Unusual Solvent-Promoted Smiles Rearrangement of Two Different Phosphorus-Containing Organolithium Compounds to the Same Lithium Phosphide. Crystal Structure of $MeP\{C_6H_4\text{-}2\text{-}CH(C_6H_4\text{-}2\text{-}CH_2NMe_2)NMe_2\}Li(THF)_2$

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Treatment of the tertiary phosphines $RP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (R = Me, **1**; R = *i*-Pr, **4**) with *n*-BuLi in THF yields the lithium phosphides $[RP\{C_6H_4\text{-}2\text{-}CH(C_6H_4\text{-}2\text{-}CH_2NMe_2)NMe_2\}]Li(THF)_2$ (R = Me, **5**; R = *i*-Pr, **6**) as the sole phosphorus-containing products. Compound **5** is also obtained when either the lithium phosphinomethanide $Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}$ (**3**) or the benzyllithium complex $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$ (**2**) is dissolved in THF. Conversion of **2** to **5** is extremely rapid, whereas conversion of **3** to **5** takes several days at room temperature. The deuterium-labeled compound $Li\{CH_2P(C_6H_4\text{-}2\text{-}CD_2NMe_2)_2\}$ (**3a**) isomerizes in THF to $DCH_2P(C_6H_4\text{-}2\text{-}CD(C_6H_4\text{-}2\text{-}CD_2NMe_2)NMe_2\}Li(THF)_2$ (**5a**) and shows a strong kinetic isotope effect in comparison to the isomerization of **3**. Compounds **5** and **6** have been characterized by multinuclear NMR spectroscopy and X-ray crystallography, and a mechanism for their formation from **1**−**4** is proposed.

Introduction

Organolithium compounds rank among the most potent and versatile reagents available to the synthetic organic/organometallic chemist.[1] Typically, such compounds are synthesized by the deprotonation of a suitable C−H acid using a strong base such as BuLi or $Li(N\text{-}i\text{-}Pr_2)$. However, even in quite simple organic substrates, several sites may be subject to deprotonation and the exact metalation site will depend on a variety of factors, including the nature of the deprotonating agent, the precise reaction conditions, and the presence of additional donor ligands such as tmeda (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[2] For example, *N*,*N*-dimethylbenzylamine undergoes ortho metalation upon reaction with *n*-BuLi in diethyl ether to give $Li\{C_6H_4\text{-}2\text{-}CH_2NMe_2\}$, whereas use of the superbase *n*-BuLi/KO-*t*-Bu under similar conditions results in deprotonation at the benzylic position to give $K\{CH(NMe_2)\text{-}C_6H_5\}$.[3,4] Similarly, metalation of *p*-fluoroanisole with *n*-BuLi occurs ortho to the methoxy group, whereas metalation with either *n*-BuLi/pmdeta or *n*-BuLi/KO-*t*-Bu occurs ortho to the fluorine substituent (pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine).[5]

We recently reported the synthesis and metalation behavior of the amino-functionalized tertiary phosphine $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (**1**).[6,7] This phosphine may potentially undergo deprotonation at any of four positions (Scheme 1): (i) at the methyl group adjacent to phosphorus to give a P-stabilized carbanion,[8] (ii) at the ring positions adjacent to the phosphorus or (dimethylamino)methyl substituents via an ortho-metalation reaction,[3] or (iii) at the benzylic position adjacent to nitrogen.[4,9] We found that the site of metalation could

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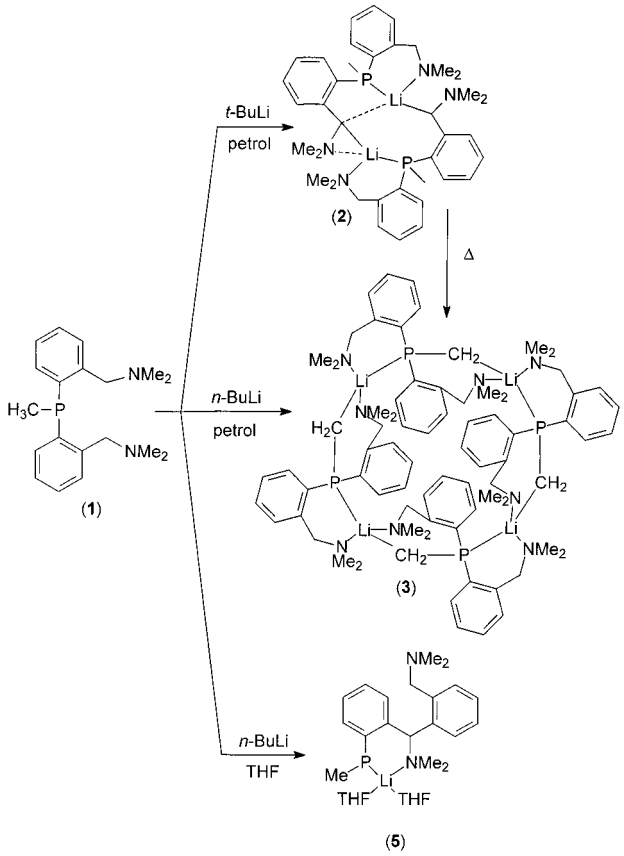
Scheme 1



