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Versatile Coordination Behavior of Aryl-Substituted Phosphiniminate and Phosphoranate Anions: Synthesis and Structural Characterization of Lithium Complexes with η^0, η^1, and η^6-Arene Coordination

Musa Said,[†] Mark Thornton-Pett,[‡] and Manfred Bochmann*,[†]

Wolfson Materials and Catalysis Centre, School of Chemical Sciences,
University of East Anglia, Norwich, NR4 7TJ, U.K., and School of Chemistry,
University of Leeds, Leeds, LS2 9JT, U.K.

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Metalation of the bulky phosphinimine 4-MeC$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$ (**1**) with *n*-butyllithium followed by recrystallization from benzene affords [Li{4-MeC$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$}]$_2$ (**3**), while Li(THF)$_2${4-MeC$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$} (**2**) is formed in the presence of THF. Similarly, treatment of the N-mesityl compound 4-Bu^{t}C$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6 (**4**) with Bu^{n}Li in the presence of THF produced Li(THF)$_2${4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} (**5**), while lithiation of the new phosphorus ylid 4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2${=C(SiMe$_3$)C$_6$H$_4$Bu^t-4} (**6**) afforded Li(THF)$_2${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$C(SiMe$_3$)C$_6$H$_4$-Bu^t-4} (**7**). The solid-state structures of **2**, **3**, **5**, and **7** were determined. Whereas the anion in **2** acts simply as a C−N chelate, the MeC$_6$H$_4$ moieties in the dimeric compound **3** are η^6-bonded. On the other hand, compound **5** contains an aryl substituent that is η^1-coordinated to Li$^+$ via its *ipso*-carbon, while the ylid anion **7** displays an unusual η^1-coordination to one *ortho*-C atom of a strongly tilted arene ring. The results demonstrate the surprisingly variable coordination behavior of aryl-substituted [CPN]$^-$ and [CPC]$^-$ anions and the importance of aryl substituents in stabilizing electron-deficient metal centers.

Introduction

Phosphiniminato anions[1] [CHR^1-PR$^2_2$=NR^3]$^-$ have attracted much attention recently as C−N chelating ligands. The first structurally characterized lithium salt, Li(THF)$_2$(CH$_2$PPh$_2$NPh), was reported in 1995 and is prototypical for a solvent-stabilized complex where the phosphorus ligand acts as a C−N chelate (Chart 1, structure **A**).[2] Complexes without donor solvents tend to adopt an oligomeric structure, such as the tetrameric [LiCH$_2$PMe$_2$NSiMe$_3$]$_4$[3] and the dimeric compounds **B**,[3] **C**,[4] **D**,[5] and **E**.[6] These structures are based on LiCPN four-membered rings with bridging alkyl-carbons, usually supported by additional bridging interactions between the lithium ions and the imino-nitrogen atoms. Closely related structural principles are found in alkali metal bis(iminophosphino)methanides M[CH{Ph$_2$P=NSiMe$_3$}$_2$] (M = Li, Na).[7] Complexes bearing phosphiniminato ligands have recently attracted interest for use in ethene polymerization catalysis.[8,9] As part of our interest in the coordination chemistry and reactivity of phosphinimine and phosphiniminato complexes of early[10] and late[11] transition metals, we report here the synthesis and crystal structures of lithium phosphiniminates carrying bulky −C(SiMe$_3$)(aryl) substituents. The results show that, depending on subtle details of the ligand structure and the presence or absence of donor solvents, these ligands have the ability to accommodate a surprising variety of coordination modes through variable metal−arene interactions.

Results and Discussion

The new benzylic phosphinimine 4-MeC$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$ (**1**) was prepared by lithiation of 4-MeC$_6$H$_4$CH$_2$P(Ph)$_2$=NSiMe$_3$ followed by treatment with Me$_3$SiCl. Addition of *n*-butyllithium to **1** in light petroleum gave a white precipitate, which on recrys-

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[†] University of East Anglia.

[‡] University of Leeds.

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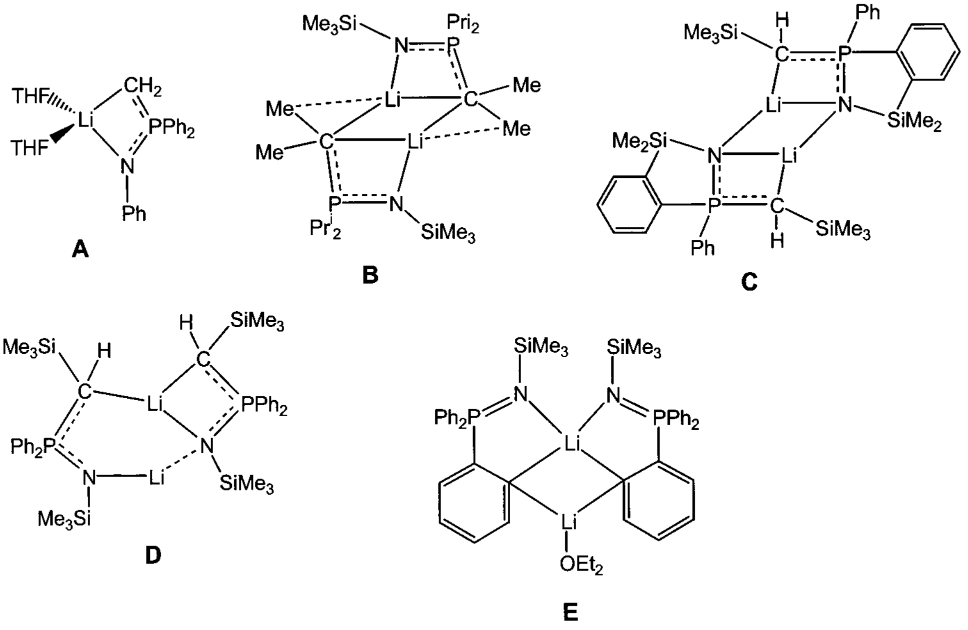
Chart 1



tallization in the presence of THF afforded Li(THF)$_2$-{4-MeC$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$} (**2**) as colorless prisms (Scheme 1). On the other hand, recrystallization from benzene gave solvent-free crystals, which were identified as the dimeric compound [Li{4-MeC$_6$H$_4$C-(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$}]$_2$ (**3**). Similarly, treatment of the N-mesityl analogue 4-Bu^{t}C$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6 (**4**) with Bu^{n}Li in the presence of THF produced crystalline Li(THF)$_2${4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P-(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} (**5**) (Scheme 2).

