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Structural studies of lithiated enaminones: the 1-oxa-5-azapentadienyllithium fluxional heterocubane [(Pr$^{i}\overline{\text{NCMeCHCMeOLi}}$)$_4$] and its dimeric hexamethylphosphoric triamide complex [{Pr$^{i}\overline{\text{NCMeCHCMeOLi}}$·OP(NMe$_2$)$_3$}$_2$]

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Lithiation of 4-isopropylaminopent-3-en-2-one in hexane gave a 1-oxa-5-azapentadienyl compound [(Pr$^{i}\overline{\text{NCMeCHCMeOLi}}$)$_4$] **1**, which comprises a tetrameric aggregate of Li_4 and O_4 interpenetrating tetrahedra in which chelating terminal nitrogens undergo a fluxional process around each face of the Li_4 tetrahedron in toluene solution. Addition of hexamethylphosphoric triamide (hmpa) produced a dimeric complex **2** in which oxygen bridges are retained. The crystal structures of both compounds were determined. Bond lengths indicate that an iminoenolate form of the ligand predominates, irrespective of aggregation state. The data are used to rationalise the selectivity of dimetallations of enaminones.

A recent report highlighted the current interest in early main-group metal co-ordination chemistry of pentadienyl-type ligands,[1] including those with p-block heteroatoms. The geometry of such ligands is amenable to fine-tuning to give close control of the co-ordination environment of the metal. While this is relevant to the design of homogeneous catalysts[2] and low-molecular-weight precursors for metal–organic chemical vapour deposition,[3] the pseudo-aromatic nature of the ligands and the variety of possible co-ordination modes provides a more fundamental stimulus. As an extension to our previous work on diazapentadienyl ligands,[4] we present this account of our studies on a 1-oxa-5-azapentadienyllithium compound. In this case the nature of the deprotonated ligand as a resonance hybrid of enolate and amidolithium gives added interest in the field of organic synthesis, where such systems in general have found a variety of uses.[5] Furthermore, lithiated enaminones in particular have been intensively investigated by Bartoli and co-workers[6] for their synthetic utility, though to date no structural information on the intermediates, save for some *ab initio* calculations on monomeric models,[6d] has been available.

Experimental

General

All manipulations were carried out under a protective argon blanket, either in a double-manifold argon/vacuum line or argon-filled recirculating glove-box. All solvents were used freshly distilled under argon from sodium–benzophenone. Hexamethylphosphoric triamide, P(NMe$_2$)$_3$O (hmpa), was dried over molecular sieves 13X. (**CAUTION:** hmpa is a suspected carcinogen. Avoid skin contact and exposure to vapour.) 4-Isopropylaminopent-3-en-2-one was prepared by a literature method.[7] Cryoscopic grade benzene was dried over 4 Å molecular sieves and purged with nitrogen prior to use. Other materials were used as received. Proton, ^{13}C and ^{7}Li NMR spectra were recorded on a Bruker MSL 300 spectrometer; ^{1}H and ^{13}C were referenced to residual solvent peaks, 0.1 M Li_2SO_4 in D_2O was used as an external reference for ^{7}Li. The ^{31}P NMR spectra were recorded on a Bruker AC200 spectrometer, and referenced to a secondary external standard of PPh_3 in C_6D_6 at δ −6.0.

