

IV.10 Carbopalladation via Palladacyclopropanes and Palladacycloprenes

IV.10.1 Palladium-Catalyzed Oligomerization and Polymerization of Dienes and Related Compounds

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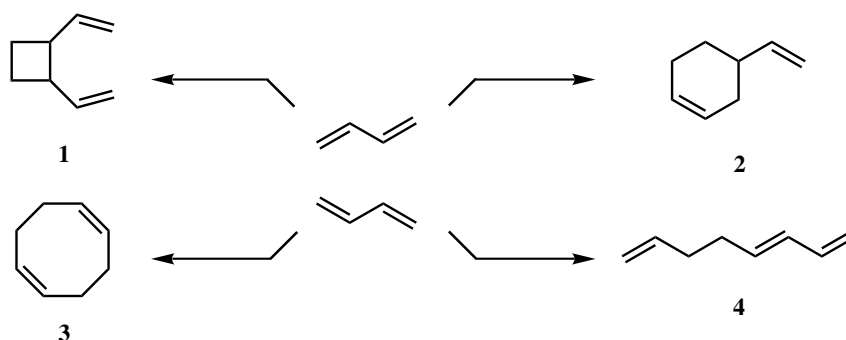
A. INTRODUCTION

Simple 1,3-dienes such as 1,3-butadiene, isoprene, and related compounds undergo efficient metal-catalyzed oligomerization. Under palladium catalysis, diene dimerization is the most common oligomerization reaction observed. Four modes of dimerization have been reported (**Scheme 1**): (i) [2 + 2] cycloaddition to afford 1,2-divinylcyclobutane (**1**); (ii) [4 + 2] cycloaddition to afford 4-vinylcyclohexene (**2**); (iii) [4 + 4] cycloaddition to afford 1,4-cyclooctadiene (**3**); and (iv) linear dimerization to afford 1,3,7-octatriene (**4**).

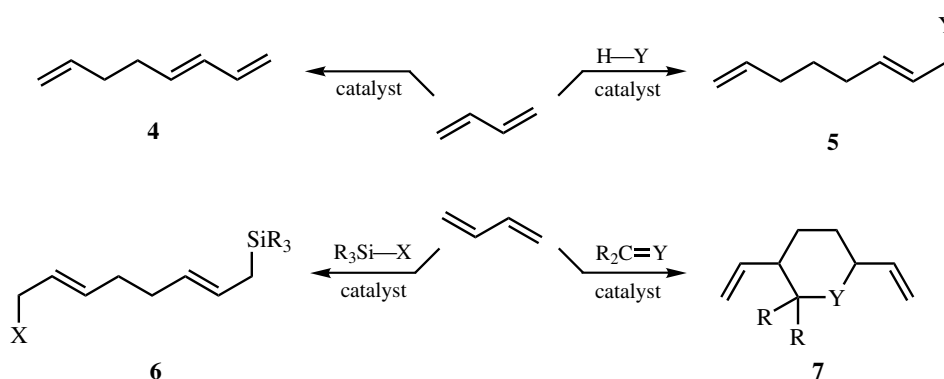
A number of catalyst systems have been uncovered that produce some 1,2-divinylcyclobutane as a significant component of a product mixture, but, at present, there are no generally applicable, preparative useful catalyst systems that afford 1,2-divinylcyclobutanes with high mode selectivity. Selective diene dimerization via the [4 + 2] cycloaddition mode^[1] or [4 + 4] cycloaddition mode^[2] is best obtained using nickel catalysis, and, in particular, the latter mode has proved very useful for the synthesis of a wide range of functionalized cyclooctadienes.^{[3],[4]} Selective linear dimerization can be accomplished via a variety of metals, including nickel,^[5] platinum,^[6] rhodium,^{[7]–[9]} cobalt,^{[8],[9]} and iridium^{[8],[9]}; albeit, some of these metal catalyst systems are described only in isolated reports. Generally, palladium is the catalyst of choice for this mode of diene oligomerization.

A.i. Palladium-Catalyzed Linear Dimerization: Reaction Modes

Four related Pd-catalyzed linear dimerization modes have been observed for the intermolecular reaction of 1,3-dienes (**Scheme 2**). While potentially of industrial importance for bulk



Scheme 1

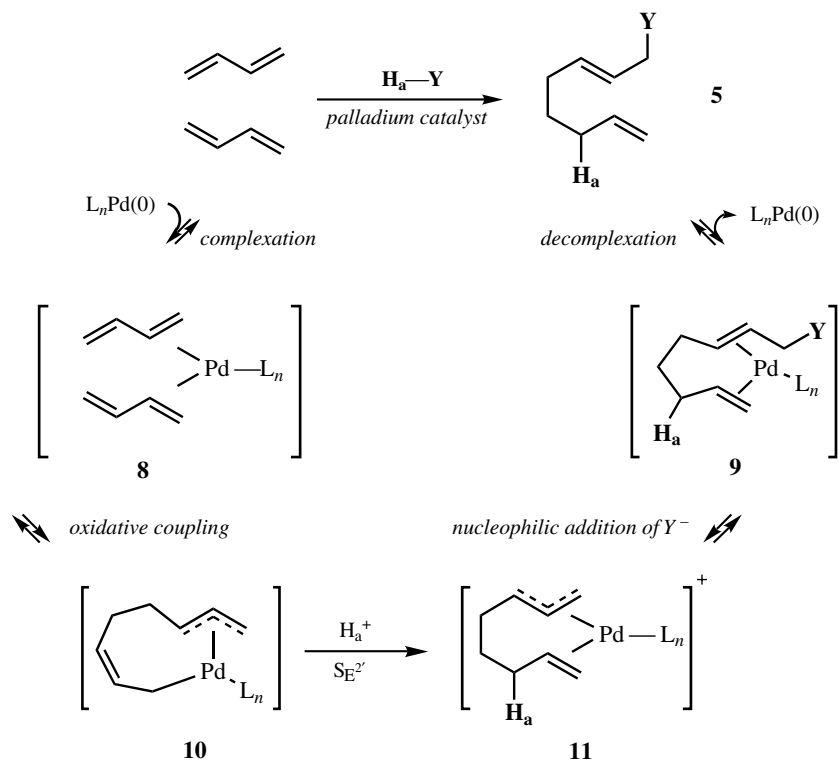


Scheme 2

chemical production, the relatively least developed of these is the linear dimerization to 1,3,7-octatriene (**4**) or its substituted derivatives. The coupling of two diene molecules with incorporation of a third component (trapping reagent) is much more common. Three types of trapping reagents have been employed. (i) Protic trapping reagents (e.g., H—Y = an alcohol, a phenol, a carboxylic acid, a 1°- or 2°-amine, a sulfinic acid, an active methylene or methine compound, a nitroalkane, or an enamine) afford predominantly 1-substituted 2,7-octadienes **5**. (ii) Silanes, stannanes (e.g., R₃Si—X or R₃Sn—X; X = H), or disilanes (e.g., R₃Si—X, X = SiR₃) afford predominantly 2,6-octadiene derivatives **6**. (iii) Finally, certain R₂C=Y reagents (e.g., aldehydes, ketones, imines, carbon dioxide, or isocyanates) yield **7**, the products of a net cycloaddition reaction. Several other miscellaneous trapping reactions are also known.

A.ii. Palladium-Catalyzed Linear Dimerization: Mechanism

Most of the work on the mechanism of Pd-catalyzed linear diene dimerization has been done on the variant involving dimerization with trapping by a protic trapping reagent H—Y, and a particularly interesting series of papers has been published by Jolly and co-workers.^{[10]–[14]} In these and related papers, structural and spectroscopic data are presented that support the catalytic cycle shown in **Scheme 3**.^{[15]–[17]} While the Jolly catalytic cycle is not without some controversy,^[18] it provides a good working model to rationalize the observed coupling chemistry.



Scheme 3

The active catalyst is presumably a palladium(0) species,^{[19]–[22]} and the dienes must in some way complex about the metal (e.g., **8**).^[23] The first directly observed intermediate, the palladacycle **10**, is the result of oxidative coupling of the dienes; that is, the dienes undergo oxidative addition onto the palladium concomitant with coupling. In the case of palladium, as well as nickel^[24] and platinum,^[9] metallacycles of type **10** have been characterized both crystallographically and spectroscopically.^{[13],[25],[26]} An isolated palladacycle **10** was stoichiometrically protonated by H—Y (i.e., methanol) at low temperature (−80 °C). The observed site of protonation was at the η^1 -allyl moiety in an $\text{S}_{\text{E}}^{2'}$ fashion to afford an intermediate, the NMR spectrum of which is consistent with the chelated π -allylpalladium intermediate **11**. Upon warming (−35 °C), addition of the nucleophile Y^- afforded the presumed chelate **9**, a species shown to be a competent catalyst for further consumption of butadiene.^{[16],[17]} It has been suggested on the basis of calorimetric analysis that, at least under certain conditions, release of product from chelate **9** may be rate determining.^{[19],[27]} The model in **Scheme 3** nicely accounts for the selective formation of the 2,7-octadienyl isomer as well as the site of selective deuteration upon reaction with isotopically labeled ^2H —Y trapping reagents; for example, reaction with CH_3OD or $\text{H}_3\text{CO}_2\text{D}$ affords **5** wherein the proton labeled H_a is replaced by deuterium.

Recent advances in each of the four Pd-catalyzed linear diene dimerization modes (**Scheme 2**: dimerization without trapping; dimerization with incorporation of protic H—Y trapping reagents; dimerization with incorporation of silanes or disilanes; and

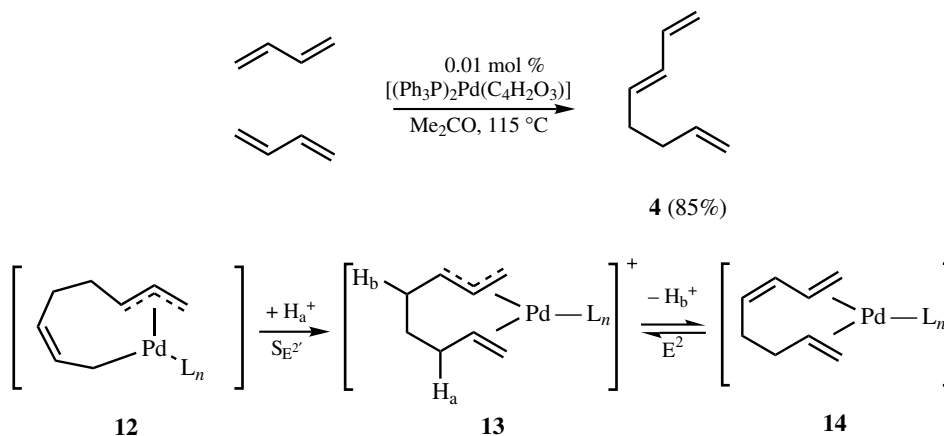
dimerization with incorporation of $R_2C=Y$ reagents) are discussed below (**Sects. B–E**). In some cases both the intermolecular reaction of 1,3-dienes as well as recent examples of the corresponding intramolecular cyclization reaction of bisdiene substrates are discussed. For additional details, especially of the older literature in this area, the reader is referred to a number of previous review articles.^{[25],[28]–[34]}

B. DIMERIZATION WITHOUT TRAPPING

B.i. Intermolecular Linear Dimerization of Hydrocarbon Dienes

The Pd-catalyzed linear dimerization of butadiene or isoprene in the absence of trapping reagent affords the linear dimer 1,3,7-octatriene (**4**) or its methylated derivative.^{[29],[35]–[37]} Hagihara and co-workers^[38] originally reported that, in the absence of trapping reagent, treatment of butadiene with the bis(triphenylphosphine)(maleic anhydride)palladium(0) complex (0.01 mol %, acetone, 115 °C) affords 1,3,7-octatriene in 85% yield. Nickel^{[39]–[43]} and cobalt^[44] catalyst systems have also been described.

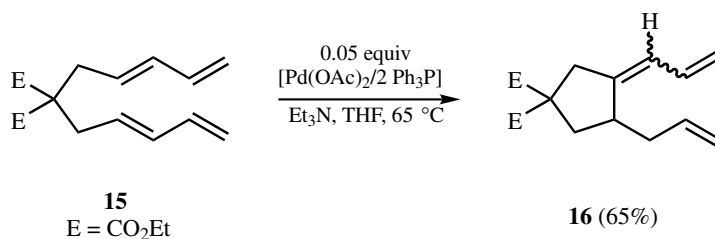
Mechanistically, this reaction can be understood on the basis of the Jolly mechanism. As before, oxidative coupling affords the palladacycle **12**, and protonation (adding H_a^+ in an $S_{E2'}$ fashion) leads to the chelated π -allyl intermediate **13**. In the absence of a good nucleophile, **13** loses proton H_b to afford a palladium(0) complex of the observed triene product (**Scheme 4**). It should be noted that the initially formed triene may subsequently undergo Pd-catalyzed double bond isomerization and thus in some cases product mixtures will be observed.



Scheme 4

B.ii. Intramolecular Diene Coupling of Alkyl-Substituted Dienes: Bisdiene to Enediene Cycloisomerization

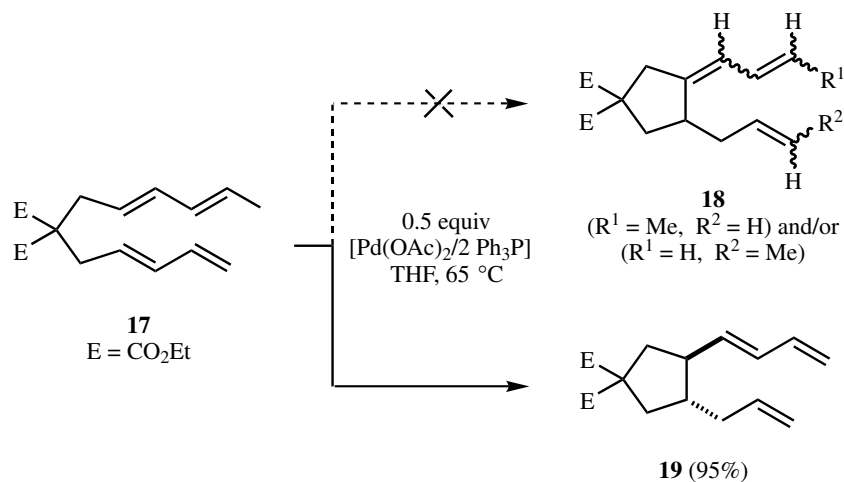
The intramolecular version of Hagihara's dimerization of 1,3-butadiene to 1,3,7-octatriene, that is, a bisdiene to enediene cycloisomerization, is also feasible. In the absence of any trapping reagent, bisdiene **15** (**Scheme 5**) undergoes Pd-catalyzed



Scheme 5

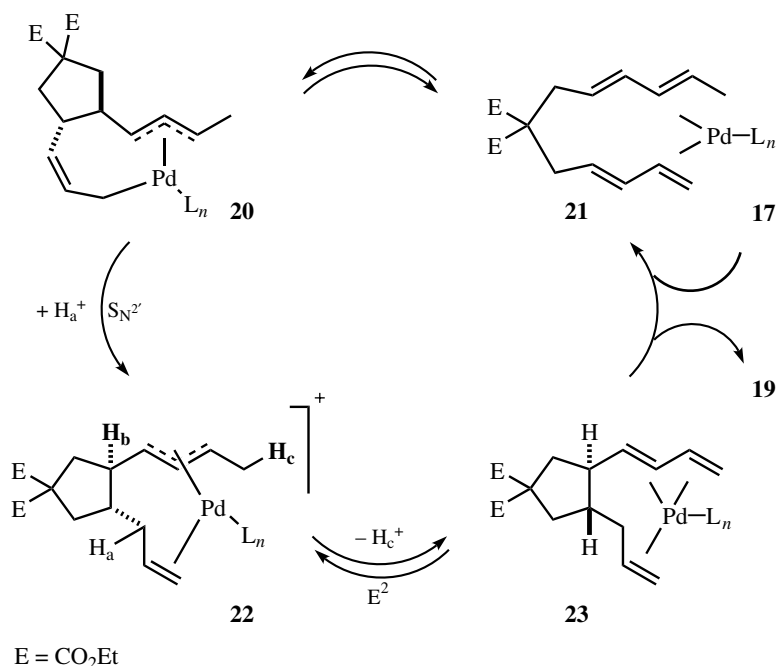
cycloisomerization to give **16** in 65% yield (0.05 equiv [Pd(OAc)₂/2 Ph₃P], Et₃N, THF, 65 °C).^{[45],[46]} This reaction, however, is not particularly facile under the conditions examined. The enediyne **16** is formed as a 1:1 mixture of diastereomers, and although in some cases one of the diastereomers was formed preferentially, the cycloisomerization of the homologous bisdiene leading to a six-membered ring compound proceeded in lower yield.

At first glance bisdiene substrates in which the two 1,3-diene subunits are substituted differently (e.g., **Scheme 6**, **17**) appear to be improper candidates for Pd-catalyzed cycloisomerization, as they would probably lead to a mixture of isomers (e.g., **18**). This is known for the linear dimerization of simple substituted 1,3-dienes (e.g., isoprene or piperylene). The attempted selective cross-coupling of different 1,3-dienes usually affords a complex mixture of isomeric products (*vide infra*). Nonetheless, the Pd-catalyzed cyclization of bisdiene **17** does not form any of the isomeric **18** structures, but instead affords the single enediyne **19** in near quantitative yield (95%).



Scheme 6

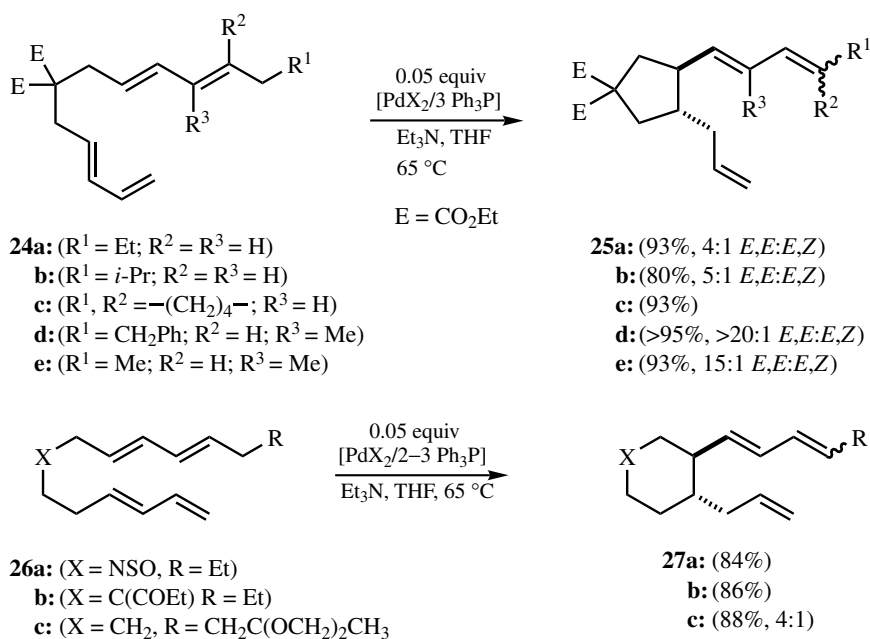
This conversion of an acyclic bisdiene to a cyclized enediyne constitutes a new Pd-mediated reaction mode, which can be rationalized as outlined in **Scheme 7**. Complexation of bisdiene **17** following oxidative cyclization (i.e., oxidative addition with intramolecular coupling of the diene moieties) affords palladacycle **20**. Protonation in an



Scheme 7

S_E2' fashion (labeled H_a in structure **22**) leads to the chelated π -allylpalladium intermediate **22**, which can potentially lose either of two protons (labeled H_b and H_c in structure **22**) to afford either **18** or **19**, respectively. From recent work in the literature, notably that of Krafft and co-workers,^{[47],[48]} it is recognized that chelated π -allylpalladium intermediates can show unusual regioselectivity in addition reactions. Perhaps related factors govern the regioselective loss of H_c to afford intermediate **23** and, ultimately, the enediene product **19**; there is evidence suggesting that loss of proton H_c occurs via an E2 rather than β -hydride elimination pathway.^{[46],[49]}

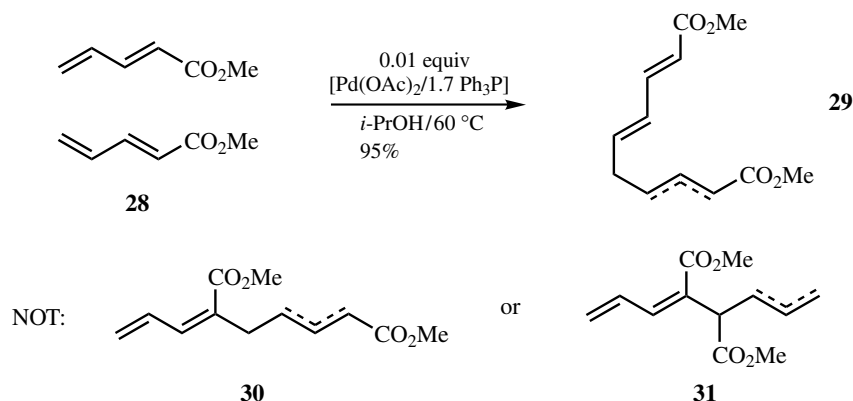
The Pd-catalyzed bisdiene to enediene cycloisomerization appears to be reasonably general. A variety of palladium catalyst precursors can be employed ([Pd(OAc)₂/2 Ph₃P] and [(MeCN)₂Pd(BF₄)₂/2 Ph₃P] appear to be quite generally applicable), and as illustrated by the reactions summarized in **Scheme 8**, five- and six-membered carbocyclic and heterocyclic ring systems are generally formed in high yields and with high diastereoselectivities. For both ring sizes, the cyclization establishes the *trans* configuration between the unsaturated side chains on the newly formed ring. Control over the double bond configurations can be high, although in some cases, mixtures arise from the failure to control the configuration of the double bond most remote from the newly formed C—C bond (e.g., **25a-b**). In such cases, an additional diene substituent can help control the geometry (e.g., **25d-e**). In general, electron-donating substituents on the diene slow down the rate of cycloisomerization. Labeling studies show that the hydrogen lost (i.e., H_c in **Scheme 7**) is not transferred intramolecularly (i.e., $H_a \neq H_c$), and a large isotope effect associated with the loss of H_c suggests that deprotonation rather than β -hydride elimination is mechanistically important.



