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Synthesis and Multinuclear NMR Characterization of Iminophosphoranyl Phosphines and Silanes

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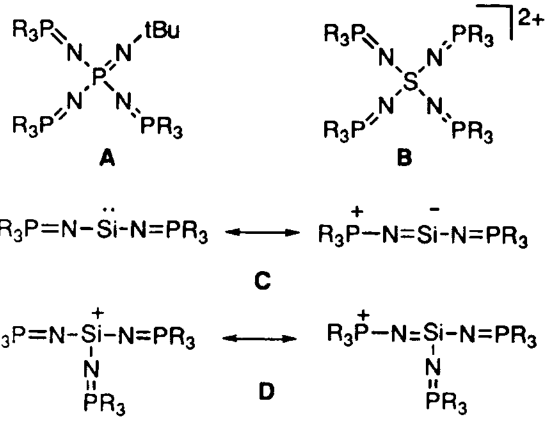
ABSTRACT

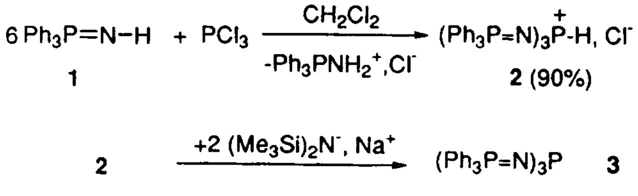
Tris(iminotriphenylphosphoranyl)phosphonium chloride **2**, *tris(iminotriphenylphosphoranyl)phosphine* **3**, *bis(iminotriphenylphosphoranyl)dichlorosilane* **4**, *tris(iminotriphenylphosphoranyl)-chlorosilane* **5** *and -hydrogenosilane* **6** *have been prepared by reacting the iminotriphenylphosphorane* **1** *with trichlorophosphine or the corresponding chlorosilanes. A multinuclear NMR study of these compounds is presented.* *© 1996 John Wiley & Sons, Inc.*

INTRODUCTION

The electron-releasing properties of the R_3PN^- ligand readily explain that the phosphazene base (P_4tBu) **A** is one of the strongest non-ionic bases known [1], and thus it was of interest to prepare the corresponding phosphine, which could well exhibit a similar basicity [2]. Moreover, phosphorane iminato ligands have been used to stabilize metals in high oxidation states [3] and allowed Dehnicke et al. to isolate a dication of hexavalent sulfur **B** [4]. Therefore, it seemed clear that low coordinate main group species such as silylenes [5] and silicenium cations [6] should be stabilized by the R_3PN^- ligand, as shown by the resonance structures **C** and **D** (Scheme 1). Here we report the synthesis of the tris(imino-



SCHEME 1



$$6\,Ph_3P{=}N{-}H + PCl_3 \xrightarrow[-Ph_3PNH_2^+,Cl^-]{CH_2Cl_2} (Ph_3P{=}N)_3\overset{+}{P}{-}H,\ Cl^-$$

1 ⟶ 2 (90%)

