Sterically Controlled Mono- or Dimetalation of a Thioether-Functionalized Phosphine and an Unusual Light-Induced Phosphide−Thiolate Rearrangement

Stuart Blair, Keith Izod,* Ross W. Harrington, and William Clegg

Department of Chemistry, Bedson Building, University of Newcastle, Newcastle upon Tyne, NE1 7RU, United Kingdom

Received October 3, 2002

The thioanisole-functionalized secondary phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}SMe)$ (**1**) is readily accessible via the reaction of $2\text{-}LiC_6H_4SMe$ and $\{(Me_3Si)_2CH\}PCl_2$, followed by reduction with $LiAlH_4$. Compound **1** reacts with 1 equiv of *n*-BuLi in the presence of 1 equiv of tmeda in diethyl ether to give the lithium phosphide $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}SMe)]Li(tmeda)$ (**2**) [tmeda = *N*,*N*,*N*,*N*-tetramethylethylenediamine]. In the absence of tmeda, compound **1** reacts with either 1 or 2 equiv of *n*-BuLi to give the phosphide−thiolate complex $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}S)]\{Li(OEt_2)\}_2$ (**4a**), which may be recrystallized in the presence of tmeda as the adduct $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}S)]\{Li(tmeda)\}_2$ (**4b**). Compound **2** undergoes an unusual rearrangement on photolysis with white light to give the lithium thiolate $[\{(Me_3Si)_2CH\}P(Me)(C_6H_4\text{-}2\text{-}S)]Li(tmeda)$ (**6a**), which may be recrystallized in the presence of 12-crown-4 as the adduct $[\{(Me_3Si)_2CH\}P(Me)(C_6H_4\text{-}2\text{-}S)]Li(12\text{-}crown\text{-}4)$ (**6b**). EPR experiments suggest that this rearrangement does not involve radical intermediates, but consists of a concerted migration of a methyl group from sulfur to phosphorus. Compounds **1**, **2**, **4a**, **4b**, **6a**, and **6b** have been characterized by multielement NMR spectroscopy; in addition, compounds **2**, **4b**, and **6b** have been structurally characterized by X-ray crystallography.

Introduction

Organolithiums such as *n*-BuLi or MeLi are ubiquitous reagents for the generation of anions by the abstraction of a proton from a weakly acidic substrate. In many cases the weak acidity of a substrate may require activation of the organolithium by complexation with a polydentate tertiary amine such as tmeda or pmdeta [tmeda = *N*,*N*,*N*,*N*-tetramethylethylenediamine; pmdeta = *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine].[1] However, this strategy can have two major drawbacks: (i) under certain circumstances metalation of the tertiary amine itself may occur,[2] and (ii) the polydentate co-ligand may remain associated with the metal center, significantly affecting the structure and reactivity of the metalated product. Frequently, however, such co-ligand complexation is desirable, since coordination of the co-ligand may result in lower aggregation states and hence higher solubility of the metalated substrate, enabling ready crystallization and characterization.[1,3]

In many instances a particular substrate may potentially undergo deprotonation at one of several sites, the favored deprotonation site often depending on the nature of the deprotonating agent, the precise reaction conditions, and the presence of additional donor ligands. Polydentate tertiary amine co-ligands such as tmeda and pmdeta may greatly influence the regioselectivity of a deprotonation reaction; for example, whereas metalation of *p*-fluoroanisole with *n*-BuLi occurs ortho to the methoxy group, metalation with *n*-BuLi/pmdeta occurs ortho to the fluorine substituent.[4]

In this regard, we recently reported that deprotonation of the tertiary phosphine $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ with *n*-BuLi in the absence of donor solvents gives the tetrameric phosphinomethanide $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4$, whereas deprotonation with *t*-BuLi under the same conditions gives the dimeric benzyllithium complex $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$.[5] In contrast, the reaction of $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ with *n*-BuLi in THF or in the presence of tmeda yields the secondary phosphide complex $[MeP\{C_6H_4\text{-}2\text{-}CH(C_6H_4\text{-}2\text{-}CH_2NMe_2)NMe_2\}]LiL_n$ via an unusual example of the Smiles rearrangement [L_n = $(THF)_2$, tmeda].[6]

Bonding interactions between hard alkali metal cations and soft phosphorus donor ligands are expected to be relatively weak. We recently reported the synthesis and crystal structures of the alkali metal complexes $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}CH_2NMe_2)]M(L)$ [M(L) = Li-

---

(1) (a) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, UK, 1982; Vol. 1, Chapter. 2. (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, UK, 1974. (c) Gray, M.; Tinkl, M.; Sniekus, V. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, UK, 1991; Vol. 11, Chapter 1.

(2) (a) Harder, S.; Lutz, M. *Organometallics* **1994**, *13*, 5173. (b) Smith, W. N. *Adv. Chem. Ser.* **1974**, *No. 130*, 21.

(3) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

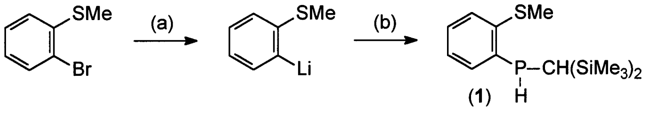
(4) Katsoulos, G.; Takagishi, S.; Schlosser, M. *Synlett* **1991**, 731.

(5) (a) Clegg, W.; Izod, K.; McFarlane, W.; O'Shaughnessy, P. *Organometallics* **1999**, *18*, 3950. (b) Izod, K.; O'Shaughnessy, P.; Clegg, W.; Liddle, S. T. *Organometallics* **2001**, *20*, 648.

(6) (a) Izod, K.; O'Shaughnessy, P.; Clegg, W. *Organometallics* **2002**, *21*, 641. (b) Izod, K.; O'Shaughnessy, P. Unpublished results.

