DALTON
FULL PAPER

Reactions of 1,3,5-triazine with organolithium compounds containing trimethylsilyl substituents; X-ray structures of 1,3,5-triaza- and 1,3,5,7-tetraaza-heptatrienyllithium compounds†

W. Marco Boesveld, Peter B. Hitchcock and Michael F. Lappert*

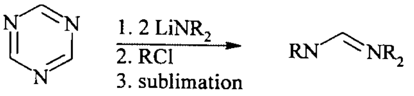
The Chemistry Laboratory, University of Sussex, Falmer, Brighton, UK BN1 9QJ

Received 13th September 1999, Accepted 11th October 1999

While treatment of 1,3,5-triazine $\overline{NC(H)NC(H)NC}H$ **1** with **a** $[LiCH_2R]_6$, **b** $[LiCHR_2]_\infty$ or **c** $[LiSiR_3(thf)_3]$ ($R = SiMe_3$) was believed to yield the 1,4-adducts $Li\overline{NC(H)NC(H)(R')NC}H$ **2a**–**c**, by contrast, **1** with $[LiNR_2]_3$ or $[Li(thf)_4][Li(CR_3)_2]$ under similar conditions gave the 1,3,5,7-tetraazaheptatrienyllithium $[Li_3\{RNC(H)NC(H)NC(H)NR\}_3]$ **4** or 1,3,5-triazaheptatrienyllithium $[Li_2\{RNC(H)NC(H)NC(H)CR_2\}_2(\mu\text{-thf})]$ **5** compounds, implicating a trimethylsilyl-shift and subsequent ring-scission. For **2b**, the transformation to the 1,3,5-triazaheptatrienyllithium compound $[Li_4\{RNC(H)NC(H)NC(H)C(H)R\}_4]$ **7** was accomplished by heating the solid to 140 °C. Although compound **4** was unreactive towards tmen or pmdien, from the triazaheptatrienyllithium compound **5** and pmdien, the lithium compound $[Li\{RNC(H)NC(H)NC(H)CR_2\}(pmdien)]$ **6** was isolated. The tri- **4**, di- **5**, tetra- **7** and mono-nuclear **6** lithium compounds have been fully characterised, including their X-ray crystal structures.

Introduction

1,3,5-Triazine **1** has been well investigated for its use in organic synthesis, in particular by Grundmann and Kreutzberger.[1] The aromatic heterocycle **1** was shown to be a useful synthon for hydrogen cyanide, for example in Gatterman's aldehyde synthesis.[2] Some attention has been paid to the mechanism believed to consist of either (i) one or more additions to the heterocycle and then ring-opening or (ii) initial depolymerisation to HCN units.[3] Organometallic derivatives of triazine are scarce and attention has focused on derivatives formed by the cyclotrimerisation of organonitriles, induced by alkyllithium compounds.[4] Oakley and co-workers prepared the formamidine $RNC(H)NR_2$ by the reaction of **1** with 2/3 $[LiNR_2]_3$, treatment with RCl and sublimation, eqn. (1) ($R = SiMe_3$).[5]



1

(1)

This reaction led us to anticipitate that **1** might behave as an HCN synthon with $LiCHR_2$ and thus furnish the lithium 1-azaallyl $Li\{N(R)C(H)C(H)R\}$ or β-diketiminate $Li[\{N(R)C(H)\}_2CH]$, by analogy with the reaction of $[LiCHR_2]_\infty$ and a nitrile free from α-hydrogen, *e.g.*, yielding $[Li\{N(R)C(Bu^t)C(H)R\}]_2$ with Bu^tCN or $[Li\{N(R)C(Ph)\}_2CH]_2$ with PhCN.[6] However, a 1,4-adduct $Li\overline{NC(H)NC(H)(CHR_2)NC}H$ **2b** was formed, analogous to the reaction between an alkyllithium compound and 2,4,6-triphenyl-1,3,5-triazine.[7] This result and the notion that *mono*-substituted dihydrotriazines **3** were considered unstable,[8] prompted us to investigate the reaction of **1** with a variety of lithium alkyls and amides. A preliminary communication has been published describing the reaction of **1** with $LiCHR_2$, $LiCR_3(thf)_2$ or $LiNR_2$ and including the X-ray crystal structure of the triazaheptatrienyllithium compound **5**;[9] full experimental details and extensions are now reported.