be directed simply by the choice of deprotonating agent: deprotonation of **1** with *t*-BuLi in light petroleum gives the unusual dimeric benzyllithium complex [MeP-(C_6H_4-2-CH_2NMe_2){C_6H_4-2-CH(Li)NMe_2}]$_2$ (**2**) as the sole product,[6] whereas deprotonation of **1** with *n*-BuLi in the same solvent yields the tetrameric phosphinomethanide complex [Li{$CH_2P(C_6H_4$-2-$CH_2NMe_2)_2$}]$_4$ (**3**) as the major product (small amounts of **2** are also formed during this latter reaction).[7] No evidence was observed for the formation of ortho-metalated species in either reaction. Moderate heating of toluene solutions of **2** resulted in its complete isomerization to **3**, clearly demonstrating that compound **3** is the thermodynamically favored deprotonation product. We now report that metalation of **1** in THF proceeds in an entirely different manner to give a lithium phosphide via an unexpected ligand rearrangement. We also comment on evidence for a possible mechanism for this process.

Results and Discussion

Synthesis and Solid-State Structures of [RP{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)NMe_2}]Li(THF)$_2$ (R = Me, *i*-Pr). The tertiary phosphines $RP(C_6H_4CH_2NMe_2)_2$ (R = Me (**1**),[7] *i*-Pr (**4**)) are readily prepared by the reaction of $RPCl_2$ with 2 equiv of $Li(C_6H_4CH_2NMe_2)$ in ether/THF, according to eq 1.

$$RPCl_2 + 2Li(C_6H_4CH_2NMe_2) \xrightarrow{Et_2O/THF} RP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2 + 2LiCl \quad (1)$$

R = Me (**1**), *i*-Pr (**4**)

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the new phosphine **4** are as expected; the isopropyl methyl groups

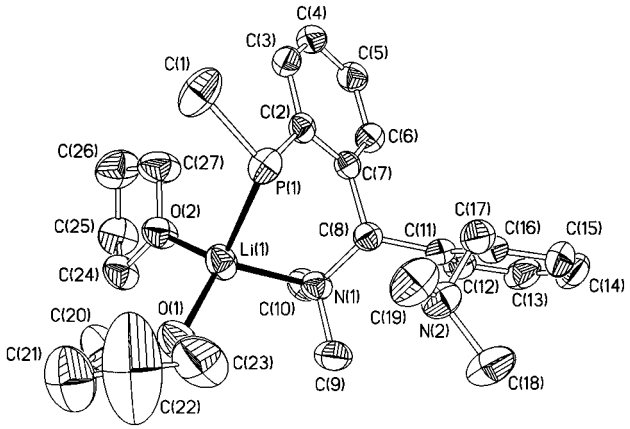


Figure 1. Structure of one independent molecule of **5** with 50% thermal ellipsoids and with H atoms omitted for clarity.

and the benzylic protons are diastereotopic and give rise to a pair of doublets in the ^{1}H NMR spectrum in each case (the benzylic signals also exhibit coupling to phosphorus).

Although treatment of a solution of **1** in light petroleum with *t*-BuLi or *n*-BuLi yields the benzyllithium complex **2** and the phosphinomethanide **3**, respectively, treatment of a THF solution of **1** with *n*-BuLi at room temperature yields the lithium phosphide [MeP{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)NMe_2}]Li(THF)$_2$ (**5**) as the exclusive product (Scheme 1). The reaction is essentially complete within 2 min, and ^{31}P NMR spectra obtained on the reaction solution suggest that neither **2** nor **3** is present under these conditions. Similarly, treatment of the related tertiary phosphine *i*-PrP($C_6H_4CH_2NMe_2$)$_2$ (**4**) with *n*-BuLi in THF yields the lithium phosphide [*i*-PrP{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)NMe_2}]Li(THF)$_2$ (**6**). The ^{31}P{^{1}H} NMR spectra of **5** and **6** exhibit singlets at −76.4 and −21.6 ppm, respectively; only a single, averaged signal is observed for the two diastereomers in each case due to rapid, reversible P−Li bond cleavage on the NMR time scale. The ^{1}H NMR spectra of these two compounds each exhibit eight signals for the aromatic protons, two separate NMe_2 signals, and two separate signals for the benzylic CH_2 and CH groups; the last of these appear at 6.05 and 6.06 ppm, for **5** and **6**, respectively, clearly identifying the new phosphide ligands present in each case.

