experiment of this same mixture would provide evidence for the back-reaction only (eq 9) and could not reveal the actual sequence of events leading to this final step. A variety of redox products can be produced by electron-transfer quenching of more than one excited-state molecule. Judicious adjustment of the concentrations of photosensitizers and quenchers can be used to vary the relative amounts of these redox products.

Note the distinction between the system described here using a nonabsorbing quencher (Fe^{3+}) and those described previously in which quenching occurs via the ground state of a photoactive partner.[1–3] In the present case, the rapid intervening reaction (eq 3) results in the exclusive production of only two redox products, $Ru(trpy)(bpy)(NH_3)^{3+}$ and Fe^{2+}, which undergo a relatively slow back-reaction (eq 9).

The important point to be made is that the oxidized photoactive species with the lower reduction potential is produced in the intervening reaction (eq 3). Therefore, in the design of light energy conversion schemes based on this approach, the reduction potentials of *all* photoactive species should be large enough to produce the desired reaction. Regardless of the details of the reactions, a common feature of all the schemes involving photoactive mixtures described so far is the production of only two redox products. (An exception to this statement is the special case of the $Ru(bpy)_3^{2+}/Ru(phen)_3^{2+}$ mixture,[8] in which both photosensitizers have the same reduction potential (1.30 V) for the $RuL_3^{3+/2+}$ couple).

There has been a report in which a mixture of three photoactive species was used.[19] In that case MV^{2+} was photoreduced by a mixture of tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II), (tetraphenylporporphyrinato)zinc(II), and hematoporphyrin. Assuming only MV^{2+} quenching of the excited states and hematoporphyrin to be the most easily oxidized of the three photoactive species, the net redox products should be $MV^{+\cdot}$ and oxidized hematoporphyrin.[20] A flash photolysis experiment of the type described here would enable this prediction to be tested.

Acknowledgment is made to the National Science Foundation (Grant CHE-14405 A02) and Du Pont (Grant 64511-5026) for support of this research.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(trpy)(bpy)(NH_3)^{2+}$, 58452-44-1.

---

(19) Okura, I.; Kim-Thuan, N. *Inorg. Chim. Acta* **1981**, *54*, L56.

(20) Bonnett, R.; Lambert, C.; Land, E. J.; Scourides, P. A.; Sinclair, R. S.; Truscott, T. G. *Photochem. Photobiol.* **1983**, *38*, 1–8.

Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

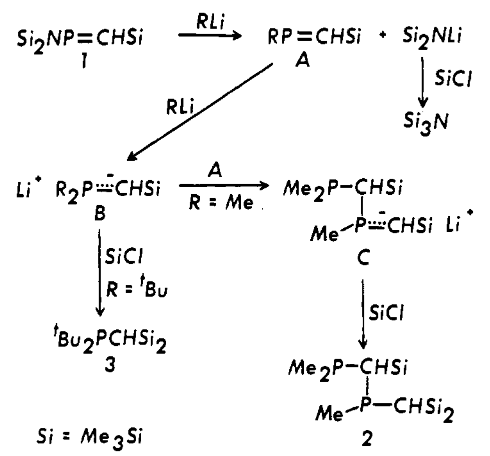
Substitution and Addition Reactions of a Methylenephosphine with Alkyllithium Reagents

Bei-Li Li and Robert H. Neilson*

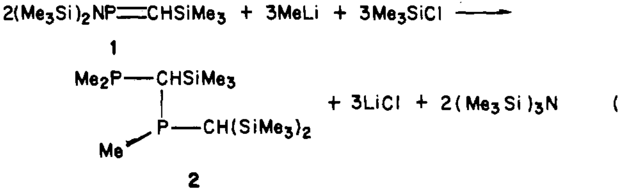
Received February 23, 1984

Many recent reports have dealt with the preparative chemistry of methylenephosphines $RP{=}CR'_2$ as well as their structural and bonding characteristics.[1] Moreover, some relatively clear and consistent patterns of reactivity of such compounds are now emerging. The types of reactions of methylenephosphines reported thus far include: (1) addition of polar electrophilic reagents to the P=C bond;[2] (2) oxidation to 3-coordinate P(V) derivatives;[3] (3) complexation of transition metals to the phosphorus lone pair or to the P=C π bond;[4] (4) various cycloaddition processes such as Diels–Alder reactions.[5] In another general mode of reactivity, we find that these coordinatively unsaturated phosphorus compounds will also react smoothly with nucleophiles.[6] We report here some novel examples involving both substitution and addition reactions of a bis[(trimethylsilyl)amino]-substituted methylenephosphine with alkyllithium reagents.

