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Volume XVII

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INORGANIC SYNTHESES

Volume XVII

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PREFACE

The format used in this volume follows the organizational pattern used in recent volumes. An attempt is made to group syntheses in different chapters in accordance with specific areas of interest. Chapter One, which describes compounds containing metal-hydrogen bonds, is divided into two parts: main group hydrides and transition metal hydride complexes. For convenience, transition metal compounds not containing a metal-hydrogen bond are treated separately. Those compounds containing only carbonyl, phosphine, olefin, and similar types of ligands are grouped together in Chapter Two; all other types of transition metal compounds are described in Chapter Three. Chapter Four contains all compounds of the main group elements with the exception of the metal hydrides which are, as noted above, described in Section I of Chapter One.

Inorganic Syntheses, Inc., is a nonprofit organization dedicated to the selection and presentation of tested procedures for the preparation of compounds of more than routine interest. The Editorial Board seeks the cooperation of the entire scientific community in realizing these goals. The editor for Volume XVIII is B. E. Douglas; for Volume XIX, D. F. Shriver; and for Volume XX, D. H. Busch Directions for submitting preparations follow this preface.

I am particularly indebted to the many scientists who have willingly contributed their time and materials to checking the syntheses and to the authors for collaborating with the checkers where appropriate, in changing their manuscripts for greater clarity.

Finally, I wish to thank those members of Inorganic Syntheses, Inc., who read the original manuscripts and gave me much valuable advice and help. I am especially indebted to Professors Eugene C. Ashby and Herbert D. Kaesz who contacted prospective authors for the syntheses of main group hydrides and transition metal hydrides, respectively. I also wish to thank Warren H. Powell and Mr. Thomas E. Sloan for their invaluable assistance in nomenclature matters and in the copy-editing of the manuscripts as well as Professor W. Conard Fernelius for his meticulous reading of proof for the entire volume.

Alan G. MacDiarmid

NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESES series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing INORGANIC SYNTHESES by offering their advice and assistance in both the formulation of and the laboratory evaluation of outstanding syntheses. Help of this kind will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of INORGANIC SYNTHESES. The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be stated clearly. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be delineated clearly. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References*, all pertinent literature citations should be listed in order.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis must be satisfactorily reproduced in a different laboratory from that from which it was submitted.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Jay H. Worrell, Department of Chemistry, University of South Florida, Tampa, FL 33620. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in *Nomenclature of Inorganic Chemistry, Second Edition, Definitive Rules. 1970 Issue of the IUPAC Commission on Nomenclature of Inorganic Chemistry.* Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry.*

Inorganic Syntheses, Volume XVII
Edited by Alan G. MacDiarmid

Chapter One

METAL HYDRIDES

I. MAIN GROUP HYDRIDES

(E. C. ASHBY*)

Simple and complex metal hydrides of the main group elements have found widespread use in both inorganic and organic synthesis. The purpose of this chapter is to provide synthetic preparations for a variety of typical main group metal hydrides. In this connection both simple and complex metal hydride preparations are provided involving zinc, magnesium, boron, and gallium compounds. Some of the hydrides such as MgH_2 and ZnH_2 are well known. However, the present methods of preparation provide simple routes to these compounds as well as compounds of unusual reactivity. Other hydrides presented here, such as $Li[ZnH_3]$, $Li_2[ZnH_4]$, $Na[Zn_2(CH_3)_2H_3]$, $Na[ZnH_3]$, and $K[(sec\text{-}C_4H_9)_3BH]$, are relatively new but have significant potential utility as reducing agents. Simple and excellent methods of preparation are provided for the aminoboranes, aluminum hydride complexes, and for the metal hydrido gallium complexes which should make these compounds more available for future exploration. The methods described for $Ca(BH_4)_2$ and the quaternary ammonium and phosphonium heptahydrodiborates should result in the ready availability of these rather fundamental classes of hydroborates for more extensive use as reducing agents and as intermediates in inorganic synthesis.

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1. MAGNESIUM DIHYDRIDE

$$Li[AlH_4] + 4n\text{-}C_4H_9MgBr \longrightarrow 2MgH_2 + MgBr_2 + BrMg[Al(n\text{-}C_4H_9)_4] + LiBr$$

Submitted by E. C. ASHBY* and R. D. SCHWARTZ*
Checked by G. L. BRATTEN† and J. A. DILTS†

There are four general methods for preparing magnesium dihydride.[1]

$$(C_2H_5)_2Mg \xrightarrow{175^\circ} MgH_2 + 2C_2H_4 \tag{1}$$

$$Li[AlH_4] + 2(C_2H_5)_2Mg \longrightarrow 2MgH_2 + Li[Al(C_2H_5)_4] \tag{2}$$

$$2NaH + MgBr_2 \xrightarrow{THF} MgH_2 + 2NaCl \tag{3}$$

$$Mg + H_2 \xrightarrow[200\text{ atm}]{570^\circ} MgH_2 \tag{4}$$

The pyrolysis of diethylmagnesium[2] (Eq. 1), the reaction of diethylmagnesium with lithium tetrahydridoaluminate(1−)[3] (Eq. 2), and the reaction of sodium hydride with magnesium dibromide[4] (Eq. 3) provide an active form of magnesium hydride which is pyrophoric in air and reacts violently with water or other protic compounds. In contrast, reaction of magnesium metal with hydrogen (Eq. 4) produces a form of magnesium dihydride which is unreactive toward air and water.

Although the reaction of lithium tetrahydridoaluminate(1−) and diethylmagnesium produces an active form of pure magnesium dihydride, diethylmagnesium is not commercially available and hence must be prepared separately. This is also true of the route involving pyrolysis of diethylmagnesium. The reaction of sodium hydride with magnesium dibromide in diethyl ether represents an economic route to reactive magnesium dihydride from readily available starting materials; however, reaction times are long and the product is contaminated with sodium bromide. The present method[5] provides the most convenient route to magnesium dihydride by adding an ether solution of commercially available lithium tetrahydridoaluminate(1−) to an ether solution of a Grignard reagent. Magnesium dihydride is important as a reducing agent for both organic and inorganic compounds and as a source of active hydrogen. The compound is sensitive to protic compounds, especially water, and to the moisture in air; therefore the preparation should be carried out in a dry, airfree atmosphere.[6]

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Solvents and Reagents

■ **Caution.** *The drying of tetrahydrofuran (THF) may result in serious explosions under certain conditions.* [See *Inorganic Syntheses*, **12:** 111, 317 (1970); also this volume, Synthesis 4 and the information given below.]

The tetrahydrofuran used in the synthesis is dried immediately prior to use and is purified by atmospheric-pressure distillation over sodium tetrahydridoaluminate(1 –)* under a nitrogen atmosphere. The use of lithium tetrahydridoaluminate(1 –) is to be avoided because of reports that it explodes on distillation. The following precautions should be observed when distilling tetrahydrofuran over sodium tetrahydridoaluminate(1 –).

1. Predry fresh tetrahydrofuran with calcium dihydride.
2. Do not use a large excess of sodium tetrahydridoaluminate(1 –) (10 g of sodium tetrahydridoaluminate(1 –) per liter of tetrahydrofuran is recommended).
3. Do not continue the distillation beyond the point where the flask is one-third full.
4. Carry out the distillation behind a shield in a hood. Alternate methods of drying and purifying tetrahydrofuran are available, such as distillation over sodium benzophenone ketyl.[2]

Sodium tetrahydridoaluminate(1 –) has been found to be superior to lithium tetrahydridoaluminate(1 –) as a drying agent over which tetrahydrofuran is distilled. Tetrahydrofuran distills at 65°, a temperature at which lithium tetrahydridoaluminate(1 –) is already decomposing slowly. As tetrahydrofuran is distilled from a flask containing lithium tetrahydridoaluminate(1 –) the temperature of the pot increases and can reach a temperature of 90°, at which lithium tetrahydridoaluminate(1 –) decomposes rapidly and has been known to detonate. On the other hand, sodium tetrahydridoaluminate(1 –) decomposes at 185°, a temperature far above temperatures expected in the distillation flask during distillation. Under no condition should the distillation of tetrahydrofuran over sodium tetrahydridoaluminate(1 –) be allowed to proceed to dryness. Preferably the distillation should be stopped just as the solvent layer reaches the top of the heating mantle.

Diethyl ether (Fisher Certified) was distilled over lithium tetrahydridoaluminate(1 –)* immediately prior to use. It is perfectly safe to distill diethyl ether over lithium tetrahydridoaluminate(1 –) since diethyl ether boils (34°) sufficiently below the decomposition point of lithium tetrahydridoaluminate(1 –) provided normal precautions are taken. See Synthesis 3.

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* Available from Ventron Corporation, Alfa Products, P.O. Box 299, Danvers, MA 01923.

n-Butylmagnesium bromide was prepared from *n*-butyl bromide and magnesium in ether by the usual procedure.[7] Bromide ion was determined by the Volhard method.[8] Magnesium was determined by titration with ethylenediaminetetraacetic acid (EDTA).[9] Hydridic hydrogen was determined by hydrolyzing a weighed sample on a standard vacuum line[10] and measuring the hydrogen evolved.

Procedure

■ **Caution.** *Magnesium dihydride prepared by this method is pyrophoric and reacts violently with water or other protic compounds.*

To a dry, nitrogen-filled, three-necked, 250-mL, round-bottomed flask, equipped with a Teflon stirring bar, water-cooled condenser, 100-mL dropping funnel, and a three-way stopcock, is added 75 mL of a 0.58*M* ether solution of *n*-butylmagnesium bromide (0.034 mol) (see Fig. 1). Oxygen and moisture are removed from the apparatus prior to addition of the Grignard reagent by closing pinch clamp *E*, opening stopcock *H*, and flash-flaming the apparatus with a Bunsen burner while nitrogen is flushed through the system. The Grignard reagent is added to the flask *C* via the three-way stopcock *G* via a 100-mL syringe. To the stirred solution of the Grignard reagent at room temperature is added dropwise 45 mL of a 0.242*M* ether solution of lithium tetrahydridoaluminate(1−) (0.011 mol) via dropping

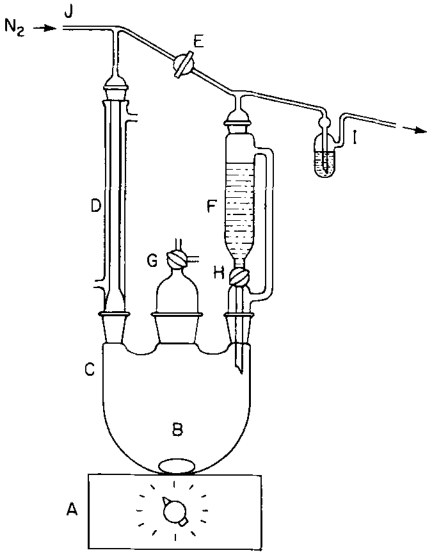

Fig. 1. Apparatus for the preparation of magnesium dihydride: A, *magnetic stirrer;* B, *Teflon-coated stirring bar;* C, *250-ml, three-necked, round-bottomed flask;* D, *water-cooled condenser;* E, *pinch clamp;* F, *100-mL dropping funnel;* G, *three-way stopcock;* H, *stopcock to addition funnel;* I, *mineral-oil bubbler;* J, *Tygon tubing.*

funnel *F*. A white precipitate begins to form immediately* and the solution is stirred for 5 min after the addition of lithium tetrahydridoaluminate(1 −) is complete.

The white precipitate is isolated via filtration in a dry box[6] through a medium sintered-glass filter and is washed with three 25-mL portions of ether. The filtrate is destroyed by pouring it into 200 mL of kerosene and adding isopropyl alcohol dropwise with stirring. The solid product is dried for 1 hr under vacuum to yield 1.73 g of product (91%). *Anal.* Calcd. for $MgH_2 \cdot 0.8(C_2H_5)_2O$: Mg, 28.3; H, 2.34; $(C_2H_5)_2O$, 69.4. Found: Mg, 28.0; H, 2.12; $(C_2H_5)_2O$, 71.5.† Mg/H ratio, found: 1.0 : 1.96.

Properties

Magnesium dihydride is a white, granular solid which decomposes at 310° to magnesium metal and hydrogen.[11] It is stable indefinitely at room temperature when protected from moisture and oxygen. It is pyrophoric in air and reacts violently with water. The infrared spectrum of magnesium dihydride shows two broad envelopes. One is at 1400–800 cm^{-1}, the other at 800–400 cm^{-1}. The x-ray powder diffraction (nickel-filtered CuK_α) pattern shows lines at 3.17 Å (s); 2.50 Å (m); 2.25 Å (m); 1.67 Å (w).

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* The checkers noted a delay in the formation of solid magnesium dihydride, which did not begin to precipitate until nearly all the lithium tetrahydridoaluminate(1 −) had been added.

† The diethyl ether was determined by difference in the gravimetric analysis.

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2. ZINC DIHYDRIDE

$$(CH_3)_2Zn + AlH_3 \longrightarrow ZnH_2 + (CH_3)_2AlH$$

Submitted by E. C. ASHBY* and JOHN J. WATKINS*
Checked by D. GREIG† and D. F. SHRIVER†

When dimethylzinc is allowed to react with an equivalent amount of aluminum trihydride, in diethyl ether or tetrahydrofuran (THF) as solvent, zinc dihydride and dimethylaluminum hydride are formed. The reaction, carried out at room temperature, is quantitative, with the zinc dihydride precipitating and the dimethylaluminum hydride remaining in solution. Zinc dihydride can also be obtained by reacting dimethylzinc with lithium tetrahydridoaluminate(1−) in diethyl ether.[1] However, zinc dihydride prepared in this manner is always contaminated with lithium and aluminum. Zinc dihydride prepared according to the present procedure does not contain either of these impurities. Zinc dihydride is sensitive to air; therefore the preparation of this compound must be carried out in an airfree atmosphere (nitrogen or argon). Like all main group metal hydrides, it is useful as a reducing agent in organic syntheses.

Reagents and Solvents

■ **Caution.** *The drying of tetrahydrofuran may be accompanied by serious explosions under certain conditions.* [See *Inorganic Syntheses*, **12:** 111, 317 (1970); also this volume, Synthesis 1.]

The solution of aluminum trihydride used in this synthesis is prepared by the reaction of 100% sulfuric acid with lithium tetrahydridoaluminate(1−) in dry tetrahydrofuran.[3] Under nitrogen flow, a stoichiometric amount of the sulfuric acid is added dropwise by syringe at 0° to a solution of lithium tetrahydridoaluminate(1−) in dry tetrahydrofuran. The apparatus used is just like that shown in Fig. 2, except that an ice bath is used to cool the reaction flask and thus prevent ether cleavage. As the sulfuric acid is added to the lithium tetrahydridoaluminate(1−), a precipitate of lithium sulfate forms and hydrogen is evolved. For this reason, the reaction must be carried out in a hood. After all the sulfuric acid has been added, the resulting slurry is stirred for 2 hr, then filtered in a glove box.[4,5] The filtrate, a clear solution of aluminum trihydride in tetrahydrofuran, is stored in the refrigerator at −20° until it is needed.

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The solution of dimethylzinc in dry tetrahydrofuran is prepared by the method of Noller.[6] The methyl iodide is dried over anhydrous magnesium sulfate and distilled prior to use. The Zn/Cu couple was flamed and dried under vacuum overnight prior to use. The reaction of the Zn/Cu couple with methyl iodide was allowed to proceed overnight.* The dimethylzinc was distilled from the reaction mixture at atmospheric pressure under nitrogen.

Procedure

The apparatus used to carry out the above reaction is shown in Fig. 2. The 50-mL round-bottomed flask *G*, containing a magnetic stirring bar and a

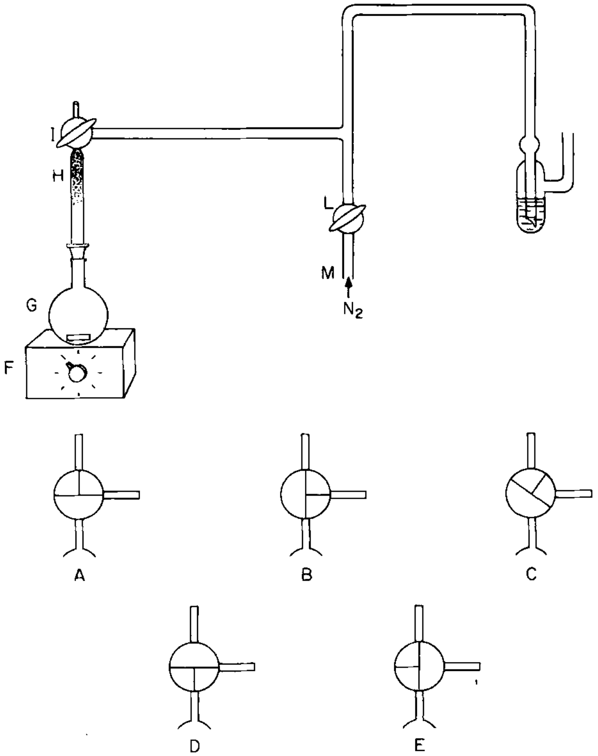

Fig. 2. Apparatus used to prepare ZnH_2. A, B, C, D, *and* E *represent the different positions of the three-way stopcock used in this preparation;* F *is a magnetic stirrer,* G *is a 50-mL round-bottomed flask,* H *is a glass-wool plug,* I *is a three-way stopcock,* L *is a needle valve,* M *is the position of the nitrogen source, and* N *is a mercury pool (any type of mercury bubble will do).*

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* The checkers found it necessary to reflux methyl iodide twice over fresh Zn/Cu couple to obtain dimethylzinc that was not significantly contaminated with methyl iodide.

piece of glass wool at the neck, is evacuated, flamed under vacuum, and filled with nitrogen. This procedure is repeated twice and is accomplished by setting stopcock *I* to position *E* in order to obtain the vacuum and then opening valve *L* and changing stopcock *I* to position *D*. When one is ready to add the reactants to the flask, stopcock *I* is set in position *B*, and valve *L* is opened in order to allow nitrogen to be flushed through the entire apparatus.

The magnetic stirrer is turned on, and by means of syringes, previously dried and flushed with nitrogen, 6.1 mL of a 0.820*M* solution of dimethylzinc (0.005 mol) in dry tetrahydrofuran is added to the flask followed by 9.0 mL of a 0.555*M* solution of aluminum trihydride (0.005 mol) in dry tetrahydrofuran. After the reactants are added, stopcock *I* is returned to position *D*. Zinc dihydride forms as a white, granular precipitate within a few seconds after reagent addition. The mixture is stirred for 1 hr and the zinc dihydride is allowed to settle. The supernatant solution (dimethylaluminum hydride in tetrahydrofuran) is withdrawn with a syringe by bringing stopcock *I* to position *B*. The contents of the syringe are added to 200 mL of kerosene (in hood) and the dimethylaluminum hydride is destroyed by slowly adding isopropyl alcohol dropwise.

The remaining precipitate of zinc dihydride is washed with three 25-mL portions of freshly distilled tetrahydrofuran. This is accomplished by setting stopcock *I* at position *B* with valve *L* open. The 25-mL portions of tetrahydrofuran are added through stopcock *I*; the mixture is stirred for 5 min, with stopcock *I* in position *C*; the zinc dihydride is allowed to settle; and the supernatant liquid is removed via syringe by returning stopcock *I* to position *B*. The wash solution is destroyed in the same way as that described earlier for the more concentrated solution of dimethylaluminum hydride.

The washed precipitate is dried under vacuum at room temperature by returning stopcock *I* to position *E*. The vacuum must be applied slowly so that the zinc dihydride is not sucked up into the vacuum system (this is the reason for the glass-wool plug). The zinc dihydride is left under vacuum overnight for drying. The yield of zinc dihydride is 0.330 g (0.00493 mol), which is quantitative. *Anal.* Calcd. for ZnH_2: Zn, 97.03; H, 2.97. Found: Zn, 75.67; H, 2.35; THF, 22.08. The molar ratio of Zn/H/THF is 1.00 : 2.03 : 0.27.

Properties

Zinc dihydride is a white, granular solid which decomposes at 90° to zinc metal and hydrogen. The THF of solvation is liberated gradually during the process of heating to 90°; however, it is difficult to remove all of the THF below 90° without decomposition of the zinc dihydride. After standing at room temperature for a period of several days, the white solid slowly turns black, although the compound is stable for a period of several days when it is stored at Dry Ice temperature. Zinc dihydride is not soluble in ethereal solvents and is both water- and oxygen-sensitive. The hydrolysis of zinc dihydride with water occurs slowly, but it is violent with aqueous acids.

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3. LITHIUM TRIHYDRIDOZINCATE(1−) AND LITHIUM TETRAHYDRIDOZINCATE(2−)

Submitted by E. C. ASHBY* and JOHN WATKINS*
Checked by D. GREIG† and D. F. SHRIVER†

The reaction of methyllithium with dimethylzinc in 1 : 1 and 2 : 1 molar ratios in diethyl ether solution produces lithium tri- and tetramethylzincates.[1] Two equivalents of lithium trimethylzincate(1−) react with three equivalents of lithium tetrahydridoaluminate(1−), and one equivalent of lithium tetramethylzincate(2−) reacts with two equivalents of lithium tetrahydridoaluminate(1−) to give lithium trihydridozincate(1−) and lithium tetrahydridozincate(2−), respectively, in quantitative yields. Both reactions proceed in diethyl ether at room temperature and are complete within 5 min. The compounds are air-sensitive and therefore must be prepared in an airfree atmosphere (nitrogen or argon). They may be used as reducing agents in organic syntheses.

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† Department of Chemistry, Northwestern University, Evanston, IL 60201.

Reagents and Solvent

■ **Caution.** *The distillation of diethyl ether over lithium tetrahydridoaluminate(1 –) can be dangerous if the distillation is allowed to proceed to dryness.* (See this volume, Synthesis 1.)

The diethyl ether used herein is purified and dried prior to use by atmospheric-pressure distillation over lithium tetrahydridoaluminate(1 –)* under a nitrogen atmosphere. The lithium tetrahydridoaluminate(1 –) should be added to the diethyl ether in a nitrogen-filled dry box, and the distillation should not be carried out past the point where the distillation flask is one-quarter full.

The solution of dimethylzinc in diethyl ether, used in both these syntheses, is prepared by the method of Noller.[2] The methyl iodide is dried over anhydrous magnesium sulfate and distilled prior to use. The Zn/Cu couple is flamed and dried under vacuum overnight prior to use. The reaction of Zn/Cu couple with methyl iodide is allowed to proceed overnight.† The dimethylzinc is distilled from the reaction mixture at atmospheric pressure under nitrogen. The solution of lithium tetrahydridoaluminate(1 –) is prepared by refluxing pulverized lumps of lithium tetrahydridoaluminate(1 –) in diethyl ether overnight. The next morning the remaining solids are filtered off‡ (using medium-porosity glass frit with a 1-in. layer of predried Celite filter aid) in the dry box, leaving a clear solution of lithium tetrahydridoaluminate(1 –) in ether. This solution is standardized for aluminum by titration with ethylenediamine tetraacetic acid (EDTA).

The methyllithium§ is obtained as a 5% solution in diethyl ether. It is stored in a refrigerator at –20° until ready for use. The solution is standardized by measuring the amount of methane gas evolved when a sample is added to methanol. The gas analyses are carried out by hydrolyzing the sample on a standard vacuum line equipped with a Toepler pump.[3]

A. LITHIUM TRIHYDRIDOZINCATE(1 –)

$$\mathrm{Li[Zn(CH_3)_2]} + \tfrac{3}{2}\mathrm{Li[AlH_4]} \longrightarrow \mathrm{Li[ZnH_3]} + \tfrac{3}{2}\mathrm{Li[Al(CH_3)_2H_2]}$$

Procedure

The apparatus used to carry out this reaction is the same as that shown in Fig. 2. The 50-mL round-bottomed flask *G*, containing a magnetic stirring

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* Available from Ventron Corporation, Alfa Products, P.O. Box 299, Danvers, MA 01923.

† The checkers found it necessary to reflux methyl iodide twice over fresh Zn/Cu couple to obtain dimethylzinc without significant contamination of methyl iodide.

‡ Centrifuging is also satisfactory for separating the solid material from the clear solution.

§ Available from Foote Mineral Co., Route 100, Exton, PA 19341.

bar is evacuated, flamed while under vacuum, and filled with nitrogen. This is accomplished by setting stopcock *I* to position *E* so as to place the flask under vacuum, then by opening valve *L* and setting stopcock *I* to position *D* in order to fill the flask with nitrogen. This procedure should be repeated twice. Then, by placing stopcock *I* in position *B* with valve *L* open, 6.1 mL of a 0.820*M* solution of dimethylzinc (0.005 mol) in diethyl ether is added to the flask. All additions to the reaction flask are made by using a syringe. After the stirrer is turned on, a 1.68*M* solution of methyllithium (0.005 mol) in diethyl ether is added rapidly. The resulting solution is stirred at room temperature for 10 min, then 14.4 mL of a 0.520*M* solution of lithium tetrahydridoaluminate(1 −) (0.0075 mol) in diethyl ether is added. A white precipitate of lithium trihydridozincate(1 −) forms immediately. The mixture is stirred at room temperature for an additional 10 min, then stopcock *I* is placed in position *C*, and the flask *G* is placed in a nitrogen-filled glove box[4] for filtration of the solid product. The filtration is carried out under vacuum using a 260-mL, medium-frit filter funnel. The white solid is then washed three times with 30-mL portions of freshly distilled diethyl ether.* If a glove box is not available, the solid can be separated from the ether solution by centrifugation followed by decantation.†

The resulting solid is then dried under vacuum at room temperature overnight. This drying procedure removes essentially all of the diethyl ether. The apparatus used for drying is the same as that shown in Fig. 2, except that a piece of glass wool *H* is inserted below stopcock *C* in order to prevent the solids from being sucked up into the vacuum system. The yield of lithium trihydridozincate(1 −) is 0.365 g (0.005 mol), which is quantitative. *Anal.* Calcd. for $Li[ZnH_3]$: Li, 9.2; Zn, 86.9; H, 4.0. Found: Li, 9.2; Zn, 86.5; H, 4.30. The molar ratio of Li/Zn/H in the white solid is 1.00 : 1.00 : 3.21. Aluminum is absent.

Properties

Lithium trihydridozincate(1 −) is a white, granular solid which slowly turns black on standing at room temperature. If it is stored at Dry Ice temperature, it remains white for an indefinite period of time. It is not soluble to any extent in ethereal solvents, and it is very sensitive to air and moisture. It is best identified by its x-ray powder diffraction (nickel-filtered CuK_α) pattern. The predominant interplanar spacing and the corresponding relative intensities (estimated visually) are: $d = 6.25$ Å (m); 4.45 Å (vs); 4.30 Å (m);

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* The ether wash solution is destroyed by adding it to twice its volume of kerosene under the hood and then carefully adding isopropyl alcohol (50 mL) with stirring.

† A procedure for doing this is described on pages 157–158 of Ref. 2. The checkers prefer the centrifugation method.

4.19 Å (m); 3.81 Å (ms); 3.24 Å (vs); 3.10 Å (m); 2.94 Å (s); 2.81 Å (s); 2.35 Å (m); 2.41 Å (m).

It decomposes under vacuum at 97° to give lithium tetrahydridozincate(2 –) and zinc metal.

B. LITHIUM TETRAHYDRIDOZINCATE(2 –)

$$Li_2[Zn(CH_3)_4] + 2Li[AlH_4] \longrightarrow Li_2[ZnH_4] + 2Li[Al(CH_3)_2H_2]$$

Procedure

The apparatus and method used to carry out this reaction are exactly the same as those described in Sec. A for the preparation of lithium trihydridozincate(1 –). After flash-flaming flask *G* under vacuum and filling it with nitrogen, 12.2 mL of a 0.820*M* solution of dimethylzinc (0.010 mol) in diethyl ether is added to the 50-mL flask with valve *L* open and stopcock *I* in position *B*. The magnetic stirrer is turned on; then 11.9 mL of a 1.68*M* solution of methyllithium (0.020 mol) in diethyl ether is added rapidly. The resulting solution is stirred at room temperature for 10 min; then 38.50 mL of a 0.520*M* solution of lithium tetrahydridoaluminate(1 –) (0.020 mol) in diethyl ether is added. A white precipitate of lithium tetrahydridozincate(2 –) forms immediately. This mixture is stirred at room temperature for an additional 10 min; filtration of the precipitate in a glove box follows.* The precipitate is washed three times with 30-mL portions of diethyl ether.† Drying the resulting solid under vacuum overnight removes essentially all of the diethyl ether. The yield of lithium tetrahydridozincate(2 –) is 0.810 g (0.010 mol), which is quantitative. *Anal.* Calcd. for Li_2ZnH_4: Li, 16.7; Zn, 78.5; H, 4.85. Found: Li, 14.8; Zn, 80.4; H, 4.85. The molar ratio of Li/Zn/H in the solid is 1.73 : 1.00 : 3.94. Aluminum is absent.

Properties

The properties and uses of lithium tetrahydridozincate(2 –) are similar to those of lithium trihydrozincate(1 –). It decomposes at 136° to give lithium hydride and zinc metal.

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* Centrifugation is also a satisfactory method for separating the solid material from the clear solution.

† The ether solution of lithium dihydridodimethylaluminate(1 –) removed in the filtration and the ether wash solutions are combined and destroyed by adding them to 200 mL of kerosene (in the hood) and then adding isopropyl alcohol dropwise.

The predominant interplanar spacing and the corresponding relative intensities of the x-ray (nickel-filtered CuK_α) diffraction pattern (estimated visually) are: $d = 5.02$ Å (m); 4.25 Å (s); 3.84 Å (vs); 3.65 Å (m); 3.42 Å (ms); 2.94 Å (ms); 2.46 Å (s); 2.42 Å (s); 2.32 Å (m); 2.12 Å (m).

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4. SODIUM TRIHYDRIDODIMETHYLDIZINCATE(1−) AND SODIUM TRIHYDRIDOZINCATE(1−)

Submitted by G. J. KUBAS* and D. F. SHRIVER*
Checked by J. A. DILTS†

One route to Zn—H bonds involves metathesis of a hydride with Zn—X or Zn—R (R = alkyl) bonds.[1] A second route, used in the preparation of anionic zinc hydride complexes, involves donor-acceptor interaction between H^- and diorganozinc.[2] For example[3]

$$\text{Zn}(\text{C}_6\text{F}_5)_2 + \text{NaH} \longrightarrow \text{Na}[\text{ZnH}(\text{C}_6\text{F}_5)_2]$$

The reaction described here of methylzinc iodide with sodium hydride, to produce $\text{Na}[\text{Zn}_2(\text{CH}_3)_2\text{H}_3]$, may be pictured as a combination of the two reaction types named above. Unlike many hydride preparations, the synthesis of sodium trihydridodimethyldizincate(1−) is easily performed using ordinary Schlenk-type bench-top techniques and commercially available starting materials.[4] Sodium trihydridozincate(1−) is easily prepared by exposing $\text{Na}[\text{Zn}_2(\text{CH}_3)_2\text{H}_3]\cdot x\text{THF}$ to high vacuum.[4]

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A. SODIUM TRIHYDRIDODIMETHYLDIZINCATE(1−)

$$Zn/Cu + CH_3I \xrightarrow{THF} CH_3ZnI + Cu$$

$$2CH_3ZnI + 3NaH \xrightarrow{THF} Na[Zn_2(CH_3)_2H_3]\cdot xTHF + 2NaI$$

Procedure

■ **Caution.** *The drying of tetrahydrofuran (THF) may be accompanied by serious explosions under certain conditions.* [See *Inorganic Syntheses*, **12:** 111, 317 (1970) and also this volume, Synthesis 1.]

All manipulations of reactants and products should be carried out in an inert atmosphere using dry, Schlenk-type glassware.[5] Under a nitrogen atmosphere, commercial THF is refluxed with sodium wire plus ca. 0.2 g benzophenone until a blue color develops. The THF is then distilled from the sodium benzophenone ketyl solution and the dry THF is collected under nitrogen. About 50 mL of the dried THF is placed in a 100-mL round-bottomed flask containing 15 g (0.23 mol) of a Zn/Cu couple* (5–8% Cu). Methyl iodide (22.8 g, 0.16 mol) is added, and the mixture is refluxed for 8 hr,[6] cooled, and filtered through a Schlenk frit into a 250-mL round-bottomed flask equipped with a magnetic stirring bar. About 150 mL of distilled THF is added to the filtrate and the colorless or pale-yellow solution of methylzinc iodide is cooled to 0° in an ice bath. While the solution is being stirred vigorously, sodium hydride† (6.5 g, 0.27 mol) is added rapidly. After 2 hr of stirring at 0°, the mixture is allowed to warm to room temperature and stirring is continued for an additional 14 hr. A precipitate of sodium iodide, ranging in color from white to light-gray, forms and is filtered off by means of a Schlenk frit containing Celite filter aid. The colorless filtrate should be stored at −20° to prevent the slow decomposition to metallic zinc which occurs at room temperature. The net composition of the filtrate (excluding the sodium iodide content) can be represented by the formula $NaH[(CH_3)_{2-n}ZnH_n]_2$ where n has been found to be 0.86 ± 0.08 in four different preparations. *Anal.* Calcd. for $NaZn_2(CH_3)_2H_3$: ratio Na/Zn/CH_4 (upon hydrolysis)/H_2 (upon hydrolysis), 1.0/2.0/2.0/3.0. Found ratio: 1.02 : 2.00 : 2.06 : 2.82. (The foregoing sodium value is corrected for sodium iodide content, which can approach 0.28 molar.)

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* Prepared by melting together a mixture of coarsely granulated or mossy zinc (not zinc powder) with brass turnings (ca. 80% Cu), pouring the melt into test tubes, and turning the resulting rods on a lathe. Commercial material also may be suitable.

† The sodium hydride should be oilfree. An excellent commercial material, used here, can be purchased from Fluka AG Chemische Fabrik (Buchs, Switzerland). It is obtained in the form of nearly colorless, oilfree pellets, which were found by us to be 99% pure by sodium and hydrogen analysis. Finely divided sodium hydride is pyrophoric and should be handled in a glove box or a glove bag. It may be destroyed with water-saturated nitrogen gas. See footnote, page 15.

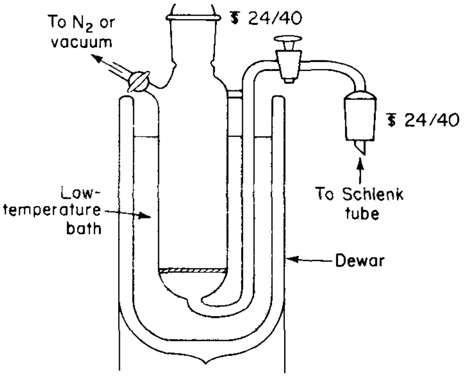

Fig. 3. Low-temperature filter. The main chamber is 50-mm o.d. and ca. 200 mm from the frit to the bottom of the standard-taper joint. A medium-porosity frit is employed.

Solid $Na[Zn_2(CH_3)_2H_3]$ can be isolated in high yield by cooling the solution in a Dry Ice bath for several days, whereupon large, colorless, needle-like crystals form. These may be filtered off at −78° using the apparatus shown in Fig. 3. After the crystals are washed with several 10-mL portions of cold, dry THF, they are held under vacuum at −22° (carbon tetrachloride slush bath)[7] for several hours to remove excess THF. Under these conditions, the crystals lose solvent to form a white powder, which unlike the parent crystals does not melt upon warming to room temperature. *Anal.* Found: $Na/Zn/CH_3/H$, 1.01 : 1.98 : 1.98 : 3.01. In addition, 2.3 mol of THF was retained per mole of $Na[Zn_2(CH_3)_2H_3]$ for this sample; however, the exact value varies from one preparation to another. No iodide was detected in the product.

B. SODIUM TRIHYDRIDOZINCATE(1−)

$$Na[Zn_2(CH_3)_2H_3]\cdot x\text{THF} \longrightarrow Na[ZnH_3] + Zn(CH_3)_2 + x\text{THF}$$

Procedure

When a sample of $Na[Zn_2(CH_3)_2H_3]\cdot x$THF is exposed to high vacuum at room temperature, both dimethylzinc (■ **Caution.** *Spontaneously flammable in air.*) and THF are slowly evolved. After 3 hr of pumping at room temperature, followed by about 1 hr of pumping at 80°, the evolution of volatiles, which are collected in a trap cooled with liquid nitrogen, should cease.* If not, more pumping is required. Care must be exercised in adjusting

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* Upon completion of the preparation the cold trap should be vented with nitrogen or another inert gas. The dimethylzinc may be safely disposed of by passing a slow stream of water-saturated nitrogen gas through the trap at room temperature. This process should be conducted in a hood and away from solvents.

the evolution rate to prevent entrainment of solid particles in the stream of volatiles. Solid, white to light-gray $Na[ZnH_3]$ is obtained in a quantitative yield. If pure, white $Na[ZnH_3]$ is required, its precursor, $Na[Zn_2(CH_3)_2H_3]$, must also be white. *Anal.* Calcd. for H_3NaZn: H, 3.3; Na, 25.2; Zn, 71.5. Found: H, 3.3; Na, 24.6; Zn, 71.5.

Properties

$Na[Zn_2(CH_3)_2H_3]\cdot x$THF is sensitive to air, moisture, and heat and must be stored in a closed container at −78°. At room temperature, the compound slowly decomposes, changing from a white powder to first yellow, then gray, aggregates. It loses dimethylzinc and THF readily at room temperature, eventually becoming sodium trihydridozincate(1−).

The crude $Na[Zn_2(CH_3)_2H_3]$ solution in THF may be used as a reducing agent.[4] Like lithium tetrahydridoaluminate(1−), the zinc reagent reduces aliphatic ketones and esters to the corresponding alcohols and aliphatic nitriles to amines. However, of the two, the zinc compound is a somewhat milder reducing agent as shown by the reduction of benzonitrile to the corresponding imine under conditions in which lithium tetrahydridoaluminate(1−) yields the amine.

Sodium trihydridozincate(1−) is air- and moisture-sensitive, but can be stored at room temperature under vacuum or an inert atmosphere. Because of this stability $Na[ZnH_3]$ is a promising compound for the preparation of zinc hydride derivatives. The infrared spectrum and x-ray powder pattern of $Na[ZnH_3]$ are reported,[4] and an alternate preparation has been mentioned.[8]

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Inorganic Syntheses, Volume XVII
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5. CALCIUM BIS[TETRAHYDROBORATE(1−)]

$$CaH_2 + 2(CH_3CH_2)_3N\cdot BH_3 \longrightarrow Ca[BH_4]_2 + 2(CH_3CH_2)_3N$$

Submitted by R. KÖSTER* and H. HUBER*
Checked by P. C. KELLER† and P. BRANT†

The tetrahydroborate salts of alkali metals, $M[BH_4]$ (M = Li, Na, K),[1] are important because they serve as starting materials for the preparation of other boron hydrides[2,3] and because they are used frequently as reducing agents.[4] The lithium and sodium salts are prepared on a technical scale.[5–9] The tetrahydroborate salts of the alkaline earth metals, $M[BH_4]_2$ (M = Mg, Ca, Sr, Ba), have not as yet been used extensively; however, calcium bis[tetrahydroborate(1−)], $Ca(BH_4)_2$,[10] is very soluble in tetrahydrofuran (THF) and it therefore has considerable potential application as a substitute for the lithium and sodium salts.

Calcium bis[tetrahydroborate(1−)] may be prepared from sodium tetrahydroborate(1−) and calcium dichloride by cation exchange[11] in a suitable solvent such as dimethylformamide,[12] an amine[13,14] or an alcohol.[13,14] A particularly good preparation of very pure $Ca[BH_4]_2$ involves the reaction of calcium dihydride with the triethylamine-borane adduct.[15,16] This method may also be used for the preparation of other tetrahydroborates of alkali and alkaline earth metals. The triethylamine-borane adduct[17] may be synthesized in a variety of ways, e.g., from triethylamine, sodium tetrahydroborate(1−), and trichloroborane;[18] from a trialkoxyborane, aluminum metal, and hydrogen in the presence of triethylamine;[19] or by hydrogenation under pressure of a mixture of triethylborane and triethylamine.[20] The triethylamine-borane adduct is a colorless liquid (mp −2°). It is stable to air and moisture at room temperature and it is easily purified by vacuum distillation (bp 95–96°/12 torr).

The preparation of calcium bis[tetrahydroborate(1−)] described here is recommended because high yields of pure product are usually obtained without difficulty. If the material should be contaminated by impurities from the calcium hydride, then it may be extracted with THF. Needles of $Ca[BH_4]\cdot 2THF$[11,21,22] may be obtained from this solution. The THF can then be readily removed by heating and pumping.

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■ **Caution.** *Calcium dihydride and calcium bis[tetrahydroborate(1−)] react vigorously with water, alcohols, and other compounds which contain acidic hydrogen atoms, sometimes with spontaneous ignition. The reaction should be carried out in an efficient hood and the reagents and products should be handled under an inert gas.*

The drying of tetrahydrofuran may be accompanied by serious explosions under certain conditions. For the recommended drying procedure and related information see Synthesis 1.

Procedure

The apparatus consists of a 2-L three-necked flask equipped with a dropping funnel, a powerful metal stirrer, a thermometer pocket, and a Claisen condenser connected to a 1-L receiver (see Fig. 4). After the reagents are added to the flask but before the dropping funnel is put in place, the apparatus is flushed with a stream of dry argon, which enters as shown in the figure and exits at *A*. A constant pressure of argon is maintained in the apparatus throughout the experiment by the setup shown in the figure. A dropping-funnel assembly, which eliminates the use of a greased stopcock, is employed.*

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* A conventional dropping funnel with a Teflon stopcock may be used, if desired. The dropping funnel shown in the diagram is available from Normag, 6238 Hofheim am Taunus, Postfach 1269, West Germany.

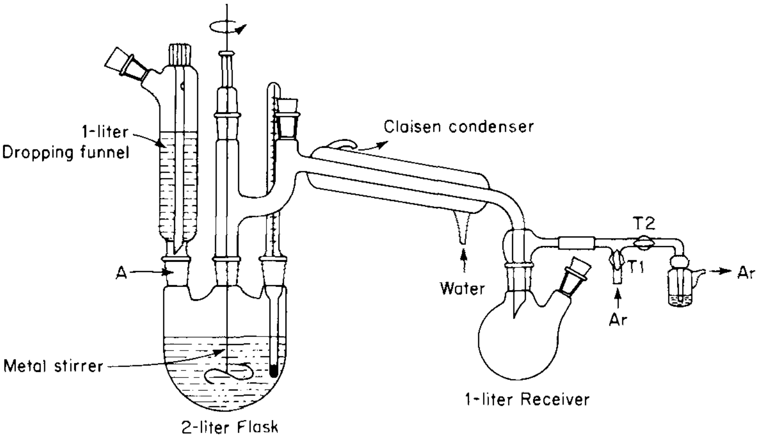

Fig. 4. Apparatus for the synthesis of $Ca[BH_4]_2$.

Over 3 hr 486 g (4.22 mol) of triethylamine-borane adduct* is added dropwise to a well-stirred fine suspension of 68.7 g (1.63 mol) of calcium dihydride† in 500 mL of hexahydrocumene‡ at 140–150° (bath temperature). The triethylamine which is liberated distills over together with some solvent. The temperature of the reaction mixture adjusts itself to ca. 135°. After approximately 400 mL has distilled, the bath temperature is raised to ca. 175°, under which conditions most of the hexahydrocumene distills. On cooling the reaction mixture, one obtains a gray, viscous slurry. As the argon stream is continued, the dropping-funnel assembly is removed and replaced by a ground-glass stopcock against the countercurrent of argon. A new 500-mL receiver is fitted to the apparatus against the countercurrent of argon, with care being taken to keep diffusion of air into the apparatus to a minimum. Stopcocks T_1 and T_2 are closed and the remaining solvent is removed *in vacuo* (bp 43–45°/15 torr; bath temperature, ca. 80°). The excess triethylamine-borane adduct is then removed by distillation at reduced pressure (bp 93–97°/15–16 torr, bath temperature, max 160°), and after the flask cools to room temperature the apparatus is filled with argon to 1 atm pressure by *slowly* opening stopcock T_1. When atmospheric pressure has been attained T_2 is again opened. Calcium bis[tetrahydroborate(1−)] [153.9 g, (94.6% yield); 91.2% pure] is obtained as the residue from 98 g (2.33 mol) calcium dihydride (in 1 L hexahydrocumene) and 556.6 g (4.85 mol) triethylamine-borane adduct using the method described above.

If desired, the calcium bis[tetrahydroborate(1−)] may be purified as follows. Against the countercurrent of argon admitted via a stopcock which has been inserted at *A* (see Fig. 4), the Claisen condenser is replaced by a reflux condenser. A total of 1.4 L of purified THF is carefully added in small portions (50–100 mL) through the top of the reflux condenser. (■ **Caution.** *A very exothermic reaction occurs.*) During the addition of the THF the flask is occasionally stirred and is cooled in a water bath. A dark gray, extremely fine suspension, which is difficult to filter, is obtained. It is centrifuged in portions. The centrifuging is carried out by transferring the entire assembly to a large argon-filled dry centrifuge.§ The clear, dark-brown solution is separated from the precipitate, composed of impurities from the

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* Aldrich Chemical Co., Inc., Milwaukee, Wisconsin; Fluka A.G., Buchs, Switzerland.

† The calcium dihydride should be ground to a fine powder under hexahydrocumene (isopropylcyclohexane). A ball mill may be used.

‡ Other saturated hydrocarbons [e.g., decahydronaphthalene (decalin)] which have a boiling point similar to or higher than that of hexahydrocumene (isopropylcyclohexane) may also be used.

§ Complete details for centrifuging materials in an inert atmosphere may be obtained from reference 23.

calcium dihydride, by decanting or siphoning* under a slow stream of argon.

The bulk of the THF is removed by distillation at atmospheric pressure (bp 65–66°, bath temperature, max 120°) under an atmosphere of argon by means of the apparatus shown in the figure. The receiver is then changed and the remaining solvent is removed *in vacuo* (15–16 torr). Finally, the crystalline $Ca[BH_4]_2 \cdot 2THF$ is heated for 3–4 hr at a maximum bath temperature of 240° *in vacuo* (0.4–0.6 torr). On cooling, argon is admitted to 1 atm pressure. One obtains 108 g (95% yield)† of solvent-free calcium bis[tetrahydroborate(1−)] of 94% purity‡ as a light, off-white powder.

Properties

Calcium bis[tetrahydroborate(1−)] is obtained as a fine powder which must be stored in well-sealed containers. It is stable in dry air at room temperature but traces of moisture decompose it with liberation of hydrogen. The gas evolution is quantitative when dilute hydrochloric acid is added. The compound decomposes at ca. 260°. The solvate $Ca[BH_4]_2 \cdot 2THF$ loses THF on heating to 240° *in vacuo*. Calcium bis[tetrahydroborate(1−)] dissolves exothermally in THF and crystalline $Ca[BH_4]_2 \cdot 2THF$ may be isolated from the solution. The $Ca[BH_4]_2 \cdot 2THF$ is very soluble in dimethyl sulfoxide, in hexamethylphosphoric triamide, and in bis(2-methoxyethyl) ether (diglyme).

The infrared spectrum shows a B—H stretching vibration at 2245 cm^{-1}. The ^1H nmr spectrum in THF solution consists of a quartet at $\tau 10.16$ ($J_{^{11}BH} = 81.1$ Hz). The ^{11}B nmr spectrum in THF solution consists of a quintet at $\delta 36$ downfield from $(C_2H_5)_2O \cdot BF_3$; ($J_{^{11}BH}$, ca. 80 Hz).

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* Less preferably, the solution may be decanted in an argon atmosphere in a dry box.

† The checkers obtained a yield of 90% on carrying out the synthesis on a one-twentieth scale.

‡ The compound is analyzed by measuring the volume of hydrogen liberated when first water, and then hydrochloric acid, is added.

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6. QUATERNARY AMMONIUM AND PHOSPHONIUM HEPTAHYDRODIBORATES

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Checked by R. SCHAEFFER‡ and D. C. MOODY‡

Several quaternary ammonium and phosphonium heptahydrodiborates, notably $[N(C_2H_5)_4][B_2H_7]$,[1,2] $[N(n\text{-}C_4H_9)_4][B_2H_7]$,[2-4] $[N(C_8H_{17})_3C_3H_7][B_2H_7]$,[5] and $[P(C_6H_5)_3CH_3][B_2H_7]$[4] have been isolated and studied. These salts are formed by reacting the corresponding $[BH_4]^-$ salt with one-half equivalent of diborane(6). The $[B_2H_7]^-$ ion contains a single B—H—B bond and so is useful for studying this particular feature of boron hydride chemistry. We shall discuss the preparation of $[N(n\text{-}C_4H_9)_4][B_2H_7]$ and $[P(C_6H_5)_3CH_3][B_2H_7]$, although similar procedures may be applied to many quaternary ammonium and phosphonium heptahydrodiborates.

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A. METHYLTRIPHENYLPHOSPHONIUM TETRAHYDROBORATE(1 −)

$$P(C_6H_5)_3 + CH_3I \longrightarrow [P(C_6H_5)_3CH_3]I$$

$$[P(C_6H_5)_3CH_3]I \xrightarrow{\text{Dowex 1-X8}} [P(C_6H_5)_3CH_3]Cl$$

$$[P(C_6H_5)_3CH_3]Cl + Na[BH_4] \longrightarrow [P(C_6H_5)_3CH_3][BH_4] + NaCl$$

Procedure

A solution of triphenylphosphine (26.2 g, 100 mmol) in 400 mL of diethyl ether is prepared. To this solution is added 17.0 g (7.5 mL, 120 mmol) of methyl iodide with stirring. A white precipitate of $[P(C_6H_5)_3CH_3]I$ begins to form almost immediately. The mixture is stirred for 36 hr. A 2.8-g (1.2 mL, 20 mmol) portion of methyl iodide is added after 12 hr and another portion after 24 hr to replace evaporation losses. Use of an excess of methyl iodide makes recrystallization unnecessary. The white precipitate is filtered, washed with diethyl ether, and dried under vacuum to yield 38.7 g (95.7 mmol, 95.7%) of $[P(C_6H_5)_3CH_3]I$.

The $[P(C_6H_5)_3CH_3]I$ is converted to chloride by dissolving it in a minimum quantity of absolute ethanol and passing it through a column of Dowex 1-X8 anion exchange resin.* The column must contain little or no water and should be eluted with absolute ethanol. Care should be taken to ascertain that the column is of sufficient capacity to handle all of the iodide. The progress of the elution can be followed by adding an occasional drop of elutant to a silver nitrate solution. The exchange is rapid and quantitative. The $[P(C_6H_5)_3CH_3]Cl$ need not be isolated, but may be used directly.†

Sodium tetrahydroborate(1 −) (2.4 g, 64 mmol) dissolved in 100 mL of absolute ethanol is added with stirring to a solution of $[P(C_6H_5)_3CH_3]Cl$ (7.8 g, 25 mmol) in 200 mL of absolute ethanol. After 2 hr of stirring the solution is filtered to remove precipitated sodium chloride and is evaporated to dryness by means of a rotary evaporator connected to a water aspirator. The residue is extracted with two 25-mL portions of methylene chloride. The extract is concentrated to 15 mL. The product is precipitated with 60 mL of diethyl ether, washed with diethyl ether, and dried under vacuum to yield 6.40 g (21.9 mmol, 87.6%) of $[P(C_6H_5)_3CH_3]BH_4$. *Anal.* Calcd. for $C_{19}H_{22}BP$: B, 3.70; hydridic H, 1.38. Found: B, 3.60; hydridic H, 1.34.

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* Registered trademark of the Dow Chemical Company. Available from J. T. Baker Chemical Co., Phillipsburg, NJ 08865.

† $[P(C_6H_5)_3CH_3]I$ may *not* be used directly in the next step because of the slight solubility of sodium iodide in ethanol and methylene chloride (dichloromethane).

Properties

Methyltriphenylphosphonium tetrahydroborate(1 −) is a white, crystalline solid, moderately stable in air at room temperature. It is soluble in methylene chloride, chloroform, ethanol, and water but insoluble in diethyl ether, pentane, tetrahydrofuran, and benzene. The ^1H nmr spectrum in methylene chloride at room temperature consists of a phenyl resonance centered at $\tau 2.20$, a methyl doublet at $\tau 6.83$ ($J_{PH} = 13.6$ Hz), and a 1 : 1 : 1 : 1 quartet at $\tau 10.05$ ($J_{BH} = 81$ Hz) due to $[BH_4]^-$.*

The ^{11}B nmr spectrum of $[P(C_6H_5)_3CH_3]^+[BH_4]^-$ consists of a quintet at $\delta 36.7$ ($J_{BH} = 82$ Hz) relative to $BF_3 \cdot O(C_2H_5)_2$.

B. TETRABUTYLAMMONIUM TETRAHYDROBORATE(1 −)

$$[N(n\text{-}C_4H_9)_4]OH + Na[BH_4] \longrightarrow [N(n\text{-}C_4H_9)_4][BH_4] + NaOH$$

Procedure

A commercially available solution of tetrabutylammonium hydroxide in methanol (30 mL of 31.4% $[N(n\text{-}C_4H_9)_4]OH$, 30.6 mmol) was added with stirring to a solution of 2.73 g (72.2 mmol) of sodium tetrahydroborate(1 −) in 30 mL of 10% methanolic sodium hydroxide.† The solution is stirred for 2 hr and evaporated to dryness by means of a rotary evaporator connected to a water aspirator. Care should be taken to remove all the methanol, or the product may be contaminated with sodium hydroxide.

The residue from the evaporation is extracted with 60 mL of methylene chloride in 20-mL portions. The extract is concentrated to 25 mL, and $[N(n\text{-}C_4H_9)_4][BH_4]$ is precipitated with 50 mL of diethyl ether.‡ The precipitate is filtered, washed with diethyl ether, and dried under vacuum to yield 7.6 g (29.6 mmol, 96.8%) of pure product. *Anal.* Calcd. for $C_{16}H_{40}NB$: B, 4.20; hydridic H, 1.57. Found: B, 4.12; hydridic H, 1.54.