$$2 \xrightarrow{+2\,(Me_3Si)_2N^-,\ Na^+} (Ph_3P{=}N)_3P \quad 3$$

SCHEME 2

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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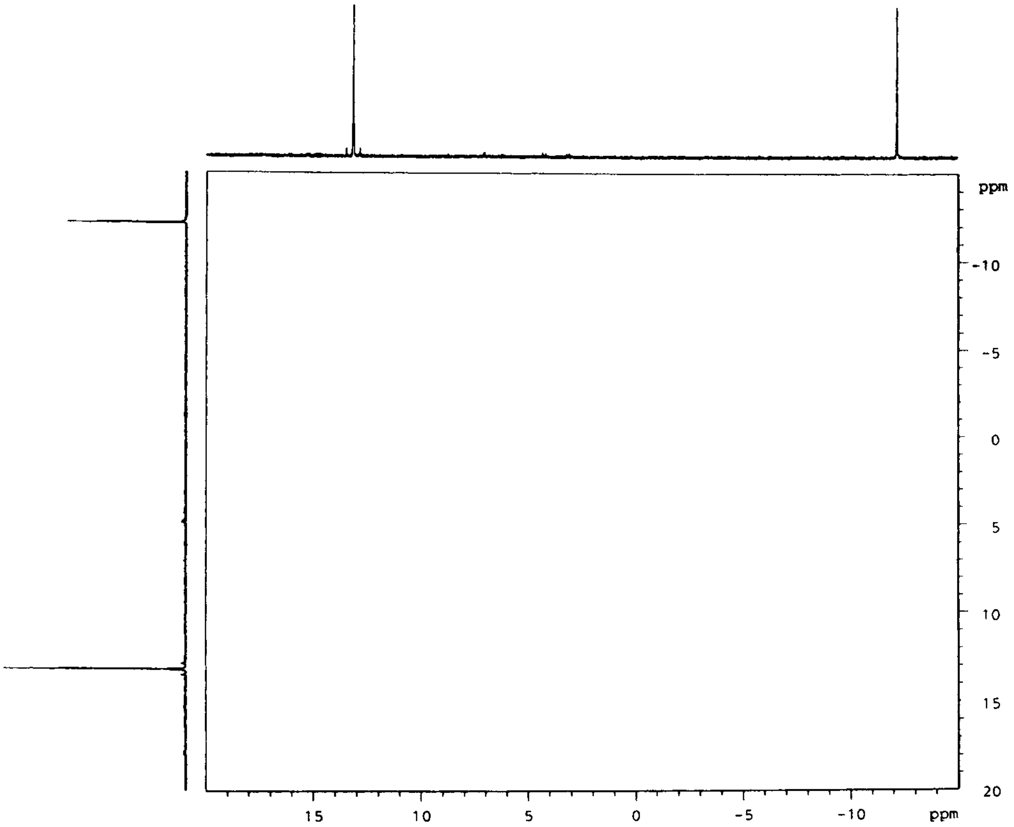
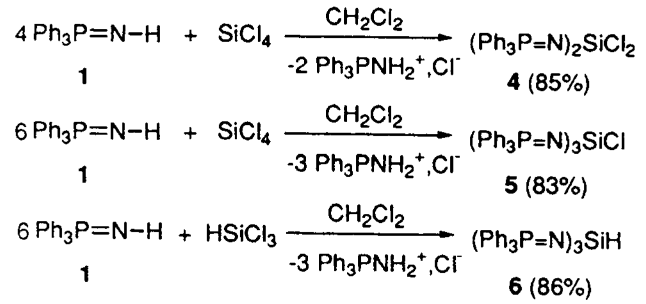


FIGURE 1 2D NMR ^{31}P-^{31}P GE-COSYDQF{^{1}H} experiment for compound **2**.



SCHEME 3

triphenylphosphoranyl)phosphine **3** [7] and of the silylene and silicenium precursors **4**, **5**, and **6**. In all cases, heteronuclear NMR spectroscopy appeared to be the most powerful tool for characterization [8].

No clean reaction was observed by treating the silylated phosphorane imine $R_3PNSiMe_3$ [9] with phosphorus trichloride. However, six equivalents of **1** reacted at room temperature with a dichloromethane solution of PCl_3 affording **2** as a white powder (Scheme 2). The ^{31}P NMR spectrum showed a singlet at $+12.1$ and a doublet at -13.0 ($^{1}J_{PH} = 582$ Hz), suggesting the formation of a phosphonium salt featuring a PH bond; however, no PP coupling constant was observable. Thanks to a 2D NMR ^{31}P-^{31}P GE-COSYDQF {^{1}H} experiment, it appeared that a $^{2}J_{PP}$ coupling constant smaller than 0.5 Hz did exist (Figure 1). Therefore, we could conclude that **2** was the tris(iminotriphenylphosphoranyl)phosphonium salt (90% yield), which was confirmed by mass spectroscopy. The presence of a phosphonium unit demonstrates that the corresponding phosphine **3** is more basic than phosphazene **1**! Indeed, deprotonation of **2** only occurred in the presence of a very strong base, such as sodium bis(trimethylsilyl)amide. The structure of **3** (a highly water- and oxygen-sensitive material) was clear from ^{31}P NMR spectroscopy ($+104.4$, q, $^{2}J_{PP} = 87.9$ Hz; $+7.5$, d, $^{2}J_{PP} = 87.9$ Hz).

Four equivalents of **1** reacted at room temperature with tetrachlorosilane in dichloromethane affording the desired dichlorosilane **4** in 85% isolated yield. In the same way, using six equivalents of **1** with tetrachlorosilane and trichlorosilane, tris(iminotriphenylphosphoranyl)chlorosilane **5** and -hydrogenosilane **6** were obtained in 83% and 86% yield, respectively, as white powders (Scheme 3).