The identities of **5** and **6** were confirmed by X-ray crystallography. The molecular structures of **5** and **6** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles for both compounds are given in Table 1. Compound **5** crystallizes with two independent molecules in the unit cell, which differ only trivially in their bond lengths and angles, together with disordered THF solvent molecules (the THF solvent of crystallization is rapidly lost under vacuum and is not observed in NMR spectra of samples of **5** that had been exposed to vacuum for 2 min). The lithium atom in each case is bound by the P and one of the N atoms of the ligands, generating a six-membered chelate ring with a bite angle of 97.39(15)° [97.49(16)°] and 95.4(2)° for **5** and **6**, respectively (values in brackets refer to the second molecule). These compare with a bite angle of 93.8(3)° [94.5(3)°] observed in the closely related com-

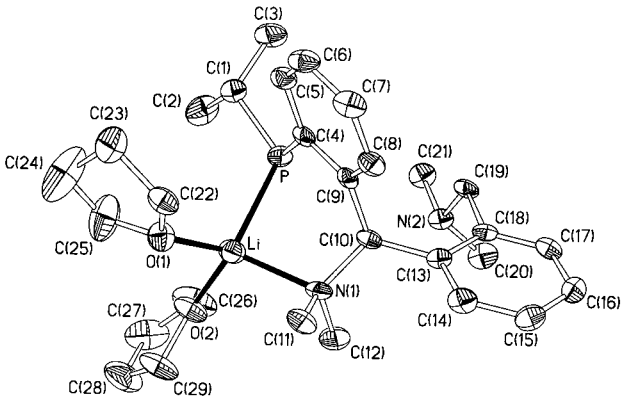


Figure 2. Molecular structure of **6** with 50% thermal ellipsoids and with H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5 and 6

Compound **5**

Molecule 1

Li(1)−N(1)	2.152(4)	Li(1)−O(1)	1.954(4)	Li(1)−O(2)	1.944(4)
Li(1)−P(1)	2.518(4)	P(1)−C(1)	1.866(2)	P(1)−C(2)	1.808(2)

O(1)−Li(1)−O(2)	108.64(19)	O(1)−Li(1)−N(1)	113.50(19)
O(1)−Li(1)−P(1)	110.72(17)	O(2)−Li(1)−P(1)	115.35(18)
N(1)−Li(1)−P(1)	97.39(15)	O(2)−Li(1)−N(1)	111.04(19)

Molecule 2

Li(2)−N(3)	2.164(4)	Li(2)−O(3)	1.968(4)	Li(2)−O(4)	1.953(4)
Li(2)−P(2)	2.522(4)	P(2)−C(28)	1.869(3)	P(2)−C(29)	1.809(2)

O(3)−Li(2)−O(4)	107.3(2)	O(3)−Li(2)−N(3)	109.5(2)
O(3)−Li(2)−P(2)	118.97(19)	O(4)−Li(2)−P(2)	109.63(19)
N(3)−Li(2)−P(2)	97.49(16)	O(4)−Li(2)−N(3)	114.0(2)

Compound **6**

Li−N(1)	2.108(6)	Li−O(1)	1.952(7)	Li−O(2)	1.961(6)
Li−P	2.509(6)	P−C(1)	1.859(4)	P−C(4)	1.808(3)

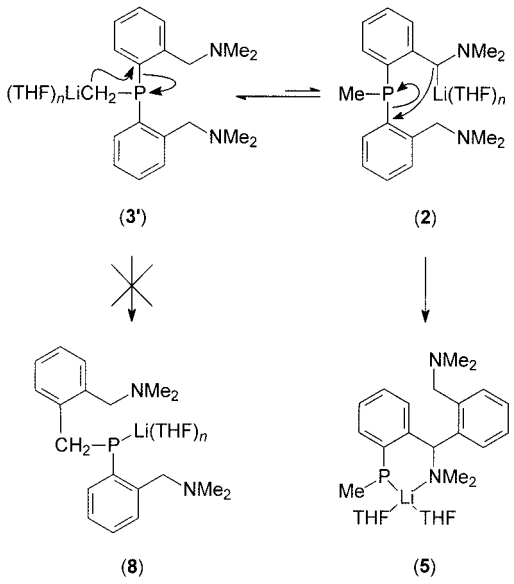
O(1)−Li−O(2)	99.1(3)	O(1)−Li−N(1)	117.4(3)
O(1)−Li−P	114.5(3)	O(2)−Li−P	121.5(3)
N(1)−Li−P	95.4(2)	O(2)−Li−N(1)	110.3(3)

plex Li[P{CH(SiMe$_3$)$_2$}(C$_6$H$_4$-2-CH$_2$NMe$_2$)](THF)$_2$ (**7**).[10] The coordination sphere of each lithium is completed by two molecules of THF to give a distorted-tetrahedral geometry; there is no contact between the lithium atoms and the second NMe$_2$ group in the phosphide ligands in either **5** or **6**.

The Li−P distances of 2.518(4) Å [2.522(4) Å] and 2.509(6) Å for **5** and **6**, respectively, are typical for such bonds. For example, the P−Li distance in **7** is 2.535(7) Å [2.535(8) Å],[10] while the Li−P distances in polymeric [Li(PCy$_2$)(THF)]$_x$[11] are 2.455(9) and 2.543(9) Å and in the monomeric complex [Li(PPh$_2$)(pmdeta)][12] the Li−P distance is 2.567(6) Å. The remaining distances and angles within **5** and **6** are also typical for such species and require no further comment.[8a]

Isomerization of 2 and 3: A Key to the Mechanism of Formation of 5. Although we were initially surprised by the facile formation of **5** and **6** from the tertiary phosphines **1** and **4**, investigation of the behavior of the metalated phosphines **2** and **3** in THF suggested a possible rationale for their formation.