The structures of compounds **2**, **3**, and **5** were determined by single-crystal X-ray diffraction. Selected bonding parameters are collected in Table 1. Comparison of the geometries with those of previously determined examples shows that certain parameters remain fairly constant, irrespective of the ligand framework and the presence or absence of coordinated solvent molecules. Representative examples are listed in Table 2. For example, the P−N and P−C bond lengths fall, with few exceptions, within the narrow range of 1.57−1.60 Å and 1.7−1.76 Å, respectively, and the C−Li−N and P−C−Li angles are close to 77−80° and are smaller by ca. 10−15° than the corresponding P−N−Li angles. The geometry around the phosphorus atoms, too, shows little distortion from tetrahedral in all cases, with C−P−N angles from 105.6° to 113.2°. The coordinated imino-nitrogen atoms are trigonal-planar, with intra-annular angles of 90−110° and typical exocyclic P−N−substituent and Li−N−substituent angles of 125−128°.

The lithium−carbon distances are subject to wider variation. Thus in sterically undemanding compounds such as Li(THF)$_2$(CH$_2$PPh$_2$NPh) the Li−C bond length is 2.23(1) Å, while the tetramer [LiCH$_2$PMe$_2$NSiMe$_3$]$_4$, with triply bridging CH$_2$ groups, shows a range of distances from 2.28(1) to 2.50(1) Å. The Li−C(1) distance in **2** is rather long, 2.386(3) Å, about 0.1 Å longer than in the closely related Li(OEt$_2$)$_2${CH(SiMe$_3$)PPh$_2$NSiMe$_3$}.[5] In other respects the structure of **2** (Figure 1) closely resembles that of previously reported ether-stabilized lithium compounds, with the phosphorus ligand acting as $\kappa C,\kappa N$-chelate.

A very different bonding situation is found in the solvent-free analogue [Li{4-MeC$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NSiMe$_3$}]$_2$ (**3**). Whereas the Li−C(1) and Li−N(1) bond lengths (2.395(8) and 1.991(7) Å, respectively) are very similar to the values found for **2**, in this case the coordination sphere of the lithium ions is completed by η^6-coordination to a methylphenyl substituent of a neighboring molecule, thus forming a dimeric structure (Figure 2). Carbons C(133) and C(132) are tilted slightly toward Li, with relatively short Li−C bond lengths of 2.434(7) and 2.497(7) Å, while the distances to the other phenyl ring carbons range from 2.503 to 2.677 Å but remain within bonding range. The benzylic C(SiMe$_3$)-C$_6$H$_4$Me moieties therefore act as $\mu,\eta^1:\eta^6$ ligands. In previous cases, dimer formation in solvent-free lithium phosphiniminates was made possible by P=N and/or alkyl bridges,[4,5,7] with the possible participation of agostic interactions, e.g., in **B**.[3]

An interrogation of the Cambridge crystallographic database for compounds with Li−C bonds showed a spread of bond distances from ca. 2.0 to 2.7 Å, with a pronounced maximum at 2.27 Å, the typical Li−C σ-bond length in most lithium aryls.[12] Similar bond lengths are characteristic for sterically less hindered lithium phosphiniminates. Lithium−arene π-interactions, on the other hand, are much more variable. While Li···C distances from 2.2 to 2.5 Å are common, longer range interactions of over 2.7 Å are sometimes observed.[13]