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* The $[P(C_6H_5)_3CH_3]^+$ cation is useful for ^1H nmr work involving boron hydride anions for several reasons; e.g., salts of $[P(C_6H_5)_3CH_3]^+$ are usually soluble in good nmr solvents such as chloroform and methylene chloride, and there are no $[P(C_6H_5)_3CH_3]^+$ resonances in the region above $\tau 7$, where most boron hydride resonances fall.

† The concentration of commercially available solutions of $[N(n\text{-}C_4H_9)_4]OH$ is often higher than the label states because of evaporation of methanol; therefore, it is wise to titrate a portion of the solution with standard hydrochloric acid to obtain the true concentration before adding to the sodium tetrahydroborate(1 −) solution.

‡ The checkers suggest that additional diethyl ether should be employed if an oil, rather than a crystalline product, is obtained in this step.

Properties

Tetrabutylammonium tetrahydroborate(1 −) is a white, crystalline solid, moderately stable in air at room temperature. It is soluble in methylene chloride, chloroform, methanol, ethanol, water, tetrahydrofuran, and benzene, but insoluble in diethyl ether and pentane. Its ^1H nmr spectrum consists of $[N(n\text{-}C_4H_9)_4]^+$ multiplets centered at τ6.73, τ8.49, and τ9.03 and a sharp 1 : 1 : 1 : 1 quartet (τ10.17, $J_{BH} = 82$ Hz) characteristic of $[BH_4]^-$. The ^{11}B nmr spectrum is similar to that of $[P(C_6H_5)_3CH_3][BH_4]$.

C. METHYLTRIPHENYLPHOSPHONIUM HEPTAHYDRODIBORATE(1 −)

$$[P(C_6H_5)_3CH_3][BH_4] + \tfrac{1}{2}B_2H_6 \longrightarrow [P(C_6H_5)_3CH_3][B_2H_7]$$

Procedure

■ **Caution.** *Diborane*(6) *is a highly toxic, extremely flammable gas* (*bp* −86.5°). *Serious explosions have resulted from exposure of diborane*(6) *to atmospheric oxygen. All apparatus to be used for handling diborane*(6) *should be checked carefully for leaks. Suitable safety shields should be employed.*

Standard high-vacuum techniques[6-8] are used throughout this preparation.

A 20-mm-diam. reaction tube containing 0.877 g (3.00 mmol) of $[P(C_6H_5)_3CH_3][BH_4]$ and a Teflon stirring bar is fitted with an adapter having a stopcock. The vessel is transferred to the vacuum line and evacuated. The $[P(C_6H_5)_3CH_3][BH_4]$ is dissolved by distilling 5 mL of methylene chloride (dried over lithium tetrahydridoaluminate(1 −) for 2 days) into the vessel. It is not necessary that all the $[P(C_6H_5)_3CH_3][BH_4]$ dissolve.

The vessel is cooled with liquid nitrogen, and 2 mmol of diborane(6)* is condensed into it. The tube is warmed to −78°, and the solution is stirred for 6 hr. The excess diborane(6) may be recovered and measured to check for completeness of reaction. The methylene chloride is distilled off to give a quantitative yield of $[P(C_6H_5)_3CH_3][B_2H_7]$. Alternatively, $[P(C_6H_5)_3CH_3][B_2H_7]$ may be precipitated with diethyl ether, filtered from the solution, and dried under vacuum. *Anal.* Calcd. for $[P(C_6H_5)_3CH_3]B_2H_7$: B, 7.06; hydridic H, 2.31. Found: B, 6.85; hydridic H, 2.24.

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* Diborane(6) may be purchased from Callery Chemical Company, Callery, PA 16024, or it may be prepared by one of the methods referenced by A. D. Norman and W. L. Jolly, *Inorganic Syntheses*, **11**, 15 (1968).

Properties

Methyltriphenylphosphonium heptahydrodiborate(1 −) is a white, crystalline, air-sensitive compound. It is moderately stable at room temperature, but decomposes readily at 100°. It is soluble in methylene chloride, chloroform, and 1,1,2,2-tetrachloroethane, but insoluble in benzene, pentane, tetrahydrofuran (THF), diethyl ether, dimethyl ether, and diglyme [bis(2-methoxyethyl) ether].

The ^1H nmr spectrum of $[P(C_6H_5)_3CH_3][B_2H_7]$ in methylene chloride at room temperature consists of a phenyl resonance ($\tau 2.2$), a methyl doublet ($\tau 7.02$, $J_{PH} = 13.2$ Hz), a broad quartet ($\tau 8.6$, $J_{BH} = 106$ Hz) due to terminal B—H, and a very broad unresolved resonance ($\tau 14.2$) due to bridge B—H—B. The ^{11}B nmr spectrum is a broad quartet ($\delta 24.5$ relative to $BF_3 \cdot O(C_2H_5)_2$, $J_{BH} = 83$ Hz).[4]

D. TETRABUTYLAMMONIUM HEPTAHYDRODIBORATE(1 −)

$$[N(n\text{-}C_4H_9)_4][BH_4] + \tfrac{1}{2}B_2H_6 \longrightarrow [N(n\text{-}C_4H_9)_4][B_2H_7]$$

Procedure

The synthesis of $[N(n\text{-}C_4H_9)_4][B_2H_7]$ is completely analogous to that of $[P(C_6H_5)_3CH_3][B_2H_7]$. *Anal.* Calcd. for $C_{16}H_{43}B_2N$: B, 7.97; hydridic H, 2.60. Found: B, 7.81; hydridic H, 2.51.

Properties

Tetrabutylammonium heptahydrodiborate(1 −) possesses properties similar to those of $[P(C_6H_5)CH_3][B_2H_7]$. It is, however, soluble in benzene, diglyme [bis(2-methoxyethyl) ether], and tetrahydrofuran as well as in the common chlorinated hydrocarbons. The ^1H nmr spectrum in methylene chloride at room temperature consists of $[N(n\text{-}C_4H_9)_4]^+$ multiplets centered at $\tau 6.80$, $\tau 8.45$, and $\tau 8.97$ and an extremely broad resonance centered at $\tau 14.5$ assigned to the B—H—B bridge hydrogen. One arm of the terminal B—H quartet appears at $\tau 10.3$. The other three arms are obscured by the $[N(n\text{-}C_4H_9)_4]^+$ resonances. The ^{11}B nmr spectrum is similar to that of $[P(C_6H_5)_3CH_3][B_2H_7]$.

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7. POTASSIUM TRI(*sec*-BUTYL)HYDROBORATE(1 −)

$$(sec\text{-}C_4H_9)_3B + KH(s) \xrightarrow{\text{THF}} K^+[(sec\text{-}C_4H_9)_3BH]^-$$

Submitted by CHARLES ALLAN BROWN*
Checked by SHELDON G. SHORE† and GEORGE MEDFORD†

Simple trialkylhydroborates, $M^+[R_3BH]^-$ (R = CH_3 or C_2H_5, M = Li or Na) are formed readily through direct reaction of unhindered trialkylboranes with lithium hydride or sodium hydride.[1–3] However, increases in steric hindrance about boron resulting from greater bulk of the alkyl groups (R) retard or even preclude such direct reactions.[1,4] Hindered lithium trialkylhydroborates have been prepared recently by two indirect routes involving either lithium hydridotrimethoxyaluminate(1 −) or *t*-butyllithium[5] as the hydride source. The former route, although evidently general, is complicated by the formation of an aluminum methoxide gel during reaction, while the latter is apparently limited to organoboranes too hindered to form tetraalkylborates. Potassium hydride reacts directly with a wide range of organoboranes in tetrahydrofuran solution at room temperature.[6] As potassium hydride is insoluble in tetrahydrofuran, the resulting solutions are readily separated from excess hydride by decantation; the method appears entirely general.

Lithium tri(*sec*-butyl)hydroborate(1 −) is a highly active reducing agent with exceptional stereoselectivity for reduction of ketones to alcohols.[4] The potassium analog exhibits equal or greater stereoselectivity.

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† Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Reagents and Solvent

■ **Caution.** *The drying of tetrahydrofuran (THF) may be accompanied by serious explosions under certain conditions.* [See *Inorganic Syntheses,* **12,** 111, 317 (1970) and Synthesis 1 in this volume for information on drying THF.]

Reactions were carried out in THF freshly distilled from lithium tetrahydridoaluminate(1−) under nitrogen or argon.[8] Since THF readily forms explosive hydroperoxides in contact with air, only THF from freshly opened bottles was used, and only a sufficient quantity for immediate use was distilled from the drying agent.

Tri(*sec*-butyl)borane was formed by hydroboration of 2-butene in THF.[1]* The solvent was removed with water-aspirator vacuum at room temperature with a final warming to 40°. Distillation is unnecessary for preparation of potassium tri(*sec*-butyl)hydroborate(1−), but it may be accomplished under reduced pressure using a slow nitrogen bleed; the organoborane distills at 63–64°/3 torr.[9]† Tri(*sec*-butyl)borane—unlike lower organoboranes—is not spontaneously flammable in bulk but will smoke when exposed to air. (■ **Caution.** *Ignition may occur if the liquid is absorbed by a high-surface-area material such as tissue paper.*) The borane should be stored under argon or nitrogen at all times and transferred by means of a syringe.[10]

Procedure

■ **Caution.** *Disposal of organic solvents containing even small amounts of suspended potassium hydride directly into sinks may result in fires.‡ Dry potassium hydride powder may ignite spontaneously in air.*

A 125-mL flask equipped with a Teflon-covered magnetic stirring bar and an injection inlet closed by a serum stopper is dried in an oven (125° or higher), then cooled and purged with dry argon.§ Into this flask is weighed

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* Commercially available solutions of $H_3B \cdot THF$ in THF (Aldrich-Boranes, Inc., 2371 N. 30th St., Milwaukee, WI 53210) which are used in this synthesis, contain approximately 5% of sodium tetrahydroborate(1−) as a stabilizer. Tri(*sec*-butyl)borane prepared from these solutions should be distilled. An alternative commercial (Aldrich-Boranes, Inc.) hydroborating agent free of sodium tetrahydroborate(1−) is borane-methyl sulfide.

† This reference contains many detailed procedures regarding properties, reactions, handling, and analysis of organoboranes.

‡ Potassium hydride in oil reacts only slowly with atmospheric oxygen or moisture but will generally ignite if it is placed in water. Excess potassium hydride is safely decomposed by treatment with a 10% solution of a secondary alcohol (e.g., 2-butanol) in a hydrocarbon of low volatility (e.g., kerosine, toluene); utensils coated with the oil dispersion are cleaned by washing with such a solution.

§ Argon is preferred because it is denser than nitrogen and provides a "blanket" from the atmosphere during the brief time required for weighing the potassium hydride. Alternatively, an inert atmosphere chamber or glove bag may be used.

75 mmol of potassium hydride (10.0 g of 33 wt% dispersion in mineral oil*). The dispersion should be thoroughly stirred before weighing to ensure uniformity; resegregation of the dispersion is slow enough not to interfere with weighing.

The flask is attached to a reflux condenser vented through a mercury bubbler and is thoroughly purged with dry argon or nitrogen admitted through the injection inlet with a hypodermic needle (20 gage or larger). The oil is removed from the potassium hydride by three stir-settle-decant cycles using a 30-mL portion of dry pentane in each cycle. The pentane-oil mixture is removed with a syringe equipped with a long needle.† Residual pentane is evaporated in a stream of dry argon or nitrogen. With a syringe, first 38 mL of dry THF is added and then 50 mL (12.0 mmol) of tri(*sec*-butyl)borane. The reaction mixture is stirred for 1 hr at 20–25°; then it is allowed to stand for several hours to allow excess potassium hydride and any sediment to settle. The product is then removed with a syringe or transferred under inert-gas pressure through a thin, stainless-steel tube of approximately 18 gage (often called a "double-ended needle"). The yield of potassium tri(*sec*-butyl)tetrahydroborate(1−) is essentially quantitative, with a 1 : 1 : 1 ratio of K/H/B. A typical analysis is described below.

Hydride is determined as hydrogen gas following hydrolysis. A 2.0-mL aliquot of the product is quenched in 20 mL of a 3 : 1 mixture of glycerine and deionized water to which has been added 3.00 mL of 1.00*N* aqueous hydrochloric acid. Hydrolysis should be carried out in an apparatus previously flushed with argon or nitrogen. The liberated gas is passed through a gas-washing tube containing water and is collected over water. The hydrolyzed mixture is treated with 20 mL of deionized water and titrated, under argon or nitrogen, with base to a methyl red end point. Potassium (as base) in the product normally corresponds to active hydride (as hydrogen) within ±3%.

Boron is determined by oxidation of tri(*sec*-butyl)borane to 2-butanol.[9,11,12] A 4.0-mL aliquot of the potassium tri(*sec*-butyl)hydroborate(1−) solution is hydrolyzed by adding it, with stirring, to a mixture of

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* Dispersions of potassium hydride in mineral oil are available from Pressure Chemical Co., 3419 Smallman Street, Pittsburgh, PA 15201 and Ventron Corp., Alfa Products, P.O. Box 299, Danvers, MA 01923.

† Such needles are available from the Hamilton Co., P.O. Box 10030, Reno, NV 89510, and Aldrich-Boranes, Milwaukee, WI 53210. A convenient size is 8 in. long with an 18-gage diameter. A flat end is useful for maximum efficiency in removing pentane; with such a needle, it is necessary to puncture the serum stopper first with a regular pointed needle. It is desirable to avoid drawing potassium hydride powder into the syringe as it may collect between plunger and barrel, causing the syringe to seize. Disposal of the pentane washes should be carried out with the precautions previously described for excess potassium hydride.

6 mL of THF and 2 mL of water, under inert gas. The mixture is rendered strongly alkaline by addition of 1.5 mL of 3*N* aqueous sodium or potassium hydroxide solution. The mixture is cooled in an ice bath, and 1.5 mL of 30% hydrogen peroxide is added over 15–30 min. (■ **Caution.** *The oxidation is highly exothermic and care should be exercised, especially during the initial stages of the addition.*) After all the hydrogen peroxide is added, the solution is heated for 10 min at 50°, cooled to room temperature, and treated with crystalline potassium carbonate to produce a saturated lower aqueous layer and a clear upper THF layer. Dodecane is added as an internal standard, and the THF solution is analyzed by gas chromatography using a polar liquid phase such as Carbowax 20M or Ucon Polar. The analysis for boron generally agrees with active hydride to ±3%. In computing the boron analysis it should be noted that each mole of organoborane yields stoichiometrically *three* moles of 2-butanol. The yield of the oxidation reaction using pure, distilled tri(*sec*-butyl)borane is 95–98%.

Properties

Pure potassium tri(*sec*-butyl)hydroborate(1−) has not been isolated. The solution in THF is clear and water-white to yellow, the color largely depending upon the degree of coloration of the potassium hydride reagent used. Coloration is independent of yield and analysis. Solutions of 1.0*M* concentration show substantially greater viscosity than pure THF; above 2.0*M* the viscosity makes handling difficult, and further concentration produces a glassy material. The solutions may be stored indefinitely under argon or nitrogen in flasks fitted with a side arm closed by a stopcock and capped by a rubber serum stopper. Solutions sealed with a rubber stopper alone show progressive concentration due to selective evaporation of THF through the rubber. Potassium tri(*sec*-butyl)hydroborate(1−) reacts vigorously with water but ignition is not observed either when it is added to water or when a thin layer of the solution is spread on a glass plate in air. Solutions cause skin irritation and may cause chemical burns. The infrared spectrum in sodium chloride cells previously equilibrated with an aliquot of the solution (0.05–0.1 mm, THF reference) shows a characteristic broad band (B—H stretch) at 2025 cm^{-1}.

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8. BIS(DIMETHYLAMINO)BORANE

$$4B[N(CH_3)_2]_3 + B_2H_6 \longrightarrow 6HB[N(CH_3)_2]_2$$

Submitted by PHILIP C. KELLER*
Checked by HOWARD D. JOHNSON, II†

Bis(dimethylamino)borane may be prepared by the reduction of $ClB[N(CH_3)_2]_2$[1] or by gas-phase exchange of hydride and dimethylamino groups on boron.[2,3] The latter method, using diborane(6) and excess $B[N(CH_3)_2]_3$ and described here, is the most convenient for the synthesis of a few millimoles of product. The basic vacuum-line techniques necessary to carry out this synthesis are detailed in reference 4.

Procedure

■ **Caution.** *Diborane*(6) *reacts explosively with atmospheric oxygen and is extremely toxic. This highly volatile substance must be handled in a vacuum line at all times. The pyrolysis bulb must be inspected as detailed in the synthesis of* $[(CH_3)_2NBH_2]_2$ (*p.* 32). *The aminoboranes should be regarded as toxic.*

A dry 500-mL pyrolysis bulb similar to that used for the synthesis of $[(CH_3)_2NBH_2]_2$ (Fig. 5) is evacuated and checked for leaks on the vacuum line. The lower portion of the vessel is cooled with liquid nitrogen, and into

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this are condensed 1.43 g (10 mmol) of $B[N(CH_3)_2]_3$ * and 2.0 mmol of diborane(6).† The vessel is sealed with a hand torch at the constriction *A* and carefully placed in an oven which is then warmed from room temperature to 185° and maintained at that temperature for 24 hr. The oven is then turned off and allowed to cool before the sample is removed. A magnetic breaker is inserted in the side arm *B* and the vessel is attached to the vacuum system and evacuated. The lower part is cooled with liquid nitrogen and the break seal is opened. Usually little or no hydrogen is present. The product is pumped from the bulb into a trap at −78° (Dry Ice–trichloroethylene slush) and is subsequently purified by slow fractionation through a trap held at −30.8° (bromobenzene slush),‡ into a trap immersed in liquid nitrogen, in which the bis(dimethylamino)borane condenses. The yield is typically ca. 90%.

Properties

Bis(dimethylamino)borane is monomeric and has a vapor pressure of 8.5 torr at 0°. The gas-phase infrared spectrum shows the following absorptions: 3000 (s), 2880 (vs), 2800 (s), 2450 (s), 2400 (w, sh), 2290 (vw), 2220 (vw), 1525 (vs), 1460 (s), 1400 (vs), 1350 (m), 1300 (m), 1230 (s), 1160 (s), 1070 (s), 875 (m), 725 (m) cm^{-1}. The compound undergoes further redistribution reactions with greater quantities of diborane(6) in the gas phase at elevated temperatures,[2,5] but at 25°, in ether solution, either $[(CH_3)_2NBH_2]_2$ or μ-$[(CH_3)_2N]_2B_3H_7$ is formed with a deficiency or an excess of diborane(6), respectively.[6] The ^{11}B nmr spectrum of bis(dimethylamino)borane consists of a doublet ($J_{BH} = 126$ Hz) at $\delta 28.6$ relative to $(C_2H_5)_2O \cdot BF_3$.[7]

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* Available from Alfred Bader Chemicals, Aldrich Chemical Company, Inc., 940 West St. Paul Ave., Milwaukee, WI 53233. Prior to use the compound should be purified on the vacuum line by fractional condensation at −45° (chlorobenzene slush) to eliminate any dimethylamine formed through possible exposure to atmospheric moisture.

† Prepared as described by A. D. Norman and W. L. Jolly, *Inorganic Syntheses*, **11**, 15 (1968).

‡ The material passing −78° is a small quantity of μ-$[(CH_3)_2N]B_2H_5$. This by-product may be destroyed by condensing it into a vessel containing methanol. The material condensing at −30.8° is unreacted, excess $B[N(CH_3)_2]_3$.

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9. BIS-μ-(DIMETHYLAMINO)-DIBORANE(6)

$$2(CH_3)_2NH\cdot BH_3 \longrightarrow [(CH_3)_2NBH_2]_2 + 2H_2$$

Submitted by PHILIP C. KELLER*
Checked by GEORGE E. RYSCHKEWITSCH†

The compound bis-μ-(dimethylamino)-diborane(6), $[(CH_3)_2NBH_2]_2$, has been prepared by the pyrolysis of dimethylamine-borane, $(CH_3)_2NH\cdot BH_3$,[1–3] and by a novel iodination-deprotonation of $(CH_3)_2NH\cdot BH_3$.[4] The gas-phase pyrolysis described here is the simplest and most convenient method for the preparation of small samples, since no solvent is involved and separation problems are thus minimized. The basic vacuum-line techniques necessary for this synthesis are outlined in reference 7.

Procedure

■ **Caution.** *Although neither reactants nor products are spontaneously flammable, the boron compounds are toxic and should be handled with care. The pyrolysis bulb should be carefully inspected to ensure that it is completely free from cracks or imperfections that could result in an implosion upon evacuation. The volume of the bulb is such that the gas pressure at pyrolysis temperature is no more than 1.5 atm. If the scale of this synthesis is changed, the bulb size should be altered accordingly.*

A dry pyrolysis bulb (Fig. 5), constructed from a 500-mL round-bottomed flask and previously checked for leaks, is charged with 1.18 g (20 mmol) of dimethylamine-borane.‡ The vessel is quickly evacuated to less than 1 torr,

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‡ Available from Research Organic/Inorganic Chemical Corp., 11686 Sheldon St., Sun Valley, CA 91352. A convenient synthesis is detailed in reference 6.

the lower portion is cooled with liquid nitrogen to prevent sublimation of the reactant, and the bulb is pumped down to a high vacuum and torch-sealed at the constriction *A*. The bulb is placed in an oven which is then turned on and warmed to 180°. The pyrolysis is carried out at this temperature for 2 hr; then the oven is turned off and allowed to cool before the bulb is removed. Neither temperature nor heating time should be *less* than these values. A magnetic breaker is inserted in the side arm *B*, and the vessel is attached to the vacuum line and evacuated. The lower portion of the apparatus is cooled with liquid nitrogen and the break seal is opened. Because the sudden release of hydrogen pressure into the vacuum line can sometimes propel the breaker upward with considerable speed, it is advisable to cushion the upper surface of the inlet port with glass wool to avoid possible breakage.

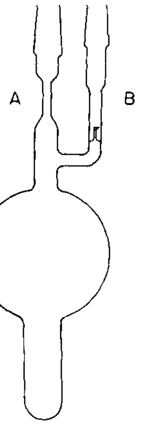

Fig. 5. Pyrolysis bulb.

For purification and isolation, the volatile products are pumped through U traps maintained at −30.8° (bromobenzene) and −63.5° (chloroform). Pure crystals of $[(CH_3)_2NBH_2]_2$ (yield ca. 90%), having the properties given below, slowly condense in the trap held at −63.5°.

Properties

The vapor pressure of $[(CH_3)_2NBH_2]_2$ obeys the relationship $\log P = 10.1970 - 2721.4/T$[1] (8 torr/20°). The gas-phase infrared spectrum shows absorptions at 3025 (m), 2980 (s), 2970 (s), 2875 (m), 2820 (w), 2450 (vs), 2370 (s), 2230 (w), 1475 (m), 1370 (w), 1240 (m), 1200 (m), 1189 (m), 1150 (vs), 1050 (w), 1042 (w), 960 (s), 810 (w) cm^{-1}. The compound is a dimer at room temperature, but above 180° an appreciable concentration of monomer is present.[5] The mass spectrum shows only peaks characteristic of the monomer (parent ion *m/e* 57) when a heated inlet system is used; if all inlet heaters are turned off, the spectrum shows an envelope of peaks characteristic of the dimer (parent ion *m/e* 114). The melting point is 74.5–75°.[3]

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10. μ-(DIMETHYLAMINO)-DIBORANE(6)

$$(CH_3)_2NH\cdot BH_3 + K \longrightarrow K[(CH_3)_2NBH_3] + \tfrac{1}{2}H_2$$

$$K[(CH_3)_2NBH_3] + 2NaBH_4 + \tfrac{1}{2}I_2 \longrightarrow Na[[(CH_3)_2N](BH_3)_2] + K[BH_4] + NaI + \tfrac{1}{2}H_2$$

$$Na[[(CH_3)_2N](BH_3)_2] + \tfrac{1}{2}I_2 \longrightarrow \mu\text{-}[(CH_3)_2N]B_2H_5 + NaI + \tfrac{1}{2}H_2$$

Submitted by PHILIP C. KELLER*
Checked by GEORGE E. RYSCHKEWITSCH†

The volatile compound μ-$[(CH_3)_2N]B_2H_5$ has been prepared by the gas-phase reaction of $[(CH_3)_2NBH_2]_2$ with diborane(6) at 80°,[1] and by the reaction of $Na[(CH_3)_2NBH_3]$[2] or $Li[N(CH_3)_2]$[3] with excess diborane(6) in diethyl ether solution. The method described here[4] offers the advantages that diborane(6) is not used and that reactions are carried out with bench apparatus with a vacuum line employed only for final separation and purification. Basic vacuum-line techniques are outlined in reference 9.

Procedure

■ **Caution.** *The product* μ-$[(CH_3)_2N]B_2H_5$ *is toxic and spontaneously flammable. It should be handled in a vacuum line. All apparatus should be carefully inspected for cracks or flaws that could cause an implosion on evacuation.*

The apparatus shown in Fig. 6 is purged with nitrogen, and 1.18 g (20 mmol) of $(CH_3)_2NH\cdot BH_3$‡ is added to the flask; this is followed by

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‡ Available from Research Organic/Inorganic Chemical Corp., 11686 Sheldon St., Sun Valley, CA 91352. A convenient synthesis is detailed in reference 10.

75 mL of dry diglyme.* A 2.4-g piece of freshly cut potassium metal† is then dropped into the vessel and the solution is stirred magnetically until hydrogen evolution stops (about 3 hr). The remaining piece of potassium is removed, under nitrogen flow, with long forceps. A 2.25-g (60.0 mmol) portion of sodium tetrahydroborate(1 −) is added to the flask, and the addition funnel is filled with a solution of iodine (5.08 g, 20.0 mmol) in 30 mL of dry diglyme. While the mixture is stirred vigorously, the iodine solution is added dropwise over a 1-hr period. The gas outlet on the addition funnel is then replaced with a stopper and the apparatus is quickly evacuated. A −45° slush (chlorobenzene) is added to the Dewar condenser and an oil bath maintained at 60° is placed around the reaction flask. The diglyme is allowed to reflux against the −45° condenser as more volatile materials evaporating from the apparatus are pumped through traps at −45° and −196°. During the approximately 80 min required for the refluxing, it is necessary to keep the chlorobenzene slush at −45° by occasionally adding a small quantity of liquid nitrogen and carefully stirring with a wooden dowel. Fractionation of

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* Diglyme [bis(2-methoxyethyl) ether] is very hygroscopic. It should be dried with and distilled from sodium hydride prior to use. The checkers dried the diglyme over sodium/benzophenone until a blue color appeared.

† Potassium metal is extremely reactive and should be exposed only briefly to the atmosphere. The checkers added the potassium in an inert-atmosphere box.

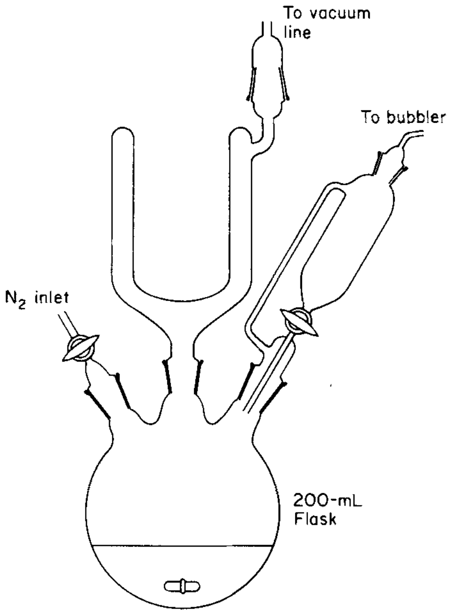

Fig. 6. Apparatus for the preparation of μ-(dimethylamino)-diborane(6).

the material in the −196° trap through −126° (methylcyclohexane slush) separates pure μ-$[(CH_3)_2N]B_2H_5$ from a small amount of diborane(6) by-product. The latter may be destroyed by condensing it into a bulb containing methanol. Yields are typically 40–50%.

Properties

The vapor pressure of μ-$[(CH_3)_2N]B_2H_5$ obeys the relationship $\log P = 2158.56/T + 1.75 \log T - 0.008061T + 7.51883$[1] (101 torr at 0°). The gas-phase infrared spectrum has been reported in detail.[5] The compound is a useful intermediate in the synthesis of other boron nitrogen compounds, including those containing NBNB[6] and PBNB[7] chains, and $Na[(CH_3)_2N(BH_3)_2]$.[8] The compound can be stored at 25° for months in sealed, evacuated Pyrex tubes. It is soluble in ethers and aromatic hydrocarbons, but is attacked by protic solvents.

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11. TRIHYDRIDO(TRIMETHYLAMINE)ALUMINUM AND (DIETHYLAMINO)HYDRIDOALUMINUM COMPLEXES

Submitted by ROGER A. KOVAR* and JOHN OWEN CALLAWAY†
Checked by CHARLES H. VAN DYKE‡ and NEMESIO D. MIRO‡

While lithium tetrahydridoaluminate(1−) is used extensively as a reducing agent,[1] relatively little is known about the utility of amine and/or amino complexes (compounds of the general formulas $H_3Al(NR_3)$ and $H_{3-n}Al$-

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$(NR_2)_n$; $n = 1$ and 2, respectively). Limited uses of these derivatives as polymerization catalysts,[2] reducing agents,[3] and synthetic intermediates[4] have been described.

The following procedures, based on modification of literature methods,[5–9] describe the preparation of benzene solutions of trihydrido(trimethylamine)aluminum, $(CH_3)_3N \cdot AlH_3$; (diethylamino)dihydridoaluminum, $H_2Al[N(C_2H_5)_2]$; and bis(diethylamino)hydridoaluminum, $HAl[N(C_2H_5)_2]_2$. The products can be isolated from solution by removal of benzene under vacuum. They can be purified further by vacuum sublimation in the case of $(CH_3)_3N \cdot AlH_3$ and $H_2Al[N(C_2H_5)_2]$ and by vacuum distillation in the case of $HAl[N(C_2H_5)_2]_2$. Additional aminohydridoaluminum complexes can be prepared by the procedures described here by substituting other secondary amines for diethylamine.[6]

■ **Caution.** *Hydride compounds of aluminum are extremely air- and moisture-sensitive and may ignite if exposed to air. The use of Schlenk ware, syringes, and/or an inert atmosphere are necessary for handling these compounds. An excellent reference of necessary techniques is given by Shriver.*[10] *All reactions should be conducted in a well-ventilated fume hood.*

A. TRIHYDRIDO(TRIMETHYLAMINE)ALUMINUM

$$Li[AlH_4] + [(CH_3)_3NH]Cl \xrightarrow{\text{benzene}} (CH_3)_3N \cdot AlH_3 + LiCl + H_2$$

Procedure

Lithium tetrahydridoaluminate(1−) may be used as obtained commercially.* Trimethylammonium chloride† is dried under vacuum at 100° for 1 hr. The benzene solvent should be dried by heating at the reflux temperature for a period in excess of 1 hr over lithium tetrahydridoaluminate(1−) followed by distillation under a nitrogen atmosphere. In a nitrogen-filled dry box, 47.8 g (0.50 mol) of trimethylammonium chloride is transferred to a Schlenk tube. To a 1000-mL three-necked flask containing a large, egg-shaped stirring bar, 22.8 g (0.60 mol) of lithium tetrahydridoaluminate(1−) is added. A 20% excess of lithium tetrahydridoaluminate(1−) is used in order to eliminate the possibility of obtaining

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chloro aluminum complexes. The apparatus depicted in Fig. 7 is assembled and securely clamped on the bench top while proper precautions are taken to avoid air contamination. Dry benzene (500 mL) is added to the lithium tetrahydridoaluminate(1 −), by means of a syringe, through the rubber septum of the T-type hose connector. The magnetic stirring motor is started as soon as possible with the first addition of benzene to avoid caking of the tetrahydridoaluminate. The reaction is initiated by slow addition of trimethylammonium chloride. This is accomplished by slowly rotating the gooseneck attached to the Schlenk tube, thereby allowing the white solid to fall into the lithium tetrahydridoaluminate(1 −)-benzene mixture. After the addition of 3–5% of the trimethylammonium chloride over a period of 5–15 min, frothing is observed in the reaction flask. Rapid addition of trimethylammonium chloride should be avoided, since the reaction is exothermic and much frothing will occur. The remaining trimethylammonium chloride is added slowly over a period of approximately 2 hr. After all the trimethylammonium chloride has been added, a dark-gray mixture of unreacted lithium tetrahydridoaluminate and by-product lithium chloride will remain in the reaction flask. Filtration of the mixture is carried out by means

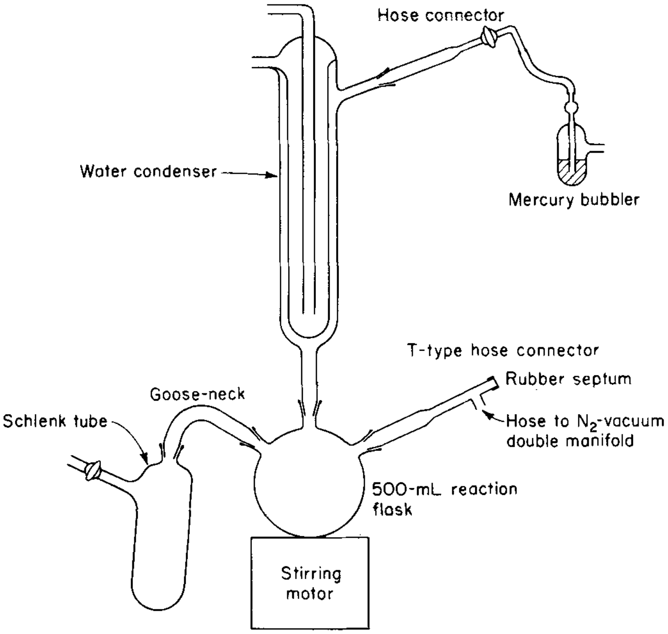

Fig. 7. Apparatus for the preparation of trihydrido(trimethylamino)aluminum.

of a fritted-filter funnel of medium porosity.* Unreacted lithium tetrahydridoaluminate(1−) will remain in both the reaction flask and the filter funnel and should be decomposed carefully by adding an inert diluent such as heptane or kerosene, then carefully adding ethanol and, finally, water while stirring the mixture. The filtrate is a clear, colorless solution of $(CH_3)_3N \cdot AlH_3$ in benzene. Yields of $(CH_3)_3N \cdot AlH_3$ based on the experimental concentration and volume of the filtrate are found to range from 70 to 80%.

Analysis is accomplished by standard vacuum-line techniques. A 1.00-mL aliquot of $(CH_3)_3N \cdot AlH_3$ in benzene solution is placed in an ampul and attached to a multipurpose vacuum line equipped with gas-separation traps and a Toepler pump and is hydrolyzed by using a mixture composed of equal amounts of water and concentrated hydrochloric acid.

$$H_3Al \cdot N(CH_3)_3 + 4HCl(aq) \longrightarrow AlCl_3 + 3H_2 \uparrow + [HN(CH_3)_3]Cl$$

The number of moles of hydrogen gas evolved is measured from standard *PVT* relationships. The aluminum trichloride remaining in solution is analyzed for aluminum by using standard EDTA† solution and dithizone indicator. The active hydride/aluminum ratio was found to be 3.0 : 1.0 in all preparations.

A separate 1.00-mL aliquot is hydrolyzed with water and analyzed for Cl^- with a modified Volhard procedure. All samples were found to be chlorine-free. Solid $(CH_3)_3N \cdot AlH_3$ is obtained by removing the benzene solvent under vacuum and allowing the solid to dry in a stream of dry nitrogen. Complete removal of benzene under vacuum should not be attempted because the vapor pressure of $(CH_3)_3N \cdot AlH_3$ is reasonably high at room temperature, and significant quantities will be transferred in the process. Solid $(CH_3)_3N \cdot AlH_3$ having a melting point of 77–78° is obtained in 66% yield by allowing benzene to evaporate under a stream of dry nitrogen.

Properties

A ^1H nmr spectrum using a Varian A-60-A instrument is clearly diagnostic of $(CH_3)_3N \cdot AlH_3$. Signals occurring at $\tau 7.93$ (singlet) and $\tau 6.02$ (singlet) of relative intensities 3.15 : 1.00 are assigned to methyl hydrogen atoms and hydridic hydrogen atoms, respectively (benzene solvent signal as internal standard). Benzene solutions of $(CH_3)_3N \cdot AlH_3$ are stable and remain clear and colorless for periods in excess of one year at temperatures

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* See reference 10, page 147.

† Ethylenediamine tetraacetic acid.

of 10° or lower. Storage of benzene solutions of $(CH_3)_3N \cdot AlH_3$ at or above room temperature should be avoided since these solutions develop relatively large quantities of aluminum metal flakes and liberate hydrogen on standing for periods in excess of 24 hr.

B. (DIETHYLAMINO)DIHYDROIDALUMINUM

$$(CH_3)_3N \cdot AlH_3 + (C_2H_5)_2NH \xrightarrow{\text{benzene}} H_2Al[N(C_2H_5)_2] + H_2 + N(CH_3)_3$$

Procedure

An apparatus consisting of a 250-mL side-arm Schlenk flask fitted with a Claisen head to which are attached a 50-mL pressure-equalizing dropping funnel and a water condenser is assembled. The water condenser is connected to a mercury-filled bubbler by means of a hose connector. The addition funnel is fitted with a T-type hose connector one arm of which is fitted with a septum and the other arm of which is attached to a source of dry nitrogen and/or a vacuum. A magnetic stirring bar is placed in the Schlenk flask and the apparatus is evacuated to remove air and moisture. Dry nitrogen is admitted and a benzene solution of $(CH_3)_3N \cdot AlH_3$ (120 mL of a 0.775*M* soln, 0.093 mol) is added to the reaction flask through the side arm by means of a syringe. Diethylamine* (9.57 mL, 0.093 mol) which is distilled under nitrogen atmosphere and stored over 8–12 mesh molecular sieve† is added with a syringe to the 50-mL pressure-equalizing dropping funnel. Diethylamine is added to the magnetically stirred benzene solution of $(CH_3)_3N \cdot AlH_3$ in a dropwise fashion over a 30-min period. Continuous bubbling occurs during the addition; the reaction solution remains clear and colorless. Three 5-mL portions of dry benzene are used to rinse any residual diethylamine from the walls of the dropping funnel into the reaction flask. The $H_2Al[N(C_2H_5)_2]$ is isolated by removing the benzene solvent and trimethylamine under vacuum at room temperature. The conversion is found to be essentially quantitative.

The H/Al ratio, as well as percent composition of active hydride and aluminum are determined by analysis of a weighed portion of a solid sample using techniques described in the analysis of $(CH_3)_3N \cdot AlH_3$. The H/Al ratio is found to be 2.00 : 1.00. *Anal.* Calcd. for wt % of active hydride and aluminum: H, 1.99; Al, 26.7. Found: H, 2.00; Al, 26.6.

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† J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ 08865.

Properties

Solid $H_2Al[N(C_2H_5)_2]$ (mp 45°) can be sublimed under vacuum at room temperature. The infrared spectrum of this compound as a mull in Nujol exhibits Al—H stretching and deformation frequencies at 1839 and 734 cm^{-1}, respectively. The compound is thermally unstable above the melting point, forming hydrogen, aluminum, and $HAl[N(C_2H_5)_2]_2$ at 180°.[6]

$$2H_2Al[N(C_2H_5)_2] \longrightarrow Al + \tfrac{3}{2}H_2 + HAl[N(C_2H_5)_2]_2$$

The compound can be stored indefinitely at room temperature in a water- and oxygen-free environment.

C. BIS(DIETHYLAMINO)HYDRIDOALUMINUM

$$(CH_3)_3N\cdot AlH_3 + 2(C_2H_5)_2NH \longrightarrow HAl[N(C_2H_5)_2]_2 + 2H_2 + N(CH_3)_3$$

Procedure

The apparatus described in the preparation of $H_2Al[N(C_2H_5)_2]$ is used again, but forcing conditions and additional time are required for the preparation of $HAl[N(C_2H_5)_2]_2$. The active hydride/aluminum ratio of a 2 : 1 mixture of diethylamine and $(CH_3)_3N\cdot AlH_3$ in benzene was found to be 1.53 : 1.00 after simple stirring at room temperature for 10 hr. Unreacted diethylamine is indicated by the high active hydride/aluminum ratio. This ratio was reduced to 1.13 : 1.00 and 1.02 : 1.00 after heating at reflux temperature for 7 hr and 22 hr, respectively. Bis(diethylamino)hydridoaluminum is prepared conveniently by mixing $(CH_3)_3N\cdot AlH_3$ and diethylamine in 1 : 2 molar ratio in benzene solution and heating the mixture at reflux temperature for at least 24 hr. Pure, liquid $HAl[N(C_2H_5)_2]_2$ is obtained by removing benzene under vacuum. This liquid product can be analyzed by procedures analogous to those described for analysis of $H_2Al[N(C_2H_5)_2]$. The active hydride/aluminum ratio is found to be 1.0 : 1.0. *Anal.* Calcd.: hydride, 0.582 wt %; Al, 15.7 wt %. Found: hydride, 0.412 wt %; Al, 16.0 wt %.

Properties

The infrared spectrum of neat $HAl[N(C_2H_5)_2]_2$ exhibits Al—H stretching and deformation frequencies at 1822 and 692 cm^{-1}, respectively. The compound can be distilled under high vacuum using a short-path distillation apparatus. It decomposes at 240° to give products of unknown composition.[6] The compound can be stored indefinitely at room temperature in an oxygen- and water-free environment.

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12. TRIHYDRIDO(TRIMETHYLAMINE)GALLIUM

$$Li[GaH_4] + [(CH_3)_3NH]Cl \xrightarrow{(C_2H_5)_2O} (CH_3)_3N\cdot GaH_3 + LiCl + H_2$$

Submitted by D. F. SHRIVER* and A. E. SHIRK*
Checked by J. A. DILTS†

Previously reported syntheses of the title compound have involved vacuum-line techniques.[1,2] We describe here a procedure in which commercially available Schlenk-type glassware is used.‡ The synthesis involves the reaction of the protic hydrogen of trimethylammonium chloride with a hydridic hydrogen of $[GaH_4]^-$, to liberate hydrogen and form the desired amine gallium complex.

Procedure

Prior to use, all Schlenk ware should be put through several cycles of pumping and filling with dry nitrogen. A nitrogen atmosphere or vacuum is maintained in the apparatus throughout the synthesis.[3] The source of vacuum should be a good, two-stage mechanical pump which should be protected by a Dry Ice–cooled or liquid-nitrogen–cooled trap. Lithium tetrahydridogallate§ and trimethylammonium chloride are transferred in a

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† Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, NC 27412.

‡ Kontes Glass Co., Vineland, NJ 08360.

§ $Li[GaH_4]$ may be used without isolation from Synthesis 13.

nitrogen glove bag or glove box. Finely ground commercial trimethylammonium chloride should be dried by mixing it with 2,2-dimethoxypropane and then removing the dehydrating reagent under vacuum.

In a 50-mL Schlenk flask containing a magnetic stirring bar is placed 0.65 g (8.1 mmol) of $Li[GaH_4]$ and 20 mL of dry diethyl ether. If the active hydrogen analysis is low, a proportionately greater quantity of $Li[GaH_4]$ must be employed. A solids-addition tube containing slightly *less* than the stoichiometric amount of trimethylammonium chloride (0.71 g, 7.5 mmol) is fitted on top of the Schlenk flask. The side arm of this Schlenk flask is hooked to a nitrogen source and a bubbler to allow the escape of hydrogen produced by the reaction (Fig. 8).

The Li $[GaH_4]$ solution is stirred and cooled to −78° in a Dry Ice–2-propanol bath. Trimethylammonium chloride is gradually added to the stirred $Li[GaH_4]$ solution. After the final addition, the mixture is allowed to stir for 0.5 hr; then it is warmed to 0° and stirred for an additional 2 hr to ensure complete reaction. The mixture is then cooled in the range −40 to −50° (2-propanol with occasional addition of Dry Ice works well) and the diethyl ether is removed under vacuum while the solution is being stirred.

At this point, the trihydrido(trimethylamine)gallium should be sublimed immediately into a high-vacuum line or into a Schlenk tube as illustrated in Fig. 9 and described below. A loose, glass-wool plug is employed in this apparatus to prevent lithium chloride particles from flying into the sublimation receiver. The system is evacuated through tube *A* while the sublimation receiver is cooled to −78° with Dry Ice–2-propanol. (Initial evacuation of the apparatus should be carried out slowly to prevent lithium chloride particles from being swept along with the nitrogen.) Owing to the low volatility

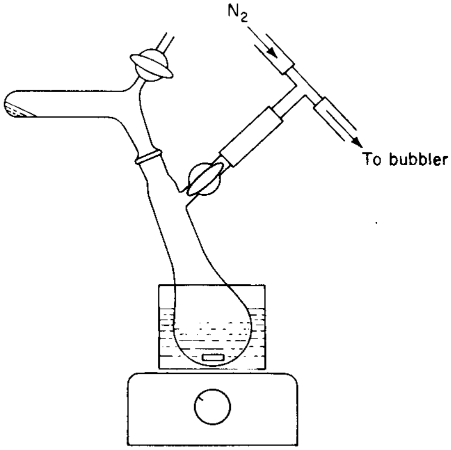

Fig. 8. Setup for the addition of $[(CH_3)_3NH]Cl$ *to* $Li[GaH_4]$. *The pear-shaped Schlenk flask facilitates solvent removal.*

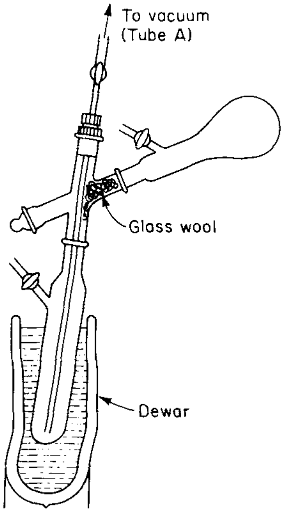

Fig. 9. Sublimation of $[(CH_3)N]GaH_3$. *The commercially available S.T. 14/20 Teflon adapter might be replaced by a properly fitting one-hole rubber stopper. An internal diameter of at least 30 mm is recommended for the receiver to reduce the problem of the sublimate bridging to the central tube.*

of trihydrido(trimethylamine)gallium, ca. 2 torr at room temperature, the system is continuously evacuated through tube *A* during the sublimation, thus preventing the buildup of noncondensables which would stop the sublimation. To avoid loss of product due to bridging of the sublimate between the receiver walls and the central tube, the receiver is cooled immediately prior to the evacuation of the apparatus and the cold zone is worked up on the receiver as the sublimation proceeds. The sublimation is judged complete when, upon cooling a spot near the top of the receiver with a small chunk of Dry Ice, no trihydrido(trimethylamine)gallium is condensed. The sublimed product must be stored under nitrogen. For long-term storage, reduced temperatures as well as an inert atmosphere are advised. The yield is about 73% based on trimethylammonium chloride. Analysis is conveniently performed by pyrolysis in a sealed tube followed by hydrogen and trimethylamine collection and measurement in a vacuum line.[4] *Anal.* Calcd. for $C_3H_{12}NGa_3$: H (from Ga—H), 2.29; $(CH_3)_3N$, 44.81. Found: H (by pyrolysis), 2.29; $(CH_3)_3N$, 44.7. Alternatively the sample may be hydrolyzed by dilute hydrochloric acid to give active hydrogen, and the resulting solution may be analyzed for gallium (see references 8 and 9 of Synthesis 13).

Properties

Trihydrido(trimethylamine)gallium generally condenses as clear needle-like crystals having a melting point of 69°.[1,2] It will add a second mole of trimethylamine, forming the five-coordinate complex trihydridobis(trimethylamine)gallium which has a trimethylamine dissociation pressure of 378 torr at 0°. Trihydrido(trimethylamine)gallium is hydrolyzed by water. It provides a good intermediate for other gallium hydride derivatives.[5,6] The vibrational spectrum and crystal structure have been reported.[1,7,8]

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13. LITHIUM TETRAHYDRIDOGALLATE(1−)

$$GaCl_3 + 4LiH \xrightarrow{(C_2H_5)_2O} Li[GaH_4] + 3LiCl\downarrow$$

Submitted by A. E. SHIRK* and D. F. SHRIVER*
Checked by J. A. DILTS† and R. W. NUTT‡

Lithium tetrahydridogallate, which was first prepared by Finholt, Bond, and Schlesinger,[1] is a very useful starting material for the preparation of gallium hydride derivatives.[2,3] The present synthesis is based on an adaptation of the original preparation.[1,4] Since gallium-hydrogen bonds are susceptible to hydrolysis, it is necessary to perform the preparation in the absence of air. The procedure described is based on the use of Schlenk-type inert-atmosphere techniques.

Procedure

All reactions are carried out in Schlenk ware which, prior to use, is put through several cycles of pumping and purging with dry nitrogen. The source of vacuum should be a two-stage mechanical pump which is in good working condition. The pump should be protected by a Dry Ice–cooled or preferably a liquid-nitrogen–cooled trap. Lithium hydride and gallium trichloride must be transferred in a glove bag or glove box under a dry nitrogen

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atmosphere. General procedures for these types of inert-atmosphere manipulations are described in detail elsewhere.[5]

In a 50-mL Schlenk flask* equipped with a magnetic stirring bar are placed 1.32 g finely powdered lithium hydride (0.166 mol)† and 10 mL of dry, freshly distilled diethyl ether. A dropping funnel equipped with a Teflon-in-glass valve and containing 1.77 g gallium(III) chloride (0.010 mol) in 10 mL of dry, freshly distilled diethyl ether (dissolution is exothermic) is fitted to the Schlenk flask and the outlet arms are linked as illustrated in Fig. 10 to equalize pressure.

The LiH-$(C_2H_5)_2O$ slurry is cooled to 0° to moderate the ensuing reaction with gallium(III) chloride,‡ and the latter solution is added dropwise with stirring over a 1-hr period. The reaction mixture is then warmed to room temperature and stirred for 5 hr. A 10-mL portion of dry toluene is

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* Schlenk ware is commercially available from Kontes Glass Co., Vineland, NJ 08360 (Airless-Ware), and Ace Glass Co., Vineland, NJ 08360 (No-Air Glassware).

† To obtain a chloride-free product a fourfold excess of *finely* powdered LiH is required.

‡ The checker notes that when working on a larger scale it is necessary to employ a lower temperature (−78° is convenient) to moderate the reaction. Slow warming of the stirred mixture also is recommended.

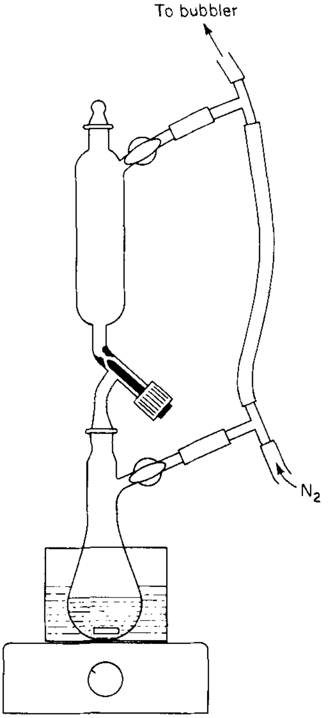

Fig. 10. Setup for the addition of $GaCl_3-(C_2H_5)_2O$ *solution to a* $LiH-(C_2H_5)_2O$ *slurry. The pressures in the dropping funnel and Schlenk flask are equalized by linking the two side arms to a common nitrogen source and bubbler.*

added, and the mixture is stirred for 0.5 hr. (Toluene is not necessary but it facilitates subsequent removal of diethyl ether from Li[GaH_4]). The mixture is then filtered with a medium-porosity Schlenk-ware filter. Prior to use this filter should be heated and put through several purging cycles to remove moisture. The filtrate is collected in a 50-mL Schlenk flask containing a magnetic stirring bar. This clear filtrate is stirred rapidly as the solvent is pumped off overnight. The resulting Li[GaH_4] forms initially as a white solid which decomposes slightly to a gray material upon complete removal of ether. The yield is 0.65 g, or 81% based on gallium(III) chloride. *Anal.* Calcd. for H_4GaLi: (hydridic H)/Ga ratio, 4.00. Found: (hydridic H)/Ga ratio, 3.97. Procedures for active hydrogen and gallium analyses are available in the literature.[8,9] Test for Cl^-, negative.

Properties

Lithium tetrahydridogallate(1−) is a moisture-sentitive solid similar in many respects to lithium tetrahydridoaluminate(1−). It reacts with protic solvents, but is soluble without reaction in a variety of ethers. The solid decomposes slowly at room temperature, but may be stored with decomposition at −78° under an inert atmosphere or in vacuum. Ether solutions are stable for at least several days. A variety of gallium hydride derivatives may be prepared from Li[GaH_4], including $(CH_3)_3N\cdot GaH_3$.[1,2,6] Infrared and Raman data have been reported for $[GaH_4]^-$.[7]

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14. SODIUM AND POTASSIUM TETRAHYDRIDOGALLATE(1 −)

Submitted by J. A. DILTS* and W. R. NUTT†
Checked by R. A. KOVAR‡

Although Finholt, Bond, and Schlesinger[1] reported the synthesis of lithium tetrahydridogallate(1 −) in 1947,[1] little is known about the sodium and potassium salts of this mild reducing agent. Unlike the corresponding lithium compound, the sodium and potassium salts are stable at room temperature. The procedure reported here is based on a modification of a report by Zakharkin and coworkers[2] and can be generalized for use in preparation of the corresponding aluminum hydride complexes. The air- and moisture-sensitive hydride compounds involved in this preparation require use of an inert-atmosphere (nitrogen) glove box or Schlenk[3] type of equipment.

