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Preparation and Properties of Bulky Secondary Phosphines[1]

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The isoelectronic bulky secondary phosphines $[(Me_3Si)_2CH]_2PH$ (**1**) and $[(Me_3Si)_2N]_2PH$ (**3**) have been prepared by $LiAlH_4$ reduction of the corresponding chlorides. Compound **1** can also be prepared by treatment of the phosphinyl radical $[((Me_3Si_2)_2CH)_2P]·$ (**2**) with C_6H_5SH. Reduction of the iminophosphine $(Me_3Si)_2NP=N(SiMe_3)$ (**4**) with $LiAlH_4$ followed by hydrolysis affords $(Me_3Si)_2NP(H)N(H)(SiMe_3)$ (**5**). Compounds **1** and **3** fail to undergo the usual deprotonation reactions; however, **5** undergoes facile deprotonation of the N–H bond to afford the corresponding iminophosphoranide anion $[(Me_3Si)_2N(Me_3SiN=)PH]^-$ (**8**). Anion **8** also results from the addition of H^- to **4**. The secondary phosphine **1** undergoes quaternization with MeI to produce the phosphonium salt $[((Me_3Si)_2CH)_2P(Me)H]^+I^-$ (**10**). The reaction of **1** with $Fe_2(CO)_9$ and $Co_2(CO)_8$ yields the complexes $[(Me_3Si)_2CH]_2P(H)Fe(CO)_4$ (**11**) and $[(Me_3Si)_2CH]_2P(H)Co_2(CO)_7$ (**12**), respectively. NMR data have been acquired for the new compounds presented in this work.

Introduction

Bulky alkyl and amido groups can confer unusual patterns of stability and reactivity on several main-group species.[2] In the context of group 5A chemistry, for example, the isoelectronic $(Me_3Si)_2CH$ and $(Me_3Si)_2N$ groups possess sufficient steric bulk to stabilize two-coordinate phosphinyl and arsinyl radicals.[3,4] The same groups have proved to be equally useful for stabilizing phosphenium ions (R_2P^+) and their transition-metal complexes.[5-7] A further useful function of these substituents is that they can undergo 1,2 elimination of silyl halide, thereby offering a synthetic pathway to compounds with novel multiple bonds such as $P=N^8$ and $P=C$.[9,10] The present paper is concerned with the syntheses and chemical properties of $[(Me_3Si)_2CH]_2PH$, $[(Me_3Si)_2N]_2PH$, and $(Me_3Si)_2NP(H)N(H)(SiMe_3)$.[11]

Results and Discussion

Preparation of $[(Me_3Si)_2CH]_2PH$ (1) and $[(Me_3Si)_2N]_2PH$ (3). Bis[bis(trimethylsilyl)methyl]phosphine (**1**) can be prepared in 75–85% yields by the $LiAlH_4$ reduction of $[(Me_3Si)_2CH]_2PCl$ in Et_2O solution. Compound **1** can also be synthesized by treatment of the phosphinyl radical, $[((Me_3Si)_2CH)_2P]·$ (**2**) with C_6H_5SH, viz.
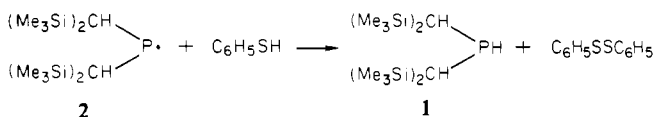
The syntheses of $[(Me_3Si)_2CH]_2PCl$ and **2** have already been described by Lappert and co-workers.[3,4] However, the present procedures for the preparation of the phosphinyl radical **2** differs from the one reported in the literature. Lappert et al.[3,4]

photolyzed $[(Me_3Si)_2CH]_2PCl$ in the presence of an electron-rich olefin, while our synthesis involves treatment of the phosphorus chloride with Na in *n*-hexane. Radical **2** is a distillable red liquid. Dissolution of the distillate in *n*-hexane followed by cooling to –20 °C produces colorless crystals of $[((Me_3Si)_2CH)_2P]_2$ (**2′**), the dimer of **2**. Recently we have determined the structures of **2** and **2′** by gas-phase electron diffraction and low-temperature X-ray crystallography, respectively.[12]