The characterization of these three products **4**–**6** is a nice illustration of the use of heteronuclear

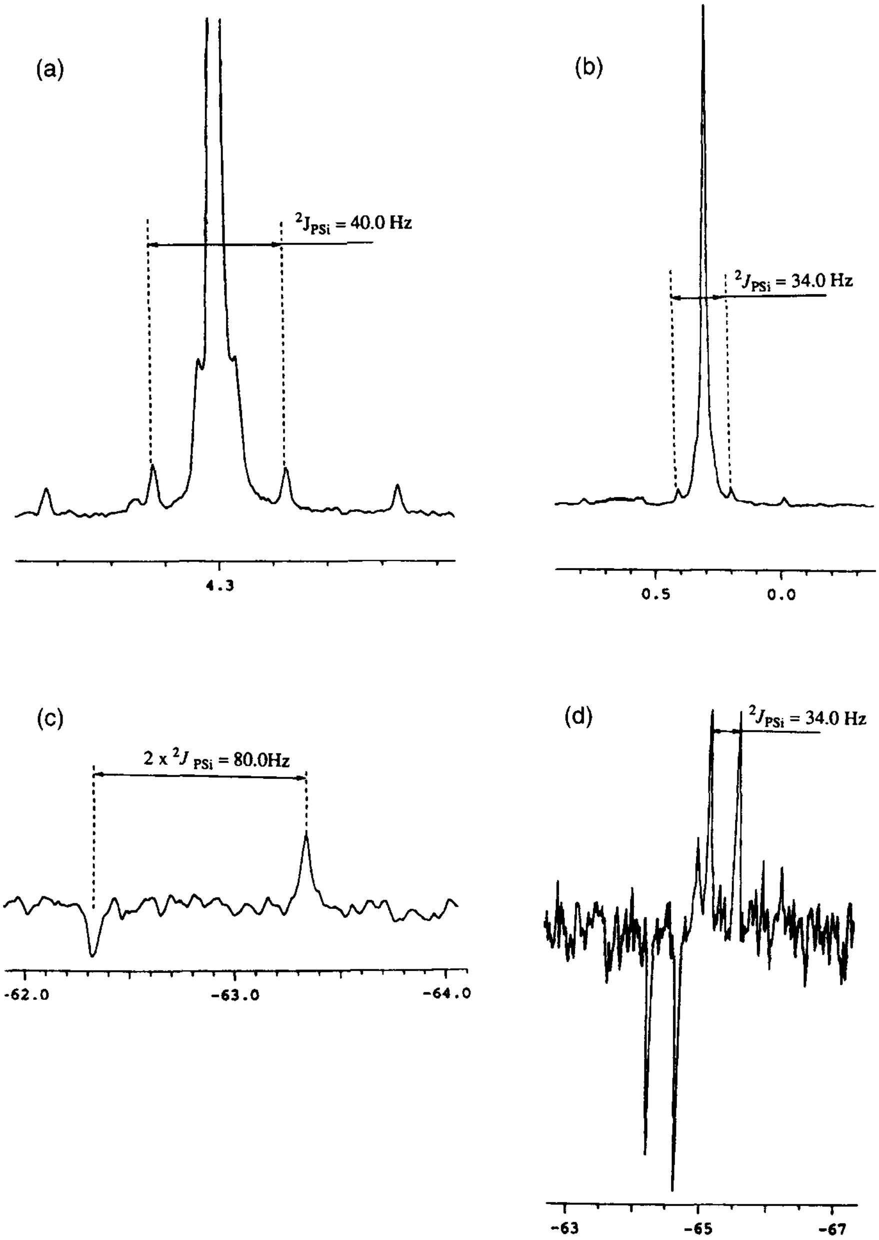


FIGURE 2 ^{31}P NMR spectra of compounds (a) **4** and (b) **5**, showing coupling constants $^2J_{PSi}$. ^{31}P-^{29}Si{^{1}H} INEPT NMR spectra of compounds (c) **4** and (d) **5**.