Solvents and Reagents

■ **Caution.** *Sodium-potassium alloy reacts vigorously with air and must be handled in a good inert-atmosphere box. Solvents should be dried first over calcium hydride or have a very low water content before one attempts to dry them further over sodium-potassium alloy.*

Except as noted, solvents used in this procedure are purified by distillation from sodium-potassium alloy–diphenylketyl under a nitrogen atmosphere.[3] Solvents are best dried initially over calcium dihydride and then decanted under a nitrogen atmosphere onto the alloy. After an initial reflux of 1–2 hr, benzophenone is added and reflux is continued until the intense blue or purple color of the ketyl is evident. Diglyme [bis(2-methoxyethyl) ether] is distilled from sodium tetrahydridoaluminate(1 −) (after first drying over calcium dihydride, overnight) under vacuum. All solvents are stored in O-ring flasks (ethylene-propylene O rings for ether solvents) which are equipped with right-angle Teflon-glass needle valves that allow for syringe withdrawal of solvent while a pure nitrogen atmosphere is maintained (Fig. 11). After several evacuation and nitrogen-refill cycles, the needle valve is opened and removed to permit syringe sampling of the contents under nitrogen purge.

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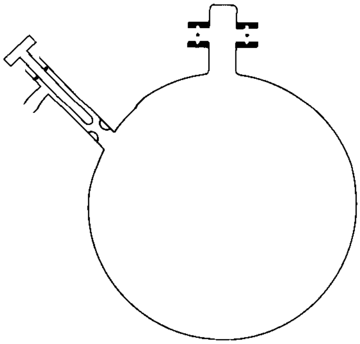

Fig. 11. O-ring storage flask for solvents and solutions of Li(GaH$_4$). *O-ring joints are standard O 9/18. Needle valve is 4-mm Teflon in glass.*

Sodium and potassium hydrides are obtained from commercial sources* as mineral oil dispersions. The mineral oil is removed by washing with dried hexane either in a Schlenk frit under a nitrogen atmosphere or in a glove box. (■ **Caution.** *After the protective mineral oil has been removed, the dry sodium and potassium hydrides are pyrophoric when exposed to moist air. They must be handled in the dry state under a nitrogen atmosphere either in a glove box or glove bag.*) The solid metal hydride is weighed into a storage tube in a glove bag or dry box; the tube is then capped and attached under nitrogen flush to the Schlenk flask containing the ether solution of Li[GaH$_4$]. The metal hydride can then be added by a combination of tipping and tapping the tube containing the solid.†

A solution of Li[GaH$_4$] in diethyl ether is prepared by the standard methods,‡[1] and is stored in a needle-valve O-ring flask. The concentration of Li[GaH$_4$]-ether solution is determined by hydrolysis of a known volume of the solution followed by gallium determination by ethylenediamine-tetraacetic acid, disodium salt using copper-PAN [1-(2-pyridylazo)-2-naphthol copper complex] as the indicator.[4] It is assumed that all the gallium is present as the tetrahydrogallate. Only an approximate concentration need be determined since an excess of sodium hydride or potassium hydride is used.

Diethyl ether solutions of Li[GaH$_4$] are converted to tetrahydrofuran (THF), monoglyme (dimethoxyethane), or diglyme solutions by adding an equal volume of the appropriate solvent to a diethyl ether solution in a Schlenk flask, and then removing the more volatile diethyl ether by vacuum distillation. In the case of THF, after the total volume of the solution has

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* Ventron Corporation, Alfa Products, P.O. Box 159, Beverly, MA 01915.

† The apparatus used is identical with that shown in Fig. 8, Synthesis 12, this volume.

‡ See Synthesis 13, this volume.

been reduced by one-half, a second equal volume of THF is added and the volume of the solution is reduced by one-half again under vacuum. When monoglyme or diglyme is used, a precipitate of the glyme–Li[GaH_4] complex will form, but this redissolves as the diethyl ether is removed.

Procedure

The preparation of sodium tetrahydridogallate(1 –). Sodium hydride (1.57 g, 65.4 mmol) is added slowly to a THF solution of Li[GaH_4] (3.43 g, 43 mmol in 150 mL THF) at room temperature.* The mixture is stirred magnetically for 32 hr under a nitrogen atmosphere and filtered through diatomaceous earth (dried at 130° under vacuum) in a Schlenk frit. After removal of the lithium hydride and excess sodium hydride, the filtrate is concentrated to a volume of 50 mL, and on addition of 150 mL of dry toluene, a white crystalline precipitate is formed. Further evaporation to a total liquid volume of 75 mL and subsequent addition of 75 mL of toluene assures more complete recovery. The resulting solid Na[GaH_4] is isolated by vacuum filtration in nitrogen to yield 3.12 g (32.3 mmol) of product (75% yield). It is desirable not to remove all the diethyl ether before the toluene is added, since difficulty may be experienced in removing all the ether from a solid ether solvate if one should form. When isolated by the method described, the Na[GaH_4] is essentially free of ether. *Anal.* (hydridic H)/Ga ratio, found: = 3.74 : 1.†

The preparation of potassium tetrahydridogallate(1 –). Basically the same procedure is used as for sodium tetrahydridogallate(1 –) except that potassium hydride is used, with monoglyme or diglyme as the solvent. A diglyme solution of Li[GaH_4] is prepared as described above (2.71 g, 34 mmol of the hydride in 60 mL). Potassium hydride (2.64 g, 65.8 mmol) is then added, and the resulting mixture is stirred magnetically for 42 hr at ambient temperature. The excess potassium hydride and lithium hydride are removed by filtration, and the volume of the filtrate is reduced to 5–10 mL under vacuum. Dry toluene (75 mL) is added to effect precipitation of the product. Precautions concerning the removal of all the diethyl ether should be taken, as described in the synthesis of Na[GaH_4]. Yield is 1.77 g (16 mmol) or 50%. *Anal.* (hydridic H)/Ga ratio, found: = 3.9 : 1.‡

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* The apparatus used is identical with that shown in Fig. 8.

† Checkers report 76% yield. *Anal.* Calcd. for Na[GaH_4]: Ga, 72.0; H, 4.1; Na, 24.0. Found: Ga, 70.4; H, 4.1; Na (by difference), 25.5.

‡ Checkers report 82% yield. *Anal.* Calcd. for K[GaH_4]: Ga, 61.4; H, 3.5; K, 35.1. Found: Ga, 60.4; H, 3.5; K (by difference), 36.1.

Properties

Both gallium hydride complexes are obtained as white, crystalline powders which remain white when stored at room temperature in the absence of air and moisture for periods in excess of one year. Their reaction with water is moderate when compared to the analogous aluminum hydride complexes. They undergo typical reactions for an $[MH_4]^-$ species, e.g.,

$$Na[GaH_4] + R_3N \cdot HCl \longrightarrow R_3N \cdot GaH_3 + NaCl + H_2$$

The sodium compound begins to decompose under an argon atmosphere at 165°, while the potassium compound begins to decompose at about 230°. Both of these compounds are considerably more stable than solid $Li[GaH_4]$ which is reported[5] to lose hydrogen rapidly at 70°.

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II. TRANSITION METAL HYDRIDE COMPLEXES

HERBERT D. KAESZ*

That studies of transition metal hydride complexes have undergone rapid expansion in recent years is attested to by the increasing number of reviews[1] and a collected volume on this subject.[2] This activity stems no doubt from the interest in the novel geometries and valence properties exhibited by the compounds in this class as well as in their identification as catalysts or intermediates in a number of processes such as hydroformylation, hydrosilylation, hydrogenation, oligomerization and/or isomerization of olefins.[1,2,3] Hydridometal complexes have also been shown to effect hydrogen/deuterium exchange in various hydrocarbons and their derivatives.[4] Such applications are mentioned where appropriate in the syntheses that are collected both in the present volume and in previous volumes. These latter are summarized in Table I. Perhaps it would be appropriate to single out for special mention the optically active complex hydridobis[(+)-diop]-rhodium(I) (see Synthesis 22 below), which is a catalyst in the recently developed area of the synthesis of optically active derivatives by hydrogenation of pro-chiral olefins.

To complement the catalytic function one may anticipate use of transition metal hydrides also as reagents for organic synthesis based on the recent elegant demonstration of hydrozirconation and related reactions by J. Schwartz and coworkers.[5] For such applications, obviously, derivatives of the less precious transition metals would be desirable.

The variety of methods available in the synthesis of hydride complexes[1,2] is well represented in the present and previously published syntheses. These include protonation of anionic derivatives, metathesis of halogen derivatives with the main group metal hydrides or complex hydrides, direct reaction with elemental hydrogen, and hydrogen transfer from coordinated groups and/or solvent. These are not presented in any systematic order because of the vagaries inherent in the process whereby syntheses are solicited and/or independently submitted. It is hoped that syntheses in this interesting and important class of compounds will continue to find their way into these collections. In this connection it should be mentioned that syntheses originally submitted for the present volume but whose processing has not been completed will be included in the next volume of *Inorganic Syntheses*.

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TABLE 1 Hydrido–Transition Metal Complexes Appearing in *Inorganic Synthesis* Vol. 2–16*

Complex	Reference(s)	Complex	Reference(s)
Nb		Fe, Ru, Os (Cont'd)	
$[(\eta^5\text{-}C_5H_5)_2Nb][BH_4]$	**16:** 109	$OsHCl(CO)(PPh_3)_3$	**15:** 53
$(\eta^5\text{-}C_5H_5)_2Nb(H)PPhMe_2$	**16:** 110	$OsH_2(CO)(PPh_3)_3$	**15:** 54
$[(\eta^5\text{-}C_5H_5)_2Nb(H)_2PPhMe_2][A]$	**16:** 110, 111	$OsH_2(CO)_2(PPh_3)_2$	**15:** 55
$A = Cl^-, BF_4^-, PF_6^-$		$OsH_4(PPh_3)_3$	**15:** 56
Cr, Mo, W		Mn, Re	
$CrH(CO)_3(C_5H_5)$*		$MnH(CO)_5$*	**7:** 198
$MoH(CO)_3(C_5H_5)$	**7:** 107	$Mn_3H_3(CO)_{12}$	**12:** 43
$WH(CO)_3(C_5H_5)$*		$Na_2[ReH_9]$	**13:** 219
$MoH_4(PMePh_2)_4$	**15:** 42, 43		
		Co, Rh, Ir	
Fe, Ru, Os†		$CoH(CO)_4$*	**2:** 240, **5:** 192
$FeH_2(CO)_4$	**2:** 243	$CoH(N_2)(PPh_3)_3$	**12:** 12, 21
$FeH_2[PPh(OEt)_2]_4$	**13:** 119	$CoH_3(PPh_3)_3$	**12:** 19
$FeHCl(depe)_2$	**15:** 23	$CoHL_4$ $L = P(OPh)_3$	**13:** 107
$[FeH(N_2)(depe)_2]^+$	**15:** 24	$L = PPh(OEt)_2$	**13:** 118
$FeH_2(dppe)_2$	**15:** 39	$RhHL_4$ $L = P(OPh)_3$	**13:** 109
$RuHCl(PPh_3)_3$	**13:** 131	$L = PPh_3$	**15:** 58
$RuHCl(CO)(PPh_3)_3$	**15:** 48	$[RhH(NH_3)_5][SO_4]$	**13:** 214
$RuH_2(CO)(PPh_3)_3$	**15:** 48	$RhH(CO)(PPh_3)_3$	**15:** 59
$RuH_2[P(OEt_3)]_4$	**15:** 40	$IrH(CO)(PPh_3)_3$	**13:** 126
$RuH_2(N_2)(PPh_3)_3$	**15:** 31	$IrH_5(PMe_3)_2$	**15:** 34
$RuH_4(PPh_3)_3$	**15:** 31		
		Pt	
		$PtHCl(PEt_3)_2$	**12:** 28

* And "Organometallic Syntheses," Vol. 1, R. B. King (Academic Press, 1965), which work contains synthesis of $(\eta^5\text{-}C_5H_5)MH_2$ [M = Mo, W] and $(\eta^5\text{-}C_5H_5)_2ReH$.

† depe = 1, 2-bis(diethylphosphino)ethane; dppe = 1, 2-bis(diphenylphosphinoethane.

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15. HYDRIDO PHOSPHINE ARENE COMPLEXES OF MOLYBDENUM

Submitted by WILLIAM E. SILVERTHORN*
Checked by M. L. H. GREEN,† J. KNIGHT,† and R. A. PARDY†

Bis(arene) metal complexes are generally unreactive toward ligand replacement reactions.[1] However, in the case of bis(arene) molybdenum complexes it has been shown that one of the arene ligands can be replaced by certain tertiary phosphine ligands or by allyl chloride under mild conditions, giving complexes of the type $Mo(PR_3)_3(\eta^6\text{-}C_6H_6)$ and $[MoCl(\eta^3\text{-}C_3H_5)(arene)]_2$ [arene = C_6H_6, $(CH_3)C_6H_5$, *sym*-$(CH_3)_3C_6H_3$ respectively].[2,3] These complexes have proved very useful in the syntheses of some unusual hydride complexes. The compounds $Mo(PR_3)_3(\eta^6\text{-}C_6H_6)$ [$PR_3 = P(C_6H_5)(CH_3)_2$, $P(C_6H_5)_2CH_3$] readily protonate in dilute acid solution giving stable hydride cations of the type $[MoH(PR_3)_3(\eta^6\text{-}C_6H_6)]^+$, and in concentrated acid solution they add a second proton, giving stable dihydrido cationic complexes of the type $[MoH_2(PR_3)_3(\eta^6\text{-}C_6H_6)]^{2+}$.[2,4] The latter reaction appears to be the only example of the addition of two protons to the same atom of a neutral molecule giving an isolable cation, thus demonstrating a high electron density on the metal atom along with a marked ability to delocalize positive charge. Sodium tetrahydroborate(1−) reduction of the complexes $[MoCl(\eta^3\text{-}C_3H_5)(arene)]_2$ in the presence of tertiary phosphines readily leads to neutral dihydrido complexes such as $MoH_2[P(C_6H_5)_3]_2(\eta^6\text{-}C_6H_6)$ in which the hydrido ligands can be replaced by dinitrogen and carbon monoxide.[3]

One of the key factors in the syntheses of benzene molybdenum complexes is the facile preparation of large quantities of bis (η^6-benzene)molybdenum. The synthesis of this compound under sealed-tube conditions has been described elsewhere.[5,6] The modified procedure described here is useful for large-scale preparations.

A. BIS(η^6-BENZENE)MOLYBDENUM

$$3MoCl_5 + 4Al + 6C_6H_6 \xrightarrow{AlCl_3} 3[Mo(\eta^6\text{-}C_6H_6)_2][AlCl_4] + AlCl_3$$

$$6[Mo(\eta^6\text{-}C_6H_6)_2]^+ + 8OH^- \longrightarrow 5[Mo(\eta^6\text{-}C_6H_6)_2] + [MoO_4]^{2-} + 4H_2O + 2C_6H_6$$

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Procedure

All operations are carried out in a dry, inert atmosphere. Schlenk apparatus capable of handling ca. 500 mL of solution is useful for the work-up of the products.* Although the intermediates may be handled briefly in air, bis(η^6-benzene)molybdenum is immediately decomposed by oxygen.

Pure molybdenum pentachloride (65 g, 238.0 mmol),† 140 g (1050.0 mmol) of anhydrous aluminum trichloride powder,‡ and 8.5 g (315 mmol) of aluminum powder are thoroughly mixed in a 500-mL, single-necked, round-bottomed flask, and 250 mL of dry benzene is added over a period of about 15 min. (■ **Caution.** *Enough heat is often generated on addition of the benzene to cause the solution to boil. An ice bath should be available in case the reaction becomes too vigorous.*) After the mixture has cooled to room temperature, the contents of the flask are thoroughly mixed by shaking and a reflux condenser is added. A Teflon sleeve should be used on the flask joint to prevent it from freezing. The reflux condenser is tightly wired to the neck of the flask by means of heavy-duty Nichrome wire. The apparatus is connected to a nitrogen line containing a mercury bubbler with a sufficient level of mercury to give an excess pressure of 15 to 17 psi. The complete apparatus is shown in Fig. 12. The flask is immersed in an oil bath,§ and a safety shield is placed in front of the apparatus. The nitrogen pressure is slowly increased until a slow stream of bubbles is emitted from the mercury bubbler. The temperature of the oil bath is slowly raised to 120°. After the reaction mixture has refluxed for about 12 hr (overnight) the apparatus is allowed to cool to room temperature and the contents are thoroughly mixed by shaking. The temperature is again raised to 120° and refluxing is continued for another 12 hr. After the mixture cools to room temperature, as much of the benzene solution as possible is decanted. The residue is washed four times with 250-mL portions of hexane. The solid is dried as far as possible ($\sim$14 hr) *in vacuo*, and the flask is shaken periodically during the drying period in order to break up the solid into small lumps.¶

A 3-L three-necked flask is equipped with a Teflon-blade stirrer and a nitrogen-inlet tube. Aqueous potassium hydroxide solution (750 g of KOH

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* See, e.g., D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," Chap. 7, McGraw-Hill Book Company, New York, 1969.

† Ventron Corporation, Alfa Products, Beverly, MA 01915.

‡ Aluminum Chloride Anhydrous AR(Powder) was purchased from Mallinckrodt Chemical Works, St. Louis, MO 63160, and used without further purification.

§ A heating mantle should not be used because localized heating will cause severe bumping.

¶ The checker found that the residue may occasionally be a stiff viscous tar.

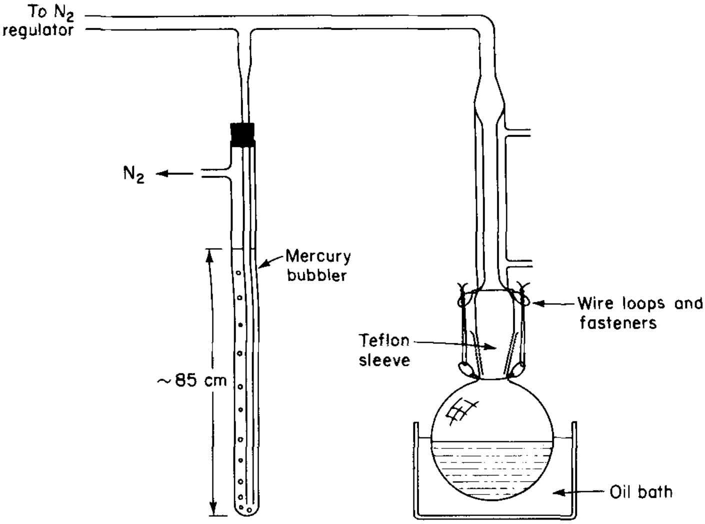

Fig. 12. Apparatus for the synthesis of bis(benzene)molybdenum.

pellets in 1750 mL H_2O) is added, and the solution and flask are purged of air by bubbling nitrogen through the solution for about 10 min. The solution is cooled to about −15° in a large ice-salt bath or Dry Ice–acetone bath. The small lumps of solid are added to the vigorously stirred solution in a strong countercurrent of nitrogen. The addition is carried out at such a rate (over ca. 2 hr) that the temperature of the solution does not exceed −5°. After the addition is complete the contents of the flask are allowed to warm slowly to room temperature, and stirring is continued for another 2 hr. The contents of the flask are filtered on a medium-porosity filter frit at least 2 in. in diameter and containing a 1-in.-thick bed of filter aid (Celite).* The solid is washed with 250 mL of water and dried *in vacuo*. (■ **Caution.** *The dry solid is highly pyrophoric.*) The solid is finely pulverized and is extracted with a total of 1 L of hot benzene. The benzene solution is filtered while hot, the green filtrate is concentrated to a volume of about 150 mL, and cooled to 6° for 1 hr. The bright-green solid is removed by filtration, washed with 100 mL of light petroleum ether, and dried *in vacuo*. Yield: 17.3 g (34.5%). *Anal.* Calcd. for $C_{12}H_{12}Mo$: C, 57.2; H, 4.8. Found: C, 55.8; H, 4.77. The reaction can be scaled up or down as desired.

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* The contents of the flask are best transferred to the filter device by forcing them through a $\frac{3}{8}$-in. section of Tygon tubing with a slight positive pressure of nitrogen. The solid material is transferred last to minimize plugging of the frit.

Bis(η^6-toluene)molybdenum and bis(η^6-mesitylene)molybdenum may be prepared in a similar manner. The reaction is carried out at atmospheric pressure, and the final product is purified by sublimation.[3] Similar yields are obtained.

B. (η^6-BENZENE)DIHYDRIDOBIS(TRIPHENYLPHOSPHINE)-MOLYBDENUM

$$2\mathrm{Mo}(\eta^6\text{-}\mathrm{C_6H_6})_2 + 2(3\text{-}\mathrm{ClC_3H_5}) \longrightarrow [\mathrm{MoCl}(\eta^3\text{-}\mathrm{C_3H_5})(\eta^6\text{-}\mathrm{C_6H_6})]_2 + 2\mathrm{C_6H_6}$$

$$[\mathrm{MoCl}(\eta^3\text{-}\mathrm{C_3H_5})(\eta^6\text{-}\mathrm{C_6H_6})]_2 + 2\mathrm{P(C_6H_5)_3} \longrightarrow 2[\mathrm{MoCl}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{P(C_6H_5)_3})(\eta^6\text{-}\mathrm{C_6H_6})]$$

$$\mathrm{MoCl}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{P(C_6H_5)_3})(\eta^6\text{-}\mathrm{C_6H_6}) \xrightarrow[\mathrm{P(C_6H_5)_3}]{\mathrm{Na[BH_4]}} \mathrm{MoH_2[P(C_6H_5)_3]_2}(\eta^6\text{-}\mathrm{C_6H_6})^*$$

Procedure

All reactions are carried out in an inert atmosphere. Solutions of (η^6-benzene)dihydridobis(triphenylphosphine)molybdenum should be handled in an inert atmosphere other than nitrogen to avoid contaminating the product with the dinitrogen complex $[\mathrm{Mo[P(C_6H_5)_3]_2}(\eta^6\text{-}\mathrm{C_6H_6})]_2\mathrm{N_2}$.

Bis(η^6-benzene)molybdenum (2 g, 7.94 mmol) in ca. 400 mL of dry benzene is treated with 1.5 mL (18.43 mmol) of allyl chloride which has been freshly distilled from P_4O_{10}. The solution is warmed to 45° in a water bath. The solution rapidly turns a red-violet color and small, purple crystals separate. After 1 hr at 40° the solution is cooled to 6° for 30 min and the light-purple supernatant liquid is decanted. The solid is washed with 100 mL of 95% ethanol and dried *in vacuo*. The yield of di-μ-chloro-bis[(η^3-allyl)(η^6-benzene)molybdenum(II)] is 1.5–1.7 g (75–85%). The solid is ground to a fine powder and transferred to a solution of 3 g (11.47 mmol) of triphenylphosphine in 100 mL of benzene. The mixture is stirred under reflux for 1 hr, and the red-purple solution is cooled and filtered. One hundred milliliters of 95% ethanol is added, and the solution is concentrated to a volume of about 75 mL *in vacuo*. The solution is then cooled to −15° for 1 hr, and the supernatant is carefully decanted. The small, purple crystals are washed with 100 mL of 95% ethanol and are dried *in vacuo*. The yield of (η^3-allyl)chloro(η^6-benzene)(triphenylphosphine)molybdenum is 2.4–2.8 g (60–70% yield based on bis(η^6-benzene)molybdenum). The solid is ground

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* The other products of this reaction have not been identified.

to a fine powder and transferred to a solution of 4.5 g of triphenylphosphine (17.18 mmol) in 150 mL of 95% ethanol. Sodium tetrahydroborate(1−) (3 g, 79.3 mmol) is added, and the mixture is stirred rapidly with a magnetic stirrer for 5 hr. The mixture is then filtered, and the solid is washed with 100 mL of 95% ethanol and dried *in vacuo*. The solid is extracted with 150 mL of benzene, and the solution is filtered through a bed of filter aid (Celite). One-hundred-fifty milliliters of 95% ethanol is added, and the solution is concentrated to about one-half its original volume or until the supernatant is a pale, orange-red color. The orange-red crystals are separated by decantation, washed twice with 100-mL portions of 95% ethanol, and dried *in vacuo*. The yield of (η^6-benzene)dihydridobis(triphenylphosphine)molybdenum is 3.1–3.6 g [55–65% based on bis(η^6-benzene)molybdenum]. *Anal.* Calcd. for $C_{24}H_{38}P_2Mo$: C, 72.0; H, 5.5. Found: C, 72.5; H, 5.7. The toluene analog can be prepared in an analogous manner starting from bis(η^6-toluene)molybdenum.

Properties

(η^6-Benzene) dihydridobis(triphenylphosphine)molybdenum can be exposed to air for brief periods without showing signs of decomposition; however, the material should be stored in an inert atmosphere. Solutions are rapidly decomposed by oxygen. The compound melts with decomposition at about 130° *in vacuo*. The compound is moderately soluble in benzene and tetrahydrofuran and is insoluble in ethanol or diethyl ether. The infrared spectrum (Nujol mull) shows metal hydride bands at 1730 (s) and 1775 (w) cm^{-1}. Treatment of a benzene solution of the compound with a slow stream of nitrogen gas causes reversible displacement of hydrogen to give the binuclear dinitrogen complex $[Mo[P(C_6H_5)_3]_2(\eta^6\text{-}C_6H_6)]_2N_2$. With carbon monoxide the hydrogen is irreversibly displaced to give $Mo[P(C_6H_5)_3]_2(CO)(\eta^6\text{-}C_6H_6)$.[3]

C. (η^6-BENZENE)TRIS(DIMETHYLPHENYLPHOSPHINE)-HYDRIDOMOLYBDENUM HEXAFLUOROPHOSPHATE(1−)

$$Mo(\eta^6\text{-}C_6H_6)_2 + 3P(C_6H_5)(CH_3)_2 \longrightarrow Mo[P(C_6H_5)(CH_3)_2]_3(\eta^6\text{-}C_6H_6) + C_6H_6$$

$$Mo([P(C_6H_5)(CH_3)_2]_3(\eta^6\text{-}C_6H_6) \xrightarrow[\text{(ii) } NH_4[PF_6]]{\text{(i) HCl (aq)}} [MoH\{P(C_6H_5)(CH_3)_2\}_3(\eta^6\text{-}C_6H_6)][PF_6]$$

■ **Caution.** *Dimethylphenylphosphine is toxic, and all operations should be carried out in a well-ventilated hood. Although it is not spontaneously flammable, it reacts with oxygen and it should be stored under an inert atmosphere.*

Procedure

All operations are carried out in an inert atmosphere. One gram (3.97 mmol) of bis(η^6-benzene)molybdenum and 2.5 mL (16.3 mmol) of dimethylphenylphosphine are stirred together at 110° in 40 mL of xylene for 12 hr. The solvent and excess phosphine are removed *in vacuo* at 100°. The residue is washed twice with 10-mL portions of cold (about −50°), light petroleum ether. The residue is extracted with 100 mL of hot heptane, and the hot solution is filtered and concentrated *in vacuo* to a volume of about 20 mL. The solution is cooled to −50° for 30 min and the supernatant is decanted. The orange-red crystals are washed three times with 10-mL portions of cold (about −50°), light petroleum ether and are dried *in vacuo* to give 2 g of (η^6-benzene)tris(dimethylphenylphosphine)molybdenum. One gram (1.7 mmol) of this material is added to 20 mL of a 1 : 1 ethanol–concentrated hydrochloric acid mixture, and the solution is stirred at 50° for 10 min, giving a clear, yellow solution. One-half gram (3.1 mmol) of ammonium hexafluorophosphate(1−) dissolved in 2 mL of water is added. The pale-yellow precipitate which forms is removed by filtration and washed three times with 5-mL portions of water. The solid is extracted with 25 mL of acetone and the solution is filtered. Ten milliliters of water are added and the volume of the solution is concentrated to about 10 mL *in vacuo*. The yellow crystals which form are removed by filtration and dried *in vacuo*. The yield of (η^6-benzene)tris(dimethylphenylphosphine)hydridomolybdenum hexafluorophosphate(1−) is 1.1 g [90% based on (η^6-benzene)tris(dimethylphenylphosphine)molybdenum]. *Anal.* Calcd. for $C_{30}H_{38}P_4F_6Mo$: C, 49.0; H, 5.4. Found: C, 48.8; H, 5.3.

The methyldiphenylphosphine analog can be prepared in an analogous manner except that hot benzene is used for the recrystallization of the neutral compound.

Properties

(η^6-Benzene)tris(dimethylphenylphosphine)hydridomolybdenum hexafluorophosphate(1−) is a moderately air-stable solid, soluble in polar solvents like acetone, methanol, and sulfur dioxide. Its ^1H nmr spectrum (in acetone-

d_6 solution at 60 MHz with external tetramethylsilane reference) shows bands centered at τ2.4 (phenyl protons), τ5.4 [8 lines ($J_{C_6H_6P} = 4.2$ Hz; $J_{HMoC_6H_6} = 2.7$ Hz)] (benzene protons), τ8.2 (methyl protons), and τ11.2 [quartet ($J_{HMoP} = 72.1$ Hz)] (Mo—H) in the expected ratios. The three ^{31}P nuclei appear equivalent down to −96°. It is thought that the hydrogen and phosphorus ligands are located at the corners of a square and are interconverting, as has been shown to occur in compounds of the type $MoH(\eta^3\text{-}C_5H_5)L_3$,[7] rather than that the molecule possesses a structure in which all of the phosphorus ligands are equivalent. The infrared spectrum shows a weak metal hydride band at 1915 cm^{-1} (KBr) which shifts to 1370 cm^{-1} (KBr) on deuteration. Other ligand absorptions are also present. The compound is readily deprotonated on treatment with ethanolic sodium hydroxide, giving $Mo[P(C_6H_5)(CH_3)_2]_3(\eta^6\text{-}C_6H_6)$.

D. (η⁶-BENZENE)TRIS(DIMETHYLPHENYLPHOSPHINE)DIHYDRIDOMOLYBDENUM BIS[HEXAFLUOROPHOSPHATE(1−)]

$$Mo[P(C_6H_5)(CH_3)_2]_3(\eta^6\text{-}C_6H_6) \xrightarrow[\text{(ii) } H[PF_6](aq.)]{\text{(i) } CF_3COOH}$$
$$[MoH_2\{P(C_6H_5)(CH_3)_2\}(\eta^6\text{-}C_6H_6)][PF_6]_2$$

Procedure

One gram (1.7 mmol) of (η^6-benzene)tris(dimethylphenylphosphine)molybdenum synthesized as described in Sec. C is dissolved in 10 mL (135.0 mmol) of freshly distilled, deoxygenated trifluoroacetic acid to give a yellow solution. Four milliliters (33.0 mmol) of 65% aqueous hexafluorophosphoric acid is added, and the solution is concentrated slowly *in vacuo* to a volume of about 5 mL. Very small, yellow crystals are produced. The mixture is centrifuged and the mother liquor is decanted off. The solid is washed three times with 5-mL portions of cold (0°) water and is dried *in vacuo*. The yield is ca. 1.1 g [75% yield based on (η^6-benzene)tris(dimethylphenylphosphine)molybdenum]. *Anal.* Calcd. for $C_{30}H_{39}P_5F_{12}Mo$: C, 40.9; H, 4.7. Found: C, 40.5; H, 4.9.

The methyldiphenylphosphine analog can be prepared by an analogous procedure.

Properties

(η^6-Benzene)tris(dimethylphenylphosphine)dihydridomolybdenum bis[hexafluorophosphate(1−)] can be exposed to air for brief periods without showing signs of decomposition, but it should be stored in a dry, inert atmosphere. The compound is soluble in trifluoroacetic acid and anhydrous sulfur dioxide. It is deprotonated in acetone solution, giving the monohydride complex $[MoH(PPhMe_2)_3(\eta^6\text{-}C_6H_6)][PF_6]$. The ^1H nmr spectrum (in trifluoroacetic acid solution at 60 MHz, with external tetramethylsilane reference) shows bands centered at $\tau 2.6$ (phenyl protons), $\tau 4.2$ (benzene protons), $\tau 8.4$ (methyl protons), and $\tau 12.3$ [quartet ($J_{HMoP} = 43.5$ Hz)] in the expected ratios. The apparent equivalence of the three ^{31}P nuclei is thought to be due to the hydrogen and phosphorus ligands interconverting rather than to the molecule possessing a structure in which all phosphorus atoms are equivalent.[4] The infrared spectrum shows a weak hydride band at 1880 cm^{-1} (Nujol mull) in addition to other ligand absorptions.

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16. BIS[ETHYLENEBIS(DIPHENYLPHOSPHINE)] HYDRIDO(2,4-PENTANEDIONATO)MOLYBDENUM(II)

$$Mo(acac)_3{}^{*} + 2(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + Al(C_2H_5)_3 \longrightarrow MoH(acac)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$$

Submitted by TAKASHI ITO† and AKIO YAMAMOTO†
Checked by WILLIAM SILVERTHORN‡

Bis[ethylenebis(diphenylphosphine)]hydrido(2,4-pentanedionato)molybdenum(II) can be obtained by reduction of tris(2,4-pentanedionato)molybdenum(III) with triethylaluminum in the presence of ethylenebis(diphenylphos-

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* acac = acetylacetonato (2,4-pentanedionato).

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phine) [1,2-bis(diphenylphosphino)ethane]* under an atmosphere of argon.[1] The use of less than a 5-molar ratio of triethylaluminum is essential in order to obtain the hydrido complex, otherwise, the ethylene complex [$Mo(C_2H_4)(diphos)_2$] is obtained as the main product.[1] The employment of argon as an inert atmosphere is indispensable, because the use of nitrogen gas in the place of argon causes the formation of the bis(dinitrogen) complex, *trans*-[$Mo(N_2)_2$ $(diphos)_2$].[2] The same hydridomolybdenum complex can be also prepared by the oxidative addition of 2,4-pentanedione to [$Mo(C_2H_4)(diphos)_2$].[1]

The complex can initiate the polymerization of acrylonitrile at room temperature[1] and may also be used as a catalyst for the low-temperature polymerization of acrylonitrile.

Procedure

■ **Caution.** *Because of the pyrophoric nature of triethylaluminum, special care should be taken to prevent it from coming in contact with air*†

A mixture of 2.87 g (7.30 mmol) of tris(2,4-pentanedionato)molybdenum(III)‡ and 6.01 g (15.1 mmol) of diphos is placed in a Schlenk-type reaction flask§ under an atmosphere of argon, and 20 mL of dry toluene is added to make a dark-brown slurry. The mixture is cooled to −40°, and 3.0 mL (22 mmol) of triethylaluminum¶ is slowly added by means of a hypodermic syringe, under vigorous stirring with a magnetic stirrer, under a stream of argon.

The temperature is raised gradually to room temperature over 5–6 hr. Stirring is continued at room temperature (10–30°) for three days during which time a deep-brown solution is formed from which a deep-brown solid finally precipitates. The precipitate is isolated from the reaction mixture by

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* 1,2-bis(diphenylphosphino)ethane is abbreviated as "diphos."

† Information concerning the handling of triethylaluminum may be obtained from "Aluminum Alkyls—Specifications, Properties, and Procedures," Texas Alkyls, Inc., Deer Park, TX 77536; or from "Handling Procedures for Aluminum Alkyl Compounds," Ethyl Corporation, Baton Rouge, LA 70801.

‡ Tris(2,4-pentanedionato)molybdenum may be prepared from molybdenum hexacarbonyl[3,4] or from $K_3[MoCl_6]$.[4] The authors used molybdenum hexacarbonyl in their preparation of the complex.

§ For the use of Schlenk-type apparatus, see D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Company, New York, 1969, or R. B. King, in "Organometallic Syntheses," J. J. Eisch and R. B. King (eds.), Vol. I, Academic Press, Inc., New York, 1965.

¶ Ethyl Corporation, Baton Rouge, LA 70801. A solution of triethylaluminum in toluene (Stauffer Chemical Company, Westport, CT 06880) may be substituted for the pure compound.

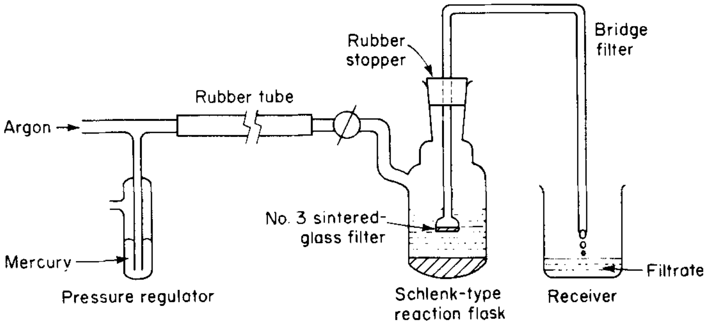

Fig. 13. Bridge-filter apparatus.

filtration using a bridge-filter method (see Fig. 13). It is washed with dry diethyl ether (30 mL × 3) and dry *n*-hexane (30 mL × 3) and dried *in vacuo*. The yield of the crude product, a brown, powdery solid, is 3.85 g, 53% based on $Mo(acac)_3$.

The product is recrystallized under argon as follows. Dry toluene is added with heating to 60° until all of the complex dissolves. The deep-brown solution thus obtained is filtered through a filter paper under an atmosphere of argon. After the filtrate is cooled to room temperature, its volume is reduced *in vacuo* to about one-fourth of its initial volume until needles form. The system is allowed to stand at −20° for two days and is then filtered by the bridge-filter method to isolate deep-brown, fine needles contaminated with a small amount of colorless prisms of diphos. The diphos is removed by washing the mixture well with degassed ethanol*† followed by diethyl ether† and *n*-hexane. Drying of the residue *in vacuo* gives deep-brown, fine needles of the pure product. *Anal.* Calcd. for $C_{57}H_{56}O_2P_4Mo$: C, 69.0; H, 5.7. Found: C, 69.2; H, 5.9.

Properties

Bis[ethylenebis(diphenylphosphine)]hydrido(2,4-pentanedionato)molybdenum(II) is diamagnetic and forms deep-brown, fine needles which are moderately stable in air. Solutions of the compound decompose rapidly in air. The compound does not have a sharp melting point but decomposes gradually at

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* Ethanol was deaerated by bubbling argon gas through it in a Schlenk-type flask for 48 hr.

† Since the product is soluble in ethanol and diethyl ether to some extent, the use of these solvents should be restricted to the minimum amounts necessary to obtain an analytically pure product. A yield of ca. 40% can be attained.

~200° *in vacuo.* It is soluble in tetrahydrofuran, toluene, and benzene and is slightly soluble in diethyl ether and ethanol. Characteristic infrared bands (KBr disk) are as follows: 1803 (m) [ν(Mo—H)], 1560 (s) [ν(C=C)], 1510 (vs) [ν(C=O)], 1478 (m), 1426 (vs), 1392 (s) (δ_{aCH_3}), 1262 (m) [ν(C—C)], 1091 (s), 872 (s), 805 (s), 743 (s), 696 (vs), 652 (s) cm^{-1}. There is a weak, broad band at 1950 cm^{-1} attributable to one of the overtones of δ_{CH} (out of plane). The absence of a band at 1970 cm^{-1} suggests that the complex does not contain, as an impurity, *trans*-[Mo(N$_2$)$_2$ (diphos)$_2$] which possesses a very strong band at 1970 cm^{-1}.[2] Contamination by free diphos is indicated by the presence of a band at 730 cm^{-1}. This strong band in free diphos completely disappears on coordination.

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17. TRIS(DIMETHYLPHENYLPHOSPHINE)PENTAHYDRIDORHENIUM (V)

$$\mathrm{K[ReO_4] + 4HCl + 5P(CH_3)_2C_6H_5 \longrightarrow}$$
$$\mathrm{ReCl_3[P(CH_3)_2C_6H_5]_3 + 2PO(CH_3)_2C_6H_5 + 2H_2O + KCl}$$
$$\mathrm{ReCl_3[P(CH_3)_2C_6H_5]_3 + Na[BH_4] \longrightarrow ReH_5[P(CH_3)_2C_6H_5]_3}$$

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The reduction of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III)[1-3] with sodium tetrahydroborate(1−), as described below, provides a clean synthesis of tris(dimethylphenylphosphine)pentahydridorhenium(V),

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in contrast to reduction with lithium tetrahydridoaluminate(1 −) which is less convenient and gives a lower yield. An analogous reduction of *trans*-tetrachlorobis(dimethylphenylphosphine)rhenium(IV)[1,2] with sodium tetrahydroborate(1 −) affords bis(dimethylphenylphosphine)heptahydridorhenium(VII).

Procedure

A mixture of 4.0 g (13.8 mmol) of potassium perrhenate(1 −) (or 3.4 g of Re_2O_7), 10.4 g (75 mmol) of dimethylphenylphosphine,[4] 13 mL of concentrated hydrochloric acid, and 220 mL of ethanol is boiled under reflux overnight in a 500-mL round-bottomed flask equipped with a condenser surmounted by a nitrogen-flushed "tee." The color changes from green to amber. On cooling to room temperature, 8.3 g (85% yield) of orange crystals of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III) separate from solution, mp 189–191.5°. The material has an infrared spectrum identical to that of an authentic sample[3] and is suitable for most synthetic applications. Further purification may be accomplished by recrystallization from ethanol.

A suspension of 3.83 g (5.4 mmol) of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III) (or its benzene solvate)[1] and 2.48 g (65 mmol) of sodium tetrahydroborate(1 −) in 100 mL of absolute ethanol is heated under nitrogen on a steam bath until the orange complex dissolves to give a colorless suspension. The solvent is evaporated under reduced pressure, and the residue is extracted with three 75-mL portions of benzene. The benzene extract is evaporated, and the residue is crystallized from 60 mL of absolute ethanol to give prisms of tris(dimethylphenylphosphine)pentahydridorhenium(V); the yield is 2.2 g (67%). *Anal.* Calcd. for $C_{24}H_{38}P_3Re$: C, 47.59; H, 6.32; P, 15.34. Found (checkers' values): C, 47.60; H, 6.24; P, 15.51.

Properties

Tris(dimethylphenylphosphine)pentahydridorhenium(V) is a white, crystalline solid, mp 97–98°. It may be remelted several times without apparent decomposition and is stable for several months at 20°. It is soluble in cold benzene but much less soluble in cold ethanol or light petroleum ether. The rhenium-hydrogen stretching vibrations, ν(Re—H), are (in Nujol mull) 1949 (w, sh), 1931 (m), 1905 (m), and 1852 (m); (in benzene solution) 1969 (sh), 1898, 1855, 1817 (sh) cm^{-1}. In the ^1H nmr spectrum (benzene at 34°) the hydridic hydrogens are apparently equivalent (fluxional molecule) and occur at τ16.1 (quartet), $J_{(\mathrm{PH})} = 14.2$ Hz: the methyl groups absorb at τ8.33 (apparent doublet). Conductimetric titration shows that $ReH_5[P(CH_3)_2(C_6H_5)]_3$ reacts very rapidly with hydrogen chloride in methanol at 0° to give the $[ReH_6\{P(CH_3)_2(C_6H_5)\}_3]^+$ ion, but this is followed by the slow evolution of molecular hydrogen, giving *fac*-$ReCl_3[P(CH_3)_2(C_6H_5)]_3$. The compound $ReH_5[P(CH_3)_2(C_6H_5)]_3$ reacts rapidly with an excess of dry hydrogen chloride in methanol at 20° to give *fac*-$ReCl_3[P(CH_3)_2(C_6H_5)]_3$ (95% yield).

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18. DODECACARBONYLTRI-μ-HYDRIDO-*triangulo*-TRIRHENIUM(I)

$$Re_2(CO)_{10} + Na[BH_4] \xrightarrow{\text{THF}} \text{anion mixture} \xrightarrow[\text{cyclohexane}]{H_3PO_4} Re_3H_3(CO)_{12} + \text{other products}$$

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Checked by C. B. COOPER, III†

The title compound has been prepared by two methods, the tetrahydroborate(1 −) reduction of $Re_2(CO)_{10}$[1] and the direct hydrogenation of $Re_2(CO)_{10}$.[2] While the latter method is simpler and more convenient, the tendency to form rhenium metal makes it less desirable for the preparation of large quantities (>0.5 g) of $Re_3H_3(CO)_{12}$. This contrasts with the syntheses of $Re_4H_4(CO)_{12}$, $Os_3H_2(CO)_{10}$, and $Os_4H_4(CO)_{12}$ which can be readily prepared by direct hydrogenation.[2] The tetrahydroborate(1 −) reduction of metal carbonyls followed by acidification is a general method for the synthesis of neutral metal carbonyl hydrides.[3] Dodecacarbonyltri-μ-hydrido-*triangulo*-trirhenium(I) can also be used as the starting material for the preparation of $Re_4H_4(CO)_{12}$[4] and substituted derivatives $Re_3H_3(CO)_{12-n}L_n$ ($L = P(C_6H_5)_3$, $P(OCH_3)_3$, $P(C_6H_5)_2CH_3$, etc., $n = 1, 2, 3$).[5]

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Procedure

■ **Caution.** *Toxic, colorless, odorless carbon monoxide is evolved in this reaction and must be properly vented. All metal carbonyls should also be considered to be toxic compounds. The drying of tetrahydrofuran (THF) may be accompanied by serious explosions under certain conditions.* [See *Inorganic Syntheses*, **12,** 111, 317 (1970); also Synthesis 1, this volume.]

The THF used in this synthesis was dried by distillation under nitrogen from calcium hydride. All operations should be carried out under an atmosphere of nitrogen[6] until the product is isolated in solid form.

Sodium tetrahydroborate(1−) (3.2 g, 84.4 mmol) and dirhenium decacarbonyl* (4.0 g, 6.14 mmol) are added to THF (100 mL) in a 250-mL Schlenk flask, and the mixture is heated to reflux with magnetic stirring. The solution rapidly becomes dark-red. After 4 hr the solution is cooled to room temperature, and the clear, red solution is removed with a syringe from the excess sodium tetrahydroborate(1−) and is transferred to the bulb of the liquid-liquid extraction apparatus shown in Fig. 14.

The solvent is then removed at water-aspirator pressure† to give a red-orange solid. The solid is broken up with a spatula, and a 500-mL Schlenk flask containing deaerated cyclohexane (300 mL) is affixed to the 24/40 joint. Finally, a magnetic stirring bar and phosphoric acid (60 mL, 85%) are carefully added to the upper bulb and a reflux condenser is fitted at the S.T. 45/50 joint. The 500-mL flask is then heated, causing the cyclohexane to reflux and to extract the $Re_3H_3(CO)_{12}$ from the acidified red solid. The mixture in the upper bulb should be heated with an auxiliary oil bath to 50–60° and stirred rapidly enough with the magnetic stirring bar to ensure

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* Available from Strem Chemicals, Inc., 150 Andover Street, Danvers, MA 01923 and from Pressure Chemicals Co., 3419 Smallman St., Pittsburgh. PA 15201.

† The checker suggested a vacuum pump to prevent back-diffusion of air or moisture.

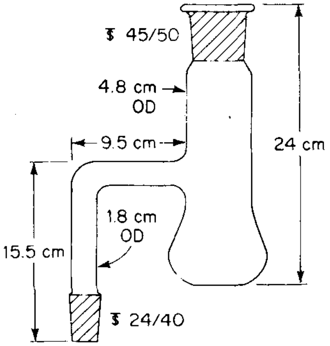

Fig. 14. Continuous liquid-liquid extraction apparatus.

efficient extraction at the cyclohexane–phosphoric acid interface but not so rapidly as to allow any of the phosphoric acid to spill over into the 500-mL flask. The cyclohexane layer becomes dark-red because of the presence of small amounts of $Re_4H_4(CO)_{12}$, and gradually colorless crystals of $Re_3H_3(CO)_{12}$ form on the cooler portions of the 500-mL flask. After 18–24 hr the solution is allowed to cool slowly for several hours.* The mother liquor is decanted from the colorless to pale-orange crystals. These are washed with two 20-mL portions of hexane and dried in *vacuo* to give nearly pure $Re_3H_3(CO)_{12}$ (1.9 g, 50% yield). This material is pure enough for use as a starting material for most reactions. If further purification is desired, the compound can be recrystallized from hot cyclohexane. *Anal.* Calcd. for $C_{12}H_3O_{12}Re_3$: C, 16.05; H, 0.34; Re, 62.23. Found: C, 16.04; H, 0.30; Re, 61.12.

Properties

The trimer is a white, crystalline material which is air-stable in the solid state but decomposes very slowly in solution. It is only slightly soluble in most organic solvents. The carbonyl stretching region of the infrared shows four principal peaks at 2093 (m), 2030 (vs), 2008 (s), and 1983 (m) cm^{-1} (cyclohexane solution, see Fig. 3 of reference 1). Because of its low solubility and its relative ease of signal saturation, proton magnetic resonance of $Re_3H_3(CO)_{12}$ can be observed only for saturated solutions in acetonitrile at 70° which show a single resonance at τ27.1.[7]

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* The checker suggested cooling under carbon monoxide with stirring to convert the small quantity of $Re_4H_4(CO)_{14}$ into $Re_3H_3(CO)_{12}$ and $ReH(CO)_5$.[4] The smaller crystals thus formed were collected on a glass frit by suction filtration.

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19. BIS[ETHYLENEBIS(DIPHENYLPHOSPHINE)]-HYDRIDOIRON COMPLEXES

Submitted by P. GIANNOCCARO* and A. SACCO*
Checked by STEVEN D. ITTEL† and MARTIN A. CUSHING, JR.†

A number of cationic hydrido complexes of transition metals, stabilized by tertiary phosphines, have been described in recent years. The bis[ethylenebis(diphenylphosphine)]hydridoiron(II) cation is of particular interest because it reacts very easily with a number of neutral ligands to give a series of cationic hydrido complexes of formula $[FeH(L)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$ (L = N_2, CO, $(CH_3)_2CO$, NH_3, Py, CH_3CN, C_6H_5CN), and with hydrogen to give the cationic hydrido complex of iron(IV) $[FeH_3\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$.[1] The synthesis of $FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ is included because this compound is the starting material for the synthesis of a number of iron complexes containing the $Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ moiety. The compound $FeH[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ which can be prepared easily by the sodium reduction of $FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ is of particular interest because it represents a very uncommon example of a stable paramagnetic hydrido complex.[4] The syntheses are carried out under an inert-gas atmosphere, using Schlenk-tube techniques.[2] A standard filtration device[3] for use on a vacuum manifold is employed.

A. CHLOROBIS[ETHYLENEBIS(DIPHENYLPHOSPHINE)]-HYDRIDOIRON(II)

$$FeCl_2 + 2(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + Na[BH_4] \longrightarrow NaCl + 0.5B_2H_6 + FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$$

Procedure

A 0.652-g (4.0 mmol) sample of iron(II) chloride dihydrate‡ and 40 mL of 95% ethanol are placed, in a countercurrent of nitrogen, in a 250-mL flask containing a magnetic stirring bar; then 3.20 g (8.1 mmol) of the bis(phos-

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† Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, DE 19898.

‡ The $FeCl_2 \cdot 2H_2O$ was prepared as described in *Inorganic Syntheses*, **5**, 179 (1957). The checkers obtained a better yield with anydrous $FeCl_2$, prepared as described in *Inorganic Syntheses*, **6**, 172 (1960) and *ibid.*, **15**, 39 (1974).

phine)* are added, the temperature is raised to 40°, and the mixture is kept at this temperature for 1 hr. At this time a solution of sodium tetrahydroborate(1 −)† (160 mg, 4.2 mmol) in 20 mL of ethanol is slowly added, and a red-violet precipitate forms. The mixture is kept at 40° for an additional hour and is then filtered, using the vacuum-filtration apparatus previously described.[3]

The precipitate is washed with 30 mL of deoxygenated water, then with 40 mL of ethanol (40–50°), and last with 40 mL of acetone. After drying *in vacuo*, 2.8 g of crude product is obtained (80% yield). The product is recrystallized in the same apparatus by dissolving it in 30 mL of dry benzene, filtering, concentrating under vacuum until some crystals appear, and finally adding light petroleum ether. After filtering, washing with light petroleum ether, and drying *in vacuo*, 1.5 g of pure, red-violet product is obtained (43% yield).‡ *Anal.* Calcd. for $C_{52}H_{49}ClP_4Fe$: C, 70.2; H, 5.6; Cl, 4.0; P, 13.9; Fe, 6.3. Found: C, 71.3; H, 6.2; Cl, 4.1; P, 13.6; Fe, 6.2.

Properties

The red-violet crystalline compound, which decomposes at 195°, is fairly stable to air; it is soluble in benzene, toluene, and THF (tetrahydrofuran). Its solutions slowly react with air. Its infrared spectrum, determined in Nujol mull, shows a broad, weak absorption band at 1955 cm^{-1}, assignable to the Fe—H stretch. When the complex is treated with solid iodine at 60°, about 0.5 mol of hydrogen is evolved per mole of complex. On treatment with iodine in benzene solution at room temperature, only 20–40% of the stoichiometric amount of hydrogen is evolved.

B. BIS[ETHYLENEBIS(DIPHENYLPHOSPHINE)]-HYDRIDOIRON(II) TETRAPHENYLBORATE(1 −)

$$FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2 + Na[B(C_6H_5)_4] \longrightarrow$$
$$[FeH\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][B(C_6H_5)_4] + NaCl$$

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* Available from Ventron Corporation, Alfa Products, P.O. Box 159, Beverly, MA 01915.

† The sodium tetrahydroborate(1 −) must be used in the stoichiometric amount; if it is used in excess, the dihydrido complex $FeH_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ is formed.

‡ The product may still contain some unreacted ethylenebis(diphenylphosphine). This can be removed by recrystallizing the product from diethyl ether or by washing it with warm acetone.

*Procedure**

A mixture of $FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ (1.00 g; 1.12 mmol) and $Na[B(C_6H_5)_4]$ (0.70 g; 2 mmol) in 10 mL of benzene is stirred at 50–60° until a blue product is formed (ca. 1 hr). After filtration, the precipitate is washed with 10 mL of benzene, then with 10 mL of ethanol at room temperature, twice with 15 mL of deoxygenated water, and last with 10 mL of ethanol. After drying *in vacuo*, 0.65 g of deep-blue product is obtained (48% yield). *Anal.* Calcd. for $C_{76}H_{69}BFeP_4$: C, 77.8; H, 5.9; Fe, 4.8; P, 10.6. Found: C, 78.0: H, 6.2; Fe, 4.8; P, 10.5; Cl, 0.2.