Synthesis of [(Pr$^{i}\overline{\text{NCMeCHCMeOLi}}$)$_4$] 1

Under a dry argon blanket, LiBu^{n} (8.9 cm^3 of a 1.6 M solution in hexanes, 14.2 mmol) was added at 273 K to a dry hexane (10 cm^3) solution of 4-isopropylaminopent-3-en-2-one (2.0 g, 14.2 mmol). A white precipitate appeared which was heated into solution. Large blocks of compound **1** (0.896 g, 43% yield) formed after standing at room temperature overnight, m.p. = 68 °C (Found: C, 64.82; H, 9.96; N, 9.27. $C_8H_{14}LiNO$ requires: C, 65.30; H, 9.59; N, 9.52%). IR: $\tilde{\nu}_{max}$ 1606 cm^{-1} (CO str). ^{1}H NMR (300.1 MHz, [$^{2}H_8$]toluene, 258 K, slow exchange): δ 0.96 (d, *J* 5.5, 3 H, *Me*CHMe), 1.25 (d, *J* 5.5, 3 H, MeCH*Me*), 1.59 (s, 3 H, Pr^{i}NC*Me*), 2.12 (s, 3 H, OCMe), 3.40 (spt, *J* 5.5 Hz, 1 H, Me*CH*Me) and 4.84 (s, 1 H, MeCC*H*CMe); the two doublets at δ 0.96 and 1.25 coalesced at 290 K to a signal which at 308 K was clearly resolved as a single doublet, centred at δ 1.12. ^{13}C NMR (75.5 MHz, C_6D_6, 293 K): δ 21.57 (Pr^{i}NC*Me*), 24.02 (*Me*CHMe), 24.21(MeCH*Me*), 27.82 (*Me*CO), 50.62 (Me*C*HMe), 96.91 (MeC*C*HMe), 169.88 (Me*C*NPr^{i}) and 182.48 (Me*C*O). ^{7}Li NMR (116.6 MHz, [$^{2}H_8$]toluene): δ −0.8 (s), invariant to temperature or concentration. Positive ^{1}H–^{1}H nuclear Overhauser enhancements were recorded between the isopropyl methyl signal and *both* the 2- and 4-methyl signals of the enaminone fragment in the fast-exchange limit. The freezing point depression of a benzene solution of compound **1** (0.029 mol dm^{-3} based on a monomeric molecular weight of 147.146) gave an average molecular mass in solution of 572 ± 17, or an association state of 3.89 ± 0.12.

Crystallographic data. Single crystal 0.4 × 0.2 × 0.2 mm from hexane mounted in a Lindemann glass capillary under argon, $C_{32}H_{56}Li_4N_4O_4$, $M = 588.57$, triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $a = 10.073(2)$, $b = 12.346(2)$, $c = 16.842(3)$ Å, $\alpha = 78.18(3)$, $\beta = 89.35(3)$, $\gamma = 70.21(3)°$, $U = 1925.0(6)$ Å^3, $D_c = 1.015$ Mg m^{-3}, μ(Mo-Kα) = 0.064 mm^{-1}, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), $F(000) = 640$. 5208 Reflections were collected at room temperature in the range $1 \le \theta \le 22°$ on a CAD4 diffractometer using the ω–2θ method, of which 4686 were considered independent ($R_{int} = 0.0152$). Data were corrected for Lorentz-polarisation effects. The structure was solved by direct methods using SHELXS 90[8] and refined on F^2 using SHELXL 93[9] with all heavy atoms anisotropic and all hydrogens in calculated positions to a conventional $R1 = 0.0695$ for reflections with $F > 4\sigma(F), wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}} = 0.2141$ for all data. Goodness of fit = 0.977, highest and lowest residual density = 0.265 and −0.263 e Å^{-3}.

CCDC reference number 186/660.

Synthesis of [{Pr^i$\overline{\text{NCMeCHCMeOL}}$i·OP(NMe$_2$)$_3$}$_2$] 2

Under a dry argon blanket, LiBu^n (4.5 cm^3 of a 1.59 M solution in hexanes) was added at 273 K to a dry hexane (10 cm^3) solution of 4-isopropylaminopent-3-en-2-one (1.01 g, 7.14 mmol). To the resultant suspension was added hmpa (1.24 cm^3, 7.14 mmol). The mixture was heated to boiling and allowed to cool to room temperature, yielding a crop of colourless *crystals* (1.70 g, 73.1%) of compound **2**, m.p. = 116 °C (Found: C, 51.24; H, 9.92; N, 16.59; P, 9.43. $C_{14}H_{32}LiN_4O_2P$ requires: C, 51.63; H, 9.88; N, 17.17; P, 9.49%). ^{1}H NMR (300.1 MHz, [^{2}H$_8$]toluene, 298 K, slow exchange): δ 1.38 (d, *J* 6.0, 6H, *Me*CH*Me*), 1.83 (s, 3 H, Pr^{i}NC*Me*), 2.13 (s, 3 H, OCMe), 2.44 (d, *J* 9, 18 H, Me$_2$NP), 3.73 (spt, *J* 6.0 Hz, 1 H, MeC*H*Me) and 4.77 (s, 1 H, MeCC*H*CMe). ^{13}C-{^{1}H} NMR (75.5 MHz, [^{2}H$_8$]toluene, 298 K): δ 19.87 (Pr^{i}NC*Me*), 24.97 (*Me*CH*Me*), 28.61 (*Me*CO), 36.70 (Me$_2$NP), 50.20 (Me*C*HMe), 97.25 (MeC*C*HMe), 163.91 (Me*C*NPr^i) and 167.50 (MeCO). ^{7}Li NMR (116.6 MHz, [^{2}H$_8$]toluene, referenced to 0.1 M Li_2SO_4 in D_2O): δ −0.96 (s). ^{31}P-{^{1}H} NMR (81.03 MHz, C_6D_6, 298 K): δ 23.3 (s).