10.1021/om0208265 CCC: $25.00
Publication on Web 12/14/2002

Scheme 1. Reagents and Conditions: (a) *n*-BuLi, Et_2O, 0 °C, 4 h; (b) (i) $\{(Me_3Si)_2CH\}PCl_2$, Et_2O, −78 °C, (ii) $LiAlH_4$, Et_2O, Reflux 4 h



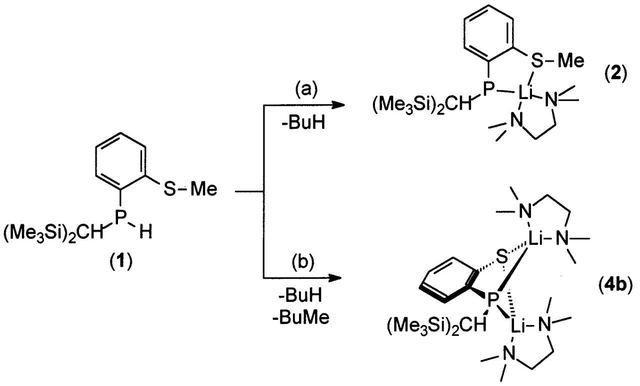
$(THF)_2$, Na(tmeda), K(pmdeta)],[7] in which coordination of the hard amino side group in the phosphide ligand combined with the ligand's steric properties and chelating nature serve to stabilize the M−P interactions. To explore further the complexation of hard cations by soft donor ligands we set out to synthesize the alkali metal complexes of a thioether-functionalized phosphide ligand, $\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}SMe)^-$, a potentially chelating ligand containing two soft donor groups. We now report that reaction between the thioanisole-substituted secondary phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}SMe)$ (**1**) and *n*-BuLi yields either a mono- or a dianion, depending upon the precise reaction conditions. We also report a highly unusual light-induced rearrangement of one of these compounds to the corresponding thiolate complex.

Results and Discussion

Synthesis of a Thioether-Functionalized Secondary Phosphine and Its Reactions with *n*-BuLi. The low-temperature reaction of 2-bromothioanisole with *n*-BuLi in diethyl ether yields the ortho-lithiated compound $LiC_6H_4\text{-}2\text{-}SMe$, which may be reacted in situ with $\{(Me_3Si)_2CH\}PCl_2$ to give the secondary chlorophosphine $\{(Me_3Si)_2CH\}P(Cl)(C_6H_4\text{-}2\text{-}SMe)$. Reduction of this chlorophosphine with $LiAlH_4$ in diethyl ether, followed by a simple aqueous workup, gives the secondary phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}SMe)$ (**1**) as a colorless, viscous oil in good yield (Scheme 1). The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **1** are as expected, although the diastereotopic $SiMe_3$ groups give rise to only a single peak in both the ^1H and ^{13}C spectra.

Treatment of a mixture of **1** and 1 equiv of tmeda in diethyl ether with 1 equiv of *n*-BuLi gives a deep red solution. Removal of solvent and recrystallization of the resulting slightly sticky solid from light petroleum yields orange, air-sensitive crystals of the expected deprotonation product, $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}SMe)]Li(tmeda)$ (**2**) (Scheme 2a). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** in d_8-toluene are consistent with this formulation: the ^1H spectrum once again exhibits a single signal for the diastereotopic $SiMe_3$ groups and exhibits signals due to the aromatic and tmeda protons, along with a sharp singlet at 2.34 ppm due to the SMe group. The single peak observed for the $SiMe_3$ protons may be due to rapid, reversible P−Li cleavage, leading to symmetrization of the complex on the NMR time scale. Similar behavior has been observed for the amino-functionalized alkali metal phosphides $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}CH_2NMe_2)]M(L)$ [M(L) = $Li(THF)_2$ (**3**), Na(tmeda), K(pmdeta)].[7] The $^{31}P\{^1H\}$ NMR spectrum of **2** in d_8-toluene consists of a broad singlet at −64.2 ppm; coupling to ^7Li is not resolved at room temperature.

Scheme 2. Reagents and Conditions: (a) *n*-BuLi/Tmeda, Et_2O, Room Temp.; (b) (i) 2 x *n*-BuLi, Et_2O, Room Temp., (ii) 2 x Tmeda



The identity of **2** was confirmed by X-ray crystallography; details of selected bond lengths and angles are given in Table 1 and the molecular structure of **2** is shown in Figure 1. Compound **2** crystallizes from warm methylcyclohexane as a discrete molecular species. The phosphide ligand binds the lithium center via both its P and S donor atoms, forming a five-membered chelate ring with a P−Li−S bite angle of 74.63(7)°. The coordination sphere of the lithium atom is completed by the two nitrogen atoms of a chelating tmeda ligand, giving the lithium center a distorted tetrahedral geometry. The P and S atoms adopt a pyramidal geometry [the sums of angles at the P and S atoms are 334.84 and 328.41°, respectively]; in Sm(II) complexes of the closely related ligands $\{(Me_3Si)_2CH\}P(C_6H_3\text{-}2\text{-}OMe\text{-}3R)^-$ [R = H, Me] the P atoms adopt either a planar or a pyramidal geometry, depending on the degree of steric crowding at the metal center.[8] The Li atom lies 1.368 Å below the C_6H_4PS plane; the dihedral angle between the "best fit" P−C(8)−C(13)-S and P−Li−S planes is 132.4°. Despite this, there is no contact between the lithium atom and the ipso-carbons.

The Li−P distance of 2.508(3) Å is at the lower end of the range found for such distances in molecular lithium phosphides and compares with a Li−P distance of 2.535(8) Å in **3**.[7,9] For comparison, the Li−P distance in the monomeric lithium phosphide $[Li(PPh_2)(pmdeta)]$ is 2.567(6) Å,[9b] while the Li−P distances in the polymeric complex $[Li(PPh_2)(OEt_2)]_n$ range from 2.469(10) to 2.492(10) Å.[9c] There are few examples of crystallographically characterized complexes containing a direct interaction between lithium and a thioether group; however, the Li−S distance of 2.543(3) Å in **2** lies within the range previously reported for these few known $Li{-}SR_2$ interactions. For example, the Li−S distances

---

(7) Clegg, W.; Doherty, S.; Izod, K.; Kagerer, H.; O'Shaughnessy, P.; Sheffield, J. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1825.