Scheme 2



Whereas in toluene solution at elevated temperatures **2** slowly isomerizes to the more thermodynamically stable **3** over a period of approximately 2 days, such solutions are stable for long periods at or below room temperature, showing no signs of decomposition even after several days. However, when crystalline **2** is dissolved in the strong donor solvent THF, a rapid rearrangement occurs at room temperature, yielding the lithium phosphide complex **5** (Scheme 2). This represents an unusual manifestation of the Smiles rearrangement,[13] i.e., nucleophilic substitution at the phosphorus-substituted aromatic position by the benzylic carbanion. No other P-containing compounds are formed during the reaction, which ^{31}P NMR spectroscopy shows is complete within two minutes.

Smiles rearrangements are well-known for O- and N-substituted arenes; for example, Davidson and coworkers have reported that the diaminoether O(C$_6$H$_4$-2-NHCH$_2$CH$_2$OMe)$_2$ undergoes a Smiles rearrangement on treatment with NaH/HMPA (HMPA = hexamethylphosphoramide) to give the sodium phenoxide [(MeOCH$_2$CH$_2$)(MeOCH$_2$CH$_2$NH-2-C$_6$H$_4$)N(C$_6$H$_4$-2-ONa)]$_2$.[14] However, there are few reports of such a rearrangement occurring in a P-substituted arene (and, as far as we are aware, none that involve nucleophilic substitution by a carbanion), although treatment of the phosphonium salt [Ph$_3$P(C$_6$H$_4$-2-OH)]I with Na$_2$CO$_3$ followed by thermolysis is reported to yield the aryl ether PhOC$_6$H$_4$-2-PPh$_2$.[15]

While the rearrangement of **2** to **5** may readily be rationalized, we were surprised to find that the lithium phosphinomethanide **3** undergoes a rearrangement in THF solutions to give the identical lithium phosphide

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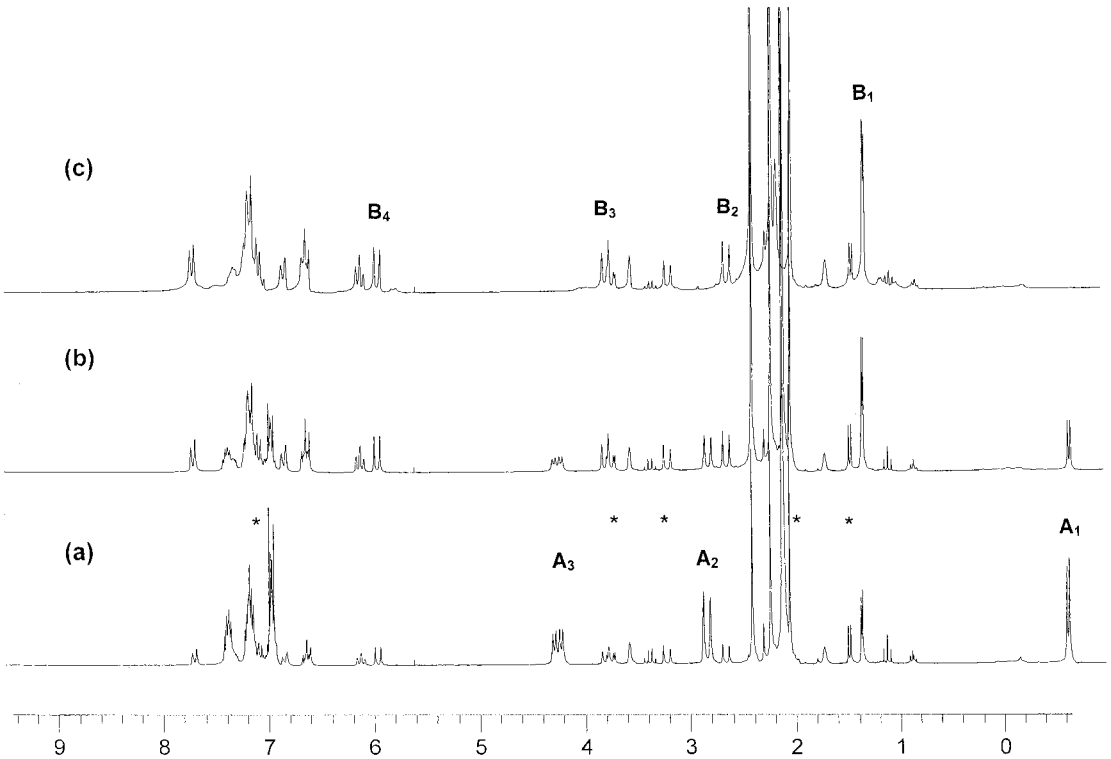

Figure 3. ^{1}H NMR spectra of **3** in d_8-THF after (a) 1 day, (b) 4 days, and (c) 8 days. Signals due to free tertiary phosphine (**1**) are labeled with an asterisk. Selected assignments: $\mathbf{A_1}$, **3′** (CH_2Li); $\mathbf{A_2}$, $\mathbf{A_3}$, **3′** (CH_2N); $\mathbf{B_1}$, **5** (PMe); $\mathbf{B_2}$, $\mathbf{B_3}$, **5** (CH_2N); $\mathbf{B_4}$, **5** (Ar_2CH).