Crystallographic data. Single crystal 0.4 × 0.2 × 0.2 mm from hexane mounted in perfluoropolyether oil in a Lindemann glass capillary under argon, $C_{28}H_{64}Li_2N_8O_4P_2$, $M = 652.69$, monoclinic, space group $P2_1/n$ (no. 14), $Z = 2$, $a = 10.675(2)$, $b = 13.433(3)$, $c = 13.741(3)$ Å, $\beta = 102.24(2)°$, $U = 1925.5(7)$ Å^3, $D_c = 1.126$ Mg m^{-3}, μ(Mo-Kα) = 0.153 mm^{-1}, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), $F(000) = 712$. 3389 Reflections were collected at 183(2) K in the range $2.1 \leqslant \theta \leqslant 25.2°$ on a Nonius MACH3 diffractometer using the ω–2θ method, of which all were independent. Data were corrected for Lorentz-polarisation effects, and for decay (the intensities of three representative reflections measured after every 150 declined monotonically by −16%). The structure was solved and refined on F^2 as above $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0699$ for 2657 reflections with $F > 4\sigma(F)$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}} = 0.1965$ for all data. Goodness of fit = 1.459, highest and lowest residual density = 0.50 and −0.76 e Å^{-3}.

CCDC reference number 186/660.

Results and Discussion

A hexane solution of 4-isopropylaminopent-3-en-2-one treated with *n*-butyllithium yielded a crop of large colourless crystals of compound **1** when left to cool. Since no co-ordinating solvent was necessary, it was clear that some molecular aggregated form of the lithiated enaminone was present. A similar *N*,*O* chelating monoanionic ligand also with an isopropyl substituent on the amino group forms two different aggregates of [{Pr^{i}NC(Ph)OLi}$_x$]. Depending on crystallisation conditions, either a bis(tetrahydrofuran)-solvated hexagonal-prismatic hexamer[10] or a dimer of cubic tetramers[11] was obtained. However, the bite angle of the azaenolate ligand in those cases was much different from that expected for **1**. It remained unclear whether **1** would adopt a hexa- or tetra-meric (or other) aggregation pattern, therefore the degree of aggregation in the solid state was determined by X-ray diffraction. This revealed the molecular structure of **1** to be an approximately S_4-symmetric tetramer with μ_3 bridging oxygens and terminal nitrogens. The tetramer is comprised of a cubic array of annulated four- and six-membered rings as shown in Fig. 1. This may be viewed in turn as a dimer of dimers formed from a stack of two Li_2O_2 rings[12] with the two six-membered metallacycles occupying cisoid positions relative to the central four-membered rings, at angles ranging from 46.1(3) to 50.9(4)° [48.2(2)° averaged over the four crystallographically independent monomers]. These dimers join orthogonally to give the S_4 tetramer in preference to an ostensibly equally probable D_2 isomer. In fact, for Li_4O_4 clusters with intramolecular co-ordination, the S_4 isomer is always observed.[13] For example, in previous structurally authenticated examples of a similar architecture, the lithium aldolate from reaction of pinacolone with pivaldehyde,[14] and the lithium enolate of 2-[2-(dimethylaminomethyl)phenyl]ethen-2-olate,[15] both exhibit an approximate S_4 arrangement (however, two organolithium structures have been reported with a tetrameric D_2 structure).[16]