(8) Izod, K.; O'Shaughnessy, P.; Sheffield, J. M.; Clegg, W.; Liddle, S. T. *Inorg. Chem.* **2000**, *39*, 4741.

(9) For examples see: (a) Izod, K. *Adv. Inorg. Chem.* **2000**, *50*, 33 and references therein. (b) Mulvey, R. E.; Wade, K.; Armstrong, D. R.; Walker, G. T.; Snaith, R.; Clegg, W.; Reed, D. *Polyhedron* **1987**, *6*, 987. (c) Bartlett, R. A.; Olmstead, M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243. (d) Stieglitz, G.; Neumüller, B.; Dehnicke, K. *Z. Naturforsch. B* **1993**, *48b*, 156. (e) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Xu, X. *Inorg. Chem.* **1987**, *26*, 1941. (f) Niediek, K.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1993**, *619*, 885. (g) Hey, E.; Weller, F. *Chem. Commun.* **1988**, 782. (h) Jones, R. A.; Stuart, A. L.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7459. (i) Hey, E.; Hitchcock, P. B.; Lappert, M. F.; Rai, A. K. *J. Organomet. Chem.* **1987**, *325*, 1. (j) Hey-Hawkins, E.; Sattler, E. *Chem. Commun.* **1992**, 775. (k) Driess, M.; Pritzkow, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1524.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Li-S	2.543(3)	Li−P	2.508(3)	Li−N(1)	2.076(3)
Li−N(2)	2.098(3)	S−C(13)	1.7762(14)	S−C(14)	1.7961(17)
P−C(1	1.8888(14)	P−C(8)	1.8041(14)	Si(1)−C(1)	1.8718(15)
Si(1)−C(2)	1.8754(17)	Si(1)−C(3)	1.8736(18)	Si(1)−C(4)	1.8825(17)
Si(2)−C(1)	1.8783(15)	Si(2)−C(5)	1.8662(17)	Si(2)−C(6)	1.8760(18)
Si(2)−C(7)	1.872(2)				
S−Li−P	74.63(7)	S−Li−N(1)	102.84(11)		
S−Li−N(2)	122.30(12)	P−Li−N(1)	118.03(12)	P−Li−N(2)	146.28(13)
N(1)−Li−N(2)	88.31(11)	Li−S−C(13)	102.17(7)	Li(1)−S−C(14)	122.42(10)
C(13)−S−C(14)	103.82(8)	Li−P−C(1)	128.51(8)		
Li−P−C(8)	100.99(8)	C(1)−P−C(8)	105.34(6)		

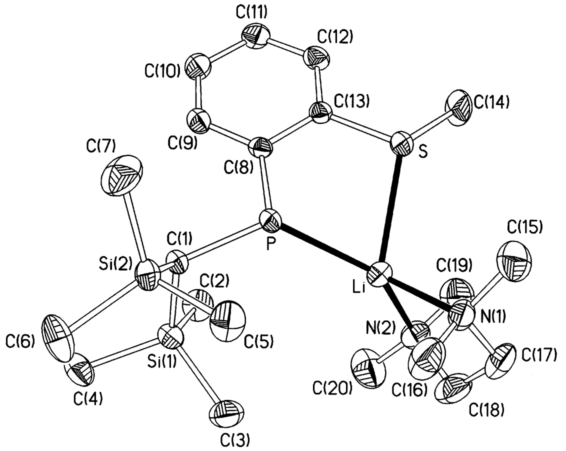


Figure 1. Molecular structure of **2** with 50% probability ellipsoids and with H atoms omitted for clarity.

in the cluster complexes $[LiPh(SMe_2)]_4$ and $[Li_3Cu_2Ph_5(SMe_2)_4]$ range from 2.576(4) to 2.635(4) Å and from 2.445(9) to 2.497 Å, respectively.[10,11]

In contrast to the facile formation of **2**, we find that treatment of **1** with 1 equiv of *n*-BuLi in diethyl ether in the *absence* of tmeda results in the rapid formation of a pale yellow precipitate. A $^{31}P\{^1H\}$ NMR spectrum of this solid in d_8-THF exhibits a singlet at −86.8 ppm, while the ^1H spectrum of this compound exhibits a singlet due to the $SiMe_3$ groups and signals due to diethyl ether and the aromatic protons; however, no signal is observed for the expected SMe group. These spectra are consistent with the formation of a lithium complex of a dianionic phosphide−thiolate ligand $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}S)]\{Li(OEt_2)\}_2$ (**4a**), generated through the combined deprotonation of the P−H group and demethylation of the S-Me group (Scheme 2b). $^{31}P\{^1H\}$ NMR spectra obtained from the reaction solution indicate that approximately half of the starting material (**1**) remains after this reaction; $^{31}P\{^1H\}$ NMR spectra show that treatment of **1** with 2 equiv of *n*-BuLi under the same conditions results in an effectively quantitative conversion of **1** to **4a**.

The demethylation of **1** was somewhat unexpected, since reactions between thioanisole and organolithiums typically yield the corresponding α-metalated species; for example, treatment of thioanisole with *n*-BuLi/tmeda results in deprotonation of the methyl group to give $[(tmeda)Li(CH_2SPh)]_2$.[12] However, it has been observed previously that certain thioethers may undergo dealkylation on treatment with strong bases. For example, treatment of $1,4\text{-}MeSC_6H_4S\text{-}i\text{-}Pr$ with NaSMe results in demethylation of the SMe group, whereas treatment of this thioether with NaOMe results in dealkylation of the S-*i*-Pr group.[13] The dealkylation of **1** is unusual in this regard in that it generates a *dianion*.