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

$Li(THF)_2\{4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3\}$ (**2**)			
Li−O(1)	1.967(3)	Li−O(2)	1.976(3)
Li−N(1)	2.039(3)	Li−C(1)	2.386(3)
N(1)−P(1)	1.5889(14)	N(1)−Si(1)	1.6897(15)
P(1)−C(1)	1.7409(17)	P(1)−C(111)	1.8245(18)
C(1)−C(131)	1.489(2)	C(1)−Si(2)	1.8448(18)
C(1)−Li−N(1)	76.81(11)	O(1)−Li−O(2)	96.60(14)
N(1)−Li−O(1)	118.48(15)	N(1)−Li−O(2)	125.41(16)
O(1)−Li−C(1)	125.35(16)	O(2)−Li−C(1)	116.73(14)
P(1)−N(1)−Si(1)	144.89(10)	P(1)−N(1)−Li	92.42(11)
Si(1)−N(1)−Li	122.66(11)	P(1)−C(1)−C(131)	114.85(12)
C(131)−C(1)−Si(2)	118.60(12)	P(1)−C(1)−Si(2)	125.55(10)
C(131)−C(1)−Li	92.38(13)	P(1)−C(1)−Li	77.73(9)
Si(2)−C(1)−Li	109.00(10)	C(1)−P(1)−N(1)	112.01(8)
$[Li\{4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3\}]_2$ (**3**)			
Li−N(1)	1.991(7)	Li−C(1)	2.3951(8)
N(1)−P(1)	1.595(3)	P(1)−C(1)	1.752(4)
N(1)−Si(1)	1.716(3)	C(1)−Si(2)	1.851(4)
C(1)−C(131)	1.478(5)	Li−C(131)	2.677(7)
Li−C(132)	2.497(7)	Li−C(133)	2.434(7)
Li−C(134)	2.503(8)	Li−C(135)	2.568(7)
Li−C(136)	2.645(7)		
C(1)−Li−N(1)	78.1(2)	Li(1)−N(1)−P(1)	92.9(2)
N(1)−P(1)−C(1)	112.36(17)	Li−C(1)−C(131)	98.8(3)
Li−C(1)−Si(2)	108.5(2)	Li−N(1)−Si(1)	129.2(3)
P(1)−N(1)−Si(1)	137.3(2)	P(1)−C(1)−Si(2)	123.3(2)
P(1)−C(1)−C(131)	114.1(3)	N(1)−Li−C(132)	175.4(4)
$Li(THF)_2\{4\text{-}Bu^tC_6H_4C(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ (**5**)			
Li−O(1)	1.957(5)	Li−O(6)	1.960(5)
Li−N(1)	1.969(5)	Li−C(1)	2.759(5)
N(1)−P(1)	1.599(2)	N(1)−C(131)	1.423(3)
P(1)−C(1)	1.717(2)	P(1)−C(111)	1.829(3)
C(1)−C(141)	1.483(3)	C(1)−Si(1)	1.853(3)
Li−C(141)	2.621(5)		
C(1)−Li−N(1)	67.37(15)	O(1)−Li−O(6)	102.2(2)
N(1)−Li−O(1)	107.4(2)	N(1)−Li−O(6)	128.3(3)
O(1)−Li−C(1)	148.2(2)	O(6)−Li−C(1)	105.0(2)
P(1)−N(1)−C(131)	128.71(16)	P(1)−N(1)−Li	106.10(17)
C(131)−N(1)−Li	125.2(2)	P(1)−C(1)−C(141)	119.68(18)
C(141)−C(1)−Si(1)	113.04(16)	P(1)−C(1)−Si(1)	124.17(14)
C(141)−C(1)−Li	68.93(15)	P(1)−C(1)−Li	75.45(13)
Si(1)−C(1)−Li	143.97(16)	C(1)−P(1)−N(1)	109.16(11)
C(1)−C(141)−Li	79.19(16)	N(1)−Li−C(141)	86.00(18)
$Li(THF)_2\{4\text{-}Bu^tC_6H_4CHP(Ph)_2C(SiMe_3)C_6H_4Bu^t\text{-}4\}$ (**7**)			
Li−O(31)	1.904(4)	Li−O(41)	1.939(4)
Li−C(1)	2.199(4)	Li−C(2)	3.543(4)
Li(1)−C(11)	2.787(4)	Li−C(211)	2.928(4)
Li−C(212)	2.463(5)	Li−C(213)	3.047(5)
Li−C(214)	3.903(5)	Li−C(215)	4.145(5)
Li−C(216)	3.731(4)	C(1)−C(11)	1.466(3)
C(1)−P(1)	1.741(2)	C(2)−P(1)	1.706(2)
C(2)−C(211)	1.491(3)	C(2)−Si(2)	1.839(2)
C(1)−Li−C(212)	100.6(2)	O(31)−Li−O(41)	102.4(2)
C(1)−Li−O(31)	121.8(2)	C(1)−Li−O(41)	118.0(2)
O(31)−Li−C(212)	111.5(2)	O(41)−Li−C(212)	100.9(2)
P(1)−C(1)−C(11)	125.6(2)	P(1)−C(1)−Li	107.94(14)
C(11)−C(1)−Li	97.0(2)	C(1)−P(1)−C(2)	114.73(10)
C(211)−C(2)−Si(2)	112.69(14)	P(1)−C(2)−Si(2)	127.29(11)

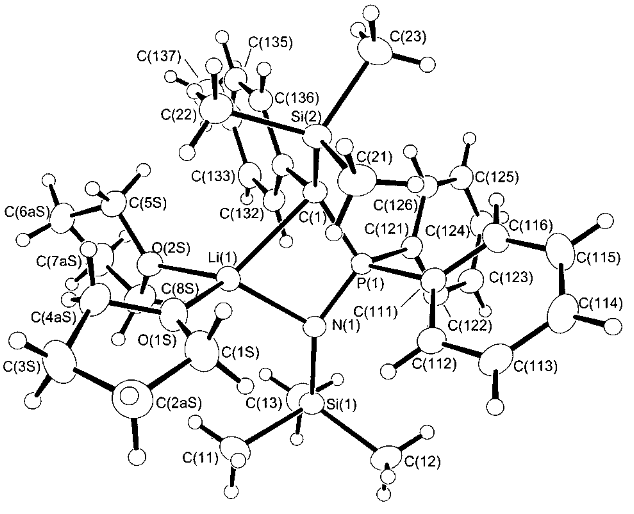

Figure 1. Molecular structure of $Li(THF)_2\{4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3\}$ (**2**), showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

Lithiation of $4\text{-}Bu^tC_6H_4CH(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ (**4**), a slightly bulkier analogue of **1** bearing an *N*-mesityl substituent, with *n*-butyllithium in hexanes in the presence of THF gives $Li(THF)_2\{4\text{-}Bu^tC_6H_4C(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ (**5**) (Figure 3). Although the composition of this compound is very similar to **2** and a similar structure might be expected, the Li−C(1) distance in **5** is 0.36 Å or 15% longer than in **2**, and more than 0.5 Å longer than in most previously determined structures of lithium phosphiniminates, such as **A**, **C**, **D**, and **E**. Long Li$\cdots$C(alkyl) distances as found in **5** are at the upper limit of what might be considered a bonding interaction. As a consequence of the Li$\cdots$C(1) elongation, the N(1)−Li−C(1) angle of only 67.37(15)° is about 10° more acute than in the previously discussed cases.

The reason for this rather dramatic structural change is the close approximation of the $Bu^tC_6H_4$ substituent and in particular of the *ipso*-carbon atom C(141), which shows a Li−C(141) distance of 2.621(5) Å. The bonding mode of the benzylic $Bu^tC_6H_4C(SiMe_3)$ moiety is therefore predominantly via η^1-coordination to C(141), while in view of the rather long Li−C(1) distance of >2.7 Å it is debatable whether there is any significant Li−C(1) σ-bond contribution.