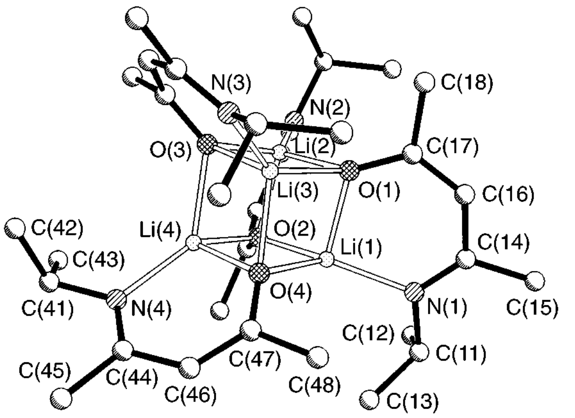


Fig. 1 Crystal structure of compound **1**. Hydrogen atoms are omitted for clarity

Distinct from these cases, however, the structure of compound **1** is the first case in which the six-membered ring is planar [root-mean-square deviation 0.056(4) Å averaged over the four crystallographically independent monomers] and delocalised (see Table 1 for selected bond lengths and angles), and thus offers an opportunity to study the effect of aggregation on the electronic structure of organic anions. Reduction of the aggregation state of **1** was therefore attempted, first without success with the chelating Lewis bases *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, underlining the robust nature of this tetramer (see below), but ultimately with hmpa a new species **2** was isolated from solution.

The substantial partial negative charge on the oxygen of hmpa[17] makes this ligand successful in breaking the aggregate **1**, since it can compete with the oxygen of the deprotonated enaminone on the strength of its co-ordination to lithium. The crystal structure of compound **2** (Fig. 2) shows that the dimers remain intact, but instead of *via* stacking the lithium atoms attain their favoured four-co-ordination *via* a terminal bond to a single hmpa each. Beyond this, the primary structural difference is that the two six-membered rings now lie transoid to the central Li_2O_2 ring [at an angle of 43.0(2)°], and that the aggregate is held by μ instead of μ_3 bridging oxygens. In this case the two monomers are related by a crystallographic centre of symmetry. Compound **2** can be seen as a dimer of monomers rather than as a true dimer in that the lithium which bonds to the nitrogen of a given anion has a significantly shorter bond to the oxygen of that anion, 1.891(5) *versus* 1.956(5) Å to the lithium of the other monomer (see Table 2). Furthermore the angle C−O−Li lies close to 120° within a given metallacycle, consistent with efficient overlap with an electron pair from an sp^2-hybridised oxygen, whereas the longer distances are also associated with greater angles [124.5(2) *versus* 133.5(2)° in **2**]. Precisely the same applies in the tetramer **1**; the view of that molecule as an aggregate of four monomers is supported by consideration of the O−Li bond lengths: the lithium which lies in the plane of each individual ligand is bonded to the oxygen of that ligand with the shortest [mean 1.905(4); range 1.899(8)–