Properties

The deep-blue, crystalline compound, which decomposes under vacuum at 145–147°, is unstable in air. It is soluble in acetone and THF, giving red solutions which turn yellow under nitrogen:

$$[FeH\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+ \xrightarrow{THF} [FeH(C_4H_8O\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+ \xrightarrow[(-THF)]{N_2} [FeH(N_2)\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$$

C. BIS[ETHYLENEBIS(DIPHENYLPHOSPHINE)]-HYDRIDOIRON(I)

$$FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2 + Na \longrightarrow FeH[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2 + NaCl$$

Procedure

■ **Caution.** *Sodium must be handled with care. A dangerous explosion may result if the metal comes into contact with water.*

A sample of $FeHCl[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ (1.35 g, 1.52 mmol) and 30 mL of anhydrous benzene are placed, in a countercurrent of nitrogen, in a 100-mL flask containing a magnetic stirring bar; then 37 mg

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* The product is very oxygen- and nitrogen-sensitive. The synthesis must be carried out under an atmosphere of pure argon (or helium) and the solvents must be argon-flushed before they are used.

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20. HYDRIDONITROSYLTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(I)

$$RuCl_3 \cdot 3H_2O \xrightarrow[\text{aqueous solution}]{NO/NO_2,\ 100^\circ C} Ru(NO)Cl_3(aq)$$

$$Ru(NO)Cl_3 + 3P(C_6H_5)_3 + 3KOH + 2C_2H_5OH \xrightarrow[\text{under nitrogen}]{\text{ethanol, } 78^\circ} RuH(NO)[P(C_6H_5)_3]_3 + 3KCl + 2CH_3CHO + 3H_2O$$

Submitted by J. S. BRADLEY* and G. WILKINSON*
Checked by S. KOMIYA† and A. YAMAMOTO†

The title compound and related complexes with substituted phosphine ligands were first prepared by the reduction of trichloronitrosylbis(triphenylphosphine)ruthenium with ethanolic potassium hydroxide, in the presence of excess tertiary phosphine.[1] The synthesis may be conveniently performed in one operation from ruthenium trichloride trihydrate; trichloronitrosylruthenium, prepared by the action of a mixture of nitric oxide and nitrogen dioxide on aqueous ruthenium trichloride,[2] is treated with an excess of triphenylphosphine in refluxing alcoholic potassium hydroxide, giving hydridonitrosyltris(triphenylphosphine)ruthenium in yields of ca. 90%. The complex is an effective catalyst for the isomerization of olefins and the hydrogenation of styrene and readily exchanges with gaseous deuterium to give the corresponding deuteride.[1]

Procedure

■ **Caution.** *Oxides of nitrogen are toxic and a good hood should be used.*

A solution of commercial ruthenium trichloride trihydrate (1.0 g, 3.8 mmol) in water (30 mL) is placed in a 100-mL two-necked flask fitted with a reflux condenser and a gas inlet. The mixture is heated to reflux, and through the dark-brown solution is bubbled a mixture of nitric oxide and nitrogen dioxide. (This mixture may be adequately obtained by periodically introducing air into the nitric oxide stream—exact proportions of nitric oxide and nitrogen dioxide are not required). After ca. 1 hr, during which

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† Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan.

time the color changes to deep-red, concentrated hydrochloric acid (10 mL) is added, and the solution is evaporated to a purple oil under reduced pressure. Ethanol (30 mL) is added, and the solution is filtered into a pressure-equalizing dropping funnel fitted to a 250-mL, three-necked flask equipped with a reflux condenser, nitrogen inlet, and magnetic stirrer. The flask is charged with ethanol (75 mL), triphenylphosphine (4.0 g, 15.2 mmol), and potassium hydroxide (0.7 g) and purged with nitrogen; then the mixture is stirred and heated to reflux. The solution of $Ru(NO)Cl_3$ is added dropwise over ca. 30 min. The red-brown, crystalline solid which separates* is collected by filtration; washed with two 20-mL portions of warm ethanol, water, and finally cold ethanol; and dried *in vacuo*. The yield is ca. 3.1 g (90% based on ruthenium), mp 197–200° (decomposes) under argon.† *Anal.* Calcd. for $C_{54}H_{46}P_3NORu$: C, 70.6; H, 5.0; N, 1.5; Ru, 11.0. Found: C, 70.2; H, 5.2; N, 1.6; Ru, 10.6.

Properties

Hydridonitrosyltris(triphenylphosphine)ruthenium(I) is stable in air in the solid state, but slowly oxidizes in solution. The infrared spectrum of the complex shows absorptions at 1965 cm^{-1} [ν(Ru—H)] and 1640 cm^{-1} [ν(N—O)]. The ^1H nmr spectrum (which is temperature-independent) shows a high-field quartet at $\tau 16.6$ ($^2J_{PH} = 30$ Hz), consistent with a trigonal bipyramidal structure with axial hydride and equatorial phosphines.[1] This structure has been confirmed in the solid state by x-ray crystallography,[3] which reveals a slightly distorted trigonal bipyramid. The axial nitrosyl is coordinated in a linear fashion (Ru—N—O angle = 176°).

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* If addition of the $Ru(NO)Cl_3$ solution is too rapid, a green solid precipitates. However, on prolonged refluxing under nitrogen this solid is converted to the desired product with no reduction in overall yield.

† The checkers, using a sealed tube, observed a decomposition temperature (uncorrected) of 194–197°.

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21. DIHYDRIDOTETRAKIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

$$RuCl_2[P(C_6H_5)_3]_3 + Na[BH_4] + P(C_6H_5)_3 \longrightarrow RuH_2[P(C_6H_5)_3]_4 + \text{other products}$$

Submitted by R. YOUNG* and G. WILKINSON*
Checked by S. KOMIYA† and A. YAMAMOTO†

The complex $RuH_2[P(C_6H_5)_3]_4$ has been obtained by (*a*) the interaction of the dichloride, $RuCl_2[P(C_6H_5)_3]_3$,[1] with sodium tetrahydroborate(1−) in the presence of excess triphenylphosphine, in hydrogen saturated benzene-methanol solution;[2] (*b*) the reaction of ruthenium trichloride or $Ru(acac)_3$,‡ triphenylphosphine, and triethylaluminum in tetrahydrofuran (as light-yellow crystals, yield 24%);[3] and (*c*) the rapid successive addition of hot ethanolic solutions of ruthenium trichloride and sodium tetrahydroborate(1−) to a well stirred, boiling ethanolic solution of triphenylphosphine (as mustard-yellow microcrystals, yield 94%).[4] The complex has also been produced by the addition of triphenylphosphine to $RuH_4[P(C_6H_5)_3]_3$ or $RuH_2(N_2)[P(C_6H_5)_3]_3$.[5] It is most conveniently and reliably made by the procedure described here. $RuH_2[P(C_6H_5)_3]_4$ in benzene is known to react with ethylene and styrene and is said to yield the complexes $Ru(C_2H_4)[P(C_6H_5)_3]_3$ and $Ru(C_6H_5CH{=}CH_2)[P(C_6H_5)_3]_3$.[6] More recently, the title compound has been used to initiate the polymerization of vinyl compounds.[7] It has also been shown[8] that the action of acids on $RuH_2[P(C_6H_5)_3]_4$ in methanol yields a solution which is an active catalyst for the hydrogenation of alkenes.

Procedure

■ **Caution.** *Hydrogen is an explosion and fire hazard. The reaction should therefore be carried out in an efficient fume hood in the absence of flame or*

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‡ "acac" = acetylacetonate (2,4-pentanedionate).

spark sources. The isolated product is somewhat air- and light-sensitive and should be stored under argon in the dark.

A mixture of benzene (60 mL) and methanol (100 mL) containing triphenylphosphine (6 g, 22.9 mmol) is placed in a 250-mL, round-bottomed, three-necked flask fitted with a reflux condenser,* a gas inlet tube which will protrude beneath the surface of the solvent, and a magnetic stirrer. After purging the apparatus with hydrogen for ca. 5 min $RuCl_2[P(C_6H_5)_3]_3$[1] (1.0 g, 0.87 mmol) is added through a side neck. Dry, finely ground sodium tetrahydroborate(1 −) (1.5 g, 0.04 mol) is added in approximately five 0.3-g portions, over a period of 20 min, with rapid stirring. The solution is stirred at room temperature for 1 hr, during which time the initial red solution changes to brown and then yellow and the complex is precipitated as bright-yellow microcrystals. Degassed methanol (100 mL) is added to the solution, and the product is collected on a sintered filter under argon, washed with argon-purged methanol, and dried *in vacuo.*† Typical yields based on ruthenium are 1.02–1.08 g (85–90%). *Anal.* Calcd. for $C_{72}H_{62}P_4Ru$: C, 75.0; H, 5.4; P, 10.7. Found: C, 75.1; H, 5.7; P, 10.4.

Properties

The complex is sparingly soluble in benzene, toluene, tetrahydrofuran, and acetone. The complex is moderately stable to air in the solid state but is readily oxidized in solution. In solution the complex dissociates to give free triphenylphosphine and $RuH_2[P(C_6H_5)_3]$, which may then reversibly add nitrogen or hydrogen to produce $Ru(N_2)H_2[P(C_6H_5)_3]_3$ and $RuH_4[P(C_6H_5)_3]_3$, respectively.[3] In addition to phosphine bands the infrared spectrum shows a single, medium-strong Ru—H stretching frequency at 2080 cm^{-1}.

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* The reflux condenser is required to prevent stripping-off of solvent during purging.

† The checkers report that the complex can be recrystallized from benzene or toluene to give a sample which has decomposed in a sealed tube at a temperature of 220° (uncorrected).

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22. HYDRIDO[η^6-PHENYL)DIPHENYLPHOSPHINE]-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) TETRAFLUOROBORATE(1 −)

$$\mathrm{RuH(CH_3CO_2)[P(C_6H_5)_3]_3} + \mathrm{HBF_4} \longrightarrow$$
$$[\mathrm{RuH\{P(C_6H_5)_3\}_2\{(\eta^6\text{-}C_6H_5)P(C_6H_5)_2\}}][\mathrm{BF_4}] + \text{other products}$$

Submitted by R. YOUNG* and G. WILKINSON*
Checked by A. G. OSBORNE†

The reaction of aqueous tetrafluoroboric acid with a methanolic suspension of (acetato)hydridotris(triphenylphosphine)ruthenium(II) leads to the precipitation of hydridotris(triphenylphosphine)ruthenium(II) cation as the fluoroborate salt.[1] The cation has also been produced by the decomposition of the $[\mathrm{RuH(P(C_6H_5)_3)_4}]^+$ cation in dichloromethane solution.[2] On the basis of proton magnetic spectra, a structure with one of the phenyl rings of one triphenylphosphine bound as an arene to the metal was proposed.[2] This structure has been confirmed by both x-ray diffraction and ^{31}P nmr spectra.[1]

Procedure

■ **Caution.** *Hydrogen is an explosion and fire hazard. The reaction should therefore be carried out in an efficient fume hood in the absence of flame or spark sources.*

A solution of 42% aqueous tetrafluoroboric acid (5 mL) in methanol (50 mL) is placed in a 250-mL, round-bottomed, three-necked flask fitted with a reflux condenser, a gas inlet tube protruding beneath the surface of

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† Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, England.

the solvent, and a magnetic stirrer. After the flask has been purged with hydrogen for 5 min, $RuH(CH_3CO_2)\{P(C_6H_5)_3\}_3$* (0.50 g, 0.53 mmol) and $P(C_6H_5)_3$ (0.50 g, 1.91 mmol) are added through a side neck, and the resulting suspension is heated to reflux, under a stream of hydrogen, with stirring. The deep-red solution produced is refluxed for 2 min, during which it lightens in color.† Upon cooling, the complex precipitates from the hot solution as pale-lemon-yellow crystals. These are collected on a sintered filter under nitrogen, washed successively with 25-mL portions of degassed methanol and ether, and dried *in vacuo* for approximately 1 hr. Typical yields based on ruthenium are 0.35–0.40 g (66–75%). The complex as isolated contains one, quite firmly held methanol of crystallization. *Anal.* Calcd. for the methanol solvate $C_{55}H_{50}OP_3BF_4Ru$: C, 65.5; H, 5.0; P, 9.2; F, 7.5. Found: C, 65.7; H, 5.1; P, 9.5; F, 7.9.

Properties

In the solid state the complex is reasonably stable to air and turns slightly green only after prolonged exposure. The methanol of crystallization is lost on long storage (2 weeks) *in vacuo*. The complex is relatively insoluble in diethyl ether and petroleum ether, and moderately soluble in halogenated solvents such as dichloromethane and chloroform, giving air-sensitive solutions. In acetone the complex is freely soluble and produces an air-sensitive yellow solution. In addition to phosphine and tetrafluoroborate bands, the infrared spectrum has a weak, broad Ru—H stretching frequency at 2035 cm^{-1}. The ^1H nmr spectrum in acetone-d_6 shows: (*a*) a broad absorption band τ2.5–3 due to the aromatic phosphine protons; (*b*) two triplets at τ4.60 and 5.68 which are assigned to the ortho and meta protons on the arene ring η^6-bonded to the metal; (*c*) a hydride resonance centered at τ18.67, split into a triplet by coupling with the two equivalent phosphorus atoms of the two normally bonded phosphines, and further split by the unique phosphorus of the η^6-bonded phosphine.

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* Prepared as described in Synthesis 23.

† The checker found that on some occasions it was desirable to filter the hot solution under nitrogen before cooling it.

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23. (ACETATO)HYDRIDOTRIS)TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

$$RuCl_2[P(C_6H_5)_3]_3 + CH_3CO_2Na + CH_3OH \longrightarrow RuH(CH_3CO_2)[P(C_6H_5)_3]_3 + \text{other products}$$

Submitted by R. YOUNG* and G. WILKINSON*
Checked by S. KOMIYA† and A. YAMAMOTO†

The acetato and other carboxylato complexes, $RuH(RCO_2)[P(C_6H_5)_3]_3$, have been made by reaction of the dichloro complex,[1] $RuCl_2[P(C_6H_5)_3]_3$ with the sodium salt of a carboxylic acid RCO_2H in methanol solution under an atmosphere of hydrogen.[2] There is no necessity to use molecular hydrogen, and the solvent, methanol, can act as the hydride source. These complexes have also been prepared by (*a*) the reaction of $RuH_2[P(C_6H_5)_3]_4$ with the appropriate carboxylic acid in boiling 2-methoxyethanol;[3] and (*b*) the rapid successive addition of ruthenium trichloride, the carboxylic acid, and potassium hydroxide to a solution of triphenylphosphine in vigorously boiling ethanol.[3] The title compound has also been prepared by the action of $RuH_2[P(C_6H_5)_3]_4$ on vinyl acetate.[4] The synthesis now described affords the product in the most crystalline state and free from green impurities. Both benzene and acidified methanolic solutions of the complex are active catalysts for the homogeneous hydrogenation of 1-alkenes of the type $RCH{=}CH_2$.[5]

Procedure

Reagent quality methanol (100 mL) is placed in a 250-mL, round-bottomed, three-necked flask fitted with a reflux condenser, a nitrogen-gas inlet tube which will protrude beneath the surface of the solvent, and a magnetic stirrer. After the flask has been purged with nitrogen for 5 min $RuCl_2[P(C_6H_5)_3]_3$ (0.6 g, 0.63 mmol) and sodium acetate trihydrate (0.71 g, 5.22 mmol) are added through a side neck. The resulting suspension

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is refluxed under nitrogen for 45 min. The hydrido complex precipitates from the hot solution as bright-yellow crystals. After cooling to room temperature, the solid is collected on a sintered filter under nitrogen; washed successively with 25-mL portions of degassed methanol, water, methanol, and diethyl ether; and dried *in vacuo*. Typical yields based on ruthenium are 0.475–0.505-g (80–85%) mp 221–223°.* *Anal.* Calcd. for $C_{56}H_{48}O_2P_3Ru$: C, 70.9; H, 5.2; P, 9.8. Found: C, 70.7; H, 5.3; P, 9.6.

Properties

At 25°, the yellow complex is sparingly soluble in benzene and toluene (saturated solutions ca. $10^{-3}M$) and is almost completely insoluble in cyclohexane, diethyl ether, petroleum ether, and similar solvents. It is freely soluble in halogenated solvents such as dichloromethane and chloroform. The infrared spectrum shows a sharp Ru—H stretching frequency at 2012 cm^{-1}. The position and value of $\Delta\nu$ [$\nu_{asym}(COO)-\nu_{sym}(COO)$] for the carboxylate frequencies is consistent with a symmetrical bidentate chelate arrangement of the carboxylate grouping. In chloroform-*d* solution, the ^1H nmr spectrum of the complex shows, besides resonances due to aliphatic and aromatic protons, a symmetrical quartet due to the hydrogen bound to the ruthenium [τ(H), 29.89] mutually *cis* to three equivalent phosphorus atoms (J_{PH}, 27 Hz). The structure has been confirmed by x-ray diffraction study.[6] In the solid state the complex is reasonably stable to air, and darkens only on prolonged exposure to light. However, in solution it is sensitive to traces of oxygen, and the solutions become dark-green.

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* The checkers report that the melting point can be raised to 250–251° by recrystallization from a tetrahydrofuran–diethyl ether mixture.

Inorganic Syntheses, Volume XVII
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24. HYDRIDOBIS[(+)-DIOP]RHODIUM(I)

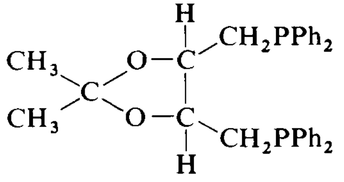
Bis[(+)-[(2,2-*dimethyl*-1,3-*dioxolane*-4,5-*diyl*)*bis*(*methylene*)]*bis*[*diphenyl*-*phosphine*]]*hydridorhodium*(I)

$$RhCl_3 \cdot 3H_2O + (+)\text{-diop} \xrightarrow[\text{ethanol}]{Na[BH_4]} HRh[(+)\text{-diop}]_2$$

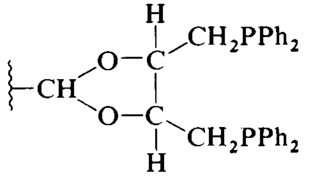
Submitted by A. FENSTER,* B. R. JAMES,* and W. R. CULLEN*
Checked by R. LINCOLN† and G. WILKINSON†

There is considerable current interest in the use of chiral catalysts for asymmetric synthesis. Studies have been reported on hydrogenation, hydrosilylation, and hydroformylation reactions using complexes of rhodium with tertiary phosphines as catalysts, in which the chirality is at either the phosphorus atom or at carbon atoms of groups attached to the phosphorus.[1-5] Useful systems, giving high optical yields (70–80%) for hydrogenation of olefins and hydrosilyation of ketones are those reported by Kagan and coworkers,[5] who have used (*a*) a homogeneous catalyst prepared *in situ* from labile $[RhCl(olefin)_2]_2$ complexes and the optically active chelating bis(phosphine), 4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane, more conveniently called "diop" (I), and (*b*) a similar catalyst that is heterogenized by attaching a modified diop ligand (II) to a polystyrene-divinylbenzene cross-linked polymer support.

The homogeneous catalyst has been prepared in alcoholic media and is a cation formed by loss of chloride. The procedure is described here for production of the neutral hydrido species $HRh[(+)\text{-diop}]_2$, which is a slower catalyst than the *in situ* species for asymmetric hydrogenation but is equally effective in terms of optical yields. The method follows that of Levison and Robinson[6] for synthesis of hydrido(triphenylphosphine)rhodium complexes.



I



II

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Procedure

The reaction is performed in a 100-mL flask fitted with a condenser, a nitrogen inlet which protrudes beneath the surface of a 60-mL solvent level, and a port for introducing reagent solutions. The nitrogen leaves the flask via the condenser which is connected to a bubbler. The solutions are stirred magnetically. The flask is purged with nitrogen and charged with 1.0 g (2.0 mmol) of (+)-diop* in 40 mL of ethanol;† this solution is stirred vigorously under reflux, and to it is added in rapid succession a solution of 0.13 g (0.5 mmol) of rhodium(III) chloride trihydrate‡ in 10 mL warm ethanol,† followed by a solution of 0.2 g (5 mmol) sodium tetrahydroborate(1−) in 10 mL ethanol.† The reaction mixture is refluxed for 10 min. The yellow solid which precipitates on cooling (1 hr at 0°) is filtered in air;§ washed with warm water to remove chloride, impurities, and ethanol; and is then dried overnight at 25° under vacuum; 0.46 g (85% yield) of essentially pure $HRh[(+)\text{-diop}]_2$ (mp with decomposition ~210°) is obtained. Redissolving in a few milliliters of dichloromethane under an inert atmosphere, followed by addition of an equal volume of light petroleum ether and cooling, yields $HRh[(+)\text{-diop}]_2 \cdot CH_2Cl_2$, mp 185° (decomposes *in vacuo*). *Anal.* Calcd. for $C_{63}H_{67}Cl_2O_4P_4Rh$: C, 63.80; H, 5.65; Cl, 5.99. Found: C, 63.3; H, 5.7; Cl, 5.7. The unsolvated complex can also be obtained by prolonged pumping on the solvate.

Properties

The solvated and unsolvated rhodium diop complexes are air-stable, yellow, crystalline solids; solutions of the complexes, however, rapidly decompose on exposure to air. $HRh[(+)\text{-diop}]_2$ is soluble in benzene, toluene, and dichloromethane; it is slightly soluble in petroleum ether and *n*-hexane, and insoluble in ethanol.

The infrared spectrum (KBr) shows an absorption in the hydride region at 2040 cm^{-1}. The ^1H nmr spectrum in benzene at 20° shows the Rh—H resonance as a doublet of quintets centered around τ28.4. The same nmr pattern has been reported[7] for $HRh(CH_3PPh_2)_4$ and was attributed to a tetragonal pyramid structure, although this has been questioned.[8]

A benzene solution of the diop complex containing 250 mg of the complex in 10 mL gives an optical rotation of −0.084 whence $[\alpha]_D^{25} = -3.4°$.

The complex in benzene-ethanol solutions is an effective hydrogenation

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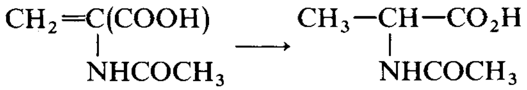
* Available from Strem Chemicals, Inc., 150 Andover Street, Danvers, MA 01923.

† The ethanol is deoxygenated before use by purging with nitrogen.

‡ Available from Johnson Matthey Ltd., Wembley HA9 0HW, Middlesex, England.

§ No decomposition is observed when this procedure is followed, but as a precautionary measure the filtration may be carried out in a nitrogen atmosphere.

catalyst for terminal olefins and unsaturated carboxylic acids;[9] for example, the pro-chiral substrate 2-acetamidoacrylic acid is converted into *N*-acetyl-(*S*)-alanine with 60% optical purity. Using an *in situ* catalyst prepared from (−)-diop (Rh/diop = 1.1), Kagan and Dang[10] formed the corresponding R conformer in 73% optical yield.



$$\mathrm{CH_2{=}\underset{\underset{\displaystyle NHCOCH_3}{|}}{C}(COOH)} \longrightarrow \mathrm{CH_3{-}\underset{\underset{\displaystyle NHCOCH_3}{|}}{C}H{-}CO_2H}$$

Acid hydrolysis gives an approach to the important optically active α-amino acids.

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25. NICKEL AND PALLADIUM CHLOROHYDRIDOBIS(PHOSPHINE) COMPLEXES

Submitted by T. SAITO,* H. MUNAKATA,† and H. IMOTO*
Checked by A. DAVISON,‡ K. JONAS,§ and B. ALBIEZ§

Nickel hydride complexes had been considered to be very unstable before the discovery of several stable hydride complexes of the type $NiHX(PR_3)_2$

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‡ Nickel complexes were checked by A. Davison, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

§ Palladium complexes were checked by K. Jonas and B. Albiez, Max-Planck Institut für Kohlenforschung, Mülheim a. d. Ruhr, West Germany.

where PR_3 is Pcy_3 (tricyclohexylphosphine)* or $P(i\text{-}Pr_3)$ (triisopropylphosphine). These complexes have been prepared by two methods. The first employs sodium tetrahydroborate(1−) for the reduction of the corresponding dihalo complex.[1] The second involves the oxidative addition of acids to μ-dinitrogen-bis[bis(tricyclohexylphosphine)nickel].[2] Derivatives can also be prepared from chlorohydrido complexes by metathesis reactions.[1]

The corresponding palladium complexes are also known.[3] Since the original preparative method is rather complicated, a simpler one[4] for the preparation of chlorohydridobis(tricyclohexylphosphine)palladium is described in this synthesis.†

■ **Caution.** *Since both tertiary phosphines and diborane-(6) are toxic, and since diborane-(6) is spontaneously flammable in air, all operations should be carried out in an argon or nitrogen atmosphere and in a well-ventilated hood.*

A. *trans*[CHLOROHYDRIDOBIS(TRICYCLOHEXYLPHOSPHINE)NICKEL]

$$NiCl_2 \cdot 6H_2O + 2Pcy_3 \longrightarrow NiCl_2(Pcy_3)_2 + 6H_2O$$

$$NiCl_2(Pcy_3)_2 + Na[BH_4] \longrightarrow trans\text{-}NiHCl(Pcy_3)_2 + \tfrac{1}{2}B_2H_6 + NaCl$$

Procedure

In view of the chemical reactivity of the tertiary phosphine and nickel hydride complexes to air, all manipulations should be carried out in a nitrogen or argon atmosphere.[6] All solvents should be distilled under a nitrogen or argon atmosphere.

Dichlorobis(tricyclohexylphosphine)nickel is first prepared by the following procedure, which is a slight modification of the original synthesis of Turco, Scatturin, and Giacometti.[7] A solution of tricyclohexylphosphine (14.0 g, 0.050 mol) in benzene (50 mL) and ethanol (300 mL) is added slowly to a solution of nickel dichloride hexahydrate (5.9 g, 0.025 mol) in ethanol (100 mL) at room temperature in a nitrogen or an argon atmosphere. A reddish, crystalline precipitate deposits immediately. After the addition is complete, the mixture is left for a few hours, then the product is filtered off, washed with ethanol, and dried *in vacuo*. (Yield: 16.4 g; 95%.)

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* Tricyclohexylphosphine may be purchased from Strem Chemicals, Inc., Danvers, MA 01923. cy = cyclohexyl.

† *Note added in proof:* A very simple preparation of hydrido(nitrato)bis(tricyclohexylphosphine)palladium, which is a good starting complex for the preparation of other derivatives, has been discovered recently in this laboratory.[4,5]

Powdered sodium tetrahydroborate(1−) (0.38 g, 0.01 mol) is added in three or four portions at about 30-min intervals to a suspension of dichlorobis(tricyclohexylphosphine)nickel (6.9 g, 0.01 mol) in diethyl ether (200 mL), benzene (40 mL), and 95% ethanol (40 mL) in a 500-mL three-necked flask with an argon inlet and a gas bubbler vented to an efficient hood. The reaction mixture is stirred for 5 hr at 20° with a magnetic stirring bar.* Gas evolution is observed, and the dichloro compound dissolves gradually. After all the nickel compound has dissolved, the yellow solution is filtered into a 500-mL two-necked flask with an argon inlet. The solvents are removed under reduced pressure to give a yellow powder. The yellow complex is dissolved in toluene (70 mL) and washed with two 100-mL portions of water. The toluene layer is separated, dried with 15 g of anhydrous sodium sulfate, and filtered. The sodium sulfate is washed with two 5-mL portions of toluene, which are then added to the main body of the toluene. Methanol (600 mL) is added to the filtrate, and the solution is cooled to −15° overnight.† The yellow-brown crystals which are formed are filtered, washed with cold methanol (50 mL), and dried *in vacuo* to give the product, mp 150° (decomposes). (Yield: 3.7 g; 56%.) *Anal.* Calcd. for $C_{36}H_{67}ClNiP_2$: C, 66.0; H, 10.2; Ni, 8.9. Found: C, 66.2; H, 10.7; Ni, 8.8.

Properties

Chlorohydridobis(tricyclohexylphosphine)nickel is a yellow-brown solid. It is thermally stable at ambient temperature but reacts with air. It is very soluble in benzene, tetrahydrofuran, and dichloromethane and is soluble in diethyl ether and petroleum ether. Carbon tetrachloride, carbon disulfide, and chloroform decompose the complex. The infrared spectrum shows a sharp ν(Ni—H) band at 1916 cm^{-1} (KBr disk and Nujol mull). The high-field ^1H nmr spectrum in benzene solution has a triplet (1 : 2 : 1) at τ34.6 (TMS) with J_{PH} 73.5 Hz. The splitting is caused by the coupling of the hydride proton with two equivalent ^{31}P nuclei. This is consistent with a trans square-planar configuration.

* The checkers found that all the nickel complex had dissolved after 2 hr at 24–25°.

† The checkers found that in one experiment, the complex crystallized very slowly during a period of 2 weeks (yield 1.8 g). In another experiment, 2.2 g of complex was obtained after 2 days at −15°, and a second crop of 0.2 g crystallized during the next 2 weeks. In yet another experiment, 3.0 g of material was obtained after 2 days at −15°.

B. *trans*-[CHLOROHYDRIDOBIS-(TRIISOPROPYLPHOSPHINE)NICKEL]

$$NiCl_2 \cdot 6H_2O + 2P(i\text{-}Pr)_3 \longrightarrow NiCl_2[P(i\text{-}Pr)_3]_2 + 6H_2O$$

$$NiCl_2[P(i\text{-}Pr)_3]_2 + Na[BH_4] \longrightarrow trans\text{-}NiHCl[P(i\text{-}Pr)_3]_2 + \tfrac{1}{2}B_2H_6 + NaCl$$

Procedure

Dichlorobis(triisopropylphosphine)nickel is first prepared by the following procedure, which is similar to the original synthesis of Giacometti and Turco.[8] Triisopropylphosphine (8.0 g, 0.050 mol) is added slowly to a solution of nickel dichloride hexahydrate (5.9 g, 0.025 mol) in ethanol (100 mL) at room temperature in a nitrogen or argon atmosphere. A red, crystalline precipitate deposits immediately. After the addition is complete, the mixture is left for 5 hr and the product is filtered off, washed with ethanol, and dried *in vacuo*. (Yield: 9.6 g, 85%.) The compound can be recrystallized by dissolving it in hot benzene (10 g in 250 mL) and by adding *n*-hexane (500 mL).

Powdered sodium tetrahydroborate(1 –) (0.37 g, 0.01 mol) is added in three portions at about 30-min intervals to a suspension of dichlorobis(triisopropylphosphine)nickel (4.5 g, 0.01 mol) in diethyl ether (300 mL) and 95% ethanol (50 mL) in a 500-mL three-necked flask with an argon inlet and a gas bubbler vented to the hood. The reaction mixture is stirred with a magnetic stirring bar at 20° for approximately 5 hr. Gas evolution is observed, and the nickel complex dissolves gradually. After all the nickel compound is dissolved, the solution is filtered into a 500-mL two-necked flask and the solvent is removed under reduced pressure. The yellow residue is extracted with petroleum ether (200 mL),* and the solution is washed with two 50-mL portions of water. The petroleum layer is separated, dried with 15 g of anhydrous sodium sulfate, which is washed with two 10-mL portions of the solvent which are added to the petroleum extract; the combined extract is then filtered and concentrated *in vacuo*. The saturated solution (approximately 100 mL) is cooled to –78° in a Dry Ice–2-propanol mixture overnight. The crystals which are formed are filtered, washed with a small amount (approximately 10 mL) of petroleum ether at 0°, and dried *in vacuo* to give brown crystals, mp 65–66° (decomposes). (Yield: 2.5 g, 60%.) *Anal.* Calcd. for $C_{18}H_{43}ClNiP_2$: C, 52.1; H, 10.4; Ni, 14.1. Found: C, 52.3; H, 9.7; Ni, 14.1.

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* The checker used pentane instead of petroleum ether.

Properties

Chlorohydridobis(triisopropylphosphine)nickel is a yellow-brown solid. It is thermally stable at ambient temperatures but reacts with air. It is very soluble in benzene and tetrahydrofuran and is soluble in diethyl ether and petroleum ether. Carbon tetrachloride, carbon disulfide, and chloroform decompose the complex. The infrared spectrum shows a sharp ν(Ni—H) band at 1937 cm^{-1} (Nujol mull). The high-field ^1H nmr spectrum in benzene solution shows a triplet (1 : 2 : 1) at τ34.3 (TMS) with J_{PH} 77.8 Hz. The splitting is caused by the coupling of the hydride proton with the two equivalent ^{31}P nuclei. The trans square-planar configuration has been confirmed by x-ray crystallography.[9]

C. *trans*-[CHLOROHYDRIDOBIS-(TRICYCLOHEXYLPHOSPHINE)PALLADIUM]

$$PdCl_2 + 2NaCl \longrightarrow Na_2[PdCl_4]$$

$$Na_2[PdCl_4] + 2P(n\text{-Bu})_3 \longrightarrow PdCl_2[P(n\text{-Bu})_3]_2 + 2NaCl$$

$$PdCl_2[P(n\text{-Bu})_3]_2 + Na[BH_4] \longrightarrow PdHCl[P(n\text{-Bu})_3]_2 + \tfrac{1}{2}B_2H_6 + NaCl$$

$$PdHCl[P(n\text{-Bu})_3]_2 + 2Pcy_3{}^{*} \longrightarrow PdHCl(Pcy_3)_2 + 2P(n\text{-Bu})_3$$

Procedure

A mixture of palladium dichloride (5.32 g, 0.030 mol) and sodium chloride (3.70 g, 0.063 mol) in water (150 mL) is boiled until the palladium dichloride has dissolved. The solution is cooled to room temperature, and tri-*n*-butylphosphine (12.5 g, 0.062 mol) in ethanol (50 mL) is added. After 2 hr of stirring, the organic layer is extracted with benzene, and the benzene is evaporated *in vacuo*. The residue is recrystallized from ethanol (70 mL) to give $PdCl_2[P(n\text{-Bu})_3]_2$. (Yield: 15.1 g, 86%.)

A solution of sodium tetrahydroborate(1 –) (0.14 g, 0.00378 mol) in 95% ethanol (80 mL) is added to a solution of dichlorobis(tri-*n*-butylphosphine)-palladium (2.00 g, 0.00344 mol) in 95% ethanol (50 mL) at 25° in a nitrogen or argon atmosphere. After 1 hr of stirring, tricyclohexylphosphine (3.50 g, 0.0125 mol) is added to the solution and it is stirred for another hour. The solution is evaporated at room temperature *in vacuo* and the residue is washed with *n*-hexane (20 mL), two 20-mL portions of 1 : 1 water-ethanol mixture, and then with methanol (15 mL). It is dried *in vacuo* to give a white

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* cy = cyclohexyl.

solid, mp 218–220° (decomposes). (Yield: 1.22 g, 50%.) The compound can be recrystallized from a toluene-methanol mixture. *Anal.* Calcd. for $C_{36}H_{67}ClP_2Pd$: C, 61.4; H, 9.6. Found: C, 61.2; H, 9.4.

Properties

Chlorohydridobis(tricyclohexylphosphine)palladium is a white solid. It is thermally stable at ambient temperatures. It is not very sensitive to air in the solid state, but it is advisable to store it in an inert atmosphere. It is soluble in benzene and tetrahydrofuran. The infrared spectrum shows a sharp ν(Pd—H) band at 2002 cm^{-1} (Nujol mull). The high-field ^1H nmr spectrum in benzene solution shows a triplet at τ24.4 (TMS) with J_{PH} 4.1 Hz. The splitting is caused by the coupling of the hydride proton with two equivalent ^{31}P nuclei. This is consistent with a trans square-planar configuration.

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26. HYDRIDO[TETRAHYDROBORATO(1 −)] NICKEL AND PALLADIUM COMPLEXES

Submitted by H. MUNAKATA* and T. SAITO†
Checked by K. JONAS‡ and B. ALBIEZ‡

The thermally stable nickel and palladium hydride complexes, *trans*-$[MHX(PR_3)_2]$, where M = Ni or Pd, R = cyclohexyl or isopropyl, and X = halogen, have been prepared by various methods.[1–5] Hydrido[tetrahydroborato(1 −)] complexes can be prepared from them by metathetical reactions.[3] The hydrido[tetrahydroborato(1 −)]bis(tricyclohexylphos-

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‡ Max-Planck Institut für Kohlenforschung, Mülheim a. d. Ruhr, West Germany.

phine)nickel and palladium complexes are thermally stable, but the triisopropylphosphine analogs are less stable. Only the synthesis of the tricyclohexylphosphine complexes are described here. During all stages in the preparation of the triisopropylphosphine complex, it is necessary to hold the temperature carefully between − 10 and − 5°, and it is recommended that the freshly recrystallized chlorohydridobis(triisopropylphosphine) complex be used as a starting material in order to obtain good yields.

The complexes, *trans*-$[MH(BH_4)(PR_3)_2]$, can be used as mild reducing agents,[3] and can act as catalysts for butadiene oligomerization.[6]

A. *trans*-[HYDRIDO[TETRAHYDROBORATO(1 −)]BIS(TRICYCLOHEXYLPHOSPHINE)NICKEL]

$$trans\text{-}[NiHCl(Pcy_3)_2] + Na[BH_4] \longrightarrow trans\text{-}[NiH(BH_4)(Pcy_3)_2] + NaCl$$

Procedure

Powdered *trans*-$[NiHCl(Pcy_3)_2]$* (6.56 g, 0.010 mol) is suspended in a mixture of 95% ethanol (40 mL) and acetone (40 mL) in a 200-mL three-necked flask equipped with an argon inlet and a gas bubbler. Powdered sodium tetrahydroborate(1 −)† (0.455 g, 0.012 mol) is added to the suspension, and the mixture is stirred magnetically at 20–25° for 3 hr. The fine, yellow crystals which form are filtered, washed with three 40-mL portions of a 1 : 1 water-ethanol mixture, and dried *in vacuo* to give the product, mp 121–125° (decomposes). (Yield: 5.4 g, 85%.) *Anal.* Calcd. for $C_{36}H_{71}BNiP_2$: C, 68.0; H, 11.3; Ni, 9.2. Found: C, 67.8; H, 11.2; Ni, 9.0.

Properties

trans-[Hydrido[tetrahydroborato(1 −)]bis(tricyclohexylphosphine)nickel] is a yellow, crystalline solid. It is soluble in benzene, but the solution decomposes in air after a few minutes. Samples of *trans*-$[NiH(BH_4)(Pcy_3)_2]$ consisting of well-formed crystals remain unchanged in air for several hours. The infrared spectrum (Nujol mull) shows a sharp band at 1920 cm^{-1} [ν(Ni—H)], and bands due to Ni—(BH_4) at 2365 cm^{-1} (terminal B—H stretching), 1140 cm^{-1} (terminal B—H deformation), 2050 cm^{-1} and

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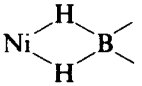
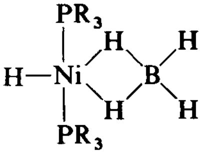
* Prepared as described in Synthesis 25. cy = cyclohexyl.

† The checkers found it desirable to use a molar ratio of $Na[BH_4]/NiHCl(Pcy_3)_2$ of approximately 3 : 1 and a reaction time of approximately 20 hr.

1872 cm^{-1} (bridging  $\mathrm{Ni}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix}{>}\mathrm{B}{<}$). The ^{1}H nmr band assigned to the hydrogen attached to the Ni atom in the complex occurs as a broad triplet (1 : 2 : 1) in benzene solution at τ30.1 (TMS) with J_{PH} 72 Hz. This suggests an equal coupling of the Ni—H with the two *cis*-^{31}P nuclei. The line broadening is presumably caused by the coupling with the *trans*-BH_4 group. The ^{1}H nmr spectrum of the triisopropylphosphine analog, *trans*-$[NiH(BH_4)\{P(i\text{-}Pr)_3\}_2]$ shows a triplet of quintets centered at τ29.7 (TMS), which is assignable to the Ni—H bond in the complex. The triplet is presumably caused by coupling of the Ni—H hydrogen with the two *cis*-^{31}P nuclei (J_{PH} = 70.5 Hz). The quintet structure results from equal coupling of the Ni—H hydrogen with all four hydrogens of BH_4 (J_{HBH_4} = 6.0 Hz). The apparent equivalence of all BH_4 hydrogens suggests that a rapid intramolecular exchange of the tetrahedral BH_4 group occurs. These data suggest the complexes have a square-planar configuration and are *trans*-$[NiH(BH_4)(PR_3)_2]$. The BH_4 group is probably attached to the nickel atom by two hydrogen bridging bonds, namely,



B. *trans*-[HYDRIDO[TETRAHYDROBORATO(1−)]BIS(TRICYCLOHEXYLPHOSPHINE)PALLADIUM]

trans-$[PdHCl(Pcy_3)_2 + Na[BH_4] \longrightarrow$ *trans*-$[PdH(BH_4)(Pcy_3)_2] + NaCl$

Procedure

Powdered *trans*-$[PdHCl(Pcy_3)_2]$* (3.0 g, 0.0043 mol) is suspended in a mixture of 95% ethanol (20 mL) and acetone (30 mL) in a 200-mL three-necked flask equipped with an argon inlet and a gas bubbler. Powdered sodium tetrahydroborate(1−)† (0.19 g, 0.0051 mol) is added to the suspension, and the mixture is stirred magnetically at 20–25° for 8 hr. The fine, white crystals which form are filtered, washed with three 30-mL portions of a 1 : 1 water-ethanol mixture, and dried *in vacuo*, to give the product, mp 135–138° (decomposes). (Yield: 2.5 g, 85%.) *Anal.* Calcd. for $C_{36}H_{71}BP_2Pd$: C, 63.3; H, 10.5. Found: C, 63.0; H, 10.1.

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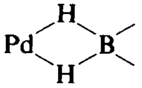
* Prepared as described in Synthesis 25. cy = cyclohexyl.

† The checkers found it desirable to use a molar ratio of $Na[BH_4]/PdHCl(Pcy_3)_2$ of approximately 3 : 1 and a reaction time of approximately 20 hr.

Properties

trans-[Hydrido[tetrahydroborato(1 −)]bis(tricyclohexylphosphine)palladium] is a white, crystalline solid. It is only slightly soluble in organic solvents such as benzene, acetone, and ethanol. The infrared spectrum shows a sharp band at 2002 cm^{-1} [ν(Pd—H)] and bands due to Pd—(BH_4) at 2330 cm^{-1} (terminal B—H stretching) and 1800 cm^{-1} (bridging  $\mathrm{Pd}\begin{smallmatrix}\mathrm{H}\\ \\ \mathrm{H}\end{smallmatrix}\mathrm{B}$). The ^1H nmr spectrum has not been measured because of the low solubility of the complex. The ^1H nmr spectrum of the triisopropylphosphine analog, *trans*-[$PdH(BH_4)\{P(i\text{-}Pr)_3\}_2$], shows five broad lines centered at τ23.2 (TMS) and these five lines may be considered to be the most intense of seven lines, if J_{PH} is approximately the same as J_{HBH_4} (ca. 9 Hz).

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27. BIS(η^5-CYCLOPENTADIENYL) [TETRAHYDROBORATO(1 −)]TITANIUM

$$2(\eta^5\text{-}C_5H_5)_2TiCl_2 + 4Na[BH_4] \longrightarrow 2Ti(\eta^5\text{-}C_5H_5)_2(BH_4) + 4NaCl + B_2H_6 + H_2$$

Submitted by C. R. LUCAS*
Checked by A. SHAVER†

The observation of catalytic activity by the title compound[1] and other derivatives of lower-valent titanium[2,3] has stimulated interest in the organic chemistry of this element. Despite the interesting and challenging problems

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presented by lower-valent titanium species,[4–7] little effort has been devoted to studying them. One of the reasons for this is undoubtedly related to the lack of good preparative methods for compounds suitable as starting materials. Herein, therefore, is described a synthesis of $Ti(\eta^5\text{-}C_5H_5)_2(BH_4)$ which has certain advantages over a previously reported procedure.[8] No difficulty has been experienced when this new procedure was scaled up or down by a factor of three. This improved synthesis can be made to yield relatively large quantities (> 10 g) of compound after three hours of work and one overnight reaction period.

■ **Caution.** *The gas evolved during the reaction contains some diborane*(6) *and hydrogen and is therefore poisonous and potentially explosive. It should be vented from the bubbler to a fume hood. When treated in this manner the dangerous gases are diluted and present no hazard.*

Procedure

The reaction is carried out in a 500-mL three-necked flask. To one neck is fitted a stopcock leading to a T-piece, of which one side is connected to an inert-gas supply (high purity, dry nitrogen or argon) and the other side is connected to a bubbler. To another neck is fitted a stopcock leading to a vacuum line. The remaining neck is used to introduce reagents and is fitted with a stopper. Reactants and solvents may be used without further purification.

A magnetic stirrer and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ * (9.96 g, 40.0 mmol), are placed in the flask and 1,2-dimethoxyethane (180 mL) is added. The flask is evacuated several times, while its contents are stirred, in order to remove dissolved oxygen; it is then refilled with inert gas and the stopcock to the bubbler is opened. Sodium tetrahydroborate(1−) (8.00 g, 210 mmol) is added to the mixture against a countercurrent of inert gas. Effervescence begins immediately, and the flask becomes warm. Reaction is allowed to proceed for several hours (preferably overnight); at the end of this time, the liquid phase is purple. The suspension is filtered† under an inert atmosphere and the residue is washed with 1,2-dimethoxyethane (50 mL) from which dissolved oxygen has been removed by the technique employed earlier.

■ **Caution.** *The residue is extremely pyrophoric in air, especially when dry. It should be destroyed by adding to it a large excess of cold water in a fume*

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† Filters tend to become clogged quickly but use of Celite or other filtering aid alleviates the problem.

hood. The gases evolved as the residue decomposes, either in water or when the dry solid ignites, are foul-smelling, poisonous, and potentially explosive and should be vented in a fume hood.

The solvent is removed from the combined filtrate and washings *in vacuo* on a water bath at 60°, and the purple residue is extracted three times with deoxygenated toluene (3 × 40 mL). The combined extracts are filtered; then pentane (40 mL), deoxygenated in the manner previously described, is added and the solution is chilled to −78°. Purple needles form during the cooling and after 1 hr they are separated by filtration and dried *in vacuo* at room temperature. Yield is 6.4 g (83% based on titanium). *Anal.* Calcd. for $C_{10}H_{14}BTi$: C, 62.3; H, 7.3; B, 5.6; Ti, 24.8. Found: C, 62.2; H, 7.2; B, 5.5; Ti, 25.2.

Properties

The purple crystals are freely soluble in all common organic solvents except aliphatic hydrocarbons, in which they are only sparingly soluble. Solutions of the compound are highly sensitive to oxidation, and rigorous exclusion of air is necessary. The appearance of yellow material, insoluble in hydrocarbons, indicates the onset of oxidation. The purple solid is pyrophoric in air but is stable indefinitely when stored under an inert atmosphere at room temperature.

Long, purple needles are obtained by subliming $Ti(\eta^5\text{-}C_5H_5)_2(BH_4)$ *in vacuo* at 80° into a 40-cm, air-cooled tube. Sublimation is accompanied by a substantial amount of thermal decomposition to an involatile residue which is pyrophoric in air. Sublimation is therefore not employed as a purification step during the preparation.

The structure of $Ti(\eta^5\text{-}C_5H_5)_2(BH_4)$ which was originally proposed on the basis of infrared spectra[8,9] and has been confirmed subsequently by x-ray techniques,[10] consists of an essentially tetrahedral array about titanium of the two C_5 ring-centroids and two hydrogen atoms. The boron atom is surrounded roughly tetrahedrally by hydrogen atoms, two of which form hydrogen bridges to the titanium atom.

The compound reacts very slowly with water to give $[Ti(\eta^5\text{-}C_5H_5)_2(OH)]_n$, but in acid solutions it decomposes more rapidly to give $[(\eta^5\text{-}C_5H_5)_2Ti]^+$. Basic solutions destroy even the cyclopentadienyl-metal system and cause precipitation of Ti_2O_3.

The compound is paramagnetic and its infrared spectrum (Nujol mull) shows absorptions at 3050 (vw), 2375 (mbr), 2045 (w), 1930 (m), 1725 (w), 1630 (w), 1555 (w), 1445 (m), 1380 (s), 1300 (vw), 1260 (vw), 1150 (s), 1010 (s), 915 (w), 845 (m), 803 (sbr), 452 (s) cm^{-1}. Slight oxidation of a sample in air does not cause great changes in its infrared spectrum, but more extensive oxidation results in loss of the band at 2375 cm^{-1} and the appearance of new bands at 725 and 595 cm^{-1}.

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Chapter Two

CARBONYL, PHOSPHINE, OLEFIN, AND RELATED TRANSITION METAL COMPLEXES

28. (CARBENE)PENTACARBONYL COMPLEXES OF CHROMIUM AND TUNGSTEN

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Checked by CHARLES M. LUKEHART† and JANE V. ZEILE†

The synthesis of the transition metal carbenoid‡ complexes, $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ and $[W(CO)_5\{C(CH_3)(OCH_3)\}]$, via the initial reaction of an organolithium reagent and a coordinated carbon monoxide molecule followed by alkylation represents one general synthetic route to a metal carbenoid complex. In addition, these particular carbenoid complexes are useful starting materials for the synthesis of a number of related metal derivatives and organic compounds.[1,2] Pentacarbonyl[1-(phenylthio)ethylidene]chromium(0) has been prepared by the reaction of $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ with neat benzenethiol at room temperature over a period of two days.[3]

This particular thiocarbenoid complex and the analogous tungsten derivative are more conveniently synthesized by an initial reaction of $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ or $[W(CO)_5\{C(CH_3)(OCH_3)\}]$ with benzenethiolate ion at room temperature followed by acidification with hydrochloric acid. This synthetic route has also been used to prepare a series of pentacarbonyl[(1-phenylthio)ethylidene]tungsten(0) complexes substituted in the 4-position of the phenyl rings.[4]

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‡ The term "methylene" is sometimes used in place of "carbene" in describing complexes of this type.

A. PENTACARBONYL(METHOXYMETHYLCARBENE)-CHROMIUM(0)

$$\mathrm{Cr(CO)_6} \xrightarrow{\mathrm{CH_3Li}} \mathrm{Li[Cr(CO)_5(COCH_3)]}$$

$$\mathrm{Li[Cr(CO)_5(COCH_3)]} \xrightarrow{\mathrm{[(CH_3)_3O][BF_4]}} \mathrm{[Cr(CO)_5\{C(CH_3)(OCH_3)\}]}$$

Procedure

A 250-mL, three-necked, round-bottomed flask, containing a magnetic stirring bar and equipped with an inlet for nitrogen at one neck, a nitrogen-bubbling tube at another neck, and a 125-mL pressure-equalizing dropping funnel at the third neck, is purged with nitrogen. The flask is then charged with 5.0 g (22.7 mmol) of $Cr(CO)_6$ and 100 mL of freshly distilled diethyl ether which has previously been dried over sodium. The dropping funnel is then charged with 25 mL of 1.0*M* methyllithium solution (0.55 mol) in diethyl ether. The methyllithium solution is then added in a dropwise fashion to the ethereal solution of $Cr(CO)_6$ during a period of ca. 15–20 min. The reaction may be deemed complete when all of the $Cr(CO)_6$ has dissolved. During the course of the reaction the solution changes from yellow to a dark-brown color. If all the $Cr(CO)_6$ has not dissolved, more methyllithium solution may be added.

The following operations are performed in the open air. The solvent is completely removed with the aid of a roto-evaporator, leaving behind the salt $Li[Cr(CO)_5\,(COCH_3)]$. At this point approximately 60–80 mL of water is added to dissolve the salt. The solution is stirred for a few minutes and then filtered by gravity. Solid trimethyloxonium tetrafluoroborate(1 –)[5] is added in small portions to the stirred solution until the solution is neutralized (pH paper). It is important to avoid over-acidification since $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ is attacked by any HBF_4 which is produced. The methylation should be carried out as quickly as possible. Once this has been completed the $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ is quickly extracted in several small portions using nitrogen-saturated *n*-pentane. The combined pentane extracts are dried over 2 g of anhydrous sodium sulfate for a few minutes with stirring and then filtered by gravity. The volume of solvent is then reduced to about 20–30 mL with the aid of a roto-evaporator.

Pentacarbonyl(methoxymethylcarbene)chromium(0) precipitates from the concentrated solution when the solution is placed in a Dry Ice–acetone slush (– 78). The complex may be recrystallized from the minimum amount of a 1 : 1 mixture of a *n*-hexane–diethyl ether; purity was confirmed by its mp. Yield is 2.0 g (35%).

Properties

Pentacarbonyl(methoxymethylcarbene)chromium(0) is a dull-yellow, crystalline solid; mp 34°. It slowly decomposes in the solid state at room temperature in air, but may be stored at 5° for a few days before appreciable decomposition is observed. It is soluble in aliphatic hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, and other common laboratory solvents such as benzene, 1,4-dioxane, tetrahydrofuran, chloroform, dichloromethane, and methanol, and is slightly soluble in ethanol. The infrared spectrum (cyclohexane solution) has $\nu(CO)$ bands at 2065, 1985, 1965, and 1950 cm^{-1}. The ^1H nmr spectrum in chloroform-*d* shows the methoxy proton resonance at $\tau 6.15$ and the methyl proton resonance at $\tau 7.70$. Other physical properties are reported in the literature.[6,7]

B. PENTACARBONYL(METHOXYMETHYLCARBENE)-TUNGSTEN(0)

$$W(CO)_6 \xrightarrow{CH_3Li} Li[W(CO)_5(COCH_3)]$$

$$Li[W(CO)_5(COCH_3)] \xrightarrow{[(CH_3)_3O][BF_4]} [W(CO)_5\{C(CH_3)(OCH_3)\}]$$

Procedure

The procedure is identical with that outlined above for $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ except for the replacement of $Cr(CO)_6$ by $W(CO)_6$ (7.2 g, 20.5 mmol); purity was confirmed by its mp. Yield is 2.75 g (55%).