It is evident that C-aryl-substituted phosphiniminato anions are able to respond to subtle electronic and steric changes by "fine-tuning" their coordination characteristics and to adopt varying degrees of π-arene interactions. This flexibility is, however, not restricted to these C−N chelates. For example, lithiation of the new phosphorus ylid $4\text{-}Bu^tC_6H_4CH_2P(Ph)_2\{{=}C(SiMe_3)C_6H_4\text{-}Bu^t\text{-}4\}$ (**6**) affords $Li(THF)_2\{4\text{-}Bu^tC_6H_4CHP(Ph)_2C(SiMe_3)C_6H_4Bu^t\text{-}4\}$ (**7**) (Scheme 3). The crystal structure of **7** confirms coordination of lithium to two THF molecules as well as to carbon C(1), with a relatively short Li−C bond length of 2.199(4) Å, typical of a σ-bond. There is, however, no bond to C(2), i.e., no CPC chelate formation (Li$\cdots$C(2) 3.543(4) Å). Instead, the fourth coordination site on Li^+ is occupied by the aryl substituent on C(2). However, unlike **5**, which showed η^1-coordination to the *ipso* carbon, in **7** the aryl substituent on C(2) is tilted to allow close approximation of one of the *ortho*-carbon atoms, to give a Li−C(212) π-bond of 2.463(5) Å. All other distances between lithium and the other ring carbon atoms range from 2.9 to >4.1 Å and are firmly outside any bonding range. Lithium−aryl π-coordination to *ortho*- rather than *ipso*-C atoms of phenyl groups have been seen previously in the terphenyllithium compound $[DppLi]_2(THF)$, which shows a very comparable Li$\cdots$C(ortho) distance (2.431(4) Å).[14]

One reason for the subtle difference in η^1-bonding mode between **5** and **7** may be the presence of the Si-

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[14] Rabe, G. W.; Sommer, R. D.; Rheingold, A. L. *Organometallics* **2000**, *19*, 5537.

Scheme 1

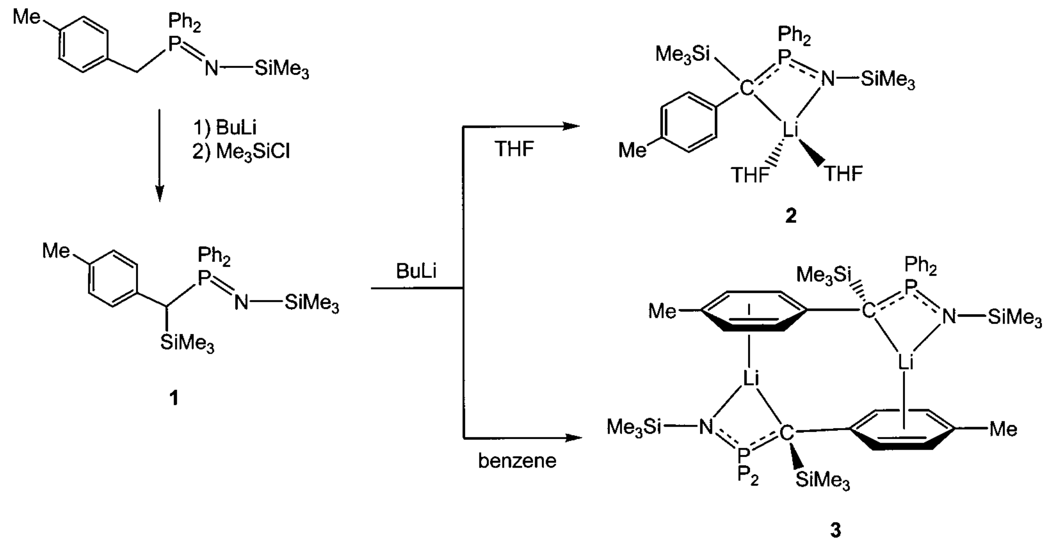
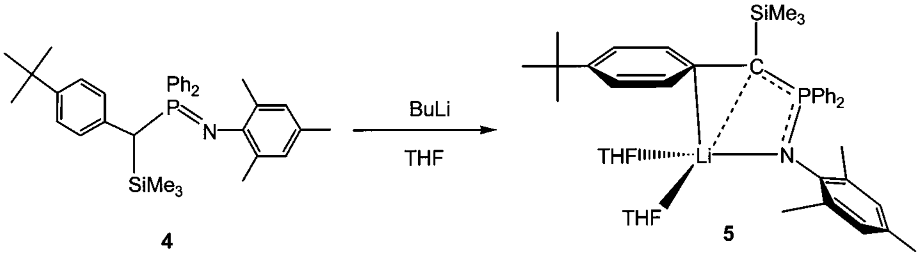


