Regioselective Metalation of a Tertiary Phosphine. Synthesis and Structural Characterization of an Unusual Tetrameric Lithium Phosphinomethanide

Keith Izod,* Paul O'Shaughnessy, William Clegg, and Stephen T. Liddle

Department of Chemistry, University of Newcastle upon Tyne,
Newcastle upon Tyne, U.K. NE1 7RU

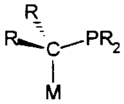
Received October 12, 2000

The tertiary phosphine $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (**3**) is conveniently prepared by the reaction of $MePCl_2$ with $Li(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ in high yields. Treatment of **3** with *n*-BuLi in light petroleum yields the tetrameric lithium phosphinomethanide complex $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4{\cdot}(PhMe)_3$ (**5a**) after recrystallization from toluene, whereas treatment of **3** with *t*-BuLi under similar conditions yields the benzyllithium complex $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\text{-}\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$ (**4**). Complex **5a** has been characterized by elemental analyses, multielement NMR spectroscopy, and X-ray crystallography. Complex **5** can also be accessed by moderate thermal treatment of **4** in toluene solution. The kinetics of this conversion were followed by ^{31}P NMR spectroscopy and show a first-order dependence upon the concentration of **4** and are independent of the concentration of **3**. Analysis of the temperature dependence of the reaction over the range $T = 308{-}338$ K yielded $\Delta H^{\ddagger} = 68.1 \pm 4.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = -124 \pm 30$ J K^{-1} mol^{-1} for this reaction, consistent with the reaction proceeding via a concerted intramolecular H−Li exchange mechanism.

Introduction

The stabilization of carbanions α to phosphorus by hyperconjugation and/or polarization effects is well documented.[1,2] Such carbanions have found widespread application in organic and organometallic synthesis and are usually generated by the metalation of tertiary phosphines containing a P−CHR$_2$ group using strong bases such as *n*-BuLi/tmeda or *t*-BuLi (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[3] The delocalization of charge from the carbanion center toward phosphorus(III) in phosphinomethanide ligands, $[R_2C{-}PR_2]^-$, enables the directly bonded, valence isoelectronic P and C atoms to compete as nucleophiles for metal centers, giving rise to a range of coordination modes, including η^1-C-donation (**I**), η^1-P-donation (**II**), η^2-P,C-donation (**III**), and bridging modes (**IV**).[4−6]

The coordination mode adopted is defined by a combination of factors including the electronic and steric properties of the substituents at P and C, the nature of the metal center(s), and the presence of additional donor ligands such as THF, tmeda, or pmdeta (pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). In general, the presence of sterically demanding, charge-stabilizing substituents such as SiR$_3$ or PR$_2$ at the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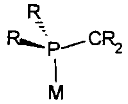
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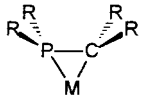
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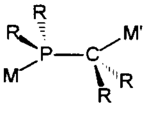
(IV)

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* Corresponding author. E-mail: k.j.izod@ncl.ac.uk.

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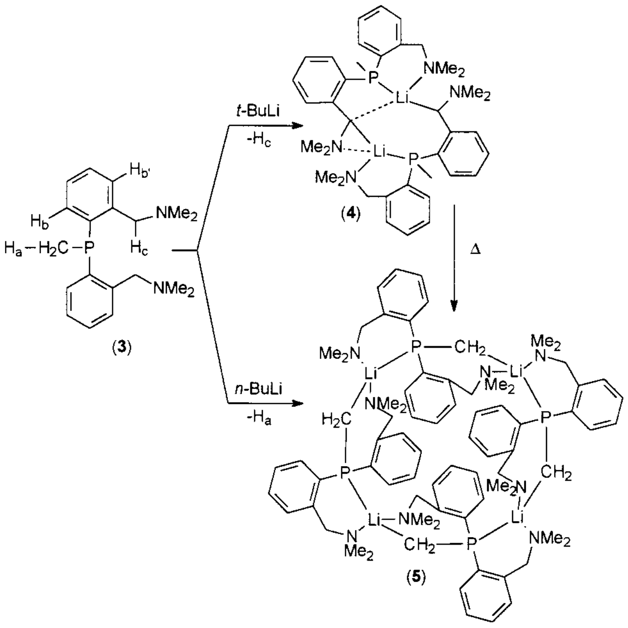
Scheme 1



carbanion center favors P- over C-coordination due to both an increase in steric congestion and a decrease in effective charge at the carbanion center.