Properties

Pentacarbonyl(methoxymethylcarbene)tungsten(0) is a dull-yellow, crystalline solid; mp 52°. It is appreciably more stable thermally and oxidatively than its chromium analog in the solid state at room temperature and may be stored at 5° for a period of 1 or 2 weeks without significant decomposition. It is soluble in aliphatic hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, and other common laboratory solvents such as benzene, 1,4-dioxane, tetrahydrofuran, chloroform, dichloromethane, and methanol; it is slightly soluble in ethanol. The infrared spectrum (cyclohexane solution) has $\nu(CO)$ bands at 2075, 1980, 1960, and 1947 cm^{-1}. The ^1H nmr spectrum in chloroform-*d* has the methoxy proton resonance at $\tau 6.17$ and the methyl proton resonance at $\tau 7.69$. Other physical properties are reported in the literature.[6,7]

C. PENTACARBONYL[1-(PHENYLTHIO)ETHYLIDENE]-CHROMIUM(0)

$$[Cr(CO)_5\{C(CH_3)(OCH_3)\}] + Na[SC_6H_5] + HCl \longrightarrow [Cr(CO)_5\{C(CH_3)(SC_6H_5)\}] + NaCl + CH_3OH$$

Procedure

A 250-mL, three-necked, round-bottomed flask is charged with 80 mL of benzene saturated with nitrogen. One neck of the flask is equipped with an inlet for nitrogen, another neck is equipped with a nitrogen-bubbling tube, and the third neck is equipped with a 125-mL pressure-equalizing dropping funnel which is charged with 35 mL of a methanolic solution of concentrated hydrochloric acid. This solution is obtained from a solution containing 6 mL of concentrated hydrochloric acid dissolved in 100 mL of methanol. A slow stream of nitrogen is passed over the solution and 2.0 g (8.0 mmol) of $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ is added to the benzene followed by the addition of 2.0 g (15.1 mmol) of sodium benzenethiolate* dissolved in 20 mL of methanol saturated with nitrogen.

The nitrogen flow is stopped and the inlet and outlet of the flask are stoppered. The benzene solution is then stirred for 5 min by means of a magnetic stirring bar. The methanolic hydrochloric acid solution is then added dropwise to the stirred benzene solution over a period of 15–20 min; during this time the solution becomes deep-red in color and sodium chloride precipitates. Stirring is continued for 2 hr. The following operations are performed in the open air. The volume of the reaction mixture is reduced to a minimum with the aid of a Roto-evaporator, and 80 mL of water and 100 mL of *n*-hexane are added successively to the residue. The aqueous layer is quickly discarded and the organic layer dried over 5 g of anhydrous sodium sulfate for a few minutes. The sodium sulfate is removed by filtration, and the volume of the filtrate is reduced with the aid of a roto-evaporator to leave a dark-red, oily residue.

A Fluorosil (100–200 mesh) column (25 cm × 3 cm) is charged with the oily residue, and elution is initiated with *n*-hexane saturated with nitrogen. The dark-red band which moves down the column is collected, and the volume of the dark-red effluent is reduced to about 5 mL with the aid of a Roto-evaporator.

* A solution of 0.60 g of NaOH and 1.5 mL of C_6H_5SH dissolved in 20 mL of methanol saturated with nitrogen may be used in place of solid sodium benzenethiolate. However, the use of this solution has been found to result in a somewhat lower yield of the final product $[Cr(CO)_5\{C(CH_3)(SC_6H_5\}]$.

The solution is then transferred to a 25-mL beaker. This solution is next concentrated in a stream of nitrogen, immersed in a Dry Ice–acetone slush (−78°). Crude $[Cr(CO)_5\{C(CH_3)(SC_6H_6)\}]$ precipitates from the solution and is collected by filtration and air-dried. Yield is 1.3 g (50%). The crude $[Cr(CO)_5\{C(CH_3)(SC_6H_5)\}]$ may be recrystallized from the minimum amount of *n*-hexane–diethyl ether (1 : 1) solution. *Anal.* Calcd. for $C_{13}H_8O_5SCr$: C, 47.55; H, 2.44. Found: C, 47.56; H, 2.65.

Properties

Pentacarbonyl[1-(phenylthio)ethylidene]chromium(0) is a dark-red, crystalline solid; mp 67°. It slowly decomposes in the solid state upon exposure to light. It may be stored for several months at 5° in the dark. It is soluble in aliphatic hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, and other common laboratory solvents such as benzene, 1,4-dioxane, tetrahydrofuran, chloroform, dichloromethane, and methanol; it is slightly soluble in ethanol. In these solvents, solutions of $[(CO)_5Cr\{C(CH)_3(SC_6H_5)\}]$ are rapidly decolorized on exposure to light. The infrared spectrum (cyclohexane solution) has ν(CO) bands at 2060, 1983, and 1960 cm^{-1}. The ^1H nmr spectrum in chloroform-*d* shows the methyl-proton resonance at τ6.71. Other physical properties are reported in the literature.[4]

D. PENTACARBONYL[1-(PHENYLTHIO)ETHYLIDENE]-TUNGSTEN(0)

$$[W(CO)_5\{C(CH_3)(OCH_3)\}] + Na[SC_6H_5] + HCl \longrightarrow [W(CO)_5\{C(CH_3)(SC_6H_5)\}] + NaCl + CH_3OH$$

Procedure

The procedure is identical with that given in Sec. C except for the replacement of $[Cr(CO)_5\{C(CH_3)(OCH_3)\}]$ by $[W(CO)_5\{C(CH_3)(OCH_3)\}]$. Solid sodium benzenethiolate may be replaced by a methanolic solution of $Na[SC_6H_5]$ generated *in situ* by the reaction of sodium hydroxide with C_6H_5SH in methanol with no appreciable decrease in yield of the final product. Yield = 1.6 g (50%). *Anal.* Calcd. for $C_{13}H_8O_5SW$: C, 33.88; H, 1.55. Found: C, 33.93; H, 2.05.

Properties

Pentacarbonyl[1-(phenylthio)ethylidene]tungsten(0) is an air-stable, dark-red, crystalline solid; mp 76°. It can be handled in the presence of light with no decomposition. It may be stored for several months at 5°. It is soluble in aliphatic hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, and other common laboratory solvents such as benzene, 1,4-dioxane, tetrahydrofuran, chloroform, dichloromethane, and methanol; it is slightly soluble in ethanol. The infrared spectrum (cyclohexane solution) shows ν(CO) bands at 2065, 1980, and 1953 cm^{-1}. The ^{1}H nmr spectrum in chloroform-*d* shows the methyl proton resonance at $\tau 6.96$. Other physical properties are reported in the literature.[4]

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29. DICARBONYL(η^5-CYCLOPENTADIENYL)(THIOCARBONYL)IRON(1 +) HEXAFLUOROPHOSPHATE(1 −) AND DICARBONYL(η^5-CYCLOPENTADIENYL)-[(METHYLTHIO)THIOCARBONYL]IRON

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^- + CS_2 \longrightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS_2)]^-$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS_2)]^- + CH_3I \longrightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2[C(S)SCH_3] + I^-$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(S)SCH_3] + HCl \longrightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+Cl^- + CH_3SH$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+Cl^- + NH_4[PF_6] \longrightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+[PF_6]^- + NH_4Cl$$

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The dicarbonyl(η^5-cyclopentadienyl)(thiocarbonyl)iron(1 +) cation, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$, has been prepared by the reaction of the $[(\eta^5\text{-}C_5H_5)$-

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$Fe(CO)_2]^-$ ion with $ClC(S)OCH_3$ or $ClC(S)OC_2H_5$ followed by treatment of the resulting intermediate with hydrogen chloride.[1,2] A second procedure[2] involved reaction of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ ion with carbon disulfide, followed by methyl iodide to give the dithioester, dicarbonyl(η^5-cyclopentadienyl)(methylthio)(thiocarbonyl)iron, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(S)SCH_3]$. On reaction with hydrogen chloride, the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$ ion was produced. The low yields obtained by this latter route made it of limited synthetic utility. Now we report an improved procedure for this reaction which provides a convenient, high-yield synthesis of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$ ion.

Procedure

■ **Caution.** *The drying of tetrahydrofuran may be accompanied by serious explosions under certain conditions.* (See *Inorganic Syntheses*, **12,** 111, 317 (1970), and Synthesis 1 of this volume for additional information on suggested drying procedures.)

The starting material, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, may be prepared[3] from iron pentacarbonyl and cyclopentadiene dimer*, or it may be purchased commercially.† Before use, dicarbonyl(η^5-cyclopentadienyl)iron dimer may be recrystallized by dissolving it in a minimum amount of dichloromethane, filtering the saturated solution through Celite filter aid, adding an equal volume of *n*-hexane to the solution, and cooling to −20°.

A 500-mL three-necked flask[4] with a stopcock fused to the bottom and equipped with a mechanical stirrer (Fig. 15), is flushed well with nitrogen, and 35 mL of mercury is added. While rapidly stirring the mercury, 2.0 g (87 mmol) of sodium is added to the flask against a countercurrent of nitrogen, in pieces of about 0.4 g cut under a hydrocarbon solvent. After the

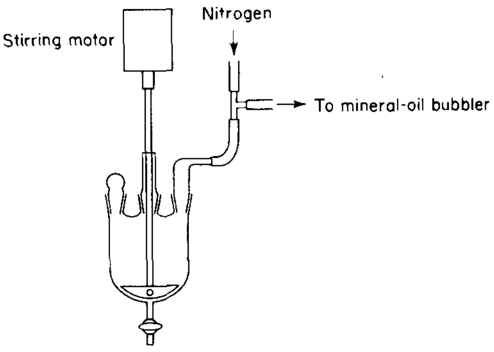

Fig. 15. Apparatus for the preparation of dicarbonyl(η^5-cyclopentadienyl)[(methylthio)thiocarbonyl]iron.

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* 3a, 4, 7, 7a-tetrahydro-4,7-methanoindene.

† Available from Strem Chemicals, Inc., 150 Andover Street, Danvers, MA 01923.

amalgam has cooled, dry tetrahydrofuran (250 mL) is added to the flask, followed by 10.0 g (28.3 mmol) of dicarbonyl(η^5-cyclopentadienyl)iron dimer. The mixture is stirred *vigorously* for ca. 1 hr.

The sodium amalgam is then drained out of the flask through the bottom stopcock. The mercury may be washed with ethanol and water and reused.[5] Carbon disulfide (5 mL, 73 mmol) is added rapidly to the solution under a nitrogen atmosphere, and the mixture is stirred for 20–30 *seconds*. Methyl iodide (5 mL, 79 mmol) is then added immediately. The mixture is stirred for ca. 5 min under a nitrogen atmosphere. *Longer reaction times reduce the yield.* The operations beyond this point may be done in air. The reaction mixture is then decanted into a 1000-mL round-bottomed flask and evaporated to dryness on a rotary evaporator.

The $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(S)SCH_3]$ may be isolated at this stage by extracting the residue with warm pentane until the wash is colorless. The solution is filtered and concentrated by evaporation under vacuum. Cooling to −20° gives 7.5–9.5 g* of brown crystals of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}[C(S)SCH_3]$ (49–62% yield). *Anal.* Calcd. for $C_9H_8FeO_2S_2$: C, 40.3; H, 2.98; S, 23.8. Found: C, 40.4; H, 2.95; S, 22.7.

In the direct preparation of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$ ion the dithioester is not normally isolated. The residue resulting from evaporation of the reaction mixture on a rotary evaporator is dissolved in 75 mL of benzene and filtered through Celite filter aid. Another 75 mL of benzene is used to wash the flask and precipitate. The benzene solution is then transferred to a 500-mL round-bottomed flask. Dry hydrogen chloride gas is bubbled rapidly through the solution for ca. 1 hr. The flask is then put on a rotary evaporator and the volume of solution is reduced by about one-third. A solution of 10.0 g of $NH_4[PF_6]$ (61 mmol) in 40 mL of anhydrous acetone is added to the benzene solution with swirling. Approximately 250 mL of diethyl ether is then added to complete precipitation. The light-colored solid is collected by suction filtration and washed with ether. It is dissolved in 250 mL of warm anhydrous acetone and filtered to remove the insoluble ammonium chloride. Approximately 75 mL of ether is added slowly, with warming of the flask on a hot-water bath, until the point of precipitation is reached. Cooling to −20° gives yellow crystals of $[(\eta^5\text{-}C_5H_5)\times Fe(CO)_2(CS)]^+[PF_6]^-$. After the product is collected and washed with ether, the filtrate is evaporated to about 100 mL, and the crystallization step is repeated, yielding a total of 10.0 to 13.0 g (48–63% yield) of the product.† A

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* The checkers report a yield of 5.6 g (37%).

† The checkers obtained a yield of 8.1 g, (39%) based on $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. They report that the second and third crops of crystals were not pure.

third crop of impure product may also be collected. *Anal.* Calcd. for $C_8H_5F_6FeO_2PS$: C, 26.2; H, 1.37; S, 8.75. Found: C, 26.6; H, 1.19; S, 8.77.

Properties

The dithioester complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(S)SCH_3]$, is an air-stable, brown solid with a melting point of 72°, soluble in polar and nonpolar organic solvents. The infrared spectrum of its hexane solutions shows two strong carbonyl absorptions at 2035* and 1988* cm^{-1}. Its ^{1}H nmr spectrum taken in carbon tetrachloride shows a singlet C_5H_5 resonance at τ5.08 and singlet $-SCH_3$ resonance at τ7.40.

The thiocarbonyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+[PF_6]^-$ crystallizes as air-stable yellow crystals from acetone or acetone-ether. It is also soluble in acetonitrile, but decomposes in dimethyl sulfoxide and dimethylformamide. The crystals darken at about 190° and decompose without melting. The infrared spectrum in acetone shows two strong carbonyl absorptions (2102† and 2072† cm^{-1}). The C—S stretching frequency at 1348 cm^{-1} may be observed in a hexachlorobutadiene mull. An x-ray crystallographic study of the compound confirms its formulation as a thiocarbonyl complex.[6] Its ^{1}H nmr spectrum taken in acetone-d_6 solvent exhibits a singlet C_5H_5 resonance at τ3.9. The thiocarbonyl ligand in this complex is very susceptible to attack by nucleophiles.[7] Conversion to the $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ ion has been observed in moist acetone or acetonitrile.[8]

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* The checkers report values of 2032 and 1985 cm^{-1}.

† The checkers report values of 2101 and 2068 cm^{-1}.

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30. TRICARBONYL-(η^5-CYCLOPENTADIENYL)SILYL COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

$$K[C_5H_5] + M(CO)_6 \longrightarrow K[M(CO)_3(\eta^5\text{-}C_5H_5)] + 3CO$$
$$SiH_3Br + K[M(CO)_3(\eta^5\text{-}C_5H_5)] \longrightarrow H_3SiM(CO)_3(\eta^5\text{-}C_5H_5) + KBr$$
$$(M = Cr, Mo, W)$$

Submitted by A. P. HAGEN* and P. J. RUSSO*
Checked by A. M. MANCE,† N. D. MIRO,† and C. H. VAN DYKE†

Organometallic compounds of the type $R_3SiM(CO)_x(\eta^5\text{-}C_5H_5)$ have been prepared in the following ways: (1) where $R = CH_3$[1] or C_6H_5[2] and $M = Fe(x = 2)$ by the interaction of an appropriate silyl halide with the metal carbonyl complex anion, $[M(CO)_x(\eta^5\text{-}C_5H_5)]^-$; (2) where R = Cl or F and M = Mo, W(x = 3),[3,4] M = Fe(x = 2),[3,5] or M = Ni(x = 1)[3] by the cleavage of the metal-metal bond in the corresponding dimer, $[M(CO)_x(\eta^5\text{-}C_5H_5)]_2$, by the Si—H bond of a silane; (3) where $R = CH_3$, M = Mo, W(x = 3)[6] by the reaction of compounds containing a silicon-nitrogen bond with the appropriate metal hydride complex, $HM(CO)_x(\eta^5\text{-}C_5H_5)$; and (4) where R = H, M = Fe(x = 2)[7] by the reaction between an $[H_3Si]^-$ anion and the halide of the metal complex, $BrM(CO)_x(\eta^5\text{-}C_5H_5)$. Until recently silyl-chromium complexes of the above general type were not known.[8,9] The present procedure describes the synthesis of silyl-metal bonds in compounds of the type $H_3SiM(CO)_3(\eta^5\text{-}C_5H_5)$; where M = Cr, Mo, W by by a gas-solid exchange reaction between bromosilane (silyl bromide) and the potassium salt of the appropriate metal carbonyl complex anion.

Synthesis of Reagents and Purification of Solvents

■ **Caution.** *Bromosilane is potentially hazardous since it is spontaneously inflammable in air. All manipulations involving this compound must be carried out in a vacuum system. Unused bromosilane may be destroyed by condensing it in small portions into a large quantity of alcoholic potassium hydroxide solution. The hydrogen which is liberated during the ensuing reaction should be pumped away continuously as it is evolved.*

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Bromosilane is synthesized from phenylsilane and anhydrous hydrogen bromide[10] and is stored in a glass vessel at −196°. Known weights of the compound are obtained by measuring the pressure of the gas when it is confined in a known volume at a given temperature.

Monomeric 1,3-cyclopentadiene is obtained by the thermal cracking of cyclopentadiene dimer which is heated at about 150° in a nitrogen atmosphere in a distillation apparatus with a water-jacketed condenser. The fraction which boils below 44° is collected at 0° and is then degassed and stored *in vacuo* at −78°.*

A preliminary purification of 1,2-dimethoxyethane (monoglyme) is carried out by refluxing it over sodium hydroxide pellets for 2–3 days, then distilling it at atmospheric pressure under a nitrogen atmosphere and collecting the distillate in a flask containing fresh lithium tetrahydridoaluminate(1−). Next, this mixture is refluxed under a nitrogen atmosphere for 24 hr and is then distilled. The distillate (bp 83–84°) is saturated with pure nitrogen immediately before use to assure a minimum oxygen concentration.

Procedure

■ **Caution.** *Potassium is a dangerous metal from which water and air must be excluded. All manipulations of this substance must be carried out in a dry, oxygen-free nitrogen-purged glove bag. Unreacted potassium may be destroyed by adding it to an excess of* n-*butanol. Also, carbon monoxide is an odorless, extremely toxic gas. It is essential that the apparatus (Fig. 16) be set up in an efficient fume hood.*

Potassium cyclopentadienide is prepared in a large glove bag† that is constantly purged with nitrogen. Approximately 125 mL of freshly distilled nitrogen-saturated 1,2-dimethoxyethane is poured into the reaction vessel containing a Teflon-coated magnetic stirring bar, and then 1,3-cyclopentadiene (4.3 mL, 51 mmol) is added. Potassium (2.0 g, 51 mmol) is cut into small pieces (approximately 2 mm on a side), washed with several portions of solvent to remove oil on the surface and then added one or two pieces at a time to the stirred solution. The slow addition prevents the reaction from becoming too vigorous. When the last piece of potassium has been added, the red solution of $K[C_5H_5]$ is stirred until either gas formation

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* The boiling points of 1,3-cyclopentadiene and cyclopentadiene dimer (3a, 4, 7, 7a-tetrahydro-4,7-methanoindene), are 40.0° and 170°, respectively.

† Model X-37-37, Instruments for Research and Industry, 108 Franklin Ave., Cheltenham, PA 19102.

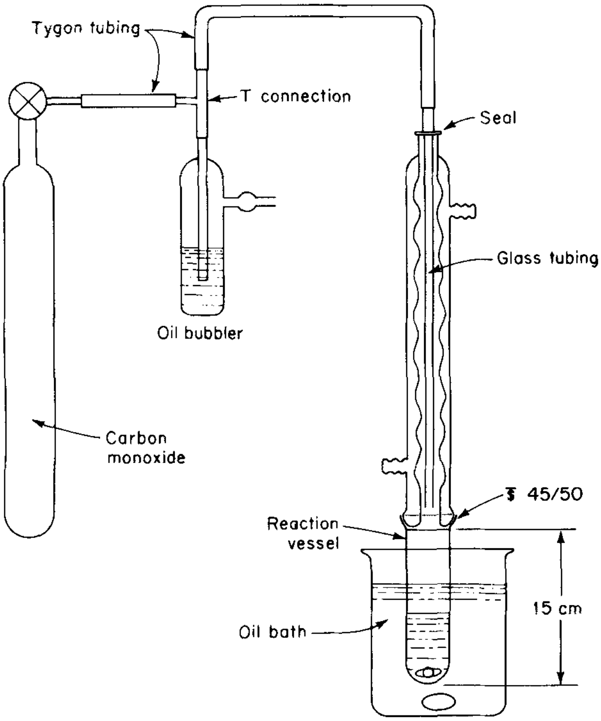

Fig. 16. Apparatus for the synthesis of $K[M(CO)_3(\eta^5\text{-}C_5H_5)]$.

on the surfaces of any remaining pieces of metal has ceased or until no further gas is evolved upon the addition of a piece of potassium to the solution. The reaction is complete after 1–2 hr, and any unreacted metal is removed from the solution with forceps.

The appropriate metal hexacarbonyl ($Cr(CO)_6$, 11.5 g, 52.3 mmol; $Mo(CO)_6$, 13.5 g, 51.3 mmol; $W(CO)_6$, 18.0 g, 51.3 mmol) is added to the $K[C_5H_5]$ solution and the resulting mixture is stirred magnetically in the glove bag for 15 min. Liberation of carbon monoxide commences immediately with molybdenum hexacarbonyl and the solution becomes red-yellow; however, for chromium hexacarbonyl and tungsten hexacarbonyl the reaction is slower. The glove bag is carefully opened at one corner and the end of an Allihn condenser, fitted with a length of glass tubing to within 2 cm of the bottom of the condenser (Fig. 16) and delivering a strong jet of carbon monoxide, is inserted into the glove bag and is attached to the reaction vessel. In order to avoid contamination of the products by grease, no grease or a Teflon sleeve is used on the joint; some difficulty is therefore sometimes experienced in separating the joints at the end of the experiment.

The reaction vessel is removed from the glove bag and is clamped so that the solution level is 2–3 cm below the oil bath level. A stream of carbon monoxide from a cylinder (lecture-bottle size) flows through the glass tubing throughout the reaction period. After 1 hr of simultaneous stirring of the oil bath and the solution by the same magnetic stirrer, a heating coil* is placed just below the oil surface and the temperature of the oil at the top is slowly raised to about 96°. After vigorous refluxing for 18 hr under a carbon monoxide atmosphere, the resulting bright-yellow solution is cooled to room temperature, the heating coil is replaced by a magnetic stirrer–hot plate, and the condenser is rapidly replaced by a distilling head. Care should be taken that air does not enter during this operation. Most of the solvent is distilled off under a carbon monoxide atmosphere and the remaining yellow slurry is then allowed to cool to room temperature. The distilling head is quickly replaced by a ground-glass joint attached to a vacuum stopcock. The solution is cooled to 0°, then *slowly* to $-78°$, and finally to $-196°$. The carbon monoxide then is pumped away. The solid is allowed to melt and the dissolved carbon monoxide which is liberated is pumped away after the solution has been refrozen at $-196°$. The remaining solvent is removed carefully at temperatures of $-20°$, then 0°, and finally room temperature and collected in a trap held at $-196°$. The reactor is then heated at 60° for 4 hr with pumping to remove any remaining hexacarbonyl. The reactor is placed in a nitrogen-purged glove bag, and the hard solid is broken into several small pieces. The solid is ground into a fine powder and then an appropriate amount of the salt $K[M(CO)_3(\eta^5-C_5H_5)]$ ($M = Cr$: 2.10 g, 87.4 mmol; $M = Mo$: 2.50 g, 88.0 mmol; $M = W$: 3.25 g, 88.0 mmol) is transferred into the bottom of the reactor (Fig. 17) using a long-stemmed funnel. The reactor is then *slowly* evacuated to prevent the powdery solid from being mechanically deposited onto the upper walls of the vessel. To ensure a dry solid the bottom of the reactor is heated at 80° for 3–4 hr with constant pumping.

■ **Caution.** *Heat is liberated during the course of the reaction with bromosilane, and it may be necessary to cool the bottom of the reactor to $-78°$. The brown residue remaining in the bottom of the reactor after sublimation of the product is pyrophoric and should be destroyed by the slow addition of* n*-butanol to the reactor.*

Bromosilane (1.46 g, 13.1 mmol) is condensed into the side arm of the reactor (Fig. 17); the Teflon stopcock is closed, and then the reactor is allowed to warm to room temperature. The gaseous bromosilane is allowed to remain in contact with the solid for approximately 30 min. The bottom of

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* The checkers indicated that decomposition may result if the coil is too close to the reaction vessel wall.

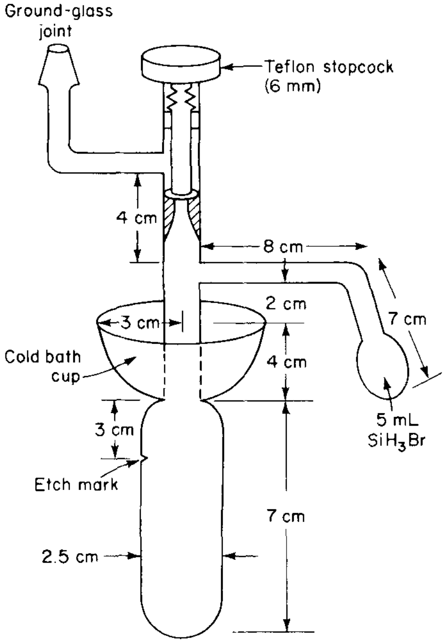

Fig. 17. Reactor for the synthesis of $H_3SiM(CO)_3(\eta^5\text{-}C_5H_5)$.

the reactor is then cooled to −196° and any noncondensable gas is pumped away. The reactor is closed, and after an additional 30 min at room temperature the bottom is cooled to −196° and any noncondensable gas is again pumped away. The bottom of the reactor is then warmed to −78° and the excess bromosilane is condensed into a trap held at −196°. The bottom of the reactor is then warmed to room temperature for the chromium complex (or to 65° for the molybdenum and tungsten complexes) with constant pumping in order to remove excess metal hexacarbonyl. Finally, the bottom of the reactor is heated to 60–75° for the chromium complex (to 75–80° for the molybdenum complex, or to 80–90° for the tungsten complex). The product sublimes and is collected at the base of the liquid-nitrogen-filled cold-bath cup. At the end of 1 hr, the entire reactor is allowed to attain room temperature, the cup is wiped free of condensed moisture, and the reactor is placed into the glove bag. The neck of the reactor is flushed with a stream of nitrogen and the stopcock is opened and closed, allowing nitrogen to enter the reactor. (■ **Caution.** *The following operation should be performed behind a safety shield, and protective gloves should be used.*) The reactor is removed from the glove bag, a previously filed etch mark is "spot" heated so that a crack begins to develop in the glass, and the reactor is quickly returned to the glove bag. The reactor is broken to separate the yellow sublimate from

TABLE I Physical Properties of $H_3SiM(CO)_3(\eta^5\text{-}C_5H_5)$

M	Color	mp, °C (with decomp.)	ν(CO), cm^{-1} (Nujol mull)	τ(Si—H)	$\tau(C_5H_5)$
Cr	bright-yellow	130	1999, 1943, 1918	5.88	5.11
Mo	yellow	94	2005, 1948, 1925	6.15	4.65
W	dull-yellow	111	2005, 1940, 1931	6.18	4.50

the brown *pyrophoric* solid residue. A 40% yield of the chromium and molybdenum compounds and a 20% yield of the tungsten compound is attained, based on the initial amount of complex anion. The compounds are stored *in vacuo* below 0°. *Anal.* Calcd. for $C_8H_8O_3SiCr$: C, 41.37; H, 3.47; Si, 12.09. Found: C, 40.60; H, 3.49; Si, 12.00. *Anal.* Calcd. for $C_8H_8O_3SiMo$: C, 34.79; H, 2.91; Si, 10.17. Found: C, 34.02; H, 3.23; Si, 10.25. *Anal.* Calcd. for $C_8H_8O_3SiW$: C, 26.39; H, 2.15; Si, 7.71. Found: C, 26.59; H, 2.28; Si, 7.97.

Properties

Tricarbonyl(η^5-cyclopentadienyl)silylchromium, -molybdenum, and -tungsten are crystalline compounds which are stable *in vacuo* below 0°. They change color rapidly even in the presence of the small amounts of oxygen and water vapor frequently present in the nitrogen atmosphere of a glove bag and they decompose rapidly upon exposure to air. The compounds are readily converted by gaseous hydrogen chloride to $MH(CO)_3(\eta^5\text{-}C_5H_5)$ and silyl chloride.[9] When combined with trimethylamine an adduct forms which contains the $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$ anion.[9] Some properties of the compounds are summarized in Table I.

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31. PHOSPHINE COMPLEXES OF RHENIUM

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Rhenium displays an unusual array of oxidation states and coordination numbers that make it the subject of much current research. The following preparation, adapted from one developed by Chatt and coworkers, provides a convenient synthesis of trichlorooxobis(triphenylphosphine)rhenium(V)[1] based on either rhenium(VII) oxide or perrhenate salts. The trichlorooxo compound is a versatile intermediate for the synthesis of other rhenium complexes such as *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III),[2] as described below. The rhenium(III) complex, in turn, provides a starting point for synthesis of other compounds such as *trans*-tetrachlorobis(dimethylphenylphosphine)rhenium(IV)[3] and tris(dimethylphenylphosphinepentahydrido)rhenium(V).[4] An alternative synthesis of the trichlorocomplex is described in the accompanying preparation by Douglas and Shaw.[4]

A. TRICHLOROOXOBIS(TRIPHENYLPHOSPHINE)-RHENIUM(V)

$$Re_2O_7 + 6HCl + 6(C_6H_5)_3P \longrightarrow 2ReOCl_3[P(C_6H_5)_3]_2 + 2(C_6H_5)_3PO + 3H_2O$$

Procedure

A 1-L two-necked flask, equipped with magnetic stirrer, addition funnel, and condenser surmounted by a nitrogen-flushed "tee" tube, is charged with 7.30 g (15 mmol) of rhenium(VII) oxide (or 8.68 g of potassium perrhenate), 50 mL of concentrated hydrochloric acid, and 250 mL of absolute ethanol. The solution is stirred and heated to boiling, and a solution of 45 g (170 mmol) of triphenylphosphine in 250 mL of hot ethanol is added. The mixture becomes green immediately, and a precipitate forms even before the addition is complete. The mixture is boiled for 30 min. It is allowed to cool to 55° and is filtered. The lime-green solid product is extracted with 100 mL

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of hot ethanol and with 250 mL of boiling benzene. The yellow residual trichlorooxobis(triphenylphosphine)rhenium(V) is pure enough for most syntheses; yield 24.8 g (99%). For further purification a 10-g portion of the crude product is dissolved in 3 L of boiling benzene. On cooling and addition of 1 L of heptane, 9.25 g of yellow, crystalline product is obtained. *Anal.* Calcd. for $C_{36}H_{30}Cl_3OP_2Re$: C, 51.89; H, 3.62; Cl, 12.76. Found: C, 52.05; H, 3.70; Cl, 12.41.

Properties[1]

Trichlorooxobis(triphenylphosphine)rhenium(V) is a yellow, diamagnetic, air-stable solid which crystallizes from benzene-heptane as monoclinic prisms, mp 211–214° with decomposition. It is slightly soluble in benzene to give nonconducting solutions. The infrared spectrum shows a strong band at 969 cm^{-1} assignable to Re=O stretching.

B. *mer*-TRICHLOROTRIS(DIMETHYLPHENYLPHOSPHINE)RHENIUM(III)

$$ReOCl_3[P(C_6H_5)_3]_2 + 4P(CH_3)_2(C_6H_5) \longrightarrow ReCl_3[P(CH_3)_2C_6H_5]_3 + 2P(C_6H_5)_3 + PO(CH_3)_2C_6H_5$$

Procedure

■ **Caution.** *Alkylphosphines are volatile and toxic and should be handled only in an efficient hood.*

A mixture of 9.0 g (10.8 mmol) of trichlorooxobis(triphenylphosphine)rhenium(V), 7.2 g (52 mmol) of dimethylphenylphosphine,[5] and 350 mL of benzene is stirred and boiled for 2 hr under nitrogen in a 1-L flask equipped with magnetic stirrer and condenser. The solution is evaporated to dryness *in vacuo* and the residue is dried under high vacuum at room temperature. The residue is dissolved in 300 mL of ethanol under nitrogen. On cooling the solution, one obtains 5.6–6.5 g of orange platelets of a benzene solvate of trichlorotris(dimethylphenylphosphine)rhenium(III), mp 153–160°. Partial evaporation of the filtrate gives 3.7 g of triphenylphosphine, mp 76–78°.

The benzene solvate, which by elemental and nmr analyses contains about one benzene per rhenium, may be used for most preparative purposes. Recrystallization from ethanol gives pure orange crystals of *mer*-trichlorotris(dimethylphenylphosphine)rhenium(III). *Anal.* Calcd. for $C_{24}H_{33}Cl_3P_3Re$: C, 40.77; H, 4.70; Cl, 15.04. Found: C, 40.96; H, 4.84; Cl, 15.14.

Properties

mer-Trichlorotris(dimethylphenylphosphine)rhenium(III) is a yellow-orange paramagnetic solid (μ_{eff}, 2.0 B.M.) which crystallizes from ethanol as needles.[2] The *meridional* configuration was established by nmr criteria. The complex is moderately soluble and stable in benzene and dichloromethane but is readily oxidized by highly halogenated solvents such as chloroform and carbon tetrachloride. The compound is stable in air for at least several days.

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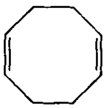
32. π-CYCLOOCTENYL-π-1,5-CYCLOOCTADIENECOBALT

[(1,2,5,6-*η*)-1,5-*cyclooctadiene*][(1,2,3-*η*)-2-*cycloocten*-1-*yl*]*cobalt*

$CoCl_2$ +  + Na $\longrightarrow$ NaCl + $Co(C_8H_{12})(C_8H_{13})$

Submitted by L. W. GOSSER* and MARTIN A. CUSHING, JR.*
Checked by HEINZ BERKE† and SIEGFRIED STENGELIN†

π-Cyclooctenyl-π-1,5-cyclooctadienecobalt is a valuable reagent for the preparation of low-oxidation-state cobalt complexes such as hydrides and olefin complexes.[1] Several preparations of this compound have been reported. It has been prepared by electrochemical or alkylaluminum reduction of bis(2,4-pentanedionato)-cobalt(II) (cobalt acetylacetonate) in the presence of 1,5-cyclooctadiene[2] or by the reduction of anhydrous cobalt chloride

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with sodium in a solution of pyridine and 1,5-cyclooctadiene.[3] The procedure described below is based on the latter method of S. Otsuka and M. Rossi.[3]

Reagents and Solvent

■ **Caution.** *The drying of tetrahydrofuran may be accompanied by serious explosions under certain conditions.* (See *Inorganic Syntheses*, **12,** 111, 317, and Synthesis 1 in this volume for additional information on suggested drying procedures.)

The solvents should be free of air and water. Pyridine and 1,5-cyclooctadiene were distilled under nitrogen. Tetrahydrofuran was distilled from lithium tetrahydridoaluminate(1−) and stored over sodium in a nitrogen atmosphere. Pentane was dried over molecular sieve and sparged with nitrogen.

Both commercial anhydrous cobalt dichloride* and anhydrous cobalt dichloride prepared by drying the hydrate under vacuum at 200° have been used successfully.

Procedure

■ **Caution.** *Sodium can ignite on contact with moisture and air. Residues from the reaction may contain unreacted sodium and should be handled with appropriate caution.*† *Air must be excluded throughout all the procedures.*‡

It is important to use sodium that has been freshly cut to the small size indicated. A glove box with a pure nitrogen or argon atmosphere greatly facilitates the cutting of the sodium, the filtrations, and other operations. An apparatus for low-temperature crystallization has been described previously[4] and a similar apparatus is available commercially.§

A 2-L, four-necked, round-bottomed flask is equipped with a mechanical stirrer, a thermometer, and a gas vent with a nitrogen bubbler to maintain a slight positive nitrogen pressure. The nitrogen-filled flask is charged with 1 L of tetrahydrofuran, 76 mL of pyridine (0.94 mol), and 57.6 g of anhydrous cobalt dichloride (0.44 mol) which has been crushed to a powder. This

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* Available from Ventron Corporation, Alfa Products, P.O. Box 299, Danvers, MA 01923.

† For information concerning the handling and disposal of sodium see L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," pp. 905, 1022, John Wiley & Sons, Inc., New York (1967).

‡ For general procedures for the manipulation of air-sensitive materials see D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Company, New York, 1969.

§ Available from Kontes Glass Company, Vineland, NJ 08360.

mixture is stirred at room temperature overnight (ca. 16 hr) under nitrogen. 1,5-Cyclooctadiene (200 mL) is added, and the mixture is cooled to 5 ± 5° with a Dry Ice–toluene bath. Sodium metal (20 g),* freshly cut into pieces 2 to 3 mm on a side, is added in ca. 5-g portions by means of a flask and a piece of flexible tubing attached to one of the necks of the flask.† The additions are made at intervals of about 20 min so that the temperature of the reaction mixture can be kept at 5° or below. Stirring at ca. 5° is continued for 2 hr after the addition of the sodium has been completed. The apparatus is allowed to warm to room temperature.‡ It is then transferred to a nitrogen-filled glove box, and the reaction mixture is filtered through diatomaceous earth. The dark-brown filtrate is concentrated under vacuum outside the glove box by flash vacuum-distillation from a flask with a large-bore stopcock and a magnetic stirrer. The result is a brown, semisolid mixture. Heat for the evaporation is supplied from a bath at or below room temperature. The brown residue is dissolved in ca. 250 mL of pentane at room temperature. The solution is filtered and the pentane and any residual volatile materials are evaporated from the filtrate under vacuum (oil pump) at room temperature. This residue is dissolved in ca. 250 mL of pentane, and this solution is cooled in a Dry Ice–acetone bath using the low-temperature crystallization apparatus. The black crystals are collected without warming and are then dried under vacuum for ca. 0.5 hr at −40° and then for ca. 3 hr at room temperature; yield 49 g (40%, based on $CoCl_2$). *Anal.* Calcd. for $C_{16}H_{25}Co$: C, 69.55; H, 9.12. Found: C, 69.53; 68.85; H, 9.56; 8.95.

Properties

When the black solid is warmed at about 2°/min in an evacuated capillary the crystals collapse at ca. 60–65°, but the material does not become fluid even at 100°. It is stable for short periods at room temperature in an inert atmosphere. It has been stored successfully for months at −35° in a nitrogen atmosphere. In solution it is quite air-sensitive. The sensitivity of the solid to air depends on crystal size.

It is quite soluble in aromatics such as benzene or toluene and is also soluble in other solvents such as pentane or tetrahydrofuran.

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* The checkers suggest using sodium sand instead of slices.

† See L. F. Fieser, "Experiments in Organic Chemistry," 3d ed., p. 265, D. C. Heath and Co., Boston, 1957.

‡ It is best to carry the procedure through from the addition of the sodium to the final isolation of the product without interruption. If it is necessary to interrupt the procedure, the materials should be stored at Dry Ice temperature in tightly sealed containers.

The ^1H nmr spectrum is shown in reference 3, as are some diagrammatic representations of the structure. An x-ray crystal analysis of the structure has also been reported.[5]

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2. H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organometal. Chem.,* **30,** 407 (1971).
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33. DODECACARBONYLTETRARHODIUM

$$[Rh(CO)_2Cl]_2 + CO \xrightarrow{NaHCO_3/H_2O} Rh_4(CO)_{12}$$

Submitted by P. E. CATTERMOLE* and A. G. OSBORNE*
Checked by L. J. KRUCZYNSKI†

Of late new methods[1] have been devised for the preparation of the polynuclear carbonyls of the Group VIII elements. Dodecarbonyltetrarhodium, $Rh_4(CO)_{12}$, has presented particular difficulties because of its ready decomposition in solution to $Rh_6(CO)_{16}$. Methods[2] for the synthesis of $Rh_4(CO)_{12}$ also suffer from the disadvantages of requiring long reaction times (up to 4 days) and the need for high-pressure autoclaves. We now report a convenient synthesis of $Rh_4(CO)_{12}$ which can be performed in a few hours and which utilizes carbon monoxide at atmospheric pressure. The method involves the reaction of $[Rh(CO)_2Cl]_2$ with carbon monoxide in the presence of sodium hydrogen carbonate with the addition of a small amount of water. For optimum yields all apparatus and chemicals must be scrupulously dried and the addition of water must be very carefully controlled.

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Procedure

■ **Caution.** *Carbon monoxide is a colorless, odorless, very poisonous gas. The reaction must be conducted in an efficient fume hood.*

A dry, 250-mL, three-necked, round-bottomed flask is equipped with a magnetic follower, a gas inlet tube, a condenser, and a serum cap for admission or withdrawal of samples via a hypodermic syringe. To ensure removal of water vapor the flask is flamed at 0.005 torr. The flask is then charged with $[Rh(CO)_2Cl]_2$ [3,*] (350 mg, 0.899 mmol), sodium bicarbonate (1.0 g, 11.9 mmol, dried at 100°), and dry, degassed *n*-hexane (150 mL). To ensure removal of oxygen, the system is twice evacuated and carbon monoxide (dried by passing over P_4O_{10}) is admitted to a pressure 1 to 2 torr greater than atmospheric pressure. The dried carbon monoxide is then passed through the solution, with stirring, for 2 hr, either from a cylinder or recycled from a reservoir using a peristaltic pump. The addition of water[†] (ca. 0.01 mL) to the stirred solution causes the rapid formation of a dark-red solution containing $Rh_4(CO)_{12}$. After a further 1–1½ hr of stirring under carbon monoxide, the solution is filtered; the solvent is then evaporated under reduced pressure to give a final volume of approximately 50 mL. Dodecacarbonyltetrarhodium is precipitated as dark-red crystals when this solution is cooled to −70°. The compound can be recrystallized by dissolution in pentane,[‡] followed by filtering and cooling to −70°. The yield varies slightly from preparation to preparation but is usually in the range 55 to 60% (0.20 g). After addition of the water, the reaction can be monitored by withdrawing a sample of liquid and recording the infrared spectrum. The reaction is complete when the band at 2027 cm^{-1} disappears.

Properties

Dodecacarbonyltetrarhodium is a dark-red solid which is soluble in most organic solvents but which readily decomposes to $Rh_6(CO)_{16}$ in the

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[*] Prepared in high yield by passing a stream of carbon monoxide, part of which has passed through methanol, over rhodium trichloride heated to 94–95°. This is conveniently done by using a glass tube (30 cm × 4.5-cm-diam.) with the rhodium trichloride and carbon monoxide inlet at one end; the other, unheated, end of the tube has a detachable outlet containing a sintered-glass disk. The $[Rh(CO)_2Cl]_2$ sublimes along the tube and collects against the disk as fine, red crystals. For optimum yield care should be taken not to saturate the carbon monoxide with methanol.

[†] Addition of larger quantities of water causes precipitation of $Rh_6(CO)_{16}$ and rhodium metal. The water may be added as soon as the solution is saturated with carbon monoxide, if desired.

[‡] The checker used toluene for recrystallization.

presence of water. It is best stored under an atmosphere of carbon monoxide. In an atmosphere of nitrogen, $Rh_4(CO)_{12}$ decomposes quantitatively at 100° to $Rh_6(CO)_{16}$ and carbon monoxide. The infrared spectrum contains absorption bands due to bridging and terminal carbonyl groups, and can be used for checking the purity of the compound ν(C—O) (*n*-hexane)[2]: 2075 (s), 2070 (s), 2062 (sh), 2044 (m), 2016 (w), 1978 (w), 1885 (s) cm^{-1} (s = strong, m = medium, w = weak, sh = shoulder). A characteristic band of $Rh_6(CO)_{16}$ at 1811 cm^{-1} should be absent.

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34. OLEFIN, ACETYLENE, PHOSPHINE, ISOCYANIDE, AND DIAZENE COMPLEXES OF NICKEL(0)

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Checked by H. BERKE,† H. DIETRICH,† J. LAMBRECHT,†
P. HÄRTER,† J. OPITZ,† and W. SPRINGER†

Complexes of Ni(0) have been investigated by a large number of workers.[1] They are interesting because they undergo oxidative addition,[2] because they are potentially catalytically active,[3] and because they exist with a wide variety of ligands including unsaturated molecules[4] and Group V donors. These complexes are easily prepared using bis(1,5-cyclooctadiene)nickel(0)[5] $[Ni(\pi\text{-}C_8H_{12})_2]$ as a starting material. Examples of the preparation of each major class of compounds, NiL_4, "NiL_2," and NiL_2(UN) (where L = phosphine, arsine, stibine, nitrogen base, or isocyanide and UN = olefin, acetylene, or azo compound), are presented.

General Procedure

■ **Caution.** *Isocyanide and phosphorus ligands are toxic and malodorous. The syntheses should therefore be carried out in a well-ventilated hood.*

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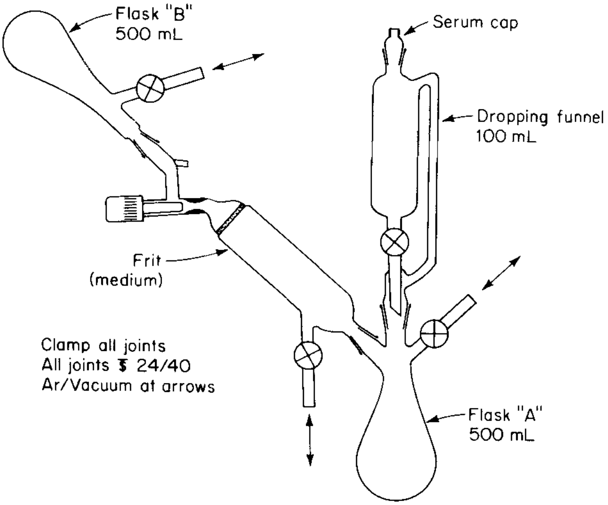

Fig. 18. Apparatus for the preparation of nickel(0) complexes.

The entire procedure must be performed in an anhydrous, oxygen-free atmosphere* using anhydrous, deoxygenated solvents.[6] The complexes rapidly decompose upon exposure to air, either as solids or in solution. The reactions may be scaled down, but yields will be somewhat lower due to mechanical losses; the method has been used to prepare as little as 0.5 g of (azobenzene-$^{15}N_2$)bis(tri-*p*-tolylphosphine)nickel(0). The Schlenk apparatus shown in Fig. 18 is useful for these preparations and also for the preparation of the starting material $Ni(\pi\text{-}C_8H_{12})_2$,[5] because it minimizes contact with stopcock grease and allows one to perform all operations without a glove box. The frit with a Teflon plug allows one to rinse the product repeatedly or to prepare a solution by pulling a suitable solvent through the frit without danger of air leakage or contaminating it with grease.

A. TETRAKIS(*t*-BUTYL ISOCYANIDE)NICKEL(0)

$$Ni(\pi\text{-}C_8H_{12})_2 + 4[(CH_3)_3CNC] \longrightarrow Ni[(CH_3)_3CNC]_4 + 2C_8H_{12}$$

Procedure (see also General Procedure)

The apparatus is set up as shown in Fig. 18, with the dropping funnel in place. Bis(1,5-cyclooctadiene)nickel(0) (10.0 g, 36.4 mmol) and a magnetic stirring bar are transferred into flask A and the system is reevacuated and

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* Either prepurified nitrogen or argon can be used. The author prefers the convenience of argon.

flushed with argon. Ether (125 mL) is injected into the dropping funnel and is allowed to run into flask A. The suspension is stirred and cooled with an ice bath. *t*-Butyl isocyanide[8] (12.2 g; 146 mmol) in ether (20 mL) is injected into the dropping funnel and allowed to flow into flask A over a period of 5 min. The reaction mixture is stirred for 30 min. The pale-yellow product is filtered under vacuum and washed twice with 50-mL portions of hexane. The product (13.5 g, 95% yield), may be recrystallized from ethanol-ether (1 : 2 mixture), with loss in yield, to give pale-yellow crystals, mp 172° (decomposes). $\nu(N{\equiv}C) = 2000\ \text{cm}^{-1}$. *Anal.* Calcd. for $C_{20}H_{36}N_4Ni$: C, 61.2; H, 9.2; N, 14.0. Found: C, 61.7; H, 9.4; N, 13.3.

The compounds listed in Table I can be conveniently prepared by this procedure. The quantities of the appropriate ligands are listed, as are the preferred solvents for each reaction; melting points and colors are listed for characterization. Several of the products require cooling or removal of solvent to cause crystallization.

Properties

The air-stabilities of the complexes in Table I vary widely. Isocyanide complexes and complexes of the alkyl phosphines are very air-sensitive or pyrophoric. The aryl phosphine complexes are moderately air-sensitive; the phosphite complexes can be handled in air but should be stored in an inert atmosphere. The phosphite complexes are insoluble in polar solvents such as

TABLE I Synthesis and Properties of Selected Nickel(0) Complexes Prepared by Procedure A

					Analysis			
					Carbon		Hydrogen	
Compound	Ligand, g	Solvent	Color	mp, °C	Calcd.	Found	Calcd.	Found
$Ni(C_6H_{11}NC)_4$	16.0	hexane	light-yellow	75	67.89	67.95	8.95	8.99
$Ni[P(CH_3)_3]_4$	11.2	pentane	yellow	198	39.70	39.29	10.00	9.81
$Ni[P(C_2H_5)_3]_4$	17.3	pentane	pale-yellow	42	54.25	54.46	11.38	11.70
$Ni[P(n\text{-}C_4H_9)_3]_4$	29.7	pentane	off-white	50	55.65	55.64	10.51	10.31
$Ni[P(CH_3)(C_6H_5)_2]_4$	29.4	ether	red-orange	170	72.26	72.71	5.32	5.38
$Ni[P(C_2H_5)_2(C_6H_5)]_4$	24.4	pentane	yellow	87	66.40	66.49	8.36	8.47
$Ni[P(OCH_3)_3]_4$	18.2	pentane	white	130	25.97	26.14	6.54	6.39
$Ni[P(OC_2H_5)_3]_4$	24.4	pentane	white	108	39.86	39.71	8.36	8.26
$Ni[P(O\text{-}i\text{-}C_3H_7)_3]_4$	30.6	pentane	white	187	48.50	48.59	9.50	9.41
$Ni[P(OCH_3)(C_6H_5)_2]_4$	31.7	pentane	yellow	185	67.63	67.58	5.68	5.78
$Ni[P(OC_6H_5)_3]_4$	45.5	benzene	white	147	66.53	66.29	4.65	4.76
$Ni[(CH_3)_2PC_2H_4P(CH_3)_2]_2$	22.0	ether	pale-yellow	121	40.15	40.00	8.99	9.17

alcohols and water, and soluble in hydrocarbons. Aryl phosphine complexes are soluble in aromatic solvents or tetrahydrofuran and insoluble in alkanes and alcohols. The alkyl phosphine complexes are soluble in ethers and hydrocarbons; the triethylphosphine complex dissociates to the deep-purple tris complex, and is protonated by alcohols.

B. TETRAKIS(TRIPHENYLPHOSPHINE)NICKEL(0)

$$Ni(\pi\text{-}C_8H_{12})_2 + 4P(C_6H_5)_3 \longrightarrow Ni[P(C_6H_5)_3]_4 + 2C_8H_{12}$$

Procedure (see also General Procedure)

A magnetic stirring bar is placed in flask A of the apparatus shown in Fig. 18. The dropping funnel is removed, and the serum-cap adapter is placed in the top of flask A before the entire system is evacuated and flushed with argon (or nitrogen). Bis(1,5-cyclooctadiene)nickel(0) (10.0 g, 36.4 mmol) is transferred into flask A, followed by finely powdered triphenylphosphine (38.2 g, 145.6 mmol). The system is reevacuated and flushed with argon; then flask A is cooled in an ice bath and 200 mL of hexane is injected through the serum cap. The stirred suspension begins to turn red at once. Stirring is continued, and the precipitate is allowed to come to room temperature. After 30 min, the ice bath is replaced; stirring is continued for 5 min, and then the entire apparatus is rotated to pour the product onto the frit. The red-brown product is filtered under vacuum and washed with one 50-mL portion of hexane and two portions of diethyl ether. The crude material may be dried under vacuum for 24 hr to give about 39 g (96% yield) of product, mp 122–124°. *Anal.* Calcd. for $C_{72}H_{60}NiP_4$: C, 78.3; H, 5.4. Found: C, 78.9; H, 5.7.

The material may be purified by extraction at 60° with 150 mL of benzene containing 10 g of triphenylphosphine. The benzene is removed on a rotary evaporator while *n*-heptane is added to keep the mixture at constant volume. The precipitated product is collected and washed with two 20-mL portions of diethyl ether.

This procedure is useful for the preparation of the compounds listed in Table II as well as many others where the ligands are solids and possibly insoluble in the reaction solvent. All of the preparations are on a scale which starts with 10.0 g of $Ni(C_8H_{12})_2$. The quantities of various ligands for each complex are listed, as is the preferred solvent for the reaction. Colors and melting points are included for characterization.

TABLE II Synthesis and Properties of Selected Nickel(0) Complexes Prepared by Procedure B

	Ligand, g					Analysis			
						Carbon		Hydrogen	
Compound	Ligand I	Ligand II	Solvent	Color	mp, °C	Calcd.	Found	Calcd.	Found
Ni$[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2$	29.0		hexane	orange	256	73.00	72.79	5.66	5.36
Ni[2,2′-bipyridine]$_2$	11.4		ether	dark-violet	155	64.74	64.71	4.35	4.39
Ni[1,10-phenanthroline]$_2$	13.2		ether	blue-black	280	68.78	68.67	3.85	3.72
Ni$[As(C_6H_5)_3]_4$	44.6		ether	orange-yellow	107	67.37	67.43	4.71	4.91
Ni$[Sb(C_6H_5)_3]_4$	51.4		ether	light-yellow	244	58.79	58.90	4.11	4.13
Ni$[(CH_3)_2AsC_6H_4As(CH_3)_2]_2$	31.8		ether	orange	195	38.08	38.18	5.11	5.27
Ni$[P(C_6H_5)_3]_2[(C_6H_5)N{=}N(C_6H_5)]$	19.2	6.63	pentane	dark-red	205	75.31	75.16	5.27	5.27
Ni$[P(C_6H_5)_3]_2[(C_6H_5)HC{=}CH(C_6H_5)]$	19.2	6.56	pentane	dark-red	205	78.65	78.37	5.55	5.71

Properties

All the compounds in Table II are soluble in aromatic solvents. They are all moderately air-sensitive, and the arsine and stibine complexes are thermally unstable, decomposing upon standing in solution—or more slowly in the solid state—to liberate nickel metal.