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

O(3)–C(37)	1.303(5)	O(3)–Li(3)	1.911(8)	N(3)–Li(3)	1.983(8)	N(2)–C(24)	1.310(6)
O(3)–Li(2)	1.965(8)	O(3)–Li(4)	2.014(8)	N(2)–C(21)	1.462(6)	N(2)–Li(2)	1.956(8)
O(2)–C(27)	1.310(5)	O(2)–Li(2)	1.902(8)	N(4)–C(44)	1.300(6)	N(4)–C(41)	1.468(6)
O(2)–Li(1)	1.999(8)	O(2)–Li(4)	2.017(8)	N(4)–Li(4)	1.993(8)	C(37)–C(36)	1.353(6)
O(1)–C(17)	1.311(5)	O(1)–Li(1)	1.909(8)	N(1)–C(14)	1.274(6)	N(1)–C(11)	1.469(6)
O(1)–Li(2)	1.998(8)	O(1)–Li(3)	2.028(8)	N(1)–Li(1)	1.974(8)	C(36)–C(34)	1.437(6)
O(4)–C(47)	1.293(5)	O(4)–Li(4)	1.899(8)	C(24)–C(26)	1.427(7)	C(26)–C(27)	1.348(6)
O(4)–Li(1)	1.977(8)	O(4)–Li(3)	2.019(8)	C(46)–C(47)	1.353(6)	C(46)–C(44)	1.420(7)
N(3)–C(34)	1.286(5)	N(3)–C(31)	1.463(6)	C(16)–C(17)	1.355(6)	C(16)–C(14)	1.434(7)
C(37)–O(3)–Li(3)	122.8(3)	C(37)–O(3)–Li(2)	128.1(4)	Li(1)–O(4)–Li(3)	86.7(3)	C(34)–N(3)–C(31)	120.1(4)
Li(3)–O(3)–Li(2)	87.6(3)	C(37)–O(3)–Li(4)	132.1(3)	C(31)–N(3)–Li(3)	121.2(4)	C(31)–N(3)–Li(3)	118.5(4)
Li(3)–O(3)–Li(4)	83.8(3)	Li(2)–O(3)–Li(4)	87.6(3)	C(24)–N(2)–C(21)	120.9(4)	C(24)–N(2)–Li(2)	120.6(4)
C(27)–O(2)–Li(2)	119.2(4)	C(27)–O(2)–Li(1)	138.3(4)	C(21)–N(2)–Li(2)	118.5(4)	C(44)–N(4)–C(41)	119.7(5)
Li(2)–O(2)–Li(1)	81.6(3)	C(27)–O(2)–Li(1)	138.3(4)	C(44)–N(4)–Li(4)	121.7(4)	C(41)–N(4)–Li(4)	118.3(4)
Li(2)–O(2)–Li(1)	81.6(3)	Li(2)–O(2)–Li(4)	89.3(3)	O(3)–C(37)–C(36)	124.1(4)	C(14)–N(1)–C(11)	120.1(5)
Li(1)–O(2)–Li(4)	85.2(3)	C(17)–O(1)–Li(1)	120.3(4)	C(14)–N(1)–Li(1)	120.4(4)	C(11)–N(1)–Li(1)	119.5(4)
C(17)–O(1)–Li(2)	138.6(4)	Li(1)–O(1)–Li(2)	81.4(3)	C(37)–C(36)–C(34)	129.8(4)	N(3)–C(34)–C(36)	123.5(4)
C(17)–O(1)–Li(3)	127.9(4)	Li(1)–O(1)–Li(3)	88.3(3)	N(2)–C(24)–C(26)	122.1(4)	C(27)–C(26)–C(24)	130.3(5)
Li(2)–O(1)–Li(3)	83.6(3)	C(47)–O(4)–Li(4)	121.8(4)	C(47)–C(46)–C(44)	129.4(5)	O(4)–C(47)–C(46)	125.9(4)
C(47)–O(4)–Li(1)	125.4(3)	Li(4)–O(4)–Li(1)	89.1(3)	C(17)–C(16)–C(14)	131.4(5)	O(1)–C(17)–C(16)	124.3(4)
C(47)–O(4)–Li(3)	135.4(4)	Li(4)–O(4)–Li(3)	84.0(3)				

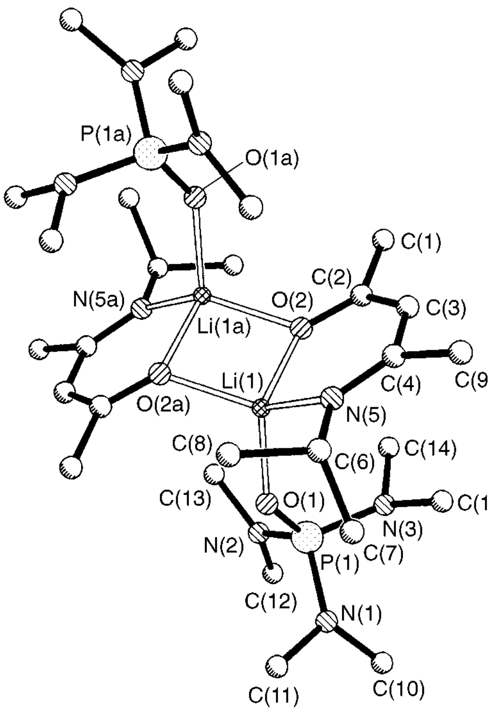


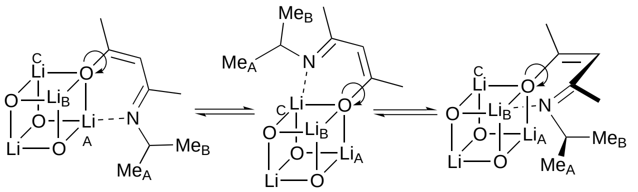
Fig. 2 Crystal structure of compound **2**. Hydrogen atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