Scheme I



Treatment of [bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphine[2c] (**1**) in Et_2O at −78 °C with MeLi, followed by quenching with Me_3SiCl, does not yield the expected[7] phosphine $(Me_3Si)_2NP(Me)CH(SiMe_3)_2$. Instead, the reaction takes a much more complicated course, forming the novel bis(phosphino)methane derivative **2** (eq 1). The product



$$2(Me_3Si)_2NP{=}CHSiMe_3 + 3MeLi + 3Me_3SiCl \longrightarrow \begin{array}{l} Me_2P{-}CHSiMe_3 \\ \quad\quad\ | \\ Me{-}P{-}CH(SiMe_3)_2 \end{array} + 3LiCl + 2(Me_3Si)_3N \quad (1)$$

2 is isolated as a colorless liquid in 88% yield by fractional

---

(1) For a general review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

(2) (a) Kleback, T. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4887. (b) Issleib, K.; Schmidt, H.; Wirkner, Ch. *Z. Anorg. Allg. Chem.* **1981**, *473*, 85. (c) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.

(3) (a) Niecke, E.; Wildbredt, D.-A. *J. Chem. Soc., Chem. Commun.* **1981**, 72. (b) Caira, M.; Neilson, R. H.; Watson, W. H.; Wisian-Neilson, P.; Xie, Z.-M. *J. Chem. Soc., Chem. Commun.* **1984**, 698.

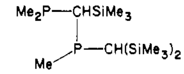
(4) (a) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. *Polyhedron* **1982**, *1*, 89. (b) van der Knaap, Th. A.; Bickelhaupt, F.; van der Poel, H.; van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756. (c) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (d) Al-Resayes, S. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (e) van der Knaap, Th. A.; Jenneskens, L. W.; Meenwissen, H. J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A. L. *J. Organomet. Chem.* **1983**, *254*, C33. (f) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132.

(5) (a) Appel, R.; Korte, S.; Halstenberg, M.; Knach, F. *Chem. Ber.* **1982**, *115*, 3610. (b) Meriem, A.; Majoral, J.-P.; Revel, M.; Navech, J. *Tetrahedron Lett.* **1983**, *24*, 1975. (c) van der Knaap, Th. A.; Bickelhaupt, F. *Tetrahedron* **1983**, *38*, 3189. (d) Appel, R.; Zimmerman, R. *Tetrahedron Lett.* **1983**, *24*, 3591.

(6) Nucleophilic displacement of chloride from chloro-substituted methylenephosphines is known: (a) Appel, R.; Kundgen, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 219. (b) Cowley, A. H.; Ebsworth, E. A. V.; Kemp, R. A.; Rankin, D. W. H.; Stewart, C. A. *Organometallics* **1982**, *1*, 1720. (c) Cowley, A. H.; Kilduff, J. E.; Pakulski, M.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 1655.

(7) Addition of MeLi to the analogous iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$ does yield the simple P–Me derivative: Cowley, A. H.; Kemp, R. A. *J. Chem. Soc., Chem. Commun.* **1982**, 319.

Table I. NMR Spectroscopic Data[a]

compd	signal	^{1}H δ	^{1}H J_{PH}	^{13}C δ	^{13}C J_{PC}	^{31}P δ
 2	$\mathit{Me}_3\mathrm{SiC}$	0.14	1.0	2.56	5.4, 1.8	−23.7, −37.9[b]
	$(\mathit{Me}_3\mathrm{Si})_2\mathrm{C}^c$	0.10	0.4	1.89	6.7	
				3.49	2.4	
	$\mathit{Me}_2\mathrm{P}^c$	1.15	4.8	*d*		
		1.16	4.2			
	$\mathit{Me}\mathrm{P}$	1.30	6.0	*d*		
	$\mathrm{Si}_2\mathit{CH}$	1.04	2.4	*d*		
	$\mathrm{P}_2\mathit{CH}$	*e*		22.80	48.0, 33.3	
$(t\text{-Bu})_2\mathrm{PCH(SiMe}_3)_2$ 3	$\mathrm{Me}_3\mathrm{Si}^c$	0.12	0.2	2.48	11.0	47.6
		0.18		5.12		
	CH	1.15	13.5	28.67	55.6	
	$\mathit{Me}_3\mathrm{C}^c$	1.17	12.3	30.20	14.0	
		1.09	10.8	32.02	16.5	
	$\mathrm{Me}_3\mathit{C}^c$			30.95	30.5	
				32.42	17.1	

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] AB pattern with $J_{PP} = 95.2$ Hz. [c] Diastereotopic groups observed in ^{1}H and/or ^{13}C NMR spectra. [d] Multiplet of ca. 16 overlapping peaks in range δ 9.8–15.1. [e] Signals obscured by MeP resonances.

distillation. The characterization of **2** is based mainly on NMR data (Table I), with the AB pattern in the ^{31}P NMR spectrum being especially diagnostic. A satisfactory elemental analysis and the appropriate mass spectral fragmentation pattern were also obtained for **2**.