This paper also has a bearing on the structural chemistry of lithium amides. Lithium amides and their complexes are valuable deprotonating reagents in organic synthesis[10] and have also been used extensively to prepare amides of other metals.[11] The structures of crystalline lithium compounds $LiNR^1R^2$ have been reviewed,[12] as well as their solutions.[13] Lithium amides with R^1 or R^2 containing additional functionalities, *e.g.*, nitrogen atoms have been omitted in reviews,[12] but include the porphyrinates,[14] phthalocyaninates,[15] amidinates,[16,17] *o*-amidopyridines[17,18] and β-diketiminates.[19]

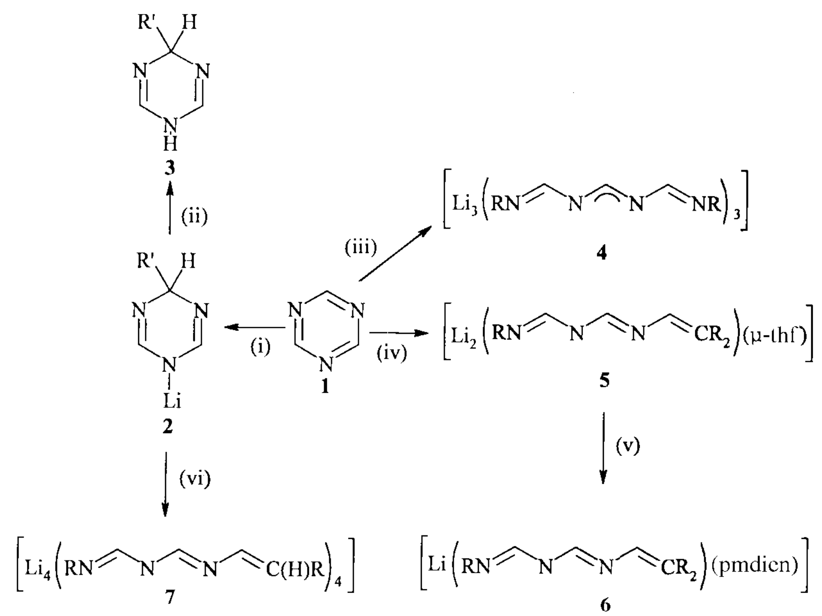
Results and discussion

The reaction of 1,3,5-triazine **1** with **a** $[LiCH_2R]_6$, **b** $[LiCHR_2]_\infty$ or **c** $[LiSiR_3(thf)_3]$ ($R = SiMe_3$) in benzene at ambient temperature gave insoluble, air-sensitive adducts **2**, (i) in Scheme 1. Due to their insolubility, they have not been characterised. Attempts to form more soluble tetramethylethylenediamine (tmen) or pentamethyldiethylenetriamine (pmdien) adducts failed. However, protolysis with one equivalent of methanol (or water), and extraction with diethyl ether, dichloromethane or tetrahydrofuran, followed by concentration afforded 1,4-dihydrotriazines **3a**–**c** in good yield (*ca.* 70%), (ii) in Scheme 1; thus providing evidence that a carbon–carbon or –silicon bond formation had taken place. These crystalline compounds **3** will be fully discussed in a separate paper.[20]

Reaction of **1** with 1/3 $[LiNR_2]_3$ under the same conditions gave an off-white suspension, (iii) in Scheme 1. After removal of volatiles *in vacuo*, the solid was extracted into pentane to yield the 1,3,5,7-tetraazaheptatrienyllithium compound $[Li_3\{RNC(H)NC(H)NC(H)NR\}_3]$ **4**. The air-sensitive compound **4** was characterised by C, H, N elemental analysis and ^1H, $^7Li\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The $^7Li\{^1H\}$ NMR spectrum showed two inequivalent nuclei in a ratio of 2:1. Mass spectrometry revealed the parent molecular ion peak at $m/z = 503$ corresponding to $[Li_3L_2]^+$ [$L = RNC(H)NC(H)NC(H)NR$]. Single crystals suitable for X-ray analysis were obtained from pentane at −20 °C and showed **4** to be trinuclear in the solid state, Fig. 1. Cryoscopy in benzene (Beckmann method) was consistent with the formula $(LiL)_{2.6}$, indicating that **4** was largely trinuclear in solution in accord with its $^7Li\{^1H\}$ NMR spectrum. Variable temperature ^1H and $^7Li\{^1H\}$ NMR spectroscopic experiments (213 to 333 K) in toluene-d_8 did not provide

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4041/



Scheme 1 The formation of compounds **2**–**7** from triazine **1**. *Reagents and conditions*; [(i)–(iv) *ca.* 20 °C, benzene] and: (i) LiR′ (R′ = **a** CH_2R, **b** CHR_2, **c** SiR_3; R = $SiMe_3$);[20] (ii) 1 equivalent MeOH; (iii) $LiNR_2$, 4 h; (iv) $LiCR_3(thf)_2$, 24 h; (v) pmdien, pentane; (vi) 140 °C, 10^{-3} mbar, 5 min.