Table 2. Comparison of Geometric Parameters of Lithium Phosphiniminato Complexes

compound	Li−C/Å	Li−N/Å	P−C/Å	P−N/Å	C−Li−N/deg	P−C−Li/deg	P−N−Li/deg	C−P−N/deg	ref
$Li(THF)_2\{CH_2PPh_2NPh\}$ **A**	2.23(1)	2.00(1)	1.707(7)	1.914(4)	77.2(4)	83.0(4)	93.4(4)	105.6(3)	2
$[LiCMe_2PPr^i{}_2NSiMe_3]_2$ **B**	2.28(1) − 2.50(1)	1.97(1)− 2.12(1)	1.765(1)− 1.93(1)	1.574(7)− 1.589(7)					3
$[LiCHSiMe_2C_6H_4P(Ph)NSiMe_3]_2$ **C**	2.232(6)	2.081(6)	1.699(3)	1.628(2)	80.1(2)	79.9(2)	86.2(2)	113.18(14)	4
$Li(OEt_2)_2\{CHSiMe_3PPh_2NSiMe_3\}$	2.289(6)	2.018(5)	1.702(3)	1.592(2)	77.4(2)	79.6(2)	91.1(2)	110.2(1)	5
$[Li\{CHSiMe_3PPh_2NSiMe_3\}]_2$ **D**	2.190(9)	2.166(9)	1.714(5)	1.617(3)	78.1(3)	82.2(3)	85.2(3)	111.0(2)	5
$Li_2(OEt_2)(C_6H_4PPh_2NSiMe_3)_2$ **E**	2.263(5)	2.037(4)	1.802(2)	1.562(2)					6
		2.027(4)							
2	2.386(3)	2.039(3)	1.7409(17)	1.5889(14)	76.91(11)	77.73(9)	92.42(11)	112.01(8)	a
3	2.395(8)	1.991(7)	1.752(4)	1.595(3)	78.1(2)	76.4(2)	92.9(2)	112.36(17)	a
5	2.759(5); 2.621(5)	1.969(5)	1.717(2)	1.599(2)	C(1): 67.37(15) C(141): 86.00(18)	75.45(13)	106.10(17)	109.16(11)	a

[a] This work.

Scheme 2



(2)Me$_3$ silyl group. A further Li···C interaction, with the *ipso*-C atom C(11) of the second aryl substituent in **7**, is probably too weak to represent a significant η^2-type bonding contribution (Li···C(11) = 2.787(4) Å).

The P−C bonds in **7** are comparable to the P−C bond lengths of phosphiniminates, with the shorter P−C(2) bond of 1.706(2) Å indicating more pronounced double bond character in this C−P−C anion system.

Conclusion

Bulky phosphiniminato and phosphoranato anions bearing aryl substituents are capable of fine-tuning their coordination behavior by adopting varying degrees of arene−metal interactions that range from no interaction, as in **2**, and at least two types of η^1-bonding to η^6-coordination. Although disruption of arene−lithium interactions by coordinating solvent molecules might be expected, arene binding is apparently competitive with THF coordination and is seen in both phosphiniminato and phosphoranato chelate complexes. While many geometric parameters in these ligands are insensitive to structural and electronic changes, the lithium−C distances are subject to wide variations and range in the present examples from ca. 2.2 Å to just under 2.8 Å. Particularly noteworthy is the Li···*o*-C π-coordination in the phosphoranato compound **7**, brought about by a

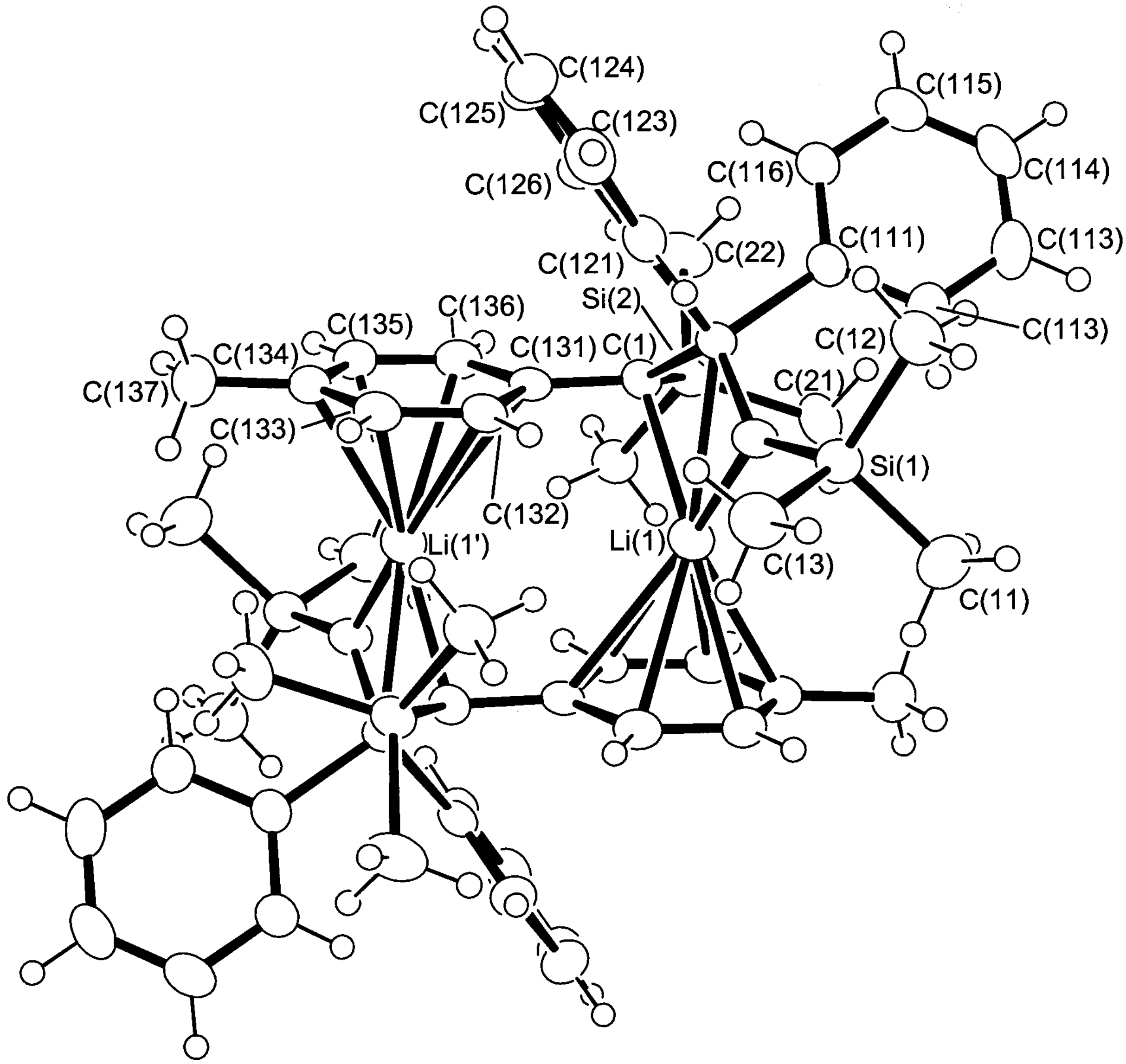


Figure 2. Molecular structure of $[Li\{4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3\}]_2$ (**3**), showing the atomic numbering scheme.

ring tilt which allows just one of the six ring carbons to approach within bonding range. The consequences of this coordinative variability in transition metal chemistry are the subject of current investigations.