Scheme 8

B.iii. Intermolecular Diene Dimerization: Influence of Ester Substituents

While the intermolecular reactions of butadiene and related methyl or simple alkyl-substituted dienes have been investigated extensively, relatively few examples of the Pd-catalyzed linear dimerization of higher dienes have been reported. Brun and co-workers^[50] in an isolated paper reported that, under palladium catalysis, reaction of methyl 2,4-pentadienoate (**Scheme 9**, **28**) affords the linear dimer **29** in high yield (95%). Two aspects of this reaction are of particular interest. (i) The dimerization yields essentially only the tail-to-tail dimer **29**, not the head-to-tail or head-to-head isomers (**30** or **31**, respectively). This is in contrast to the behavior of alkyl-substituted dienes under similar conditions (*vide infra*). (ii) Although no details are given, the authors imply that **29** is

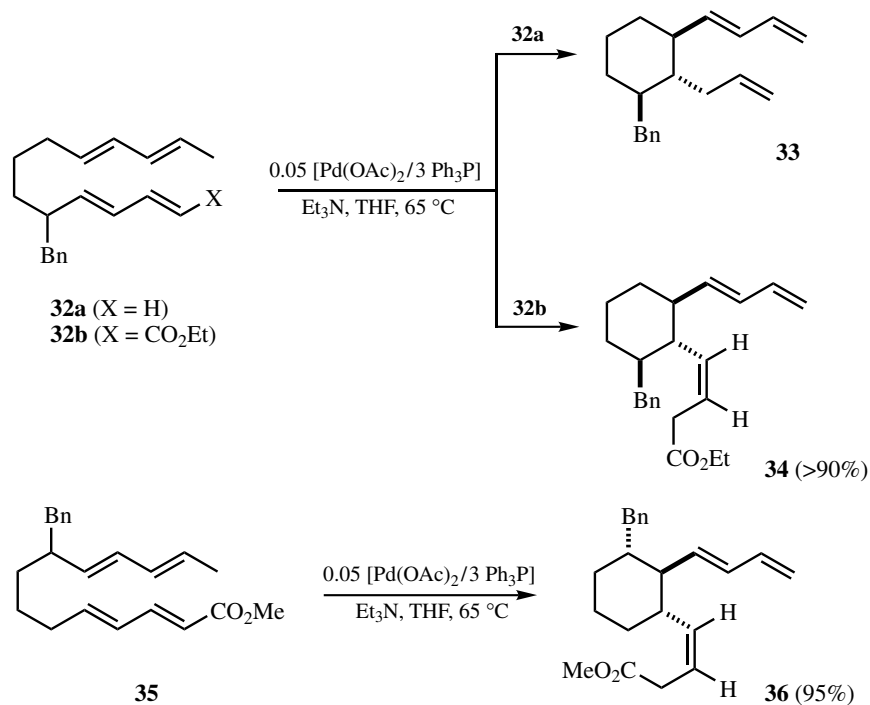


Scheme 9

formed as a mixture of α,β - and β,γ -unsaturated isomers, an aspect of regiochemistry that will be important in the intramolecular case.

B.iv. Intramolecular Diene Coupling: Influence of Ester Substituents

Pd-catalyzed cyclization of bisdiene **32a** ($X = H$) affords enediene **33**. Related bisdienes bearing an ester substituent undergo facile cycloisomerization via a complementary reaction pathway. For example, bisdiene **32b** ($X = CO_2Et$) undergoes Pd-catalyzed cycloisomerization (0.05 equiv $[Pd(OAc)_2/3 Ph_3P]$, 5 equiv Et_3N , THF, 65 °C, 12 h) to afford product **34** in high yield (>90%) and good diastereomeric purity (>90%).^[51] As in the case of **33**, the three substituents on the cyclohexane core in product **34** have predominantly the *trans,trans* relationship, and the diene side chain is formed with the (*E*) configuration. The β,γ -unsaturated ester moiety in **34** is formed selectively with a (*Z*) double bond (Scheme 10) and a deconjugated ester moiety, somewhat reminiscent of the kinetic protonation of an extended enolate and of the Brun reaction of methyl 2,4-pentadienoate discussed above.



Scheme 10

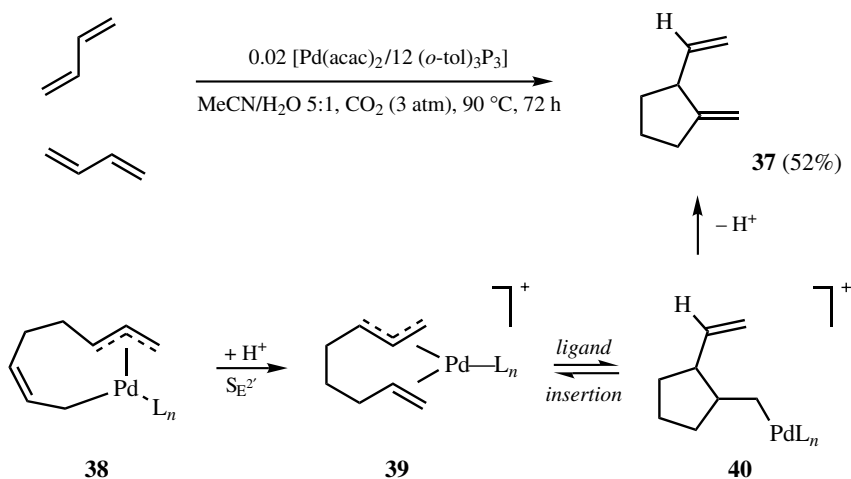
Bisdiene **35** bears a complementary substitution pattern to that of **32b**; that is, the benzyl substituent resides adjacent to the methyl-bearing 1,3-diene moiety. Bisdiene **35** also cyclizes smoothly under the conditions employed for **32b** and affords compound **36** in high yield (95%), and with good diastereoselectivity (>90% diastereomeric purity). Thus, bisdienes bearing an ester substituent undergo facile Pd-catalyzed cycloisomerization via a pathway that complements that found for substrates without the ester substituent. This defines a new bond construction that is inaccessible by classical

methods. The cyclization proceeds with good to excellent levels of stereoinduction relative to a resident asymmetric center in the bisdiene substrate and defines another control element that efficiently directs the cyclization of an unsymmetrical substrate.

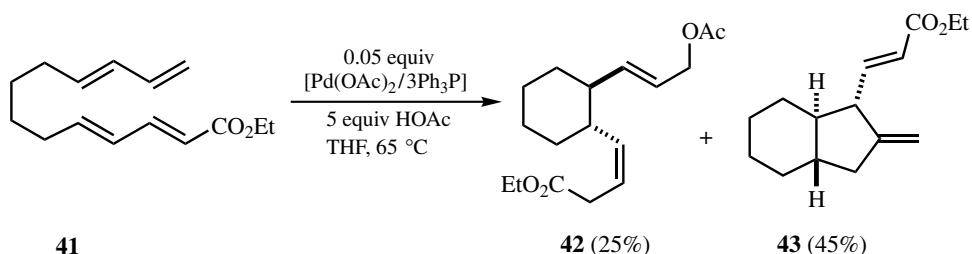
B.v. A Novel Formal [3 + 2] Cycloaddition Mode

Bergamini et al.^[52] reported an unusual variation on the linear dimerization, wherein Pd-catalyzed dimerization in acetonitrile/water and in the presence of CO₂ affords **37** selectively (52% yield, turnover number (TON) = 420). Under these conditions, only small amounts of the water-trapped product and 1,3,7-octatriene are observed as side products (**Scheme 11**). The formal intramolecular [3 + 2] cycloaddition product **37**, particularly the 1,4-diene subunit imbedded in it, is reminiscent of the products obtained from cyclization of η^3 -allylpalladium intermediates onto pendant alkenes, a process termed a “palladium-ene reaction” by Oppolzer and Gavdin,^[53] which has also been investigated by Negishi et al.^[54] and Trost and Luengo.^[55] One can account for the formation of **37** from the chelated π -allylpalladium intermediate **39** by ligand insertion to **40** followed by β -hydride elimination.

A similar cyclization mode has been observed in the intramolecular reaction of an ester-substituted bisdiene. Treatment of bisdiene **41** with 0.05 equiv of [Pd(OAc)₂/2 Ph₃P] and 5 equiv of acetic acid (THF/65 °C) affords the acetic acid-trapped product **42** (25% yield) and the [3 + 2] cycloaddition product **43** (45% yield) (**Scheme 12**).^[56]



Scheme 11

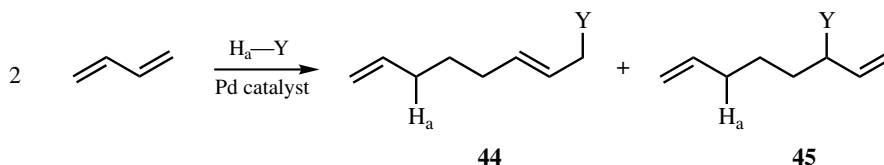


Scheme 12

C. DIENE DIMERIZATION WITH INCORPORATION OF A PROTIC H—Y TRAPPING REAGENT

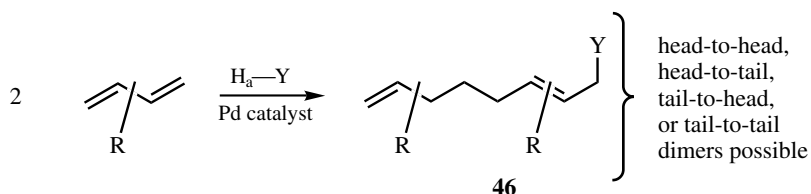
C.i. Introduction

Simple 1,3-dienes, such as 1,3-butadiene and isoprene, undergo efficient metal-catalyzed linear dimerization with incorporation of an appropriate protic H—Y trapping reagent to afford functionalized octadienes, typically as a mixture of predominantly the 1-substituted 2,7-octadiene **44** and minor amounts of the 3-substituted 1,7-octadiene isomer **45** (Scheme 13). The process, originally termed diene telomerization, was discovered in 1967 independently by Smutny^[57] and by Hagihara and co-workers.^[38] The original reports employed soluble palladium complexes as the metal catalyst precursor; however, subsequently a variety of metals, including nickel, platinum, cobalt, rhodium, and iridium, have been shown to catalyze this mode of diene dimerization.^{[28],[29]} However, among these, palladium is generally the metal catalyst of choice.



Scheme 13

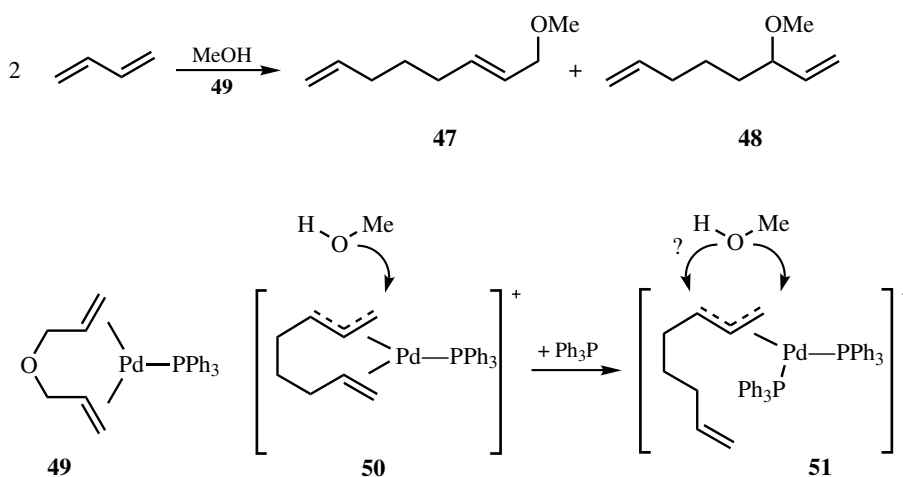
In exploring this mode of dimerization a number of issues have attracted significant attention. These include (i) the search for new protic trapping reagents (H—Y); (ii) the search for new catalysts and catalyst precursors, including enantioselective catalysts; (iii) studies directed toward defining the factors controlling the distribution of regioisomeric products **44** and **45** and controlling the distribution; (iv) studies directed toward defining the factors controlling the distribution of head-to-head, head-to-tail, tail-to-head, and tail-to-tail regioisomeric products **46** (Scheme 14) obtained from the intermolecular dimerization of unsymmetrical dienes and controlling their distribution; (v) studies directed toward defining the factors controlling the intermolecular dimerization of bisdienes; and (vi) using the Pd-catalyzed linear dimerization reaction in natural products synthesis. Recent progress toward addressing each of these issues will be discussed in the sections below, organized according to the nature of the protic H—Y trapping reagent employed: alcohols and phenols; water; carboxylic acids; formic acid; amines, amides, imides, and sulfonamides; sulfinic acids; doubly activated C—H acidic compounds; enamines; nitroalkanes; and carbon monoxide/alcohol (“H—CO₂R”).



Scheme 14

C.ii. Alcohols and Phenols as H—Y Trapping Reagents: Intermolecular Diene Dimerization

The Pd-catalyzed telomerization of butadiene and isoprene with alcohols, diols, and phenols continues to attract significant attention.^{[58]–[64]} A recent detailed study by Beller and co-workers offers new insights into the reaction of butadiene with methanol and highly optimized conditions for the selective formation of 1-methoxy-2,7-octadiene (**Scheme 15, 47**).^[16] The authors find that palladium(0) complex **49**^[17] is an excellent catalyst for the dimerization–trapping reaction of butadiene with methanol, the catalyst being active even at $-10\text{ }^{\circ}\text{C}$. Finding a convenient source of a palladium(0)–monophosphine complex is a very significant advance in this field, and one can expect that this catalyst system will find widespread use.



Scheme 15

Beller and co-workers find that the ratio of **47** to **48** is influenced by the reaction temperature, the ligand to metal ratio, and the ratio of methanol to butadiene. A high **47/48** ratio can be obtained at relatively low temperature with one phosphine per palladium and a 1:2 methanol/butadiene ratio. For example, at $30\text{ }^{\circ}\text{C}$ (2.5 h, 36% conversion, $\text{TON} = 1376$, turnover frequency (TOF) = 556 h^{-1}), the **49**-catalyzed reaction affords 34% combined yield of **47** and **48** in a 36:1 ratio. Addition of a second equivalent of phosphine per palladium decreases the regioselectivity (12:1 **47/48**). The authors suggest that disruption of the chelated π -allylpalladium intermediate **50** by displacement of the complexed alkene by the second phosphine to **51** accounts for the lower regioselectivity. At $90\text{ }^{\circ}\text{C}$, impressive TON of 10,500 and TOF of $21,000\text{ h}^{-1}$ are observed, although at higher temperature formation of 1,3,7-octatriene competes more effectively and comprises 23% of the product mixture.

Carlini and co-workers carefully studied the influence of a series of mono- and diphosphines on the $\text{Pd}(\text{dba})_2$ -catalyzed reaction of butadiene and methanol.^[22] With monophosphines (2:1 phosphine: $\text{Pd}(\text{dba})_2$) it was found that more basic ligands afford more active catalysts; for example, the catalyst activity increases in the series: $\text{Ph}_3\text{P} < \text{Ph}_2\text{PBu} < \text{PhPBu}_2 < \text{PBu}_3$. Bu_3P , $(\text{C}_6\text{H}_{11})_3\text{P}$, and $(i\text{-Pr})_3\text{P}$ afford catalysts of comparable activity;

however, steric effects influence the ratio of trapping to formation of 1,3,7-octatriene. The latter two ligands afford about 80% trapping, while Bu₃P affords 97% trapping product. In each case, the regioselectivity of trapping is high. A series of bidentate diphosphine ligands (dppm, dppe, dppp, and dppb) were also examined. The most strongly chelating ligands (dppe and dppp) gave the least active catalysts. In comparing the weakly chelating ligand dppb to the bridging ligand dppm, the former gives a higher TON and TOF (3310 and 1240 h⁻¹, respectively). Using the dppb catalyst, other primary alcohols (ethanol, *n*-propanol, *n*-hexanol) also react with butadiene; albeit somewhat slower (25–50% slower than methanol) and with lower selectivity for trapping relative to 1,3,7-octatriene formation.

In addition to the Beller catalyst system discussed above, several new catalysts have been introduced for the reaction of butadiene with methanol. For example, a number of cationic palladium complexes have been investigated. Basato and co-workers found that $[(\eta^3\text{-allyl})\text{Pd}((o\text{-C}_6\text{H}_4\text{NMe}_2)\text{PPh}_2)]\text{PF}_6$ and $[\text{Me}(\text{Ph}_3\text{P})\text{Pd}(o\text{-C}_6\text{H}_4\text{NMe}_2)\text{PPh}_2]\text{OTf}^-$ afford good catalysts, the former slightly better for the dimerization of butadiene with trapping by methanol.^[21] Good TON and TOF numbers (1700 and 466 h⁻¹, respectively) were observed for the former catalyst when activated by the addition of sodium methoxide. The aminophosphine ligand $((o\text{-C}_6\text{H}_4\text{NMe}_2)\text{PPh}_2)$ is thought to play an important role in catalyst stability, and the 1:1 combination of Pd(dba)₂ plus $(o\text{-C}_6\text{H}_4\text{NMe}_2)\text{PPh}_2$ affords an even more active catalyst. A similar conclusion regarding ligands was reached by Carlini and co-workers in comparing a series of P—O, N—N, and P—N bidentate ligands to diphosphines. For the butadiene–methanol reaction, these authors found the P—N ligands to be the best, and, in particular, a 1:1 combination of Pd(dba)₂ plus 2-diethylphosphino-1-methyl-imidazole was especially promising.^[65] Tkatchenko and co-workers reported that other cationic palladium complexes (e.g., $[(\eta^3\text{-allyl})\text{Pd}(\text{ligand})_2]^+ \text{X}^-$ (X = PF₆, ClO₄, BF₄) afford a greater percentage of higher oligomers (principally C₁₆ and C₂₄) from the reaction of butadiene with alcohols and other protic trapping reagents.^{[66],[67]} Certain cationic palladacyclic complexes behave similarly.^[68]

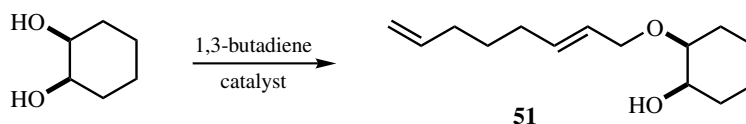
Water-soluble^{[63],[69],[70]} or polymer-bound phosphorus ligands have been examined for their potential use as recoverable metal catalysts for diene dimerization.^{[71]–[78]} For example, diphenylphosphinite functionalized cellulose binds palladium(II) chloride, which upon reduction with hydrazine forms a polymer-bound reduced palladium catalyst suitable for the linear dimerization of butadiene with methanol in benzene (97% yield).^[72] A recent study by Carlini and co-workers into the potential of polymer-bound diphosphines showed that while a polymer-bound dppp catalyst system exhibited modest catalytic activity, an analogous polymer-bound dppm catalyst system showed quite good activity for the Pd-catalyzed reaction of butadiene with methanol (TON = 199 h⁻¹). The activity is comparable to that of the corresponding soluble catalyst system (TON = 217 h⁻¹).^{[79],[80]} The authors conclude the catalyst is working as a real heterogeneous catalyst with significant potential for dimerization–trapping as well as for other Pd-catalyzed reactions.

The linear dimerization of isoprene with alcohols also continues to be of interest.^{[27],[81]–[85]} A rough correlation between the yield of octadienyl ether and the acidity of the alcohol was noted.^[84] Thus, trifluoroethanol (pK_a 12.39) and methanol (pK_a 15.09) give high yields; ethanol (pK_a 15.93), *n*-propanol (pK_a 16.1), and *n*-butanol (pK_a 16.1) give moderate yields; while *tert*-butyl alcohol (pK_a > 19) does not afford a linear dimer.

