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Coordination and Reduction of HMPA in the Lithiation of (*S*)-*N*-(α-Methylbenzyl)allylamine: Crystal Structures of {(*S*)-α-[PhC(H)CH_3](CH_2CH=CH_2)NLi·HMPA}$_2$ and [(Me$_2$N)$_2$POLi]$_6$

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Monolithiation of the chiral amine (*S*)-*N*-(α-methylbenzyl)allylamine, in the presence of the strong Lewis donor solvent hexamethylphoshoramide (HMPA), results in pale yellow crystals which have been crystallographically analysed revealing the structure of the complex to be an asymmetric *cisoid* dimer {(*S*)-α-[PhC(H)CH_3](CH_2CH=CH_2)NLi·HMPA}$_2$. Variable-temperature NMR studies show this complex can undergo a thermally induced rearrangement to a 1-azaallyl complex at ca. 90 °C. Attempted dilithiation of the chiral amine at the N and vinylic C centres with *n*BuLi and HMPA results in competitive reduction of HMPA to give crystals of the lithium dimethylamidophosphite, structurally authenticated as the hexamer [(Me$_2$N)$_2$POLi]$_6$, in which the Li cation is bonded preferentially to the O centre and not P. The effect is a reduction in the oxidation state of the P centre from (V) to (III), which is supported by ab initio calculations showing the crystal structure to represent the most thermodynamically stable of the possible isomers.

Introduction

Chiral lithium amides derived from α-methylbenzylamine are invaluable reagents in the formation of β-amino acids and β-lactams from their selective conjugate addition reaction with unsaturated β-amino esters and amides.[1] In particular, the use of lithium (*S*)-*N*-(α-methylbenzyl)allylamide, as developed by Davies and co-workers, has proved highly effective because of the ease by which deprotection of the conjugate addition product can be achieved by simple application of Wilkinson's catalyst in removing the allyl group.[1,2] Our recent endeavours in probing the causes of high selectivity have focused on establishing the structural chemistry and unexpected anion transformations which occur when the common chiral amines derived from α-methylbenzylamine are treated with *n*BuM (M = Li, Na, K) in the presence of Lewis bases. A variance in the metal, solvents and/or Lewis donors can promote dramatic and unexpected structural changes such as azaallyl and enamide formation.[3,4] In this regard, we have previously shown that the complex formed on reaction of (*S*)-*N*-(α-methylbenzyl)allylamine (= *S*-*N*-α-mba) with *n*BuNa in the presence of tmeda undergoes a 1,3-sigmatropic shift, converting from the expected allylamide to the 1-azaallylic complex, {[(*S*)-α-(PhC(H)CH_3N⁻⁻C(H)⁻⁻$CHCH_3$)]Na·tmeda}$_2$,[5] Figure 1, and because our numerous attempts at crystallising analogous lithium complexes with a variety of Lewis donors resulted only in a series of impure oils, we were unable to confirm definitively whether a similar transformation was, or could be, occurring with lithium (*S*)-*N*-(α-methylbenzyl)-allylamide.

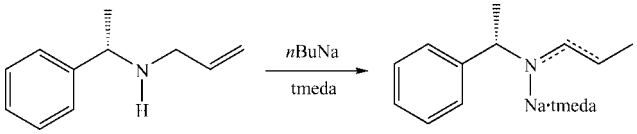

Figure 1. The 1-azaallyl structure of {[(*S*)-α-(PhC(H)CH_3N⁻⁻C(H)⁻⁻$CHCH_3$)]Na·tmeda}$_2$ derived from sodiation of (*S*)-*N*-(α-methylbenzyl)allylamine.