Bis[bis(trimethylsilyl)amino]phosphine (**3**)[13] can be prepared in 70–80% yields by the $LiAlH_4$ reduction of $[(Me_3Si)_2N]_2PCl$. The phosphorus(III) chloride $[(Me_3Si)_2N]_2PCl$ is known to be thermally unstable, undergoing facile elimination of Me_3SiCl to afford the aminoiminophosphine, $(Me_3Si)_2NP=N(SiMe_3)$ (**4**).[14] Serendipitously, however, we have discovered that $[(Me_3Si)_2N]_2PCl$ exhibits long-term stability in the presence of small quantities of the phosphinyl radical $[((Me_3Si)_2N)_2P]·$. Thus, refluxing $[(Me_3Si)_2N]_2$ PCl with Na in *n*-hexane or *n*-octane for 24 h in a sealed system resulted in no obvious changes. However, the ESR spectrum of the solution revealed the presence of $[((Me_3Si)_2N)_2P]·$, while the ^1H, ^{13}C, and ^{31}P NMR spectra corresponded exclusively to those of $[(Me_3Si)_2N]_2PCl$.[15] When the system was opened and the Me_3SiCl was allowed to escape, **4** was formed. Similar results were obtained when small quantities of the radical were generated in other ways. For example, CH_2Cl_2 solutions of $[(Me_3Si)_2N]_2PCl$ can be stored at ambient temperature for long periods of time provided a trace of electron-rich olefin is added prior to photolysis of the solution for 1 h. These observations can be explained by the reactions shown in Scheme I. A key feature of the scheme is the production of Me_3Si radicals, which react rapidly with the aminoiminophosphine **4** to generate the phosphinyl radical $[((Me_3Si_2N)_2P]·$.

Scheme I

$$[(Me_3Si)_2N]_2PCl \xrightarrow[\text{or } h\nu/\text{electron-rich olefin}]{Na/n\text{-hexane}} [((Me_3Si)_2N)_2P]·$$

$$[(Me_3Si)_2N]_2PCl \rightarrow (Me_3Si)_2NP=N(SiMe_3) + Me_3SiCl$$

$$[((Me_3Si)_2N)_2P]· + Me_3SiCl \rightarrow$$
$$[(Me_3Si)_2N]_2PCl + Me_3Si·$$

$$Me_3Si· + (Me_3Si)_2NP=N(SiMe_3) \rightarrow [((Me_3Si)_2N)_2P]·$$
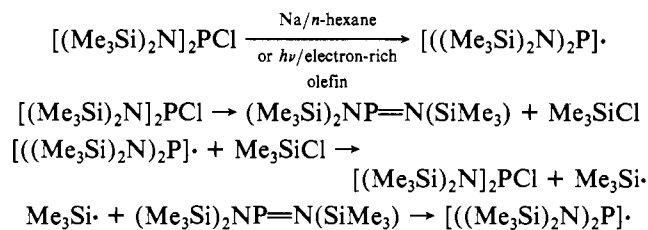
(1) This paper is dedictated to the memory of Dr. James C. Wilburn, 1953–1981.
(2) For an authoritative account for the use of the $(Me_3Si)_2CH$ group in main-group and transition-metal chemistry, see: Lappert, M. F. *Adv. Chem. Ser.* **1976**, *No. 150*, 256–272.
(3) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1976**, 623–624.
(4) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428–2433.
(5) Cowley, A. H.; Mehrotra, S. K., to be published.
(6) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916–2919.
(7) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289–4293.
(8) Numerous reports have appeared on aminoiminophosphines. See, for example: Niecke, E.; Scherer, O. J. *Nachr. Chem. Tech.* **1975**, *23*, 395–397.
(9) Niecke, E.; Schöller, W.; Wildbredt, D. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131–132.
(10) For an erudite review of P=C and P≡C chemistry, see: Appel, R.; Knoll, F; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731–744.
(11) This compound has been synthesized previously by the reaction of $(Me_3Si)_2NP=N(SiMe_3)$ with $Me_2N(H)BH_3$: Niecke, E.; Ringel, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 486–487.