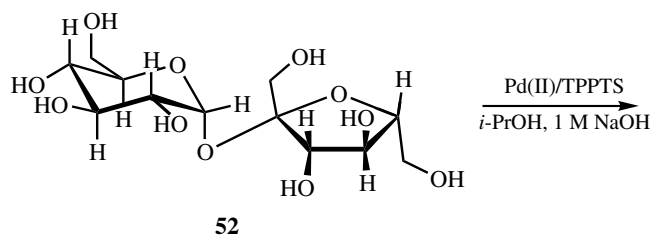
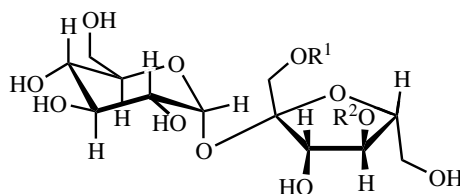
C.ii.a. Polyols. *cis*-1,2-Cyclohexanediol reacts with excess butadiene in the presence of the catalyst system [Pd(acac)₂-Ph₃P-Et₃Al] in (*tert*-BuOH, 100 °C, 10 h) to afford the

hydroxy ether **51** (Scheme 16) in 93% yield. Surprisingly, no bis(ether) formation is observed, and under forcing conditions the 2,7-isomer apparently isomerizes to the 1,7-isomer.^[60] The reaction with ethylene glycol proceeds similarly.^[71]

Two recent studies have examined the selective monoalkylation and polyalkylation of sucrose (Scheme 17, **52**). Using Pd(acac)₂/Ph₃P, sucrose was efficiently polyalkylated with butadiene in 4:1 isopropanol/water to give a mixture of 2,7-octadienyl ethers averaging 4–5 ether linkages per sucrose.^[86] While conditions for polyalkylation were found, Mortreux and co-workers also reported an alternative set of conditions that favor selective monoalkylation.^[69] Treatment of sucrose (**52**) with Pd(OAc)₂/3 TPPTS (TPPTS = tris(*m*-sulfonatophenyl)phosphine) in 5:2 isopropanol/1 M NaOH (80 °C, 30 min, 73% conversion) afforded a 2:1 mixture of mono- and diethers, from which monoethers **53a** (65%) and **53b** (18%) were isolated. The reaction is of interest for its selective alkylation, the use of a water-soluble catalyst system, and the observation that NaOH acts as a strong activator for the reaction.



Scheme 16

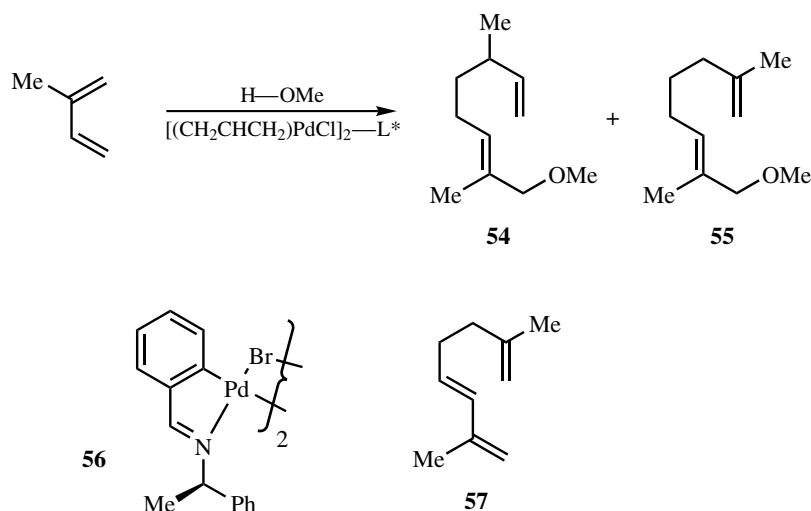
**52**

53a: (R¹ = C₈H₁₂, R² = H) (65%)

53b: (R¹ = H, R² = C₈H₁₂) (18%)

Scheme 17

C.ii.b. Enantioselective Catalysis. Hidai et al.^[87] reported enantiomeric excesses of up to 35% in a widely cited study on the influence of certain chiral phosphines in the linear dimerization of isoprene with methanol. The tail-to-head product **54** (Scheme 18) predominates (2–5:1) over the tail-to-tail isomer **55**. According to the model presented above, in this case the enantiomer ratio is set in the protonation step of the catalytic cycle



Scheme 18

(i.e., **Schemes 3, 10, and 11**). Menthyl-diisopropylphosphine affords the highest enantioselectivity in this reaction ($\text{MenP}(i\text{-Pr})_2$, 2:1 **54/55**, 35% ee for **54**), although the yield of dimers is low (14%). MenPPh_2 gives higher yields (93%) and 29% ee for **54** (2:1 **54/55**). $\text{MenP}(\text{OPh})_2$ gives an 8% ee (60% yield, 5:1 **54/55**), and *neo*- MenPPh_2 gives 13% ee (58% yield, 4:1 **54/55**).

Dupont and co-workers reported similar studies on the dimerization of isoprene with trapping by methanol (isoprene, methanol, dichloromethane, 0.1% [Pd–phosphine catalyst]; 1.3 mol% NaOMe, 25 °C, 72 h).^[88] Modest levels of enantiomeric excess were observed. These workers investigated a series of chiral ligands (i.e., (+)-neomenthyl-di-phenylphosphine ((+)-nmdpp) $\text{Ph}_2\text{P}(O\text{-menthyl})$; (*S*)-1-[(*R*)-2-diphenylphosphino]ferrocenyl]ethyl dimethylamine ((*S,R*)-ppfa), (*R*)-BINAP, (*S,S*)-DIOP, and sparteine) with four different catalyst precursors (i.e., $[(\text{MeCN})_4\text{Pd}][\text{BF}_4]_2$, $[(\text{PhCN})_2\text{PdCl}_2]$, $\text{Pd}(\text{dba})_2$, and the novel palladacycle **56**). None of the catalyst/ligand combinations surveyed gave acceptable TOFs, rates ranging from only 0.6 to 18.1 h^{-1} , and the results were largely independent of catalyst precursor. In general, the selectivity for **54** over **55** was greater than 4:1, but the enantioselectivity for the formation of **54** was always low. The ligand (+)-nmdpp achieved the highest ee, 10–12% when used in combination with $[(\text{MeCN})_4\text{Pd}][\text{BF}_4]_2$, $[(\text{PhCN})_2\text{PdCl}_2]$, or $\text{Pd}(\text{dba})_2$. Sparteine in combination with $[(\text{MeCN})_4\text{Pd}][\text{BF}_4]_2$ gave only 2% conversion and afforded predominantly 2,7-dimethyl-1,3,7-octatriene (**57**) rather than methyl ethers. Palladacycle **56** was said to be an efficient catalyst only in the presence of added phosphine; for example, in the presence of Ph_3P (21% conversion, 67:22 **54/55** (plus octatrienes), **54** in 2% ee). Recent studies have also been reported by Keim et al.^{[89]–[91]}

C.iii. Alcohols and Phenols as H—Y Trapping Reagents: Intramolecular Diene Coupling

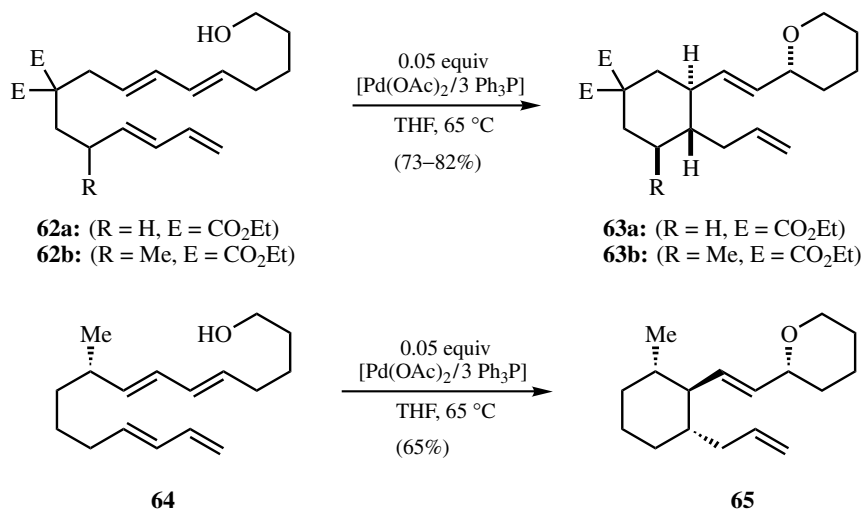
Bisdienes **58** undergoes Pd-catalyzed cyclization and trapping by phenol (0.05 $[\text{Pd}(\text{OAc})_2]/2 \text{ Ph}_3\text{P}$, 5 PhOH, THF, 65 °C) to give **59a** in 94% yield.^[92] Note the regioselective

yield (73%) (Scheme 19).



trans/cis diastereoselectivity.

Intramolecular six-membered ring formation is also efficient. Treatment of bisdiene **62a** with 0.05 equiv of a [Pd(OAc)₂]/3 Ph₃P] mixture in THF (65 °C, 24 h) affords the cyclized and intramolecularly trapped diene **63a** in good chemical yield (82%) and with good diastereoselectivity (9:1 mixture of two diastereomers) (**Scheme 20**).^[95] The conversion of **62a** to **63a** is a unique cascade cyclization in that it constructs two new six-membered rings via the net 1,4-addition of the elements carbon and oxygen across a diene subunit. Three stereochemical elements are controlled in the cyclization of **62a** to **63a**. Two of these elements, the (*E*)-configuration of the double bond and the *trans*

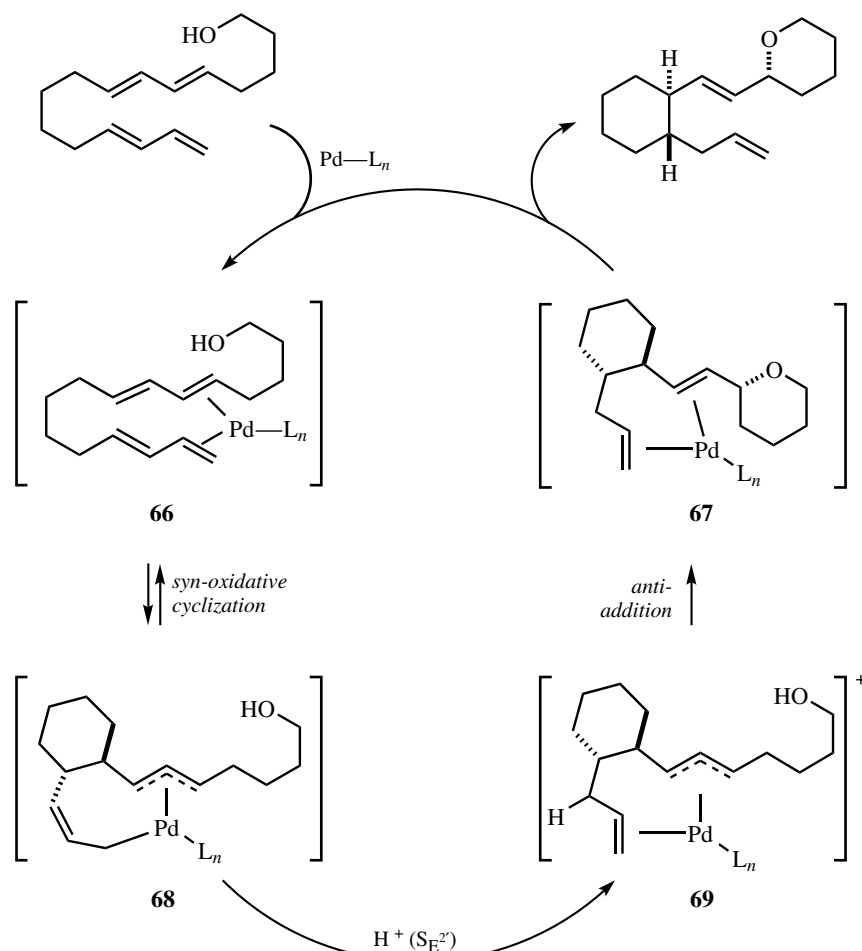


Scheme 20

relationship between the substituents on the newly formed cyclohexane ring, are easily established on the basis of spectral data and their control is consistent with results obtained in other Pd-catalyzed bisdiene cyclizations with intermolecular trapping by alcohols. The third element, the relative orientation between the newly formed carbon–carbon and carbon–oxygen bonds, could arise either via the net *anti*-1,4-addition (as depicted in **5**) or the net *syn*-1,4-addition of carbon and oxygen across the internal diene moiety.

The sense of the 1,4-stereochemical control was established by the Pd-catalyzed cyclizations of the chiral bisdiene **62b** and **64** (Scheme 20). The Pd-catalyzed cascade cyclization of the racemic bisdiene **62b** (0.05 [Pd(OTFA)₂]/3 Ph₃P], THF, 65 °C) gives comparable results to that obtained for **62a**. The cyclized product **63b** is obtained in 73% yield. Cyclization of **62b** also proceeds with the Pd(OAc)₂ catalyst mixture, but a relatively large amount (ca. 30%) of the enediene cycloisomerization product (Scheme 8) is formed. It is possible that the less basic trifluoroacetate counterion suppresses the competing cycloisomerization pathway. The stereocenter in bisdiene **62b** resides adjacent to the lower diene subunit, and the cyclization proceeds with a high level of 1,2-stereinduction (>20:1) relative to that resident stereocenter. Similarly, Pd-catalyzed cyclization of (*S*)-**64** (0.05 [Pd(OAc)₂]/3 Ph₃P], THF, 65 °C, 24 h) proceeds with a high level of 1,2-stereinduction (>20:1) from the resident methyl-bearing stereocenter. The only cyclized product isolated is **65** (65% yield), although under these conditions 35% unreacted starting material is recovered. Nonracemic **65** was used to establish the net *anti* sense of 1,4-stereocontrol during the Pd-mediated cyclization. Ozonolysis (CH₂Cl₂/EtOH, –78 °C) followed by treatment with NaBH₄ (CH₂Cl₂/EtOH, 25 °C) yielded tetrahydropyran-2-methanol for which the sign of the optical rotation indicated the (*R*) absolute configuration.

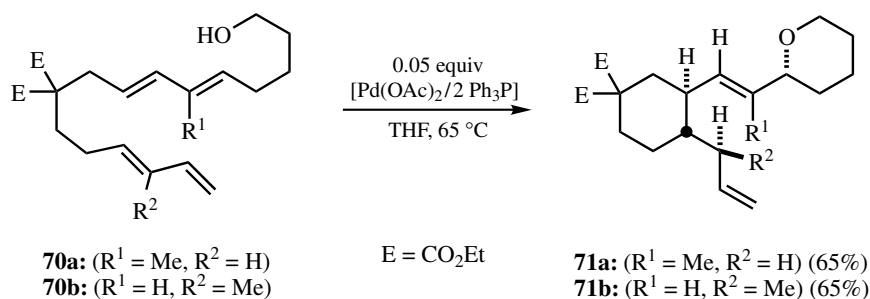
The catalytic cycle in Scheme 21 is adapted from that proposed by Jolly et al.^[11] for the dimerization of 1,3-butadiene with intermolecular trapping as discussed above. In the model the bisdiene coordinates around a reduced palladium center (e.g., **66**) and undergoes oxidative addition with cyclization (oxidative coupling) via the *syn*-addition of carbon and palladium across the diene to afford the intermediate palladacycle **68**. Protonation of the η^1 -allyl in an S_E2' fashion leads to the alkene complex **69**, and stereospecific *anti*-addition



Scheme 21

of the oxygen nucleophile to the η^3 -allylpalladium moiety to **67** completes the catalytic cycle. To account for the net *anti*-1,4-addition of carbon and oxygen across the diene, the addition of the oxygen nucleophile to the η^3 -allyl in **69** must be fast relative to the rearrangement of palladium between the diastereomeric faces of the η^3 -allylpalladium complex. It is speculated that the alkene complexed to palladium in the intermediate **69** plays a crucial role in slowing the rate of isomerization.

Metal-mediated cyclizations that rely on the initial complexation of an alkene or alkyne around a low oxidation state metal center are often sensitive to the presence of additional substituents (particularly electron-donating substituents), and relatively more stringent reaction conditions are often required for successful cyclization. This effect was noted in the Ni-catalyzed formal [4 + 4] cycloaddition reactions developed by Wender and Tebbe^[3] and is apparent when one compares the reported facility of Pd-catalyzed linear dimerization of 1,3-butadiene versus that of substituted 1,3-dienes.^[96] Similarly, the initial attempts at Pd-catalyzed cyclization of bisdiene **70a** (Scheme 22) were rather disappointing. Using 0.05 equiv of [Pd(OAc)₂/3 Ph₃P] (THF, 65 °C, 12 h), only a small



Scheme 22

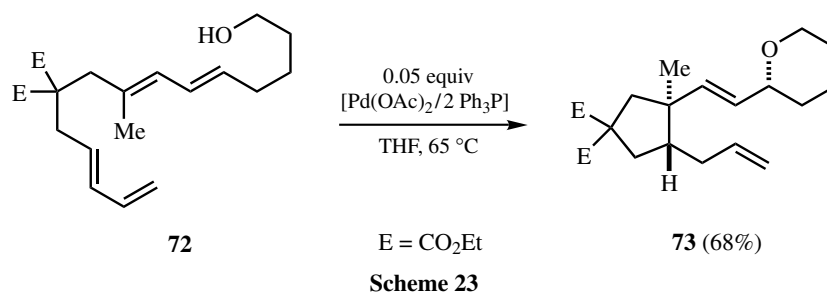
percentage reacted, and starting material was largely recovered unchanged. However, it is known that coordinately unsaturated palladium catalyst systems turn over faster in Stille coupling reactions,^[97] and the use of 2 equiv rather than 3 equiv of triphenylphosphine per palladium affords a more active cyclization catalyst. Bisdiene **70a** undergoes smooth cyclization (0.05 equiv $[\text{Pd}(\text{OAc})_2]/2 \text{ Ph}_3\text{P}$, THF, 65 °C, 12 h) affording cyclized product **71a** in 65% isolated yield and 95% diastereomeric purity.^[98] The remaining 35% of the mass is isolated as a mixture of isomeric products resulting from the bisdiene to enediene cycloisomerization pathway. The (*E*)-configuration of the newly formed trisubstituted double bond in **71a** was assigned on the basis of NOE studies. It should also be noted that the (*E*)-configuration is consistent with the working model for the catalytic cycle (Scheme 21), which assumes *transoid* η^3 -allyl-containing metallacyclic intermediates.

Upon treatment with 0.05 equiv of the $[\text{Pd}(\text{OAc})_2]/2 \text{ Ph}_3\text{P}$ mixture in refluxing THF, bisdiene **70b** cyclizes to afford product **71b** in 65% yield (97% diastereomeric purity).^[98] The methyl substitution pattern in **70b** leads to the formation of a fourth stereocenter in the cyclized product **71b** (Scheme 22). Based on the results of deuteration studies,^[99] it was anticipated that this new methyl-bearing center would be generated in a stereochemically controlled fashion. This indeed proved to be the case; the product possessed the relative configuration shown. Remarkably, the cyclization of the acyclic bisdiene **70b** generates four new stereocenters in a highly selective fashion, two of which reside exocyclic to the initially formed cyclohexane ring.

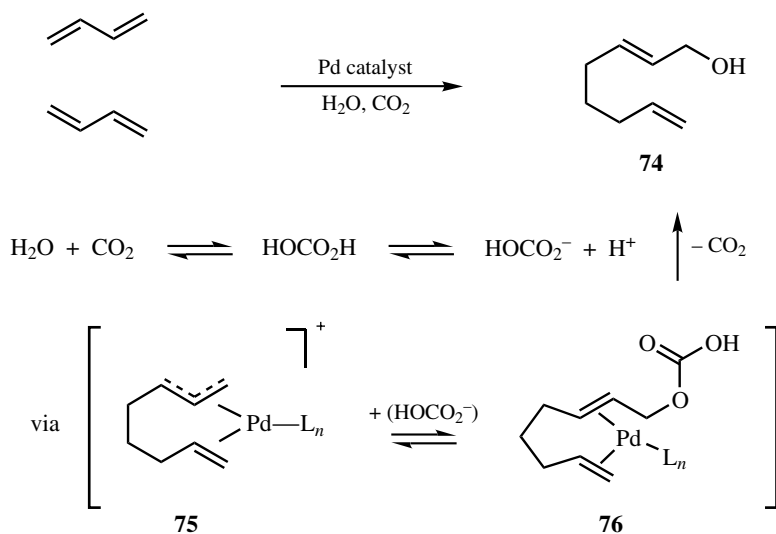
The stereocontrolled generation of quaternary centers remains a significant synthetic problem in organic synthesis.^[100] A new solution to this problem via Pd-mediated bisdiene cyclization could lead to a novel method for ultimately setting the angular methyl group at the ring fusion of a bicyclic ring system—a common structural element present in a variety of natural products. Upon treatment with 0.05 equiv of the $[\text{Pd}(\text{OAc})_2]/2 \text{ Ph}_3\text{P}$ mixture in THF (65 °C), **72** cyclizes to **73** in 68% isolated yield (94% diastereomeric purity) (Scheme 23). The successful cyclization of **72** demonstrates two important extensions of the methodology: (i) that the formation of a five-membered carbocyclic ring is efficient and (ii) that the formation of the quaternary methyl-bearing stereocenter is accomplished in a stereoselective fashion.