We recently found that donor functionalization at the periphery of a phosphinomethanide ligand can have a pronounced effect on its coordination mode: whereas $[Li\{C(SiMe_3)_2PMe_2\}(THF)]_2$ (**1**) is dimeric in the solid state,[5a] with each phosphinomethanide ligand bridging two Li centers in a six-membered $(LiPC)_2$ heterocycle, the phosphinomethanide ligand in the closely related complex $[Li\{C(SiMe_3)_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]$ (**2**) binds solely through its N and P donor atoms, with no contact between Li and the carbanion center,[6a] despite the greater steric congestion at phosphorus in **2** compared to **1**.

We now report that metalation of a related amino-functionalized tertiary phosphine, which does not contain potentially charge-stabilizing silicon substituents, may occur at two separate sites, depending on the nature of the metalating agent, to give either an unusual benzyllithium complex or a tetrameric phosphinomethanide complex. We also describe the thermally induced conversion of the former complex to the latter.

Results and Discussion

Synthesis, Characterization, and Molecular Structure of $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4\cdot(PhMe)_3$. The amino-functionalized tertiary phosphine $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (**3**) may be prepared in good yield by the reaction of $MePCl_2$ with 2 equiv of $Li(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ in ether/THF. The ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra of **3** are as expected; the diastereotopic benzylic protons give rise to an AB signal, of which the lower field component exhibits coupling to phosphorus, but the higher field component does not.

The tertiary phosphine **3** may potentially undergo deprotonation by alkyllithium reagents at any of several positions (Scheme 1): (i) at the P-Me group to give a P-stabilized carbanion (H$_a$), (ii) at the aromatic ring positions *ortho* to either the P or CH_2NMe_2 substituents (H$_b$/H$_{b'}$) to give an aryllithium complex via chelation assistance of the heteroatoms,[7] or (iii) at the position adjacent to both the NMe_2 group and the aromatic ring to give a benzyllithium complex (H$_c$).[8] We recently reported that **3** may be selectively deprotonated at one of these positions by judicious choice of the deprotonating agent: treatment of **3** with *t*-BuLi in light petroleum gives the unusual benzyllithium complex $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$ (**4**) as the exclusive product.[9] In contrast to this, we now find that treatment of **3** with *n*-BuLi under similar conditions gives a yellow precipitate of the lithium phosphinomethanide complex $Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}$ (**5**) as the major product. Although small amounts of **4** are also formed during this reaction, a ^{31}P NMR spectrum of the crude reaction mixture confirms that **5** is the major product (ratio of **4**:**5** $\approx$ 1:4.5). As was observed for the synthesis of **2**, the synthesis of **5** proceeds extremely rapidly and is essentially complete within a few hours. This compares with the metalation of $HC(PMe_2)(SiMe_3)_2$ with *n*-BuLi, which takes 3 weeks in refluxing hexane,[5b] and may be attributed to kinetic enhancement of the deprotonation reaction by chelation assistance of the amino substituents in **3**.

Purification of **5** by recrystallization from toluene gives the tetrameric complex $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4\cdot(PhMe)_3$ (**5a**) as pale yellow crystals in moderate to good yield. The solid-state structure of **5a** was shown by X-ray crystallography to consist of an unsymmetrical cyclic tetramer containing a 12-membered $\{PCLi\}_4$ core. The molecular structure of **5a** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. This tetrameric structure is unprecedented in phosphinomethanide chemistry; although polymeric systems are relatively common, the most highly aggregated *molecular* alkali metal phosphinomethanide complex previously observed is the cyclic trimeric $[Li\{C(SiMe_2Ph)(PMe_2)_2\}]_3$,[5c,d] in which lithium phosphinomethanide units are held together by η^2-aryl–Li interactions.