This lack of success in obtaining definitive structural information from the monolithiation reactions led us to subsequently examine and describe the cyclic structures of the homo- and hetero-bimetallic complexes, which result from a second deprotonation of lithium (*S*)-*N*-(α-methylbenzyl)-allylamide at the terminal vinylic site by Li, Na and K organyls.[6] The synthesis and reactions of the dilithiated complex have been described previously by Yus who used *t*BuLi to force metallation at the terminal vinylic proton,[7] though we have since noted that despite the proximity of the relative pK_a values of the terminal vinylic protons (44) and Bu*H* (50) that the dilithiated product will also form using only *n*BuLi in toluene, albeit slowly and in low yield.[6] Recent detailed structural and ab initio studies by Williard and co-workers on related *N*-silylallylamines have highlighted the importance of using ethereal solvents to increase the kinetic reactivity of the terminal vinylic protons towards *n*BuLi, and their influence in determining a *cis* stereochemi-

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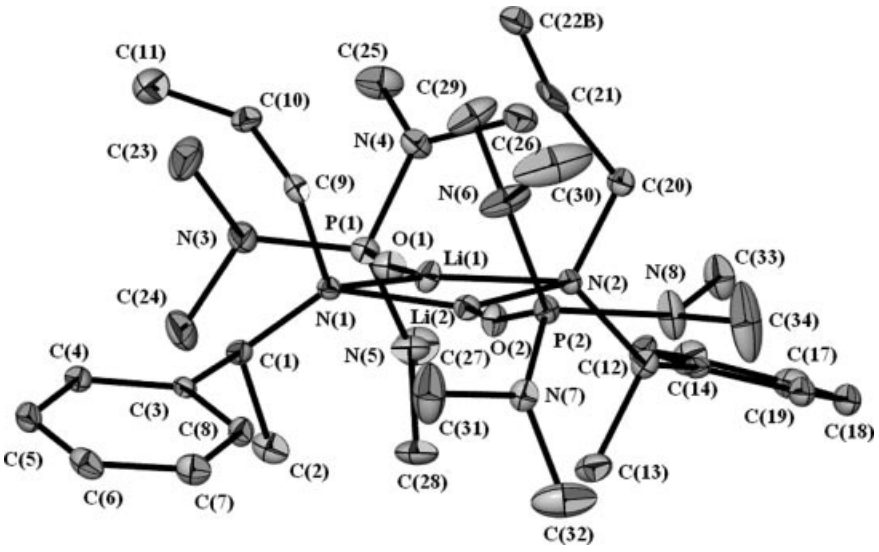


Figure 2. Structure of $\{(S)$-α-$(PhC(H)CH_3)(CH_2CH{=}CH_2)NLi{\cdot}HMPA\}_2$ (**1**). Thermal ellipsoids shown at 30% probability and all H atoms omitted for clarity. Important bond lengths [Å] and angles [°]: N(1)–Li(1) 1.994(6), N(1)–Li(2) 1.994(6), N(2)–Li(1) 2.023(7), N(2)–Li(2) 2.061(6), N(1)–C(1) 1.448(4), N(1)–C(9) 1.466(4), C(9)–C(10) 1.494(5), C(10)–C(11) 1.311(5), O(1)–Li(1) 1.858(7), O(2)–Li(2) 1.845(6); C(1)–N(1)–C(9) 109.4(3), C(1)–N(1)–Li(2) 135.7(3), C(9)–N(1)–Li(2) 101.9(3), C(1)–N(1)–Li(1) 115.9(3), C(9)–N(1)–Li(1) 114.3(3) Li(2)–N(1)–Li(1) 76.1(3), C(12)–N(2)–C(20) 109.6(3), C(12)–N(2)–Li(1) 125.8(3), C(20)–N(2)–Li(1) 110.1(3), C(12)–N(2)–Li(2) 114.0(2), C(20)–N(2)–Li(2) 120.3(3), Li(1)–N(2)–Li(2) 74.0(3), N(1)–Li(1)–N(2) 105.4(3), O(1)–Li(1)–N(1) 124.4(3), O(1)–Li(1)–N(2) 130.1(3), O(2)–Li(2)–N(1) 126.6(3), O(2)–Li(2)–N(2) 128.3(3), N(1)–Li(2)–N(2) 104.1(3).