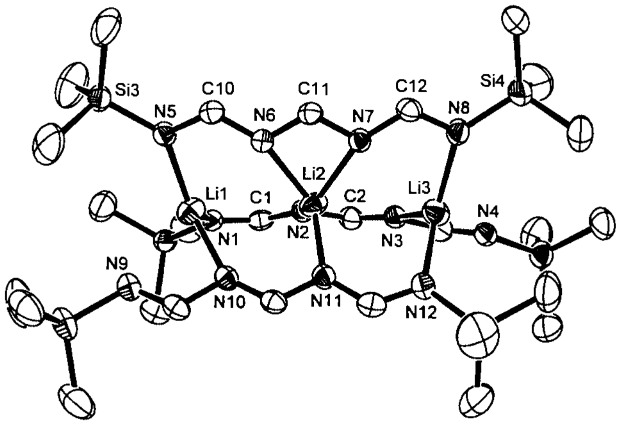


Fig. 1 The molecular structure of $[Li_3\{RNC(H)NC(H)NC(H)NR\}_3]$ **4**, with atom labelling.

more information. Further indication of the stability of this trinuclear complex is that tmen and pmdien failed to cleave the trinuclear molecule, possibly due to the steric inaccessibility of the lithium atoms. By contrast, the ligands in the triazaheptatrienyllithium compounds **5** and **7** have fewer coordination possibilities for the lithium cations; compound **5** reacted with pmdien (and **7** is expected to react similarly) to give the mononuclear adduct **6** (see below).

Reaction of **1** with 1/2 $[Li(thf)_4][Li(CR_3)_2]$, following a similar procedure as for $LiNR_2$, afforded analytically pure, yellow crystals of the 1,3,5-triazaheptatrienyllithium compound $[Li_2\{RNC(H)NC(H)NC(H)CR_2\}_2(\mu\text{-thf})]$ **5** in moderate yield (38%), (iv) in Scheme 1. Elemental analysis and mass spectrometry (parent molecular ion $m/z = 638$) are in agreement with the molecular formula of **5** taking into account the loss of a thf molecule. Colourless, single crystals suitable for X-ray analysis were obtained by recrystallisation from pentane at −20 °C and showed **5** to be dinuclear, Fig. 2. The ^1H NMR spectrum showed a broad singlet for one of the NC(H)N fragments due to fluxionality in the dinuclear molecule at 298 K. Variable temperature ^1H and $^7Li\{^1H\}$ NMR spectroscopic experiments (193 to 333 K) in toluene-d_8 led only to a change in the shape of the signals. Treatment of **5** with pmdien, (v) in Scheme 1, and crystallisation from pentane at −20 °C gave colourless, single crystals suitable for X-ray analysis which showed it to be the mononuclear 1,3,5-triazaheptatrienyllithium compound $[Li\{RNC(H)NC(H)NC(H)CR_2\}(pmdien)]$ **6**, Fig. 3. The lithium compound **6** was characterised by elemental analysis and its ^1H, $^{13}C\{^1H\}$ and $^7Li\{^1H\}$ NMR and mass spectra.

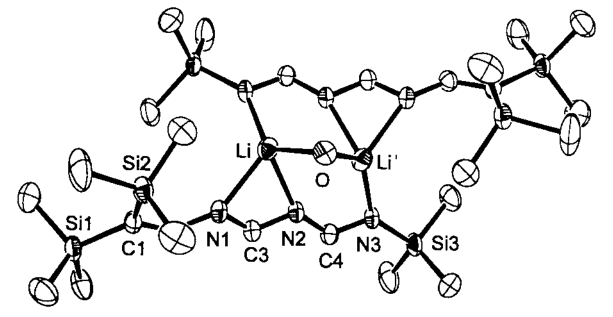


Fig. 2 The molecular structure of $[Li_2\{RNC(H)NC(H)NC(H)CR_2\}_2(\mu\text{-thf})]$ **5**, with atom labelling; only the O atom is shown for the thf molecule.