Each lithium atom in **5a** is coordinated by the carbanion center and a nitrogen atom from one ligand and by the phosphorus and a nitrogen atom from an adjacent ligand in the cycle. Thus each ligand acts as a

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

Li(1)−P(2)	2.744(3)	Li(1)−C(1)	2.167(3)	P(1)−C(1)	1.7484(15)
Li(2)−P(3)	2.718(3)	L(2)−C(20)	2.165(3)	P(2)−C(20)	1.7511(16)
Li(3)−P(4)	2.754(3)	Li(3)−C(39)	2.168(3)	P(3)−C(39)	1.7486(17)
Li(4)−P(1)	2.728(3)	Li(4)−C(58)	2.156(3)	P(4)−C(58)	1.7553(15)
Li(1)−N(1)	2.224(3)	Li(1)−N(3)	2.193(3)	P(1)−C(2)	1.8503(15)
Li(2)−N(4)	2.256(3)	Li(2)−N(5)	2.193(3)	P(1)−C(11)	1.8654(15)
Li(3)−N(6)	2.222(3)	Li(3)−N(7)	2.212(3)	P(2)−C(21)	1.8554(15)
Li(4)−N(8)	2.273(3)	Li(4)−N(2)	2.196(3)	P(2)−C(30)	1.8682(16)
P(3)−C(40)	1.8526(16)	P(4)−C(59)	1.8531(16)		
P(3)−C(49)	1.8702(15)	P(4)−C(68)	1.8643(16)		
N−Li−N′[a]	116.73	C−Li−P[b]	120.73	P−C−Li[b]	109.95

[a] Average value. [b] Average value, C = carbanion center.

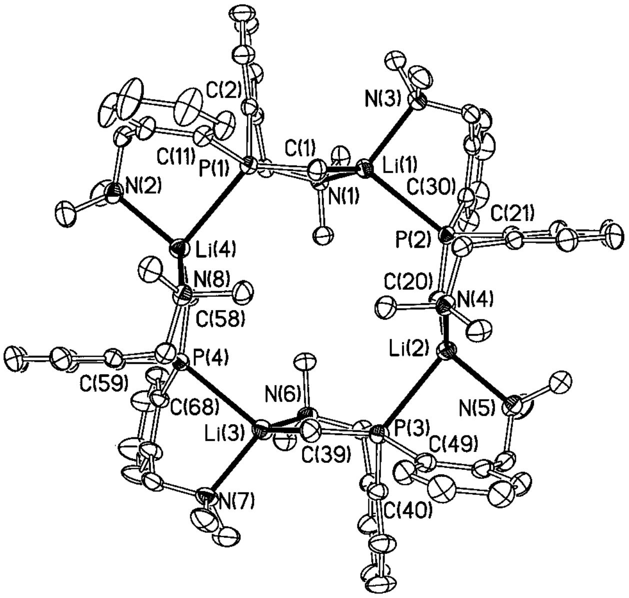

Figure 1. Molecular structure of **5a** with 40% thermal ellipsoids and with H atoms and solvent of crystallization omitted for clarity. Key atoms are labeled.

bridge between two lithium atoms, via its P and C atoms, in a manner that is reminiscent of the bridging bonding mode (**IV**) observed in several lithium monophosphinomethanides, Li(CR$_2$PR$_2$), including [Li(CH$_2$PPh$_2$)(tmeda)]$_2$[5e,f] and [Li{C(SiMe$_3$)$_2$(PMe$_2$)}(THF)]$_2$.[5a] The chelating arms of the ligands also bridge the same two adjacent lithium centers: one arm forms a six-membered (PC$_3$NLi) chelate ring to one lithium (mean N−Li−P bite angle 90.39°), while the other chelating arm forms a seven-membered (PC$_3$NLiC) chelate ring to the next lithium in the cycle (mean N−Li−C bite angle 113.55°). These chelate rings alternate in orientation with respect to the mean Li$_4$ plane such that the complex has approximate S_4 symmetry. The formation of the two chelate rings places one of the aryl groups side-on to the other in the same ligand such that the average angle between the planes of the two aryl groups within each ligand is 91.5°.