C. (AZOBENZENE)BIS(*t*-BUTYL ISOCYANIDE)NICKEL(0)

$$Ni(\pi\text{-}C_8H_{12})_2 + 2[(CH_3)_3CNC] \longrightarrow \text{“}Ni[(CH_3)_3CNC]_2\text{”} + 2C_8H_{12}$$

$$\text{“}Ni[(CH_3)_3CNC]_2\text{”} + C_6H_5N{=}NC_6H_5 \longrightarrow Ni[(CH_3)_3CNC]_2(C_6H_5N{=}NC_6H_5)$$

Procedure (see also General Procedure)

The apparatus is set up as shown in Fig. 18. Bis(1,5-cyclooctadiene-nickel(0) (10.0 g, 36.4 mmol) and a magnetic stirring bar are placed in flask A, and the entire system is reevacuated and flushed with argon. Ether (150 mL) is injected into the dropping funnel and is allowed to run into flask A. The suspension is cooled with an ice bath. *t*-Butyl isocyanide[8] (6.1 g, 73 mmol) in hexane (20 mL) is injected into the dropping funnel and is allowed to flow into the stirred reaction mixture dropwise over a period of 5 min, forming the intermediate, $Ni_4[(CH_3)_3CNC]_7$, which can be isolated at this point by vacuum filtration.*

Azobenzene† (6.7 g, 36 mmol) in ether (50 mL) is injected into the dropping funnel and is allowed to flow into flask A during the next 5 min. The mixture is stirred for 30 min and then filtered. The red, air-sensitive product is washed with two 20-mL portions of hexane and dried *in vacuo*. The yield is almost quantitative. Recrystallization from diethyl ether results in red needles which decompose at 162° ($\nu(C{\equiv}N) = 2168$, $2140\ cm^{-1}$). *Anal.* Calcd. for $C_{22}H_2N_4Ni$: C, 64.8; H, 6.9; N, 13.7. Found: C, 64.6; H, 7.0; N, 13.6.

This procedure is useful for the preparation of the compounds listed in Table III. The preparations are on a scale which starts with 10.0 g of $Ni(\pi\text{-}C_8H_{12})_2$. The quantities of the first and second ligands for each complex are listed together with the preferred solvent for the reaction. Colors and melting points are included for characterization.

* The $Ni_4[(CH_3)_3CNC]_7$ is contaminated with $Ni[(CH_3)_3CNC]_4$ to give the over-all composition, “$Ni[(CH_3)_3CNC]_2$.” If completely pure $Ni_4[(CH_3)_3CNC]_7$ is the desired product, the initial reaction should be performed with 5.34 g of *t*-butylisocyanide.

† More properly, diphenyldiazene.

TABLE III Synthesis and Properties of Selected Nickel(0) Complexes Prepared by Procedure C

	Ligand, g					Analysis			
						Carbon		Hydrogen	
Compound	Ligand I	Ligand II	Solvent	Color	mp, °C	Calcd.	Found	Calcd.	Found
$Ni[P(C_2H_5)_3]_2[C_6H_5N{=}NC_6H_5]$	8.6	6.6	ether	red	140	60.40	60.65	8.45	8.41
$Ni[t\text{-}BuNC]_2[C_6H_5N{=}NC_6H_5]$	6.1	6.6	ether	dark-red	164	64.89	64.72	6.93	6.79
$Ni[t\text{-}BuNC]_2[(NC)_2C{=}C(CN)_2]$	6.1	4.7	benzene	brown	167	54.43	54.13	5.14	5.28
$Ni[t\text{-}BuNC]_2[(NC)HC{=}CH(CN)]$	6.1	2.9	ether	yellow	124	55.49	55.57	6.65	6.71
$Ni[t\text{-}BuNC]_2[C_6H_5C{\equiv}CC_6H_5]$	6.1	6.5	ether	yellow	125	71.49	71.43	7.00	6.79

The red-brown polynuclear complex $Ni_4[(CH_3)_3CNC]_7$ can be recrystallized from diethyl ether in a Dry Ice–acetone bath to give a microcrystalline material which displays terminal and bridging isocyanide stretching frequencies at 2020 and 1605 cm^{-1}, respectively. This highly air-sensitive material may be used as an intermediate in the preparation of nickel isocyanide complexes of unsaturated molecules: simply by the addition of the desired molecules to a hexane or ether suspension.

Properties

The complexes listed in Table III are moderately to very air-sensitive. They are soluble in polar solvents such as tetrahydrofuran but decompose in halogenated solvents.

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35. (CARBOXYLATO)(TRIPHENYLPHOSPHINE) COMPLEXES OF THE PLATINUM METALS

Submitted by ALAN DOBSON,* STEPHEN D. ROBINSON,* and MICHAEL F. UTTLEY*
Checked by G. W. PARSHALL†

Carboxylic acids and their conjugate bases, the carboxylate anions, feature extensively in homogeneous catalysis systems.[1–7] In addition, the carboxylate anions are very versatile ligands capable of coordinating in unidentate,

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chelate, or bridging fashion in a wide range of transition metal complexes.[8] Platinum metal carboxylato complexes containing triphenylphosphine ligands have recently attracted considerable interest, and several compounds of this type have been shown to possess substantial catalytic activity. (Carboxylato)(triphenylphosphine) complexes have been synthesized by a variety of routes. These include addition of triphenylphosphine to metal carboxylates,[2,9–13] reaction of halophosphine complexes, $MX_n[P(C_6H_5)_3]_m$, with alkali metal[3] or silver carboxylates,[14–16] and oxidative addition of carboxylic acids to d^8 and d^{10} transition metal complexes.[17–22] A general class of oxidative addition-reductive elimination reactions based on this last technique have recently been further developed and extended in our laboratory[23–24] and now provide a convenient route to an important range of (carboxylato)(triphenylphosphine) complexes of the platinum metals. The present contribution describes syntheses of this type for a selection of acetato or trifluoroacetato complexes. The latter are described in those cases where the precursor concerned is inert to simple alkyl carboxylic acids.

General Procedure

Tetrakis(triphenylphosphine)platinum is prepared as described in *Inorganic Syntheses*, **11**;[25] all the other platinum group metal precursors employed in these syntheses are conveniently prepared using methods described in *Inorganic Syntheses*, **15**.[26] Acetic acid (glacial), trifluoroacetic acid, and the "Analar" grade solvents are used as purchased. The apparatus used comprises a two-necked 25-mL or 50-mL round-bottomed flask, fitted with ground-glass joints and equipped with a condenser and a gas inlet. Syntheses I and K are promoted by oxygen and should be performed with a slow stream of air passing through the solution; all the other syntheses are performed with slow passage of nitrogen to minimize oxygen concentrations. All products deposit from solution as crystalline solids and, with the exception of C, can be manipulated in air for short periods without decomposition. Recrystallization, where necessary, is best performed from methylene chloride–methanol. However, in our experience, products usually deposit in a pure state and do not require further purification after washing. Melting points were determined in nitrogen-filled, sealed, glass capillaries and are very dependent on heating rate.

A. BIS(ACETATO)DICARBONYLBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

$$\mathrm{Ru(CO)_3[P(C_6H_5)_3]_2 + 2CH_3COOH \longrightarrow Ru(OCOCH_3)_2(CO)_2[P(C_6H_5)_3]_2 + H_2 + CO}$$

Procedure

Acetic acid (1.0 mL) is added to a suspension of tricarbonylbis(triphenylphosphine)ruthenium (0.23 g) in 2-methoxyethanol (5.0 mL), and the mixture is heated under reflux for 15 min. The resultant solution is filtered, cooled in ice, diluted with methanol (5.0 mL), and then allowed to stand at 0° until crystallization is complete. The pale-yellow or white crystalline precipitate is washed successively with methanol (2 × 2 mL) at 0°, water (2 × 5 mL), and methanol (2 × 2 mL) at 0°, then dried *in vacuo* at 100°.

B. (ACETATO)CARBONYLCHLOROBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

$$\mathrm{RuHCl(CO)[P(C_6H_5)_3]_3 + CH_3COOH \longrightarrow RuCl(CO)(OCOCH_3)[P(C_6H_5)_3]_2 + H_2 + P(C_6H_5)_3}$$

Procedure

Acetic acid (0.5 eL) is added to a suspension of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.32 g) in 2-methoxyethanol (5.0 mL), and the mixture is heated under reflux for 10 min. During this time the suspension clears and dark-yellow crystals of the product are precipitated. The mixture is cooled and the crystals are filtered off, washed successively in methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then dried *in vacuo.*

C. (ACETATO)CARBONYLHYDRIDOBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

$$\mathrm{RuH_2(CO)[P(C_6H_5)_3]_3 + CH_3COOH \longrightarrow RuH(OCOCH_3)(CO)[P(C_6H_5)_3]_2 + H_2 + P(C_6H_5)_3}$$

Procedure

Acetic acid (1.0 mL) is added to a suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.67 g) in 2-methoxyethanol (7.5 mL), and the mixture is heated under reflux for 15 min. The resultant yellow solution is filtered, cooled, diluted with methanol (20 mL), and then left to stand until crystallization is complete. The pale-yellow, air-sensitive, crystalline precipitate is filtered off, washed successively with methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then dried *in vacuo.*

D. CARBONYLBIS(TRIFLUOROACETATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

$$\mathrm{RuH_2(CO)[P(C_6H_5)_3]_3 + 2CF_3COOH \longrightarrow Ru(OCOCF_3)_2(CO)[P(C_6H_5)_3]_2 + 2H_2 + P(C_6H_5)_3}$$

Procedure

Trifluoroacetic acid (1.0 mL) is added to a solution of carbonyldihydridotris(triphenylphosphine)ruthenium (0.46 g) in benzene (10.0 mL). The resultant yellow solution is heated under reflux for 60 min and then concentrated under reduced pressure to give a dark-yellow oil. The oil is dissolved in dichloromethane (4.0 mL) and filtered; then it is diluted with methanol (50 mL) and allowed to stand until crystallization is complete. The deep-yellow crystals are filtered off, washed successively in methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then dried *in vacuo* to yield the product as a solvate, $\mathrm{Ru(OCOCF_3)_2(CO)[P(C_6H_5)_3]_2 \cdot \frac{3}{4}CH_3OH}$.

E. NITROSYLTRIS(TRIFLUOROACETATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

$$\mathrm{2Ru(NO)_2[P(C_6H_5)_3]_2 + 6CF_3COOH \longrightarrow 2Ru(OCOCF_3)_3(NO)[P(C_6H_5)_3]_2 + 3H_2 + 2NO}$$

Procedure

Trifluoroacetic acid (1.0 mL) is added to a suspension of dinitrosylbis(triphenylphosphine)ruthenium (0.48 g) in 2-methoxyethanol (7.5 mL). The mixture is heated under reflux for 4 min; then it is concentrated to one-quarter its volume under reduced pressure, diluted with methanol (20.0 mL), and left to stand until crystallization is complete. The orange-brown crystals are filtered off, washed successively with methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then dried *in vacuo.*

F. CARBONYLCHLORO(TRIFLUOROACETATO)TRIS(TRIPHENYLPHOSPHINE)OSMIUM(II)

$$\mathrm{OsHCl(CO)[P(C_6H_5)_3]_3 + CF_3COOH \longrightarrow OsCl(OCOCF_3)(CO)[P(C_6H_5)_3]_3 + H_2}$$

Procedure

Trifluoroacetic acid (1.0 mL) is added to a suspension of carbonylchlorohydridotris(triphenylphosphine)osmium (0.4 g) in benzene (7.5 mL). The resultant solution is heated under reflux for 10 min and then concentrated under reduced pressure to give a brownish oil. The oil is dissolved in a minimum amount (3–5 mL) of methanol and allowed to stand until crystallization is complete. The white crystals are filtered off and washed successively with methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL); then they are dried *in vacuo* to yield the required product as a solvate $\mathrm{OsCl(OCOCF_3)(CO)[P(C_6H_5)_3]_3 \cdot \frac{3}{4}CH_3OH}$.

G. CARBONYLBIS(TRIFLUOROACETATO)BIS(TRIPHENYLPHOSPHINE)OSMIUM(II)

$$\mathrm{OsH_2(CO)[P(C_6H_5)_3]_3 + 2CF_3COOH \longrightarrow Os(OCOCF_3)_2(CO)[P(C_6H_5)_3]_2 + P(C_6H_5)_3 + 2H_2}$$

Procedure

Trifluoroacetic acid (1.0 mL) is added to a suspension of carbonyldihydridotris(triphenylphosphine)osmium (0.4 g) in toluene (10.0 mL). The resultant yellow-brown solution is heated under reflux for 60 min and then concentrated under reduced pressure to give a brown oil. The oil is dissolved in dichloromethane (5.0 mL), filtered, and diluted with methanol (50.0 mL). This mixture is allowed to stand until crystallization is complete; the cream-colored (or faintly greenish, if large) crystals are filtered off and washed successively in methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL); then they are dried *in vacuo* to yield the required product as a solvate $\mathrm{Os(OCOCF_3)_2CO[P(C_6H_5)_3]_2 \cdot \frac{1}{3}CH_3OH}$.

H. (ACETATO)TRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

$$RhH[P(C_6H_5)_3]_4 + CH_3COOH \longrightarrow Rh(OCOCH_3)[P(C_6H_5)_3]_3 + P(C_6H_5)_3 + H_2$$

Procedure

Acetic acid (1.0 mL) is added to a suspension of hydridotetrakis(triphenylphosphine)rhodium (0.58 g) in ethanol (15.0 mL), and the mixture is heated under reflux for 15 min. During this time the starting material dissolves and orange crystals are deposited. The mixture is cooled; the crystals are filtered off, washed successively in methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then dried *in vacuo.*

I. BIS(ACETATO)NITROSYLBIS(TRIPHENYLPHOSPHINE)RHODIUM(III)

$$Rh(NO)[P(C_6H_5)_3]_3 + 2CH_3COOH \xrightarrow{O_2} Rh(NO)(OCOCH_3)_2[P(C_6H_5)_3]_2$$

Procedure (conduct all operations in presence of air)

Acetic acid (1.0 mL) is added to nitrosyltris(triphenylphosphine)rhodium (0.4 g), and then acetone (25.0 mL) is added. The red suspension is stirred in air for 25 min; during this time the suspension darkens, turns green, and deposits a green precipitate. This precipitate is filtered off, washed successively in acetone (2 × 10 mL), water (2 × 10 mL), and acetone (2 × 10 mL), then dried *in vacuo.*

J. (ACETATO)DIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)IRIDIUM(III)

$$IrH_3[P(C_6H_5)_3]_3 + CH_3COOH \longrightarrow IrH_2(OCOCH_3)[P(C_6H_5)_3]_3 + H_2$$

Procedure

Acetic acid (1.0 mL) is added to a suspension of *mer*-trihydridotris(triphenylphosphine)iridium (0.4 g) in ethanol (15.0 mL), and the mixture is heated under reflux for 40 min. The colorless solution deposits fine, white crystals on cooling. These are filtered off and washed successively in methanol (2 × 10 mL), water (2 × 10 mL), and methanol (2 × 10 mL), then recrystallized from a mixture of dichloromethane (3.0 mL) and methanol (20 mL) and dried *in vacuo* to yield the required product as a solvate $IrH_2(OCOCH_3)[P(C_6H_5)_3]_3 \cdot CH_3OH$.

K. *cis*-[BIS(ACETATO)BIS(TRIPHENYLPHOSPHINE)-PLATINUM(II)]

$$Pt[P(C_6H_5)_3]_4 + 2CH_3COOH \xrightarrow{O_2} cis\text{-}Pt(OCOCH_3)_2[P(C_6H_5)_3]_2$$

Procedure (conduct all operations in presence of air)

Acetic acid (0.25 mL) is added to a solution of tetrakis(triphenylphosphine)platinum (0.4 g) in benzene (15.0 mL). The solution is heated to reflux over a period of 5 min and is maintained at this temperature under a slow stream of air for 60 min, during which time the initial bright-yellow color fades. The solution is then evaporated to one-half its original volume on a water bath and, while still hot, it is diluted with petroleum ether (bp 60–80°) until precipitation commences. The mixture is reduced in volume to ca. 5.0 mL by further evaporation, then diluted with petroleum ether (bp 60–80°) (5 mL), to precipitate the required product, which is filtered off from the warm suspension. Recrystallization from dichloromethane (3–5 mL) by addition of hot petroleum ether (50 mL) affords the pure product as fine, white crystals which are filtered off, washed with petroleum ether (10.0 mL), and dried *in vacuo*.

Properties

All the compounds are crystalline solids, and with the exception of $RuH(OCOCH_3)(CO)[P(C_6H_5)_3]_2$, can be manipulated in air briefly without decomposition. The platinum complex, *cis*$[Pt(OCOCH_3)_2\{P(C_6H_5)_3\}_2]$ is soluble in chloroform, dichloromethane, and methanol but practically insoluble in benzene and acetone. The other complexes are soluble in chloroform and dichloromethane, moderately soluble in benzene and acetone, and almost insoluble in light alcohols. Analytical and spectroscopic data are given in the following table. Infrared data refer to mulls in Nujol; ^1H nmr data were obtained at 90 MHz using solutions in chloroform-*d* and are referenced to TMS.

PROPERTIES, YIELDS, AND ANALYSES OF CARBOXYLATO COMPLEXES

Complex	mp, °C	ν(OCO)		ν(CO)	ν(MH)	τ(MH)	$^2J_{(PH)}$ Hz	τ(CH_3)	Yield, %	Analyses, %		
		Asym	*Sym*							C	H	P
A. $Ru(OCOCH_3)_2(CO)_2$- $[P(C_6H_5)_3]_2$	239–241	1613 1596	1370	2044 1973	—	—	—	8.87	86	calcd. 63.10 found 62.75	4.51 4.54	7.76 8.03
B. $RuCl(OCOCH_3)(CO)$- $[P(C_6H_5)_3]_2$	253–255	1507	1465	1941	—	—	—	9.49	75	calcd. 62.59 found 62.40	4.41 4.44	8.29 7.93
C. $RuH(OCOCH_3)(CO)$- $[P(C_6H_5)_3]_2$	236–237	1528	1455	1932	2020	26.45	20.0	9.38	58	calcd. 65.64 found 65.28	4.70 4.76	8.69 8.51
D. $Ru(OCOCF_3)_2(CO)$- $[P(C_6H_5)_3]_2$ [a]	236–237	1695 1665	(1440) 1408	1968	—	—	—	—	77	calcd. 55.48 found 55.14	3.59 3.59	6.85 6.85
E. $Ru(OCOCF_3)_3(NO)$- $[P(C_6H_5)_3]_2$	200–205	1728 1697	1398	1902 [f]	—	—	—	—	47	calcd. 50.70 found 50.54	3.02 3.13	6.24 6.83
F. $OsCl(OCOCF_3)(CO)$- $[P(C_6H_5)_3]_3$ [b]	182–184	1683	1410	1952	—	—	—	—	62	calcd. 58.99 found 58.79	3.94 4.04	7.91 8.25
G. $Os(OCOCF_3)_2(CO)$- $[P(C_6H_5)_3]_2$ [c]	234–236	1700 1655	(1440) 1409	1948	—	—	—	—	92	calcd. 50.83 found 50.69	3.16 3.22	6.40 6.33
H. $Rh(OCOCH_3)$- $[P(C_6H_5)_3]_3$	207–208	1598	1373	—	—	—	—	—	79	calcd. 70.90 found 70.63	5.10 5.09	9.81 10.00
I. $Rh(OCOCH_3)_2(NO)$- $[P(C_6H_5)_3]_2$	210–211	1600	1362	1614 [f]	—	—	—	—	83	calcd. 61.93 found 61.92	4.64 4.65	8.00 8.22
J. $IrH_2(OCOCH_3)$- $[P(C_6H_5)_3]_3$ [d]	212–214	1615	1378	—	2198 2157	21.1 33.5	137.0/20.0 8.0/20.0	8.28	80	calcd. 63.45 found 63.5	4.95 5.20	—
K. *cis*-$Pt(OCOCH_3)_2$- $[P(C_6H_5)_3]_2$ [e]	200–202	1636	1370	—	—	—	—	8.65	83	calcd. 57.35 found 57.1	4.30 4.25	—

[a] Solvated with CH_3OH 0.75 mol; τ(CH_3) 6.80.

[b] Solvated with CH_3OH 0.75 mol; τ(CH_3) 6.65.

[c] Solvated with CH_3OH 0.33 mol; τ(CH_3) 6.65.

[d] Solvated with CH_3OH 1.0 mol; τ(CH_3) 6.65.

[e] The ^{31}P nmr spectrum (CH_2Cl_2) shows a resonance at +5.56 ppm with respect to an external H_3PO_4 reference and a 195_{PtP} coupling of 3.823 KHz indicative of cis stereochemistry.

[f] ν(NO).

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36. *trans*-[CHLOROETHYLBIS(TRIETHYLPHOSPHINE)-PLATINUM(II)]

$$\textit{trans}\text{-}[\mathrm{PtHCl}\{\mathrm{P(C_2H_5)_3}\}_2] + \mathrm{C_2H_4} \xrightarrow{\mathrm{SnCl_2 \cdot 2H_2O}} \textit{trans}\text{-}[\mathrm{Pt(C_2H_5)Cl}\{\mathrm{P(C_2H_5)_3}\}_2]$$

Submitted by THOMAS A. WEIL*
Checked by H. C. CLARK† and C. S. WONG‡

Previous reports of the synthesis of *trans*-[chloroethylbis(triethylphosphine)-platinum(II)] have incorporated the reaction of *trans*-$[\mathrm{PtCl_2}\{\mathrm{P(C_2H_5)_3}\}_2]$

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with ethyl Grignard reagents[1] or the high-temperature–high-pressure (95°/40 atm) reaction of ethylene with *trans*-$[PtHCl\{P(C_2H_5)_3\}_2]$.[2,3] Both procedures give a low yield of product. The latter reaction can be facilitated by addition of a small amount of tin(II) chloride, and the procedure described below utilizes tin(II) chloride to catalyze the reaction between *trans*-chlorohydridobis(triethylphosphine)platinum(II) and ethylene, resulting a high yield of *trans*-[chloroethylbis(triethylphosphine)platinum(II)].[4]

Procedure

■ **Caution.** *Because of the flammability of ethylene and solvent vapors all operations should be carried out in a well-ventilated hood.*

To a 25-mL round-bottomed flask is added 0.50 g (1.1 mmol) of *trans*-chlorohydridobis(triethylphosphine)platinum(II).[5] The flask is fitted with a rubber serum cap and deoxygenated by flushing with nitrogen for 20 min. By means of a hypodermic syringe, 5 mL of absolute ethanol, which has been deoxygenated by flushing with nitrogen for 20 min, is added, giving a clear solution. A 0.06*M* solution of hydrated tin(II) chloride is prepared by placing 0.14 g of $SnCl_2 \cdot 2H_2O$ in a 25-mL flask which is then sealed with a rubber serum cap and flushed with nitrogen for 20 min. To the flask is added 10 mL of absolute ethanol which has been deoxygenated by flushing with nitrogen. By means of a syringe, 0.18 mL of the 0.06*M** tin(II) chloride solution is added to the solution of *trans*-$[PtHCl\{P(C_2H_5)_3\}_2]$, causing a yellow color to develop. A stream of ethylene is bubbled slowly through the solution while it is stirred with a magnetic stirrer for 2 hr at 25°. The ethanol is then removed by blowing a stream of nitrogen over the solution. The resulting yellow oil is dissolved in the minimum amount of diethyl ether, placed on a 2-cm by 20-cm neutral alumina column (25 g, activity "1") and eluted with diethyl ether. Approximately 50 mL of diethyl ether is collected and evaporated to dryness; a white crystalline solid remains. Further elution yields a small amount of impure material, which is discarded. The solid product is dried under vacuum: mp, 53.5-55°; yield, 0.49 g, 93%. *Anal.* Calcd. for $C_{14}H_{35}ClP_2Pt$: C, 33.90; H, 7.11. Found: C, 34.01; H, 7.00.

Properties

trans-[Chloroethylbis(triethylphosphine)platinum(II)] is a white, crystalline solid which is stable in the solid state at room temperature in air.[3,6] It is soluble in common organic solvents and is insoluble in water. At elevated

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* This corresponds to one mole percent tin(II) chloride.

temperature and pressure the compound slowly undergoes carbon monoxide insertion to give *trans*-$[Pt(CH_3CH_2CO)Cl\{P(C_2H_5)_3\}_2]$. In the presence of catalytic amounts of tin(II) chloride, the reaction proceeds at room temperature and atmospheric pressure giving high yields of the acyl complex.

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37. TETRAKIS(*t*-BUTYL ISOCYANIDE)DI-μ-CHLORO-DIPALLADIUM(I)

$$Na_2[Pd_2Cl_6] + 4[CH_3CO_2]Na + 4C_{17}H_{14}O(dba)^* + 2CH_3OH \longrightarrow 2[Pd(dba)_2] + 6NaCl + 4CH_3COOH + 2CH_2O$$

$$[Pd(dba)_2] + [PdCl_2(C_6H_5CN)_2] + 4t\text{-}C_4H_9NC \xrightarrow{C_6H_5Cl} [Pd_2Cl_2(t\text{-}C_4H_9NC)_4] + 2dba + 2C_6H_5CN$$

Submitted by M. F. RETTIG† and P. M. MAITLIS‡
Checked by F. A. COTTON§ and T. R. WEBB§

The unusual complex tetrakis(*t*-butyl isocyanide)di-μ-chlorodipalladium(I)·chlorobenzene has been prepared by Otsuka, Tatsuno, and Ataka.[1] The preparation utilized a novel coupling reaction between bis(*t*-butyl isocyanide)palladium(0) and *cis*-bis(*t*-butyl isocyanide)dichloropalladium(II) in cold chlorobenzene. Although the reported[1] yield for the final step of this synthesis was good (70%), the preparation of the precursor bis(*t*-butyl isocyanide)palladium(0) from (η^3-allyl)(η^5-cyclopentadienyl)palladium[2] is time-consuming and is accomplished in only ca. 50% yield. We have developed a greatly improved preparation of the title complex (chlorobenzene-free),

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* dba = dibenzylideneacetone. (1,5-diphenyl-1,4-pentadien-3-one).

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which utilizes readily available Pd(0) and Pd(II) compounds as starting materials, namely bis(dibenzylideneacetone)palladium(0),[3] (Pd(dba)$_2$), and *trans*-bis(benzonitrile)dichloropalladium(II).[4] In addition, since full details of the preparation of Pd(dba)$_2$ have not been reported,[3] we give a complete account of the preparation here.*

Tetrakis(*t*-butyl isocyanide)dichlorodipalladium(I) is one of a very limited number of examples of the Pd(I) oxidation state. The convenient synthesis of this stable and easily soluble complex reported here should make it a useful starting material for continued study of the Pd(I) oxidation state. The synthesis may be successfully scaled down at least fivefold.

■ **Caution.** *Although t-butyl isocyanide is apparently only weakly toxic,[7] its odor is unpleasant, and all operations involving isocyanides should be conducted in a fume hood.*

Procedure

Bis(dibenzylideneacetone)palladium(0), Pd(dba)$_2$, is first prepared by stirring 8.87 g PdCl$_2$ (0.05 mol) and 2.92 g NaCl (0.05 mol) in 250 mL of methanol at room temperature for 16 hr. The resulting solution is filtered through a plug of cotton, the filtrate is diluted to ca. 1.5 L with methanol, and the solution is heated to 60°. Dibenzylideneacetone[6] (36.5 g, 0.15 mol) is added to the warm, stirred Na$_2$[Pd$_2$Cl$_6$] solution, and stirring is continued for 15 min, followed by addition of 75 g of anhydrous sodium acetate. The reaction commences at once, and the mixture is removed from the heat and stirred for ca. 1 hr until it cools to room temperature. The dark-brown precipitate is filtered and washed successively with methanol (5 × 25 mL), water (5 × 50 mL), and acetone (5 × 15 mL). The product is air-dried. The yield is 23 g (80%). *Anal.* Calcd. for $C_{34}H_{28}O_2Pd$: C, 66.82; H, 4.92. Found: C, 66.75; H, 5.06.

Tetrakis(*t*-butyl isocyanide)di-μ-chlorodipalladium(I), Pd$_2$Cl$_2$(*t*-C$_4$H$_9$-NC)$_4$, is then synthesized by placing 90 mL of redistilled chlorobenzene in a sidearm vessel (filter flask or Schlenk tube) and bubbling argon through the chlorobenzene for 15 min. The argon is then introduced through the side arm, and 5.40 g bis(dibenzylideneacetone)palladium(0) (9.4 mmol) is added,

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* The exact nature of this complex, particularly in solution, is unclear (see reference 5), but a compound of this stoichiometry is obtained reproducibly by this method.

followed by 4.85 mL *t*-butyl isocyanide* (3.7 g, 44.5 mmol). The mixture is stirred until practically all of the dark solid dissolves to give a straw-colored solution† (ca. 15 min), and 3.60 g of solid *trans*-bis(benzonitrile)dichloropalladium(II)[4] (9.4 mmol) is added in approximately five portions during a few minutes. The yellow-brown solution is stirred under argon for 45 min, during which time crystallization commences and the color of the solution darkens. The reaction mixture is stored under argon overnight in a freezer (ca. −35°). The yellow to yellow-green precipitate is filtered and washed with 50-mL portions of anhydrous diethyl ether until the diethyl ether wash is colorless (some dibenzylideneacetone may precipitate; approximately three 50-mL washings with diethyl ether removes this impurity). The yellow to yellow-green‡ solid is air-dried. The crude product weighs 5.65 g (98% yield).

For purification, the crude product is dissolved in dichloromethane (8 mL/g) and is gravity-filtered through a fine-mesh paper (Whatman no. 542 or equivalent).† The product is precipitated by dropwise addition of anhydrous diethyl ether to the dichloromethane solution, until 5 mL ether has been added for every milliliter of dichloromethane solution originally present. The mixture is chilled for several hours at −35°, filtered, washed with diethyl ether, and air-dried.

Traces of dichloromethane are removed by vacuum drying for 2 hr at 56°/0.01 torr. The yield is 5.03 g (87% based on $Pd(dba)_2$). *Anal.* Calcd. for $C_{20}H_{36}Cl_2N_4Pd_2$: Pd, 34.55; Cl, 11.55; C, 38.98; H, 5.89; N, 9.09. Found: Pd, 34.8; Cl, 11.67, 11.50; C, 39.31, 38.77; H, 6.10, 6.13; N, 9.05, 9.33.

Properties

Tetrakis(*t*-butyl isocyanide)di-*μ*-chlorodipalladium(I) is a diamagnetic, bright-yellow powder when pure; it becomes orange above 155° and blackens above 210°. It is stable in air for months at room temperature. Its solutions in common organic solvents are also stable to air if the temperature is not elevated. It is soluble in methylene chloride, chloroform, benzene, toluene, ethyl acetate, etc., and is insoluble in diethyl ether and petroleum

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* *t*-Butyl isocyanide is readily prepared by the method of J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966). The checkers report that the *t*-butylamine used in the synthesis of *t*-butyl isocyanide should be dried, and that neutral alumina is an adequate drying agent.

† Traces of Pd metal present in the $Pd(dba)_2$ can cause the solution to appear greenish. It is also responsible for the possible presence of a small amount of dark, insoluble deposit.

‡ Traces of palladium metal can cause a precipitate to appear greenish. Palladium is removed on recrystallization.

ether. The near-infrared spectrum has major bands as follows (KBr disk, cm^{-1}): 2980 (m), 2935 (w), 2170 [s, $\nu(N{\equiv}C)$], 2160 [sh, $\nu(N{\equiv}C)$], 1475 (m), 1455 (br, m), 1400 (w), 1372 (m), 1235 (m), 1190 (s), 850 (w). The far-infrared spectrum has major absorption bands at (Nujol mull, cm^{-1}): 522 (m), 508 (m), 440 (m), 398 (m), 370 (w), 342 (w), 294 (m), and 258 (vs, possibly Pd—Cl). The pmr spectrum in $CDCl_3$ is a singlet at $\tau 8.47$. The osmometrically determined molecular weight in chloroform (0.02 molal) is 614. (Calcd. 616.) The compound is conveniently converted to the bromine and iodine analogs[1] by treatment of acetone solutions with lithium bromide or lithium iodide, respectively.

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Chapter Three

OTHER TRANSITION METAL COMPOUNDS

38. IRON(II) AND COBALT(III) CLATHROCHELATES DERIVED FROM DIOXIMES

Submitted by S. C. JACKELS,* J. ZEKTZER,* and N. J. ROSE*
Checked by VIRGIL L. GOEDKEN† and ROY CHAPMAN†

Clathrochelates comprise a new type of coordination compound containing a metal ion both coordinately saturated and encapsulated by a single ligand.[1-5] The ligands of one class of clathrochelates are derived from dioximes and various boron compounds.[1,4] Typical examples of iron and cobalt clathrochelates of this structural class are shown in Fig. 19 and Table I. These complexes are readily prepared from iron(II) or cobalt(II) salts,

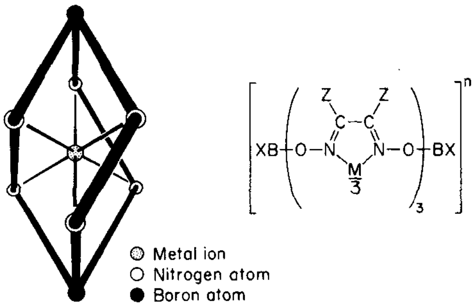

Fig. 19.

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TABLE I **Abbreviations and Formulation of Clathrochelates***

Complex	*n*	M	X	Z
$[Co(dmg)_3(BF)_2]BF_4$	+	Co(III)	F	CH_3†
$[Fe(dmg)_3(BF)_2]$	0	Fe(II)	F	CH_3†
$[Fe(nox)_3(BF)_2]$	0	Fe(II)	F	$(CH_2)_2$‡
$[Fe(dmg)_3(BOC_4H_9)_2]$	0	Fe(II)	$O(CH_2)_3CH_3$	CH_3†
$[Fe(nox)_3(BOH)_2]$	0	Fe(II)	OH	$(CH_2)_2$‡
$[Fe(dpg)_3(BOC_4H_9)_2]$	0	Fe(II)	$O(CH_2)_3CH_3$	C_6H_5§

* Column headings refer to Fig. 19 (p. 139) where n = total charge on complex, M = metal ion, and X and Z are substituent groups on the boron and dioxime "backbone" respectively.

† Complex derived from dimethylglyoxime, H_2dmg

‡ Complex derived from 1,2-cyclohexanedione dioxime, (nioxime), H_2nox

§ Complex derived from diphenylglyoxime, H_2dpg

dioximes, and either boron trifluoride or boric acid. The subject of this report is the description of the syntheses of the complexes shown in Table I.

*General Procedure**

The reagents used in the syntheses described below were obtained commercially as reagent grade and were used without further purification. All preparations were carried out in flasks open to the atmosphere. The recrystallized products were dried for ca. 12 hr at about 1 torr over Drierite or P_4O_{10}.

A. [[TRIS-[μ-[(2,3-BUTANEDIONE DIOXIMATO)-*O*:*O*′]]-DIFLUORODIBORATO(2−)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*⁗′]-COBALT(III) TETRAFLUOROBORATE(1−)

$[Co\{(dmg)_3(BF)_2\}][BF_4]$

$$2CoCl_2 + 6H_2dmg + 10(OH^-) + \tfrac{1}{2}O_2 + 12BF_3 \xrightarrow[BF_3 \cdot O(C_2H_5)_2]{n\text{-}C_4H_9OH} 2[Co\{(dmg)_3(BF)_2\}]^+ + 11H_2O + 8BF_4^- + 2Cl^-$$

Procedure

An Erlenmeyer flask (125-mL) is charged with anhydrous cobalt(II) dichloride (1.30 g, 0.01 mol), dimethylglyoxime, (H_2dmg) (3.48 g, 0.03 mol)

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* Elemental analyses were obtained from Chemalytics, Inc., Tempe, Arizona, The Materials Chemistry Section, Washington State University, or Alfred Bernhart, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

KOH (2.81 g, 0.05 mol), 1-butanol (25 mL), and a stirring bar. The flask is placed on a magnetic-stirring hot plate and *efficient stirring is maintained throughout the following procedure.* After 30 min the color of the mixture has changed to a deep, red-brown with most solids dissolved. [NOTE: It is assumed that oxygen from the atmosphere serves as the oxidizing agent for Co(II).] Heat is applied to boil the mixture for 5 min. After the mixture has cooled to room temperature (an ice bath may be used for rapid cooling), boron trifluoride–diethyl ether (10 mL) is carefully poured into the mixture. After this addition, the mixture is stirred for about 10 min and then mixing is stopped. The reaction mixture is suction-filtered through a Büchner funnel (10-cm diam., Whatman no. 1 paper) to remove salts and unreacted materials. Then the filtrate is transferred to a round-bottomed flask (200 mL) and its volume is reduced to approximately 5 mL via a rotary evaporator attached to a water aspirator. Heat may be applied to the round-bottomed flask to hasten evaporation. Typically, the temperature of the filtrate is maintained below ca. 50° during this evaporation step. Acetonitrile (25 mL) is swirled with the ca. 5 mL of syrup which results from the evaporation. The deep-brown solution is transferred to an Erlenmeyer flask (250 mL) and diethyl ether (ca. 90 mL) is added to induce precipitation of the product. After standing for 1 hr, the reddish-tan precipitate is collected in a Büchner funnel (5-cm diam., Whatman no. 1 paper) by means of suction filtration and is washed with two 10-mL portions of diethyl ether. Air is drawn through the precipitate for about 30 min to dry the product. The yield is typically about 1.65 g or 30%; however, more product may be obtained by evaporation of the filtrate.

The product (0.5 g) is recrystallized by stirring with acetonitrile (25 mL) for 5 min. The mixture is gravity-filtered through Whatman no. 1 filter paper. Then diethyl ether (about 15 mL) is added to the filtrate. The solution is stoppered and allowed to stand overnight. The rust-colored crystalline product (approximately 0.2 g) is collected and dried.* *Anal.* Calcd. for $C_{12}H_{18}N_6O_6B_3F_6Co$: C, 26.33; H, 3.34; N, 15.34; B, 5.92; F, 20.83; Co, 10.76. Found: C, 26.50; H, 3.45; N, 15.34; B, 6.00; F, 21.07; Co, 10.66.

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* The checkers point out that increased yields can be obtained in the recrystallization steps by (1) adding additional increments of water to all filtered solutions and/or (2) allowing solutions to evaporate and to stand longer than suggested. For those reactions with the lower yields, however, it must be noted that the addition of water may lead to contamination of the product by the unreacted dioxime (which is also relatively insoluble in water).

B. [[TRIS-[μ-[(2,3-BUTANEDIONE DIOXIMATO)-*O*:*O′*]]-DIFLUORODIBORATO(2−)]-*N*,*N′*,*N″*,*N‴*,*N⁗*,*N′′′′′*]IRON(II)

$[Fe\{(dmg)_3(BF)_2\}]$

$$FeCl_2{\cdot}4H_2O + 3H_2dmg + 5(OH^-) + 6BF_3 \xrightarrow[BF_3\cdot O(C_2H_5)_2]{n\text{-}C_4H_9OH} [Fe\{(dmg)_3(BF)_2\}] + H^+ + 4H_2O + 4BF_4^- + 2Cl^-$$

Procedure

An Erlenmeyer flask (250-mL) is charged with powdered iron(II) dichloride tetrahydrate (1.98 g, 0.01 mol), H_2dmg (3.48 g, 0.03 mol), 1-butanol (25 mL), and a stirring bar. The flask is placed on a magnetic stirrer, and *efficient stirring is maintained throughout the following procedure.* After 10 min, boron trifluoride–diethyl ether (10 mL) is slowly poured into the red-brown mixture. Then potassium hydroxide [2.81 g (0.05 mol) dissolved in 30 mL of 1-butanol] is added over a period of 20 min, during which the red-orange crystalline product forms. After the mixture has cooled to room temperature, the orange product is collected on a Büchner funnel (10-cm diam., Whatman no. 1 paper) by suction filtration and is washed with two 10-mL portions of petroleum ether. The crude product is dried by drawing air through it for 30 min. Salts and unreacted materials are removed from the crude product by extracting the solids with chloroform (about 200 mL total volume) until all the red product has dissolved and only a white solid remains undissolved. The chloroform solution is gravity-filtered (Whatman no. 1 paper) and then evaporated to dryness by passing a stream of dry air over it. The yield is typically about 2.25 g or 50%.

The product (1 g) is recrystallized by stirring for several minutes with a solvent composed of acetonitrile (60 mL), water (30 mL), and trifluoroacetic acid (1 drop); then the mixture is heated to boiling, whereupon most solids dissolve. After being filtered by gravity (Whatman no. 1 paper), the solution is again stirred and heated to boiling. Then water (35–40 mL) is slowly added while boiling is maintained. Finally, the volume of the solution is reduced by boiling until crystals begin to appear (generally this requires the evaporation of 5–10 mL of solution). The solution is allowed to cool slowly, whereupon more crystals deposit. The red crystals are collected and dried, yielding about 0.5 g of product. More product may be obtained by further evaporation of the remaining filtrate. *Anal.* Calcd. for $C_{12}H_{18}N_6O_6B_2F_2Fe$: C, 31.49; H, 3.69; N, 18.36. Found: C, 31.72; H, 3.98; N, 18.46.

C. [[TRIS-[μ–(1,2-CYCLOHEXANEDIONE DIOXIMATO)-*O*:*O*′]]-DIFLUORODIBORATO(2 −)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]IRON(II)

$[Fe\{(nox)_3(BF)_2\}]$

$$FeCl_2 \cdot 4H_2O + 2H_2nox + 5(OH^-) + 6BF_3 \xrightarrow[BF_3 \cdot O(C_2H_5)_2]{n\text{-}C_4H_9OH} [Fe\{(nox)_3(BF)_2\}] + H^+ + 4BF_4^- + 4H_2O + 2Cl^-$$

Procedure

An Erlenmeyer flask (125-mL) is charged with powdered iron(II) dichloride tetrahydrate (1.98 g, 0.01 mol), 1-butanol (25 mL), and a stirring bar. The flask is placed on a magnetic stirrer and *efficient stirring is maintained throughout the following procedure.* After 5 min 1,2-cyclohexanedione dioxime (nioxime, H_2nox) (4.27 g, 0.03 mol) is added. The color of the mixture changes to deep-red, and a dark-purple solid forms over a period of 10 min. Then boron trifluoride–diethyl ether (10 mL) is poured slowly into the reaction mixture. An immediate color change to orange-brown occurs, and an orange solid forms. Then potassium hydroxide [2.80 g (0.05 mol) dissolved in 50 mL of 1-butanol] is added dropwise over a period of 15 min, during which the color changes to bright orange and additional orange solid forms. Stirring is continued for 5 min, then the product is collected on a Büchner funnel (10-cm diam., Whatman no. 1 paper) by suction filtration. The orange precipitate is washed with two 20-mL portions of petroleum ether and is dried by drawing air through it for 30 min. Salts are removed from the crude product by extracting the orange product with dichloromethane (about 160 mL). The salts and unreacted materials are filtered off (Whatman no. 1 paper), and the filtrate is allowed to evaporate to dryness. The typical yield of product is 5.06 g or 94%.

The product (0.5 g) is recrystallized by stirring with a solvent mixture composed of acetonitrile (60 mL), water (10 mL), and trifluoroacetic acid (1 drop). Heat is applied to warm the mixture to 45°, and stirring is continued until the product has dissolved. After being filtered by gravity (Whatman no. 1 paper), the solution is allowed to cool slowly and evaporate. After crystallization has begun, additional water (5-mL increments) may be added. Approximate yield is 0.2 g. *Anal.* Calcd. for $C_{18}H_{24}N_6O_6B_2F_2Fe$: C, 40. 34; H, 4.51; N, 15.68. Found: C, 40.26; H, 4.65; N, 15.46.

D. [[TRIS-[μ-[(1,2-CYCLOHEXANEDIONE DIOXIMATO)-*O*:*O*′]]-DIHYDROXYDIBORATO-(2 −)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]IRON(II)

$[Fe\{(nox)_3(BOH)_2\}]$

$$FeCl_2 \cdot 4H_2O + 3H_2nox + 2B(OH)_3 \xrightarrow{H_2O} [Fe\{(nox)_3(BOH)_2\}] + 2H^+ + 10H_2O + 2Cl^-$$

Procedure

An Erlenmeyer flask (125-mL) is charged with iron(II) dichloride tetrahydrate (1.98 g, 0.01 mol), water (40 mL), and a stirring bar. The flask is placed on a magnetic stirrer and *efficient stirring is maintained throughout the following procedure.* After 5 min, 1,2-cyclohexanedione dioxime (nioxime, H_2nox) (4.27 g, 0.03 mol) is added to the iron(II) dichloride solution. The color of the mixture changes to deep red-brown as the nioxime dissolves. After the nioxime has dissolved, boric acid (1.24 g, 0.02 mol) is added, whereupon crystals of product begin to form. After 5 min, the flask is removed from the stirrer and is set aside for 5–10 hr, during which time more of the crystalline product forms. The orange product is collected on a Büchner funnel (5-cm diam., Whatman no. 1 paper) by suction filtration and is washed with two 10-mL portions of water. Air is drawn through the product for ca. 1 hr to dry it. Typical yields of product are ~5.34 g, or essentially 100%.

The product (0.5 g) is recrystallized by stirring with a solvent mixture composed of acetonitrile (50 mL or more), water (20 mL or less), and trifluoroacetic acid (1 drop). Heat is applied to warm the mixture to 45° and stirring is continued until almost all the product has dissolved. After being filtered by gravity (Whatman no. 1 paper), the solution is allowed to cool slowly to room temperature and then is kept at 2° for several days. Approximate yield is 0.25 g. *Anal.* Calcd. for $C_{18}H_{26}N_6O_8B_2Fe$: C, 40.64; H, 4.93; N, 16.02. Found: C, 40.43; H, 5.03; N, 16.02.

E. [[TRIS-[μ-[(2,3-BUTANEDIONE DIOXIMATO)-*O*:*O*′]]-DIBUTOXYDIBORATO-(2 −)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]IRON(II)

$[Fe\{(dmg)_3(BOC_4H_9)_2\}]$

$$FeCl_2 \cdot 4H_2O + 3H_2dmg + 2B(OH)_3 + 2n\text{-}C_4H_9OH \xrightarrow[\text{heat}]{n\text{-}C_4H_9OH} [Fe\{(dmg)_3(BOC_4H_9)_2\}] + 2H^+ + 10H_2O + 2Cl^-$$

Procedure

An Erlenmeyer flask (125-mL) is charged with iron(II) dichloride tetrahydrate (1.98 g, 0.01 mol), H_2dmg (3.48 g, 0.03 mol), boric acid (1.24 g, 0.02 mol), 1-butanol (50 mL), and a stirring bar. The flask is placed on a magnetic-stirring hot plate, and *efficient stirring is maintained throughout the following procedure.* Heat is applied to boil the mixture for 5 min, during which time the color of the mixture darkens to deep-red. To the boiling mixture, borax, ($Na_2B_4O_7 \cdot 10H_2O$) (1.9 g, 0.005 mol) is added slowly over a period of 5 min. Some crystals of product form during the addition. Boiling is continued for 15 min, while a gentle stream of air is directed into the flask to aid evaporation (final volume is about 20 mL). The flask is set aside to cool to room temperature. The orange, crystalline product is collected on a Büchner funnel (5-cm diam., Whatman no. 1 paper) by suction filtration and is washed with two 10-mL portions of petroleum ether. Air is drawn through the product for 30 min to dry it. Typical yields of product are 4.6 g or 90%.

The product (1 g) is recrystallized by dissolving it in acetonitrile (75 mL) by stirring and warming the mixture to 50°. The solution is filtered by gravity (Whatman no. 1 paper) while warm, and then water (35 mL) is added slowly while the temperature is maintained at about 50°. After being filtered again (as above), the solution is allowed to cool to room temperature. Approximate yield is 0.6 g. *Anal.* Calcd. for $C_{20}H_{36}N_6O_8B_2Fe$: C, 42.44; H, 6.41; N, 14.85. Found: C, 42.42; H, 6.41; N, 14.76.

F. [[TRIS-[μ-[(1,2-DIPHENYL-1,2-ETHANEDIONE DIOXIMATO)-*O*:*O*′]]-DIBUTOXYDIBORATO(2−)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]-IRON(II)

$[\mathrm{Fe}\{(\mathrm{dpg})_3(\mathrm{BOC_4H_9})_2\}]$

$$\mathrm{FeCl_2{\cdot}4H_2O} + 3\mathrm{H_2dpg} + 2\mathrm{B(OH)_3} + 2n\text{-}\mathrm{C_4H_9OH} \xrightarrow[\text{heat}]{n\text{-}\mathrm{C_4H_9OH}} \mathrm{Fe[(dpg)_3(BOC_4H_9)_2]} + 2\mathrm{H^+} + 10\mathrm{H_2O} + 2\mathrm{Cl^-}$$

Procedure

An Erlenmeyer flask (125-mL) is charged with iron(II) dichloride tetrahydrate (1.98 g, 0.01 mol), 1-butanol (50 mL), and a stirring bar. The flask is placed on a magnetic-stirring hot plate, and *efficient stirring is maintained throughout the following procedure.* After 5 min, diphenylglyoxime (H_2dpg) (7.21 g, 0.03 mol) and boric acid (1.24 g, 0.02 mol) are added to the mixture of the 1-butanol and the partially dissolved iron salt. Heat is applied to boil the mixture for 10 min, during which time the color of the mixture darkens to a deep red-brown. Then borax ($Na_2B_4O_7 \cdot 10H_2O$) (1.9 g, 0.005 mol) is added slowly over a period of 5 min while boiling is continued. The deep-red mixture is boiled an additional 5 min and then is allowed to cool to room temperature. During cooling, deep-red crystals form a solid mass. The product is collected on a Büchner funnel (10-cm diam., Whatman no. 1 paper) by suction filtration and is washed with two 10-mL portions of petroleum ether. The product is dried by drawing air through it for 30 min. Typical yield of product is 6.64 g or 71%; however, more product may be obtained by evaporating the filtrate.

The product (0.5 g) is recrystallized by stirring it with acetonitrile (20 mL) for 5 min (or until product has dissolved) and then is gravity-filtered (Whatman no. 1 paper). The filtrate is warmed to about 65°, and water (about 5 mL) is added while the solution is kept warm. Crystals usually appear upon addition of the water, and then the solution is allowed to cool to room temperature and evaporate for 24 hr. Approximate yield is 0.45 g. *Anal.* Calcd. for $C_{50}H_{48}N_6O_8B_2Fe$: C, 63.99; H, 5.16; N, 8.96. Found: C, 63.43; H, 5.12; N, 9.04.

Properties

Crystals of the iron-containing clathrochelates are orange-red to deep-red or "black," depending in part upon the crystal size. Crystals of the cobalt complex are rust-colored. All of the clathrochelates mentioned above may be handled in the atmosphere without any apparent decomposition or interaction with water or oxygen. Samples purified by recrystallization and dried *in vacuo* have shelf lives of *at least* 1 year and probably much longer than that. In general, suitable solvents for attaining concentrations of about 5×10^{-3} *M* or greater are dichloromethane, chloroform, dichloroethane, acetonitirle, or acetone. An exception to this general solubility rule occurs for $[Fe[nox)_3(BOH)_2]$, which tends to be somewhat sparingly soluble in the solvents just mentioned but is reasonably soluble in 1 : 1 v/v mixtures of water (slightly acidified with trifluoroacetic acid) and acetonitrile. In solutions made from the solvents listed above, the clathrochelates show little or no tendency to decompose. All of the clathrochelates are decomposed by boiling with concentrated hydrochloric acid. Decomposition under this condition is quite apparent: the acidic solution develops a pale-yellow color and an odor reminiscent of biacetyl (2,3-butanedione) can be detected in the case of those chelates derived from dimethylglyoxime.

The reactions described here represent a significant amount of organization in that up to eight separate ions and molecules eventually come together to make the final product. In view of the relatively high yields it must be assumed that the clathrochelate formation is highly favored thermodynamically and/or kinetically. It is anticipated that clathrochelates as a class of compounds will be particularly well suited to studies pertaining to stereochemistry,[1,3] limited-pathway intramolecular isomerizations, analysis of metal ions, and ion transport phenomena.[6]

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39. POTASSIUM *cis*-[DIAQUABIS(OXALATO)CHROMATE(III)] DIHYDRATE AND POTASSIUM *trans*-[DIAQUABIS(OXALATO)-CHROMATE(III)] TRIHYDRATE

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Checked by JOE GLIKSMAN† and JAY H. WORRELL†

The diaquabis(oxalato)chromate(III) anion forms a large number of well-crystallized salts with various cations. Their constitution was first established by Rosenheim and Cohn[1] and by Werner and Surber.[2] The salts occur in two geometrically isomeric series—cis, reddish violet, and trans, pinkish red—which are formed by reduction of dichromates by oxalic acid; the specific conditions of the reaction determine which isomer is formed.[2,3]

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In aqueous solution the equilibrium between the *cis*- and *trans*-[diaquabis(oxalato)chromate(III)] ions lies almost completely on the side of the cis isomer; pure crystals of the slightly soluble potassium salts of the trans isomer are formed by the slow evaporation of the solution at room temperature,[2,4–6] whereas the potassium salt of the cis isomer is obtained by cooling the hot solution or by allowing potassium dichromate and oxalic acid to react with only a minimal amount of water present,[2,4–6] the method given here.