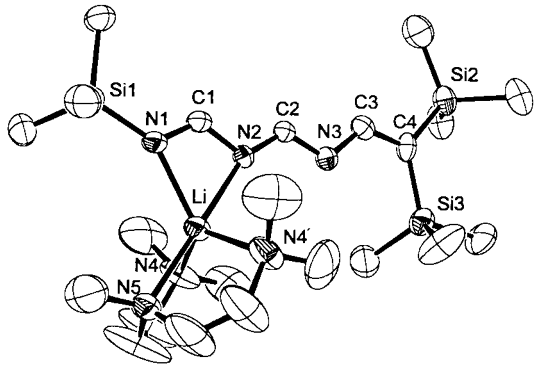


Fig. 3 The molecular structure of $[Li\{RNC(H)NC(H)NC(H)CR_2\}(pmdien)]$ **6**, with atom labelling.

The transformation of the lithium dihydrotriazine adduct $Li\overline{NC(H)NC(H)(CHR_2)NC}H$ **2b** into the 1,3,5-triazaheptatrienyllithium compound $[Li_4\{RNC(H)NC(H)NC(H)C(H)R\}_4]$ **7** was achieved by heating the green/white solid **2b** for 5 min to 140 °C under reduced pressure (10^{-3} mbar), (vi) in Scheme 1. By contrast, heating of **2a** or **2c** led to their decomposition. The analytically pure, yellow, crystalline lithium compound **7** gave satisfactory elemental analysis. The 1,3,5-triazaheptatrienyllithium compound **7** was recrystallised from hexane to give colourless single crystals suitable for X-ray

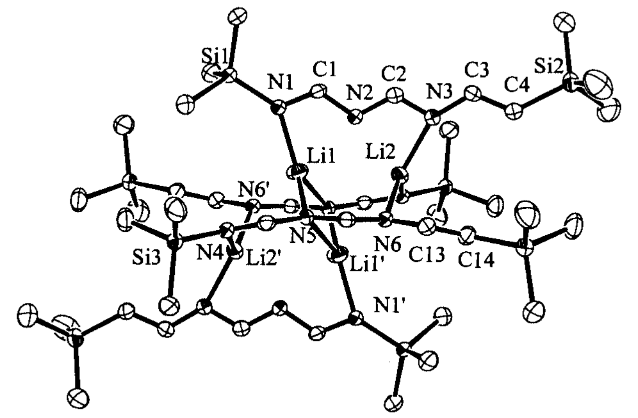


Fig. 4 The molecular structure of $[Li_4\{RNC(H)NC(H)NC(H)C(H)R\}_4]$ **7**, with atom labelling.

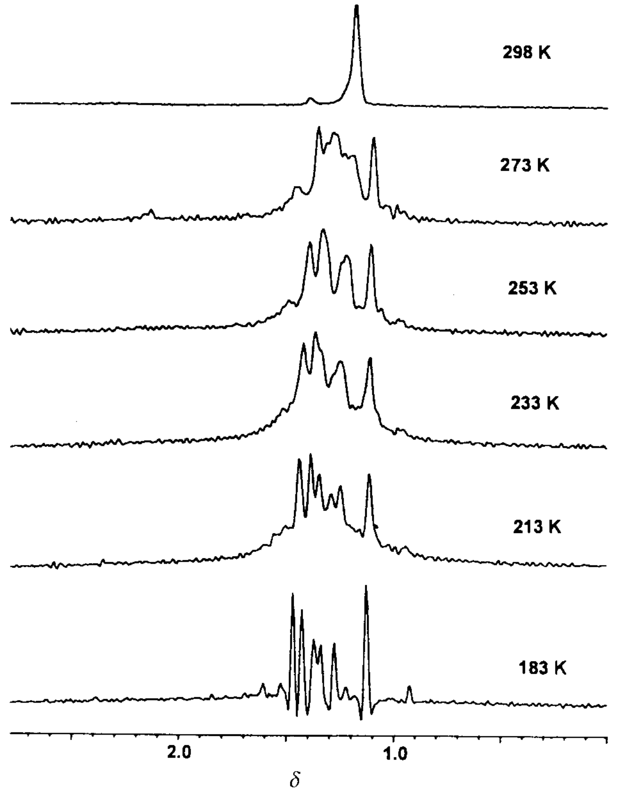


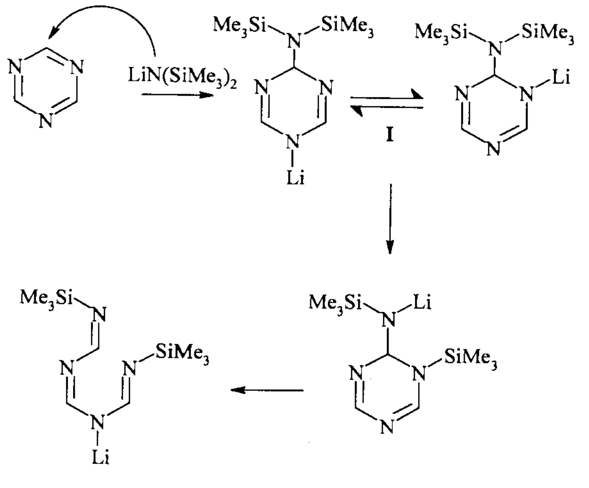
Fig. 5 The variable temperature $^7Li\{^1H\}$ NMR ($C_6D_5CD_3$, 194 MHz) spectra of the tetraazaheptatrienyllithium **7**.