C.iv. Water as the H—Y Trapping Reagent

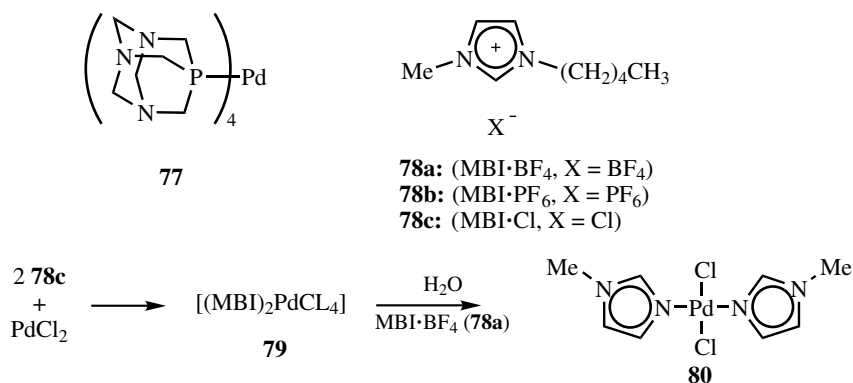
The Pd-catalyzed dimerization of butadiene^{[101]–[103]} or isoprene^{[75],[101],[104]–[106]} with trapping by water is of exceptional interest. This is especially true in the patent literature,



given the potential for a commercial route to *n*-octanol.^{[107]–[113]} The addition of carbon dioxide is reported to facilitate the reaction with water.^[101] The current postulate is that the direct addition of water to the chelated π -allylpalladium intermediate **75** is slow. The rapid equilibrium reaction between CO_2 and water affords carbonic acid and carbonate ion, and it is speculated that the carbonate ion adds to **75** to form a carbonic acid ester (**76**), which suffers decarboxylation to afford the observed 2,7-octadien-1-ol (**74**, **Scheme 24**). Minor amounts of the 1,7-octadien-3-ol isomer, 1,3,7-octatriene, and lactones are usually observed as side products.



Several interesting variations on the reaction have recently been introduced. While the reaction with water is often carried out using a sulfonated, and hence water-soluble, tri-arylphosphine, the use of a palladium(0) complex of 1,3,5-triaza-7-phosphaadamantane (**77**, **Scheme 25**) was recently reported.^[114] Monflier and co-workers reported that in addition to running the reaction under a CO_2 atmosphere, the reaction of butadiene with water is facilitated by the use of cationic^[115] or neutral (nonionic) surfactants.^[116] The role of cationic surfactants such as dodecylammonium hydroxide is conceived to be threefold:



Scheme 25

(i) to increase transport between the aqueous and the organic phase; (ii) to increase the concentration of carbonate in the organic phase; and (iii) to stabilize the palladium catalyst. In the case of the neutral surfactant, the amphiphilic nature of the addend is important. For example, reaction in the presence of $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ is superior to the reaction with no addend, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ or the PEG dimethyl ether ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_8\text{OCH}_3$). With the addition of $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$, conversion of butadiene reached 70% and the turnover number reached 230 h^{-1} . At concentrations above the critical micelle concentration, the efficiency of the surfactant-assisted reaction can be correlated to the amount of butadiene solubilized in water and, according to the authors, may result from surfactant-induced liquid-crystalline phases, association colloids, or microemulsions.

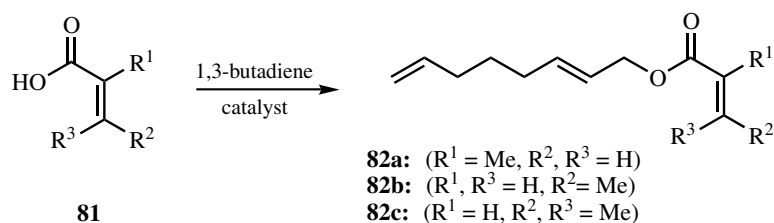
Dupont and co-workers published a very interesting study on the Pd-catalyzed reaction of butadiene with water in an ionic liquid solvent (e.g., **78a**, Scheme 25).^[117] 1-*n*-Butyl-3-methylimidazolium tetrafluoroborate ($\text{BMI} \cdot \text{BF}_4$, **78a**) is partially miscible with water at temperatures above 5°C ; water is less soluble in the corresponding PF_6 salt, **78b**. In addition, several common palladium(II) salts, for example, common diene dimerization catalyst precursors such as $\text{Pd}(\text{OAc})_2$, are soluble in **78a**. Dimerization-trapping occurs in this solvent, better in **78a** than **78b**, and the dimerization products, 2,7-octadien-1-ol and 3,6-octadien-1-ol, are immiscible below 5°C , making the product isolation via phase separation very easy. The dimerization reaction using the common palladium catalyst precursors is complicated by precipitation of palladium metal toward the end of the reaction. The authors found, however, that a new dimerization catalyst eliminates this problem. Reaction of PdCl_2 with **78c** affords complex **79**. Dissolution of **79** in ionic liquid **78a** and addition of water forms palladium complex **80**, which serves as their new dimerization catalyst. Using **79**, butadiene (28% conversion, 70°C , homogeneous reaction mixture) reacts with a TOF of 118 h^{-1} to afford 94% of the octadienol. Running the reaction under a CO_2 atmosphere (5 atm) gives 49% conversion (TOF = 204 h^{-1}) and 84% of octadienol. Given the practical advantages of this approach and the fact that the catalyst mixture was reused several times without loss of activity, the potential of this methodology seems very high.

Heterogeneous catalysis is also a very attractive alternative from an industrial perspective. Lee and co-workers reported a novel montmorillonite-supported palladium catalyst for butadiene dimerization with trapping by water.^[118] Simple solid-supported palladium(0) catalysts, such as 5% Pd/C and $\text{Pd}/\text{Al}_2\text{O}_3$, were modestly effective catalysts for

butadiene dimerization with trapping by water (surface Pd TOFs of 50–80 h⁻¹) as compared to 259 h⁻¹ for a solution phase reaction catalyzed by [Pd(OAc)₂/Ph₃P] (65 °C). Montmorillonite is a swelling-type layered silicate clay. Palladium was anchored onto montmorillonite by treating the commercially available sodium form with HCl and reacting the so-derived H–montmorillonite with 3-aminopropylethoxysilane. The resulting silane-exchanged montmorillonite was treated with Pd(OAc)₂. The resulting Pd–montmorillonite was a good catalyst for butadiene dimerization–trapping (butadiene, water, DMF, Ph₃P, CO₂ (200 psi), 65 °C, 10 h, 91% conversion) affording 77% of 1,2,7-octadienol with a TOF of 277 h⁻¹. Examining the reaction mixture after the dimerization reaction showed less than 1% palladium loss to solution, and the catalyst could be reused.

C.v. Carboxylic Acids as the H—Y Trapping Reagent: Intermolecular Diene Dimerization

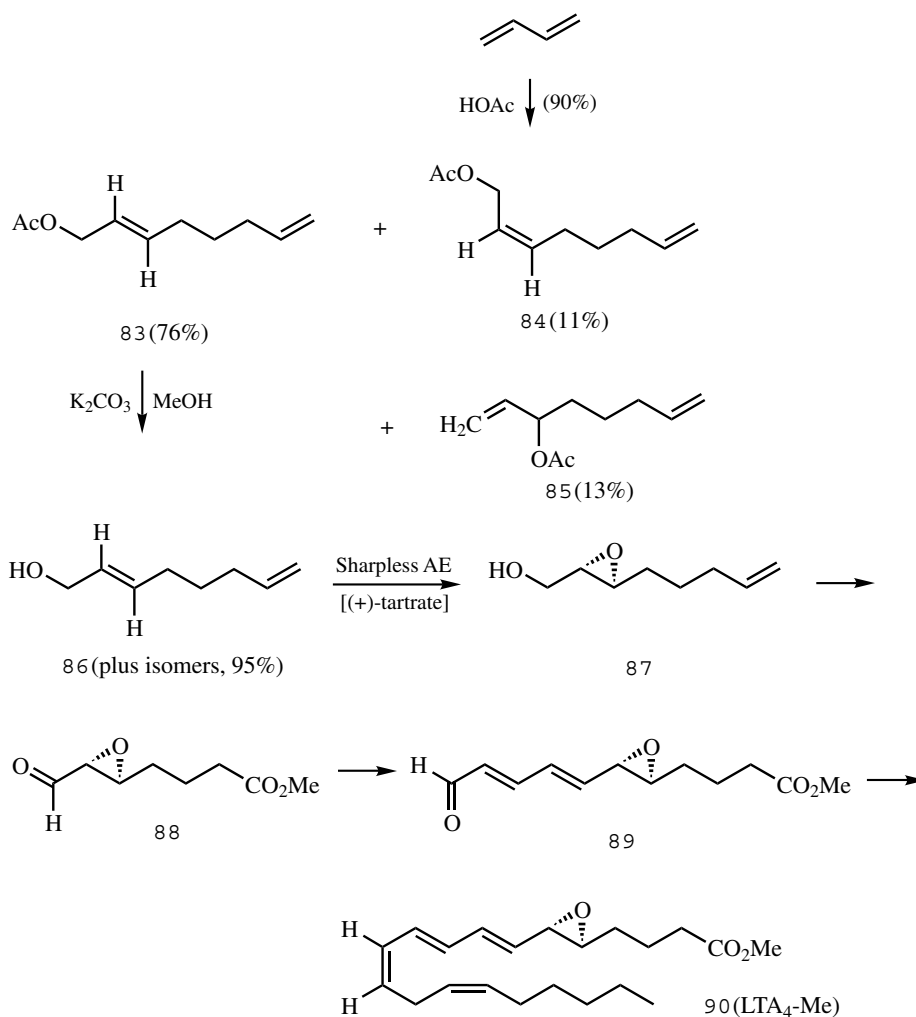
Butadiene reacts with carboxylic acids, even relatively labile carboxylic acids such as **81**, to form unsaturated esters (**Scheme 26**).^{[61],[71],[119],[120]} For example, methacrylic, β,β-dimethylacrylic, and crotonic acid react with butadiene under palladium catalysis (Pd(acac)₂/Ph₃P/Et₃Al) in THF to afford predominantly the 2,7-octadienyl esters **82** in high yields (90–95%).^[119]



Scheme 26

The product of the reaction of butadiene with acetic acid has found use in natural products synthesis. Spur and co-workers reported the total synthesis of leukotrienes starting from butadiene via its Pd-catalyzed linear dimerization with trapping by acetic acid (0.2% Pd(acac)₂, 0.2% tri(*o*-tolyl)phosphite, 3% NaOAc, 25 °C) (**Scheme 27**).^[121] These are comparatively mild conditions for butadiene dimerization; elevated temperatures are more commonly employed, but the authors report the formation of a mixture of products (90% yield) consisting of (*E*)-2,7-octadien-1-yl acetate (**83**, 76%), (*Z*)-2,7-octadien-1-yl acetate (**84**, 11%), and 1,7-octadienyl-3-acetate (**85**, 13%). It has previously been noted that, among the protic H—Y trapping reagents, carboxylic acids often give rise to a greater percentage of the isomer arising from trapping at the 3-position, and that the percentage of this isomer increases with reaction time. Observing the formation of a significant amount of (*Z*)-2,7-octadien-1-yl acetate is less common.

The mixture of isomeric acetates is converted to the corresponding mixture of alcohols and that mixture subjected to Sharpless asymmetric epoxidation. From this reaction, the chiral nonracemic epoxide **87** is isolated in 60% yield (>94% ee). Compound **87** is converted by standard transformations to **88** and **89**, ultimately affording the leukotriene methyl ester LTA₄-Me (**90**) (**Scheme 27**). A number of other leukotrienes (e.g., LTC₄, LTD₄,

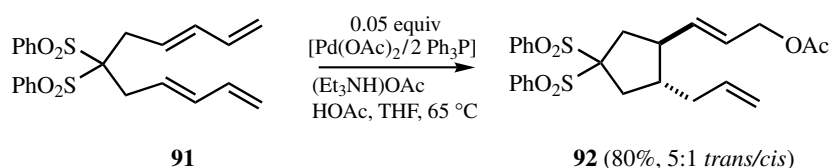


Scheme 27

LTE₄, and (14*S*,15*S*)-LTA₄ methyl ester) were also prepared from **86**. In addition, Spur and co-workers reported a conceptually similar route to lipoxins A₄ and B₄ from **86**.^[122]

C.vi. Carboxylic Acids as the H—Y Trapping Reagent: Intramolecular Diene Coupling

Due of the potential for subsequent Pd-catalyzed reaction of the allylic carboxylate product and the relatively low trapping regioselectivity reported for the intermolecular linear dimerization carboxylic acid trapping, few examples of the analogous intramolecular diene coupling followed by carboxylic acid trapping have been examined. Bisdiene **91** undergoes Pd-catalyzed cyclization in the presence of (Et₃NH)OAc and HOAc to afford predominantly the *trans*-disubstituted cyclopentane **92** (80%) (**Scheme 28**). No evidence was found for the formation of a regioisomeric allylic acetate.^[92]

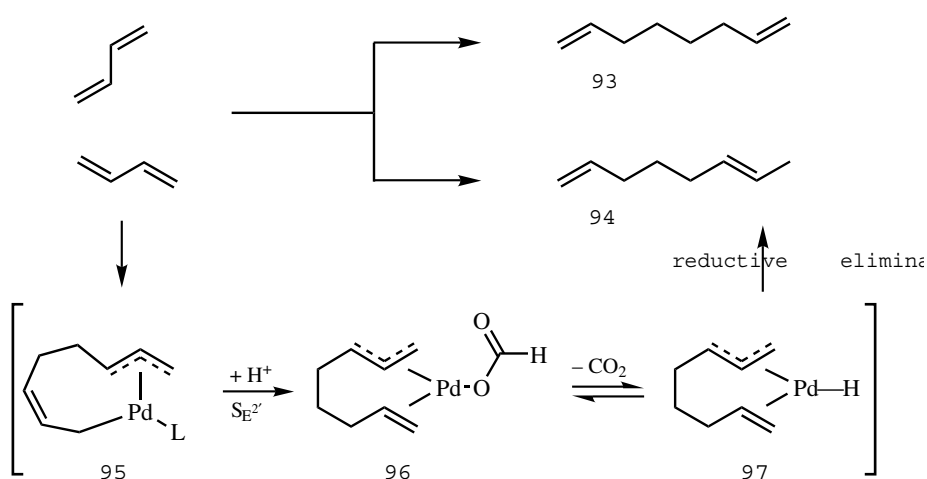


Scheme 28

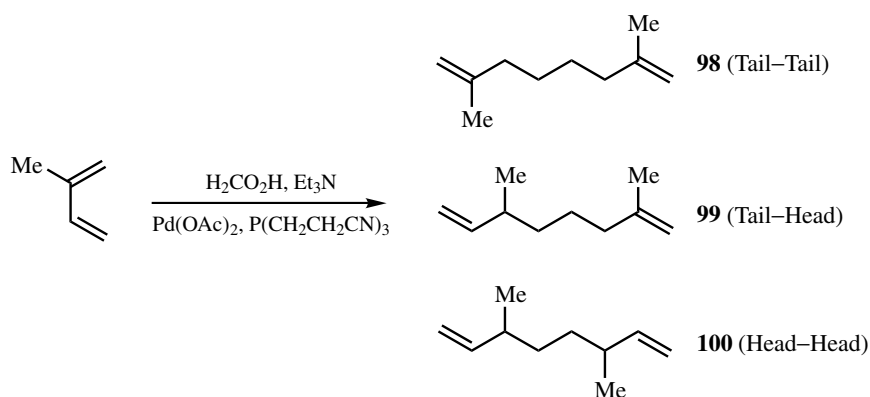
C.vii. Formic Acid as the H—Y Trapping Reagent: Intermolecular Diene Dimerization

Employing formic acid or one of its carboxylate salts as the trapping reagent effects reductive dimerization of the diene, although formation of the formate addition product has also been seen.^[123] The reaction may involve, at least under certain conditions, formation of an intermediate π -allylpalladium hydride intermediate (e.g., **97**), possibly generated from the decarboxylation of the π -allylpalladium formate **96**. For butadiene, dimerization conditions have been identified that afford either 1,7-octadiene (**93**) or 1,6-octadiene (**94**) as the reaction product (Scheme 29). 1,7-Octadiene is reported to be the near exclusive product when a phosphinated polystyrene-bound palladium(0) catalyst was used^[71] or when the reaction was carried out in solution phase using $[\text{Pd}(\text{OAc})_2/\text{Et}_3\text{P}]$.^[35] When Et_3P was omitted from the latter catalyst system or when $[\text{Pd}(\text{OAc})_2/\text{Et}_3\text{N}]$, $[\text{Pd}(\text{OAc})_2/\text{DMF}]$,^{[124],[125]} or $[\text{Pd}(\text{acac})_2/\text{Amberlyst A-21}]$ ^[123] was employed, the near exclusive product was 1,6-octadiene. While the reasons for the unusual regiocontrol in these variants is unclear, it can be suggested that recent work by Tsuji and co-workers on Pd-catalyzed reduction of allylic formates may offer some insight.^{[126],[127]}

The linear dimerization of isoprene often affords mixtures of head/tail dimers. For example, $[\text{Pd}(\text{OAc})_2, \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]$ catalyzes dimerization of isoprene with triethylammonium formate in dimethylacetamide (55 °C, 3 h), affording dimers in 97% yield as a 10:49:37 **98/99/100** mixture of head/tail coupling regioisomers (Scheme 30).^[128] It is interesting to note that, as in the case of butadiene and formic acid in the presence of phosphine-modified $\text{Pd}(\text{OAc})_2$, only 1,7-dienes are formed in this reaction of isoprene with formic acid.



Scheme 29

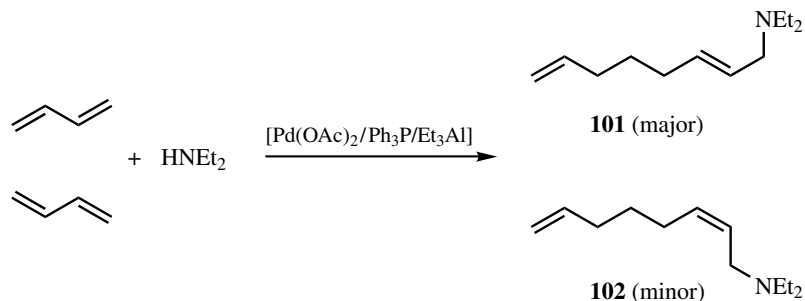


Scheme 30

C.viii. Amines, Amides, Imides, and Sulfonamides as the H—Y Trapping Reagents: Intermolecular Diene Dimerization

Butadiene undergoes efficient Pd-catalyzed linear dimerization followed by trapping with many primary and secondary amines to give predominantly 1-amino-2,7-octadienes.^{[129]–[133]} Generally, more basic amines react better.^[134] Among the more unusual amines that serve as suitable amine trapping reagents are amino alcohols,^[135] amino acids,^[136] hydroxylamines,^[137] hydrazine,^[138] aziridines,^{[139],[140]} imidazoles,^{[141]–[143]} triazoles,^[141] and pyrazolines.^[144] A range of nonbasic amine derivatives, including phthalimides,^{[145]–[147]} formamide,^{[148],[149]} and aryl- or alkylsulfonamides^{[150]–[152]} can also serve as nitrogen trapping reagents.