Diaquabis(oxalato)chromates(III) may also be prepared by the reduction of chromium(VI) oxide by oxalic acid,[7] aquation of the tris(oxalato)chromate(III) ion,[8,9] and cleavage of the $[(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2]^{4-}$ ion.[10] The mechanism of their formation from hexaaquachromium(III) and oxalate ions[11] has been established by polarographic,[12,13] conductometric,[12] and spectrophotometric[13,14] measurements.

A. POTASSIUM *cis*-[DIAQUABIS(OXALATO)-CHROMATE(III)] DIHYDRATE

$$K_2[Cr_2O_7] + 7H_2C_2O_4\cdot 2H_2O \longrightarrow 2\{K[\textit{cis}\text{-}Cr(H_2O)_2(C_2O_4)_2]\cdot 2H_2O\} + 6CO_2\uparrow + 13H_2O$$

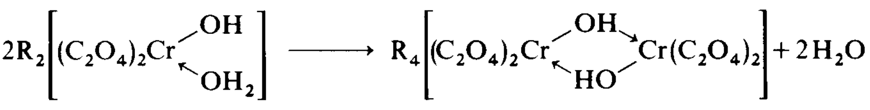
Procedure

A mixture of 4.00 g (0.0136 mol) of potassium dichromate and 12.0 g (0.0952 mol) of oxalic acid dihydrate is ground together as thoroughly as possible in a *dry* mortar. The mixture is placed in a *compact* pile in the center of a 10-cm evaporating dish whose inner surface has been moistened with water. The dish is covered with a ribbed watch glass and placed on a hot plate that is just hot to the touch. A spontaneous reaction with vigorous effervescence begins almost immediately, and the mixture liquefies to a deep-purple syrup. When the reaction appears complete (ca. 5 min), 20 mL of 95% ethanol is added, warming is continued, and the mixture is triturated, first with a spatula and then with a pestle, until the mixture solidifies. If solidification does not occur, the ethanol is decanted, an additional 20 mL of ethanol is added, and the trituration with warming is continued until the product is completely granular. The deep-purple product is collected on a 10-cm diam. Büchner funnel, washed with two 5-mL portions of 95% ethanol, 5 mL of ether, and then air-dried. The yield is 8.40 g (ca. 91.1%). *Anal.* Calcd. for $C_4H_8CrKO_{12}$: Cr, 15.33. Found: Cr, 15.36.*

* The complex readily loses its water of hydration on storage in a vacuum desiccator. The checkers obtained the following results for the anhydrous salt: *Anal.* Calcd. for $C_4H_4CrKO_{10}$: C, 15.85; H, 1.33. Found: C, 15.81; H, 1.68.

Properties

cis-[Diaquabis(oxalato)chromate(III)] salts are generally less hydrolyzed in water and are more soluble than the corresponding salts of the trans isomer. Their aqueous solutions, which give an acidic reaction, are reddish violet when dilute, while concentrated solutions exhibit red-blue dichroism. The absorption spectra of the cis and trans compounds are similar but differ greatly in intensity.[15-17] The checkers report the following absorption maxima and molar extinction coefficients: λ max (ε), 416 nm (69.4) and 562 nm (47.8). Treatment of the cis salts with aqueous ammonia or potassium hydroxide gives green *cis*-[aquahydroxobis(oxalato)chromate(III)] salts, a reaction used to differentiate them from the corresponding salts of the trans isomer.[2] Treatment of the aquahydroxo salt of the complex with mineral acid regenerates the original salt of the diaqua complex. Further loss of coordinated water results in formation of the di-μ-hydroxo-bis[bis(oxalato)chromate(III)] ion:



$$2R_2\left[(C_2O_4)_2Cr\begin{matrix}OH\\OH_2\end{matrix}\right] \longrightarrow R_4\left[(C_2O_4)_2Cr\begin{matrix}OH\\HO\end{matrix}Cr(C_2O_4)_2\right] + 2H_2O$$

Werner and Surber[2] used this "olation" reaction to assign configurations to the salts. The lilac-colored potassium salt, which crystallizes as either the di- or trihydrate, was first prepared by Werner and Surber.[2]

B. POTASSIUM *trans*-[DIAQUABIS(OXALATO)-CHROMATE(III)] TRIHYDRATE

$$K_2[Cr_2O_7] + 7H_2C_2O_4\cdot 2H_2O \longrightarrow$$
$$2\{K[\mathit{trans}\text{-}Cr(H_2O)_2(C_2O_4)_2]\cdot 3H_2O\} + 6CO_2\uparrow + 13H_2O$$

Procedure

A solution of 4.00 g (0.0136 mol) of potassium dichromate, dissolved in a minimum volume (ca. 8 mL) of *boiling* water, is added with stirring *in small portions* (■ **Caution.** *Vigorous effervescence occurs.*) to a solution of 12.0 g (0.0952 mol) of oxalic acid dihydrate, dissolved in a minimum volume (ca. 17 mL) of *boiling* water, contained in a 400-mL beaker. The beaker is covered with a watch glass while the reaction proceeds (ca. 5 min). The solution is allowed to cool to room temperature; then the dark-purple solution is transferred to a 6-cm evaporating dish and is allowed to evaporate at room temperature to ca. one-third of its original volume (ca. 24 hr).* The deposited crystals are collected on an 8-cm diam. Büchner funnel, washed with three 10-mL portions of ice water and 10 mL of 95% ethanol, and then air-dried. The yield of pink crystals is 5.70 g (58.6%). *Anal.* Calcd. for $C_4H_{10}KCrO_{13}$: Cr, 14.55; C, 13.45; H, 2.82. Found: Cr, 14.46; C, 13.34; H, 2.94.

In solution, an equilibrium in which the very soluble cis isomer is favored is established between the two isomers. However, the small solubility of the trans isomer causes its precipitation as evaporation proceeds. If evaporation proceeds too far, the precipitate of the trans isomer is contaminated by increasing amounts of the cis isomer. To test for the purity of the trans isomer, a few drops of dilute aqueous ammonia are added to a few milligrams of the product on a filter paper. If the trans isomer is pure, a light-brown, insoluble solid forms. If the cis isomer is present, a deep-green *solution* forms and spreads on the paper.

If the trans isomer is contaminated with cis isomer, it may be purified by adding, with stirring, dilute aqueous ammonia in small portions and decanting the resulting green solution. The process is continued until no further green solution is formed.† The remaining solid is collected by suction filtration, washed free of ammonia with a little ice water, and reconverted to the salt of the *trans*-diaqua compound by adding some dilute hydrochloric acid. The pure salt of the trans isomer is washed with ice water and ethanol, and air-dried as above.

Properties

trans-[Diaquabis(oxalato)chromate(III)] salts are generally less soluble in water and hydrolyze more rapidly than the corresponding salts of the cis isomer. Their aqueous solutions, which give an acidic reaction, are reddish and nondichroic when freshly prepared; on long standing or on short heating they become green or blue and form tris(oxalato)chromates(III). The absorption spectra of the cis and trans compounds are similar but differ

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* If the precipitated solid appears purple rather than pink in color, the checkers recommend carefully decanting the supernatant liquid, washing the solid with three 20-mL portions of ice water, and collecting the remaining pink product by filtration. If the mixture forms a glasslike oil, they recommend redissolving it in water and setting it aside for ca. 3 hr, whereupon a pink solid forms.

† The checkers report that the trans compound dissolves to form a brown solution. The green-to-brown color change is subtle and may result in excessive loss of purified trans compound if one is not careful.

greatly in intensity.[15–17] The checkers report the following absorption maxima and molar extinction coefficients: λ max (ε): 416 nm (28.6) and 555 nm (23.5) dissolved in water or dilute perchloric acid at 24°, based on the dihydrate formulation; the spectrum was determined 9 min after the solute was added to the solvent.*

Treatment of the salts of the trans isomer with aqueous ammonia or potassium hydroxide gives red or brown *trans*-[aquahydroxobis(oxalato)-chromate(III)] salts, a reaction used to differentiate them from the corresponding salts of the cis isomer.[2] Treatment of the aquahydroxo salt of the complex with mineral acid regenerates the original salt of the diaqua complex.

Of the very stable salts of the trans isomer only the alkali metal salts can be recrystallized from water. The commonest and best known is the potassium salt, known as Croft's salt[18] or as red potassium chromioxalate. It crystallizes with two, three, or four molecules of water and is used extensively in tanning.[19] Proof of the co-ordinative bonding of the oxalate ion to the chromium atom in this salt has been obtained by measurements of absorption spectra,[20] and its structure has been determined by x-ray diffraction.[21]

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* In the absorption spectrum, both bands rapidly become more intense as a function of time; in a typical determination, the absorption changed from 0.700 to 0.810 at 416 nm over a 6-min interval.

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40. COBALT(III), RHODIUM(III), AND IRIDIUM(III) CARBONATO COMPLEXES OF THE PENTAAMMINE TYPE

$$[M(N_5)(OH)]^{2+} + CO_2 \longrightarrow [M(N_5)(OCO_2H)]^{2+} \longrightarrow [M(N_5)(CO_3)]^{+} + H^{+}$$

$$[M = \text{Co, Rh or Ir; } (N_5) = (NH_3)_5, (en)_2(NH_3) \text{ or "tetren"*}]$$

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Checked by F. A. COTTON‡ and R. PHILENT‡

The synthesis of pentaammine(carbonato)cobalt(III) salts is readily accomplished by an air-oxidation method starting with cobalt(II) nitrate and ammonium carbonate in aqueous ammonia.[1] However, a suitable general method for making other types of monodentate amino(carbonato) metal salts is not available in the literature. The air-oxidation technique can be applied only to complexes where the ligands are all ammonia molecules or where the central metal ion is cobalt.

The procedure described here is based on the observation that amine monohydroxo complexes of cobalt(III), rhodium(III), and iridium(III) react directly with carbon dioxide to form the corresponding carbonato complexes,[2,3] without effect on the configuration of the amine ligands.[4] The amine monoaqua complex is allowed to react with lithium carbonate or carbon dioxide gas at room temperature at pH 8.0 for a few minutes, and the carbonato complex is isolated by adding alcohol. The procedure has been used to prepare salts of the following cations: pentaammine(carbonato)cobalt(III),[2] *cis*-ammine(carbonato)bis(ethylenediamine)cobalt(III),[5] *trans*-

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* "tetren" = tetraethylenepentamine.

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ammine(carbonato)bis(ethylenediamine)cobalt(III),[6] *αβsym*-(carbonato)-(tetraethylenepentaammine)cobalt(III),[7,*] pentaammine(carbonato)rhodium(III),[9] and pentaammine(carbonato)iridium(III).[10]

■ **Caution.** *Perchlorate metal ammine salts are somewhat unstable and should therefore be handled with care and in small quantities.*

Procedure

The various aquaamines from which the desired complexes were synthesized were prepared as described in the indicated references,[2,5–10] and in each case the yields obtained were as reported by the original authors.

Solid lithium carbonate is slowly added to a stirred solution containing 2 g of the $[M(N_5)(OH_2)]^{3+}$ salt in 20 mL of water until a pH of 8–8.5 is attained.† The amount of water taken is entirely dependent on the solubility of the aqua complex. It is best to start with a completely saturated solution. Approximately 2 g per 20 mL is close to the limit of saturation of the aqua complexes used.

In an alternative procedure, a filtered 10% aqueous lithium hydroxide solution is added to the aqua complex solution until the pH 8–8.5 range is reached. Then carbon dioxide is bubbled slowly through the solution, the pH being maintained by occasional dropwise additions of the lithium hydroxide solution.

After carbonato complex formation is complete, the solution is stirred for 5 min and cooled in an ice bath; then absolute ethanol is added slowly until a precipitate appears.‡ The mixture is allowed to stand near 0° for 1 hr, and

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[*] The geometry of the corresponding hydroxo compound, *αβsym*$[Co(tetren)OH](ClO_4)_2$, was incorrectly identified as the "α" configuration by the original authors.[7] Subsequent studies[8] have shown that the correct designation is "*αβsym*."

† The pH 8–8.5 range is critical, and care must be exercised to stay within this range during the addition of the lithium carbonate. *trans*-$[Co(en)_2(NH_3)(CO_3)]ClO_4$ starts precipitating in aqueous solution at about pH 6. The precipitate is filtered off, and more lithium carbonate is added to the filtrate until pH 8 is reached.

‡ *αβsym*$[Co(tetren)CO_3]ClO_4$ does not precipitate in alcohol. The solution is therefore evaporated to dryness and the crude complex salt is dissolved in a minimum amount of water. Sufficient absolute alcohol is added to the solution to precipitate the lithium carbonate and the resultant solution of the complex salt is evaporated to dryness in a vacuum desiccator.

TABLE I Analyses of the Ammine Complexes

	Calc.				Found			
Complex	C	H	N	Cl	C	H	N	Cl
$[Co(NH_3)_5(CO_3)]ClO_4 \cdot H_2O$	3.73	5.29	21.78	11.03	3.88	5.34	21.84	11.37
cis-$[Co(en)_2(NH_3)(CO_3)]Br \cdot 0.5H_2O$	20.30	6.13	17.40	—	20.62	6.00	17.21	—
trans-$[Co(en)_2(NH_3)(CO_3)]ClO_4$	16.94	5.49	19.69	10.11	16.88	5.34	19.68	9.97
αβsym-$[Co(tetren)(CO_3)]ClO_4 \cdot 3H_2O$	23.40	6.29	15.18	—	23.56	6.16	15.28	—
$[Rh(NH_3)_5(CO_3)]ClO_4 \cdot H_2O$	3.28	4.69	19.15	9.70	3.27	4.74	18.95	9.73
$[Ir(NH_3)_5(CO_3)]ClO_4$	2.75	3.46	16.03	8.20	2.68	3.31	15.74	7.96

the crude product is filtered and washed thoroughly with ethanol. The complex is then recrystallized at least twice from a minimum volume of very dilute lithium hydroxide solution ($10^{-4}M$). Recrystallization should be performed repeatedly until a constant ultraviolet-visible spectrum of carbonato salt is obtained. This is particularly important when using the carbon dioxide–bubbling procedure, since it unavoidably results in contamination by lithium carbonate. The crystals are washed with ethanol and diethyl ether and are vacuum-dried. Yield, approximately 20%.

Properties

All of the carbonato cobalt(III) complexes reported here are reddish in color and extremely soluble in water. The rhodium complex is pale-yellow, whereas the iridium salt is virtually white; they are both soluble in water. Treatment with dilute acid immediately gives the corresponding aqua complex with evolution of carbon dioxide. The characterization and the mechanistic details of acid hydrolysis of these complexes have been reported.[3,4,11]

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41. TECHNETIUM(VII) OXIDE

$$4Tc + 7O_2 \xrightarrow{450} 2Tc_2O_7$$

Submitted by A. Y. HERRELL,* R. H. BUSEY,† and K. H. GAYER*
Checked by K. SCHWOCHAU‡ and S. GUTZEIT‡

Contrary to some reports,[1-3] ditechnetium heptaoxide is not the only product formed when technetium metal is burned in an excess of oxygen—nor can it be purified by simple resublimation. The formation of small quantities of a second volatile compound (possibly TcO_3 or $HTcO_4$) has been observed by some investigators.[4-6]

Oxidation of the metal is very complex. The initial volatile product formed by reaction with oxygen at 450° may be the red pentaoxide, Tc_2O_5. Further oxidation of this intermediate oxide at 450° gives yellow Tc_2O_7 as the major product. It is suggested that the darkening in color of the Tc_2O_7 as usually obtained is caused by its reaction with Tc_2O_5 impurity to give black TcO_3.[7] These impurities can be removed by the controlled oxidation, in a sealed tube, of the initial products.

■ **Caution.** ^{99}Tc *is a weak beta emitter* ($E_{max} = 0.3$ meV; $t_{1/2} = 2.12 \times 10^5$ yr). *Technetium compounds should be handled in a well-ventilated fume hood, and normal radiochemical practices should be observed.*

Procedure

Approximately 0.3 g (3 mmol) of technetium metal,§[8,9] which has previously been degassed at 900° on a vacuum line, is contained in a suitable

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§ The technetium metal was obtained from $K[TcO_4]$ as described in reference 8. The $K[TcO_4]$ is available from the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830.

porcelain boat and placed near the closed end of a 20-mm diam., 100-cm Pyrex combustion tube that is an integral part of a modified Burg apparatus[10] (Fig. 20). The system is evacuated by means of a mechanical- and diffusion-pump system (measured pressure $< 10^{-6}$ torr), and the combustion tube is flamed (while pumping) to remove final traces of moisture. By means of a three-way stopcock (*H*), the system is switched from the vacuum pump to the supply of dry oxygen. The oxygen is dried by passing it over P_4O_{10} and then storing it over P_4O_{10} for 30 min in reservoir *E*, which contains P_4O_{10} or P_4O_{10} dispersed on glass wool. The mercury manometer connected to the combustion system is used to measure the oxygen pressure in the system and serves as a seal for one end of the closed system. When the combustion system is filled with oxygen, it is closed off from the reservoir.

A tubular furnace (not shown) is now slipped over the combustion tube, and the metal is oxidized at 450–500° for a period of 12 hr. The products which sublime out of the heated zone and condense in the cold region of the combustion tube are now resublimed as follows. The boat* is first sealed off from the combustion products which are then isolated in a 30-cm section of the combustion tube by a second sealing process.

* A white to gray residue remains in the boat when the metal employed is obtained by hydrogen reduction of $[NH_4][TcO_4]$.

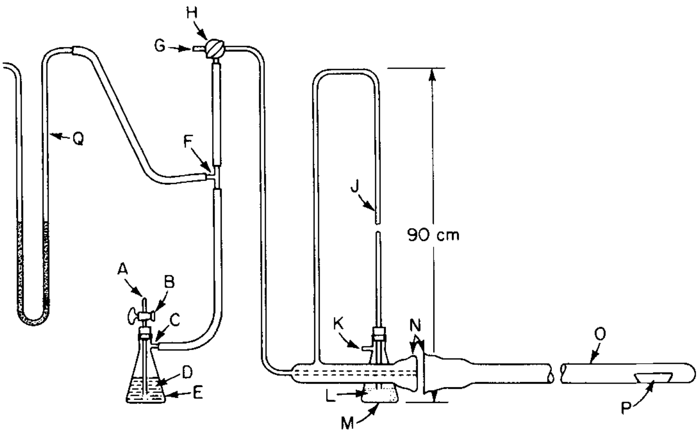

Fig. 20. Modified Burg apparatus. A, *port to oxygen supply;* B, *stopcock;* C, *glass-wool plug;* D, *moisture-indicating* P_4O_{10}; E, *500-mL suction flask;* F, *T tube; H, three-way stopcock;* J, *mercury manometer;* K, *gas exit port;* L, *150 mL mercury;* M, *500-mL suction flask;* N, *tapered ground-glass joints (65/40);* O, *Pyrex combustion tube (length: 100 cm; o.d.: 20 mm);* P, *porcelain boat;* Q, *mercury manometer.*

■ **Caution.** *In order to seal off sections of the combustion tube, the oxygen pressure in the system must be about* 50 torr *below atmospheric pressure. Failure to reduce the internal pressure will prevent a good end seal and may cause a hole to develop during the sealing process.*

This sealed-off section is now placed in a larger Pyrex tube for safety reasons (Fig. 21). (■ **Note.** *The major hazard associated with the following oxidation step is the possibility that a leak might develop at an end of the inner tube which would cause contamination of the furnace and the laboratory with radioactive material. The protective tube minimizes this potential hazard.*) The furnace is slipped over the outer tube so that the inner, sealed tube is completely covered. To ensure uniform temperature in the reaction zone, a clay plug is inserted at one end of the furnace and an aluminum reflector plug is placed inside the outer tube where it emerges from the furnace.

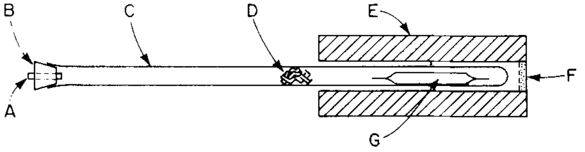

Fig. 21. Final oxidation system. A, *port to air;* B, *one-hole rubber stopper;* C, *Pyrex tube (length: 110 cm; o.d.: 42 mm);* D, *aluminum foil reflector plug;* E, *tubular furnace (length: 24 in.; bore: 2 in.);* F, *clay plug;* G, *sealed tube with sample.*

The temperature of the furnace is slowly raised to 350–450° over a period of 30 min; then the furnace is held at this temperature in order to convert the lower technetium oxides to ditechnetium heptaoxide. This oxidizing period varies from sample to sample but is usually complete in about 30 min. The protective tube is now partially withdrawn from the furnace thus exposing the sealed tube holding the product. This produces a cold region at one end of the sealed tube into which the sample sublimes. The furnace is then allowed to cool to 230°. The clay plug is removed, and the protective tube is now pushed through the furnace to provide a cold region (at the opposite end of the product tube) into which the oxide sublimes. The furnace temperature is maintained at 230°. The time required for the final sublimation is ca. 8 hr.

Because of the affinity of Tc_2O_7 for moisture, the sealed tube is transferred to a glove box filled with dry argon, where it may be broken open.

Properties

Technetium(VII) oxide is a yellow solid, crystallizing in the orthorhombic space group D_{2h}^{15}-Pbca and is one of the few known transition metal oxides having a molecular structure in the solid state.[10] It melts at 119.5° and boils at 310.6° It dissolves in water, forming pertechnetic acid. The pertechnetate ion is known to inhibit the corrosion of steel.[11] Technetium(VII) oxide is an excellent starting material for preparing pure technetium metal.

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Chapter Four

MAIN GROUP COMPOUNDS

42. TRIS(DIALKYLAMINO)BORANES

Submitted by D. T. HAWORTH*
Checked by WILLIAM R. PURDUM† and EDWIN M. KAISER†

The reaction of trichloroborane with ammonia or a primary amine hydrochloride in refluxing chlorobenzene affords the corresponding *N*-substituted 2,4,6-trichloroborazine, $B_3Cl_3N_3H_3$ and $B_3Cl_3N_3R_3$, respectively.[1] At lower temperatures, reaction of trichloroborane with a primary or secondary amine in a nonpolar solvent affords a tris(amino)borane, $B(NHR)_3$ or $B(NR_2)_3$.[2,3] The first member in this series, tris(dimethylamino)borane, $B[N(CH_3)_2]_3$,[4] was originally synthesized in the gaseous phase.[5] The procedures reported here are those of Lappert and Gerrard[2] who have reported on other derivatives of this type of aminoborane using a low-temperature, inert-solvent medium. A current paper describes the preparation of tris(amino)boranes having bulky substituents from *N*-lithioamines and boron trifluoride–diethyl ether.[6]

A. TRIS(DIETHYLAMINO)BORANE

$$BCl_3 + 6(C_2H_5)_2NH \longrightarrow B[N(C_2H_5)_2]_3 + 3(C_2H_5)_2NH\cdot HCl$$

Procedure

A 500-mL flask is fitted with a Claisen adapter having a dropping funnel and calcium chloride drying tube; the flask is charged with diethylamine

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(25 g, 0.34 mol) and pentane (100 mL) under a nitrogen atmosphere. The apparatus is placed in a Dry Ice bath. Trichloroborane (10 g, 0.085 mol) is slowly bubbled under nitrogen into a pentane-filled (50 mL) dropping funnel which has been cooled to about −35 to −40° by Dry Ice. If a jacketed funnel is not available, this cooling can be achieved by placing aluminum foil containing Dry Ice on the outside of the funnel. This solution is added dropwise (ca. 1 hr) to the cooled amine-pentane solution. After an additional 2 hr the solution is allowed to warm to room temperature. The solution is filtered under a nitrogen atmosphere, and 25 mL of pentane is used to transfer the solids to the filter funnel. The white solid is washed with an additional 25 mL of pentane, and the resulting clear solution is vacuum-stripped of the pentane solvent to yield a clear solution. For the final distillation, it is recommended that this solution be transferred to a 25-mL flask. Distillation under vacuum yields 10.5 g [81.4% yield, based on $(C_2H_5)_2NH$] of tris(diethylamino)borane, bp 47–49°/0.6 torr, n_D^{24} 1.4470 (lit.,[2] bp 50–53°/0.4 torr, n_D^{20} 1.4450). *Anal.* Calcd. for $C_{12}H_{30}BN_3$: C, 63.42; H, 13.32. Found: C, 63.58; H, 13.40.

B. TRIS[(1-METHYLPROPYL)AMINO]BORANE

$$BCl_3 + 6C_2H_5CH(CH_3)NH_2 \longrightarrow B[NHCH(CH_3)C_2H_5]_3 + 3C_2H_5CH(CH_3)NH_2\cdot HCl$$

Procedure

The procedure is identical with that described in Procedure A except for the use of *sec*-butylamine instead of the diethylamine. It may be noted that the molecular weights of *sec*-butylamine and diethylamine are identical. The yield of tris[(1-methylpropyl)amino]borane is 12.5 g [91%, based on $C_2H_5CH(CH_3)NH_2$], bp 45–47°/0.1 torr, n_D^{25} 1.4340 (lit.,[3] bp 49°/0.1 torr, n_D^{20} 1.4355). It is recommended that the distillation be performed at pressures no greater than 0.1 torr, since higher temperatures may contaminate the product with the aminoborazine, $B_3[NHCH(CH_3)C_2H_5]_3N_3[CH(CH_3)C_2H_5]_3$.[3] *Anal.* Calcd. for $C_{12}H_{30}BN_3$: C, 63.42; H, 13.32. Found: C, 63.41; H, 13.14.

Properties

Tris(diethylamino)borane and tris[(1-methylpropyl)amino]borane are clear liquids which decompose in the presence of air and moisture. The compounds are best stored under nitrogen in sealed ampuls at low temperatures. The compounds are soluble in a number of organic solvents.

The reaction of diborane(6) with bis or tris(dimethylamino)borane has recently been shown to be synthetically useful in the stepwise buildup of a boron-nitrogen chain leading to bis(μ-dimethylamino)triborane(9).[7]

Tris(acetonitrile)tricarbonylchromium and tris(acetonitrile)tricarbonyltungsten react with tris(dimethylamino)borane to give yellow, readily sublimable crystalline products of the type $[(CH_3)_2N]_3BM(CO)_3$. On the basis of their ^{11}B nmr spectrum, π-coordination of the aminoborane with a relatively strong, metal-boron interaction is suggested.[8,9]

A new class of boron compounds has been prepared by the reaction of pentacarbonyliron with dichloro(dimethylamino)borane to form $(CO)_4FeBN(CH_3)_2$, a borylene complex.[10] The mono- and dihaloaminoboranes can be prepared from the corresponding tris(amino)borane.[11,12] Pyrolysis of the tris(primary amino)borane $B(NHR)_3$ yields the borazine $B_3(NHR)_3N_3R_3$.[3]

The infrared spectrum of tris(diethylamino)borane contains major absorption bands at 2970, 2930, 2865, 2850, 1475, 1430, 1370, 1340, 1295, 1265, 1200, 1185, 1125, 1105, 1070, 1055, and 790 cm^{-1}. Its ^1H nmr spectrum (TMS standard) has absorptions centering at $\tau 7.13$ and $\tau 9.02$. The infrared spectrum of tris[(1-methylpropyl)amino]borane contains major absorption bands at 3225, 2980, 2940, 1565, 1465, 1440, 1370, 1350, 1320, 1270, 1220, 1160, 1140, 1100, 1000, 985, 900, 870, 835, 780, 720, 690, and 660 cm^{-1}. Its ^1H nmr spectrum has absorptions centering at $\tau 5.27$, 9.59, and 9.16.

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43. TRIS(*N*-METHYLANILINO)BORANE

$$C_6H_5N(CH_3)H + LiC_4H_9 \longrightarrow C_6H_5N(CH_3)Li + C_4H_{10}$$

$$3C_6H_5(CH_3)NLi + BF_3{\cdot}O(C_2H_5)_2 \longrightarrow B[N(CH_3)C_6H_5]_3 + 3LiF + (C_2H_5)_2O$$

Submitted by WILLIAM R. PURDUM* and EDWIN M. KAISER*
Checked by RICHARD L. TYSON† and JAMES C. CARTER†

Tris(*N*-methylanilino)borane has previously been prepared by the reaction of boron trifluoride–ether complexes with three equivalents each of *N*-methylaniline and a suitable Grignard reagent,[1,2] by the reaction of (*N*-methylanilino)potassium with boron trifluoride–ether complexes,[2] and by aminolysis of boron trichloride by *N*-methylaniline.[3] The present general procedure describes a convenient preparation of tris(*N*-methylanilino)borane by the reaction of (*N*-methylanilino)lithium and boron trifluoride–diethyl ether in tetrahydrofuran-hexane as solvent.

Tris(organoamino)boranes have been utilized to prepare, in reasonable yields,[4,5] mono- and dihalo(organoamino)boranes which are often difficult to obtain by direct amination of the boron trihalides. Carboxylic acids, 1,3-diketones, ketones, and β-ketoesters have been converted into carboxamides, enamino-ketones, enamines, and β-enamino-amides, respectively, by reaction with an appropriate tris(organoamino)borane under very mild conditions.[6] Sulfenamides ($R_2NSC_6H_5$) have also been prepared in high yield from selected tris(organoamino)boranes and sulfenic esters under relatively mild conditions.[7]

Procedure

■ **Caution.** *The drying of tetrahydrofuran may be accompanied by serious explosions under certain conditions.* (See *Inorganic Syntheses*, **12,** pages 111, 317.) See Synthesis 1 in this volume for additional information on suggested drying procedures.

A 500-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer, water-cooled condenser‡ topped with a calcium chloride drying

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‡ A Friedrich's condenser was employed [Fisher Scientific Company Catalog, p. 553 (1974)], but the type of condenser is not critical.

tube, addition funnel, and inert-atmosphere* inlet, is charged under the inert atmosphere with 16.1 g (0.15 mol) of freshly distilled *N*-methylaniline and 200 mL of anhydrous tetrahydrofuran. The mixture is cooled to 0° and 96 mL (0.15 mol) of 1.6*M* *n*-butyllithium in hexane† is added with a hypodermic syringe over a period of 5 min and is stirred at 0° for an additional 30 min to give the solution of (*N*-methylanilino)lithium.

Commercial boron trifluoride–diethyl ether‡ is purified by distillation at 46°/10 torr from small amounts of calcium hydride.[8] (The resulting pot residue may be destroyed by the cautious addition of ice.)

Boron trifluoride–diethyl ether (7.1 g, 0.05 mol) is added during 5 min to the previously prepared solution of (*N*-methylanilino)lithium. The pale-yellow slurry is then refluxed for 3 hr. At the end of this time, the mixed solvent is concentrated to approximately one-half of its original volume by distillation from the reaction vessel. The reaction mixture is cooled to 0° and subjected to a vacuum filtration through a 9-cm Büchner funnel to afford 22.0 g of a tan precipitate. This solid is placed in 200 mL of toluene, which is then brought to a boil; the mixture is subjected to a hot vacuum-filtration in order to remove the lithium fluoride co-product. A considerable reduction in yield may result unless a steam-jacketed Büchner funnel or hot sintered-glass filter is used. Upon cooling, the toluene filtrate deposits white crystals, which are collected by filtration. Yield: 13.7 g (83%) of tris(*N*-methylanilino)borane, mp 211–213° (lit. mp 210°;[1] 214–216°[3]).§

The above procedure has also been applied to the preparation of the symmetrical tris(organoamino)boranes derived from the following amines (% yields): dimethylamine (92%), bp 145–151° (lit.[2] bp 146°); diethylamine (92%), bp 100°/15 torr (lit.[2] bp 95°/11 torr); di-*n*-propylamine (94%), bp 85–88°/0.05 torr (lit.[9] bp 101°/0.15 torr); di-*n*-butylamine (61%), bp 130–135°/0.10 torr (lit.[9] bp 139°/0.20 torr); pyrrolidine (89%), bp 120–123°/1.0 torr (lit.[1] bp 164°/13 torr); piperidine (89%), bp 168–178°/10 torr (lit.[6] bp 142–149°/1.0 torr), mp 68–70 (lit.[3] mp 70.5°); *N*-ethylaniline (84%), mp 164–165° (lit.[2] mp 164–165°); diphenylamine (83%), mp 245–247° (lit.[10] mp 247–248°); *N*-phenylbenzylamine (71%), mp 199–201° (lit.[11] mp 200–201°); dibenzylamine (75%), mp 271–273° (lit.[5] mp 266–268°); 1,2,3,4-tetrahydrocarbazole (70%), mp 335–337° (lit.[2] mp 338°).

It should be noted that not all of the solid tris(organoamino)boranes are as stable to hydrolysis as is tris(*N*-methylanilino)borane; thus, application

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* Nitrogen, argon, or helium may be used.

† Purchased from Apache Chemicals, P.O. Box 126, Seward, IL 61077.

‡ Purchased from Eastman Kodak Company, Rochester, NY 14650.

§ The checkers obtained a yield of 32% and a melting point of 216–217°.

of this procedure to other solid tris(organoamino)boranes may have to involve vacuum filtrations with a minimum exposure to moisture. Those tris(organoamino)boranes which are distillable liquids need not be filtered and may be purified by distillation from the lithium fluoride by-product.

Properties

Tris(*N*-methylanilino)borane is a white, crystalline material having very little odor, mp 211–213°. It is relatively stable to hydrolysis by atmospheric moisture. It is not appreciably soluble in most common, nonprotonic, anhydrous, organic solvents at room temperature. Important bands in the infrared spectrum (Nujol mull) include:[12] 1598, 762, and 693 cm^{-1} (aromatic ring vibrations); 1354 cm^{-1} [$\nu(^{11}B—N)$]; 1285 cm^{-1} [aromatic $\nu(C—N)$]; 1109 cm^{-1} [alkyl $\nu(C—N)$].

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44. 1,3-DIAZA-2-BORACYCLOALKANES

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Checked by NORMAN E. MILLER†

1,3-Diaza-2-boracycloalkanes have been prepared by the condensation of bis(dimethylamino)borane, $HB[N(CH_3)_2]_2$, with α,ω-diamines[1] or by the reaction of the latter with diborane(6).[2] The borane was freshly generated *in*

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situ either from the reaction of iodine with sodium tetrahydroborate or from trimethylamine-borane, $(CH_3)_3NBH_3$. The second method appears to be the most convenient laboratory procedure since it can be performed in the absence of solvents and all by-products are highly volatile.

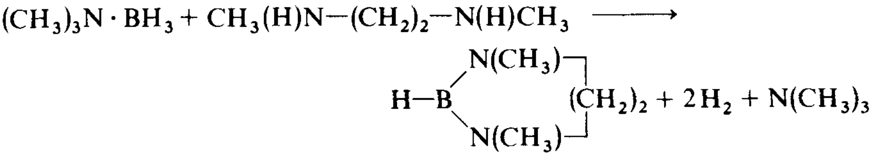
Since the successful dehydrogenation of the organic ring moiety has been described recently,[3,4] the five-membered heterocycle may deserve particular interest as potential precursor of a cyclic six π-electron donor ligand.

The method illustrated below can be used for the preparation of up to 100-g quantities of the desired product in one run. The total working time is ca. 6 hr, most of which (reflux period) does not require constant supervision.

■ **Caution.** *1,3-Diaza-2-boracycloalkanes are moisture-sensitive and react readily with protonic materials. Alcohols, in particular, may occasionally cause an explosive solvolysis reaction on contact with these heterocycles. The compounds should be handled under dry inert gas (nitrogen or argon) to avoid their contamination. The possible toxicity of boron compounds has not yet been explored.*

A. 1,3-DIMETHYL-1,3-DIAZA-2-BORACYCLOPENTANE

(1,3-Dimethyl-1,3,2-diazaborolane)



$$(CH_3)_3N\cdot BH_3 + CH_3(H)N{-}(CH_2)_2{-}N(H)CH_3 \longrightarrow H{-}B\begin{matrix}N(CH_3)\\ N(CH_3)\end{matrix}(CH_2)_2 + 2H_2 + N(CH_3)_3$$

Procedure

A 100-mL round-bottomed flask is equipped with a reflux condenser topped with a potassium hydroxide drying tube. The equipment is flame-dried while a stream of dry nitrogen passes through it, and the flask is then charged with 17.0 g (0.233 mol) of trimethylamine-borane* and 20.3 g (0.230 mol) of *N*,*N*′-dimethylethylenediamine† and a few boiling chips. The mixture is slowly warmed to achieve complete liquefaction of materials and is then heated at gentle reflux for 3 hr. The reaction flask is cooled to room

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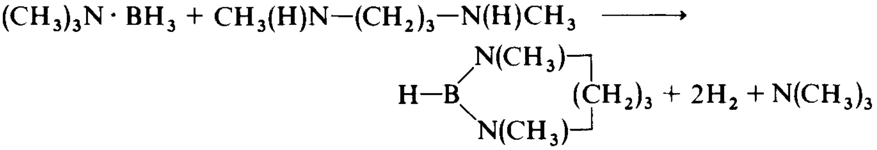
* Columbia Organic Chemicals Co., Inc., Columbia, South Carolina. The material was used as received.

† Ames Laboratories, Milford, Connecticut. The diamines were stored for a minimum of 3 days over potassium hydroxide pellets and were freshly distilled before use.

temperature and is then quickly connected to a flame-dried, one-plate distillation apparatus which is protected against atmospheric moisture with a potassium hydroxide tube. Distillation under atmospheric pressure yields ca. 18–19 g of product, bp 94–95°/734 torr; typical yields by this method are 80–95%. *Anal.* Calcd. for $C_4H_{11}N_2B$: C, 49.05; H, 11.32; N, 28.60; B, 11.04. Found: C, 48.9; H, 11.1; N, 28.5; B, 11.0.

B. 1,3-DIMETHYL-1,3-DIAZA-2-BORACYCLOHEXANE

(1,3-Dimethyl-1,3,2-diazaborinane)



$$(CH_3)_3N \cdot BH_3 + CH_3(H)N{-}(CH_2)_3{-}N(H)CH_3 \longrightarrow$$

Procedure

Using the same equipment as described in Procedure A and working in an analogous fashion, 20.0 g (0.274 mol) of trimethylamine-borane* and 28.1 g (0.280 mol) of *N,N′*-dimethyl-1,3-propanediamine† are permitted to reflux for 5 hr. Work-up of the reaction mixture as described above yields about 24 g of product, bp 129–130°/738 torr; typical yields range from 80 to 90%. *Anal.* Calcd. for $C_5H_{13}N_2B$: C, 53.63; H, 11.70; N, 25.02; B, 9.65. Found: C, 53.5; H, 11.6; N, 25.0; B, 9.6.

Properties

Both 1,3-dimethyl-1,3,2-diazaborolane and the corresponding borinane are mobile liquids which slowly hydrolyze on exposure to atmospheric moisture. The compounds are characterized by medium to strong B—H stretching modes in the 2500–2600 cm^{-1} region of their infrared spectra and intense B—N valence vibrations near 1500 cm^{-1}. They are miscible with common, aprotic, anhydrous, organic solvents and have been stored in sealed ampuls for several months without noticeable decomposition.

Infrared spectra were recorded on liquid films of the compounds using a Perkin-Elmer Model 621 instrument under standard operating conditions

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* Columbia Organic Chemicals Co., Inc., Columbia, South Carolina. The material was used as received.

† Ames Laboratories, Milford, Connecticut. The diamines were stored for a minimum of 3 days over potassium hydroxide pellets and were freshly distilled before use.

and CsI crystals. Frequencies in cm^{-1} are as follows. $(-CH_2-NCH_3-)_2BH$: 2970 (s), 2940 (s), 2860 (s), 2790 (s), 2750 (sh), 2690 (w-m), 2620 (w-m), 2595 (m-s), 2550 (s), 2520 (s), 2490 (sh), 1560 (sh), 1510 (s), 1475 (s), 1445 (s), 1410 (s), 1370 (m-s), 1340 (w-m), 1290 (s), 1245 (s), 1225 (s), 1200 (sh), 1170 (m-s), 1130 (sh), 1120 (m-s), 1085 (sh), 1065 (s), 1045 (sh), 1020 (s), 965 (w), 920 (w), 895 (w-m), 885 (m-s), 875 (m-s), 865 (s), 810 (m-s), 595 (m-s), 370 (m-s). $CH_2(-CH_2-NCH_3-)_2BH$: 2970 (s), 2940 (sh), 2920 (s), 2860 (s), 2820 (sh), 2780 (s), 2720 (w-m), 2650 (w-m), 2605 (sh), 2590 (w-m), 2550 (sh), 2490 (s), 2475 (sh), 2430 (sh), 2410 (sh), 1635 (w-m), 1595 (w-m), 1540 (sh), 1520 (s), 1485 (s), 1465 (sh), 1445 (s), 1423 (sh), 1408 (s), 1350 (sh), 1335 (s), 1320 (s), 1275 (s), 1238 (s), 1214 (s), 1135 (m-s), 1125 (sh), 1110 (w-m), 1100 (m-s), 1070 (s), 1060 (s), 1020 (w-m), 990 (w), 878 (m-s), 865 (s), 848 (w-m), 775 (w), 575 (w), 465 (w-m), 430 (w-m), 380 (m-s).

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45. GALLIUM TRICHLORIDE

$$2Ga + 3Cl_2 \xrightarrow{\Delta} 2GaCl_3$$

Submitted by ROGER A. KOVAR*
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Research in the organometallic and hydride chemistry of gallium is hampered by the absence of a convenient, reliable preparation of gallium trichloride, which is the common starting material in most preparations.

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† Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, NC 27412.

Existing methods for the preparation of gallium trichloride involve reactions of 1–2 g of gallium metal with either hydrogen chloride or chlorine at elevated temperatures.[1–3] These methods prove to be unsatisfactory in efforts to prepare gallium trichloride in larger quantities (1–2 mol) because of difficulties encountered in collecting the light, finely divided product and because of physical obstruction caused by deposition of the voluminous quantities of gallium trichloride in certain sections of the apparatus. Attempts to collect the finely divided product quantitatively, including cooling a section of the apparatus with liquid nitrogen, passing the reactant gas containing particles of the finely-divided product through diethyl ether or benzene, or allowing the product to settle in a closed section of the tube have been unsuccessful. In all of these cases a significant quantity of product is lost through the bubbler incorporated into the system to prevent buildup of internal pressure.[4]

The following preparation of gallium trichloride is applicable to both large- and small-scale reactions.[4] Gallium trichloride is produced quantitatively and in high purity. Directions for the manipulation of this air-sensitive compound on the bench top or in a dry box are included.

Procedure

■ **Caution.** *This procedure makes use of gaseous chlorine, a powerful irritant, and all operations should be conducted in a well-ventilated fume hood.*

Commercial gallium metal (99.9%)* is used without further purification. Chlorine† is dried by passing the gas through a 12-in. P_4O_{10} column. The generator for the preparation of gallium trichloride is constructed from two 50-mm-i.d. O-ring joints‡ (see Fig. 22). The generator bottom is constructed by sealing a test tube end to one of the O-ring-joint tubes approximately 20 cm from the joint end. The other O-ring joint is joined to a 40-cm length of 2.5-cm-i.d. glass tubing. The opposite end of this tube is joined to an outer 24-40 S.T. joint.§ A 4-mm Teflon stopcock,§ which serves as an outlet for excess gas, is attached to the 2.5-cm-i.d. tube near the end containing the 24-40 female S.T. joint. A gas-delivery tube is constructed from a full-length 24-40 male S.T. joint with reduced-diameter lower and upper tubes.‡ A 4-mm Teflon stopcock§ is joined to the upper

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* Alcoa Company, 1501 Alcoa Building, Pittsburgh, PA 15219.

† Matheson Gas Products, 932 Paterson Plank Road, E. Rutherford, NJ 07073.

‡ Kontes Glass Company, Spruce Street, Vineland, NJ 08360.

§ Both gallium trichloride and chlorine attack silicone stopcock grease. It is important that all stopcocks and joints be of the grease-free, Teflon variety or if this is not possible that Kel-F grease be employed.

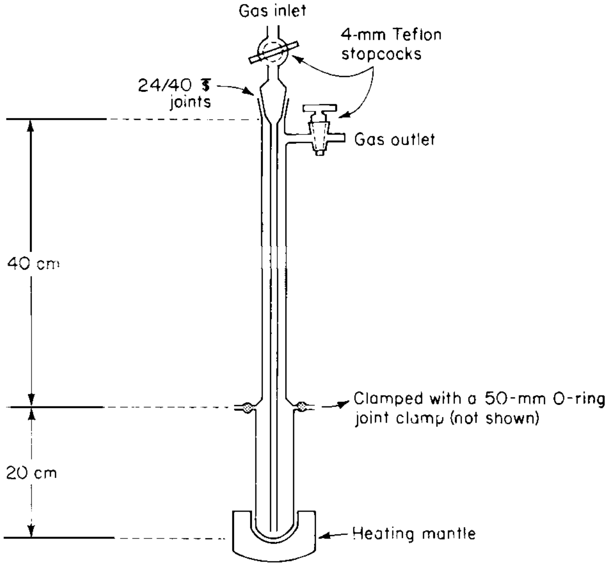

Fig. 22. Gallium trichloride generator.

tube. The lower tube is constricted and joined to a 2–4 mm-i.d. tube of sufficient length to extend to within 20 mm of the bottom of the generator when fully assembled (Fig. 22). The gas inlet tube is connected by means of Tygon tubing directly to the chlorine source through a three-way, 4-mm Teflon stopcock. The three-way stopcock is also connected to a vacuum system through which nitrogen can also be admitted.[5] The gas outlet tube is connected to a mercury-filled bubbler, the vertical length of which is sufficient to accommodate the mercury when the apparatus is under full vacuum. It is important that the bubbler be filled with a liquid of high density (such as mercury) to prevent pulling air into the reactor through the bubbler when the reaction is in progress. Reaction of chlorine and gallium is rapid, and the apparatus will have an internal pressure somewhat lower than atmospheric. There will be a slight reaction of chlorine with the mercury, however, and, if desired, Fluorolube can be used in place of mercury. The rate of chlorine introduction becomes an important factor if Fluorolube is used.

The desired quantity (1–100 g) of liquid gallium is poured into the apparatus through the 50-mm O-ring joint. The apparatus is reassembled* and

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* Gallium trichloride will attack Buna-N O-rings, thus causing discoloration and contamination of the product. Viton O-rings are not attacked and are highly recommended for this preparation.

flushed with dry nitrogen until the air is displaced. The apparatus is wrapped with heating tape from the gas-outlet connection to just below the 50-mm O-ring joint. The bottom of the generator is fitted with a 100-mL heating mantle. Current to each of these heat sources is controlled independently by means of variable voltage devices. Approximate temperatures of 100° at both upper and lower sections of the apparatus are achieved with voltages of approximately 35–40 V. After the gallium metal has melted, the flow of nitrogen is stopped, and chlorine is introduced at a moderate rate. Introduction of considerable quantities of chlorine before the gallium melts results in a rapid reaction that is difficult to control when melting occurs. Gas will escape through the outlet until chlorine has displaced much of the nitrogen. Reaction is observed when chlorine comes in contact with the gallium. The heating mantle serves to keep the product molten while the heating tape serves to melt and return to the bottom of the generator much of the product which is formed as a finely divided, white powder. At early stages in the reaction the reactor contains unreacted gallium and liquid product as two layers. The system will be under negative internal pressure even when the chlorine is being introduced because of the rapid reaction of the chlorine with the two-layer system. As the reaction proceeds the product layer increases in volume relative to the gallium layer. In the final stages of the reaction the gallium layer will be absent. The liquid product that remains may continue to react with the chlorine and thus increase substantially in volume. This is presumably due to the presence of relatively large quantities of liquid gallium(I) tetrachlorogallate(III)[4] which is further oxidized by chlorine to gallium trichloride. The reaction is judged to be complete when the liquid product turns light-yellow in color and when chlorine is observed to escape through the bubbler.

The gas inlet tube is withdrawn from the generator while a nitrogen purge is maintained through the tube, and the upper 24-40 joint is then stoppered. The heating tape and mantle are removed, and the product is allowed to solidify. The generator is evacuated in order to remove excess chlorine after the solid has cooled to room temperature. The bottom of the generator containing the gallium trichloride can be connected to a water-cooled finger sublimator* on the bench top under nitrogen purge. Up to 50-g quantities of gallium trichloride can be sublimed under vacuum over a period of 1 hr at 60° with this apparatus. The sublimator is transferred to a nitrogen-filled dry

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* The generator is designed to fit a vacuum sublimator which contains 50-mm-i.d. O-ring joints (no. 855600) which are available from Kontes Glass Company, Spruce Street, Vineland, NJ 08360.

box, and the product is removed from the cold finger for storage and subsequent use. Using this procedure, 47.5 g of gallium trichloride was produced by the reaction of 20.0 g (94% yield)* of gallium during 4 hr. The product melted sharply at 78–79° (lit.,[1] 77.9°).

Analysis was performed by hydrolyzing a sample and then using edta (ethylenediaminetetraacetic acid) analysis for gallium[6] and a Volhard procedure for chlorine. *Anal.* Calcd. for $GaCl_3$: Ga, 39.6; Cl, 60.40. Found: Ga, 39.3; Cl, 60.4.

Alternatively, by means of Schlenk techniques, liquid gallium trichloride can be poured under nitrogen purge into tared round-bottomed flasks directly from the reactor. These flasks can be stoppered and stored for subsequent use. In one experiment, 0.25 mol of gallium trichloride was transferred into a 1-L round-bottomed flask under nitrogen purge. Approximately 500 mL of dry benzene was distilled into the flask; this readily dissolved the gallium trichloride. Aliquot samples were removed with a syringe for hydrolysis and subsequent analysis for gallium and chlorine. The following results were obtained by analysis of the freshly prepared solution: Ga, 0.555*M*; chlorine, 1.63*M*; atomic ratio, Cl/Ga = 2.93 : 1.00. Re-analysis, after the solution was allowed to stand at room temperature for 60 days, gave essentially the same results. Diethyl ether can be used in place of benzene as the solvent for gallium trichloride. The procedure is the same as that described when benzene is used except that the distillation flask containing the gallium trichloride should be cooled because of the relatively high heat of solution of gallium trichloride in diethyl ether.

Properties

Gallium trichloride is a solid (mp 78–79°) which reacts with air. It is soluble in both hydrocarbons and ether-type solvents. Both the solid compound and its solutions can be stored in a waterfree environment for relatively long periods. Gallium trichloride undergoes typical metathetical displacement of one, two, or all three chlorine atoms in reactions with one, two, or three molar equivalents of an alkyllithium compound, respectively:[4]

$$GaCl_3 + n\text{RLi} \xrightarrow{\text{benzene}} \text{R}_n\text{GaCl}_{3-n} + \text{LiCl}$$

$$(\text{where } n = 1\text{–}3 \text{ and R} = n\text{-Bu})$$

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* A yield of 83% of $GaCl_3$ (mp 78°) was obtained by the checkers when 15 g of gallium was used.

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46. CYCLOPENTADIENYLSILANE AND (METHYLCYCLOPENTADIENYL)SILANE

Submitted by A. P. HAGEN* and P. J. RUSSO*
Checked by P. C. ANGUS† and S. R. STOBART‡

Silyl cyclopentadienes[1,2,3] have been formed through the interaction of a cyclopentadienide prepared *in situ* with an appropriate silicon halide; however, purification of the desired product required filtration, removal of solvent, and vacuum distillation at elevated temperatures. The synthesis of the silicon compounds, $C_5H_5(SiH_3)$ and $C_5H_4(CH_3)(SiH_3)$, described here utilizes a low-temperature reaction between liquid bromosilane and the salt $K[RC_5H_4]$ (where $R = H, CH_3$), in a 1 : 2 mole ratio, respectively.[4,5]

A. CYCLOPENTADIENYLSILANE

$$K + C_5H_6 \longrightarrow K[C_5H_5] + \tfrac{1}{2}H_2$$
$$SiH_3Br + K[C_5H_5] \longrightarrow C_5H_5(SiH_3) + KBr$$

Procedure

■ **Caution.** *Potassium is a dangerous metal from which water and air must be excluded. All manipulations of this substance must be carried out in a dry, oxygen-free, nitrogen-purged glove bag. Unreacted potassium may be destroyed by treating it with* n*-butanol. Bromosilane is potentially hazardous because it is spontaneously flammable in air. All manipulation of this compound should be carried out in a vacuum system. Known weights of bromosilane may*

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be safely and conveniently obtained by measuring the pressure of the gas when it is contained in a known volume at a given temperature.

In a nitrogen-purged glove bag, freshly cleaned potassium (0.50 g, 13 mmol), which has been cut into small pieces no larger than 2 mm on a side, is transferred into a 100-mL long-necked flask fitted with a ground-glass joint containing a Teflon-coated magnetic stirring bar. It is then fitted with a greased vacuum-stopcock adapter containing a loose plug of glass wool in the neck portion of the ground-glass connecting joint. The flask is evacuated on a vacuum system, then it is cooled to −196°, and approximately 25 mL of anhydrous diethyl ether (refluxed 2 days over lithium tetrahydridoaluminate(1−) and then vacuum-distilled) is condensed into the flask. Freshly prepared 1,3-cyclopentadiene* (1.00 g, 15.0 mmol) is then added. With the stopcock of the adapter open to a manometer, the cold (−196°) bath is removed and replaced by a Dewar flask filled with crushed Dry Ice–acetone mixture (−78°). Rapid gas evolution commences as soon as the ether melts, and mixing with the magnetic stirring bar allows the 1,3-cyclopentadiene to contact the pieces of potassium. The reaction is essentially complete after 6 hr, when white $K[C_5H_5]$ has precipitated from the low-temperature solution. To ensure complete reaction, the −78° bath is removed temporarily, allowing the contents of the flask to warm slowly to 0°. In the meanwhile the solution is stirred vigorously to circulate the white solid and any unreacted pieces of potassium. If the solution develops a light-pink tinge as more $K[C_5H_5]$ dissolves near 0°, the flask is cooled slowly to −78° and then warmed again to 0°. This process should be repeated until all the potassium has reacted. The solution next is cooled slowly to −78°; then it is frozen at −196° and the noncondensable gas (hydrogen) is pumped away slowly through a trap. The manometer serves as a gage to estimate the rate of evacuation. The frozen solution is warmed to −78°, thereby releasing more dissolved noncondensable gas which is removed after freezing the solution. Degassing three times in this manner removes the noncondensable gas from the solution. The −78° bath is removed and replaced by a cold (−34°) slush bath (*o*-chlorotoluene). The stopcock of the adapter is opened so that excess 1,3-cyclopentadiene and solvent distill slowly (6 hr) from the flask into a trap held at −196°. Removal of any remaining volatile material is accomplished by surrounding the flask with an ice bath which is allowed to melt and reach room temperature. (■ **Caution.** *The following operations should be conducted behind a safety shield, and protective gloves should be worn.*) The white solid is then heated to 60° for 2 hr with pumping.