Experimental Section

All manipulations were performed under a dinitrogen atmosphere using standard vacuum line techniques. Solvents were distilled under N_2 over sodium benzophenone (THF, diethyl ether), sodium (toluene), or sodium−potassium alloy (light petroleum, bp 40−60 °C). NMR solvents were dried over activated molecular sieves and degassed through several freeze−thaw cycles. NMR spectra were recorded on Bruker DPX300 or DRX500 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C). ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. Azidotrimethylsilane was used as purchased, and mesityl azide[15] and $4\text{-}Bu^tC_6H_4CH_2P(Ph)_2{=}N{-}C_6H_2Me_3\text{-}2,4,6$[17] were prepared according to a literature procedures. $4\text{-}Bu^tC_6H_4CH_2PPh_2$ and $4\text{-}MeC_6H_4CH_2PPh_2$ were prepared following the procedure given for $PhCH_2PPh_2$.[16] $4\text{-}MeC_6H_4CH_2P(Ph)_2{=}NSiMe_3$ was prepared as described for $4\text{-}Bu^tC_6H_4CH_2P(Ph)_2{=}NSiMe_3$.[10b]

Preparation of $Li(THF)_2[4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3]$ (2) and $[Li\{4\text{-}MeC_6H_4C(SiMe_3)P(Ph)_2{=}NSiMe_3\}]_2$ (3). In a one-pot procedure, a round-bottom flask charged with $4\text{-}MeC_6H_4CH_2P(Ph)_2{=}NSiMe_3$ (1.5 g, 3.97 mmol) was dissolved in toluene (60 mL) and cooled to 0 °C. *n*-BuLi (2.48 mL, 3.97 mmol) was added dropwise. The mixture was brought to ambient temperature and stirred until the reaction was complete (ca. 2 h), as indicated by a ^{31}P NMR signal at δ 16.5. An excess of trimethylchlorosilane (1.51 mL, 11.91 mmol) was added, and the mixture was heated at 70 °C until the silylation was complete (ca. 3 h; ^{31}P NMR δ 1.1). After cooling to room temperature, all volatiles were removed, light petroleum (50 mL) was added to the residue, and the mixture was warmed gently until it formed a clear solution. After cooling to 0 °C, Bu^nLi (2.48 mL, 3.97 mmol) was added dropwise to yield a light-yellow precipitate of **3**, which was filtered and washed with light petroleum (2 × 25 mL), yield 1.4 g (77%). Anal. Calcd for $C_{26}H_{35}LiNPSi_2$: C, 68.53; H, 7.74; N, 3.07. Found: C, 66.85; H, 7.90; N, 3.15. ^1H NMR (300.13 MHz, C_6D_6, 20 °C): δ 0.16 (s, 9H, $SiMe_3$), 0.39 (s, 9H, $NSiMe_3$), 2.14 (s, 3H, CH_3), 6.88−7.84 (m, 14H, Ph). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6, 20 °C): δ 3.91 ($SiMe_3$), 5.31 ($NSiMe_3$), 20.02 (CH_3), 125.85−150.0 (many

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Scheme 3

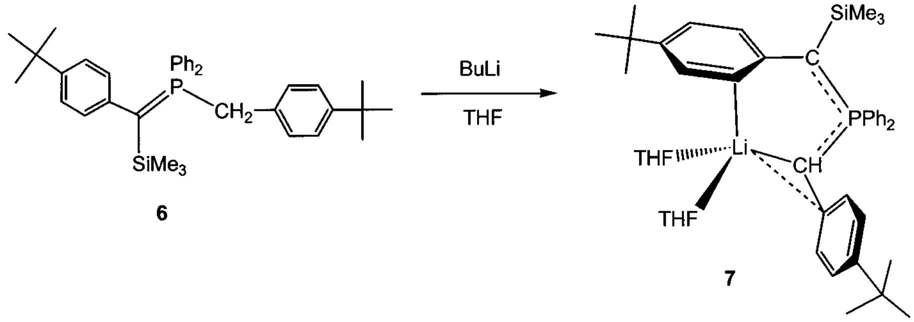

Table 3. Crystal Data and Data Collection for Lithium Chelate Complexes

	2	3	5	7
formula	$C_{34}H_{51}LiNO_2PSi_2$	$C_{26}H_{35}LiNPSi_2$	$C_{43}H_{61}LiNO_2PSi$	$C_{45}H_{62}LiO_2PSi$
fw	599.85	455.64	689.93	700.95
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	10.2320(2)	10.2817(2)	11.6119(3)	12.2198(3)
b, Å	20.9928(5)	9.7193(4)	35.9861(11)	22.3822(9)
c, Å	16.7208(2)	26.7191(10)	10.6714(3)	151746(5)
β, deg	101.799(2)	100.387(2)	114.768(2)	91.414(2)
V, Å^3	3515.71(12)	2626.31(15)	4049.0(2)	4149.1(2)
D_{calc}, g cm^{-3}	1.133	1.152	1.132	1.122
Z	4	4	4	4
μ, mm^{-1}	0.175	0.209	0.132	0.13
no. of ind/obsd reflns	6882/5789	5103/4226	7899/5602	8132/5896
F(000)	1296	976	1496	1520
R_{int}[a]	0.0599	0.0653	0.0557	0.0615
R_1 [$I > 2\sigma(I)$][b]	0.0425	0.0716	0.0561	0.0498
wR_2 (all data)[c]	0.1112	0.1772	0.1585	0.1315
GOF on F^2	1.024	1.125	1.022	1.02

[a] $\sum|F_o^2 - F_o^2(\mathrm{mean})|/\sum F_o^2$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [2F_c^2 + \max(F_o^2,0)]/3$.