The Li−P distances in **5a** range from 2.718(3) to 2.754(3) Å (average 2.736 Å). These distances are at the longer end of the range of Li−P distances observed in lithium phosphinomethanides containing a bridging Li−PC−Li unit. For example, the Li−P distances in [Li(CH$_2$PPh$_2$)(tmeda)]$_2$[5e,f] are 2.686(5) Å and in [Li(CH$_2$PMe$_2$)(tmeda)]$_2$ and [Li(CH$_2$PhMe)(tmeda)]$_2$ are 2.593(7) [2.615(6)] and 2.67(1) [2.61(1)] Å,[5g] respectively (values in square brackets refer to a second independent molecule in the unit cell). This contrasts with the PN$_2$-bonded **2**, in which the P−Li bond (2.427(6) Å) is quite short. The Li−C(carbanion center) distances in **5a** range from 2.156(3) to 2.168(3) Å (average 2.164 Å). These are at the shorter end of the range of Li−C distances in lithium phosphinomethanide complexes and compare with Li−C distances of 2.150(8) and 2.141(6) Å in [Li{CH$_2$PMe$_2$}(tmeda)]$_2$,[5g] 2.172(4) Å in [Li{C(SiMe$_3$)$_2$PMe$_2$}]$_x$,[5b] and 2.202(6) Å in [Li{C(SiMe$_3$)$_2$PMe$_2$}(THF)]$_2$.[5a] The P−C(carbanion center) distances in **5a** lie in the range 1.7484(15)−1.7553(16) Å (average 1.7509 Å) and are similar to those observed in several other lithium phosphinomethanide complexes. For example, the P−C(carbanion center) distances in [Li{CH$_2$PPh$_2$}(tmeda)]$_2$[5e,f] and [Li{CH$_2$PMe$_2$}(tmeda)]$_2$[5g] are 1.752(3) and 1.751(3)/1.754(5) Å, respectively. This relatively short P−C distance is consistent with significant charge delocalization due to negative hyperconjugation and/or polarization effects. The Li−N distances (2.193(3)−2.273(3) Å) are typical of similar distances where lithium is complexed by a tertiary amine center.[10]

The somewhat limited solubility of **5a** in noncoordinating solvents and recurrent problems with incomplete removal of the solvent of crystallization prevented measurement of the molecular weight of this compound by cryoscopy. However, multielement NMR studies suggest that a more symmetrical form of the solid-state structure is retained in toluene solution. Only a single set of ligand resonances is observed in the ^{1}H and ^{13}C NMR spectra of **5a**. The room-temperature ^{31}P and ^{7}Li NMR spectra of **5a** consist of a sharp 1:1:1:1 quartet and doublet, respectively (J_{PLi} = 36.0 Hz), consistent with each lithium coupling to one phosphorus and vice versa.

The ^{1}H NMR spectrum of **5a** exhibits a pair of doublets at 0.25 and 0.35 ppm (J_{HH} = 4.8 Hz) due to the diastereotopic methylenic protons of the carbanion center, which are further split by coupling to the adjacent phosphorus atom (J_{PH} = 16.8 and 21.1 Hz). The NMe$_2$ protons give rise to two very broad resonances at 1.34 and 2.23 ppm, while all of the benzylic protons are chemically inequivalent and give rise to doublets at 2.14 and 3.47 ppm (J_{HH} = 12.2 Hz) and at 2.89 and 5.76 ppm (J_{HH} = 13.1 Hz), the latter signal showing additional coupling to phosphorus (J_{PH} = 8.3 Hz). Similarly, all eight aromatic protons are clearly resolved at room temperature, spanning the range 6.86−8.86 ppm. The ^{13}C{^{1}H} NMR spectrum of **5a** exhibits a very broad signal due to the carbanion center, this broadness possibly arising from unresolved coupling to lithium. Individual signals are present for the two NMe$_2$ groups,