N(5)–C(4)	1.289(4)	N(6)–C(6)	1.471(4)
O(2)–C(2)	1.282(4)	N(5)–Li(1)	2.026(5)
O(2)–Li(1)	1.891(5)	O(2)–Li(1a)	1.956(5)
C(2)–C(3)	1.376(5)	O(1)–Li(1)	1.908(5)
C(3)–C(4)	1.439(5)		
C(6)–N(5)–Li(1)	118.3(2)	O(2)–C(2)–C(3)	125.8(3)
C(2)–C(3)–C(4)	127.5(3)	N(5)–C(4)–C(3)	123.4(3)
C(2)–O(2)–Li(1)	124.5(2)	C(2)–O(2)–Li(1a)	133.5(2)
Li(1)–O(2)–Li(1a)	87.3(2)	P(1)–O(1)–Li(1)	137.7(2)
O(2)–Li(1)–O(2a)	92.7(2)	O(2)–Li(1)–O(1)	119.4(3)
O(2)–Li(1)–N(5)	95.6(2)	O(2a)–Li(1)–O(1)	106.7(2)
O(2a)–Li(1)–N(5)	130.8(3)	O(1)–Li(1)–N(5)	110.8(3)
C(4)–N(5)–C(6)	119.8(3)	C(4)–N(5)–Li(1)	118.3(2)

1.911(8) Å] of the bonds within the cubane [mean of others 2.002(4); range 1.965(8)–2.028(8) Å]. The intramonomer C–O–Li angles lie in the range 119.2(4) to 122.8(3)°, while the intermonomer ones lie in the range 125.4(3) to 138.3(4)°. From amidolithium chemistry, it has been shown that such lone-pair directional effects can have a structural influence even where substantial ionic bonding prevails.[18] Unfortunately, the quality of the structural data for **1** and **2** precludes a more detailed analysis of cluster bond angles.

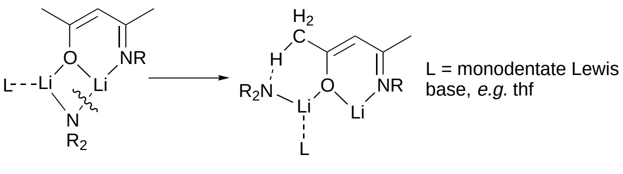
Returning to the gross structure of compound **2**, it is instructive to compare it with the closely related lithium diazapentadienyl hmpa dimer $[\{\mathrm{Ph}\overline{\mathrm{N(CH)_3NPhLi}}\cdot\mathrm{hmpa}\}_2]$. In this case[4] both nitrogens adopt a terminal role as expected for an extensively delocalised anion of this sort, leaving the oxygen of hmpa to form the bridge. A similar structure might have been expected for **2**. The observed C–O bridging in **2** is especially notable in view of the fact that $[\{\overline{\mathrm{OC(OEt)CHCO(OEt)Li}}\cdot\mathrm{hmpa}\}_2]$ also shows a terminal anion bridging hmpa structural motif.[19] It seems that while a symmetrically delocalised 1,5-diaza-[4] or 1,5-dioxa[19]-pentadienyl anion prefers a terminal role, the mixed 1-oxa-5-aza pentadienyl anion in **2** retains more iminoenolate than enamidoketone character, surpassing hmpa in its tendency to bridge. This is clearly shown in the bond lengths within the six-membered metallacycles. These stay remarkably invariant in the two different aggregation states, and while the robust nature of the bridging prevented us from obtaining structural data on a truly monomeric complex, the HF/6-31G *ab initio* calculations on lithium-4-(methylamino)-pent-3-en-2-one available in the supplementary data to ref. 6(*d*) provide valuable comparisons. In the monomer,[6d] dimer and tetramer the C–O bond lengths (mean, [range]), are 1.2841, 1.282(4) and 1.304(3) [1.293(5)–1.311(5)] respectively, the (O)C–C lengths are 1.3773, 1.376(5) and 1.352(3) [1.348(6)–1.355(6)], the C–C(N) lengths are 1.4214, 1.439(5) and 1.429(4) [1.420(7)–1.437(6)], the C–N lengths are 1.3019, 1.289(4) and 1.293(3) [1.274(6)–1.310(6)], the intramonomer Li–O lengths are 1.7134, 1.891(5) and 1.905(4) [1.899(8)–1.911(8)] and the Li–N lengths 1.8678, 2.026(5) and 1.977(4) [1.956(8)–1.993(8)] Å. The differences in Li–N and Li–O lengths are readily interpreted in terms of solvation differences. All other differences are small, distances often being close to identical within error. The terminal oxygen in the computed monomer bonds more tightly to both the lithium and the oxygen than in the experimental bridged cases, as might be expected. This signifies that lithiation of the enaminone converts the system into a delocalised 1-oxa-5-azapentadienyl anion with contributions from enamidoketone, carbanion and