Recrystallization of **4a** from light petroleum in the presence of 2 equiv of tmeda yields the complex $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}S)]\{Li(tmeda)\}_2$ (**4b**) as yellow, air-sensitive crystals suitable for X-ray crystallography. Details of selected bond lengths and angles for **4b** are given in Table 2 and the molecular structure of **4b** is shown in Figure 2.

Complex **4b** crystallizes as a discrete molecular species in which the two lithium atoms lie either side of the C_6H_4PS plane of the phosphide−thiolate ligand, coordinated by both the P and S atoms of the ligand; the dihedral angle between the two LiPS planes is 136.9°. The coordination sphere of each lithium is completed by the nitrogen atoms of a chelating tmeda molecule, giving the lithium atoms a distorted tetrahedral geometry. The coordination mode of the phosphine−thiolate ligand closely resembles that of the corresponding diphosphide ligand in the complex $[C_6H_4\text{-}1,2\text{-}\{P(SiMe_3)\}_2]\{Li(tmeda)\}_2$ (**5**),[14] in which the two lithium atoms lie either side of the plane of the 1,2-diphosphide ligand. However, in **5** the two lithium atoms are crystallographically equivalent, whereas in **4b** the two lithium atoms are in quite different environments. While Li(1) is bonded solely to the P and S atoms of the phosphide−thiolate ligand and the two N atoms of tmeda, Li(2) has additional, weak contacts with the ipso-carbon atoms of the aromatic ring [Li(2)···C(1) 2.703(3), Li(2)···C(6) 2.776(3) Å]. These distances are relatively long and compare with a Li···C(ipso) distance of 2.405(3) Å in the benzyllithium complex $[\{(Me_2P)CHC_6H_5\}Li(OEt_2)]_2$[15] and a Li···C(ipso) distance of 2.496(5) Å in $[Li(CH_2C_6H_3\text{-}2\text{-}OLi\text{-}3\text{-}t\text{-}Bu)(Me_2NCH_2CH_2NMeCH_2)Li(tmeda)]_2$.[2a] The Li(2)···C(ipso) contacts in **4b** are accompanied by a significant narrowing of the Li(2)−S−C(1) and Li(2)−P−C(6) angles [77.30(8) and 76.38(8)°, respectively] compared with the corresponding angles for Li(1) [the Li(1)−S−C(1) and Li(1)−P−C(6) angles are 97.42(8) and 94.10(8)°, respectively].

---

[10] Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 8008.

[11] Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4135.

[12] (a) Amstutz, R.; Laube, T.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 224. (b) Taube, R.; Steinborn, D.; Adler, B. *J. Organomet. Chem.* **1984**, *275*, 1. (c) Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1131. (d) Screttas, C. G.; Smonou, I. C. *J. Organomet. Chem.* **1988**, *342*, 143.

[13] Tiecco, M.; Tingoli, M.; Testaferri, L.; Chianelli, D.; Maiolo, F. *Synthesis* **1982**, 478.

[14] (a) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Yin, P. *J. Chem. Soc., Dalton Trans.* **1995**, 3925. (b) Hitchcock, P. B.; Lappert, M. F.; Yin, P. *Chem. Commun.* **1992**, 1598.

[15] Müller, G.; Abicht, H.-P.; Waldkircher, M.; Lachmann, J.; Lutz, M.; Winkler, M. *J. Organomet. Chem.* **2001**, *622*, 121.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4b

Li(1)−N(2)	2.111(3)	Li(1)−N(1)	2.146(3)	Li(1)−S	2.403(3)
Li(1)−P	2.551(3)	Li(2)−N(3)	2.139(3)	Li(2)−N(4)	2.139(3)
Li(2)−S	2.464(3)	Li(2)−P	2.566(3)	Li(2)−C(1	2.703(3)
Li(2)−C(6)	2.776(3)	S−C(1)	1.7787(15)	P−C(6)	1.8251(15)
P−C(7)	1.8891(14)	Si(1)−C(8)	1.8704(18)	Si(1)−C(9)	1.8717(18)
Si(1)−C(10)	1.8753(19)	Si(1)−C(7	1.8779(15)	Si(2)−C(7)	1.8683(15)
Si(2)−C(11)	1.8699(19)	Si(2)−C(13)	1.8777(19)	Si(2)−C(12	1.8783(18)
N(2)−Li(1)−N(1)	85.50(11)	N(2)−Li(1)−S	113.81(13)	N(1)−Li(1)−S	128.87(14)
N(2)−Li(1)−P	125.58(14)	N(1)−Li(1)−P	128.73(13)	S−Li(1)−P	79.11(8)
N(3)−Li(2)−N(4)	87.30(11)	N(3)−Li(2)−S	120.74(13)	N(4)−Li(2)−S	113.27(12)
N(3)−Li(2)−P	130.29(13)	N(4)−Li(2)−P	130.32(14)	S−Li(2)−P	77.73(7)
N(3)−Li(2)−C(1)	158.24(14)	N(4)−Li(2)−C(1)	93.27(11)	C(1)−S−Li(1)	97.42(8)
C(1)−S−Li(2)	77.30(8)	Li(1)−S−Li(2)	95.20(9)	C(6)−P−C(7)	104.44(7)
C(6)−P−Li(1)	94.10(8)	C(7)−P−Li(1)	141.45(8)	C(6)−P−Li(2)	76.38(8)
C(7)−P−Li(2)	127.61(8)	Li(1)−P−Li(2)	89.24(9)		

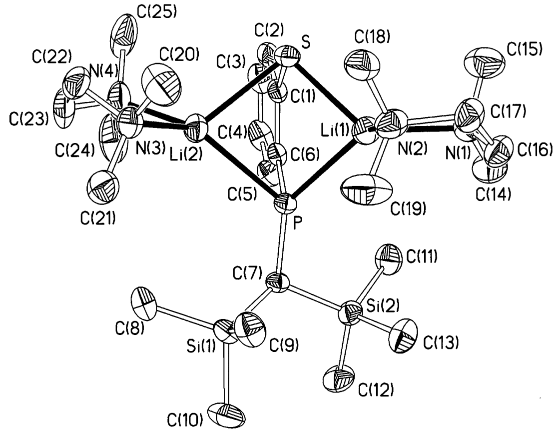


Figure 2. Molecular structure of **4b** with 50% probability ellipsoids. H atoms and minor disorder components omitted for clarity.