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Table 2. Kinetic Data for the Thermal Rearrangement of 4 into 5

run	concentration of **4** (mol dm^{-3})	temp (K)	k ($10^6 \times$ s^{-1})
1	0.07	303	4.1
2	0.07	308	4.9
3	0.07	311	8.0
4	0.07	333	40.0
5	0.07	338	80.0
6	0.05	311	9.0
7[a]	0.05	311	6.8
8[b]	0.05	311	6.6

[a] In the presence of additional **3**. [b] In the presence of additional **3** and PPh$_3$.

both benzylic and all 12 aromatic carbons. Assignment of the aromatic resonances to the two rings of the ligand was achieved with the aid of 2D ^{1}H−^{1}H COSY and ^{1}H−^{13}C correlation experiments.

These data suggest that both the C and P centers of the ligand are bound to lithium in solution. The two chelate arms of the ligand are clearly different at room temperature. Although the two chelate arms of the related phosphinomethanide ligand in the monomeric complex **2** also give rise to two separate sets of ^{1}H resonances, this is only observed at low temperatures, where fluxionality due to Li−P/N exchange and/or conformational changes in the chelate rings is frozen out.[6a,c] In the less sterically hindered complex **5**, where such fluxional processes would be expected to be more facile if a similar monomeric structure were adopted in solution, the two arms of the ligand are inequivalent at room temperature. The large chemical shift range observed for the aryl and benzyl protons suggests that one of the aromatic rings of the ligand lies side-on to the other as in the solid state. These spectra are thus consistent with complex **5** maintaining a structure in solution which is similar to that observed in the solid state. The inequivalence of the chelate arms of the ligand may be ascribed to their participation in two different chelate rings, one six-membered (PC$_3$NLi) and one seven-membered (PC$_3$NLiC). The lack of fluxionality in **5** suggests that the tetrameric structure is essentially conformationally rigid in toluene solution.

Thermal Rearrangement of 4 to 5. While toluene solutions of **4** are essentially stable over long periods below room temperature, moderate heating causes this complex slowly to rearrange to complex **5**. This clearly demonstrates that the benzyllithium complex (**4**) isolated on deprotonation of **3** by *t*-BuLi is kinetically favored and that the lithium phosphinomethanide (**5**) obtained on treatment of **3** with *n*-BuLi is the thermodynamically favored product. The progress of this rearrangement is relatively slow (complete conversion takes approximately 2 days at 311 K) and may conveniently be monitored by ^{31}P NMR spectroscopy; compounds **4** and **5** exhibit characteristic peaks at −47.6 ppm (septet, $J_{\mathrm{PLi}} = 31.6$ Hz) and −17.8 ppm (quartet, $J_{\mathrm{PLi}} = 36.0$ Hz), respectively, in toluene-d_8 at room temperature. The reaction was monitored at several temperatures between 303 and 338 K, at concentrations of **4** of 0.05 and 0.07 mol dm^{-3} in toluene or toluene-d_8. Results of these experiments are listed in Table 2. Variation in the concentrations of **4** and **5** was measured by comparison of the integrals of their respective signals with that of the residual free ligand (**3**) (a consistent impurity). That the concentration of **3** did not change significantly with time was confirmed by monitoring the variation in concentration of **3**, **4**, and **5** in the presence of nonreacting PPh$_3$ at 311 K (run 8).