analysis, showing it to be tetranuclear, Fig. 4. The ^1H and $^7Li\{^1H\}$ NMR spectra showed broad signals at 298 K. At lower temperatures the spectra were very complicated. The $^7Li\{^1H\}$ NMR spectrum at 183 K revealed several signals of varying intensity, Fig. 5; the ^1H NMR spectrum at 213 K showed twelve signals for the $SiMe_3$ groups indicating the existence of six isomers. The ^1H NMR spectrum at 333 K clearly showed the C(H) fragments, including the vinylic coupling for $C(H)C(H)R$ ($^3J_{HH} = 15.9$ Hz). Variable temperature NMR spectroscopic experiments indicated the existence of a complex equilibrium between several oligomers. This equilibrium was absent after the addition of tetrahydrofuran. Synthesis of the solvent-free analogue, the 1,7,7-tris(trimethylsilyl)-1,3,5-triazaheptatrienyllithium compound, from 1/2 $[LiCR_3]_2$ and 1,3,5-triazine **1**, showed similar behaviour in NMR spectroscopic experiments.

The pathway leading stereospecifically to the *trans*-product **4**, **5** or **7** is believed to implicate the 1,4-addition of the lithium reagent to triazine **1** forming the 1,4-dihydrotriazinyllithium complex, analogous to **2**, followed successively by a 1,3-Me_3Si shift from NR_2 or CR_3 and then its ring-scission. This is illustrated for the system **1** + $LiNR_2 \longrightarrow$ **4** in Scheme 2.

Table 1 Selected intramolecular distances (Å) and angles (°) for $[Li_3\{RNC(H)NC(H)NC(H)NR\}_3]$ **4**

Li(1)–N(1)	2.117(7)	N(1)–C(1)	1.281(4)
Li(1)–N(5)	2.123(7)	C(1)–N(2)	1.371(4)
Li(1)···N(9)	2.461(7)	N(2)–C(2)	1.327(4)
Li(1)–N(10)	2.077(7)	C(2)–N(3)	1.313(5)
Li(2)–N(2)	1.968(7)	N(3)–C(3)	1.377(4)
Li(2)–N(6)	2.079(7)	C(3)–N(4)	1.274(5)
Li(2)–N(7)	2.077(7)	N(5)–C(10)	1.280(4)
Li(2)–N(11)	1.972(7)	C(10)–N(6)	1.358(4)
Si(1)–N(1)	1.747(3)	N(6)–C(11)	1.328(4)
Si(1)–C(4)	1.856(4)	C(11)–N(7)	1.317(4)
Si(3)–N(5)	1.742(3)	N(7)–C(12)	1.365(4)
Si(3)–C(13)	1.844(5)	C(12)–N(8)	1.281(4)
N(1)–Li(1)–N(5)	123.5(3)	Li(1)–N(5)–C(10)	102.9(3)
N(1)–Li(1)–N(10)	107.9(3)	Li(2)–N(6)–C(10)	154.2(3)
N(5)–Li(1)–N(10)	125.3(3)	Li(2)–N(6)–C(11)	87.1(3)
N(2)–Li(2)–N(6)	110.2(3)	Si(3)–N(5)–C(10)	121.6(3)
N(2)–Li(2)–N(7)	124.4(4)	N(5)–C(10)–N(6)	122.0(3)
N(2)–Li(2)–N(11)	115.0(3)	N(6)–C(11)–N(7)	118.7(3)
N(6)–Li(2)–N(7)	66.4(2)		



Scheme 2 Reaction pathway for **1** + $LiNR_2$ to 1,3,5,7-tetraazaheptatrienyllithium **4**.