NMR spectroscopy. To differentiate between the di- and tri-substituted chlorosilanes 4 and 5, ^{1}H and ^{13}C NMR are useless. The ^{31}P NMR chemical shifts are very close (4: + 4.3; 5: + 0.3); however, the phosphorus-silicon coupling constants can be measured (4: 40 Hz; 5: 34 Hz) (Figures 2a and 2b). Starting from these values, the ^{31}P-^{29}Si{^{1}H} INEPT NMR spectra can be recorded (Figures 2c and 2d), and give the definitive proof for the structure. Note that in the case of 4, the two pics centered at -62.8 are separated by 80 Hz, which is double the value of the $^2J_{PSi}$ coupling constant, demonstrating that the signal is a triplet and, thus, the presence of two phosphazene units.

The structure of hydrogenosilane 6 can be deduced from the ^{1}H NMR spectrum that features a quartet centered at 5.4 ($^3J_{PH}$ = 7.7 Hz); moreover, the presence of satellites allows for the determination of the value of the $^1J_{SiH}$ coupling constant (218 Hz) (Figure 3a). The ^{1}H-^{29}Si INEPT spectrum appears as a doublet of quartets centered at -64.9 (Figure 3b). Of particular importance is the infrared stretching

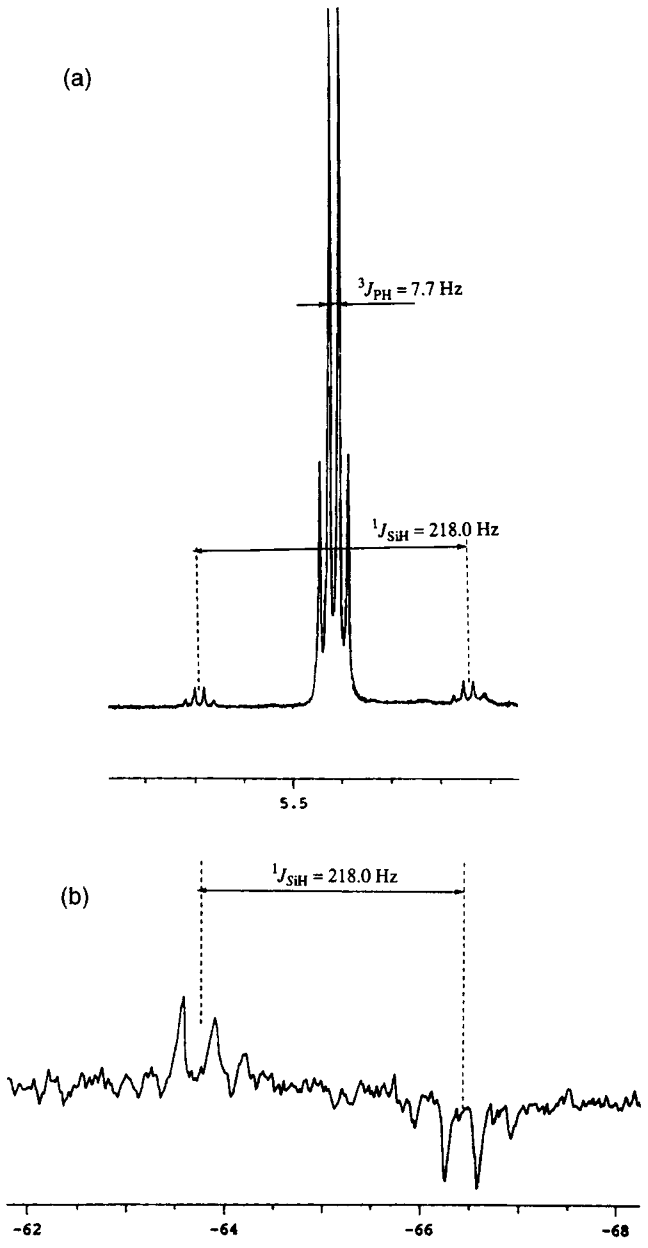


FIGURE 3 (a) Details of ^{1}H NMR spectrum of compound **6**, showing the coupling constants $^1J_{SiH}$ and $^3J_{PH}$. (b) ^{1}H-^{29}Si INEPT NMR spectrum of compound **6**.

frequency of the Si–H group at 1975 cm^{-1}, which is out of the usual range and implies a considerable lengthening of the SiH bond.

Attempts to generate the corresponding silylene from **4** and silicenium cation from **5** and **6** are under active investigation.