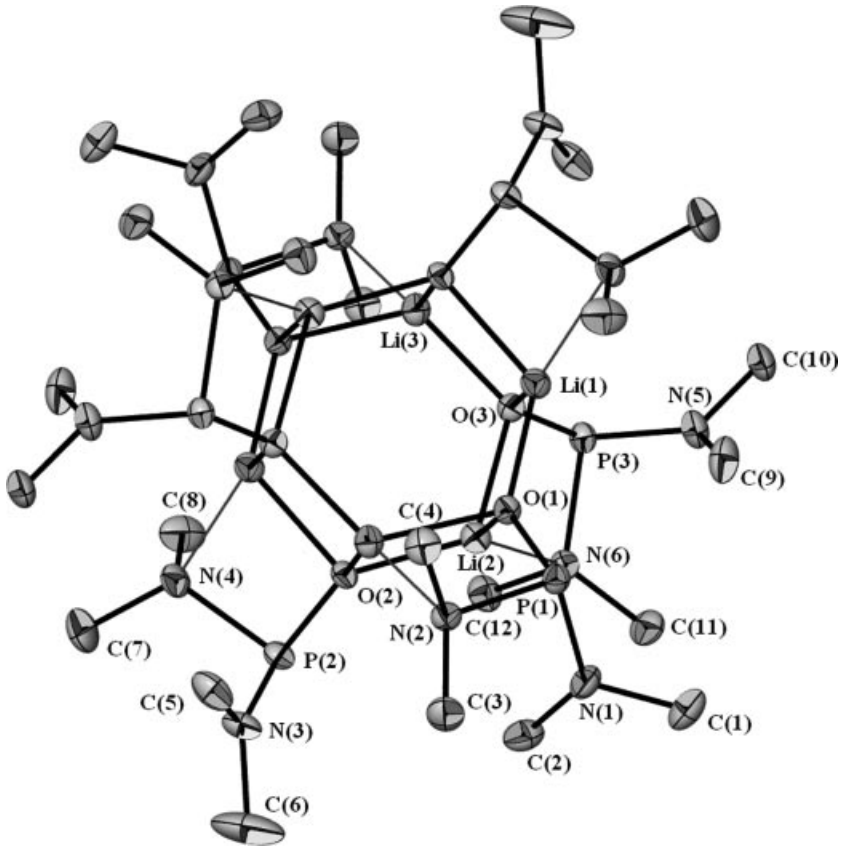


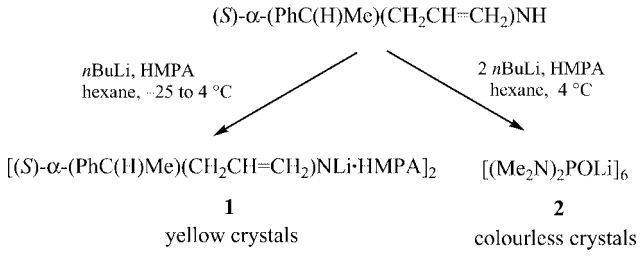
Figure 3. Structure of $\{(Me_2N)_2POLi\}_6$ (**2**). Thermal ellipsoids shown at 50% probability and all H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: O(2)–Li(2) 1.909(3), O(2)–Li(3′) 1.983(3), O(2)–Li(1′) 1.994(4), O(3)–Li(3) 1.906(4), O(3)–Li(1) 1.970(3), O(3)–Li(2) 1.996(3), O(1)–Li(1) 1.911(3), O(1)–Li(2) 1.953(3), O(1)–Li(3′) 1.982(3): O(1)–P(1)–N(1) 107.2(1), O(1)–P(1)–N(2) 95.9(1), N(1)–P(1)–N(2) 99.9(1), P(1)–O(1)–Li(1) 134.0(1), P(1)–O(1)–Li(2) 128.1 (1), Li(1)–O(1)–Li(2) 84.2(1), P(1)–O(1)–Li(3′) 100.9(1), Li(1)–O(1)–Li(3′) 116.8(2), C(2)–N(1)–P(1) 126.0(2), C(1)–N(1)–P(1) 118.2(2), C(3)–N(2)–P(1) 116.5(2), C(4)–N(2)–P(1) 108.4(1).

cal outcome for the dilithiated complex, even when the solvents are used in catalytic amounts.[8,9]

Because structural information is crucial in establishing and understanding the causes of stereo- and regioselectivies, and observed enantioselectivities, we have re-examined both the mono- and dilithiation reactions of *n*BuLi with *S*-*N*-α-mba in the presence of HMPA, and now report the crystal structure of the formerly elusive $[(S)$-α-$(PhC(H)CH_3)$-$(CH_2CH{=}CH_2)NLi{\cdot}HMPA]_2$ complex (**1**), Figure 2, and the unexpected reduction of HMPA in the attempted dilithiation reaction to give the hexameric lithium dimethylamidophosphite, $[(Me_2N)_2POLi]_6$ (**2**), Figure 3, as the only isolated crystalline product.