(12) Cowley, A. H.; Ebsworth, E. A. V.; Rankin, D. W. H.; et al., to be submitted for publication.
(13) This aminophosphine was been prepared independently by R. H. Neilson and co-workers. We thank Professor Neilson for discussing his work prior to publication.
(14) (a) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585–586. (b) Scherer, O. J.; Kuhn, N. *Chem. Ber.* **1974**, *107*, 2123–2125.
(15) ESR data for $[((Me_3Si)_2N)_2P]·$ have been published by Lappert et al.[3,4] NMR data for $[(Me_3Si)_2N]_2PCl$ are also availble in the literature.[6,14b]

Scheme II

9a   **9b**
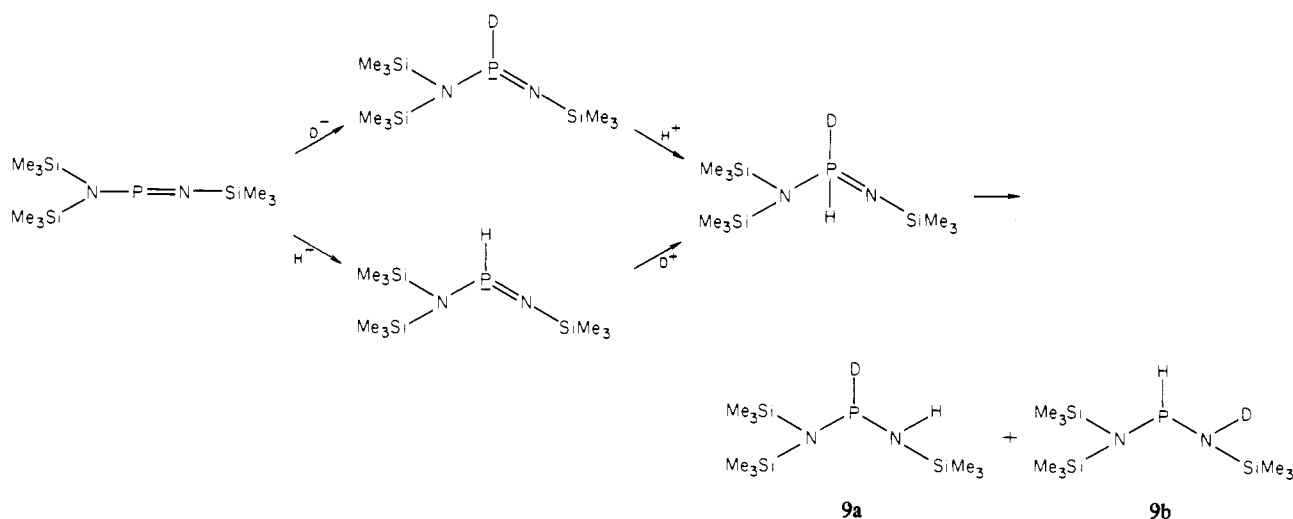
The secondary aminophosphine **5** can be prepared by the reaction of the iminophosphine **4** with $LiAlH_4$ in Et_2O followed by hydrolysis with neutral H_2O. The net reaction is, of course, the addition of H_2 across the P=N bond. Compound **5** has, in fact, been prepared previously by Niecke and co-workers by a different route.[11] However, we believe that the present procedure is simpler and more convenient. There is a certain amount of interest in the mechanism of formation of **5** using the $LiAlH_4/H_2O$ route. Addition of H^- to **4** could, in principle, result in phosphide (**6**), amide (**7**), or iminophosphoranide (**8**)

6   **7**

8
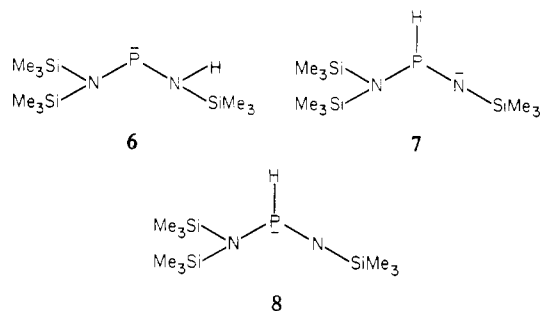
anions. Treatment of **4** with $LiAlD_4$ followed by H_2O, or $LiAlH_4$ followed by D_2O, affords an equimolar mixture of **9a/9b** on the basis of ^{31}P NMR and IR spectroscopy. These

9a   **9b**
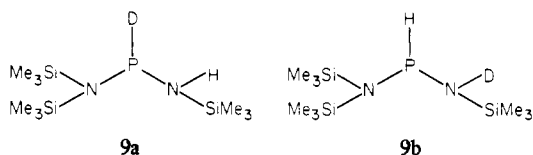
deuteration experiments rule out anion structures **6** and **7** since anion **6** should afford a 100% yield of the P–D bonded aminophosphine, **9a**, while anion **7** should result in the exclusive formation of **9b**.[16] The reactions shown in Scheme II account for our observations. Note that the final product arises by H^+ or D^+ attack on the iminophosphoranide anion followed by