The Li(1)−P and Li(2)−P distances of 2.551(3) and 2.566(3) Å, respectively, are significantly longer than the Li−P distance in **2** but are within the range of previously reported Li−P contacts;[9] the Li−P distances in **4b** compare with Li−P distances of 2.508(7) and 2.544(8) Å in **5**. The Li(1)−S and Li(2)−S distances of 2.403(3) and 2.464(3) Å, respectively, are also similar to previously reported Li−S distances in lithium thiolates;[16] of particular relevance to **4b** is the phosphine−dithiolate complex $[Li_2\{PhP(C_6H_4\text{-}2\text{-}S\text{-}3\text{-}SiMe_3)_2\}(DME)]_2$,[16b] reported by Lappert and co-workers, in which the Li−S distances range from 2.383(11) to 2.677(11) Å.

The reaction between **1** and 2 equiv of BuLi in the *presence* of either 1 or 2 equiv of tmeda does not proceed cleanly. $^{31}P\{^1H\}$ NMR spectra of the crude reaction solutions exhibit several peaks in the range −20 to −90 ppm, including signals due to **2** and **4**; however, these are only minor components of the reaction mixture under these conditions. We have so far been unable to isolate and characterize the other components of these mixtures.

It therefore appears that the product of the reaction between **1** and *n*-BuLi is greatly influenced by the presence of tmeda. We attribute the observed order of reactivity to a steric effect. In the absence of tmeda the initial product of the reaction between **1** and *n*-BuLi in diethyl ether is likely to be the phosphide $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}SMe)]Li(OEt_2)_n$, in which the lithium atom is ligated by the sterically demanding phosphide ligand and by one or more molecules of the relatively labile ether solvent. This species is still sterically unencumbered enough to undergo rapid nucleophilic attack by a second equivalent of *n*-BuLi at the SMe group, generating the dianion, which precipitates from solution. However, in the presence of tmeda, the initial product of the reaction between **1** and *n*-BuLi is the adduct $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}SMe)]Li(tmeda)$ (**2**), in which the more substitutionally inert, chelating tmeda ligand impedes the approach of a second equivalent of *n*-BuLi at the thioether group. In the absence of excess *n*-BuLi this favors the formation of **2** and, in the presence of excess *n*-BuLi, this favors alternative reaction pathways.

We recently reported that the closely related dianion $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}O)]^{2-}$ is formed upon metathesis of the potassium salt $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}OMe)]K$ with YbI_2 in THF.[17] This reaction yields the Yb(II) heterocubane cluster $\{[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}O)]Yb(THF)\}_4$ and the tertiary phosphine $\{(Me_3Si)_2CH\}P(Me)C_6H_4\text{-}2\text{-}OMe$ via an unusual ligand cleavage process involving the intramolecular migration of a methyl group from the oxygen atom of one coordinated phosphide ligand to the phosphorus atom of another. This suggests that dianions of the form $RP(C_6H_4\text{-}2\text{-}E)^{2-}$ [E = O, S] may be accessible via several routes. It is interesting, therefore, that the lithium phosphide $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}OMe)]Li$ and its potassium analogue are stable toward excess *n*-BuLi and show no signs of C−O cleavage under the same conditions that result in C−S cleavage in **1**.

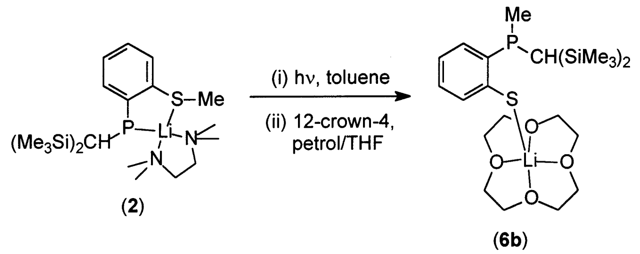
Photolytically Induced Isomerization of 2. In the absence of light compound **2** is stable indefinitely, both in the solid state and in solution. However, exposure of a yellow solution of **2** in toluene to natural daylight results in complete decolorization after ca. 60 h. A $^{31}P\{^1H\}$ NMR spectrum of the solution after this time

---

(16) For examples see: (a) Englich, U.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2000**, *210*, 135 and references therein. (b) Froelich, N.; Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1996**, 1941. (c) Ruhlandt-Senge, K.; Englich, U.; Senge, M. O.; Chadwick, S. *Inorg. Chem.* **1996**, *35*, 5820. (d) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K. *Organometallics* **1997**, *16*, 5792. (e) Ellison, J. J.; Power, P. P *Inorg. Chem.* **1994**, *33*, 4231. (f) Niemeyer, N.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 7264. (g) Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Sigel, G. E. *Chem. Commun.* **1985**, 1674. (h) Banister, A. J.; Clegg, W.; Gill, W. R. *Chem. Commun.* **1987**, 850. (i) Janssen, M. D.; Rijnberg, E.; de Wolf, C. A.; Hogerheide, M. P.; Kruis, D.; Kooijman, H.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 6735.

(17) Clegg, W.; Izod, K.; Liddle, S. T.; O'Shaughnessy, P.; Sheffield, J. M. *Organometallics* **2000**, *19*, 2090.