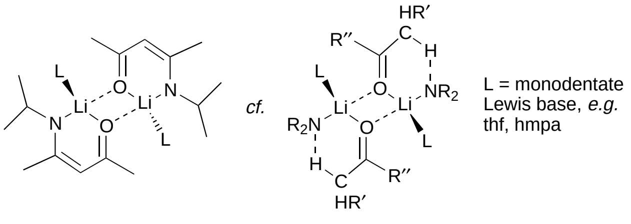
Scheme 1

iminoenolate resonance forms, but with a most predominant contribution from the iminoenolate form, essentially *irrespective* of aggregation state. For example, typical enolate C–O and C=C distances are 1.333(4) and 1.338(5) Å respectively,[15] only marginally longer and shorter than the values observed in **1** and **2**. However, the only neutral unmetallated imines structurally characterised co-ordinated to an alkali metal[20] have C=N distances of 1.256(7) and 1.266(7) Å, marginally but significantly shorter than those in **1** and **2**; while the iminoenolate form predominates, significant contributions from the enamidoketone form exist. The predominance of the iminoenolate form, even in the monomer, is presumably fundamental to the preferences of the anion and not simply dictated by the hard-acid character of lithium, since $[\mathrm{Pr^i}\overline{\mathrm{NCCF_3CHCCF_3OC}}\mathrm{u}]\cdot\mathrm{PMe_3}$, with a very similar ligand environment but a soft, copper(I) metal ion, exhibits bond lengths [C–O 1.26, (O)C–C 1.34, C–C(N) 1.41 and C–N 1.30 Å] different only in a slight shortening of C–O, ascribable to its non-bridging role in this monomeric complex.[21]