Results and Discussion

The synthesis of **1** and **2** are shown in Scheme 1. While all other standard aprotic Lewis bases produced only oils on their addition to lithium (*S*)-*N*-(α-methylbenzyl)allylamide we found that with HMPA a yellow powder could be forced to precipitate by rapid cooling. This precipitate, which is often accompanied by an orange oil, can be readily redissolved and, with slow cooling and storage at 4 °C, produces fine yellow needles. These crystals were analysed by single-crystal X-ray diffraction and revealed the solid-state structure to be unusual on two counts: the dimer itself is asymmetric, comprised of two independent lithium amide monomers, and adopts an atypical *cisoid* arrangement of the allyl and benzyl groups relative to the planar $(NLi)_2$ ring, in what is generally considered an energetically less favourable arrangement for such dimers.[10] The few other crystallographically characterised lithium amide dimers complexed by HMPA all display a symmetrical *trans* arrangement of the amido moieties relative to the central $(NLi)_2$ ring.[11–15] The structure of **1** is shown in Figure 2.



Scheme 1. Synthesis of compounds **1** and **2**.

Importantly, and in contrast to the sodium analogue, the allylic nature of the chiral amide is retained [N(1)–C(9) 1.466(4), C(9)–C(10) 1.494(5), C(10)–C(11) 1.311(5) Å] supporting the structural assumptions made in its application in conjugate addition reactions. Though one of the allyl groups is slightly disordered, mainly at the terminal vinylic carbon, they are clearly oriented differently relative to the Li centres, and both appear on the same side of the Li_2N_2 plane. This inequivalency is evident from an analysis of the bonding environment of the Li centres with the closest Li to allylic C(H_2) distances being 2.707 Å for Li(2)–C(9) and 2.871 Å for Li(1)–C(20), both of which are within the range for agostic bonding.

NMR studies in C_6D_6 indicate that the solution-state structure is consistent with that observed for the monomeric unit in the solid state. In comparison to the free amine, the NCH_2CH protons are diastereotopic (δ = 3.91 and 3.66 ppm) and because these are the same protons that are involved in the agostic interactions observed in the solid-state structure of **1**, it suggests that these interactions with the lithium centre are retained in solution. Variable-temperature studies in C_7D_8, in the range –60 °C to 90 °C, revealed an interesting transformation. At lower temperatures only a broadening of the peaks occurs. However, upon heating to 80 °C, followed by sustained heating at 90 °C for 10 min, the complex undergoes significant rearrangement to the 1-azaallyl isomer, as observed in $\{[(S)$-α-$(PhC(H)CH_3N{\cdots}C(H){\cdots}CHCH_3)]Na{\cdot}tmeda\}_2$. This is most clearly indicated by a decrease in the multiplet for –CH=CH_2 at δ = 6.23 ppm, which is mirrored by the emergence of a new multiplet for this proton at δ = 3.81 ppm. The two dd of dd for NCH_2 at δ = 3.77 and 3.54 ppm decrease with the concomitant emergence of a doublet (N···CH···C) at δ = 6.77 ppm. The new Me group appears as a doublet at δ = 1.83 ppm with a coincident diminution of signals for the =CH_2 protons at δ = 5.09 and 4.96 ppm. The overall transformation at this temperature was ca. 75% complete. As we observed for related 2-azaallyl formation in group-1 (α-methylbenzyl)benzylamides, the effect of using sodium is to induce anion changes which require thermal promotion for Li.[4]

HMPA, despite its acknowledged carcinogenicity, is still a ubiquitous, highly useful and remarkably versatile ligand in organolithium chemistry. In the vast majority of cases it behaves simply as a highly polar solvent and/or a strongly coordinating Lewis base; however, it has been observed, through chemical trapping reactions, to undergo decomposition on addition of *n*BuLi, MeLi or with NaH at elevated temperatures.[16,17] We now present unequivocal structural evidence of this decomposition and the nature of the lithiated species.