Evidence for the Meisenheimer complex **I** (or its CR_3 analogue for **5**) is supported by NMR spectroscopic experiments involving treatment of an excess of 1,3,5-triazine **1** with $LiNR_2$ in benzene-d_6. Apart from **4**, the formation of an intermediate **I** was observed, having chemical shifts and coupling patterns resembling those of the dihydrotriazines **3**; ^1H δ 7.37 (d, $^4J = 2.1$ Hz, 2H), 6.60 (t, 1H), 1.01 (s, 18H). Additionally, we have isolated the analogous intermediate $[Na\{\overline{NC(H)NC(H)(CHR_2)NC}H\}(pmdien)]_2$ from **1** and $NaCHR_2$.[21] Precedents exist for anionic 1,3-Me_3Si shifts from N→N[22] or C→N.[6]

Each of the lithium compounds **4**–**7** was characterised by X-ray crystallography. The X-ray molecular structure of the crystalline tetraazaheptatrienyllithium compound **4**, with atom labelling, is shown in Fig. 1, selected geometric parameters being in Table 1. The projection down its Li–Li–Li axis shows it to have close to C_3-symmetry, Fig. 6. The lithium compound **4** has a rather unusual structure. Three lithium atoms form a cationic rod surrounded by the three negatively charged ligands. The atoms Li(1) and Li(3) are both three-coordinate, with the sum of the angles at each being 354.7 and 355.5°, respectively, while Li(2) is four-coordinate with a bond angle of

Table 2 Selected intramolecular distances (Å) and angles (°) for [Li$_2${RNC(H)NC(H)NC(H)CR$_2$}$_2$(μ-thf)] **5**

Li–O	2.133(7)	Si(3)–N(3)	1.738(3)
Li–N(1)	2.197(7)	Si(3)–C(11)	1.863(5)
Li–N(2)	2.096(7)	C(1)–C(2)	1.351(5)
Li′–N(3)	2.058(7)	C(2)–N(1)	1.406(4)
Si(1)–C(1)	1.854(4)	N(1)–C(3)	1.303(4)
Si(1)–C(5)	1.858(5)	C(3)–N(2)	1.346(4)
Si(2)–C(1)	1.867(4)	N(2)–C(4)	1.346(4)
Si(2)–C(8)	1.866(4)	C(4)–N(3)	1.292(4)
N(1)–Li–N(2)	63.9(2)	C(2)–C(1)–Si(1)	116.5(3)
N(1)–Li–N(3′)	115.3(3)	N(1)–C(2)–C(1)	124.6(4)
N(1)–Li–O	114.0(3)	C(2)–N(1)–C(3)	116.2(3)
Li–O–Li′	77.4(4)	N(1)–C(3)–N(2)	118.2(3)
Si(1)–C(1)–Si(2)	123.8(2)	N(2)–C(4)–N(3)	120.5(3)
		C(4)–N(3)–Si(3)	122.8(3)

Table 3 Selected intramolecular distances (Å) and angles (°) for [Li{RNC(H)NC(H)NC(H)CR$_2$}(pmdien)] **6**

Li–N(1)	2.135(11)	Si(3)–C(4)	1.864(6)
Li–N(2)	2.147(10)	Si(3)–C(9)	1.870(6)
Li–N(4)	2.113(6)	N(1)–C(1)	1.287(7)
Li–N(5)	2.219(11)	C(1)–N(2)	1.346(7)
Si(1)–N(1)	1.730(5)	N(2)–C(2)	1.335(7)
Si(1)–C(5)	1.850(5)	C(2)–N(3)	1.296(7)
Si(2)–C(4)	1.849(6)	N(3)–C(3)	1.390(7)
Si(2)–C(8)	1.869(5)	C(3)–C(4)	1.351(8)
N(1)–Li–N(2)	64.8(3)	Si(1)–N(1)–C(1)	124.5(4)
N(1)–Li–N(4)	117.3(3)	Si(2)–C(4)–Si(3)	124.5(3)
N(1)–Li–N(5)	114.9(5)	Si(2)–C(4)–C(3)	118.4(5)
N(2)–Li–N(4)	97.6(3)	N(1)–C(1)–N(2)	121.1(5)
N(2)–Li–N(5)	179.6(5)	C(1)–N(2)–C(2)	117.0(5)
N(4)–Li–N(4′)	124.6(5)	N(2)–C(2)–N(3)	124.1(5)
N(4)–Li–N(5)	82.6(3)	N(3)–C(3)–C(4)	126.2(6)

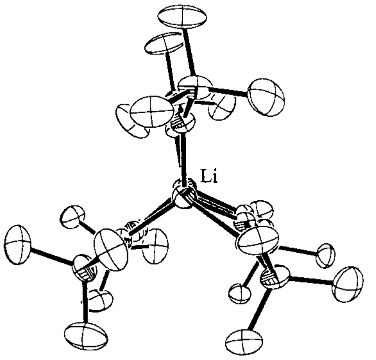


Fig. 6 Projection of the trinuclear complex **4** down its Li–Li–Li axis.