(16) In principle, this result could also arise from an equilibrium between **6** and **7** for which $K = 1$. However, the intermediacy of the iminophosphoranide anion is supported by analogous methylation experiments. Thus, **4** reacts readily with MeLi in Et_2O solution at −78 °C. Hydrolysis of the reaction mixture affords an iminophosphorane, presumably via the corresponding iminophosphoranide anion:

a rearrangement via an H or a D atom shift.

Reactions of [(Me₃Si)₂CH]₂PH (1), [(Me₃Si)₂N]₂PH (3), and (Me₃Si)₂NP(H)N(H)(SiMe₃) (5). To our knowledge, compound **1** is the first example of an air-stable secondary phosphine. While our work was in progress, Issleib et al.[17] prepared the primary alkylphosphine, $(Me_3Si)_3CPH_2$ and found that it is also stable to air. In both cases, the air stability can be attributed to the steric bulk of the alkyl substituents.

The significance of compounds **3** and **5** is that they involve the coexistence of amido and H ligands on the same phosphorus atom. Normally, uncoordinated primary and secondary aminophosphines are unstable.[18] Some of the stability of **3**, **5**, and the recently reported[19] primary aminophosphine $(Me_3Si)_2NPH_2$ might be due to N→Si π bonding; however, the predominant effect is probably steric in origin.

Steric effects also appear to be responsible for the resistance of **1** and **3** to deprotonation. Thus, **1** and **3** fail to react with *n*-BuLi, *n*-BuLi/TMEDA, MeLi, or KH. When the steric bulk is reduced, deprotonation becomes possible. Thus, **5** reacts readily with *n*-BuLi. It was not clear, however, whether deprotonation occurred at nitrogen or phosphorus, i.e., whether anions **6**, **7**, or **8** were produced. Treatment of **5** with *n*-BuLi followed by D_2O quenching of the reaction mixture results in **9a,b**. It is therefore apparent that deprotonation of **5** occurs at nitrogen to produce the iminophosphoranide anion **8**, the same anion that is produced by addition of H^- to the iminophosphine **3**.

Despite the steric bulk of the ligands in **1**, this secondary phosphine will undergo quaternization with MeI to afford the phosphonium salt $[((Me_3Si)_2CH)_2P(Me)H]^+I^-$ (**10**). Compound **1** is also capable of acting as a ligand. For example, reaction of **1** with $Fe_2(CO)_9$ produces the $Fe(CO)_4$ complex **11**. Since ν_{PH} and $^1J_{PH}$ are detectable in IR and NMR experiments, respectively, we deduce that **11** is a normal secondary phosphine complex, i.e., $[(Me_3Si)_2CH]_2P(H)Fe(CO)_4$, and not a hydrido complex.[20] The reaction of **1** with $Co_2(CO)_8$ affords a thermally unstable complex, $[(Me_3Si)_2CH]_2P(H)Co_2(CO)_7$ (**12**), which we could only characterize spectroscopically. The pattern of CO stretching frequencies for **12** is similar to those reported for $(C_6H_5)_3P$-

(17) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Chem.* **1980**, *20*, 153.
(18) Coordinated aminophosphines of this type are stable, however. See: Huttner, G.; Muller, H. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 571–572. Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488–1492.
(19) Niecke, E.; Rüger, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 62.
(20) Several other primary and secondary phosphines produce $LFe(CO)_4$ complexes. See: Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1972**, *11*, 1609–1615.

Table I. Summary of Pertinent NMR and IR Data for $(Me_3Si)_2CH$- and $(Me_3Si)_2N$-Substituted Phosphorus Compounds