The addition of one equiv. of HMPA to promote the second lithiation of (*S*)-*N*-(α-methylbenzyl)allylamine at the terminal vinylic proton resulted only in isolation of large colourless crystals, which were identified by single-crystal X-ray diffraction to be $[(Me_2N)_2POLi]_6$ (**2**). The structure is shown in Figure 3 and indicates that the asymmetric unit comprises three Li atoms and three dimethylamidophospite units with the hexameric inner core resembling two stacked trimers. While analogous stacked trimer-type structures have been previously reported for lithium imides,[18] enolates[19] and alkoxides (e.g. $[PhOLi{\cdot}thf]_6$),[20,21] the structure of the monomeric unit of **2**, $(Me_2N)_2POLi$, is unique.

The loss of Me_2N^-, believed to occur through electron transfer from RLi to HMPA with elimination of RH,[16] is accompanied by reduction of the P centre from oxidation state (V) to (III). This stands in contrast to previous assumptions that the lithium dimethylphosphite could still be viewed as a P^V compound and formulated as $(Me_2N)_2P$-

(=O)Li, assuming a covalent P–Li bond. The preference for the Li^+ cation to bond with the O atom has previously been observed in related lithiated P^V phosphane oxide complexes derived from deprotonation of alkyl[22] and amino substituents,[23,24] and though these may be functionally related to **2** there is no P^{III} centre formed and the P–O bonds retain most of their double bond character. A close analysis of the structure adopted by **2** reveals an interesting bonding arrangement within the unique lithiated dimethylamidophosphite moiety, and a comparison is given with the datively bound intact HMPA molecule in **1** in Figure 4.

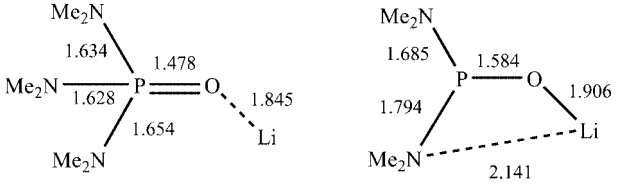


Figure 4. Comparison of the bonding arrangements for coordinated HMPA and the structurally determined dimethylamidophosphite anion in **1** and **2**, respectively. Bond lengths in Å.

There are two differing N–P bond lengths, with the longest found for the N, which datively bonds with a nearby Li cation [range 2.14(4) to 2.16(9) Å]; elongation presumably resulting from removal of the lone-pair electrons from any contribution to the N–P bond itself. This affects the bonding angles around the two N centres which differ substantially, with the longer datively bound N displaying the more acute C–*N*–P angles. Each O is bound to three Li atoms and, as is typical of stacked trimers, show a range of short, medium and longer bonds [e.g. O(3)–Li(1), 1.906(4); O(3)–Li(2), 1.970(3); O(3)–Li(3), 1.996(3) Å].

To further probe the nature of the amidophosphite intermediate ab initio calculations were performed using the Gaussian03 suite of programs.[25] Figure 5 shows structures obtained at the MP2/6-311G(d,p) level, while relative energies are reported in Table 1. Structure **2a** shows the tetrahedral complex previously proposed as the reaction intermediate.[16,17] This structure is not a potential energy minimum – it can be obtained only by constraining the angle Li–P–O. When this angle is allowed to optimize, **2a** undergoes a rearrangement to the form **2a′** which is 100 kJ·mol^{-1} more stable. It is clear that **2a** is not a viable structure. Structures **2b** and **2c** are a further 50 kJ·mol^{-1} more stable than **2a′**. Structures **2b** and **2c** both show pyramidal bonding at the phosphorus, with the Li atom preferring to be associated with the oxygen (and nitrogen) atoms. The structure **2c** consistent with the X-ray data is preferred over **2b** by just 1.6 kJ·mol^{-1} at the MP2/6-311G(d,p) level and by a larger margin of 14.6 kJ·mol^{-1} at the B3LYP/6-311+G(d,p) level. The N atom interacting with the Li also has its N–P bond lengthened relative to the other N atom in **2c**, as is evident in the crystal structure.