66.4(2)° for N(6)–Li(2)–N(7) and between 110 and 125° for the other N–Li(2)–N′ angles. The Li–N bond distances are 2.10 ± 0.02 Å, except for the Li(2)–N(2) and Li(2)–N(11) which are significantly shorter, *ca.* 1.97 Å. The organic backbone is planar. A zig-zag conformation for the anionic ligand has been predicted to be the most stable.[23] The intraligand C–N bond lengths are unremarkable, 1.28 Å for N(1)–C(1) [C(sp^2)=N(sp^2)], 1.37 Å for C(1)–N(2) [C(sp^2)–N(sp^2)] and 1.33 Å for C(2)–N(2) [delocalised C(sp^2)$\cdots$N(sp^2)].

The X-ray molecular structure of the crystalline lithium compound **5**, with atom labelling is shown in Fig. 2; selected molecular parameters are in Table 2. Compound **5** is dinuclear and lies on a crystallographic two-fold rotation axis. The lithium atoms are four-coordinate and bridged by a thf molecule, a rare phenomenon.[24] Each Li–O distance is *ca.* 2.13 Å and the Li–O–Li′ angle 77°. The Li–N distances range from 2.06 to 2.20 Å with Li–N(3′) being the shortest. The N(1)–Li–N(2), N(1)–Li–N(3′) and N(2)–Li–N(3′) angles are 64, 115 and 125°, respectively. The atoms C(1), C(2), N(1), C(3), N(2), C(4) and N(3) are coplanar and comparison of the bond lengths with known formamidinates[16,25,26] suggests that the NC(H)NC(H)N unit has some delocalisation, while the values of 1.41 Å for N(1)–C(2) and 1.35 Å for C(2)–C(1) are unexceptional for a N(sp^2)–C(sp^2) and C(sp^2)=C(sp^2) bond, respectively.[27]

Table 4 Selected intramolecular distances (Å) and angles (°) for [Li$_4${RNC(H)NC(H)NC(H)C(H)R}$_4$] **7**

Li(1)–N(1)	2.019(5)	N(1)–C(1)	1.292(3)
Li(1)–N(5)	2.118(5)	C(1)–N(2)	1.355(3)
Li(1)–N(5′)	2.157(5)	N(2)–C(2)	1.345(3)
Li(2)–N(3)	2.026(5)	C(2)–N(3)	1.297(3)
Li(2)–N(4′)	2.041(5)	N(3)–C(3)	1.399(3)
Li(2)–N(6)	2.080(5)	C(3)–C(4)	1.316(4)
Si(1)–N(1)	1.735(2)	N(4)–C(11)	1.281(3)
Si(1)–C(5)	1.857(3)	C(11)–N(5)	1.370(3)
Si(2)–C(4)	1.841(3)	N(5)–C(12)	1.345(3)
Si(2)–C(8)	1.862(4)	C(12)–N(6)	1.305(3)
Si(3)–N(4)	1.756(2)	N(6)–C(13)	1.406(3)
Si(3)–C(15)	1.856(3)	C(13)–C(14)	1.331(4)
N(1)–Li(1)–N(5)	124.8(3)	Si(3)–N(4)–C(11)	121.6(2)
N(1)–Li(1)–N(5′)	134.0(3)	N(1)–C(1)–N(2)	121.9(2)
N(5)–Li(1)–N(5′)	99.4(2)	C(1)–N(2)–C(2)	115.7(2)
N(3)–Li(2)–N(6)	117.8(3)	N(2)–C(2)–N(3)	119.6(2)
N(3)–Li(2)–N(4′)	117.6(2)	N(3)–C(3)–C(4)	124.7(3)
N(4′)–Li(2)–N(6)	121.2(2)	N(4)–C(11)–N(5)	122.9(2)
Si(1)–N(1)–Li(1)	139.3(2)	N(5)–C(12)–N(6)	121.0(2)
Si(1)–N(1)–C(1)	123.3(2)	N(6)–C(13)–C(14)	124.2(3)
Si(2)–C(4)–C(3)	127.6(2)		

The X-ray molecular structure of the crystalline pmdien adduct **6** of **5** shows it to be mononuclear and to lie on a crystallographic mirror plane, Fig. 3; selected molecular parameters are in Table 3. The bond lengths in the anionic organic backbone are comparable with those of **5** showing some delocalisation in the NC(H)NC(H)N unit. The lithium atom is five-coordinate, capped by the chelating pmdien ligand with distances of *ca.* 2.11 Å for Li–N(4), 2.22 Å for Li–N(5) and 2.14 Å to both N(1) and N(2); the bite angle N(1)–Li–N(2) is 64.8(3)°.