	chem shifts, ppm[a,b]				
compd	^{31}P	^{13}C	^1H	J, Hz	IR, cm^{-1}
$[(Me_3Si)_2CH]_2PH$ (1)	-72.2	1.66 (SiMe$_3$) 1.93 (SiMe$_3'$) 7.53 (CH)	0.16 (br,[c] SiMe$_3$, SiMe$_3'$) 1.2 (CH)	J_{PH} = 195.3, J_{PC} = 47.8 J_{PCSiC} = 1.0, $J_{PCSiC'}$ = 4.4 J_{PCH} = 6.2	ν_{PH} = 2300
$[((Me_3Si)_2CH)_2P]_2$ (2')	19.0	4.49 (SiMe$_3$) 6.12 (SiMe$_3'$)			
$[(Me_3Si)_2N]_2PH$ (3)	59.6			J_{PH} = 207.0	ν_{PH} = 2220, 2300
$(Me_3Si)_2NP(H)N(H)SiMe_3$ (5)	33.8		0.12 (NSiMe$_3$) 0.21 (N(SiMe$_3$)$_2$) 6.93 (br,[c] PH)	J_{PH} = 220.0 J_{PNSiCH} = 0.75 (NSiMe$_3$) J_{PNSiCH} = 1.2 (N(SiMe$_3$)$_2$)	ν_{PH} = 2265 ν_{NH} = 3180 (br),[c] 3400
$(Me_3Si)_2NP(D)N(H)SiMe_3$ (9a)	33.8		0.15 (NSiMe$_3$) 0.23 (N(SiMe$_3$)$_2$)	J_{PD} = 33.0 J_{PNSiCH} = 0.8 (NSiMe$_3$)	ν_{PD} = 1640 ν_{NH} = 3160 (br),[c] 3350
$(Me_3Si)_2NP(H)N(D)SiMe_3$ (9b)	33.8		0.15 (NSiMe$_3$) 0.23 (N(SiMe$_3$)$_2$)	J_{PH} = 219.7 J_{PNSiCH} = 1.2 (N(SiMe$_3$)$_2$)	ν_{PH} = 2245 ν_{ND} = 2480
$[((Me_3Si)_2CH)_2P(Me)H]^+I^-$ (10)	1.6	1.98 (SiMe$_3$) 3.02 (SiMe$_3'$) 9.59 (Me)	0.32 (SiMe$_3$, SiMe$_3'$) 0.78 (CH) 1.92 (Me)	J_{PH} = 481.7, J_{PSiC} = 3.4 $J_{PSiC'}$ = 3.0, J_{PC} = 20.5 J_{PCH} = 21.9 (CH) J_{HPCH} = 6.0 (CH) J_{PCH} = 13.5 (Me) J_{HPCH} = 5.5 (Me)	
$[(Me_3Si)_2CH]_2PHFe(CO)_4$ (11)	3.1	1.89 (SiMe$_3$) 3.06 (SiMe$_3'$) 18.6 (CH) 216.5 (CO)	-0.03 (SiMe$_3$, SiMe$_3'$) 0.60 (CH) 5.58 (PH)	J_{PH} = 348.6, $J_{PSiC'}$ = 2.9 J_{PC} = 5.9, J_{PFeC} = 16.2 J_{PCSiCH} = 2.5, J_{PCH} = 16.4 J_{HPCH} = 4.5	ν_{PH} = 2330 ν_{CO} = 1925 (br),[c] 1955, 2045
$[(Me_3Si)_2CH]_2PHCo_2(CO)_7$ (12)	6.5			J_{PH} = 380.0	ν_{PH} = 2350 ν_{CO} = 1970, 1995, 2030, 2060, 2080 (sh)[c]

[a] See Experimental Section for statement of references used. [b] A positive value means downfield (deshielded). [c] br = broad; sh = shoulder.

$Co_2(CO)_7$ by Markó and co-workers.[21] Moreover, ν_{PH} and $^1J_{PH}$ are detectable in IR and NMR experiments, respectively, thus suggesting the following structure assignment for **12**.

12
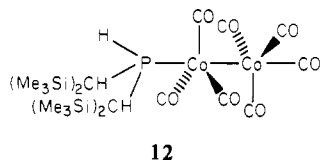
NMR and IR Spectra. A summary of pertinent NMR and IR spectral data is assembled in Table I. The interpretation of most of these data is straightforward, and extensive discussion is not required. It might be helpful, however, to note that **1** and related compounds possess three prochiral centers (•):[22]
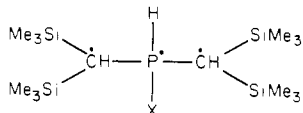
The anticipated diastereotopy is evident in the ^1H and ^{13}C NMR spectra in most instances. However, in some cases there is overlapping of peaks or accidental chemical shift degeneracy.