Scheme 3



exhibits a single peak at −33.1 ppm (cf. −64.2 ppm for **2**); there is no signal for residual **2**. The proton NMR spectrum of a similarly treated solution of **2** in d_8-toluene exhibits two signals of equal intensity at 0.13 and 0.28 ppm due to the $SiMe_3$ groups, along with peaks due to the aromatic protons and tmeda; there is no evidence for the presence of an S-Me group in this complex. However, this spectrum exhibits a new doublet signal at 1.49 ppm [J_{PH} = 4.0 Hz], which appears to be due to a newly formed P-Me group. These spectra are consistent with the formation of a lithium thiolate of composition [{$(Me_3Si)_2CH$}P(Me)(C_6H_4-2-S)]Li(tmeda) (**6a**), formed via the migration of a methyl group from the sulfur to the phosphorus atom (Scheme 3).

The identity of this rearrangement product was confirmed by X-ray crystallography. Although crystalline material could not be obtained for **6a**, addition of 12-crown-4 to a solution of **6a** in diethyl ether results in the immediate formation of a very pale yellow precipitate, which may be recrystallized from methylcyclohexane/THF as colorless plates of the adduct [{$(Me_3Si)_2CH$}P(Me)(C_6H_4-2-S)]Li(12-crown-4) (**6b**) suitable for X-ray crystallography. The molecular structure of **6b** is shown in Figure 3 and selected bond lengths and angles are listed in Table 3.

Compound **6b** crystallizes as a discrete molecular species. The five-coordinate lithium is coordinated by the thiolate sulfur atom and the four oxygen atoms of the 12-crown-4 ligand in a square-pyramidal geometry; there is no contact between the coordinatively saturated lithium and the tertiary phosphine center. The Li−S−C(13) angle of 102.46(16)° is somewhat smaller than the Li−S−C angle of 113.96(12)° observed in the closely related complex {$(Ph_3C)S$}Li(12-crown-4) (**7**),[16c] in which the lithium atom is in a similar coordination environment. The Li−S and Li−O distances in **6b** are close to those observed in **7**, although the Li−O distances fall into a smaller range in the former than in the latter complex [**6b**: Li−S 2.389(5) Å, Li−O 2.088(5)−2.147(5) Å; **7**: Li−S 2.399(4) Å, Li−O 1.895(6)−2.450(5) Å].

To confirm that the rearrangement of **2** to **6a** was photolytically rather than thermally induced, a solution of **2** in toluene was warmed to 40 °C in the absence of light within the magnet of an NMR spectrometer. ^{31}P NMR spectra of this solution recorded over 2 days showed negligible change. In contrast, irradiation of a toluene solution of **2** immersed in an ice bath with a 20-W fluorescent lamp resulted in complete conversion to **6a** after just 15 min. EPR spectra obtained from a toluene solution of **2** irradiated in situ with white light from a tungsten filament bulb showed no evidence for radical intermediates in the rearrangement; ^{31}P NMR spectra of this solution recorded after irradiation indicated complete conversion of **2** to **6a** under these conditions. This suggests that the rearrangement of **2** to **6a** is a photolytically induced reaction that proceeds via a concerted mechanism involving the migration of the methyl group from sulfur to phosphorus.

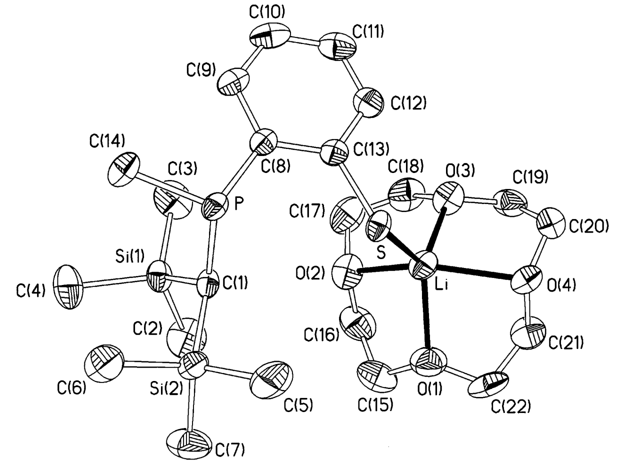


Figure 3. Molecular structure of **6b** with 50% probability ellipsoids. H atoms and minor disorder components omitted for clarity.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether, methylcyclohexane, THF, and light petroleum (bp 40−60 °C) were distilled from sodium, potassium, or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (except THF, which was stored over activated 4A molecular sieves). Deuterated toluene and THF were distilled from potassium and were deoxygenated by 3 freeze−pump−thaw cycles and stored over activated 4A molecular sieves; $CDCl_3$ was distilled from CaH_2 and was deoxygenated and stored in the same way. Tmeda was dried over CaH_2 and distilled under nitrogen; *n*-butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes. The compound $(Me_3Si)_2CHPCl_2$ was prepared by a previously published procedure.[18] All other compounds were obtained from commercial sources and were used as supplied.

^{31}P and ^{7}Li NMR spectra were recorded on a Bruker WM300 spectrometer and ^{1}H and ^{13}C spectra on a JEOL Lambda500 spectrometer operating at 121.5, 116.6, 500.0, and 125.6 MHz, respectively. ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane, ^{31}P chemical shifts are quoted in ppm relative to external 85% H_3PO_4 and ^{7}Li chemical shifts are quoted in ppm relative to external 0.1 M LiCl. Elemental analyses for **1** and **2** were obtained by the Elemental Analysis Service of the University of North London, UK; satisfactory elemental analyses could not be obtained for **4a** or **4b** due to their extreme sensitivity to air. X-band EPR spectra were recorded at room temperature on a Bruker EMX spectrometer at the EPSRC National EPR Service at the University of Manchester, UK.