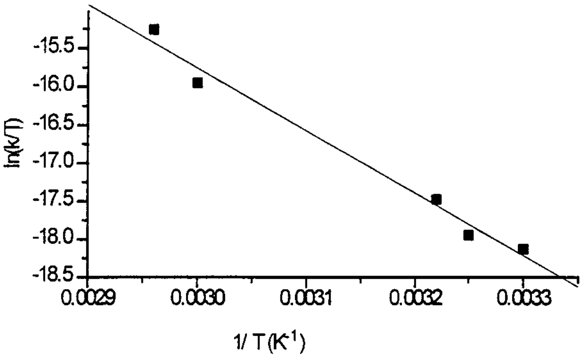
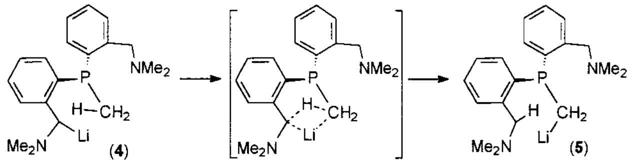


Figure 2. Plot of ln(k/T) vs 1/T for the thermal conversion of **4** to **5**.

Scheme 2. Rearrangement of 4 into 5 via a 1,5-Sigmatropic Shift within One Ligand Subunit



It has been demonstrated by variable-temperature multielement NMR spectroscopy that **4** retains its dimeric structure in toluene solution.[9] The kinetic data obtained for the rearrangement of **4** demonstrate that the reaction follows a first-order dependence on the concentration of the dimer and that the rate is unaffected by the presence of excess free ligand (**3**). This indicates that the rate-determining step of the rearrangement is a unimolecular process, rather than a bimolecular process involving deprotonation by **4** of the methyl group either of a molecule of **3** or of a second molecule of **4**. Reactions carried out in toluene-d_8 show no incorporation of deuterium in the final product and so effectively rule out the involvement of a solvent deprotonation step during the reaction. A plot of ln(k/T) versus 1/T (Figure 2) gives a straight line, from which the enthalpy and entropy of activation for the rearrangement process have been calculated as 68.1 ± 4.0 kJ mol^{-1} and −124 ± 30 J K^{-1} mol^{-1}, respectively.

The rearrangement reaction essentially consists of the exchange of H and Li between two sites and involves both C−H/C−Li bond cleavage and bond formation (Scheme 2); the former is likely to constitute the rate-determining step in any such rearrangement. The value of $\Delta H^‡$ is rather low and the value of $\Delta S^‡$ is rather negative for unimolecular C−H cleavage, where bond breaking should lead to a high value of $\Delta H^‡$ and the associated increased degrees of freedom caused by bond breaking should give a positive or low negative value of $\Delta S^‡$.[11] [It has been estimated that the C−H bond dissociation energy for PMe$_3$ is approximately 401.7 kJ mol^{-1}.][12] The experimentally determined activation parameters are more consistent with a rate-determining step involving a concerted bimolecular process. This may

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(11) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford (UK), 1998.

be accounted for by the dimeric nature of **4**: a concerted intradimer H−Li exchange process would be pseudo-bimolecular with respect to the individual benzyllithium subunits involved but unimolecular with respect to the dimeric units in which the exchange is taking place. Such an intradimer rearrangement may proceed either within the same ligand subunit (a 1,5-sigmatropic shift, via a six-membered cyclic transition state, Scheme 2) or in a "cross-dimer" fashion (effectively a 1,4-sigmatropic shift, via a five-membered cyclic transition state); it is not possible to distinguish between these two mechanisms on the current evidence. In either case the reaction would appear to be first order with respect to the concentration of dimer, while the concerted nature of the rearrangement would be reflected by a low value of $\Delta H^{\ddagger}$. The highly ordered cyclic transition state would similarly necessitate a highly negative entropy of activation, as is observed. The available data therefore suggest that the rate-determining step in the conversion of **4** to **5** consists of a concerted, intramolecular 1,4- or 1,5- sigmatropic rearrangement.

Conclusions

The products of the deprotonation of the tertiary phosphine $MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (**3**) are highly sensitive to the nature of the deprotonating agent. Deprotonation of **3** with *t*-BuLi leads to the formation of the kinetically favored dimeric benzyllithium complex $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$ (**4**), while treatment of **3** with *n*-BuLi under the same conditions yields the thermodynamically favored tetrameric phosphinomethanide complex $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4\cdot(PhMe)_3$ (**5a**). The thermodynamic instability of **4** is demonstrated by its ready thermal rearrangement to **5** under very mild conditions. Multielement NMR experiments coupled with kinetic studies suggest that the rate-determining step for this rearrangement involves intramolecular H−Li exchange.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. Ether, THF, light petroleum (bp 40−60 °C), and toluene were distilled from sodium, potassium, or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (or activated 4 Å molecular sieves in the case of THF). Deuterated toluene was distilled from potassium and was deoxygenated by three freeze−pump−thaw cycles and stored over activated 4 Å molecular sieves. Butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes; $MePCl_2$ was purchased from Acros Organics and used without further purification.