Experimental Section

Materials and General Procedures. The chlorophosphine $[(Me_3Si)_2CH]_2PCl$ was made by the procedure of Lappert et al.[3,4] However, the preparation of compound was greatly aided by our convenient one-pot synthesis of the precursor $(Me_3Si)_2CHCl$.[23] Literature procedures were also employed for the syntheses of $[(Me_3Si)_2N]_2PCl$,[24] $(Me_3Si)_2NP=N(SiMe_3)$,[14] and $Fe_2(CO)_9$.[25] All

(21) Szabó, P.; Fekete, L.; Bor, G.; Nagy-Magos, Z.; Markó, L. *J. Organomet. Chem.* **1968**, *12*, 245-248.

(22) For an excellent review of the NMR aspects of prochiral assemblies, see: Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307-322.

(23) Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 591-595.

(24) This compound was prepared originally by Schere and Kuhn.[14b] See ref 6 for the low-temperature crystallization procedure and additional NMR data.

other compounds were procured commerically and, in most instances, used without further purification. All solvents were dried and distilled prior to use.

Most of the materials described herein are air and/or moisture sensitive. Accordingly, all operations were performed in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanalytical Services, Ltd., Vancouver, B.C., Canada.

Spectroscopic Measurements. The ^{13}C (20.0-MHz) and ^{31}P (32.384-MHz) NMR spectra were measured in the FT mode on Varian FT 80 instruments. Dichloromethane (54.2 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra. All ^1H (90.0-MHz) spectra were measured on a Varian EM 390 spectrometer and are referenced with respect to internal Me_4Si.

IR spectra were obtained on a Perkin-Elmer 337 instrument using polystyrene as an external reference. Medium- and high-resolution mass spectra were determined on Du Pont-Consolidated Model 21-491 and 21-100 instruments, respectively. Perfluorokerosine was used as calibrant for the HRMS.

Preparation of $[(Me_3Si)_2CH]_2PH$ (1) Using LiAlH$_4$. The chlorophosphine $[(Me_3Si)_2CH]_2PCl$ (5.16 g, 13.4 mmol) in 20 mL of Et_2O was added via a double-tipped needle to a stirred slurry of LiAlH$_4$ (0.272 g, 7.2 mmol) in 50 mL of Et_2O. This slurry was stirred at ambient temperature for 1 h whereupon it was quenched *very slowly* with ~5.0 mL of acidified water. The solution was filtered, and the organic layer was separated from the aqueous layer and dried over Linde 4-Å molecular sieves. Ether was removed in vacuo, and the resulting clear liquid was fractionally distilled on a short-path column to yield $[(Me_3Si)_2CH]_2PH$ (1) (3.86 g, 11.0 mmol) as an air-stable, colorless liquid, bp 65-75 °C (0.04 torr), in 82% yield. HRMS: calcd 350.1865; found 350.1874. The NMR and IR data for **1** are listed in Table I.

Preparation of the Phosphinyl Radical $[((Me_3Si)_2CH)_2P]$• (2) and the Diphosphine $[((Me_3Si)_2CH)_2P]_2$ (2'). A solution of $[(Me_3Si)_2CH]_2PCl$ (6.67 g, 17.3 mmol) in 75 mL of *n*-hexane was heated with Na chips (0.437 g, 19.0 mmol) at 80 °C for 24 h. The bright red solution was evacuated to remove all traces of solvent. The resulting orange-red liquid/solid mixture was distilled on a short-path column to afford a mixture of $[((Me_3Si)_2CH)_2P]$• (2) and $[(Me_3Si)_2CH]_2PH$ (1) as a bright red liquid, bp 70-78 °C (0.03 torr).

(25) Braye, E. H.; Hübel, W. *Inorg. Synth.* **1966**, *8*, 178-181.

Recrystallization of this mixture from an equal volume of *n*-hexane at -20 °C produced colorless crystals of [((Me₃Si)₂CH)₂P]₂ (2'), the dimer of the phosphinyl radical **2**. The effective yield of **2** was 41% based on obtaining 2.49 g (3.56 mmol) of **2'**. Upon warming to room temperature, the crystals of **2'** retained their morphology although a definite orange color became perceptible. Gentle warming caused melting and the production of bright red liquid phosphinyl radical **2**. Some NMR data for **2'** are presented in Table I. Compounds **2** and **2'** have been characterized by electron diffraction and low-temperature X-ray crystallography, respectively.[12]

Preparation of [(Me₃Si)₂CH]₂PH (1) from the Phosphinyl Radical [((Me₃Si)₂CH)₂P]· (2). Thiophenol (0.35 g, 3.18 mmol) in 5 mL of *n*-hexane was added dropwise to a stirred solution of [((Me₃Si)₂CH)₂P]· (2) (1.11 g, 3.18 mmol) in 10 mL of *n*-hexane. The red color of the phosphinyl radical was completely discharged at the end of the addition. The yield of [(Me₃Si)₂CH]₂PH (1) was virtually quantitative. Samples prepared by this method and the LiAlH₄ route were identical spectroscopically.