(**5**). In contrast to the rapid rearrangement of **2**, compound **3** rearranges to **5** only slowly, taking 8 days at 22 °C for complete conversion.

Multielement (^{1}H, ^{13}C, and ^{31}P) NMR spectra of d_8-THF solutions of **3** obtained immediately after preparation clearly indicate the presence of a more symmetrical, possibly monomeric, form of **3** in solution (**3′**), in which the carbanion center is still located at the methyl carbon adjacent to phosphorus (Figure 3a). The $LiCH_2$ protons are no longer diastereotopic, possibly due to rapid inversion at the carbanion center in THF, and thus give rise to a doublet at high field in the ^{1}H NMR spectrum (δ −0.64, J_{PH} = 5.0 Hz). The NMe_2 groups are also equivalent in this solvent, and the aromatic protons give rise to only four signals; i.e., the two chelating arms of the ligand are equivalent due to rapid, reversible Li−N bond cleavage and/or the conformational mobility of the chelate rings. This is in contrast to the situation observed for **3** in d_8-toluene, where retention of the tetrameric structure in solution leads to inequivalent chelate rings and the observation of all eight inequivalent aryl ring protons.[7] Over a period of several days signals in the ^{1}H NMR spectrum due to **3′** are gradually replaced by signals due to **5** (Figure 3); no other species are detected during this time.

The identity of the isomerization product of **3′** is somewhat surprising, since a Smiles-type rearrangement of this compound similar to that observed for **2** would entail nucleophilic attack by the methyl carbanion center at the P-substituted position of the aromatic ring and would therefore be expected to generate the isomeric phosphide [($Me_2NCH_2C_6H_4$)($Me_2NCH_2C_6H_4$-2-CH_2)P]Li (**8**). However, such a rearrangement is likely to be disfavored due to the formation of a three-membered transition state (Scheme 2). That **2** converts to the same lithium phosphide as **3′** suggests that both reactions are likely to proceed via the same intermediate and hence suggests that the isomerization of **2** to **3′** is *reversible* in THF solution. Thus, we propose that the mechanism for the isomerization of **3′** to **5** consists of the slow isomerization of a monomeric, solvated form of **3′** to **2** (the rate-determining step), followed by rapid Smiles rearrangement of **2** to **5**. The intramolecular Smiles rearrangement of the intermediate **2** is extremely rapid (see above), so that NMR spectroscopy is unable to identify this species.

Isomerization experiments on the deuterium-labeled phosphinomethanide [Li{$CH_2P(C_6H_4$-2-$CD_2NMe_2)_2$}]$_4$ (**3a**) in nondeuterated THF show the sole product to be [DH_2-CP{C_6H_4-2-CD(C_6H_4-2-CD_2NMe_2)NMe_2}]Li(THF)$_2$ (**5a**). No H−D scrambling is observed, and there is no evidence for the incorporation of deuterium into the solvent. The rearrangement of **3**(**a**) to **5**(**a**) does not appear to follow simple first or second-order kinetics. However, the rearrangement of **3a** to **5a** is approximately 7 times slower than the rearrangement of **3′** to **5** under similar conditions of temperature and concentration, clearly demonstrating a significant kinetic isotope effect associated with the breaking of a C−H/D bond during the rate-determining step of the reaction. Although this behavior does not rule out an alternative isomerization mechanism, it is consistent with that proposed in Scheme 2.

The above observations imply that the initial reaction between *n*-BuLi and **1** in THF consists of the formation of a benzylic carbanion similar to **2** and that this rapidly undergoes a Smiles rearrangement to the lithium phosphide **5**. The presence of the strong donor solvent THF

is apparently sufficient to reverse the regioselectivity previously observed in light petroleum, which favors formation of the phosphinomethanide **3** on reaction of **1** with *n*-BuLi. An alternative mechanism involving initial formation of **3′** followed by rapid isomerization to **5** is unlikely, due to the slow rate of isomerization of **3′** in THF.

Finally, it is noteworthy that the closely related alkali-metal phosphinomethanides [{$(Me_3Si)_2C$}$P(C_6H_4$-2-$CH_2NMe_2)_2$]M (M = Li, Na, K) are stable even in refluxing THF,[16] clearly demonstrating that the presence of additional silicon substituents greatly increases the stability of the carbanion center, disfavoring isomerization to a benzylic carbanion and thus preventing any rearrangement.