^{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 relative to external 85% H_3PO_4, and ^{7}Li chemical shifts are quoted relative to external 1.0 M LiCl(aq).

The compounds $Li(C_6H_4\text{-}2\text{-}CH_2NMe_2)$[7d] and $[MeP(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{C_6H_4\text{-}2\text{-}CH(Li)NMe_2\}]_2$[9] were prepared by published procedures.

Preparation of $CH_3P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$ (3). To a solution of $MePCl_2$ (2.00 g, 17 mmol) in cold (0 °C) ether (15 mL) was added, dropwise over 0.5 h, a solution of $Li(C_6H_4\text{-}2\text{-}CH_2NMe_2)$ (4.80 g, 35 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 **3** as a colorless oil, which crystallized on standing for a period of several weeks. Yield: 3.46 g, 65%. Anal. Calcd for $C_{19}H_{27}N_2P$: C, 72.58; H, 8.66; N, 8.91. Found: C, 72.75; H, 8.60, N, 8.95. ^{1}H NMR (toluene-d_8, 297 K): δ 1.41 (d, $J_{PH} = 4.8$ Hz, 3H, PMe), 1.95 (s, 12H, NMe_2), 3.23 (d, $J_{HH} = 13.0$ Hz, 2H, CH_2N), 3.76 (dd, $J_{HH} = 13.0$ Hz, $J_{PH} = 3.1$ Hz, 2H, CH_2N), 6.85−7.30 (m, 8H, ArH). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, 297 K): δ 13.0 (d, $J_{PC} = 15.5$ Hz, PMe), 44.9 (NMe_2), 63.1 (CH_2N), 125.6, 127.3 (Ar), 129.4 (d, $J_{PC} = 3.1$ Hz, Ar), 131.7 (Ar), 141.2 (d, $J_{PC} = 16.6$ Hz, Ar), 143.5 (d, $J_{PC} = 21.7$ Hz, Ar). $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 297 K): δ −46.1.