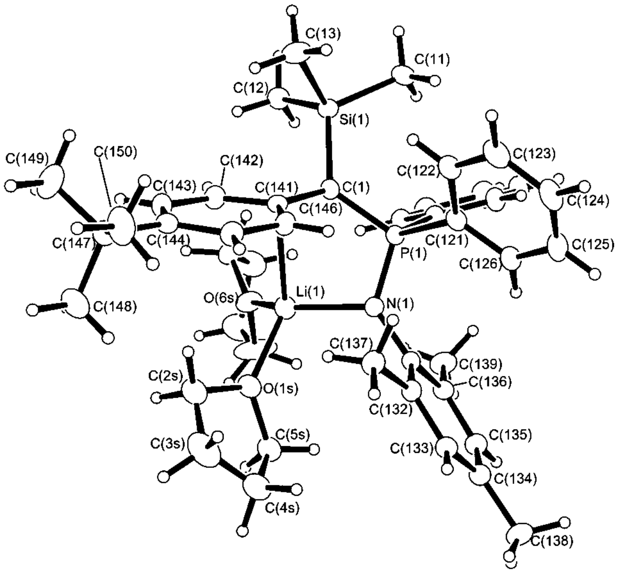

Figure 3. Molecular structure of Li(THF)$_2${4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} (**5**), showing the atomic numbering scheme.

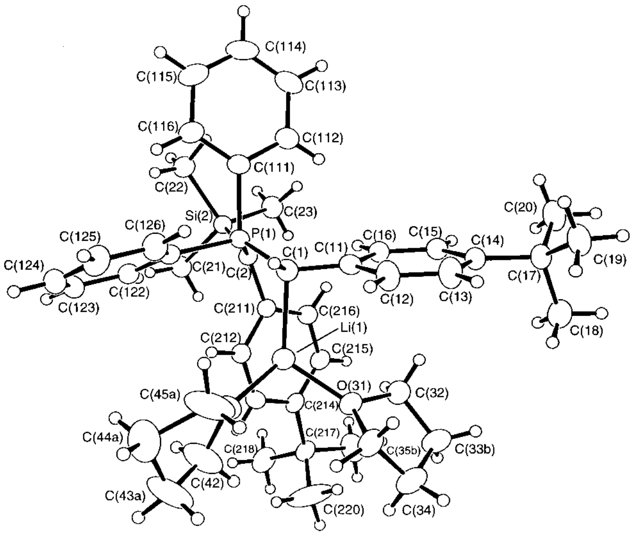

Figure 4. Molecular structure of Li(THF)$_2${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$C(SiMe$_3$)C$_6$H$_4$Bu^t-4} (**7**), showing the atomic numbering scheme.

peaks, Ph). ^{31}P NMR (121.49 MHz, C$_6$D$_6$, 20 °C): δ 23.22. Suitable crystals of **3** were obtained by keeping the above C$_6$D$_6$ solution overnight. Recrystallization of **3** from THF/light petroleum (1:1) gave **2** as yellow prisms. The compound was identified crystallographically.

Li{4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6}. To a suspension of 4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=N−C$_6$H$_2$Me$_3$-2,4,6 in light petroleum at −78 °C was added dropwise Bu^{n}Li (17 mL, 27.2 mmol). After stirring the mixture for 3 h at ambient temperature, the light yellow precipitate was filtered off and washed with light petroleum (2 × 20 mL), yield 9.50 g (84%). Anal. Calcd for C$_{32}$H$_{35}$LiNP: C, 81.51; H, 7.48; N, 2.97. Found: C, 80.63; H, 7.62; N, 3.05. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300.13 MHz): δ 1.24 (s, 9H, CMe$_3$), 1.85 (s, 6H, Me), 2.22 (s, 3H, Me), 3.04 (d, J_{HP} = 13.9 Hz, 1H, CH), 6.79−7.79 (m, 16H, aryl). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 20.59 (Me), 21.42 (2Me), 31.17 (C*Me*$_3$), 33.65 (*C*Me$_3$), 36.96 (d, J_{CP} = 138.1 Hz, CH), 119.81−138.36 (aryl). ^{31}P NMR (CDCl$_3$, 20 °C): δ 11.66.

4-Bu^{t}C$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6 (4). In an inert atmosphere drybox Li{4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} (3.30 g, 7.00 mmol) was weighed into a 100 mL Schlenk flask and dissolved in toluene (50 mL). An excess of trimethylchlorosilane (1.52 g, 14 mmol) was added. The mixture was heated at 70 °C for 2 h and filtered. After removal of volatiles the product was recrystallized from light petroleum to give **4**, yield 2.5 g (66%). Anal. Calcd for C$_{35}$H$_{44}$NPSi: C, 78.17; H, 8.25; N, 2.60. Found: C, 78.00; H, 8.20; N, 2.30. ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 0.09 (s, 9H, SiMe$_3$), 1.19 (s, 9H, CMe$_3$), 2.31 (s, 3H, CH$_3$), 2.38 (s, 6H, CH$_3$), 3.3 (d, J_{HP} = 13.90 Hz, 1H, CH), 6.80−7.90 (m, 16H, aryl). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 0.24 (SiMe$_3$), 20.61 (Me), 22.46 (2Me), 31.22 (C*Me*$_3$), 34.10 (*C*Me$_3$), 42.24 (d, J_{CP} = 80.8 Hz, CH), 124.90−148.52 (aryl). ^{31}P NMR (C$_6$D$_6$, 20 °C): δ −5.21.