Preparation of {$(Me_3Si)_2CH$}PH(C_6H_4-2-SMe) (1). To a solution of 2-bromothioanisole (3.34 g, 16.4 mmol) in diethyl ether (20 mL) at 0 °C was added *n*-BuLi (6.7 mL, 16.4 mmol). The solution was stirred at this temperature for 4 h, and was then added, dropwise, to a cold (−78 °C) solution of $(Me_3Si)_2CHPCl_2$ (4.30 g, 16.4 mmol) in diethyl ether (20 mL). The solution was slowly allowed to attain room temperature and was stirred for 16 h. The precipitate was removed by

---

[18] Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6b

Li(1)−S	2.389(5)	Li(1)−O(1	2.088(5)	Li(1)−O(2)	2.131(6)
Li(1)−O(3)	2.097(5)	Li(1)−O(4	2.147(5)	S−C(13)	1.759(3)
P−C(14	1.835(3)	Si(1)−C(1)	1.876(3)	Si(1)−C(2)	1.876(4)
Si(1)−C(3)	1.875(4)	Si(1)−C(4)	1.869(4)	Si(2)−C(1)	1.887(3)
Si(2)−C(6)	1.869(4)	Si(2)−C(7	1.867(4)		
S−Li(1)−O(1)	122.8(2)	S−Li(1)−O(2)	107.9(2)	S−Li(1)−O(3)	118.3(2)
S−Li(1)−O(4)	117.1(2)	O(1)−Li(1)−O(2)	79.7(2)	O(1)−Li(1)−O(3)	118.8(2)
O(1)−Li(1)−O(4)	78.2(2)	O(2)−Li(1)−O(3)	78.8(2)	O(2)−Li(1)−O(4)	135.0(3)
O(3)−Li(1)−O(4)	78.34(19)	Li(1)−S−C(13)	102.46(16)		

Table 4. Crystallographic Data for 2, 4b, and 6b

	2	4b	6b
molecular formula	$C_{20}H_{42}LiN_2PSSi_2$	$C_{25}H_{55}Li_2N_4PSSi_2$	$C_{22}H_{42}LiO_4PSSi_2$
fw	436.7	544.8	469.7
cryst size, mm	1.0 × 1.0 × 0.5	0.7 × 0.7 × 0.7	0.6 × 0.6 × 0.05
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a, Å	11.8664(4)	9.6026(5)	8.5421(6)
b, Å	15.2844(5)	11.7841(6)	14.8239(11)
c, Å	14.9184(5)	16.6685(9)	22.0627(16)
α, deg		103.822(2)	
β, deg	99.220(1)	93.069(2)	
γ, deg		107.490(2)	
V, Å^3	2670.80(15)	2931.2(3)	2794.8(4)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.086	1.045	1.180
μ, mm^{-1}	0.279	0.227	0.282
no. reflns measd	23667	14520	24478
no. unique reflns	6530	7635	6746
no. reflns with $F^2 > 2\sigma(F^2)$	5504	6391	4923
transmission coeff range	0.77−0.87	0.76−0.86	0.85−0.99
R_{int} (on F^2)	0.0231	0.0174	0.612
R^a	0.0350	0.0381	0.0453
R_w^{b}	0.0975	0.0997	0.1147
no. of params	255	359	306
GoF^c on F^2	1.038	1.057	1.047
max, min diff map, e Å^{-3}	1.06, −0.34	0.40, −0.34	0.53, −0.28

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [c] GoF = $[\sum w(F_o^2 - F_c^2)^2/(\text{no. of unique data} - \text{no. of parameters})]^{1/2}$.

filtration, $LiAlH_4$ (0.40 g, 10.5 mmol) was added to the filtrate, and this mixture was heated under reflux for 4 h. Excess $LiAlH_4$ was destroyed by the addition of deoxygenated water (~20 mL), the organic phase was extracted into light petroleum (3 × 20 mL), and the combined organic extracts were dried over activated 4 Å molecular sieves. Solvent was removed in vacuo to give **1** as a colorless oil. Yield 4.23 g, 82%. Anal. Calcd for $C_{14}H_{27}PSSi_2$: C, 53.45; H, 8.65. Found: C, 53.00; H, 8.71. ^1H NMR ($CDCl_3$, 297 K): δ 0.02 (s, 18H, $SiMe_3$), 0.73 (s, 1H, CHP), 2.42 (s, 3H, SMe), 4.40 (d, $J_{PH} = 216.3$ Hz, 1H, PH), 7.02 (m, 1H, ArH), 7.11 (m, 1H, ArH), 7.18 (m, 1H, ArH), 7.38 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 0.79 ($SiMe_3$), 5.05 (d, $J_{PC} = 42.7$ Hz, CHP), 16.52 (SMe), 124.63, 125.47, 128.73, 133.76 (Ar), 136.40 (d, $J_{PC} = 19.6$ Hz, Ar), 142.80 (Ar). ^{31}P NMR ($CDCl_3$, 297 K): δ −67.0 (d, $J_{PH} = 212.3$ Hz).

Preparation of [{$(Me_3Si)_2CH$}P(C_6H_4-2-SMe)]Li(tmeda) (2). To a solution of {$(Me_3Si)_2CH$}PH(C_6H_4-2-SMe) (1.31 g, 4.17 mmol) and tmeda (0.62 mL, 4.17 mmol) in diethyl ether (20 mL) was added *n*-BuLi (1.74 mL, 4.17 mmol). The deep red solution was stirred for 16 h and then solvent was removed in vacuo to leave a red/orange solid. This solid was recrystallized from warm light petroleum as orange plates of **2**. Crystals of **2** suitable for X-ray analysis were obtained from warm methylcyclohexane. Yield 1.03 g, 57%. Anal. Calcd for $C_{20}H_{42}LiN_2PSSi_2$: C, 55.01; H, 9.69; N, 6.41. Found: C, 54.66; H, 9.91; N, 6.07. ^1H NMR (d_8-toluene, 297 K): δ 0.30 (s, 18H, $SiMe_3$), 0.51 (s, 1H, CHP), 1.66 (s, br, 4H, NCH_2), 1.78 (s, br, 12H, NCH_3), 2.34 (s, 3H, SMe), 6.41 (m, 1H, ArH), 6.91 (m, 1H, ArH), 7.07 (m, 1H, ArH), 7.13 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-toluene, 297 K): 1.76 ($SiMe_3$), 4.00 (d, $J_{PC} = 61.9$ Hz, CHP), 15.76 (SMe), 45.69 (NCH_3), 56.64 (NCH_2), 115.24, 126.51, 131.82 (Ar), 165.72 (d, $J_{PC} = 53.8$ Hz, Ar). ^{31}P NMR (d_8-toluene, 297 K): −64.2 (s, br).