EXPERIMENTAL

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points were obtained on an Electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P, and ^{29}Si NMR spectra were recorded on a Bruker AMX400 spectrometer. ^{1}H and ^{29}Si chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

General Procedure. To a room temperature dichloromethane solution (15 mL) of phosphazene **1** (1.66 g, 6 mmol) was added the corresponding amount of PCl_3 (1 mmol), $SiCl_4$ (1 or 1.5 mmol), or $HSiCl_3$ (1 mmol). After stirring of the reaction mixture for 2 hours at room temperature, the phosphonium salts were eliminated by filtration. Evaporation of the solvent in vacuo afforded compounds **2**, **4**, **5**, and **6** as white powders, which were purified by washing with toluene (2 × 5 mL).

Tris(iminotriphenylphosphoranyl)phosphonium Chloride **2**. Yield 90%, mp 49–50°C; ^{31}P NMR (CD_2Cl_2) $\delta = +12.1$ (s br, Ph–P), -13.0 (d, $^1J_{PH} =$ 582.0 Hz, P–H); CIMS *m/z* 860 ($M^+ - Cl^-$). Anal. calcd for $C_{54}H_{46}N_3P_4Cl$ (896.33): C, 72.35; H, 5.17; N, 4.69. Found: C, 72.40; H, 5.21; N, 4.72.

Bis(iminotriphenylphosphoranyl)dichlorosilane **4**. Yield 85%, mp 215°C (dec); ^{31}P{^{1}H} NMR ($CDCl_3$) $\delta = +4.3$ (s); ^{31}P – ^{29}Si{^{1}H} INEPT NMR ($CDCl_3$) $\delta = -62.8$ (t, $^2J_{PSi} = 40.0$ Hz); CIMS *m/z* 651 ($M^+ + 1$). Anal. calcd for $C_{36}H_{30}N_2SiP_2Cl_2$ (651.58): C, 66.36; H, 4.64; N, 4.30. Found: C, 66.30; H, 4.58; N, 4.35.

Tris(iminotriphenylphosphoranyl)chlorosilane **5**. Yield 83%, mp 226°C (dec); ^{31}P {^{1}H} NMR (CD_2Cl_2) $\delta = +0.3$ (s); ^{31}P – ^{29}Si{^{1}H} INEPT NMR (CD_2Cl_2) $\delta = -64.6$ (q, $^2J_{PSi} = 34.0$ Hz); CIMS *m/z* 892 ($M^+ + 1$). Anal. calcd for $C_{54}H_{45}N_3SiP_3Cl$ (892.43): C, 72.67; H, 5.08; N, 4.71. Found: C, 72.78; H, 5.18; N, 4.62.

Tris(iminotriphenylphosphoranyl)silane **6**. Yield 86%, mp > 300°C; ^{31}P{^{1}H} NMR (CD_2Cl_2) $\delta = +0.0$ (s); ^{1}H-^{29}Si INEPT NMR (CD_2Cl_2) $\delta = -64.9$ (dq, $^2J_{PSi} = 26.2$ Hz); ^{1}H NMR (CD_2Cl_2) $\delta = 5.4$ (q, $^3J_{PH} = 7.7$ Hz, $^1J_{SiH} = 218.0$ Hz, Si–H), 7.0 (m, aromatic H); IR (CH_2Cl_2): $\nu = 1975$ cm^{-1} (Si–H). Anal. calcd for $C_{54}H_{46}N_3SiP_3$ (857.99): C, 75.59; H, 5.40; N, 4.90. Found: C, 75.48; H, 5.32; N, 4.65.

Synthesis of Tris(iminotriphenylphosphoranyl)-phosphine **3**. To a room temperature benzene solution (10 mL) of phosphonium salt **2** (0.73 g, 0.81 mmol) was added a suspension of sodium bis(trimethylsilyl)amide (0.30 g, 1.63 mmol) in benzene (5 mL). The reaction was monitored by ^{31}P NMR spectroscopy and was complete after 30 minutes at room temperature. Due to its extreme sensitivity, compound **3** could only be characterized in solution: $^{31}P\{^1H\}$ NMR (C_6H_6) $\delta = +7.5$ (d, $^2J_{PP} = 87.9$ Hz, Ph–P), $+104.4$ (q, $^2J_{PP} = 87.9$ Hz, N_3P).

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