

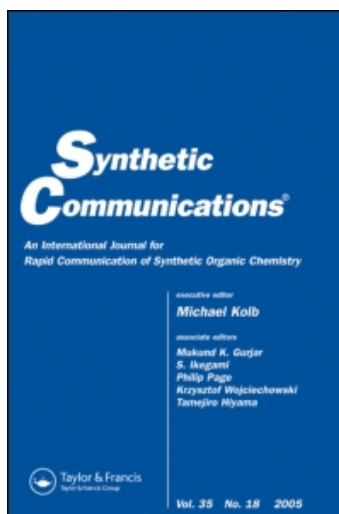
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Cai Jia^a; Fengxian Yu^{ab}; Fang Wang^a; Wangsuo Wu^b; Jing Chen^a

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China ^b Institute of Radiochemistry and Nuclear Environment, Lanzhou University, Gansu Province, China

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CONVENIENT SYNTHESIS OF DICYCLOHEXYLDITHIOPHOSPHINIC ACID

Cai Jia,¹ Fengxian Yu,^{1,2} Fang Wang,¹
Wangsuo Wu,² and Jing Chen¹

¹Institute of Nuclear and New Energy Technology, Tsinghua University,
Beijing, China

²Institute of Radiochemistry and Nuclear Environment, Lanzhou University,
Gansu Province, China

Dicyclohexyldithiophosphinic acid was synthesized by a three-step strategy through the Grignard reaction of PSCl_3 with $\text{cyclo-C}_6\text{H}_{11}\text{MgBr}$ and the P-P bond-cleavage reaction of the intermediate. The ^1H NMR data of ammonium dicyclohexyldithiophosphinate 4 and dicyclohexyldithiophosphinic acid 5 were characterized by ^1H - ^1H correlation spectra.

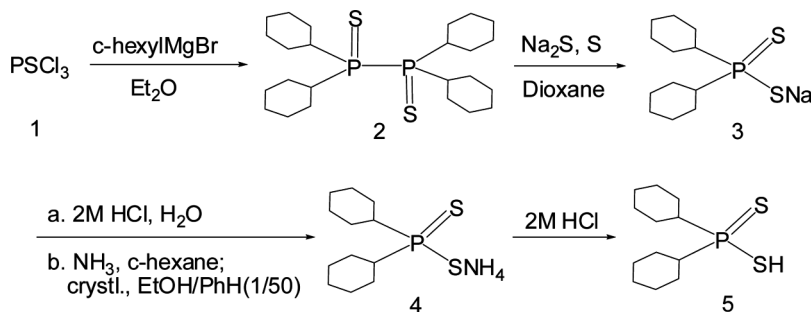
Keywords: Actinides/lanthanides separation; dithiophosphinic acid; synthesis

Diorganyldithiophosphinic acids as well as their derivatives have been investigated for decades. The early research focused on their applications as lubricant additives, insecticides, ore flotation agents, and rubber accelerators.^[1] In recent years, many reports have been delivered on the metal complexes of dithiophosphinic acids, especially on the separation of trivalent actinides from lanthanides,^[2] which is very important for the advanced nuclear fuel cycle and the exploration of sustainable nuclear energy.

Because of the different substituent groups, there are various synthetic routes. Diaryldithiophosphinic acids were obtained mainly by the Higgins's method with P_2S_5 , benzene or substituted benzene, and AlCl_3 .^[3] Di(n-alkyl)dithiophosphinic acids were formed by the Grignard reaction of thiophosphoryl chloride (PSCl_3) with alkylmagnesium halides (RMgX), followed by treatment with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and S powder.^[4] Another method, reacting dialkylphosphine with S in diluted aq. NH_4OH or NaOH and acidifying the resulting intermediate, gave not only the products of aryl groups or n-alkyls but also those of sec-alkyls.^[5] There have been some other methods^[6] reported on the synthesis of dithiophosphinic acid. Dicyclohexyldithiophosphinic acid was most frequently obtained by reaction of dicyclohexylphosphine with S in aq. NH_4OH or NaOH. Herein, we discuss the synthesis of the title compound through the Grignard reaction of PSCl_3 with $\text{c-C}_6\text{H}_{11}\text{MgBr}$ and the

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Address correspondence to Jing Chen, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 102201, China. E-mail: jingxia@tsinghua.edu.cn



Scheme 1. Synthesis of dicyclohexyldithiophosphinic acid.