Preparation of $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4\cdot(PhMe)_3$ (5a). To a solution of **3** (1.25 g, 3.98 mmol) in light petroleum (10 mL) was added BuLi (1.60 mL, 4.01 mmol). This solution was stirred for 2 h at room temperature, and then the orange precipitate was isolated by filtration and washed with light petroleum (2 × 10 mL). Recrystallization of the resulting solid from cold (−30 °C) toluene gave pale yellow crystals of **5a**. Yield: 0.88 g, 54%. Anal. Calcd for $C_{19}H_{26}LiN_2P$ (i.e., monomer unit without solvent of crystallization): C, 71.24; H, 8.18; N, 8.74. Found: C, 70.49; H, 7.90; N, 8.29. ^{1}H NMR (toluene-d_8, 297 K): δ 0.25 (dd, $J_{PH} = 16.8$ Hz, $J_{HH} = 4.8$ Hz, 1H, CH_2P), 0.35 (dd, $J_{PH} = 21.1$ Hz, $J_{HH} = 4.8$ Hz, 1H, CH_2P), 1.34 (s, br., 6H, NMe_2), 2.14 (d, $J_{HH} = 12.2$ Hz, 1H, CH_2N), 2.23 (s, br.; 6H, NMe_2), 2.89 (d, $J_{HH} = 13.1$ Hz, 1H, CH_2N), 3.47 (d, $J_{HH} = 12.2$ Hz, 1H, CH_2N), 5.76 (dd, $J_{PH} = 8.3$ Hz, $J_{HH} = 13.1$ Hz, 1H, CH_2N), 6.86 (m, 1H, ArH^A), 6.95 (m, 1H, ArH^B), 7.04 (m, 2H, ArH^B), 7.23 (m, 1H, ArH^B), 7.28 (m, 1H, ArH^A), 7.68 (m, 1H, ArH^A), 8.86 (m, 1H, ArH^A). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, 297 K): δ 0.7 (br, CH_2Li), 44.6 (br, NMe_2), 51.2 (br, NMe_2), 65.4 (d, $J_{PC} = 12.6$ Hz, CH_2N), 65.6 (d, $J_{PC} = 3.8$ Hz, CH_2N), 126.9 (Ar^B), 127.1 (Ar^A), 128.5 (Ar^B), 129.1 (Ar^A), 131.5 (d, $J_{PC} = 3.8$ Hz, Ar^B), 131.9 (Ar^A), 132.8 (d, $J_{PC} = 2.5$ Hz, Ar^B), 133.7 (d, $J_{PC} = 10.1$ Hz, Ar^A), 139.7 (d, $J_{PC} = 10.0$ Hz, Ar_{ipso}), 141.8 (d, $J_{PC} = 17.0$ Hz, Ar_{ipso}), 152.3 (d, $J_{PC} = 22.6$ Hz, Ar_{ipso}), 152.6 (d, $J_{PC} = 40.2$ Hz, Ar_{ipso}). $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 297 K): δ −17.8 (q, $J_{PLi} = 36.0$ Hz). ^{7}Li NMR (toluene-d_8, 297 K): δ 1.59 (d, $J_{PLi} = 36.0$ Hz).

Thermal Conversion of 4 to 5. Solutions of **4** in toluene (0.07 M) were heated at 303, 308, 311, 333, and 338 K in sealed NMR tubes, and ^{31}P NMR spectra were recorded at 1 h intervals. Spectra were also recorded on samples of similar concentration (0.05 M) in toluene containing (i) extra **3** and (ii) extra **3** along with a small amount of PPh_3. The latter spectrum showed that the concentration of **3** did not vary with time and thus that integration of the ^{31}P NMR signal for **3** could be used as an internal standard.

Data Collection, Refinement, and Structure Determination for 5a. Data were collected at 160 K on a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{97}H_{128}Li_4N_8P_4$, $M = 1557.7$, triclinic, space group $P\bar{1}$, $a = 16.6255(7)$, $b = 16.8352(7)$, $c = 19.2871(8)$ Å, $\alpha = 113.890(2)°$, $\beta = 92.138(2)°$, $\gamma = 90.708(2)°$, $V = 4930.2(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.049$ g cm^{-3}, $\mu = 0.122$ mm^{-1}, crystal size 0.68 × 0.46 × 0.34 mm. Structure solution by direct methods, refinement on F^2 for all 22 464 unique absorption-corrected data ($2\theta < 28.63°$); $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1061$ (all data), conventional $R = 0.0423$ on F values of 14 152 reflections with $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 0.878, final difference synthesis within ±0.27 e Å^{-3}. Highly disordered toluene solvent molecules, for which individual atoms could not be refined, were treated by the

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(12) (a) Römer, B.; Gatev, G. G.; Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 2919. (b) Schleyer, P. von R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

SQUEEZE procedure of PLATON.[13] Electron density and volume of the solvent-occupied spaces are consistent with six molecules of toluene per unit cell, as indicated in the chemical formula for **5a**. Other programs: Bruker AXS SMART (diffractometer control), SAINT (data integration), and SHELXTL[14] (structure solution and refinement).

Acknowledgment. The authors wish to thank Dr. M. N. S. Hill for obtaining the NMR spectra. This work was carried out with the support of the EPSRC and the Royal Society.

Supporting Information Available: For **5a** details of 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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(13) Spek, A. L. *PLATON, a multi-purpose crystallographic package*; University of Utrecht: The Netherlands, 2000.

(14) Sheldrick, G. M. *SHELXTL* version 5.1; Bruker AXS Inc.: Madison, WI, 1997.