Preparation of [{$(Me_3Si)_2CH$}P(C_6H_4-2-S)]{Li(tmeda)}$_2$ (4b). To a solution of {$(Me_3Si)_2CH$}PH(C_6H_4-2-SMe) (2.31 g, 7.35 mmol) in diethyl ether (30 mL) was added *n*-BuLi (6.1 mL, 14.70 mmol) and this mixture was stirred for 16 h. The pale yellow precipitate was isolated by filtration and washed with light petroleum (3 × 10 mL). Residual solvent was removed under reduced pressure to leave [{$(Me_3Si)_2CH$}P(C_6H_4-2-S)]{Li(OEt_2)}$_2$ (**4a**) as a pale yellow powder (isolated yield 1.98 g, 58%). To a suspension of this solid in light petroleum (~30 mL) was added tmeda (1.29 mL, 8.60 mmol). Concentration of the orange solution obtained to ca. 15 mL and cooling to +6 °C over 16 h gave yellow crystals of **4b** suitable for X-ray analysis (1.65 g, 70% based on **4a**). Compounds **4a** and **4b** proved too air sensitive for reproducible CHN analysis. **4a**: ^1H NMR (d_8-THF, 297 K) δ 0.05 (s, 18H, $SiMe_3$), 0.17 (d, $J_{PH} = 1.2$ Hz, 1H, CHP), 1.09 (t, 12H, Et_2O), 3.35 (q, 8H, Et_2O), 6.10−6.90 (m, 4H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 297 K): δ 1.74 ($SiMe_3$), 4.69 (d, $J_{PC} = 62.1$ Hz, CHP), 15.65 (Et_2O), 66.39 (Et_2O), 116.65, 120.94, 124.64, 132.28, 145.16 (Ar), 159.78 (d, $J_{PC} = 40.2$ Hz, Ar). ^{31}P NMR (d_8-THF, 297 K): δ −86.5. **4b**: ^1H NMR (d_8-THF, 297 K) δ 0.10 (s, 18H, $SiMe_3$), 0.35 (s, 1H, CHP), 2.16 (s, br, 24H, NCH_3), 2.32 (s, br, 8H, NCH_2), 6.15 (m, 1H, ArH), 6.49 (m, 1H, ArH), 6.59 (m, 1H, ArH), 6.95 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 297 K): δ 2.40 ($SiMe_3$), 5.27 (d, $J_{PC} = 60.9$ Hz, CHP), 46.79 (NCH_3), 59.29 (NCH_2), 117.34, 121.55, 125.40, 132.96, 145.71 (Ar), 160.17 (d, $J_{PC} = 40.2$ Hz, Ar). ^{31}P NMR (d_8-THF, 297K): δ −86.2. ^7Li NMR (d_8-toluene, 297K): δ +1.77.

Isomerization of 2 to 6. Preparation of [{$(Me_3Si)_2CH$}P(Me)(C_6H_4-2-S)]Li(12-C-4) (6b). A yellow solution of **2** (0.56

g, 1.28 mmol) in toluene (20 mL) was irradiated with white light from a 20 W fluorescent lamp for 15 min. After this time solvent was removed in vacuo to give a slightly sticky pale yellow solid. This was dissolved in diethyl ether (15 mL) and 12-crown-4 (0.23 g, 0.21 mL, 1.28 mmol) was added, resulting in the formation of a pale yellow precipitate that was isolated by filtration and dissolved in a mixture of methylcyclohexane and THF (12:4 mL). Concentration of the resulting solution to ca. 10 mL and slow cooling to +6 °C gave **6b** as colorless plates. Yield 0.45 g, 71%. Anal. Calcd for $C_{22}H_{42}LiO_4PSSi_2$: C, 53.20; H, 8.52. Found: C, 53.31; H, 8.45. ^{1}H NMR (d_8-THF): δ −0.12 (s, 9H, SiMe$_3$), 0.13 (d, 1H, $J_{PH} = 1.2$ Hz, CHP), 0.20 (s, 9H, SiMe$_3$), 1.38 (d, $J_{PH} = 6.5$ Hz, 3H, PMe), 3.61 (s, 16H, 12-crown-4), 6.59 (m, 1H, ArH), 6.69 (m, 1H, ArH), 6.95 (m, 1H, ArH), 7.23 (m, 1H, ArH). ^{13}C{^{1}H} NMR (d_8-THF): δ 2.06, 3.33 (SiMe$_3$), 12.15 (d, $J_{PC} = 15.5$ Hz, PMe), 71.08 (12-crown-4), 118.82, 126.22, 129.02, 129.06, 135.44, 142.09 (Ar). ^{31}P{^{1}H} NMR (d_8-THF): δ −32.9.

Crystal Structure Determination of 2, 4b, and 6b. All measurements were made at 160 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and narrow (0.3° in ω) frame exposures. Cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. Table 4 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[19] One tmeda ligand in **4b** was found to be disordered. It was possible to resolve two sites for some of the atoms and these were refined with the aid of restraints, giving approximately equal occupancy factors for the two components. A similar 2-fold disorder was resolved for one CH_2CH_2 segment of the crown ligand in **6b**, which could be refined without restraints.

Acknowledgment. The authors wish to thank Dr. Jing P. Zhao at the EPSRC National EPR Service (Manchester) for obtaining the EPR spectra. The authors gratefully acknowledge the support of the University of Newcastle and the Royal Society.

Supporting Information Available: Details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters for **2**, **4b**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0208265

---

(19) (a) SMART and SAINT software for CCD diffractometers; Bruker AXS Inc., Madison, WI, 1997. (b) Sheldrick, G. M. SHELXTL user manual, version 5.1; Bruker AXS Inc.: Madison, WI, 1997.