P-P bond-cleavage reaction of the intermediate compound, which avoids the formation and application of extremely stimulating dicyclohexylphosphine.

PSCl₃ reacted with the Grignard reagent from cyclohexyl bromide and Mg in Et₂O to form tetracyclohexyl-diphosphine disulfide **2**. Formation of this intermediate was confirmed by Issleib and Tzschach.^[7] Similar to the analogs of Me, Et, and Bu, dicyclohexyldiphosphine disulfide exists in the *trans* (C_{2h}) conformation.^[8] This crude intermediate reacted with Na₂S·9H₂O and S in dioxane, giving sodium dicyclohexyldithiophosphinate **3**. Acidification of compound **3** with 2 M HCl afforded a crude product of the title compound. Treating this crude with NH₃ and recrystallizing the resulting ammonium salt gave the white crystal powder **4**. Acidification of **4** with 2 M HCl was achieved to give pure title compound **5** (Scheme 1).

The key for interpretation of ¹H NMR spectra of compounds **4** and **5** lies in the obvious chemical shift difference between equatorial and axial protons. The equatorial protons occur at a lower field than the respective axial ones as a result of the deshielding effect of the fields of C-C bonds. The signs of protons from low to high field in the ¹H-¹H correlation (COSY) spectrum of compound **4** are shown in Fig. 1. This is similar to the ¹H-¹H COSY spectrum of the title compound **5** (Fig. 2).

In summary, we have described a new convenient synthesis of dicyclohexyldithiophosphinic acid. Our chemistry with dialkyldithiophosphinic acids will be reported in due course.

EXPERIMENTAL

Melting points were determined with an Electrothermal IA9100 and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Nexus 470 Fourier transform IR (FTIR) spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Jeol ECA-600 FT-NMR spectrometer. Both low- and high-resolution mass spectra were carried out on GCT-MS Micromass UK or Bruker Apex IX (7.0T) instruments. Anhydrous ethyl ether (Et₂O) and dioxane were prepared by a solvent purification system. All experiments were performed under a nitrogen atmosphere.

Tetracyclohexyldiphosphine Disulfide (2)

Twenty were added ml of the solution of cyclohexyl bromide (61 ml, 0.5 mol) in ethyl ether (130 ml) to a mixture of Mg dust (12.2 g, 0.5 mol), dried Et₂O (20 ml), and