Preparation of [(Me₃Si)₂N]₂PH (3). Freshly recrystallized[24] [(Me₃Si)₂N]₂PCl (9.08 g, 23.5 mmol) in 20 mL of Et₂O was added slowly to a stirred slurry of LiAlH₄ (0.662 g, 17.4 mmol) in 50 mL of Et₂O at 0 °C by means of a double-tipped needle. The slurry was stirred at room temperature for 1 h and then quenched with 10 mL of neutral water *very slowly*. Filtration, followed by removal of the aqueous layer and drying of the organic layer, afforded a pale yellow solution. Removal of the solvent followed by distillation under reduced pressure yielded [(Me₃Si)₂N]₂PH (3) (6.45 g, 18.3 mmol), bp 60–72 °C (0.02 torr), as a colorless liquid, which solidified upon standing. Yields ranged from 75 to 80%. Some NMR and IR data for **3** are listed in Table I. HRMS: calcd 352.1771; found 352.1781.

Preparation of (Me₃Si)₂NP(H)N(H)(SiMe₃) (5). The amino-iminophosphine (Me₃Si)₂NP=N(SiMe₃) (4) (12.85 g, 46.2 mmol) in 15 mL of Et₂O was added dropwise at 0 °C to a stirred slurry of LiAlH₄ (1.70 g, 44.8 mmol) in 50 mL of Et₂O. The solution was allowed to warm to room temperature for 30 min prior to *slow* quenching of the reaction mixture with neutral, degassed H₂O. The Li and Al salts were filtered off, and the aqueous layer was removed from the organic filtrate by means of a syringe. The organic layer was concentrated under vacuum and the resulting yellow liquid was distilled to give (Me₃Si)₂NP(H)N(H)(SiMe₃) (5), bp 55–60 °C (0.03 torr), in 41% yield (5.30 g, 18.9 mmol). The compound is identical with that reported by Niecke and Ringel.[11] Some NMR and IR data for **5** are presented in Table I.

Preparation of (Me₃Si)₂NP(D)N(H)(SiMe₃) (9a) and (Me₃Si)₂NP(H)N(D)(SiMe₃) (9b). These compounds were prepared in a manner identical with that for the perprotio compound **5**. One experiment employed LiAlH₄ reduction followed by D₂O quenching of the reaction mixture; the other utilized LiAlD₄ reduction and H₂O quenching of the reaction mixture. Both experiments resulted in a 50/50 mixture of **9a** and **9b** on the basis of ³¹P NMR and IR spectroscopy (Table I).

Attempts To Deprotonate [(Me₃Si)₂CH]₂PH (1) and [(Me₃Si)₂N]₂PH (3) with *n*-BuLi, MeLi, and KH. Compounds **1** and **3** failed to react with *n*-BuLi, *n*-BuLi/TMEDA, MeLi, or KH. The systems were monitored by ³¹P NMR spectroscopy.

Deprotonation of (Me₃Si)₂NP(H)N(H)(SiMe₃) (5). Compound **5** (0.56 g, 2.0 mmol) in 5 mL of *n*-hexane was treated with *n*-BuLi (1.25 mL of a 1.6 M solution in *n*-hexane). After the reaction mixture was stirred at -78 °C for 30 min, it was quenched with D₂O and allowed to warm slowly to room temperature. Measurement of the ³¹P NMR spectrum of the solution indicated that an equimolar mixture of **9a** and **9b** had been formed.