Conclusions

The product of metalation of the amino-functionalized tertiary phosphine **1** is highly dependent on the nature of both the metalating agent and the solvent. Reaction of **1** with *n*-BuLi or *t*-BuLi in light petroleum yields the benzyllithium and phosphinomethanide complexes **2** and **3**, respectively. In contrast, metalation of **1** with *n*-BuLi in THF proceeds via a Smiles rearrangement of the intermediate benzyllithium **2**, which has only transient existence in THF, to give the novel lithium phosphide complex **5**. A similar rearrangement is observed on deprotonation of the isopropyl-substituted tertiary phosphine **4**, yielding the analogous lithium phosphide **6**. Compound **5** is also accessible via the rapid isomerization of **2** or the slow isomerization of **3** in THF solution.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ether, THF, and light petroleum (bp 40−60 °C) were distilled from potassium or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (or activated 4A molecular sieves in the case of THF). Deuterated toluene, THF, and C_6D_6 were distilled from potassium, deoxygenated by three freeze−pump−thaw cycles, and stored over activated 4A molecular sieves; $CDCl_3$ was distilled from CaH_2 and was deoxygenated and stored as for C_6D_6. Butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes; *i*-$PrPCl_2$ and $MePCl_2$ were purchased from Acros Organics and used without further purification. The compounds Li(C_6H_4-2-CH_2NMe_2),[17] $MeP(C_6H_4$-2-$CH_2NMe_2)_2$ (**1**),[7] [$MeP(C_6H_4$-2-CH_2NMe_2){C_6H_4-2-CH(Li)NMe_2}]$_2$ (**2**),[6] and [Li{$CH_2P(C_6H_4$-2-$CH_2NMe_2)_2$}]$_4$ (**3**)[7] were prepared by published procedures.

^{31}P NMR spectra were recorded on a Bruker WM300 spectrometer and ^1H and ^{13}C spectra on a JEOL Lambda500 spectrometer operating at 121.5, 500.0, and 125.6 MHz, respectively. ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane; ^{31}P chemical shifts are quoted relative to external 85% H_3PO_4.

Preparation of *i*-PrP(C_6H_4-2-$CH_2NMe_2)_2$ (4). To a solution of Pr^iPCl_2 (1.00 g, 6.90 mmol) in cold (0 °C) ether (20 mL) was added, dropwise over 0.5 h, a solution of Li(C_6H_4-2-CH_2NMe_2) (1.92 g, 13.60 mmol) in THF (20 mL). This mixture was stirred for 2 h, and solvent was removed in vacuo. The oily solid was extracted into light petroleum (3 × 10 mL) and filtered. Removal of solvent in vacuo from the filtrate yielded essentially pure **4** as a colorless oil. Yield: 1.27 g, 55%. Anal. Calcd for $C_{21}H_{31}N_2P$: C, 73.64; H, 9.12; N, 8.18. Found: C, 73.01; H, 9.63; N, 8.06. ^1H NMR ($CDCl_3$, 297 K): δ 0.98 (d, J_{HH} = 6.7 Hz, 3H, CHMe), 1.01 (d, J_{HH} = 6.7 Hz, 3H, CHMe), 2.13 (s, 12H, NMe_2), 2.30 (septet, J_{HH} = 6.7 Hz, 1H, CHMe), 3.58 (dd, J_{HH} = 13.7 Hz, J_{PH} = 2.4 Hz, 2H, CH_2N), 3.70 (dd, J_{HH} = 13.7 Hz, J_{PH} = 2.4 Hz, 2H, CH_2N), 7.10−7.44 (m, 8H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 20.1 (d, J_{PC} = 20.2 Hz, Me_2CH), 26.3 (d, J_{PC} = 9.6 Hz, $CHMe_2$), 45.7 (NMe_2), 62.0 (d, J_{PC} = 22.3 Hz, CH_2N), 126.8, 128.5 (Ar), 128.9 (d, J_{PC} = 5.5 Hz, Ar), 131.9 (Ar), 137.1 (d, J_{PC} = 16.6 Hz, *ipso*-Ar), 144.2 (d, J_{PC} = 22.2 Hz, *ipso*-Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 297 K): δ −27.9.

Preparation of MeP{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)NMe_2}Li$(THF)_2$ (5). Method a. To a solution of **1** (0.87 g, 2.77 mmol) in THF (30 mL) was added BuLi (1.11 mL, 2.78 mmol). This mixture was stirred for 2 h, and the solution was concentrated to ∼2 mL. Addition of light petroleum (10 mL) and cooling to −30 °C for 3 days gave a crop of **5** as yellow plates, which were isolated by filtration, washed with a small amount of light petroleum, and dried in vacuo. Yield: 0.70 g, 58%.