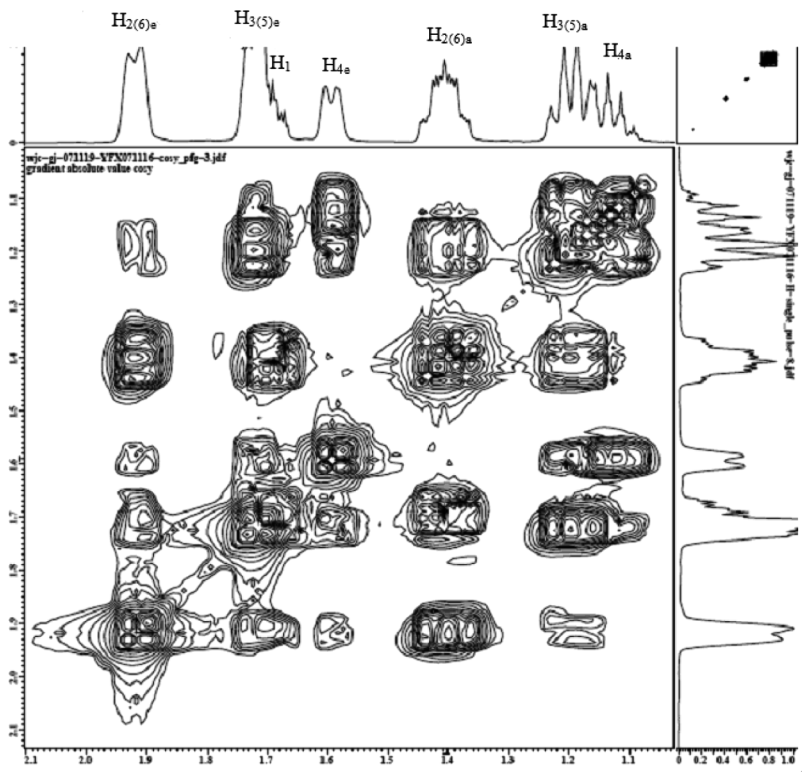


Figure 1. ^1H - ^1H COSY spectrum of compound **4**.

a little I_2 to initiate the reaction. The rest of cyclohexyl bromide in ether was added dropwise when stirring, keeping the reaction mixture mild refluxing. After the addition of bromide, the solution was refluxed by heating until the Mg dust almost disappeared. The resulted Grignard reagent was cooled down to less than 10°C . Under N_2 , PSCl_3 (13 ml, 0.125 mol) was dropped into the stirred Grignard solution in an ice-water bath, keeping the reaction temperature at less than 10°C . After 24 h of stirring at room temperature, the reaction mixture was poured into 0°C 10% H_2SO_4 solution and stirred for a few minutes. The aqueous layer was extracted twice with ether. The organic layers were combined, dried, and condensed, giving colorless oil **2** (22.7 g, 80%), which was directly subjected to the next step.

Ammonium Dicyclohexyldithiophosphate (**4**)

The mixture of compound **2** (22.7 g, 0.05 mol), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (11.9 g, 0.05 mol), and S powder (1.6 g, 0.05 mol) in dioxane (200 ml) was refluxed for 24 h. The hot reaction solution was filtered, and the resulting light-yellow filtrate was condensed to give a red brown solid (22.3 g). This solid was dissolved in water. After removal of the upper oily layer, the aqueous layer was washed twice with petroleum ether. The aqueous layer was adjusted to pH 1 with 2 M HCl and filtered, giving 20 g light-yellow