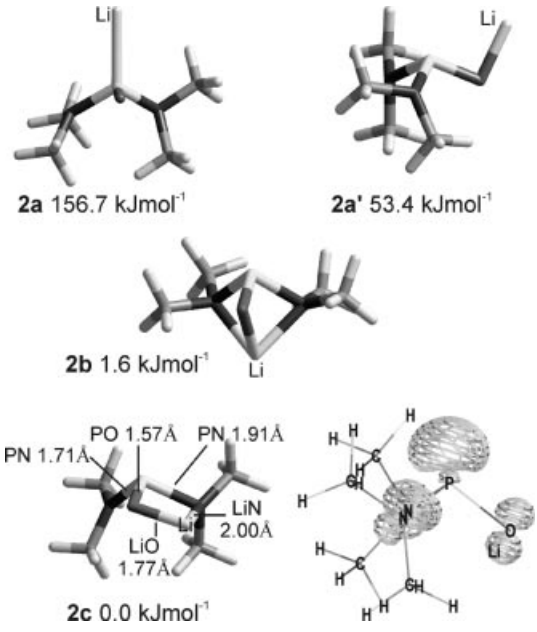


Figure 5. Li···OP[N(CH$_3$)$_2$]$_2$ structures computed at MP2/6-311G(d,p) level, together with their relative energies and HOMO of **2c**.

Calculated Mulliken charges on the P atom, at the MP2 level are given in Table 1. There is a large and significant difference between the charge of 1.8 e found in Li^+[OP[N(CH$_3$)$_2$]$_3$], and the charges of around 1.0 e found in structures **2a**–**2c**. This strongly suggests that the phosphorus atom in these forms has been reduced to P^{III}. The HOMO orbital for **2c** plotted in Figure 5 has the character of a "lone pair" on the phosphorus, consistent with this conclusion.

The first step in aggregation has also been investigated by computing dimeric structures based on **2b** and **2c**. These are shown in Figure 6. In the dimer structures, the energetic preference for **2c** is further increased: 7.6 kJ·mol^{-1} at the MP2/6-311G(d,p)//MP2/6-31G(d,p) level and 45 kJ·mol^{-1} at the B3LYP/6-311+G(d,p) level (Table 2). This is presumably due to the formation of slightly stronger, shorter LiO bonds – see Figure 6. In regard to larger aggregates, the lithium and oxygen atoms of **2c** are more accessible steri-

Table 1. Calculated Mulliken charges on the P atom, and relative energies of alternative LiOP[N(CH$_3$)$_2$]$_2$ structures at the MP2/6-311G(d,p) level.

Structure	Li^+[OP[N(CH$_3$)$_2$]$_3$]	**2a**	**2a′**	**2b**	**2c**
Mulliken charge on P (MP2)	1.77	1.06	0.88	0.96	1.00
E_{rel} (B3LYP)[a] [kJ·mol^{-1}]		148.9	49.1	12.4	0.0
E_{rel} (B3LYP+z.p.)[a],[b] [kJ·mol^{-1}]		–	47.8	14.6	0.0
E_{rel} (MP2)[c] [kJ·mol^{-1}]		156.7	53.4	1.6	0.0
E_{rel} (MP2+z.p.)[b,c] [kJ·mol^{-1}]		–	52.1	3.8	0.0

[a] B3LYP/6-311+G(d,p) level. [b] Including B3LYP/6-311+G(d,p) zero point correction. [c] MP2/6-311G(d,p) level.

cally so that it is able to form the hexamer found in the crystal structure with each lithium atom coordinated to three oxygen atoms. This arrangement is precluded in **2b** due to the increased steric crowding.

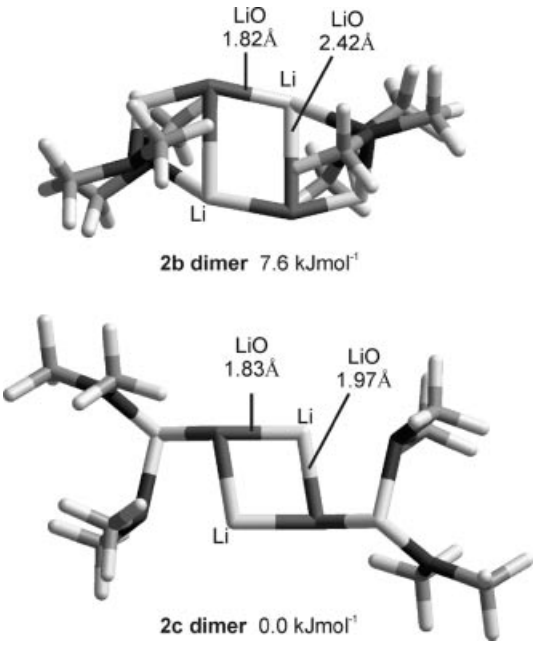


Figure 6. Dimeric structures, together with their relative energies computed at MP2/6-311G(d,p)//MP2/6-31G(d,p) level.