Method b. A crystalline sample of **2** (1.20 g, 1.64 mmol) was dissolved in THF (10 mL) and the solution stirred at room temperature for 2 h. The solution was concentrated to ∼2 mL, and light petroleum (10 mL) was added. This solution was cooled to −30 °C for 1 week, after which yellow crystals of **5** were isolated and washed with a small amount of light petroleum. Yield: 0.92 g, 53%. Anal. Calcd for $C_{27}H_{42}LiN_2O_2P$: C, 69.81; H, 9.11; N, 6.03. Found: C, 69.89; H, 10.15; N, 6.20. ^1H NMR (THF-d_8, 297 K): δ 1.44 (d, J_{PH} = 2.78 Hz, 3H, MeP), 2.33 (s, 6H, NMe_2), 2.53 (s, 6H, NMe_2), 2.74 (d, J_{HH} = 12.6 Hz, 1H, CH_2N), 3.89 (d, J_{HH} = 12.6 Hz, 1H, CH_2N), 6.05 (d, J_{PH} = 10.6 Hz, 1H, CH(Ar)N), 6.22 (m, 1H, Ar H), 6.73 (m, 2H, Ar H), 6.94 (m, 1H, Ar H), 7.20 (m, 1H, Ar H), 7.41 (m, 2H, Ar H), 7.81 (m, 1H, Ar H). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K): δ 6.8 (d, J_{PC} = 31.2 Hz, MeP), 42.5 (NMe_2), 46.3 (NMe_2), 62.6 (CH_2N), 64.5 (d, J_{PC} = 29.0 Hz, CH(Ar)N), 114.3 (d, J_{PC} = 3.1 Hz, Ar), 125.8 (d, J_{PC} = 5.2 Hz, Ar), 126.4 (d, J_{PC} = 25.9 Hz, Ar), 128.0, 128.6 (Ar), 129.3 (d, J_{PC} = 3.1 Hz, Ar), 130.0 (Ar), 135.5 (d, J_{PC} = 22.7 Hz, Ar). $^{31}P\{^1H\}$ NMR (THF-d_8, 297 K): δ −76.4.

Preparation of *i*-PrP{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)-NMe_2}Li$(THF)_2$ (6). To a solution of **4** (0.52 g, 1.52 mmol) in THF was added *n*-BuLi (0.61 mL, 1.52 mmol). This solution was stirred for 2 h and concentrated to ∼2 mL, and light petroleum (5 mL) was added. After 2 days at −30 °C, the yellow plates of **6** were isolated, washed with a small amount of light petroleum, and dried in vacuo. Yield: 0.34 g, 52%. Anal. Calcd for $C_{29}H_{46}LiN_2O_2P$: C, 70.71; H, 9.41; N, 5.69. Found: C, 69.76; H, 9.34; N, 6.14. ^1H NMR (C_6D_6, 297 K): δ 1.35 (m, 8H, THF), 1.42 (dd, J_{HH} = 6.8 Hz, J_{PH} = 15.2 Hz, 3H, $CHMe_2$), 1.55 (dd, J_{HH} = 6.8 Hz, J_{PH} = 11.6 Hz, 3H, $CHMe_2$), 2.21 (s, 6H, NMe_2), 2.35 (s, 6H, NMe_2), 2.61 (m, 1H, $CHMe_2$), 2.62 (d, J_{HH} = 13.3 Hz, 1H, CH_2N), 3.44 (m, 8H, THF), 3.85 (d, J_{HH} = 13.3 Hz, 1H, CH_2N), 6.06 (d, J_{PH} = 11.0 Hz, 1H, CH(Ar)N), 6.30 (m, 1H, Ar H), 6.75 (m, 2H, Ar H), 7.13 (m, 1H, Ar H), 7.20 (m, 1H, Ar H), 7.21 (m, 1H, Ar H), 7.25 (m, 1H, Ar H), 7.64 (m, 1H, Ar H). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 23.2 (d, J_{PC} = 36.2 Hz, CHP), 25.0 (Me_2C), 25.9 (THF), 41.9 (NMe_2), 45.9 (NMe_2), 61.9 (CH_2N), 64.2 (d, J_{PC} = 28.9 Hz, CH(Ar)N), 114.2, 126.1, 126.4, 128.9, 129.6, 132.1 (Ar), 134.5 (d, J_{PC} = 20.6 Hz), 140.6, 141.7 (Ar), 163.6 (d, J_{PC} = 57.8 Hz, Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 297 K): δ −21.6 (br).

Preparation of MeP(C_6H_4-2-$CD_2NMe_2)_2$ (1a). To a solution of $C_6H_5CH_2NMe_2$ (5.84 mL, 38.87 mmol) and KO-*t*-Bu (4.36 g, 38.85 mmol) in ether at −10 °C was added *n*-BuLi

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(15.54 mL, 38.85 mmol). This mixture was stirred for 12 h, and then D_2O (3 mL) was added. The organic phase was diluted with light petroleum, separated, and dried over $MgSO_4$. Solvent was removed on a rotary evaporator to give partially deuterated *N*,*N*-dimethylbenzylamine. This was remetalated and treated with D_2O in the manner described above a further three times, giving C_6H_4-2-CD_2NMe_2 as a colorless liquid. Yield: 3.47 g, 66%.

To a solution of C_6H_4-2-CD_2NMe_2 (3.47 g, 25.29 mmol) in diethyl ether (15 mL) was added *n*-BuLi (10.11 mL, 25.28 mmol). This mixture was stirred for 16 h, and the pale yellow solids [Li(C_6H_4-2-CD_2NMe_2)] were isolated by filtration and washed with ether (2 × 20 mL). Yield: 1.70 g, 47%.