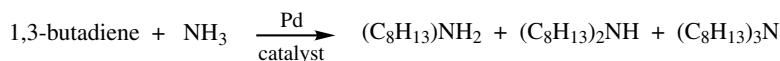
There are a number of features within this variant of protic H—Y trapping reagents that have attracted significant interest. For example, Antonsson et al.^[153] carefully examined the stereochemistry of the $\text{C}^2=\text{C}^3$ double bond as a function of catalyst composition using a $[\text{Pd}(\text{OAc})_2]$, phosphine, Et_3Al catalyst system. Using $[\text{Pd}(\text{OAc})_2]$, 2 Ph_3P without the addition of Et_3Al , a mixture of **101** and **102** with an (*E*)/(*Z*) ratio of 96:4 was obtained in 93% yield. The catalyst system $[\text{Pd}(\text{OAc})_2]$, 2 Ph_3P , 2 Et_3Al affords >99% (*E*)-product **101** in 75% yield (Scheme 31). The amount of butadiene is also important as a large excess leads to an increased amount of a C_{16} product, and a catalyst using polymer-bound phosphine gives a good (*E*)/(*Z*) ratio when the Al/Pd ratio is high. It is not clear whether



Scheme 31

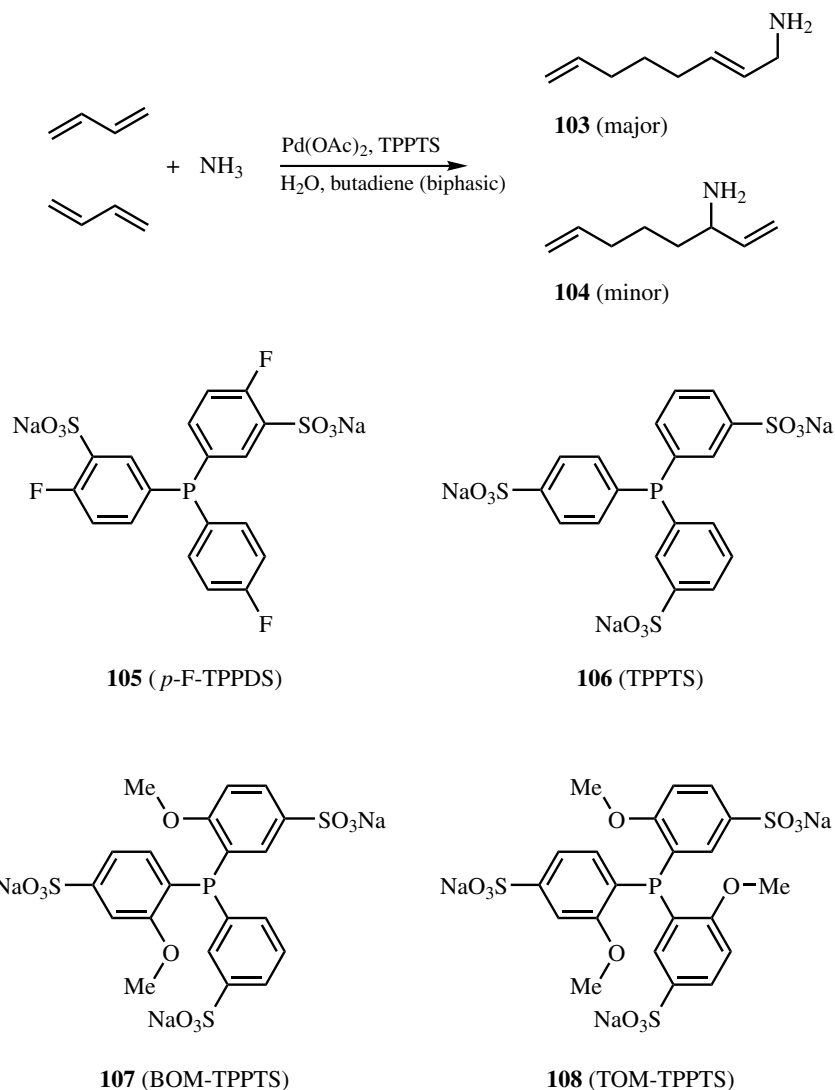
the role of Et_3Al is solely that of a reducing agent for the reduction of Pd(II) to Pd(0) or if its Lewis acidity is an important component to its success. However, other workers have found that the $\text{Pd}(\text{acac})_2$ -catalyzed reaction of butadiene with a variety of secondary amines (including diethylamine) is greatly facilitated by the addition of BF_3 .^{[154],[155]} For example, a catalyst system derived from 1:15 ($\text{Pd}(\text{acac})_2$)/ BF_3 exhibits a TOF of greater than 625 h^{-1} at 70°C and an 80% yield of **101** after 7 h at 50°C .

Generally, more basic amines are better trapping reagents than less basic ones, and consequently, the reaction of ammonia or a primary amine does not stop after the addition of one octadienyl moiety; the resulting monooctadienylated amine product reacts faster than the starting amine. Thus, for ammonia, one typically forms the tertiary octadienylamine ($(\text{C}_8\text{H}_{13})_3\text{N}$) as the major product. For example, butadiene and ammonia (10:1) undergo Pd-catalyzed reaction (1 mol % (relative to NH_3) [$\text{Pd}(\text{OAc})_2$, 3.4 Ph_3P], $t\text{-BuOH}$, 100°C , 1 h) to afford 1:2:31 ratio of mono/di/tri(octadienyl)amine (21% total yield based on ammonia) (**Scheme 32**). To improve selectivity of the mono(octadienyl)amine, Prinz et al.^[156] examined the corresponding liquid/liquid two-phase reaction. The idea behind their study is that, using a water-soluble phosphine (3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt, TPPTS), the palladium catalyst can be sequestered in an aqueous ammonia phase, while the mono(octadienyl)amine (and higher amines) will be sequestered in the organic phase. The strategy shows good potential. The biphasic reaction of butadiene and ammonia (10:1) under conditions similar to those above (1 mol % (relative to NH_3) [$\text{Pd}(\text{OAc})_2$, 4 TPPTS], 2:1 $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$, 100°C , 1 h) afforded a 21:17:1 ratio of mono/di/tri(octadienyl)amine (24% yield). Optimized conditions (75 mmol butadiene, 300 mmol ammonia, 0.15 mmol $\text{Pd}(\text{OAc})_2$, 0.6 mmol TPPTS, 20 mL H_2O , 12.5 mL toluene, 80°C , 1.5 h) afford a 13:1:0 ratio of mono/di/tri(octadienyl)amine in 55% yield.



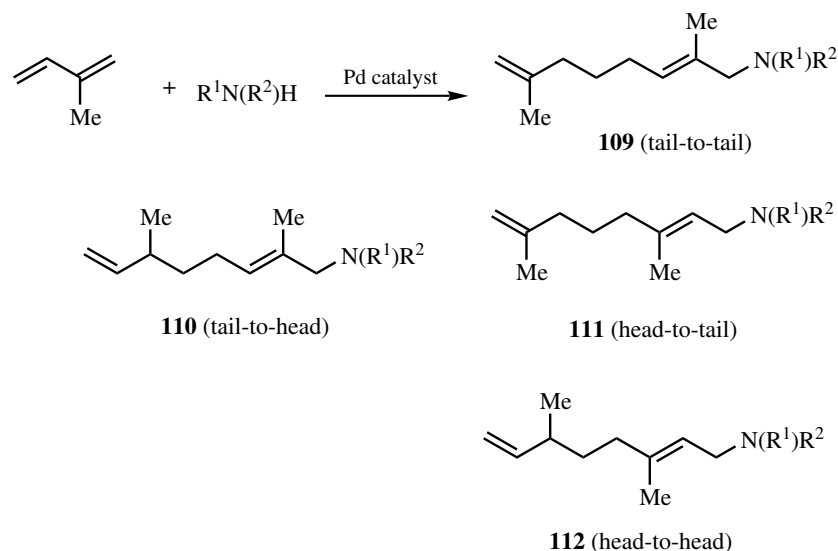
Scheme 32

As noted above, certain protic $\text{H}-\text{Y}$ trapping reagents (e.g., carboxylic acids) can give rise to a significant percentage of the isomer arising from trapping at the 3-position of the octadienyl chain. Prinz and Driessen-Hölscher^[157] examined the liquid/liquid two-phase reaction of butadiene with ammonia (a water/liquid butadiene biphasic mixture) in an effort to optimize for the selective formation of 1-amino-2,7-octadiene (**103**). They found that the reaction rate and regioselectivity (**103/104**) are a function of ammonia concentration, catalyst concentration, Pd/ligand ratio, and the nature of the ligand. A series of water-soluble ligands were screened under a standard set of reaction conditions (1:1 [$\text{Pd}(\text{OAc})_2$ /ligand], 80°C) (**Scheme 33**). The authors find a trade-off between regioselectivity and reaction rate (TOF) in this series: *p*-F-TPPDS (**105**, 1.4:1 **103/104**, TOF = 357 h^{-1}); TPPTS (**106**, 3.0:1 **103/104**, TOF = 252 h^{-1}); BOM-TPPTS (**107**, 13:1 **103/104**, TOF = 128 h^{-1}); and TOM-TPPTS (**108**, 36:1 **103/104**, TOF = 47 h^{-1}). They conclude that both steric and electronic factors influence the regioselectivity. The reactions are run under the author's biphasic conditions, and as expected from their prior studies, they proceed with high selectivity for the mono(octadienyl)amine (i.e., **103** or **104**); each of the four catalyst systems shows 6% or less of the di(octadienyl)amine product.



Scheme 33

The linear dimerization of isoprene with amines continues to be of interest; particularly with respect to controlling the four possible modes of coupling, tail-to-tail **109**, tail-to-head **110**, head-to-tail **111**, or head-to-head **112** (Scheme 34).^{[154],[158]–[164]} With amine trapping reagents the tail-to-tail mode is typically preferred, but ligands can strongly influence the ratio. For example, the linear dimerization of isoprene with *N*-methylaniline mediated by $[\text{Pd}(\text{acac})_2\text{-P}(\text{OBu})_3]$ in acetonitrile affords a 48% yield of trapped dimers of which 85% is the tail-to-tail isomer (85:5.5:9.5:1 **109/110/111/112** ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$)). In contrast, the same reaction mediated by $[\text{Pd}(\text{acac})_2/\text{Ph}_3\text{P}]$ in methanol affords a 52% yield of linear dimers of which 89% is the tail-to-head isomer (10:89:1:1 **109/110/111/112** ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$)).^[159]

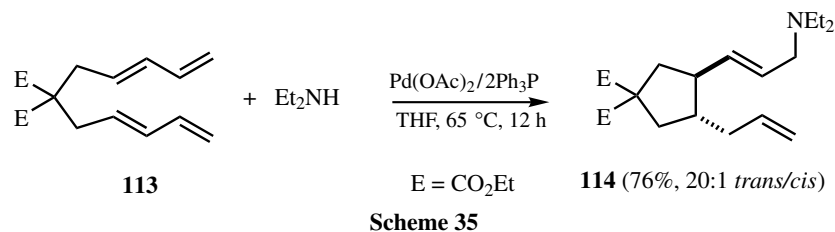


Scheme 34

The head-to-head isomer **112** can be favored by appropriate combinations of cationic palladium catalysts and ligand. Röper and co-workers had shown that cationic palladium complexes were particularly active catalyst precursors for linear diene dimerization, and the cationic palladium complex $[\text{Pd}(\text{dppe})(\text{py})_2(\text{BF}_4)_2]$ affords a 7:43:8:39 **109/110/111/112** ($\text{R}^1, \text{R}^2 = \text{Et}$) ratio in 81% yield (0.5 mol % catalyst, acetonitrile, 25 °C) (Scheme 34).^[163] The addition of a Lewis acid^{[154],[165]} as a cocatalyst also influences the isomer distribution; carbon dioxide and Brønsted acids act similarly. For example, the reaction of isoprene with diethylamine and the catalyst system $[\text{Pd}(\text{acac})_2, 4 \text{ P}(c\text{-C}_6\text{H}_{11})_3, 20 \text{ BF}_3\text{-OEt}_2]$ in acetonitrile (70 °C, 16 h) affords a 91% yield of dimers of which 60% is the head-to-head isomer (4:32:3:60 **109/110/111/112** ($\text{R}^1, \text{R}^2 = \text{Et}$)).^[162] A recent study by Maddock and Finn is particularly striking.^[166] A large number of ligands was screened in the reaction of isoprene with diethylamine; other secondary amines were also examined. The combination of a cationic palladium complex $[(\text{C}_3\text{H}_5)\text{Pd}(\text{cod})\text{BF}_4]$ and tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) affords a 93% yield of the head-to-head isomer **112** as a mixture of (*E*)- and (*Z*)-isomers with only 6.1% of the tail-to-head isomer **110** (5 mmol isoprene, 4.8 mmol Et_2NH , 0.025 mmol $[(\text{C}_3\text{H}_5)\text{Pd}(\text{cod})\text{BF}_4]/1.5 \text{ TTMPP}$, 1 mL methanol, 25 °C, 72 h). The beneficial effect of TTMPP is thought to be a result of both steric and electronic effects; tris(*o*-tolyl)phosphine, a ligand that is sterically similar to TTMPP, shows poor activity and poor selectivity.

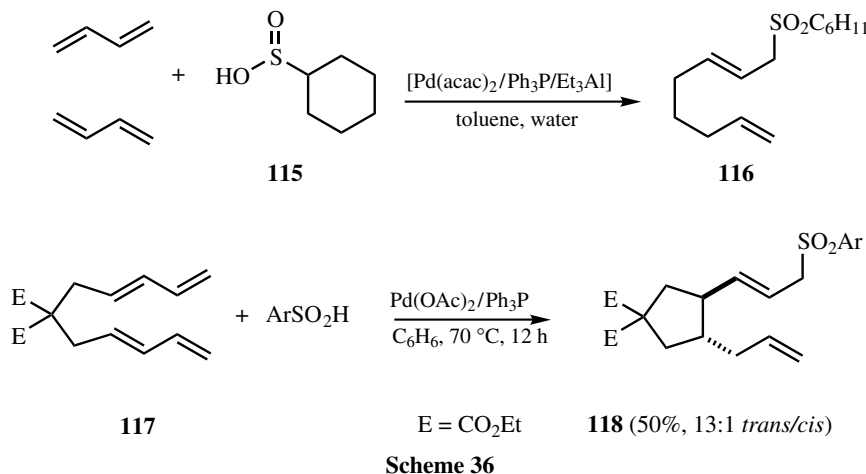
C.ix. Amines as the H—Y Trapping Reagent: Intramolecular Diene Coupling

The intramolecular diene dimerization with trapping by amines has also been shown to be viable.^[92] Bisdiene **113** is trapped by diethylamine (0.05 $[\text{Pd}(\text{OAc})_2/2 \text{ Ph}_3\text{P}]$, THF, 65 °C) to afford allylic amine **114** (73%, >20:1 *trans/cis* ring substitution) (Scheme 35).



**C.x. Sulfinic Acids as the H—Y Trapping Reagents:
Inter- and Intramolecular Diene Coupling**

Sulfinic acids, or their alkali metal salts, add to butadiene after dimerization to form octadienyl sulfone derivatives.^[167] For example, butadiene reacts with cyclohexylsulfinic acid (**115**) under palladium catalysis [$\text{Pd}(\text{acac})_2\text{-Ph}_3\text{P-Et}_3\text{Al}$] in a toluene–water mixture to afford the allylic sulfone **116** in 95% yield and high isomeric purity (**Scheme 36**).^{[168]–[170]} Under these conditions, isoprene, piperylene, cyclopentadiene, and cyclohexadiene give 1:1 and/or bis-sulfones, not linear dimerization products.^{[168],[169]} Carbon dioxide reportedly promotes the Pd-catalyzed reaction of dienes with sulfinic acids.^[171] Sulfides such as benzyl, phenyl, and *ortho*-tolyl sulfides react with butadiene to give a mixture of butenylsulfide, octadienylsulfide, and disulfide.^[172]

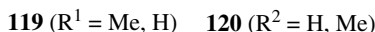


The intramolecular diene coupling with trapping by sulfinic acid has also been shown to be viable.^[92] Bisdiene **117** is trapped by *p*-toluenesulfinic acid (0.05 [$\text{Pd}(\text{OAc})_2/2\text{Ph}_3\text{P}$], benzene, 70 °C) to afford allylic sulfone **118** in moderate yield (50%, 13:1 *trans/cis* ring substitution).

C.xi. Doubly Activated Methylene and Methines (C—H Acidic Compounds) as the H—Y Trapping Reagent: Inter- and Intramolecular Diene Coupling

A number of types of carbon nucleophiles participate as protic H—Y trapping reagents in Pd-catalyzed linear diene dimerization. Among these, doubly activated methylene and

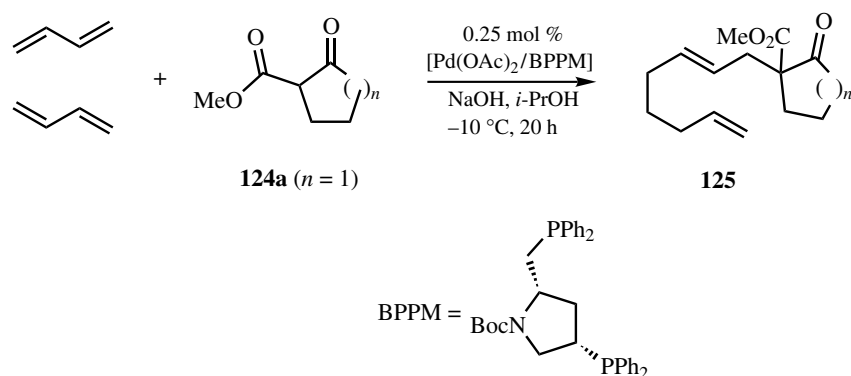
ligands are employed.^{[175],[176]}



Scheme 37

>20:1 *trans/cis* ring substitution).

C.xi.a. Enantioselective Catalysis. The influence of certain chiral bidentate diphosphine ligands (L^*) was examined in the $[Pd(OAc)_2-L^*]$ -catalyzed reactions of butadiene with two cyclic β -ketoesters.^{[76],[90],[91],[177]} The reaction of butadiene with 2-(methoxycarbonyl)cyclohexanone (**124a**) using a 1:1 ratio of $Pd(OAc)_2/BPPM$ ($BPPM = (2S, 4S)$ -*N*-*t*-butoxycarbonyl-2,4-bis(diphenylphosphino)methylpyrrolidine) in isopropanol ($-10\text{ }^\circ\text{C}$, 20 h) gave product **125a** (86% yield and 46% ee) (**Scheme 38**). Note that the new chiral center is on the trapping reagent, not the dienes, and arises from asymmetric alkylation of the π -allylpalladium moiety. Under similar conditions, 2-(methoxycarbonyl)cyclopentanone gave comparable results (86% yield, 41% ee).^[177] DIOP, NORPHOS, and

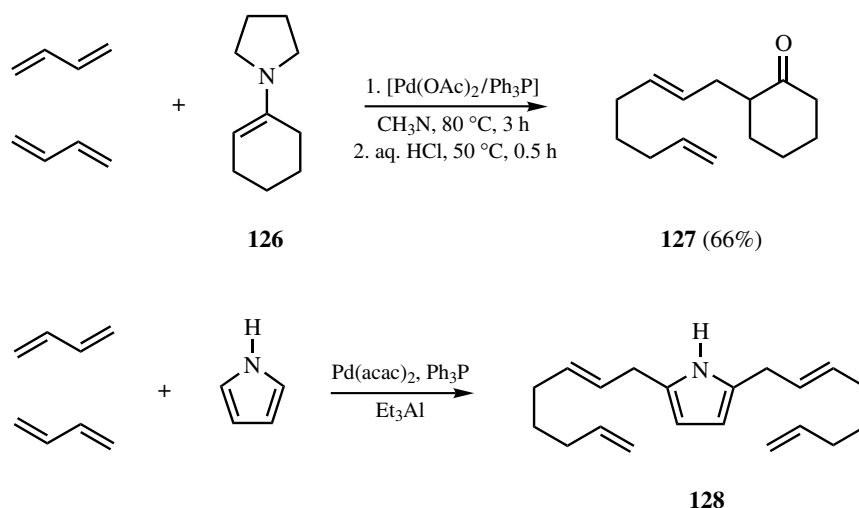


Scheme 38

(2*R*, 3*R*)-2,3-bis(diphenylphosphino)butane gave *ees* values of 10% or less. Heterogeneous versions of this reaction gave similar results.^[91]

C.xii. Enamines as the H—Y Trapping Reagent: Inter- and Intramolecular Diene Coupling

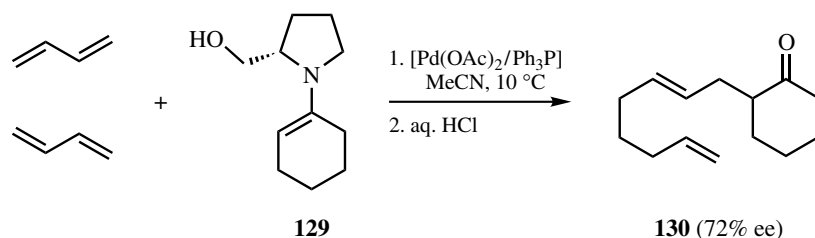
Under certain conditions less activated ketones (e.g., acetone, cyclopentanone, cyclohexanone, and cyclohexenone) can participate in the reaction with butadiene^[178] or isoprene,^{[179],[180]} but more commonly enamine derivatives are employed. For example, Tsuji reported that butadiene undergoes Pd-catalyzed linear dimerization with trapping by the pyrrolidocyclohexene **126** (Scheme 39) (Pd(OAc)₂, Ph₃P, CH₃CN, 80 °C, 3 h) to afford the octadienyl derivative **127** in 66% yield after hydrolysis (aq. HCl, 50 °C, 0.5 h).^[181] In addition, 22% of the α,α' -dialkylated product was isolated.