Table 2. Calculated relative energies of dimers formed from **2b** and **2c**.

Dimer	$(\mathbf{2b})_2$	$(\mathbf{2c})_2$
E_{rel} (B3LYP + z.p.)[a] [kJ·mol^{-1}]	44.7	0.0
E_{rel} (MP2)[b] [kJ·mol^{-1}]	7.6	0.0
E_{rel} (MP2 + z.p.)[a,b] [kJ·mol^{-1}]	10.0	0.0

[a] Including B3LYP/6-311+G(d,p) zero point correction. [b] MP2/6-311G(d,p)//MP2/6-31G(d,p) level.

Thus, while the results of Williard[9] indicate that the presence of thf produces a particular structural dimer, which facilitates deprotonation of the terminal vinylic group, it seems from our results that HMPA is preferentially cleaved, and that this most likely occurs at a greater rate than deprotonation can occur. One reason for this, which may support Williard's findings, is that the HMPA molecule is just too bulky to promote close interaction of the vinylic group and lithium base in the particular mixed aggregate structure required for deprotonation.

Experimental Section

Compound manipulations were carried out under strict inert atmosphere and dry conditions using a vacuum/argon line Schlenk techniques and a high purity argon gas recirculating dry box. Prior to use, solvents were dried by reflux over Na/K alloy and stored over molecular sieves (4 Å). (*S*)-*N*-(α-methylbenzyl)allylamine was prepared by a literature procedure.[7] *n*BuLi was purchased from Aldrich (2.5 M solution in heptane). NMR spectra were obtained on Bruker DRX-400 spectrometer with chemical shifts referenced to the appropriate deuterated solvent. Elemental analyses were carried out by CMAS, Australia.

Synthesis of $[(S)$-α-$(PhC(H)CH_3)(CH_2CH{=}CH_2)NLi{\cdot}HMPA]_2$ (1): A solution of *n*BuLi (2 mL, 2.5 M in heptane, 5 mmol) was added dropwise to a stirring solution of *S*-*N*-α-mba (0.81 g, 5 mmol) in hexane (≈ 25 mL) at room temperature. The solution was stirred for 30 min, during which time the colour changed from clear to pale yellow. The solution was then cooled to 0 °C. HMPA (0.87 mL, 5 mmol) was then added dropwise. The resulting cloudy solution was stirred and warmed to room temperature, changing to a clear yellow colour. The solution was cooled rapidly to –25 °C resulting in the precipitation of a yellow solid. The mixture was gently heated in order to dissolve the precipitate and cooled slowly to room temperature before being stored at 4 °C. This resulted in the formation of needle-like crystals. The pale yellow crystals of **1** were filtered, washed with cold hexane and dried under vacuum. Yield 1.28 g, 74%. M.p. 84–86 °C. ^{1}H NMR (300 MHz, C_6D_6, 30 °C): δ = 7.86 (d, ^1J = 6.9 Hz, 2 H, *ortho*-H), 7.38 (t, ^1J = 7.2 Hz, 2 H, *meta*-H), 7.24 (t, ^1J = 7.2 Hz, 1 H, *para*-H), 6.43 (m, 1 H, $CH_2CH{=}CH_2$), 5.28 (dd, ^1J = 3.0 Hz, ^2J = 17.1 Hz, 1 H, $CH_2CH{=}CH_2^a$), 5.14 (dd, ^1J = 3.0 Hz, ^2J = 9.9 Hz, 1 H, $CH_2CH{=}CH_2^b$), 4.44 [q, ^1J = 6.7 Hz, ^2J = 13.2 Hz, 1 H, PhC(*H*)-CH_3], 3.90 (dd, ^1J = 5.7 Hz, ^2J = 13.3 Hz, 1 H, $CH_2^aCH{=}CH_2$), 3.66 (dd, ^1J = 7.5 Hz, ^2J = 13.2 Hz, 1 H, $CH_2^bCH{=}CH_2$), 2.38 (d, ^1J = 3.03 Hz, 18 H, $PO[N(CH_3)_2]_3$), 1.81 [d, ^1J = 6.0 Hz, 3 H, $PhC(H)CH_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 30 °C): δ = 156.4 ($CH_2CH{=}CH_2$), 146.3 ($CH_2CH{=}CH_2$), 129.3 (*o*-C), 128.7 (*m*-C), 125.8 (*p*-C), 111.8 (*ipso*-C), 65.7 [$PhCH)CH_3$], 59.4 ($CH_2CH{=}CH_2$) 37.6 ($PO[N(CH_3)_2]_3$), 29.2 [$PhC(H)CH_3$] ppm. $C_{34}H_{64}LiN_4OP$ (582.8): calcd. C 59.0, H 9.3, N 16.2; found C 58.9, H 9.4, N 16.0.