To a solution of $MePCl_2$ (0.53 mL, 5.90 mmol) in ether (20 mL) was added, dropwise, with stirring, a solution of the previously prepared Li(C_6H_4-2-CD_2NMe_2) (1.70 g, 11.88 mmol) in THF (30 mL). This mixture was stirred for 12 h, and solvent was removed in vacuo. The oily solid was extracted into light petroleum (3 × 20 mL) and filtered. Removal of solvent in vacuo from the filtrate yielded essentially pure **1a** as a colorless oil. Yield: 1.17 g, 62%. ^{1}H NMR ($CDCl_3$, 297 K): δ 1.51 (d, J_{PH} = 4.8 Hz, 3H, MeP), 2.04 (s, 12H, NMe_2), 7.01−7.42 (m, 8H, Ar H). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 13.2 (d, J_{PC} = 23.1 Hz, 3H, MeP), 45.0 (NMe_2), 62.4 (quintet, J_{CD} = 18.9 Hz, CD_2), 127.3, 128.1 (Ar), 129.5 (d, J_{PC} = 4.9 Hz, Ar), 131.8 (Ar), 141.2 (d, J_{PC} = 16.9 Hz, Ar), 143.2 (d, J_{PC} = 22.6 Hz, Ar). ^{31}P{^{1}H} NMR (C_6D_6, 297 K): δ −47.1.

Preparation of [Li{$CH_2P(C_6H_4$-2-$CD_2NMe_2)_2$}]$_4$ (3a). Compound **3a** was synthesized by a procedure analogous to that for **3** from **1a** (1.17 g, 3.675 mmol) and *n*-BuLi (1.47 mL, 3.675 mmol) in light petroleum (20 mL) and was isolated as a pale yellow powder. Yield: 0.97 g, 81%. ^{1}H NMR (d_8-THF, 297 K): δ −0.64 (d, J_{PH} = 5.0 Hz, 2H CH_2Li), 2.11 (s, 12H, NMe_2), 6.97 (m, 4H, Ar H), 7.20 (m, 2H, Ar H), 7.39 (m, 2H, Ar H). ^{13}C{^{1}H} NMR (THF, 297 K): δ 1.4 (d, J_{PC} = 49.6 Hz, LiCH_2P), 46.3 (NMe_2), 62.9 (quintet, J_{DC} = 19.1 Hz, CD_2), 125.8, 128.7, 130.1, 133.1 (Ar), 141.0 (d, J_{PC} = 18.6 Hz, Ar), 153.7 (d, J_{PC} = 24.8 Hz, Ar). ^{31}P{^{1}H} NMR (THF, 297 K): δ −18.8.

Isomerization of 3 to 5. Samples of **3** in d_8-THF (ca. 0.05 M) were sealed in NMR tubes, and ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded at room temperature at intervals of approximately 12 h. The decrease in the concentration of **3′** with time was monitored by integration of the methylenic proton signal at −0.61 ppm and comparison with the signal due to the Me(P) group of the free ligand at 1.50 ppm (the free ligand **1** was a consistent impurity). The data obtained did not give simple straight line plots for ln[**3′**] vs *T* and 1/[**3′**] vs *T* and are therefore inconsistent with simple first- or second-order kinetics. Similar data were obtained for solutions of **3a** in d_8-THF. The complete disappearance of signals due to **3′** and **3a** occurred after 8 and 53 days, respectively.

Crystal Structure Determination of 5 and 6. All measurements were made on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 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, on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data.

Table 2. Crystallographic Data for 5 and 6

	5	6
mol formula	$C_{27}H_{42}LiN_2O_2P\cdot C_4H_8O$	$C_{29}H_{46}LiN_2O_2P$
fw	536.6	492.6
cryst size, mm	0.52 × 0.32 × 0.10	0.34 × 0.24 × 0.10
temp, K	160	160
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	19.3421(7)	17.0332(9)
b, Å	20.8431(7)	9.3310(5)
c, Å	16.3715(5)	18.4701(9)
β, deg	110.635(2)	93.069(2)
V, Å^3	6176.7(4)	2931.2(3)
Z	8	4
D_{calcd}, g cm^{-3}	1.154	1.116
μ, mm^{-1}	0.121	0.120
no. of rflns measd	35542	14487
no. of unique rflns	10873	5136
no. of rflns with $F^2 > 2\sigma(F^2)$	6882	2921
transmissn coeff range	0.94−0.99	0.96−0.99
R_{int} (on F^2)	0.037	0.078
R^a	0.051	0.068
$R_w{}^b$	0.144	0.180
no. of params	606	323
GOF^c on F^2	1.051	0.912
max, min diff map, e Å^{-3}	0.33, −0.32	0.62, −0.39

[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 = $[\sum w(F_o^2 - F_c^2)^2/((\text{no. of unique rflns}) - (\text{no. of params}))]^{1/2}$.

Table 2 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.[18] Disordered solvent molecules in **5** could not be resolved and refined with a model of individual atoms. They were treated by the SQUEEZE procedure of PLATON,[19] which models diffuse electron density. The observed electron density and void volumes are consistent with eight THF molecules per unit cell: i.e., a THF monosolvate. High displacement parameters of coordinated THF indicate possible unresolved disorder.

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Supporting Information Available: For **5** and **6**, tables giving details of the structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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