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* See Synthesis 30 for the conversion of cyclopentadiene dimer to 1,3-cyclopentadiene.

The flask is tapped gently in order to free the magnetic stirring bar, and the white solid is converted to a fine, air-sensitive and pyrophoric powder by *careful* yet vigorous agitation of the flask. The flask is heated to 60° for 4–6 hr with constant pumping, after which time the salt is considered to be dry.

Bromosilane[6] (0.71 g, 6.4 mmol) is condensed into the flask containing the white $K[C_5H_5]$ at $-196°$. The contents of the flask are then warmed to $-78°$. As soon as the bromosilane melts, it contacts the white solid to form a yellow-brown solid. After 30 min, unreacted bromosilane is distilled from the flask and condensed into a trap held at $-196°$ with occasional pumping. After 1 hr the volatile material which has collected in the $-196°$ trap is transferred to a take-off tube labeled "used SiH_3Br" and stored at $-196°$. The contents of the flask are warmed to $-34°$ and the volatile material which distills slowly from the flask is collected in a $-196°$ trap. The $-34°$ bath is removed after 2 hr and the flask is allowed to warm to room temperature.

The crude product which collects in the $-196°$ trap is purified as follows: The volatile material in the $-196°$ trap is allowed to warm slowly to room temperature as it distills through a cold-temperature ($-63°$) slush bath (chloroform) into a $-196°$ trap, the distillation being repeated six times on the $-63°$ fraction. Pure product collects in the $-63°$ trap. If the "used SiH_3Br" is condensed onto the partly reacted $K[C_5H_5]$ remaining after these operations, and a similar purification process is employed, 0.60 g (6.2 mmol; 95% yield) of product is obtained. *Anal.* Calcd. for C_5H_8Si: C, 62.42; H, 8.38; Si, 29.19. Found: C, 62.70; H, 8.62; Si, 28.81.

Properties

Cyclopentadienylsilane is an odorous, colorless liquid (mp $-94°$; bp 60°; $n_D^{25°}$ 1.4750; d. (25°) 0.8211 g/cc)[5] which does not react with air or water. The infrared spectrum (gas-phase, 15 torr) shows characteristic bands at 3100 (w), 2920 (vw), 2160 (vs), 998 (m), 929 (vs), 921 (vs), 825 (w), 798 (w), 700 (s), 655 (w), 646 (w), 560 (w) cm^{-1}. The ^1H nmr spectrum (neat liquid) displays the following resonances: $\tau 6.50$ (SiH_3, singlet); $\tau 3.70$ (vinylic, broad).

B. (METHYLCYCLOPENTADIENYL)SILANE

$$K + C_5H_5CH_3 \longrightarrow K[C_5H_4(CH_3)] + \tfrac{1}{2}H_2$$

$$SiH_3Br + K[C_5H_4(CH_3)] \longrightarrow C_5H_4(CH_3)(SiH_3) + KBr$$

Procedure

■ **Caution.** *See cautionary note for Procedure A.*

The procedure for preparing the dry salt, $K[C_5H_4(CH_3)]$, is identical with that previously described in Sec. A for $K[C_5H_5]$, except that methylcyclopentadiene (1.210 g, 15.1 mmol) is used in place of the 1,3-cyclopentadiene. Methylcyclopentadiene (isomer mixture) is obtained from the thermal cracking at 200° of commercially available methylcyclopentadiene dimer.[4] The fraction distilling between 73 and 75° is collected at 0°. The distillate is then redistilled under nitrogen at atmospheric pressure, collected at 0°, and stored at $-78°$ *in vacuo* after degassing.

Bromosilane (0.71 g, 6.4 mmol) is condensed into the flask containing the dry $K[C_5H_4(CH_3)]$ at $-196°$ and is allowed to react for 30–60 min at $-78°$. Unreacted bromosilane is then distilled from the flask at $-78°$ with occasional pumping. The crude product is separated from the solid in the flask and is collected in a $-196°$ trap by warming the flask to $-34°$. Pure product (0.66 g, 6.0 mmol) is obtained in better than 95% yield if the "used SiH_3Br" is condensed back and forth into the reaction flask several times. Purification of the crude product is carried out by repeated distillation of the volatile material according to the method described in Procedure A. *Anal.* Calcd. for $C_6H_{10}Si$: C, 65.38; H, 9.14; Si, 25.28. Found: C, 65.17; H, 9.17; Si, 25.28.

Properties

(Methylcyclopentadienyl)silane is an odorous, colorless liquid (mp $-146°$; bp 109°; $n_D^{25°}$ 1.4744; d. (25°) 0.8319 g/cc)[5] which forms a clear glass at $-146°$ *in vacuo*. It does not react with air or water. The infrared spectrum (gas-phase 5 torr) exhibits characteristic bands at 3100 (w), 2990 (w), 2940 (w), 2150 (vs), 990 (m), 930 (vs), 920 (vs), 691 (m), 650 (w) cm^{-1}. The ^1H nmr spectrum (neat liquid) has the following resonances: τ7.99 (methyl, singlet); τ6.51 (silyl, singlet); τ3.73 (vinylic, broad).

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47. CYCLOPENTADIENYLGERMANE

$$GeH_3Br + K[C_5H_5] \longrightarrow C_5H_5(GeH_3) + KBr$$

Submitted by PHILIP C. ANGUS* and STEPHEN R. STOBART*
Checked by E. A. V. EBSWORTH† and S. G. HENDERSON†

Cyclopentadienylgermane provides an example of a simple monoorganogermane whose variable-temperature ^1H nmr spectrum shows it to be a fluxional molecule.[1] Its synthesis from bromogermane, described below, parallels that of the silyl analog detailed in Synthesis 46. (■ **Caution.** *Potassium is a dangerous metal from which air and water must be excluded. All manipulations of this substance must be carried out in a dry, oxygen-free, nitrogen-purged glove bag. Unreacted potassium may be destroyed by treating it with* n-*butanol.*)

Procedure

The entire synthesis is conducted in a conventional high-vacuum manifold suitable for the manipulation and trap-to-trap fractionation of volatile compounds.[2]

Potassium metal (0.39 g, 10.0 mmol), cut into small pieces (cubes having ca. 2-mm edges‡) under paraffin oil, is washed with dry petroleum ether and is weighed in a glove bag filled with nitrogen. It is transferred to a dry, 250-mL, round-bottomed flask which is connected to the vacuum system via a stopcock adapter and is then immediately evacuated. Addition of diethyl ether (50 mL) is achieved after cooling the flask to −196° by allowing it to distill directly from a degassed stock supply stored over lithium tetrahydridoaluminate(1−) in a reservoir attached to the vacuum manifold. Next, excess freshly prepared 1,3-cyclopentadiene monomer§ (1.00 g,

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‡ The checkers found it necessary to use smaller pieces of potassium in order for all of it to react in 4 hr.

§ Bp 42–44°, obtained from thermal cracking of cyclopentadiene dimer at ca. 150°, as described in Synthesis 30.

15 mmol) is distilled into the flask, which is cooled to −196°. By means of a Dry-Ice–acetone slush bath the temperature of the reaction flask is raised from −196 to −78°; reaction commences and is accompanied by hydrogen evolution. Complete reaction is indicated by disappearance of the potassium metal (ca. 4 hr), and is ensured by briefly (5 min) raising the reaction temperature to 15° after first cooling to −196° and pumping away the hydrogen gas produced. The product dissolves in the diethyl ether at room temperature; it is reprecipitated by cooling again to −25° (*o*-xylene slush). At this temperature volatile material is slowly (3 hr) removed from the reaction flask; prolonged pumping (24 hr) continues at room temperature and leaves behind potassium cyclopentadienide as a dry, snowy-white powder. (■ **Caution.** *This powder is very air-sensitive and is pyrophoric.*)

Bromogermane (0.74 g, 4.7 mmol), synthesized by direct bromination of monogermane at low temperature as described elsewhere,[3] is condensed onto the dry potassium cyclopentadienide by freezing the reaction vessel to −196°. The flask is then warmed to room temperature during ca. 30 min. This is accomplished by first surrounding it with chlorobenzene slush (−46°), which is then replaced by an empty Dewar vessel. Volatile products are fractionated by slow pumping through two traps maintained at −63° (chloroform slush) into a trap held at −196° during 2 hr. A dry, yellow residue remains in the reaction vessel. (■ **Caution.** *This material may be pyrophoric. After the container has been restored to atmospheric pressure by admitting nitrogen gas the yellow residue should be destroyed by very cautious treatment with water.*) The trap held at −196° condenses traces of germane and 1,3-cyclopentadiene. The fraction collected in the two traps maintained at −63° is slightly impure product; repeated condensation at the same temperature affords spectroscopically pure cyclopentadienylgermane (0.541 g, 3.6 mmol, 76% yield based on bromogermane consumed).

Properties

Cyclopentadienylgermane is a colorless liquid, v.p.[1] 10.8 torr/0.1°, 31.8 torr/20.4°. The ^1H nmr spectrum, measured at 35° in chloroform-*d* solution, consists of a broad, low-field singlet at $\tau 3.97$ due to the ring-proton resonance and a sharp signal at $\tau 6.25$ arising from the germyl protons. Its infrared spectrum contains characteristic absorptions due to vibrations of the GeH_3 group as follows (cm^{-1}): 2120 (s, sh); 2099 (vs); 2088 (vs); 830, 823, 815 (RQP) (vs); and 520 (m).

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48. CYCLOPENTADIENYLTRIMETHYLSTANNANE

$$(n\text{-}C_4H_9)Li + C_5H_6 \longrightarrow (C_5H_5)Li + n\text{-}C_4H_{10}$$

$$(C_5H_5)Li + (CH_3)_3SnCl \longrightarrow (CH_3)_3Sn(C_5H_5) + LiCl$$

Submitted by MARGARET A. LYLE* and STEPHEN R. STOBART*
Checked by A. P. HAGEN†

Cyclopentadienyltrimethylstannane belongs to the class of 1,3-cyclopentadiene derivatives, known for both transition and nontransition elements, in which there is sigma bonding between the ring and the metal atom. It is of significance not only as a typical example of a fluxional (stereochemically nonrigid) molecule[1] but also in possessing a reactive tin to ring-carbon linkage[2] which renders it a moderately versatile source of the trimethylstannyl group in synthesis.

■ **Caution.** *Because of its toxicity and volatility, care should be taken to avoid inhalation of trimetyltin chloride (chlorotrimethylstannane) or contact of its solutions with the skin. Cyclopentadienyltrimethylstannane has a pungent odor and may be assumed to possess toxic properties similar to those of trimethyltin chloride.*

Procedure

In all of the following operations and in particular in the handling of the product, which is very sensitive to air or moisture, an atmosphere of dry nitrogen gas must be maintained. All glassware is dried in an oven at 110° and is allowed to cool while being flushed with nitrogen. In addition, it is useful to avoid contamination with stopcock grease by sealing ground-glass

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joints with Teflon collars wherever they will come into contact with refluxing solvent.

The solvent required for the reaction is diethyl ether. This is first dried over sodium and redistilled; then it is cautiously treated with lithium tetrahydridoaluminate(1 −) in a distillation apparatus to remove residual traces of water.

■ **Caution.** *Care should be taken in drying the diethyl ether with lithium tetrahydridoaluminate*(1 −) *because of the danger of fire if the ether is very wet.* See also Synthesis 1 for additional information.

The reaction vessel consists of a 250-mL, two-necked, round-bottomed flask containing a large Teflon-covered stirring bar that enables the reactants to be agitated magnetically. The vertical neck of the flask is equipped with a reflux condenser; a gas inlet at the top of the condenser allows admission of a slight positive pressure of nitrogen. The side-arm neck is fitted with a receiver adapter connected to the distillation apparatus containing the diethyl ether. This enables approximately 75 mL of solvent to be distilled directly off the lithium tetrahydridoaluminate(1 −) into the reaction vessel, after which the receiver adapter is disconnected and replaced by a rubber serum cap. The reaction flask is then immersed in an ice-water bath.

Metallation of 1,3-cyclopentadiene is achieved by reacting it with a commercially available* solution of *n*-butyllithium in hexane. With a 20-mL syringe which has been thoroughly flushed with nitrogen gas, 21.7 mL of a 2.3*M* hexane solution† of *n*-butyllithium (0.05 mol) is added to the diethyl ether in the reaction vessel *via* the rubber seal.

A further 20 mL of dry diethyl ether is distilled into a single-necked 100-mL flask which is then cooled to 0° and sealed with a serum cap. A syringe is used to add 4.2 mL (0.05 mol) of freshly prepared 1,3-cyclopentadiene‡ (bp 40.8°/772 torr) through the serum cap. The ether solution of 1,3-cyclopentadiene thus prepared is added slowly over a period of 1 hr to the butyllithium solution, by means of a syringe through the side-arm serum cap on the reaction vessel. Throughout the addition the temperature of the

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* Available from Ventron Corporation, Alfa Products, Beverly, MA 01915.

† The molarity of the butyllithium solution may be checked before use by the procedure devised by Gilman.[3] This involves careful hydrolysis of a measured sample using excess distilled water, followed by titration against standard hydrochloric acid solution with phenolphthalein as indicator. Since the butyllithium solution may contain some lithium hydroxide, it is necessary to carry out an identical titration of a sample which has undergone complete reaction with benzyl chloride in order to determine the lithium hydroxide present. From the difference between the two titrations, the molarity of the butyllithium may be calculated.

‡ The procedure used for the formation of 1,3-cyclopentadiene from cyclopentadiene dimer is given in Synthesis 30.

reaction is maintained at 0° by means of the ice bath and the solution is stirred continuously. A heavy, chalk-white precipitate* of lithium cyclopentadienide is formed and may render the stirring operation difficult, in which event more freshly distilled diethyl ether should be added through a syringe.

A solution of 9.66 g (0.05 mol) of trimethyltin chloride† is prepared in 20 mL of dry diethyl ether. The solution is cooled to 0° and is slowly injected through the serum cap into the lithium cyclopentadienide solution. This operation is carried out over a period of 1 hr with continuous stirring, during which time the white precipitate gradually becomes buff-colored. When all of the trimethyltin chloride solution has been added, the flask is allowed to reach room temperature and the reaction mixture is finally gently refluxed for 6 hr.

In order to isolate the product, a gas inlet is connected to the side-arm neck of the reaction vessel, and, against a countercurrent of nitrogen, the reflux condenser is exchanged for an assembly suitable for distillation at reduced pressure. The assembly consists of a still-head, a thermometer, a condenser, and a receiver flask with a vacuum outlet. The apparatus is evacuated via a rotary oil-filled pump, and diethyl ether and hexane are removed at room temperature by pumping through a distillation trap cooled to liquid nitrogen temperature. On distilling the residual cloudy yellow liquid, 8.9 g (0.04 mol, 80% yield) of clear, pale-yellow cyclopentadienyl(trimethyl)stannane, bp 35°/0.1 torr, is collected.‡ *Anal.* Calcd. for $C_8H_{14}Sn$: C, 41.98; H, 6.16. Found: C, 41.69; H, 5.91.

Properties

Cyclopentadienyltrimethylstannane is a pale-yellow liquid which is extremely air- and moisture-sensitive. Its ^1H nmr spectrum in chloroform-*d* solution at 35° consists of signals at $\tau 3.85$ and $\tau 9.84$ in a ratio of 5 : 9, attributable to ring and methyl protons, respectively. Spin-coupling between proton and tin nuclei gives rise to characteristic satellite signals around both resonances, with $J(^{117}Sn, {}^{119}Sn{-}H_{ring})_{av.} = 23.0$ Hz (^{117}Sn, ^{119}Sn com-

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* Darkening of the reaction mixture to brown or black at this stage is indicative of contamination by oxygen or moisture; in this event it is probably best to discontinue the synthesis and to repeat the foregoing procedure.

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‡ Manipulation and/or further purification of the product may be achieved using high-vacuum system techniques[4] with condensation in a trap maintained at 0°, but such handling at a laboratory temperature of 20° is tediously slow even at pressures lower than 5×10^{-4} torr.

ponents not resolved) and $J(^{117}Sn—H_{CH_3}) = 53.0$ Hz, $J(^{119}Sn—H_{CH_3}) = 55.0$ Hz. Reactions of $(CH_3)_3Sn(C_5H_5)$ to give tin-to-transition metal bonded complexes have been described.[2]

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49. BIS(TRIMETHYLTIN) OXIDE

(Hexamethyldistannoxane)

$$2(CH_3)_3SnOH + CaH_2 \longrightarrow [(CH_3)_3Sn]_2O + CaO + H_2$$

Submitted by D. A. ARMITAGE,* R. N. ROBINSON,† and E. W. ABEL†
Checked by M. E. BISHOP,‡ C. D. SCHAEFFER, JR.,‡ T. W. THEYSON,‡
and J. J. ZUCKERMAN‡

The stability of trialkyltin hydroxides (trialkylhydroxystannanes) (R_3SnOH) relative to the oxide in the presence of water appears to be largely dependent on the substituent.[1] Tri-*n*-butyltin hydroxide dehydrates very readily, while the ethyl homolog must be dehydrated under reduced pressure.[2] With $R = CH_3$, however, the hydroxide is readily formed from the oxide and water, and the preparation of bis(trimethyltin) oxide relies on dehydration of the hydroxide. However, the use of sodium in boiling benzene as a dehydrating agent does not always give reproducible results.[3] The method described here uses calcium hydride§ and gives reproducible results with yields greater than 70%, using commercially available trimethyltin hydroxide.§

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§ Calcium hydride may be purchased from B.D.H. Chemicals Ltd., Poole, Dorset BH12 4NN, England. Trimethyltin hydroxide may be purchased from either Orgmet, Inc., Main Street, Hampstead, NH 03841, or Digby Chemical Service, 103 Ebury Street, London SW1W 9QU, England.

The difficulty of synthesizing $[(CH_3)_3Sn]_2O$ has precluded a wide study of its chemical properties, but its reactions with protic compounds and multiple bonds should be similar to those involving $[(n\text{-}C_4H_9)_3Sn]_2O$.[4]

The more unusual chemical properties of this compound include the formation of a crystalline oxonium adduct with trimethyltin halides,[5] as would be expected from its strong donating power,[6] namely:

$$[(CH_3)_3Sn]_2O + (CH_3)_3SnX \longrightarrow [(CH_3)_3Sn]_3O^+X^-$$

With NSF_3, a tin-nitrogen product results which eliminates $(CH_3)_3SnF$ on heating, giving sulfanuryl fluoride.[7]

$$[(CH_3)_3Sn]_2O + NSF_3 \longrightarrow (CH_3)_3SnN{=}S(O)F_2 \longrightarrow N_3S_3O_3F_3$$

Procedure

■ **Caution.** *Since trialkyltin compounds are generally toxic, it is advisable to perform the synthesis in a well-ventilated fume hood.*

Dry benzene* (30 mL) is placed in a 100-mL two-necked flask containing a magnetic stirring bar. A T-piece, through which a stream of dry nitrogen is passed, is attached via a condenser to one neck of the flask and the apparatus is flushed thoroughly with nitrogen. This allows the reaction to be carried out in an inert atmosphere, free of oxygen and carbon dioxide. This is especially important since carbon dioxide reacts readily with compounds containing Sn—O bonds. Trimethyltin hydroxide (13.6 g, 75.2 mmol) is added through the other neck of the flask; then excess powdered calcium dihydride† (8.0 g, 190 mmol) was added. (■ **Caution.** *Care should be taken to keep calcium dihydride away from water, with which it reacts vigorously.) The* calcium dihydride is added slowly to avoid excessive frothing and blocking of the neck of the flask.

The mixture is stirred for 24 hr; then it is filtered under nitrogen and the solvent is removed by distillation at 40° and 20 torr. Vacuum distillation of the residual liquid at 3 torr yields bis(trimethyltin) oxide (yield 8.6 g, 70%). *Anal.* Calcd. for $C_6H_{18}Sn_2O$: C, 20.93; H, 5.23. Found: C, 21.00; H, 5.22.

The calcium dihydride residue can be destroyed by carefully adding it, a spatula-full at a time, to a beaker of water. Methyltin compounds have an unpleasant, persistent smell, hence apparatus should be washed in a fume hood with organic solvents, and the residues should be transferred to a residue bottle and destroyed.

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* The benzene was dried by refluxing over sodium wire under a calcium chloride drying tube.

† Calcium dihydride is normally obtained in small lumps. These can be ground to a powder easily and should be used immediately.

Properties

Bis(trimethyltin) oxide is a hygroscopic colorless liquid, bp 48°/3 torr, n_D^{21} 1.4892 and $d_4{}^{20}$ 1.59. The ^{1}H nmr spectrum shows a singlet methyl resonance at $\tau 9.78$[8] with $J_{^{117}\text{SnCH}} = 53.6$ and $J_{^{119}\text{SnCH}} = 56.1$ Hz (± 0.2 Hz). Characteristic peaks occur in the infrared spectrum at 1187 cm^{-1}, 740 cm^{-1} (shoulder at 770 cm^{-1}) [ν_{as}(SnOSn)], 530 and 510 cm^{-1} [ν_{as} and ν_s(SnC)], and 415 cm^{-1} [ν_s(SnOSn)].[9]

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50. METHYLDIPHENYLPHOSPHINE OXIDE AND DIMETHYLPHENYLPHOSPHINE OXIDE

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Checked by C. DAVID SCHMULBACH†

The tertiary phosphine oxides are most commonly prepared by simple oxidation of the parent phosphine with hydrogen peroxide,[1] alkylation of a trihalophosphine oxide,[2] or by oxidation of an appropriate phosphonium salt by moist silver(I) oxide.[3] The simplest and quickest method is the peroxide oxidation of the parent phosphine. Inasmuch as appropriate syntheses

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using that procedure have not been published in detail, the following syntheses were developed for the preparation of small amounts of unsymmetrical phosphine oxides. This method can be modified to prepare larger quantities of some symmetrical phosphine oxides. The only limitations of the procedure are that the parent phosphine should be slightly soluble in water and that the phosphine oxide must not form a stable hydrate which would make product isolation difficult. Consequently, neither triphenylphosphine oxide nor trimethylphosphine oxide can be prepared efficiently by this procedure.

A. METHYLDIPHENYLPHOSPHINE OXIDE

$$CH_3(C_6H_5)_2P + H_2O_2 \longrightarrow CH_3(C_6H_5)_2PO + H_2O$$

Procedure

■ **Caution.** *Organophosphines are toxic chemicals having obnoxious odors. A good fume hood is required for all procedures in which the phosphine may be evolved in the atmosphere.*

Approximately 5 mL of 15% hydrogen peroxide (0.03 mol) is placed in a 100-mL three-necked flask equipped with a magnetic stirrer. In one neck of the flask is a pressure-equalizing dropping funnel containing 1.0 g (0.005 mol) of methyldiphenylphosphine* in 10 mL of diethyl ether; the other two necks contain a nitrogen inlet and an outlet which is connected to a mineral-oil bubbler. A slow stream of nitrogen is passed through the vessel as the phosphine is added with stirring (Teflon magnetic stirring bar) over a period of 10 min. After an additional 10 minutes have elapsed, a small amount of catalase* (approximately 5–10 mg) is added as stirring continues. After all the excess peroxide has been destroyed,† the solution is evaporated to dryness either by allowing it to stand in a hood overnight or by using a rotary evaporator. The residue is recrystallized twice from toluene, giving 1.08 g (0.005 mol) (100% yield) of the white, solid phosphine oxide, mp 113° (lit. 113–114°).[3] *Anal.* Calcd. for $C_{13}H_{13}PO$: C, 72.22; H, 6.02; P, 14.35. Found: C, 72.43; H, 6.15; P, 14.46.

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* Both of these phosphines may be purchased from K & K Laboratory, 26203 Miles Road, Cleveland, OH 44128. The catalase (2000–5000 units/mg) was purchased from Sigma Chemical Company, P.O. Box 14508, St. Louis, MO 63178.

† The checker suggests adding a drop of reaction mixture to a solution of potassium iodide to find out the extent of reaction. A brown color, due to formation of iodine, would indicate hydrogen peroxide was still present.

Properties

The ^{1}H nmr spectrum in chloroform-*d* consisted of a doublet due to methyl protons being split by phosphorus at τ8.0 ($J_{HCP} = 12.5$ Hz) and a multiplet due to phenyl protons at τ2.30 (TMS reference). The phosphoryl stretching frequency has been reported at 1192 cm^{-1}.[3]

B. DIMETHYLPHENYLPHOSPHINE OXIDE

$$(CH_3)_2(C_6H_5)P + H_2O_2 \longrightarrow (CH_3)_2(C_6H_5)PO + H_2O$$

Procedure

■ **Caution.** *The oxidation of the* $(CH_3)_2C_6H_5P$ *may be very violent if it is added too rapidly to the peroxide solution.*

The oxidation of dimethylphenylphosphine,* (1.0 g, 0.007 mol), is carried out by the above method through the first evaporation step. The residue from evaporation is then dissolved in anhydrous acetonitrile and filtered; then the solvent is evaporated. The remaining solid is then transferred to a cold-finger sublimation apparatus where it is sublimed under vacuum (10^{-3} torr) at 100°. The product is isolated as a white solid (0.62 g, 0.004 mol, 57% yield) having a melting point of 115° (lit., 119°).[3] *Anal.* Calcd. for $C_8H_{11}PO$: C, 62.34; H, 7.14; P, 20.13. Found: C, 61.93; H, 7.30; P, 19.90.

Properties

The ^{1}H nmr spectrum in chloroform-*d* consisted of a doublet at τ8.28 due to methyl protons on phosphorus ($J_{HCP} = 13$ Hz) and a multiplet centered at τ2.45 due to phenyl protons (TMS reference). These data are in good agreement with previous work.[4] The phosphoryl stretching frequency has been reported at 1174 cm^{-1}.[3] Dimethylphenylphosphine oxide is quite hygroscopic and should be stored in a desiccator over P_4O_{10}.

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* See first footnote for Sec. A.

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Edited by Alan G. MacDiarmid

51. LITHIUM DIPHENYLPHOSPHIDE AND DIPHENYL(TRIMETHYLSILYL)PHOSPHINE

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Checked by DANIEL COX† and KIM COHN†

A previous description of the synthesis of $(CH_3)_3SiP(C_6H_5)_2$ in *Inorganic Syntheses*[1] involves the initial preparation of sodium diphenylphosphide from diphenylphosphinous chloride. This method of preparation of the diphenylphosphide anion requires rigorous conditions and long reaction times. At least two other easier methods of preparation of the diphenylphosphide anion (lithium counterion) are known. One synthesis uses diphenylphosphine and *n*-butyllithium[2] as reactants, whereas the second uses triphenylphosphine and elemental lithium.[3,4] The second method is described here.

The phosphorus-carbon bond of triphenylphosphine is easily cleaved by lithium in THF (tetrahydrofuran) at room temperature. The phenyllithium which is also formed in this reaction is destroyed *in situ* by allowing it to react with 2-chloro-2-methylpropane. Isobutylene gas is given off and the diphenylphosphide ion is then allowed to react with chlorotrimethylsilane. The product, diphenyl(trimethylsilyl)phosphine, is formed in 80% yield. The diphenylphosphide ion is usually formed in 85–95% yield, based on the lithium consumed.

■ **Caution.** *All phosphines are toxic. The diphenylphosphide ion and silylphosphine are very sensitive to oxygen and moisture. All operations involving these materials should be carried out in an inert atmosphere and in a good hood. Any excess lithium metal should be destroyed with* 1-*propanol in an inert atmosphere. The tetrahydrofuran* (THF) *should be handled and dried carefully as previously described.*[5] (See also Synthesis 1 of this volume for dangers involved in drying THF.)

A. LITHIUM DIPHENYLPHOSPHIDE

$$(C_6H_5)_3P + 2Li \xrightarrow{THF} (C_6H_5)_2PLi + C_6H_5Li$$

$$C_6H_5Li + (CH_3)_3CCl \xrightarrow{THF} C_6H_6 + LiCl + (CH_3)_2C{=}CH_2$$

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Procedure

A clean, dry, 100-mL, two-necked, round-bottomed flask is set up with a reflux condenser (air-cooled) in a nitrogen-filled glove bag. To the second neck, a septum is attached. Twenty-five milliliters of freshly-dried THF and 10.5 g (0.04 mol) of triphenylphosphine are added to the flask, which contains a Teflon-coated magnetic stirring bar. Lithium metal (0.55 g, 0.08 mol) from which oil has been cleaned, is scraped, cut, and pressed into flat rods and is added to the THF-phosphine solution. After the solution is stirred, a red color forms which indicates formation of the diphenylphosphide ion. The air-cooled condenser is used because the heat liberated by this reaction causes the solvent to reflux. Within 2 hr the reaction is 85–95% complete, based on unreacted lithium, and the solution is dark-red. It has been observed that the smaller the amount of THF used, the faster the reaction proceeds and the greater is the rate of refluxing.

To the dark-red solution a sample of 2-chloro-2-methylpropane (3.7 g, 0.04 mol) is added slowly by means of a syringe. The formation of white precipitate and bubbling of solvent occurs. If the 2-chloro-2-methylpropane is added too quickly, the vigorous evolution of gas may cause difficulty. The dark-red color remains. This solution is then filtered in the glove bag, and the filtrate is placed into a pressure-equalized dropping funnel. The $(C_6H_5)_2PLi$ solution may now be used as a reagent for the introduction of the $(C_6H_5)_2P$ group into a variety of compounds.

B. DIPHENYL(TRIMETHYLSILYL)PHOSPHINE

$$(C_6H_5)_2PLi + (CH_3)_3SiCl \xrightarrow{\text{THF}} (CH_3)_3SiP(C_6H_5)_2 + LiCl$$

Procedure

The dropping funnel described in Sec. A, containing the $(C_6H_5)_2PLi$ solution, is attached to a 200-mL two-necked flask which contains chlorotrimethylsilane (4.32 g, 0.04 mol) in 25 mL of THF. The other neck contains an air-cooled condenser. The $(C_6H_5)_2PLi$ solution is added slowly, in a nitrogen-filled glove bag, to the chlorotrimethylsilane solution over a period of a half-hour. A white precipitate forms together with a clear or slightly yellow-colored solution. This mixture is filtered and washed with THF in the nitrogen-filled glove bag. The solvent is then removed by distillation under an atmosphere of nitrogen, and the residual material is purified by distillation at 1 torr. The 8.3-g (80% yield) fraction collected has bp 126–127°/1 torr, n_D^{25} 1.600 (lit.,[6] bp 126–127°/1 torr, n_D^{20} 1.600). When the reaction is carried out on a 0.1-mole scale, similar yields are obtained.

Properties

The properties of $(CH_3)_3SiP(C_6H_5)_2$ have been described previously in *Inorganic Syntheses.*[1]

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52. PENTATHIAZYL, $[S_5N_5]^+$, SALTS

Submitted by A. J. BANISTER* and H. G. CLARKE*
Checked by T. CHIVERS† and J. BOJES†

The pentathiazyl ion, $[S_5N_5]^+$, is the first 14π-electron member of the series of "electron-rich" aromatic sulfur-nitrogen heterocycles.[1,2] The preparations of the related species $S_2N_2(6\pi)$, $S_3N_2Cl_2$ (containing the 6π pseudo-aromatic $[S_3N_2Cl]^+$ cation), and salts of $[S_4N_3]^+(10\pi)$ have been described[3,4] in earlier volumes of *Inorganic Syntheses.* The monocyclic structure of the $[S_5N_5]^+$ ion has been established by x-ray diffraction methods.[5,6]

Pentathiazyl salts can be prepared in high yield in thionyl chloride solution at room temperature by adding solid tetrasulfur tetranitride to a 1 : 3 mixture of trichlorocyclotrithiazene,‡ $(NSCl)_3$, and a chloride ion acceptor such as iron(III) chloride, aluminum trichloride or antimony(V) chloride.[7,8] The adducts, $(NSCl)_3\cdot 2FeCl_3$, $(NSCl)_3\cdot 2AlCl_3$, and $(NSCl)_3\cdot 3SbCl_5$, respectively, are first formed. The $(NSCl)_3\cdot 2MCl_3$ adduct and an equimolar excess of MCl_3, or alternatively the $(NSCl)_3\cdot 3SbCl_5$ adduct can be regarded

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‡ 2,4,6-trichloro-1,3,5,2,4,6-trithiatriazine

as a potential source of $[NS]^+$, which is abstracted on addition of the tetrasulfur tetranitride to give $[S_5N_5]^+$, e.g.:

$$\tfrac{1}{3}(NSCl)_3 + SbCl_5 \longrightarrow [NS]^+[SbCl_6]^- \xrightarrow{S_4N_4} [S_5N_5]^+[SbCl_6]^-$$

The usual time required to prepare any of the three $S_5N_5{}^+$ salts is ca. 4 hr; the reaction can be left unattended for much of the time. Subsequent purification is by recrystallization or solvent extraction.

Preparation and Purification of Reagents

■ **Caution.** *Tetrasulfur tetranitride has been reported to explode when subjected to percussion, friction, sudden heating, or temperatures close to its melting point.*[9,12] *It should be handled with care and only in relatively small quantities. See Appendix (p. 197) for general safety notes.*

Tetrasulfur tetranitride is prepared from disulfur dichloride, chlorine, and ammonia as described by Villena-Blanco and Jolly.[9] Thionyl chloride is purified by distillation from triphenyl phosphite.[10] (■ **Note.** *Both thionyl chloride and sulfuryl chloride (purified by distillation to give a colorless liquid) should be handled in an efficient hood.*)

The metal chlorides should be carefully purified before use. The iron(III) chloride is obtained from the commercial anhydrous material by heating for about an hour under refluxing thionyl chloride (~ 10 mL per gram of iron(III) chloride). The solvent is then removed by distillation. The aluminum trichloride is sublimed *in vacuo* at ca. 120° onto a cold water finger; the antimony(V) chloride is freshly distilled (e.g., at 68°/14 torr) under dry nitrogen.

The trichlorocyclotrithiazene is obtained[11] by stirring tetrasulfur tetranitride or $S_3N_2Cl_2$ with excess sulfuryl chloride (2–3 mL per gram of sulfur compound) for ca. 24 hr at room temperature, in a flask fitted with an exit bubbler. After excess solvent has been removed by distillation (at ca. 20° under reduced pressure) and the residue has been pumped dry, the $(NSCl)_3$ is obtained as a pale-yellow powder. Further purification is usually unnecessary but if analyses or a darker color indicate that some decomposition has occurred (e.g., through exposure to atmospheric moisture), it can be recrystallized from thionyl chloride or sulfuryl chloride. To obtain a good recovery, the mixture should be filtered at ca. $-10°$.

Since $(NSCl)_3$, the metal chlorides, $[S_5N_5]^+[FeCl_4]^-$ and $[S_5N_5]^+$-$[AlCl_4]^-$ are moisture-sensitive solids, they should be handled in a dry box and kept under nitrogen during the preparation. High-vacuum silicone grease can be used on ground-glass joints. Since thionyl chloride and $(NSCl)_3$ attack the grease, apparatus should be dismantled fairly promptly after use; this prevents the joints from seizing.

Procedure

A. PENTATHIAZYL TETRACHLOROFERRATE(1−) AND PENTATHIAZYL TETRACHLOROALUMINATE(1−)

$$(NSCl)_3 + 2MCl_3 \longrightarrow (NSCl)_3\cdot 2MCl_3$$
$$(NSCl)_3\cdot 2MCl_3 + MCl_3 + 3S_4N_4 \longrightarrow 3[S_5N_5]^+[MCl_4]^-$$
$$(M = Fe, Al)$$

The molar ratio of the reactants $(NSCl)_3$, $FeCl_3$ (or $AlCl_3$), and S_4N_4 is 1 : 3 : 3. Excess $(NSCl)_3$ (up to threefold) speeds the reaction, but it is important to avoid a simultaneous excess of $(NSCl)_3$ and metal halide because these combine to form a sparingly soluble and highly air-sensitive adduct. Excess tetrasulfur tetranitride is avoided because it reacts[13] with the solvent to give S_4N_3Cl. A typical procedure is given below.

Trichlorocyclotrithiazene (1.22 g, 5 mmol) is added to ca. 30 mL of thionyl chloride in a round-bottomed flask containing a Teflon-coated magnetic stirrer. Powdered iron(III) chloride (2.43 g, 15 mmol) [or aluminum trichloride 15 mmol] is added to the pale-yellow solution and the mixture is stirred for ca. 1 hr. A precipitate of $(NSCl)_3\cdot 2FeCl_3$ (rust-colored) [or $(NSCl)_3\cdot 2AlCl_3$ (yellow-orange)] gradually forms; unreacted solid metal chloride is also present. Tetrasulfur tetranitride (2.76 g, 15 mmol) is then added to the vigorously stirred mixture over a period of several minutes. When the tetrasulfur tetranitride is added, the solution immediately becomes deep-green and the trichlorocyclotrithiazene–metal chloride adduct dissolves. The mixture is stirred vigorously for ca. 2 hr, during which time the $[S_5N_5]^+$ salt gradually precipitates out. Poor stirring reduces the yield of $[S_5N_5]^+$ salt.

The solution is reduced in volume to about 15 mL by distillation at the boiling point and is then cooled to about −10°. The precipitated crude product (iron salt, brown; aluminum salt, orange) is filtered under nitrogen, dried *in vacuo* and recrystallized to constant melting point by dissolving it in refluxing thionyl chloride and then cooling the solution to −10°. The $[S_5N_5]^+[AlCl_4]^-$ is somewhat more soluble than $[S_5N_5]^+[FeCl_4]^-$ in thionyl chloride. The crystals are filtered under nitrogen and pumped dry *in vacuo.* After several recrystallizations, $[S_5N_5]^+[FeCl_4]^-$ is obtained as orange-brown crystals (mp 181°, decomposes) and $[S_5N_5]^+[AlCl_4]^-$ as light-orange needles (mp 181°, decomposes); the orange needles are similar in appearance to tetrasulfur tetranitride. The yields of the iron and aluminum compounds are approximately 90% and 70%, respectively, for the crude products and 80% (ca. 5.1 g) and 40% (ca. 2.4 g), respectively, for the recrystallized materials. Both $[S_5N_5]^+$ salts show a distinctive somewhat broad infrared absorption[8] at 1143 cm^{-1}. If an impurity should be present, it is most likely to be the salt $[S_4N_3]^+[MCl_4]^-$, which has a characteristic strong, sharp infrared absorption[8] at 1032 cm^{-1}. *Anal.* Calcd. for $Cl_4FeN_5S_5$: S, 37.5; N, 16.4; Fe, 13.0; Cl, 33.1. Found: S, 37.3; N, 16.3; Fe, 13.6; Cl, 32.5. Calcd. for $AlCl_4N_5S_5$: S, 40.2; N, 17.5; Al, 6.8; Cl, 35.5. Found: S, 39.7; N, 17.5; Al, 6.7; Cl, 35.3.

B. PENTATHIAZYL HEXACHLOROANTIMONATE(1 −)

$$(NSCl)_3 + 3SbCl_5 \longrightarrow (NSCl)_3 \cdot 3SbCl_5$$

$$(NSCl)_3 \cdot 3SbCl_5 + 3S_4N_4 \longrightarrow 3[S_5N_5]^+[SbCl_6]^-$$

The preparation of this salt is similar in many respects to that of the tetrachloroferrate(1 −) and tetrachloroaluminate(1 −) salts. The molar ratios of reactants are the same. Small quantities are chosen because purification (by Soxhlet extraction) is slow.

Trichlorocyclotrithiazene (0.86 g, 3.5 mmol) is dissolved in ca. 40 mL of thionyl chloride, and freshly distilled antimony(V) chloride (3.14 g, 1.34 mL, 10.5 mmol) is slowly added to the stirred solution via a graduated syringe. Slow addition is recommended since the reaction is fairly exothermic. Yellow $(NSCl)_3 \cdot 3SbCl_5$ precipitates immediately, but the solution is stirred for a further 20–30 min to ensure complete reaction. Tetrasulfur tetranitride (1.93 g, 10.5 mmol) is added slowly to the vigorously stirred mixture as before. The yellow adduct dissolves immediately to give a deep-green solution. Dark-yellow impure $[S_5N_5]^+[SbCl_6]^-$ slowly precipitates (the reaction is complete after ca. 2 hr). The product is filtered, washed with fresh, cold thionyl chloride (in which it is only sparingly soluble), and purified by Soxhlet extraction with ca. 50 mL of hot thionyl chloride on a fritted-glass thimble. The slow extraction gives a yellow powder (mp 188°, decomposes; yield 4.7 g, 80%). *Anal.* Calcd. for $Cl_6N_5S_5Sb$: S, 28.4; N, 12.4; Sb, 21.6; Cl, 37.6. Found: S, 28.3; N, 12.3; Cl, 37.6.

Properties

Pentathiazyl tetrachloroaluminate(1−) and, to a lesser extent, pentathiazyl tetrachloroferrate(1−) are moisture-sensitive; both are soluble in thionyl chloride, anhydrous formic acid, and concentrated sulfuric and nitric acids. On dissolution in acid, hydrogen chloride is evolved because of decomposition of the anion. The solution in anhydrous formic acid can be used to prepare other salts by metathesis.[7] The hexachloroantimonate(1−) undergoes almost no reaction when exposed to water or moist air for 24 hr.

The crystals of the tetrachloroaluminate(1−) are birefringent[14] and slightly photosensitive, slowly darkening on exposure to light over a period of months. The characteristic infrared absorptions of the $[S_5N_5]^+$ ion in the tetrachloroaluminate(1−) and tetrachloroferrate(1−) salts occur[8] at 1143 (s), 1048 (w), 1020 (w, sh), 733 (m), 722 (w, sh), 687 (w), 610 (w), and 529 (s) cm^{-1}. Slight shifts to higher wavenumbers occur for the hexachloroantimonate(1−) salt. Solutions of the tetrachloroaluminate(1−) and tetrachloroferrate(1−) in concentrated sulfuric acid absorb in the ultraviolet-visible region (190–700 nm) at 327 nm ($\varepsilon = 3.48 \times 10^4$) and at 426 nm ($\varepsilon = 2.47 \times 10^3$).[8,15] The electronic spectrum of $[S_5N_5]^+$ has been interpreted in terms of a modified π electronic LCI-SCF method which considers σ-core polarization.[15] The π-electron densities and bond orders give further support to the conclusion that $[S_5N_5]^+$ is an aromatic 14π system.[1,2]

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53. IMPORTANCE OF EXCESS BASE IN THE SYNTHESIS OF SODIUM MONOTHIOPHOSPHATE

(Sodium Phosphorothioate)

$$PSCl_3 + 6NaOH \longrightarrow Na_3PO_3S + 3NaCl + 3H_2O$$

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Checked by JACK L. LAMBERT† and FRANK C. MCCLELLAND†

In the synthesis of sodium phosphorothioate from thiophosphoryl chloride and sodium hydroxide according to the method of Yasuda and Lambert,[1] problems were encountered in the duplication of their reported yield and sometimes even in the isolation of any of the desired product. Yasuda and Lambert noted that the yield of the reaction was dependent upon the purity of the sodium hydroxide used but gave no explanation as to why this should be the case. Although the sodium hydroxide which we were using was an analytical grade, the bottle had previously been opened and the sodium hydroxide may have absorbed some carbon dioxide owing to exposure to air. Since the stoichiometry of the reaction demands six moles of sodium hydroxide per mole of thiophosphoryl chloride, the exact ratio called for in Yasuda and Lambert's procedure, the presence of any sodium carbonate would detract from the required quantity of base. Since sodium phosphorothioate is known[1] to decompose upon heating in neutral solution, it is most likely that a deficient quantity of base would cause the final pH to approach neutrality, resulting in decomposition of the compound in the hot solution (103–109°).

To circumvent this problem it was found advantageous to use a slight excess of sodium hydroxide in the reaction, i.e., a 5% excess of the required 6 molar equivalents. This ensures that the solution is basic enough to prevent decomposition of the sodium phosphorothioate once it is formed. Yasuda and Lambert reported a percentage yield of 57% of the theoretical. In a series of three preparations on roughly a 1-mol scale where 5% excess base was used, we obtained an average yield of 67%. It was also possible to scale down the reaction to permit synthesis of ^{35}S-labeled sodium phosphorothioate. In a series of four syntheses on a 4–5-millimol scale an average yield of 59% was achieved.

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Akerfeldt[2] reported that the hydrolysis of the phosphorothioate ion in alkaline medium is catalyzed by silicone grease. It is therefore recommended that the ground-glass joints of the apparatus not be treated with silicone grease.

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Appendix

CAUTIONARY NOTE CONCERNING THE STORING AND HANDLING OF TETRASULFUR TETRANITRIDE, S_4N_4

A. J. BANISTER*

Tetrasulfur tetranitride, particularly in the pure state or in the form of large crystals, is likely to explode if it is subjected to percussion, friction, sudden heating, or temperatures close to the melting point; it should, therefore, be handled with care.[1,2] The decomposition of large crystals by impact, or simply through a change in temperature, may cause a spark owing to triboluminescence and this serves to detonate the rest of the mass.[3] No serious accidents with tetrasulfur tetranitride have been reported, but a research worker was badly cut on the hand when 0.5 g of the compound which she was crushing with a glass rod in a small beaker detonated violently.[2]

Tetrasulfur tetranitride is not toxic.[4] Men working continuously with it for a year or more have shown neither acute, chronic, nor delayed symptoms, apart from temporary skin irritation in some cases (which may not be due to tetrasulfur tetranitride itself). The mode of hydrolysis does not suggest any particular toxic hazard.[4]

Probably the best way[3] of storing tetrasulfur tetranitride is as the crude product obtained by the procedure described by M. Villena-Blanco and W. L. Jolly[1] but with the omission of the chlorination step which converts disulfur dichloride to sulfur dichloride. The total yield of tetrasulfur tetranitride is thereby reduced by a factor of two;[1] the crude product contains

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about 30–40% sulfur. This mixture does not explode under the usual conditions which detonate pure tetrasulfur tetranitride (e.g., hitting with a hammer). Relatively large quantities of the crude product can then be stored safely in dark bottles (e.g., up to 1-kg capacity).[3] One can *not* assume that deliberate mixing of pure tetrasulfur tetranitride and sulfur produces a safe mixture. Initial purification (removal of S_8 and S_7NH) is achieved by agitating with carbon disulfide (solubility S_4N_4, 9.41 g/L at 20°).[2] For example, treatment of 30 g of the reaction product (containing 17.4 g of S_8 and 12.6 g of S_4N_4) with carbon disulfide (60 cc, 20°) gave a residue of 12.0 g of moderately pure S_4N_4.[3] Further loss of tetrasulfur tetranitride, which accompanies any subsequent washing with carbon disulfide, can be minimized if the same sample of carbon disulfide is used several times to wash the crystals and tetrasulfur tetranitride is recovered from the solution by concentration, refrigeration, and filtration. Final purification is by recrystallization from chloroform or benzene or by vacuum sublimation at ca. 80–90°.[5]

The following safety precautions are recommended:

1. Do not store more than a few grams of pure tetrasulfur tetranitride in one container. Do not use bottles with ground-glass stoppers; beware of trapping tetrasulfur tetranitride crystals in a screw cap or between ground-glass joints.
2. Do not touch tetrasulfur tetranitride with a metal spatula (especially in a dry box where there is danger from static discharge).
3. Where possible, carry out reactions with tetrasulfur tetranitride in an inert solvent, either in solution or as a suspension. The use of an inert solvent is particularly recommended for reactions with strong nucleophiles or electrophiles.[5]
4. In exploratory reactions do not use more than 0.1 g and keep reaction temperatures down to a minimum and below 100°. Reactions with metal carbonyls are especially hazardous.[6,7] A total of up to about 10 g can be used in a well-tested preparation of a compound of known stability, but it is advisable to add the tetrasulfur tetranitride in portions of not more than 0.5 g and to allow each portion to react before adding more.
5. Always wear safety goggles and place a polycarbonate safety screen in front of the apparatus.

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SUBJECT INDEX

Names used in this cumulative Subject Index for Volumes XVI and XVII, as well as in the text, are based for the most part upon "Nomenclature of Inorganic Chemistry, Definitive Rules 1970" Report of the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry, Butterworths, London, 1971 [see *Pure Appl. Chem.* **27**(1), 1–110]; also on the "Tentative Rules of Organic Chemistry—Section D"; and "Nomenclature of Inorganic Boron Compounds" [Commission on Nomenclature of Inorganic Chemistry, IUPAC, published in *Pure Appl. Chem.* **30**(3–4), 683–710 (1972)]. All of these rules have been approved by the ACS Committee on Nomenclature. Conformity with approved organic usage is also one of the aims of the nomenclature used here.

In line, to some extent, with *Chemical Abstracts* practice, more or less inverted forms are used for many entries, with the substituents or ligands given in alphabetical order (even though they may not be in the text); for example, derivatives of arsine, phosphine, silane, germane, and the like; organic compounds; metal alkyls, aryls, 1,3-diketone and other derivatives and relatively simple specific coordination complexes: *Iron, cyclopentadienyl-* (also as *Ferrocene*); *Cobalt(II), bis*(2,4-*pentanedionato*)- [instead of *Cobalt (II) acetylacetonate*]. In this way, or by the use of formulas, many entries beginning with numerical prefixes are avoided; thus *Vanadate(III), tetrachloro-*. Numerical and some other prefixes are also avoided by restricting entries to group headings where possible: *Sulfur imides*, with formulas; *Molybdenum carbonyl*, $Mo(CO)_6$; both *Perxenate*, $HXeO_6^{3-}$, and *Xenate(VIII)*, $HXeO_6^{3-}$. In cases where the cation (or anion) is of little or no significance in comparison with the emphasis given to the anion (or cation), one ion has been omitted; e.g., also with less well-known complex anions (or cations): $CsB_{10}H_{12}CH$ is entered only as *Carbaundecaborate*(1−), *tridecahydro-* (and as $B_{10}CH_{13}^-$ in the Formula Index).

Under general headings such as *Cobalt(III) complexes* and *Ammines*, used for grouping coordination complexes of similar types having names considered unsuitable for individual headings, formulas or names of specific compounds are not usually given. Hence it is imperative to consult the Formula Index for entries for specific complexes.

As in *Chemical Abstracts* indexes, headings that are phrases are alphabetized straight through letter by letter, not word by word, whereas inverted headings are alphabetized first as far as the comma and then by the inverted part of the name. Stock Roman numerals and Ewens-Bassett Arabic numbers with charges are ignored in alphabetizing unless two or more names are otherwise the same. Footnotes are indicated by *n.* following the page number.

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FORMULA INDEX

The Formula Index, as well as the Subject Index, is a cumulative index for Volumes XVI and XVII. The chief aim of this index, like that of other formula indexes, is to help in locating specific compounds or ions, or even groups of compounds, that might not be easily found in the Subject Index, or in the case of many coordination complexes are to be found only as general entries in the Subject Index. *All* specific compounds, or in some cases ions, with definite formulas (or even a few less definite) are entered in this index or noted under a related compound, whether entered specifically in the Subject Index or not.

Wherever it seemed best, formulas have been entered in their usual form (i.e., as used in the text) for easy recognition: Si_2H_6, XeO_3, NOBr. However, for the less simple compounds, including coordination complexes, the significant or central atom has been placed first in the formula in order to throw together as many related compounds as possible. This procedure often involves placing the cation last as being of relatively minor interest (e.g., alkali and alkaline earth metals), or dropping it altogether: MnO_4Ba; $Mo(CN)_8K_4 \cdot 2H_2O$; $Co(C_5H_7O_2)_3Na$; $B_{12}H_{12}{}^{2-}$. Where there may be almost equal interest in two or more parts of a formula, two or more entries have been made: Fe_2O_4Ni and $NiFe_2O_4$; $NH(SO_2F)_2$, $(SO_2F)_2NH$, and $(FSO_2)_2NH$ (halogens other than fluorine are entered only under the other elements or groups in most cases); $(B_{10}CH_{11})_2Ni^{2-}$ and $Ni(B_{10}CH_{11})_2{}^{2-}$.

Formulas for organic compounds are structural or semistructural so far as feasible: $CH_3COCH(NHCH_3)CH_3$. Consideration has been given to probable interest for inorganic chemists, i.e., any element other than carbon, hydrogen, or oxygen in an organic molecule is given priority in the formula if only one entry is made, or equal rating if more than one entry: only $Co(C_5H_7O_2)_2$, but $AsO(+)\text{-}C_4H_4O_6Na$ and $(+)\text{-}C_4H_4O_6AsONa$. Names are given only where the formula for an organic compound, ligand, or radical may not be self-evident, but not for frequently occurring relatively simple ones like C_5H_5(cyclopentadienyl), $C_5H_7O_2$(2,4-pentanedionato), C_6H_{11}(cyclohexyl), C_5H_5N(pyridine). A few abbreviations for ligands used in the text are retained here for simplicity and are alphabetized as such, "bipy" for bipyridine, "en" for ethylenediamine or 1,2-ethanediamine, "diop" for 4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane, "diphos" for ethylenebis(diphenylphosphine) or 1,2-bis(diphenylphosphino)ethane or 1,2-ethanediylbis(diphenylphosphine), "dmg" for dimethylglyoxime(2,3-butanedione dioxime), "dpg" for diphenylglyoxime, "nox" for 1,2 cyclohexanedione dioxime, and "tmeda" for N,N,N′,N′-tetramethylethylenediamine or N,N,N′,N′-tetramethyl-1,2-ethanediamine.

Footnotes are indicated by *n.* following the page number.