Scheme 39

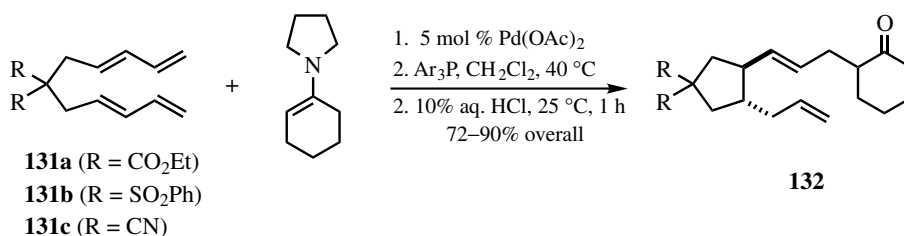
In a sense, pyrrole can be considered enamine-like in its reactivity, and Dzhemilev and co-workers reported that it acts as a carbon nucleophile, reacting twice with butadiene under palladium catalysis to afford **128**.^{[141],[182]}

C.xii.a. Enantioselective Trapping. Keim et al.^{[90],[177]} evaluated the influence of chiral trapping reagents and chiral ligands on the formation of a new stereogenic center at the site of reaction on the trapping nucleophile. For example, the $[\text{Pd}(\text{OAc})_2/\text{Ph}_3\text{P}]$ -catalyzed reaction of butadiene with the (*S*)-2-(methoxymethyl)pyrrolidine-derived enamine of cyclohexanone **129** affords, after hydrolysis, the 2-(2,7-octadienyl)cyclohexanone (**130**) with 72% ee (**Scheme 40**). Note that the new chiral center is generated on the trapping reagent, not the dienes, and arises from asymmetric alkylation of the chiral trapping reagent by the π -allylpalladium moiety.



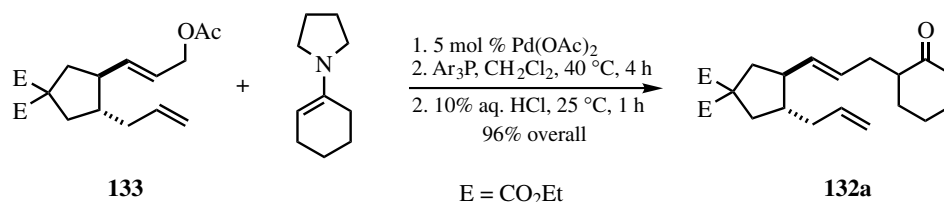
Scheme 40

C.xii.b. Intramolecular Diene Coupling. Treatment of the simple bisdiene derivatives **131a–c** with 2 equiv of 1-pyrrolidino-1-cyclohexene and 5 mol % $[\text{Pd}(\text{OAc})_2/2 \text{ Ar}_3\text{P}]$ (Ar = C_6H_5 or *o*- $\text{CH}_3\text{C}_6\text{H}_4$) in refluxing methylene chloride solution effects facile carbocyclization with incorporation of the enamine trapping reagent. Hydrolysis of the crude reaction mixture yields the α -alkylated cyclohexanones **132** in good to excellent yields (**131a** 90%, **131b** 72%, **131c** 83%) as mixtures of epimers with respect to the stereogenic center in the cyclohexyl ring (**Scheme 41**). The chemical yield and diastereoselectivity for the cyclization of bisdiene **131a** are highly dependent on the solvent, ligand, and nature of the enamine. In THF or benzene solution, cycloisomerization to an enediene competes with trapping by the enamine. This side reaction is suppressed in dichloromethane, chloroform, or acetonitrile. With respect to chemical yield and reaction time required for the cyclization, triarylphosphines are superior ligands to trialkylphosphines or to phosphites. Finally, the pyrrolidinocycloalkene is superior to the morpholino derivative as the trapping reagent in trapping by either cyclohexanone- or cyclopentanone-derived enamines.



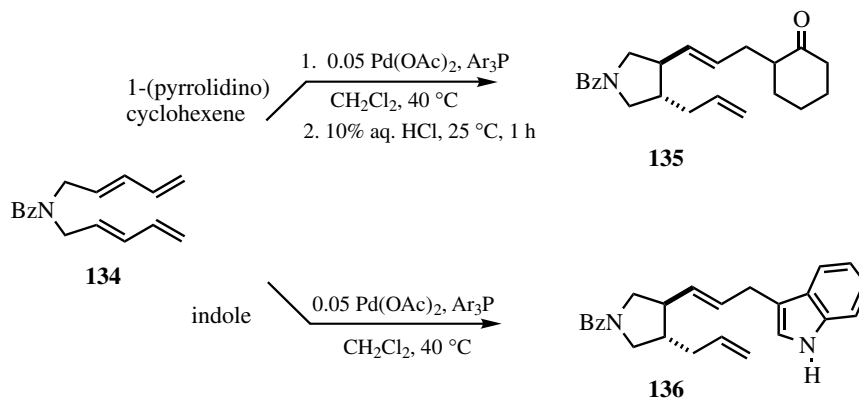
Scheme 41

With regard to the intramolecular reaction, it is conceivable that catalytic amounts of acetate ion in this $[\text{Pd}(\text{OAc})_2/2 \text{Ar}_3\text{P}]$ -catalyzed carbocyclization reaction serve to shuttle the bisdiene to an intermediate allylic acetate, which subsequently undergoes Pd-catalyzed reaction with the enamine. The action of the enamine trapping reagent could, in principle, be entirely independent from the carbocyclization event. In fact, treatment of the independently prepared allylic acetate **133** under the enamine carbocyclization conditions (2 equiv of 1-pyrrolidino-1-cyclohexene, 5 mol % $[\text{Pd}(\text{OAc})_2/2 (o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]$, CH_2Cl_2 , 40 °C, 5 h) gave **132a** in 96% yield after hydrolysis (**Scheme 42**). However, the presence of acetate ion is not required for successful allylation of the enamine. Treatment of bisdiene **131a** with 1-pyrrolidino-1-cyclohexene in the presence of 5 mol % $\text{Pd}(\text{acac})_2$ (i.e., an acetate-free palladium catalyst used in place of $\text{Pd}(\text{OAc})_2$) still gives **132a** in 81% yield (2 $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$, CH_2Cl_2 , 40 °C, 25 h). Thus, reaction via allylic acetate **133** is a viable, but not an obligatory, pathway for the conversion of bisdiene **131a** to **132a**.



Scheme 42

The benzamide bisdiene **134** proved to be a particularly good substrate for the carbocyclization with 1-pyrrolidino-1-cyclohexene. Its cyclization using 2 equiv of triphenylphosphine or tris(*o*-tolyl)phosphine or 1 equiv of diphenylphosphinoethane (dppe) in conjunction with $\text{Pd}(\text{OAc})_2$ proceeds in about 90% overall yield to the substituted *N*-acylpyrrolidine **135** (**Scheme 43**). Notably, indole also proves to be an effective trapping reagent in the reaction of **134**. The adduct **136** is obtained in 91% yield from the palladium acetate-catalyzed reaction in the presence of tris(*o*-tolyl)phosphine.

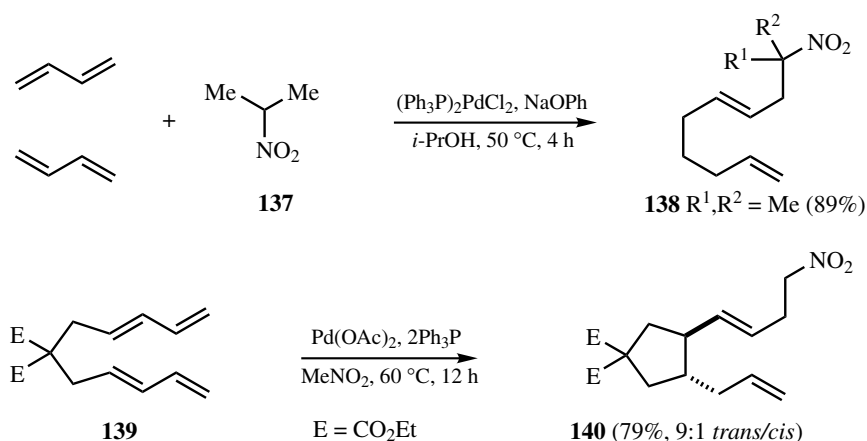


Scheme 43

**C.xiii. Nitroalkanes as the H—Y Trapping Reagent:
Inter- and Intramolecular Diene Coupling**

While relatively few examples have been reported, nitroalkanes can serve as efficient carbon nucleophiles in the Pd-catalyzed linear dimerization reaction.^[183] For example, butadiene reacts with 2-nitropropane (**137**, $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, KOH, *i*-PrOH, 50 °C, 4 h) to afford 9-methyl-9-nitro-1,6-decadiene (**138** $\text{R}^1, \text{R}^2 = \text{Me}$) in 89% yield (**Scheme 44**). Nitromethane or primary nitroalkanes also react but can give a mixture of polyalkylation products. Keim and co-workers found that butadiene undergoes $[(\text{DIOP})\text{Pd}(\text{OAc})_2]$ -catalyzed dimerization with trapping by 1-nitropropane to afford **138** ($\text{R}^1 = \text{H}, \text{R}^2 = \text{CH}_2\text{CH}_3$) with 16% ee.^[177]

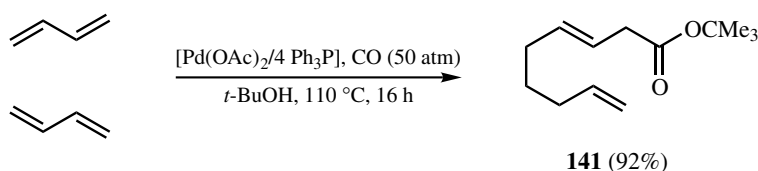
The intramolecular diene coupling with trapping by nitromethane has also been shown to be viable.^[92] Using an excess of nitromethane, polyalkylation is not a problem. Bisdien **139** is trapped by nitromethane (0.05 $[\text{Pd}(\text{OAc})_2/2 \text{ Ph}_3\text{P}]$, CH_3NO_2 (solvent), 60 °C) to afford cyclopentane **140** (79%, 9:1 *trans/cis* ring substitution).



Scheme 44

**C.xiv. CO/ROH, an Equivalent of “H—CO₂R” as the H—Y Trapping Reagent:
Intermolecular Diene Dimerization**

Butadiene reacts with carbon monoxide and alcohols^{[184],[185]} or amines^[186] to form 3,8-nonadienoic acid derivatives. A variety of alcohols, even relatively bulky ones, can be used. For example, reaction of butadiene with CO (50 atm) in *tert*-butyl alcohol ($\text{Pd}(\text{OAc})_2/4 \text{ Ph}_3\text{P}$, 110 °C, 16 h) affords the β,γ -unsaturated *tert*-butyl ester **141** in 92% yield (**Scheme 45**).^[187] CO pressures greater than 50 atm slow the reaction as do $\text{Ph}_3\text{P}/\text{Pd}$ ratios greater than or less than 4:1.

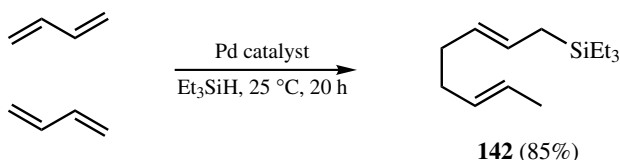


Scheme 45

D. DIENE DIMERIZATION WITH INCORPORATION OF SILANES, DISILANES, AND RELATED COMPOUNDS

D.i. Intermolecular Diene Dimerization

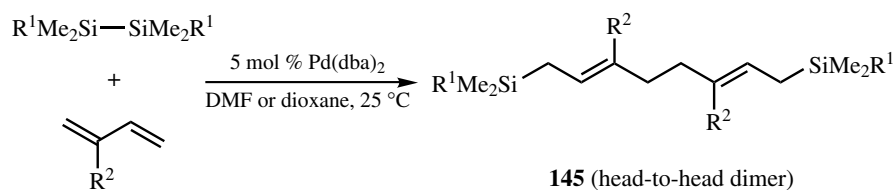
Butadiene undergoes Pd-catalyzed linear dimerization with trapping by silanes, disilanes, and distannanes to afford 2,6-octadiene derivatives (e.g., **Schemes 2** and **6**).^[29] For example, reaction of butadiene with triethylsilane catalyzed by a phosphinated polystyrene-bound palladium(0) complex affords the 1-silyl-2,6-octadiene derivative **142** (85%) (**Scheme 46**).^[71] The highly selective formation of the 2,6- rather than 2,7-octadiene is what differentiates this class of trapping agents from the protic H—Y trapping reagents discussed above.^{[188]–[194]} The change in regioselectivity may reflect a change in mechanism for this class of Pd-catalyzed linear dimerization reactions with subsequent trapping (*vide infra*). Substituted 1,3-dienes (e.g., isoprene, piperylene) give predominantly to exclusively simple hydrosilylation products rather than linear dimerization products.



Scheme 46

Disilane trapping reagents behave in a conceptually similar fashion.^[195] Tsuji and co-workers found that a variety of simple dienes (**143**, e.g., butadiene, isoprene, 2-phenyl-1,3-butadiene, 2-trimethylsilyloxy-1,3-butadiene) undergo efficient Pd(dba)₂-catalyzed linear dimerization disilane trapping with a variety of simple disilanes **144** to afford bis(allylsilane) products **145** (41–92% yield) (**Scheme 47**).^[196] Cyclic disilanes afford macrocyclic bis(allylsilane) products.^[197]

144 (R¹ = Me, Ph, CH=CH₂, CH₂CH=CH)



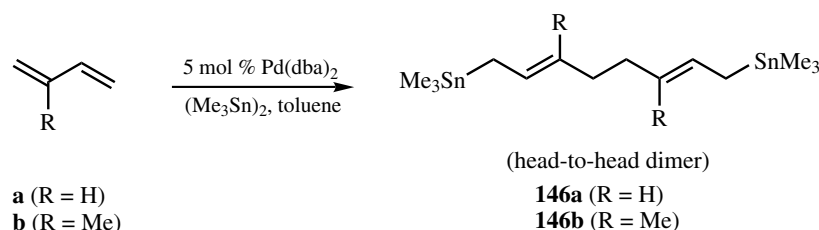
143 (R² = H, Me, Ph, OSiMe₃)

Scheme 47

There are a number of remarkable features in this very facile linear dimerization reaction with trapping by disilanes. (i) In contrast to silanes with which substituted 1,3-dienes (e.g., isoprene, piperylene) give predominantly to exclusively simple hydrosilylation products rather than linear dimerization products, disilanes afford only disilylated linear dimers—no disilylated monomer. (ii) Only the head-to-head dimerization products

(i.e., (*E,E*)-**145**) are observed from 2-substituted dienes (**Scheme 47**); this is in contrast to many other dimerization–trapping reactions of substituted dienes in which mixtures of head-to-tail dimers are formed. (iii) It is of particular note that 2-substituted 1,3-diene derivatives other than isoprene can successfully be dimerized under these conditions; for example, the 2-phenyl derivative (82% yield, $R^1 = \text{Me}$, DMF) and the 2-trimethylsilyloxy derivative (63% yield, $R^1 = \text{Me}$, DMF) afford linear dimers. However, it is reported that 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-cyclohexadiene do not react under these or even more vigorous reaction conditions. (iv) Other palladium catalysts work as well (e.g., Ph_4Pd , $(\text{PhCN})_2\text{PdCl}_2$, $[(\text{C}_3\text{H}_5)\text{Pd}(\text{cod})\text{BF}_4]$, $[(\text{C}_3\text{H}_5)\text{Pd}(\text{Cl})]$), but $\text{Pd}(\text{dba})_2$ shows the highest activity. (v) DMF and dioxane are superior to benzene, toluene, THF, HMPA, or dichloromethane as reaction solvent. (vi) Finally, no crossover products are observed when reacting an equimolar mixture of disilanes **144** ($R^1 = \text{Me}$ and $R^1 = \text{Ph}$) with isoprene. Both silicon atoms of the disilane trapping reagent are transferred to the same isoprene dimer, a remarkable observation given the facile Pd-catalyzed metathesis of disilanes.^[198]

Tsuji and Kakehi reported the analogous linear dimerization of 1,3-dienes with subsequent trapping by distannanes.^[199] For example, 1,3-butadiene undergoes efficient $\text{Pd}(\text{dba})_2$ -catalyzed linear dimerization trapping with hexamethyldistannane (0 °C, 0.05 h) to afford **146a** (78% yield) (**Scheme 48**). Isoprene reacts analogously (25 °C, 5 h) to afford (*E,E*)-**146b** (62% yield). Again, only the head-to-head dimerization product is observed. When the hexabutyldistannane is used in place of the hexamethyl derivative dimeric products are not formed.

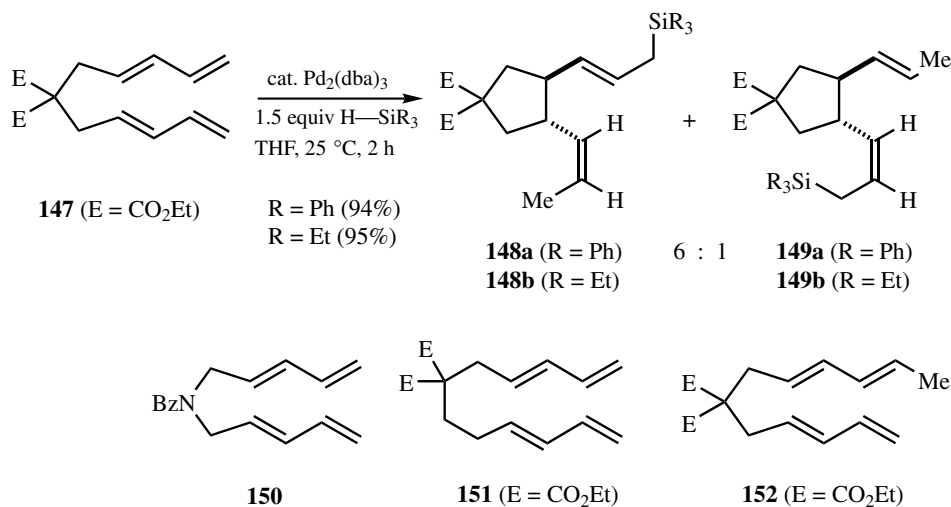


Scheme 48

D.ii. Intramolecular Diene Coupling

Treatment of bisdiene **147** with 1.5 equiv of triphenylsilane in the presence of a palladium catalyst (3 mol % $\text{Pd}_2(\text{dba})_3$, THF, 25 °C, 1–2 h) effects rapid cyclization of the bisdiene.^[200] A 6:1 mixture of two diastereomeric cyclopentanes, **148a** and **149a**, is obtained in excellent yield (94%) (**Scheme 49**). Similar products are obtained when dimethylphenylsilane (95%) or triethylsilane (95%) is employed. The reactions of three related bisdiene substrates have been investigated. The *N*-acylpyrrolidine precursor **150** (Ph_3SiH , 82%), the six-membered ring precursor **151** (Ph_3SiH , 80%), and the methyl-substituted bisdiene **152** (Ph_3SiH , 57%) also undergo Pd-catalyzed cyclization. About 65% of the products obtained in the cyclization of **152** are derived from addition of the silyl group to the less substituted diene subunit.

The structures of diastereomers **148** and **149** are related in an unusual way. Six contiguous stereochemical centers are formed as a consequence of the carbocyclization. Yet,



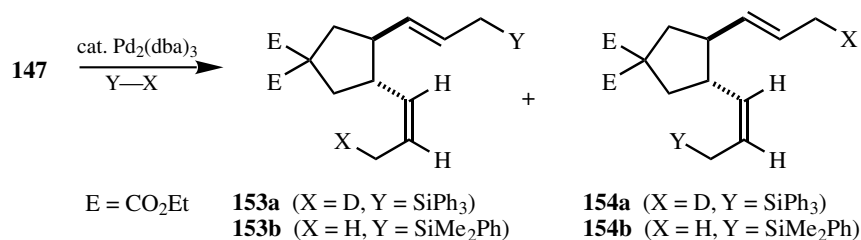
Scheme 49

out of the multitude of possible stereoisomeric products, the overall configuration of the carbon skeleton is identical in both diastereomeric products. Structures **148** and **149** differ only with respect to which of the termini in the newly formed carbon skeleton the triphenylsilyl group and the hydrogen, respectively, become attached. In essence, while **148** and **149** are formally stereoisomers, they result from regioisomeric modes of H—Si addition. The Pd-catalyzed carbocyclization to assemble the carbon skeleton of the product apparently proceeds with very high levels of relative diastereoselectivity and alkene stereoselectivity. This curious relationship between **148** and **149** must somehow relate to the role of the metal in the catalytic process leading to the cyclization.

It has long been a puzzle as to why linear dimerization of butadiene with hydrosilane trapping gives 2,6-octadienes while protic H—Y trapping reagents give 2,7-octadienes. To explain the formation of 1-silyl-2,6-octadiene, it is generally postulated that the reaction proceeds via the initial partial hydrosilylation of one butadiene molecule followed by capture of the intermediate π -allylpalladium complex (i.e., $[\pi\text{-(CH}_2\text{CHCHCH}_3\text{)]Pd(SiR}_3\text{)}_m$) by insertion of another butadiene unit. This mechanism is in contrast to the one discussed in the introductory section that has been postulated for the reaction with protic trapping reagents, that is, C—C bond formation via initial oxidative coupling of two molecules of butadiene.