Li(THF)$_2${4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} (5). To a solution of **4** (1.39 g, 2.59 mmol) in light petroleum (60 mL) at 0 °C was added dropwise Bu^{n}Li (2 mL, 3.20 mmol). The mixture was stirred for 3 h at room temperature. The resulting yellow precipitate was filtered and washed with light petroleum (2 × 30 mL), yield 0.9 g (64%). Anal. Calcd for C$_{35}$H$_{43}$LiNPSi: C, 77.31; H, 7.97; N, 2.58. Found: C, 76.75; H, 8.14; N, 2.75. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 20 °C): δ 0.04 (s, 9H, SiMe$_3$), 1.37 (s, 9H, CMe$_3$), 1.56 (s, 6H, 2CH$_3$), 2.38 (s, 3H, CH$_3$), 6.71−7.48 (m, 16H, aryl). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): δ 4.57 (SiMe$_3$), 20.48 (CH$_3$), 21.83 (2CH$_3$), 31.46 (C*Me*$_3$), 33.85 (*C*Me$_3$), 124.90−148.52 (aryl). The C−P signal was not found. ^{31}P NMR (C$_6$D$_6$, 20 °C, 121.49 MHz): δ 18.28. Crystals suitable for X-ray diffraction were grown from THF/light petroleum to give **5**.

Ph$_2$P(CH$_2$C$_6$H$_4$Bu^t-4)(=CHC$_6$H$_4$Bu^t-4). This compound was prepared following a procedure described before by Harder.[18] Anal. Calcd for C$_{34}$H$_{39}$P: C, 85.93; H, 8.15. Found: C, 84.93; H, 8.21. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300.13 MHz): δ 1.38 (s, 9H, CMe$_3$), 1.55 (s, 9H, CMe$_3$), 2.77 (d, J_{HP} = 17.74 Hz, 1H, CH), 3.81 (d, J_{HP} = 13.02 Hz, 2H, CH$_2$), 6.88−7.84 (m, 18H, aryl). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, 75.46 MHz): δ 22.04 (C*Me*$_3$), 23.75 (C*Me*$_3$), 31.22 (*C*Me$_3$), 31.77 (*C*Me$_3$), 32.89 (d, J_{CP} = 51.3 Hz, CH), 33.96 (d, J_{CP} = 34.0 Hz, CH$_2$), 121.06−144.10 (many peaks, aryl). ^{31}P NMR (C$_6$D$_6$, 20 °C, 121.49 MHz): δ 7.42.

Ph$_2$P(CH$_2$C$_6$H$_4$Bu^t-4)(=C(SiMe$_3$)C$_6$H$_4$Bu^t-4) (6), Li[4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$CH$_2$C$_6$H$_4$Bu^t-4], and Li(THF)$_2$[4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$CH$_2$C$_6$H$_4$Bu^t-4] (7). Ph$_2$P(CH$_2$C$_6$H$_4$-Bu^t-4)(=CHC$_6$H$_4$Bu^t-4) (2.0 g, 4.18 mmol) was dissolved in toluene (50 mL) and cooled to 0 °C. Bu^{n}Li (2.61 mL, 4.18 mmol) was added dropwise. After stirring at room temperature until the reaction was complete (2 h, monitored by ^{31}P NMR δ 1.86), an excess of trimethylchlorosilane (1.59 mL, 12.54 mmol) was then added. The mixture was heated at 70 °C until the silylation was complete (ca. 3 h; ^{31}P NMR δ16.2). The product Ph$_2$P(CH$_2$C$_6$H$_4$Bu^t-4)(=C(SiMe$_3$)C$_6$H$_4$Bu^t-4) (**6**) was isolated by removing all volatiles and used without further purification.

Compound **6** thus prepared was dissolved in light petroleum (50 mL), and Bu^{n}Li (2.61 mL, 4.18 mmol) was added to give a yellow precipitate, which was collected and washed with light petroleum (30 mL), yield 1.8 g (61%). Anal. Calcd for C$_{37}$H$_{46}$-LiPSi: C, 77.10; H, 8.92. Found: C, 77.05; H, 9.05. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300.13 MHz): δ 0.24 (s, 9H, SiMe$_3$), 1.26 (s, 9H, CMe$_3$), 1.41 (s, 9H, CMe$_3$), 2.87 (d, J_{HP} = 6.84 Hz, 1H, CH), 7.06−8.08 (m, 18H, aryl). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, 75.46 MHz): δ 4.45 (SiMe$_3$), 31.44 (C*Me*$_3$), 31.65 (C*Me*$_3$), 33.64 (*C*Me$_3$), 121.00−149.43 (aryl). The C−P signals were not located. ^{31}P NMR (C$_6$D$_6$, 20 °C, 121.49 MHz): δ 14.7.

Crystals of composition Li(THF)$_2$[4-Bu^{t}C$_6$H$_4$C(SiMe$_3$)P(Ph)$_2$-CH$_2$C$_6$H$_4$Bu^t-4] (**7**) suitable for crystallography were grown from THF/light petroleum (1:1) and characterized crystallographically.

X-ray Crystallography. In each case a suitable crystal was coated in an inert perfluoropolyether oil and mounted in a nitrogen stream at 150(2) K on a Nonius Kappa CCD area-detector diffractometer. Data collection was performed using Mo Kα radiation (λ = 0.71073 Å) with the CCD detector placed 30 mm from the sample via a mixture of 1° ϕ and ω scans at different θ and κ settings using the program COLLECT.[19] The raw data were processed to produce conventional data using the program DENZO-SMN.[20] The data sets were corrected for absorption using the program SORTAV.[21] All structures were solved by heavy-atom methods using SHELXS-97[22] and were refined by full-matrix least squares refinement (on F^2) using SHELXL-97.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized positions. Crystallographic data for compounds **2**, **3**, **5**, and **7** are summarized in Table 3.

Acknowledgment. This work was supported by the Engineering and Physical Sciences Research Council.

Supporting Information Available: X-ray crystallographic files for the structures of **2**, **3**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010762I

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