Under similar conditions, the reaction of **1** with *t*-BuLi occurs in a 1:2 stoichiometry (eq 2) to afford the di-*tert*-butylphosphine, **3**, in 69% yield rather than a P–C–P product analogous to **2**.

$$\underset{\mathbf{1}}{(\mathrm{Me_3Si})_2\mathrm{NP{=}CHSiMe_3}} + 2t\text{-BuLi} + 2\mathrm{Me_3SiCl} \rightarrow \underset{\mathbf{3}}{(t\text{-Bu})_2\mathrm{PCH(SiMe_3)_2}} + 2\mathrm{LiCl} + (\mathrm{Me_3Si})_3\mathrm{N} \quad (2)$$

These remarkably clean reactions of the methylenephosphine **1** with alkyllithium reagents must involve both nucleophilic displacement of the bis(trimethylsilyl)amide group as well as addition across the P═C bond. The reaction pathway proposed in Scheme I is strongly suggested by the following experimental observations: (1) The byproduct $(Me_3Si)_3N$ can be isolated and identified by NMR, indicating that $(Me_3Si)_2NLi$ is indeed formed.[8] Moreover, the ^{1}H NMR integration of the crude reaction product is consistent with the stoichiometry given by eq 1. (2) The use of 1:1 mole ratios of **1** to RLi yields only unreacted **1** in addition to products **2** or **3**. (3) The formation of **3** in the *t*-BuLi reaction rather than a product similar to **2** is consistent with increased steric hindrance at phosphorus in intermediates **A** and **B** when R = *t*-Bu. (4) When the reaction with MeLi is monitored by low-temperature ^{31}P NMR, the methylenephosphine intermediate **A** is not seen but an AB pattern (δ_A −1.8, δ_B −6.8, J_{AB} = 69.3 Hz) assignable to the diphosphorus anion **C** is clearly observed prior to the addition of Me_3SiCl.

A final point of interest concerns the ^{1}H and ^{13}C NMR spectra of the di-*tert*-butylphosphine **3** which reveal nonequivalence of the *t*-Bu signals at room temperature. A high-temperature ^{1}H NMR study shows that the two *tert*-butyl doublets coalesce to a single doublet at 65 °C (in C_6H_6 solution), indicating a barrier to rotation about the P–CH$(SiMe_3)_2$ bond of approximately 17.7 kcal/mol. The extreme steric hindrance caused by the bis(trimethylsilyl)methyl group in phosphorus(III) compounds has been previously noted.[9]

Experimental Section

Materials and General Procedures. The methylenephosphine **1** was prepared according to the published procedure.[2c] Alkyllithium reagents were used as received from commercial sources. Ether and hexane were distilled from CaH_2 prior to use. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P, both with ^{1}H decoupling, were obtained on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnigan OWA 1020 GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described below are typical of those that gave the best yields of compounds **2** and **3**. Preliminary experiments using equimolar quantities of **1** and the alkyllithium reagents afforded the same products together with unreacted methylenephosphine.

Reaction of 1 with MeLi. Methyllithium (30 mmol, 21.5 mL, 1.4 M in Et_2O) was added at −78 °C to a stirred solution of **1** (20 mmol, 5.6 g) in Et_2O (50 mL) to yield a light yellow precipitate, presumably anion **C** (Scheme I). After the mixture was stirred for 2.5 h at −78 °C, Me_3SiCl (30 mmol, 3.8 mL) was added and the mixture was allowed to warm to room temperature. After the mixture was stirred overnight, Et_2O was removed under vacuum and hexane (20 mL) was added. The mixture was then filtered and the solvent and $(Me_3Si)_3N$ (identified by ^{1}H NMR) were removed under vacuum. Distillation through a short-path column afforded compound **2** as a colorless liquid: yield 3.1 g (87%); bp 99–105 °C (0.05 mm). Anal. Calcd: C, 47.73; H, 10.80. Found: C, 47.51; H, 10.77. Mass spectrum, *m/e* (relative intensity): 352 (2), 337 (9), 291 (22), 279 (6), 205 (4), 193 (10), 147 (14), 73 (100).

Reaction of 1 with *t*-BuLi. By means of a similar procedure, **1** (20 mmol) was treated with *t*-BuLi (40 mmol, 22.2 mL, 1.8 M in pentane) at −78 °C in Et_2O (50 mL). After the quenching with Me_3SiCl (40 mmol) and workup as described above, distillation gave **3** as a colorless liquid: yield 4.2 g (69%); bp 82–83 °C (0.15 mm). Anal. Calcd: C, 59.21; H, 12.17. Found: C, 59.08; H, 12.05. Mass spectrum, *m/e* (relative intensity): 304 (22), 289 (25), 248 (81), 159 (28), 145 (14), 73 (100).

Acknowledgment. We thank the U.S. Office of Naval Research and the Robert A. Welch Foundation for generous financial support.

Registry No. 1, 76173-65-4; 2, 89982-68-3; 3, 89982-67-2; MeLi, 917-54-4; *t*-BuLi, 594-19-4; Me_3SiCl, 75-77-4.

---

(8) Displacement of the $(Me_3Si)_2N$ group from the analogous iminophosphine by very bulky organolithium compounds has recently been reported: Romanenko, V. D.; Ruben, A. V.; Markovski, L. N. *J. Chem. Soc., Chem. Commun.* **1983**, 187.

(9) Goldwhite, H.; Power, P. P. *Org. Magn. Reson.* **1978**, *11*, 499.