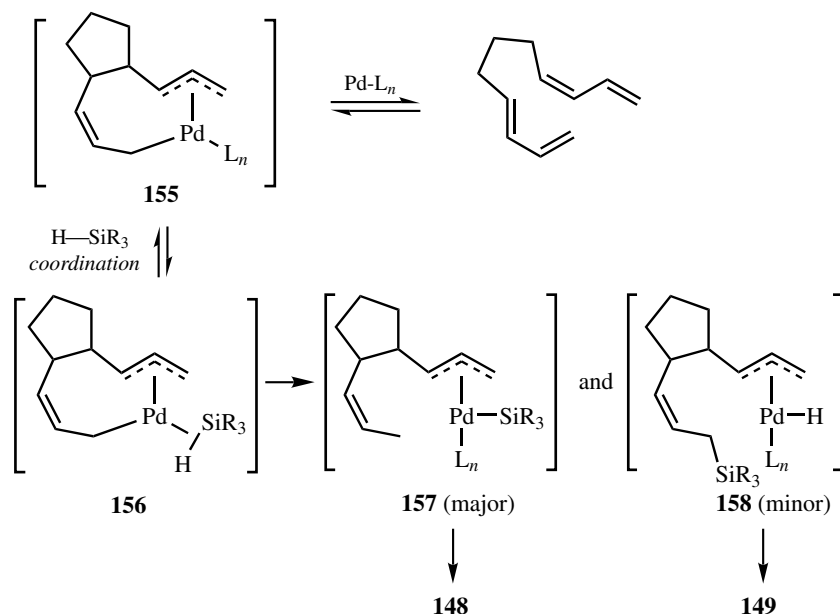
The Pd-catalyzed reaction of bisdiene **147** with [*D*]-triphenylsilane gives the regiospecifically monodeuterated products corresponding to **148** and **149** (i.e., **153a** (X = D, Y = SiPh₃) and **154a** (X = D, Y = SiPh₃)); that is, the cyclized product picks up its hydrogen (deuterium) from the silane trapping reagent. When admixed in the absence of bisdiene **147**, Pd₂(dba)₃ catalyzes the rapid H/D exchange and competitive dehydrogenative coupling of a mixture of deuteriosilane and hydrosilane (0.03 mmol Pd₂(dba)₃/0.75 mmol Ph₃SiD/0.75 mmol Me₂PhSiH/5 mL THF/25 °C/0.5 h). Nonetheless, a competition experiment in which a limiting amount of bisdiene **147** is reacted under otherwise standard conditions with a mixture of [*D*]-triphenylsilane and dimethylphenylsilane yields only four cyclized products (0.03 mmol Pd₂(dba)₃/1.0 mmol **147**/0.75 mmol Ph₃SiD/0.75 mmol Me₂PhSiH/5 mL THF/25 °C/3 h/98% combined yield of products). Triphenylsilyl-containing products are separated from dimethylphenylsilyl-containing products by chromatography

on silica. Analysis of the product mixture containing the triphenylsilyl moiety shows that this material also has stoichiometric deuterium incorporation; that is, a mixture of **153a** (X = D, Y = SiPh₃) and **154a** (X = D, Y = SiPh₃) is isolated (46%) (Scheme 50). Products containing the dimethylphenylsilyl moiety show no deuterium incorporation; only **153b** (X = H, Y = SiMe₂Ph) and **154b** (X = H, Y = SiMe₂Ph) are isolated (52%). This experiment shows that no crossover products are formed; both the hydrogen (or deuterium) and the silyl group come from the same molecule of silane.



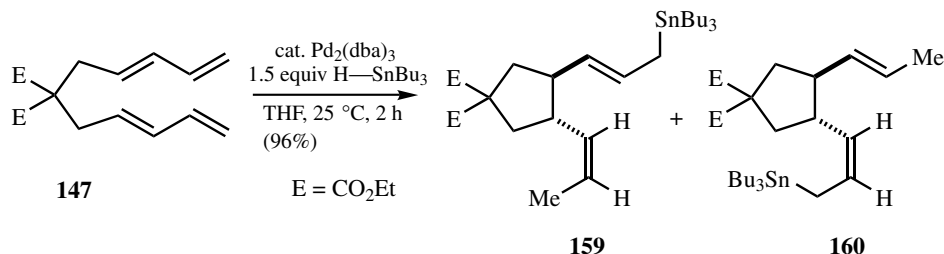
Scheme 50

The results of the crossover experiments argue against a mechanism initiated by hydrosilylation. An alternative mechanistic possibility, which is consistent with all of the data and which adequately accounts for the stereoselective formation of only diastereomers **148** and **149**, is given in Scheme 51. Complexation of the silane to an initially formed palladacycle such as **155** would afford a complex such as **156**. Sigma bond metathesis to a mixture of π -allylpalladium complexes **157** (presumed major) and **158** (presumed minor) followed by reductive elimination from each of these would generate the observed products **148** (major) and **149** (minor).



Scheme 51

The Pd-catalyzed reaction of bisdiene **147**, using tributylstannane in place of the hydrosilane, provides one example where tin can be used in place of silicon. The mixture of allylstannanes **159** and **160** is obtained in excellent yield (96%) (**Scheme 52**).



Scheme 52

E. DIENE DIMERIZATION WITH INCORPORATION OF A R¹(R²)C=Y TRAPPING REAGENT

E.i. Introduction

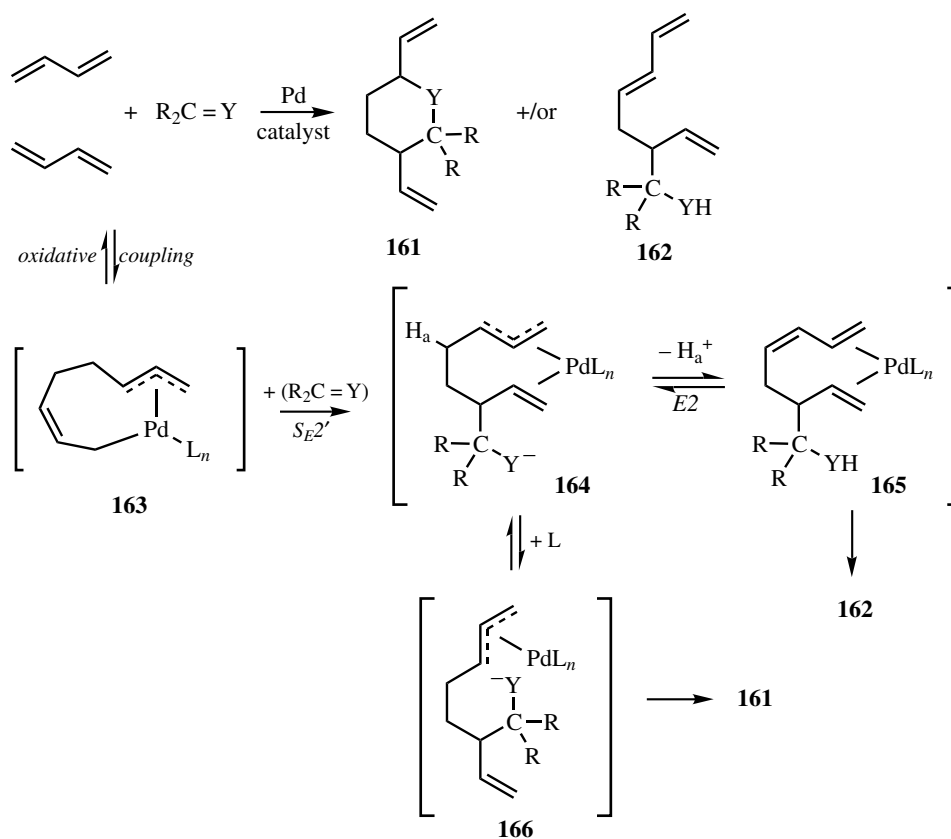
At first glance the products obtained from the dimerization of dienes with R¹(R²)C=Y trapping reagents (e.g., aldehydes, ketones, imines, carbon dioxide, and isocyanates),^[29] especially those obtained via the cycloaddition mode, look quite different from those obtained via the other three trapping modes. Nonetheless, as illustrated in **Scheme 53** for the reaction of 1,3-butadiene with a hypothetical R¹(R²)C=Y trapping reagent (for simplicity, R¹ = R²), the products can be thought of as arising via a mechanism that is conceptually quite similar to that discussed in **Sects. A–C**.

Pd-catalyzed oxidative coupling of butadiene to the palladacycle **163** followed by addition of the carbon electrophile to the η^1 -allyl moiety in an S_E2' fashion (i.e., a reaction akin to S_E2' protonation in the case of proton H—Y trapping reagents) leads to a chelated π -allylpalladium intermediate such as **164**. At this juncture, one option is deprotonation, that is, the same pathway postulated in **Sect. B** to account for the intermolecular linear dimerization with trapping. Loss of the proton labeled H_a would lead to chelate **165**, and upon decomplexation, triene **162**. In practice, products of this sort are seen when the Pd/phosphine ratio is less than 2 (*vide infra*). The more common reaction mode (favored when the Pd/phosphine ratio is greater than 2) leads to the cyclized product **161**. Its formation can be rationalized via decomplexation of chelate **164** to **166** followed by addition of the newly generated nucleophile Y[−] to the η^3 -allylpalladium, a pathway akin to that postulated in **Sect. C** for trapping by protic H—Y trapping reagents, but here an intramolecular variation.

The following discussion is organized according to the nature of the R¹(R²)C=Y trapping reagent employed: aldehydes and ketones, imines, and carbon dioxide and isocyanates.

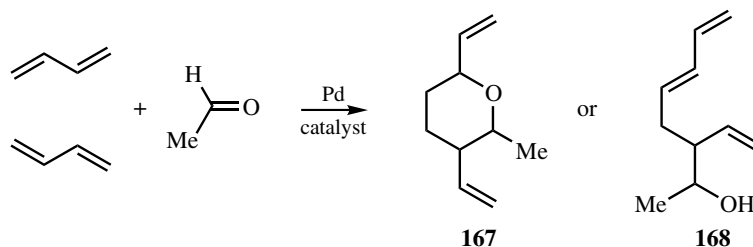
E.ii. Aldehydes and Ketones as Trapping Agents: Intermolecular Diene Dimerization

A variety of aldehydes (formaldehyde, aliphatic, and aromatic aldehydes) and some electrophilic ketones (e.g., α -diketones and hexafluoroacetone) have been shown to serve as



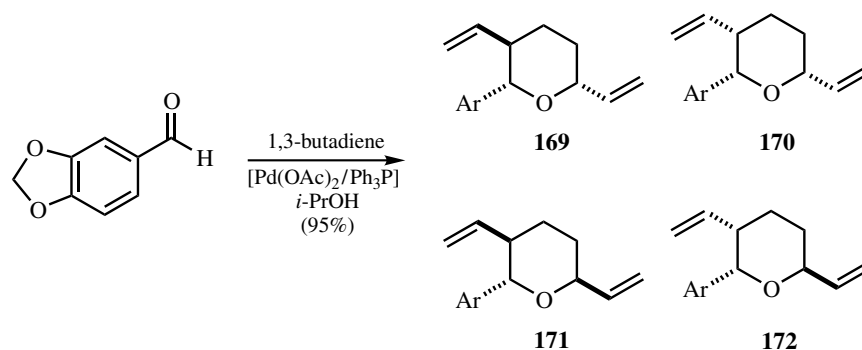
Scheme 53

trapping reagents.^{[201]–[204]} The formation of linear or cyclic products depends on the Pd/phosphine ratio. For example, the reaction of butadiene with acetaldehyde ($\text{Pd}(\text{acac})_2$, n Ph_3P , 25 °C, 60 h, ca. 0.5–2.0 mmol Pd/mol butadiene) in the presence of 4 equiv of Ph_3P per Pd affords predominantly **167** (70% yield) (Scheme 54).^[201] The same reaction run in the presence of 1 equiv of Ph_3P per Pd affords predominantly **168** (70% yield). The reaction is said to be more facile when run in an alcohol solvent, as illustrated by the following two sets of reaction conditions: (i) ($\text{Pd}(\text{acac})_2$, 4 Ph_3P , EtOH, 80 °C, 2 h) yields **167** (74%) and **168** (6%); and (ii) ($\text{Pd}(\text{acac})_2$, 1 Ph_3P , *i*-PrOH, 80 °C, 3 h) yields **167** (8%) and **168** (75%).



Scheme 54

In general, when the reaction is run so as to favor formation of the cyclic (here, divinyltetrahydropyran) product, a mixture of four racemic diastereomers is formed. For example, butadiene reacts with aromatic aldehydes such as 3,4-(methylenedioxy)benzaldehyde to afford a 33:33:24:10 mixture of substituted divinylpyrans (**169–172**) in high yield (70–95%) (**Scheme 55**).^{[205],[206]}



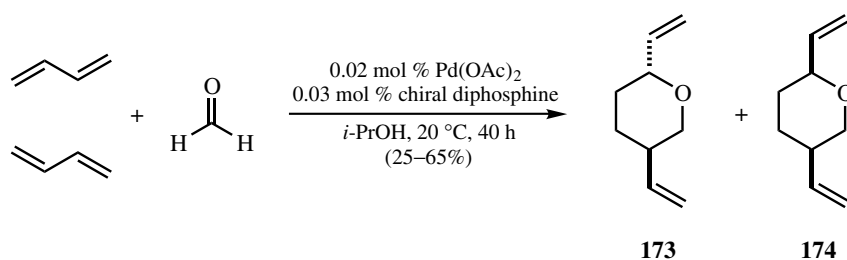
Scheme 55

E.ii.a. Enantioselective Catalysis. Keim and co-workers examined the enantioselective butadiene dimerization with aldehyde trapping. For example, Pd-catalyzed reaction of butadiene with formaldehyde (0.02 mol % $\text{Pd}(\text{OAc})_2$, 0.03 mol % chiral diphosphine, *i*-PrOH, 20 °C, 40 h) affords a mixture of *cis*- and *trans*-divinyltetrahydropyrans, **173** and **174**, respectively.^{[177],[207]} (The absolute configurations of **173** and **174** were not assigned by the authors; the configurations illustrated in **Scheme 56** were chosen arbitrarily.) **Table 1** summarizes the results obtained for several chiral phosphines. The reaction with formaldehyde affords a 2.6–5.6:1 ratio of *trans*- and *cis*-2,5-divinyltetrahydropyran in 25–65% chemical yield. Among the chiral ligands examined, DIOP (**173** 18% ee; **174** 26% ee), NORPHOS (**173** 3% ee; **174** 36% ee), and *neo*-MenPPh₂ (**173** 13% ee; **174** 30% ee) gave the highest levels of enantioselectivity.

TABLE 1. Enantioselective Dimerization of Butadiene Followed by Trapping with Formaldehyde

Chiral Ligand ^a	Yield (%)	173/174	173 ee (%)	174 ee (%)
(+)-DIOP	65	5.0 : 1	18	26
(-)-DIOP	64	5.5 : 1	17	25
BPPM	45	2.6 : 1	2	5
CIRA	30	3.6 : 1	15	20
NORPHOS	55	5.6 : 1	3	36
NMDPP	25	3.9 : 1	13	30
PHEN	45	3.9 : 1	5	24

^aBPPM = (2*S*,4*S*)-*N*-*t*-butoxycarbonyl-2,4-bis(diphenylphosphino)methylpyrrolidinone; CIRA = (2*R*,3*R*)-2,3-bis(diphenylphosphino)butane; NORPHOS = (2*R*,3*R*)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene; NMDPP = (1*R*,2*R*,5*S*)-neomenthyl-diphenylphosphine; PHEN = (*R*)-1,2-bis(diphenylphosphino)-3-phenylpropane.



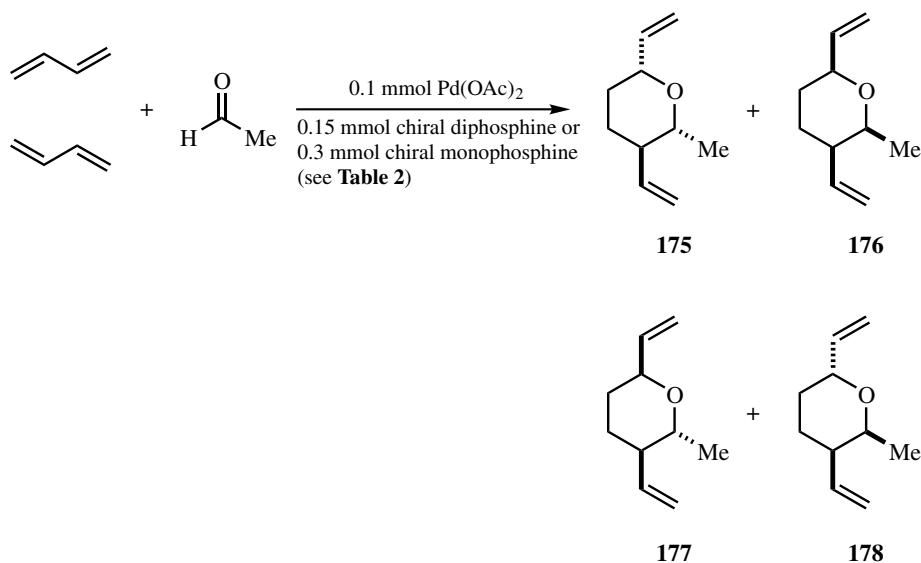
Scheme 56

As shown above, the reaction with an aldehyde other than formaldehyde can form four chiral diastereomers. Keim and Mastrolilli examined the reaction of butadiene with acetaldehyde using chiral diphosphine ligands (0.1 mmol $\text{Pd}(\text{OAc})_2$, 0.15 mmol chiral diphosphine or 0.3 mmol chiral monophosphine, 20 mmol acetaldehyde, 42 mmol 1,3-butadiene, *i*-PrOH).^[208] The products **175**–**178** are shown in **Scheme 57** with the correct relative configuration within each structure, but arbitrarily chosen absolute configuration. The authors state that the ratio of chiral diastereomers is typically found to be 48:35:5:12 (**175/176/177/178**). It seems difficult to draw many conclusions from the numbers in **Table 2**, given the mixture of products. The authors report that BINAP and CHIRAPHOS did not afford active catalysts, and among the bidentate ligands that were successful, DIOP was the best. The best enantiomeric excesses were obtained with chiral monophosphines, but these gave significant amounts of the triene product. In one case, $\text{Pd}(\text{acac})_2$ was substituted for $\text{Pd}(\text{OAc})_2$ with similar results, but $\text{Pd}(\text{dba})_2$ failed to give an active catalyst with DIOP.

TABLE 2. Enantioselective Dimerization of Butadiene Followed by Trapping with Acetaldehyde

Ligand ^a	Time	Temperature (°C)	Yield (%)	175 ee (%)	176 ee (%)	177 ee (%)	178 ee (%)
BPPM	66 h	21	58	21	21	25	6
BPPM	13 d	0	3	62	29	23	22
(+)-NORPHOS	3 d	45	55	10	33	25	11
(+)-NORPHOS	14 d	15	9	10	46	26	22
(–)-NORPHOS	12 d	21	23	52	2	27	7
(–)-NORPHOS	12 d	10	5	60	6	32	7
(+)-DIOP	5 d	21	75	47	2	7	0
(+)-DIOP	14 d	15	77	50	1	7	4
(–)-DIOP	66 h	21	52	1	27	7	1
NMDPP	4 d	21	5	63	77	16	48
NMDPP	9 d	0	28	37	47	33	16
TMP	4 d	21	42	23	50	35	10
TMP	9 d	0	3	1	76	8	61

^aBPPM = (2*S*,4*S*)-*N*-*t*-butoxycarbonyl-2,4-bis(diphenylphosphino)methylpyrrolidinone; CIRA = (2*R*,3*R*)-2,3-bis(diphenylphosphino)butane; NORPHOS = (2*R*,3*R*)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene; NMDPP = (1*R*,2*R*,5*S*)-neomenthylidiphenylphosphine; PHEN = (*R*)-1,2-bis(diphenylphosphino)-3-phenylpropane; TMP = trimethylphosphite.