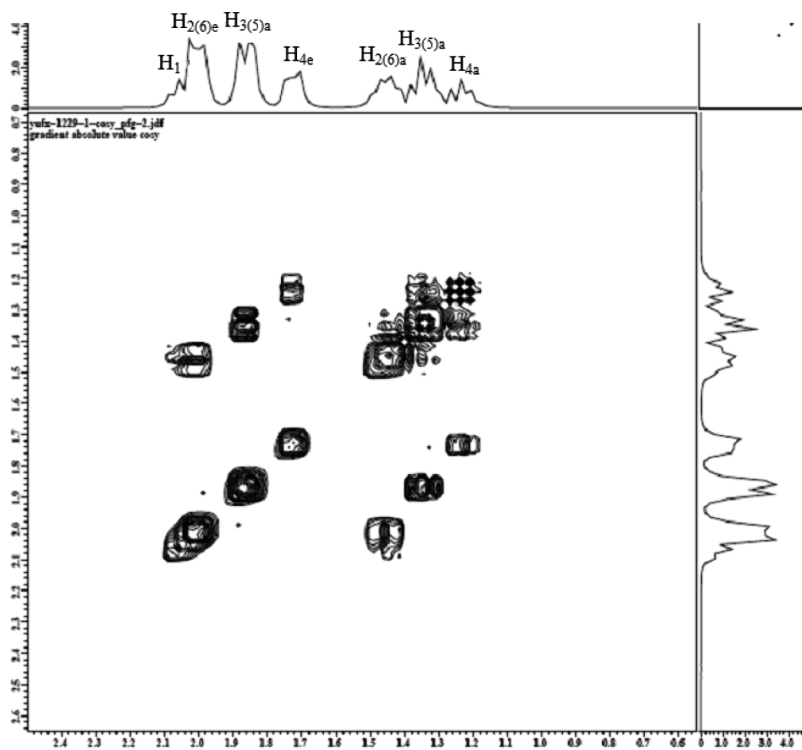


Figure 2. ^1H - ^1H COSY spectrum of title compound **5**.

solid. The product was dissolved in cyclohexane, and dry NH_3 gas was bubbled in, with a light yellow solid (18.5 g) obtained. This solid was recrystallized with alcohol/benzene (1/50, v/v), giving white crystal powder **4** (16 g, 0.057 mol, 57%), mp 179–180 °C. ^1H NMR (600 MHz, CD_3OD) δ ppm 1.17 (m, 6H, 2H_{4a} , 2H_{3a} , 2H_{5a}), 1.40 (m, 4H, 2H_{2a} , 2H_{6a}), 1.59 (d, $J_{4e,4a} = 11.7$ Hz, 2H, 2H_{4e}), 1.71 (m, 6H, 2H_1 , 2H_{3e} , 2H_{5e}), 1.92 (d, $I_{2a,2e} = J_{6a,6e} = 13$ Hz, 4H, 2H_{2e} , 2H_{6e}). ^{13}C NMR (150 MHz, CD_3OD) δ ppm 43.6, 43.3 (2C_1), 26.5, 26.4 (2C_3 , 2C_5), 26.1 (2C_4), 25.8 (2C_2 , 2C_6). ^{31}P NMR (240 MHz, CD_3OD) δ ppm 86.1. HRMS-ESI calcd. for $\text{C}_{12}\text{H}_{26}\text{NPS}_2$ ($\text{M} + \text{NH}_4$) $^+$: 261.0906. Found: 261.0903.

Dicyclohexyldithiophosphinic Acid (**5**)

The white crystal **4** (0.975 g, 0.0035 mol) was dissolved in water (10 ml) and centrifuged. The solution was mixed with 2 M HCl (5 ml) and extracted twice with ether (10 ml). The ether layers were combined, dried, and evaporated to give white crystal powder **5** (0.79 g, 0.0030 mol, 86%), mp 101–102 °C. ^1H NMR (600 MHz, CD_3OD) δ ppm 1.13 (q, $J_{4a,3a} = J_{4a,5a} = 13.0$ Hz, $J_{4a,4e} = 12.4$ Hz, 2H_{4a}), 1.24 (q, $J_{3a,3e} = J_{5a,5e} = 12.4$ Hz, $J_{3a,2a} = J_{3a,4a} = J_{5a,6a} = J_{5a,4a} = 13.0$ Hz, 4H, 2H_{3a} , 2H_{5a}), 1.36 (m, 4H, 2H_{2a} , 2H_{6a}), 1.63 (d, $J_{4a,4e} = 12.4$ Hz, 2H_{4e}), 1.76 (d, $J_{3a,3e} = J_{5a,5e} = 11.04$ Hz, 4H, 2H_{3e} , 2H_{5e}), 1.90 (s, 4H, 2H_{2e} , 2H_{6e}), 1.96 (m, 2H_1). ^{13}C NMR

(150 MHz, CD₃OD) δ ppm 25.56, 25.58, 25.67, 25.83, 25.93 (10C), 41.49, 41.80 (2C₁). ³¹P NMR (240 MHz, CD₃OD) δ ppm 87.33. HRMS-TOF EI⁺ calc. for C₁₂H₂₃PS₂ M⁺: 262.0979. Found: 262.0981.

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