Synthesis of $\{(Me_2N)_2P{=}OLi\}_6$ (2): A solution of *n*BuLi (4 mL, 2.5 M in heptane, 10 mmol) was added dropwise to a stirred solution of S-*N*-α-mba (0.81 g, 5 mmol) in hexane (≈ 25 mL) at room temperature. The solution changed to a yellow colour and was further stirred for 1 hour. It was then cooled to 0 °C and HMPA (0.87 mL, 5 mmol) was added slowly. The solution became cloudy and dark yellow in colour, and warming to room temperature resulted in a dark orange oil falling out of solution. The emulsion was homogenised and filtered, and the mother liquor subsequently reduced by 50%. The solution was stored at 4 °C overnight resulting in the precipitation of colourless block crystals of **2**. Yield (0.23 g, 32%). M.p. 187–189 °C (dec.) ^{1}H NMR (300 MHz, C_6D_6, 30 °C): δ = 2.60 (d, ^1J = 8.8 Hz, 12 H, $PO[N(CH_3)_2]_2$) ppm. ^{13}C NMR (300 MHz, C_6D_6, 30 °C): δ = 38.5 (d, ^1J = 19.8 Hz, 4 C, $PO[N(CH_3)_2]_2$) ppm. $C_4H_9LiN_2OP$ (142): calcd: C 33.8, H 8.5, N 19.7; found C 33.9, H 8.4, N 19.6.

Crystallography: Single crystals of **1** and **2** were coated in oil under argon in a dry box, mounted on a fibre and data collected with an Enraf Nonius KappaCCD at 123 K with Mo-K_a radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS 97)[26] and refined by full-matrix least-squares on F^2. All H were placed in calculated positions (C–H 0.95 Å) and included in the final least-squares refinement. All other atoms were located and refined anisotropically.

CCDC-297298 and -297299 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for 1: $C_{34}H_{64}LiN_4OP$, M = 582.8, T = 123 K, orthorhombic $P2_12_12_1$, a = 8.5429(17), b = 15.629(3), c = 31.008(6) Å β = 90°, V = 4140.0(14) Å^3, $D_{calcd.}$ = 1.403 g/cm^3, Z =

6, $F(000)$ = 1932, $\mu_{mo\text{-}K}$ = 0.138 mm^{-1}, $2\theta_{max}$ = 56.6°, final R, R_w = 0.0669, 0.1113 N_o = 5041 "observed" [$I > 2\sigma(I)$] reflections out of N = 9946, R_{int} = 0.1368, GooF = 0.990. Disorder in the terminal vinylic carbon C22 which was modelled at 50% occupancy at each site.

Crystallographic Data for 2: $C_{12}H_{36}Li_3N_6O_3P_3$, M = 426.2, T = 123 K, orthorhombic *Pbca*, a = 14.648(3), b = 16.236(3), c = 20.038(4) Å, β = 90°, V = 4765.5(16) Å^3, $D_{calcd.}$ = 1.188 g/cm^3, Z = 8, $F(000)$ = 1824, $\mu_{Mo\text{-}K}$ = 0.271 mm^{-1}, $2\theta_{max}$ = 56.6°, final R, R_w = 0.024, 0.0840, N_o = 3975 "observed" [$I > 2\sigma(I)$] reflections out of N = 5886, R_{int} = 0.086. GooF = 1.021.

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