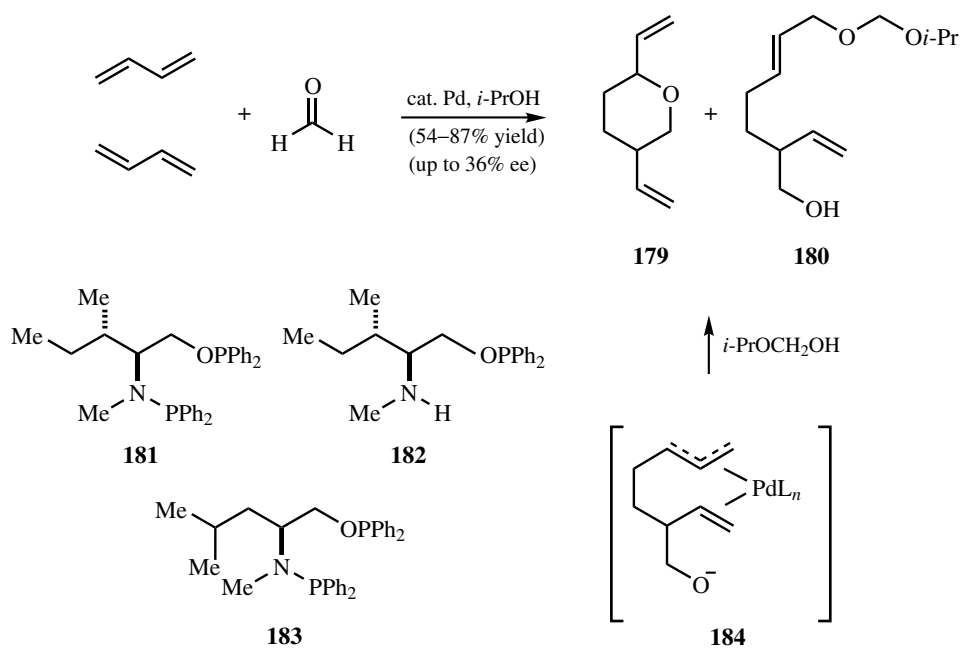


Scheme 57

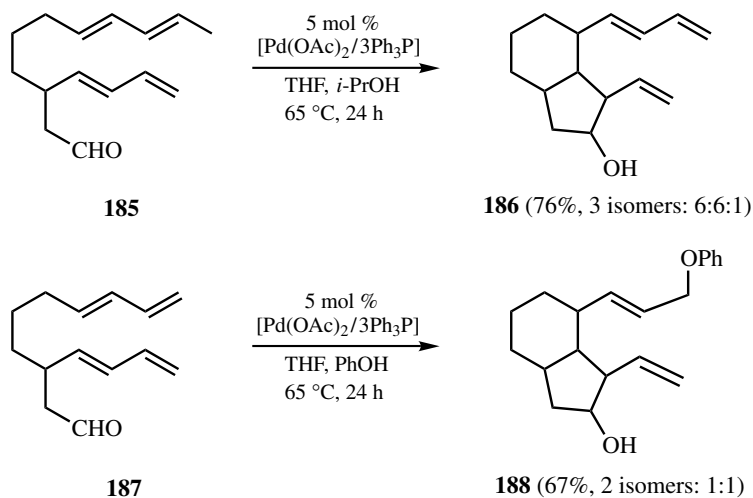
Peiffer and co-workers found an unusual variation in which butadiene dimerization was coupled to incorporation of separate $\text{R}^1(\text{R}^2)\text{C}=\text{Y}$ and protic $\text{H}-\text{Y}$ trapping reagents.^[209] Treatment of butadiene and paraformaldehyde in isopropanol (50 mmol paraformaldehyde, 97 mmol butadiene, 0.1 mmol Pd(OAc)_2 , 0.15 mmol diphosphine or 0.3 mmol monophosphine chiral ligand, *i*-PrOH (10 mL), 25 °C, 24 h) in the presence of aminophosphinephosphinite (AMPP) **181** (IleNOP) affords mostly 2,5-divinyltetrahydropyran (**179**, 74% yield, 5:1 *trans/cis*, 1–4% ee) along with minor amounts of linear dimers; **180** is formed in 13% yield (3% ee). In contrast, when aminophosphinite (**182** (IleOP) is used, the major product is the linear dimer **180** (66% yield, racemic); **179** is formed in 13% yield under these conditions (3:1 *trans* (3% ee)/*cis* (36% ee)). In compound **180** two molecules of formaldehyde have been incorporated, one as a $\text{R}^1(\text{R}^2)\text{C}=\text{Y}$ trapping reagent and one that has condensed with a molecule of *i*-PrOH to form a novel protic $\text{H}-\text{Y}$ trapping reagent (*i*-PrOCH₂OH). Formation of **180** can be rationalized via the addition of *i*-PrOCH₂OH to an intermediate such as **184** (Scheme 58). Surprisingly, AMPPs other than the one derived from isoleucine (i.e., IleNOP, **181**) were found to afford mostly the linear dimer **180**. Of these, the AMMP derived from leucine (i.e., LeuNOP, **183**) gave **180** with the highest ee (20% ee, 54% yield).

E.iii. Aldehydes and Ketones as Trapping Agents: Intramolecular Diene Coupling

Preliminary studies into the doubly intramolecular variant of the linear diene dimerization with aldehyde trapping show promise.^[56] Two versions of the reaction have been demonstrated. Because of the ring constraints, it is unlikely that the aldehyde oxygen can add to the π -allylpalladium, and, therefore, the cycloisomerization reaction was investigated. Bisdien **185** undergoes Pd-catalyzed cyclization to afford the bicyclic ring system **186** (Scheme 59). A 6:6:1 mixture of three diastereomers was obtained in 76% yield. Bisdien **187** undergoes Pd-catalyzed cyclization in the presence of the external protic $\text{H}-\text{Y}$



Scheme 58



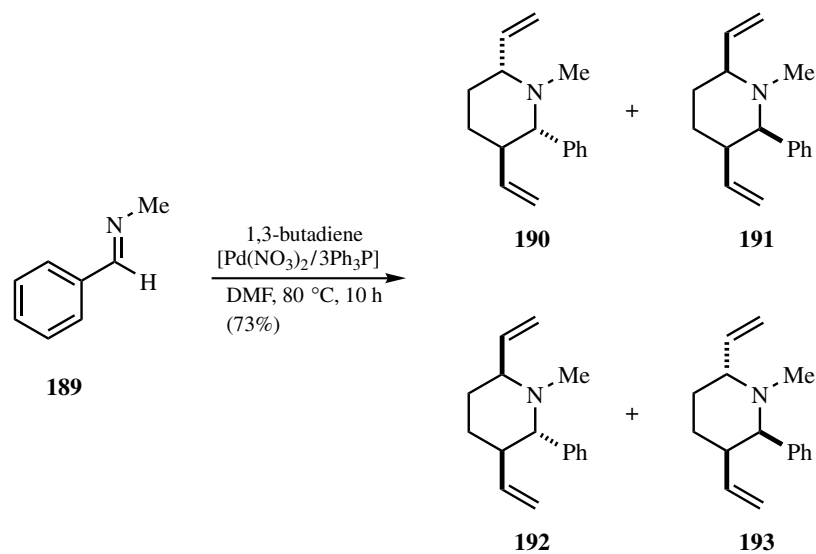
Scheme 59

trapping reagent phenol to the doubly cyclized and trapped product **188** (67%, 1:1 mixture of diastereomers).

E.iv. Imines as the Trapping Agent: Intermolecular Diene Dimerization

The reaction of dienes with imines has not been widely studied.^[210] The results obtained thus far are very similar to those obtained with aldehydes. For example, the reaction of

butadiene with imine **189** ($\text{Pd}(\text{NO}_3)_2$, 3 Ph_3P , DMF, 80 °C, 10 h) affords a mixture of divinylpiperidines **190–193** (73%) in a ratio of 37:11:17:34 (**Scheme 60**). At longer reaction times (40 h, 91% yield), the ratio of products is 45:40:9:6, suggesting that the products equilibrate. This was verified independently by resubjecting the isolated products to the catalyst system. The authors report that $\text{Pd}(\text{acac})_2$ is not a suitable catalyst precursor and that other simple imines behave similarly to **189**.

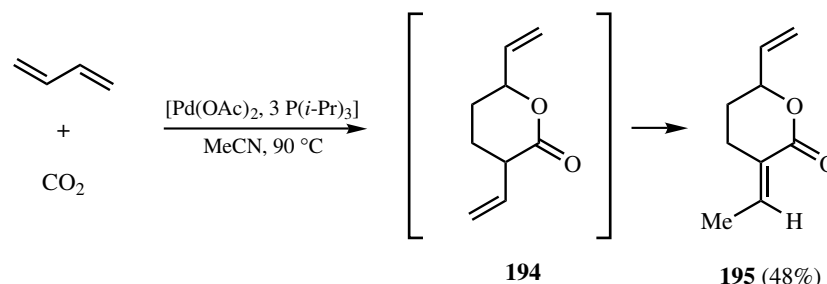


Scheme 60

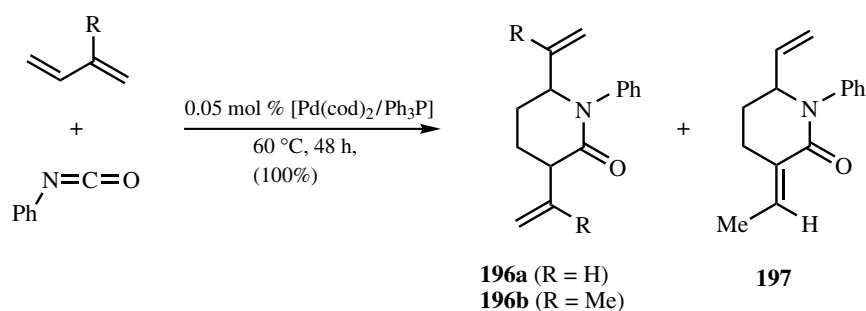
E.v. Carbon Dioxide and Isocyanates as Trapping Agents: Intermolecular Diene Dimerization

As discussed above, carbon dioxide plays an important role in facilitating the reaction of dienes with water. In the absence of water, CO_2 reacts with butadiene to afford a number of addition products.^{[211]–[213]} Given the potential commercial importance of CO_2 as a C_1 building block,^{[214]–[216]} the diene dimerization– CO_2 trapping reaction has been examined in great detail in an effort to optimize the selectivity.^{[20],[217],[218]} Much progress has been made, and now high selectivity for formation of the δ -lactone and yields approaching 60% have been reported. For example, Behr and co-workers reported the reaction catalyzed by $[\text{Pd}(\text{OAc})_2, 3 \text{P}(i\text{-Pr})_3]$ (MeCN, 90 °C) affords the δ -lactone **195** in 48% yield (**Scheme 61**).^[217] The reaction presumably involves the intermediacy of the divinyl derivative **194**, but it isomerizes under the reaction conditions to the more stable α,β -unsaturated derivative **195**. Nonetheless, the scope of the CO_2 -trapping reaction is still rather limited. Under conditions such as those described above, isoprene fails to react or reacts to only very low conversion.^{[20],[219]}

The corresponding reaction with isocyanates has been less widely studied but overall seems to be qualitatively similar. For example, the reaction of butadiene with phenyl isocyanate (0.05 mol % $[\text{Pd}(\text{cod})_2, \text{Ph}_3\text{P} (1:1)]$, 60 °C, 48 h) affords a 1:1 mixture of **196a** ($\text{R} = \text{H}$) and **197** in quantitative yield (**Scheme 62**).^[204] In contrast to the reaction of CO_2 , phenyl isocyanate is reported to readily react with isoprene to afford **196b** ($\text{R} = \text{Me}$, 1:1 *cis/trans*).^[220]



Scheme 61



Scheme 62

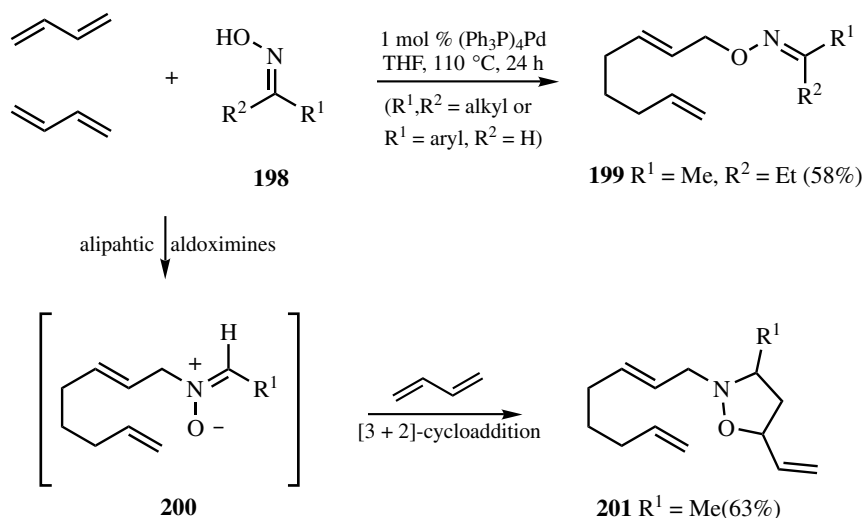
F. MISCELLANEOUS TRAPPING MODES: INTERMOLECULAR DIENE DIMERIZATION

F.i. Oximes as the Trapping Reagent

The reaction of dienes with oximes has not been extensively investigated^[221]; however, it has been shown that the reaction mode depends on the nature of the oxime **198**. Oximes derived from aromatic aldehydes or from ketones afford mixtures of 1-substituted 2,7-octadienyl (e.g., **199**) and 3-substituted 1,7-octadienyl oxime ethers. Such oxime trapping reagents apparently function as typical protic $\text{H}-\text{Y}$ trapping reagents. For example, butadiene undergoes a Pd-catalyzed reaction with methyl ethyl ketone oxime (180 mmol butadiene, 30 mmol oxime **198**, 0.3 mmol $\text{Pd}(\text{Ph}_3\text{P})_4$ or [1:1 $\text{Pd}(\text{NO}_3)_2\text{-Ph}_3\text{P}$], THF (10 mL), 110°C , 4–12 h) to afford **199** and its 3-substituted isomer (9:1, 58%) (**Scheme 63**). In contrast, the reaction of butadiene with the oxime derived from an aliphatic aldehyde (e.g., **198** $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) affords the isoxazolidine containing product **201** (63%). Its formation can be rationalized via initial alkylation on nitrogen, generating a 1,3-dipole (i.e., **200**), which under the reaction conditions undergoes $[3 + 2]$ cycloaddition with a third molecule of butadiene to give the observed product **201**.

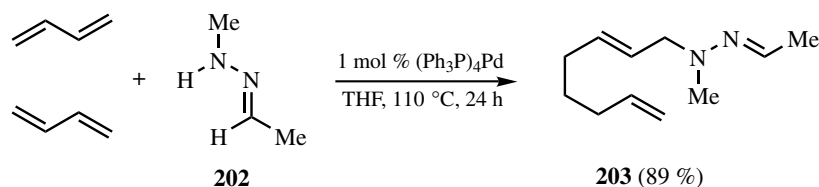
F.ii. Hydrazones as the Trapping Reagent

The reaction of dienes with hydrazones has not been extensively investigated. Nonetheless, the results obtained to date show an unusual dependency on the nature of the substituents.



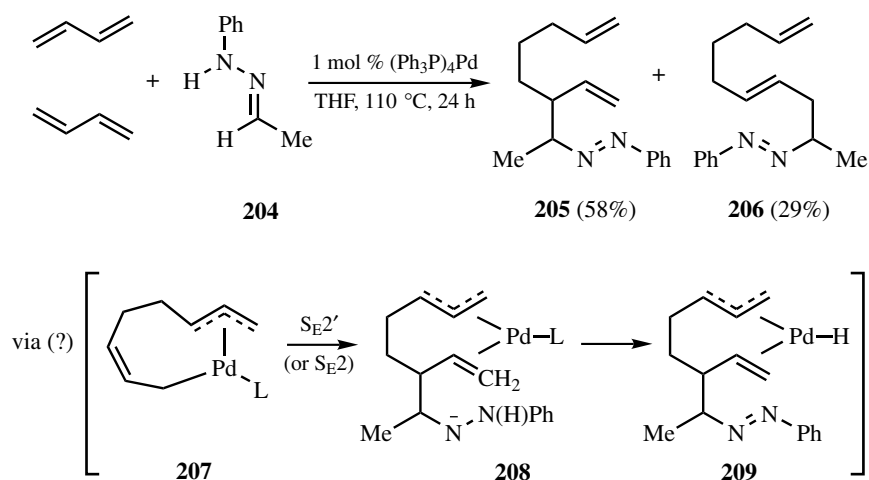
Scheme 63

Methylhydrazones act just like protic $\text{H}-\text{Y}$ trapping reagents.^[222] For example, the methylhydrazone of acetaldehyde **202** undergoes Pd-catalyzed reaction with butadiene to afford linear dimer **203** (1 mol % $(\text{Ph}_3\text{P})_4\text{Pd}$, THF, 110°C , 24 h, 89%) (Scheme 64). Methylhydrazones derived from propanal, acetone, and methyl ethyl ketone behave similarly (80–86% yield).



Scheme 64

Phenylhydrazones exhibit another mode of reaction (Scheme 65).^[223] The reaction of butadiene with the phenylhydrazone of acetaldehyde **204** (1 mol % $(\text{Ph}_3\text{P})_4\text{Pd}$, THF, 110°C , 24 h) affords a 2:1 mixture of **205** and **206** (86%). A small amount of the protic ($\text{H}-\text{Y}$) trapping product was also observed. The formation of **205** can be rationalized by addition of the phenylhydrazone in the fashion of a $\text{R}^1(\text{R}^1)\text{C}=\text{Y}$ -type electrophile to a palladacycle in an $\text{S}_{\text{E}}2'$ fashion to **208** followed by hydride transfer to **209**. Reductive elimination could account for the formation of **205**. Thus, **206** could be formed via a similar pathway, by addition of the phenylhydrazone in an $\text{S}_{\text{E}}2$ rather than $\text{S}_{\text{E}}2'$ fashion. The proposed hydride transfer invoked to rationalize the formation of the observed products offers interesting possibilities and appears worthy of further investigation. Phenylhydrazones derived from propanal, acetone, and methyl ethyl ketone behave similarly (60–95% yield), although the ratio of **205/206** and the proportion of the protic ($\text{H}-\text{Y}$ -type) trapping product vary.



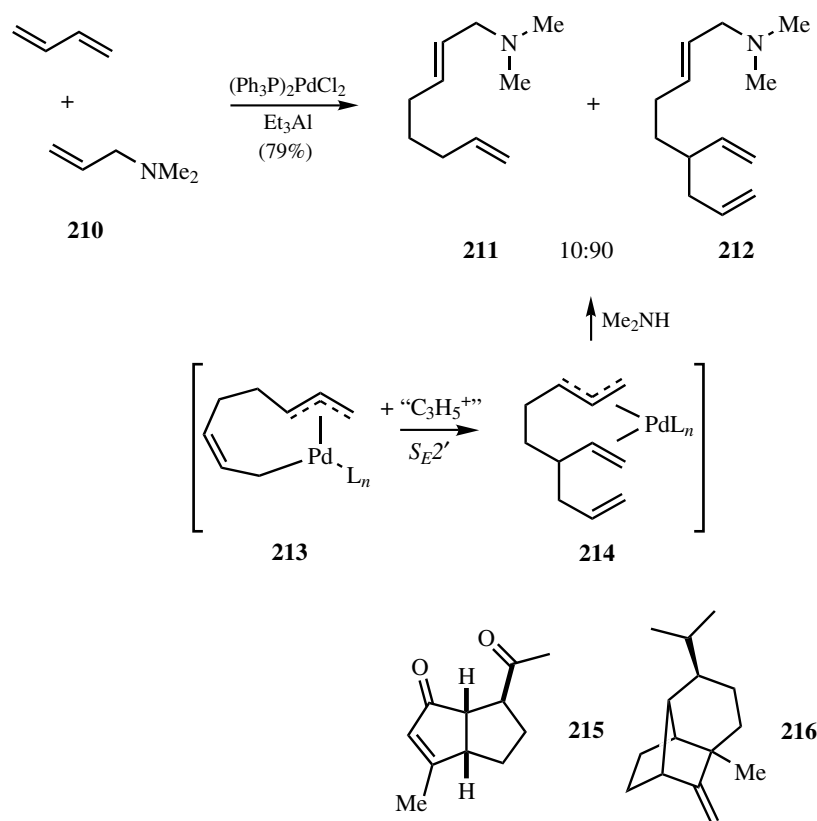
Scheme 65

F.iii. Dimethylallylamine as the Trapping Reagent

The $[(\text{Ph}_3\text{P})_2\text{PdCl}_2\text{-Et}_3\text{Al}]$ -catalyzed reaction of butadiene with *N,N*-dimethylallylamine is a particularly intriguing linear dimerization reaction.^[224] It appears to involve a carbon electrophile (allyl cation or an equivalent). The reaction affords a 1:9 mixture of 1-(*N,N*-dimethylamino)-2,7-octadiene (**211**) and **212** in 79% yield (Scheme 66). The formation of **211** requires dimethylamine and hence requires that *N,N*-dimethylallylamine must decompose under the reaction conditions. Its decomposition could liberate allyl cation or an equivalent (e.g., a π -allylpalladium). The formation of **212** could arise via addition of the allyl electrophile to the palladacycle **213** in an $\text{S}_{\text{E}}2'$ fashion to afford **214** and be completed by subsequent addition of dimethylamine. The adduct **212** has been used as an intermediate in the synthesis of the diquinane **215**^[225] and the natural product (+)-sativene (**216**).^[226]

G. CONCLUDING REMARKS

Diene telomerization has attracted much attention over the years, perhaps not surprisingly so. The reaction can be quite efficient, even industrially practical. It uses relatively stable unactivated substrates and a catalyst to effect bond formations between two, three, or even four components, with considerable flexibility in the choice and combination of those components. These are very desirable features. A number of recent advances hold significant promise for the future. The use of ionic liquids, biphasic conditions, and heterogeneous catalyst systems are exciting developments to the field, as are the discoveries of new, more efficient homogeneous catalysts, a better understanding of the mechanism, and new ligands and catalyst systems that render the reaction more selective. The use of chiral catalysts is as yet modestly effective, but this area is sure to attract much more research. The intramolecular diene coupling and the intramolecular diene coupling with intramolecular trapping constitute a relatively new direction for this chemistry and promise to offer novel ways to efficiently assemble complex ring systems. These advances mark



Scheme 66

growth areas for the chemistry and suggest it will continue to attract intense research efforts in the coming years.

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