In solutions of compound **1** the robust nature of the tetramer hinted at by the lack of reaction with chelating amine electron donors was borne out by all the other evidence. Cryoscopy in benzene indicates that the tetramer remains intact. In toluene there was no NMR evidence for anything other than a single species. At low temperature the two prochiral methyl groups of the isopropyl group are anisochronous in the ^{1}H NMR spectrum lacking a molecular plane of symmetry bisecting them in the slow-exchange limit. This is consistent with retention of the solid-state structure. These two doublets coalesce to a single doublet upon warming. Calculation of the approximate rate of this two-site exchange process[22] at coalescence ($\approx\pi\Delta\nu/\sqrt{2}$) gave a value of 193 $\mathrm{s^{-1}}$ at 290 K, which gave $\Delta G^{\ddagger} = 58.3$ kJ $\mathrm{mol^{-1}}$ at 290 K using the Eyring equation. No other gross changes in the spectra were apparent. No other aggregates or D_2 isomers, and no changes in the ^{7}Li NMR spectra with either temperature (−70 to +60 °C) or concentration (ten-fold range) were observed. The ^{7}Li NMR spectrum was particularly sharp throughout, indicative of retention of a near-tetrahedral local geometry. We propose that the methyl groups coalesce because the nitrogens undergo an intramolecular fluxional motion (Scheme 1) around a triangular face of the $\mathrm{Li_4}$ tetrahedron accompanied by rotation of the C–O bond, thereby generating a time-averaged symmetry. In support of this is the cryoscopic evidence for retention of the tetrameric structure, and the observation of nuclear Overhauser enhancements, even at the fast-exchange limit, to the 4-methyl group from the isopropyl methyl groups, which can only occur in an aggregated form. We do not believe that the $\mathrm{Li_4O_4}$ core rearranges, since more profound changes in the ^{7}Li NMR spectra would be expected, and since each bond within the core has an electron pair directed along its vector. This contrasts with the situation in $(\mathrm{LiBu^t})_4$ for example, thought to rearrange *via* an eight-membered ring intermediate,[23] or in vinyllithium in diethyl ether, like **1**, another solvated heterocubane, also thought to undergo a fluxion of the μ_3 substituent around a triangular face of a $\mathrm{Li_4}$ tetrahedron.[24] In that case the barrier was much lower, since no two-centre, two-electron co-ordinate σ bond needed to be broken in order for the process to occur, and since the steric barriers were lower, requiring less co-operativity in the molecular motion. In **1** the Li–N bond scission and necessary co-operativity of the intramolecular iminelithium exchange contribute to the comparatively high barrier to fluxion.



Scheme 2



Scheme 3

For compound **2**, no coalescences were revealed by NMR study down to 258 K; only data consistent with a time-average was obtained (since in the static structure there exists no molecular symmetry plane passing through the isopropyl methine carbon). The averaging could be a result of a monomer–dimer equilibrium or a low-energy intramolecular *cis–trans* fluxion around the central $\mathrm{Li_2O_2}$ ring proceeding *via* a planar transition state. The ^{31}P chemical shift ruled out the possibility of a bridge–terminal ligand-exchange process, since the recorded shift was well within the range for monodentate hmpa, and quite far removed from the range for bridging hmpa.[4]

The knowledge gathered on these systems may be of some value in interpreting the extensive work of Bartoli and coworkers,[6] who have used lithiated enaminones in a variety of synthetic transformation, for example in synthesis of N-substituted furylidene ketones,[6b] pyridin-4-ones and pyran-4-ones,[6c] pyridines and pyrimidines,[6f] *etc.* Most of these transformations proceed *via* dilithiated intermediates, and methods have been developed to direct the second metallation at the α-methyl group (kinetic) or the γ-methyl group (thermodynamic).[6d] Inspection of the structures of compounds **1** and **2** would seem to offer little ready explanation of the tendency for bulky bases to favour α- (next to oxygen) over γ-metallation (next to nitrogen). Both seem equally well protected sterically, in the aggregated forms, a factor presumably responsible for the sluggish nature of the second metallation, which required temperatures above 273 K to proceed satisfactorily.[6d] However, the answer may lie in the pronounced tendency here discovered for the oxygen to form bridges. The reaction may proceed *via* a lithium imino–enolate–amidolithium mixed aggregate (Scheme 2).[25] Such a postulate puts the amido group in close proximity to the α-methyl group and able to attack it *via* an open-dimer intermediate,[26] but prevented from approaching the γ-methyl by the substituent on nitrogen. Indeed, a correlation was found between the bulkiness of the substituent on the nitrogen and selectivity of α-metallation.[6d] We hope to substantiate these postulates with future work on mixed aggregates and on isolation of the dimetallated species themselves, as has been recently achieved for the parent dilithium acetylacetonate.[27]

A further intriguing point of more general importance in synthesis regards the structure of compound **2**. If instead of the predominant iminoenolate resonance form the minor enamidoketone form is emphasised, then **2** may be viewed as a dimeric amidolithium with terminal amido groups and bridging neutral ketone (Scheme 3). This is a possible transition-state model for enolisation reactions, an alternative or addition to the open-dimer model currently gaining acceptance.[26b] We are currently searching for structural data exhibiting true neutral ketones in a bridging role to substantiate this alternative mechanism.

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