Preparation of [((Me₃Si)₂CH)₂P(Me)H]⁺I⁻ (10). Methyl iodide (0.91 g, 6.4 mmol) was added by means of a syringe to a stirred solution of [(Me₃Si)₂CH]₂PH (1) (1.12 g, 3.2 mmol) in 5 mL of Et₂O. A white precipitate formed slowly. After 6 h the Et₂O was removed by evacuation and the residual white solid was recrystallized from a CH₂Cl₂/Et₂O mixture at -10 °C. Filtration followed by drying in vacuo afforded 1.12 g (2.27 mmol) of white crystalline [((Me₃Si)₂CH)₂P(Me)H]⁺I⁻ (10) in 71% yield. Anal. Calcd for C₁₅H₄₂IPSi₄: C, 36.6; H, 8.6. Found: C, 36.3; H, 8.7. Some NMR data for **10** are presented in Table I.

Preparation of [(Me₃Si)₂CH]₂PHFe(CO)₄ (11). A mixture of [(Me₃Si)₂CH]₂PH (1) (0.397 g, 1.1 mmol) and Fe₂(CO)₉ (0.449 g, 1.23 mmol) in 10 mL of *n*-hexane was stirred at room temperature for 24 h. Filtration of the reaction mixture through a medium-porosity frit followed by prolonged pumping to remove all volatiles afforded 0.456 g (0.88 mmol) of pure dark brown liquid [(Me₃Si)₂CH]₂PHFe(CO)₄ (11) in 80% yield. Anal. Calcd for C₁₈H₃₉FeO₄PSi: C, 41.7; H, 7.6. Found: C, 41.7; H, 8.2. Some NMR and IR data for **11** are presented in Table I.

Preparation of [(Me₃Si)₂CH]₂PHCo₂(CO)₇ (12). The phosphine [(Me₃Si)₂CH]₂PH (1) (0.446 g, 1.28 mmol) was syringed into a stirred solution of Co₂(CO)₈ (0.438 g, 1.28 mmol) in 5 mL of *n*-hexane at room temperature. The product, [(Me₃Si)₂CH]₂PHCo₂(CO)₇ (12), undergoes decomposition upon heating or standing overnight; hence it was possible to characterize this compound only by the NMR and IR spectroscopic data presented in Table I.

Note Added in Proof. The reaction of [(Me₃Si)₂CH]₂PCl with Na in hydrocarbon solvents has also been studied by: Power, P. P. D.Phil. Thesis, University of Sussex, 1977. We thank Professor Power for bringing this earlier work to our attention.

Registry No. **1**, 83436-92-4; **2**, 63429-86-7; **2'**, 83436-91-3; **3**, 81072-86-8; **4**, 50732-21-3; **5**, 63104-54-1; **9a**, 83928-53-4; **9b**, 83928-54-5; **10**, 83928-55-6; **11**, 83928-52-3; **12**, 83947-19-7; C₆H₅SH, 108-98-5; [(Me₃Si)₂CH]₂PCl, 63429-87-8; [(Me₃Si)₂N]₂PCl, 53327-45-0; Fe₂(CO)₉, 15321-51-4; Co₂(CO)₈, 10210-68-1; Co, 7440-48-4.

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Kinetics of the Hexaammineruthenium(II)–(Ethylenediaminetetraacetato)iron(III) Reaction. A Relative Marcus Theory Evaluation

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Kinetic parameters for the outer-sphere reaction between Ru(NH₃)₆²⁺ and Fe(EDTA)⁻ have been determined at I = 1.00 M: k = (2.2 ± 0.2) × 10⁶ M⁻¹ s⁻¹ (25 °C), ΔH^* = 3.6 ± 0.3 kcal mol⁻¹, and ΔS^* = -17 ± 1 eu. With the reported variation of k with I, these results provide the basis for a detailed evaluation of the Marcus cross-reaction relationships for ΔG^*, ΔH^*, and ΔS^*. At I = 0.00 M the agreement with extrapolated experimental results is excellent when the work terms are taken properly into account. Major components of the substantial corrections they provide to ΔG_0^*, ΔH_0^*, and S_0^* are attributable to differences in solvation shell polarization relative to the respective self-exchanges. At I = 0.10 M, ΔH^* and ΔS^* are less well accounted for than is ΔG^*, with the deviations suggesting an exaggerated shielding of charge by the supporting electrolyte within the Debye–Hückel model for ΔH^w and ΔS^w.

Outer-sphere electron transfer processes have been modeled by Marcus and others[1-4] in terms[5-8] of (a) the kinetic barriers

attending a self-exchange and (b) the relationship between the kinetic parameters of a cross reaction and the corresponding