The X-ray molecular structure of the crystalline lithium complex **7** shows it to be tetranuclear lying on a crystallographic inversion centre, Fig. 4; selected molecular parameters are in Table 4. There are two distinct ligands in the tetramer. One binds with two of its remote nitrogen atoms, N(1) and N(3), to the lithium atoms, while the other uses all three nitrogen atoms for coordination. This does not significantly affect the bond lengths or angles, consistent with the electrostatic nature of the interactions between the anionic heptatrienyl ligands and the cationic lithium atoms. The bond lengths of the anionic backbone show similar distances to those of **5** and **6**, a partly delocalised NC(H)NC(H)N unit. The lithium atoms Li(1) and Li(2) are both three-coordinate, the sum of the angles at these being 358.2 and 356.6°, respectively. The angles N(5′)–Li(1)–N(2) and N(5′)–Li(1)–N(5) are the narrower, *ca.* 99°, thus keeping the ligands together. The Li–N distances range from *ca.* 2.02 Å [Li(1)–N(1) and Li(2)–N(3)] to 2.16 Å for Li(1)–N(5′), while there may be additional stabilising interactions between lithium and nitrogen atoms; for example the Li(1)–N(6′) distance is *ca.* 2.37 Å.

The X-ray structures show that the bond lengths in the anionic organic backbone are more or less independent of the location and bonding of the lithium cations. This suggests that the formation of the aggregates is largely governed by electrostatic interactions, the nitrogen atoms providing ample opportunities for coordination in solution and in the solid state. In solution the trinuclear structure of **4** is retained, while each of the solvent-free bis- and tris-(trimethylsilyl)-1,3,5-triazaheptatrienyllithium complexes appear to form a complicated mixture of oligomers.

Table 5 Crystal data and refinement parameters for lithium compounds **4**–**7**

Formula	$C_{27}H_{63}Li_3N_{12}Si_6\cdot(C_5H_{12})_{\frac{1}{2}}$ **4**	$C_{30}H_{68}Li_2N_6OSi_6$ **5**	$C_{22}H_{53}LiN_6Si_3$ **6**	$C_{40}H_{88}Li_4N_{12}Si_8$ **7**
M	781.3	711.3	492.91	989.70
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2/n$ (no. 13)	*P*nma (no. 62)	$P\bar{1}$ (no. 2)
a/Å	18.869(7)	13.022(3)	28.389(5)	10.047(3)
b/Å	14.603(4)	8.134(4)	11.343(2)	12.148(4)
c/Å	19.523(4)	22.607(6)	10.290(2)	13.646(3)
α/°				82.42(2)
β/°	112.10(2)	106.43(2)		76.68(2)
γ/°				76.74(2)
U/Å^3	4984(3)	2296.8(14)	3313.5(10)	1572.0(8)
Z	4	2	4	1
μ(Mo-Kα)/cm^{-1}	2.0	2.1	1.6	2.1
Reflections collected	9027	4220	4037	5516
Independent reflections (R_{int})	8753 (0.0334)	4041 (0.0347)	2149 (0.0907)	5516
Reflections observed [$I > 2\sigma(I)$]	5240	2570	1400	4010
*R*1 [$I > 2\sigma(I)$], *wR*2 all data	0.061, 0.161	0.062, 0.162	0.061, 0.158	0.048, 0.124

Experimental

General procedures

All manipulations of organometallic compounds were performed under an argon atmosphere using standard Schlenk techniques. Solvents were pre-dried over sodium wire and distilled over potassium–sodium alloy under nitrogen gas. Hexane, pentane and benzene were stored over a potassium mirror, while tetrahydrofuran, diethyl ether and deuterated solvents were stored over molecular sieves (4 Å). $[LiCR_3]_2$,[28] $[Li(thf)_4]\{Li[C(SiMe_3)_3]_2\}$,[29] $[LiCH(SiMe_3)_2]_\infty$[30] and $[LiN(SiMe_3)_2]_3$[31] were prepared by established procedures. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (tmen) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdien) were obtained from Aldrich and were distilled over CaH_2 prior to use. 1,3,5-Triazine **1** (Aldrich) was used without further purification.

Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex or the Canadian Micro-analytical Service Ltd., Delta, Canada. The NMR spectra were recorded using a WM-300 Bruker at 300.13 MHz (^1H), 75.42 [$^{13}C\{^1H\}$], 116.64 [$^7Li\{^1H\}$], or an AMX-500 Bruker spectrometer at 500 MHz (^1H) at *ca.* 295 K in benzene-d_6 and referenced internally to residual solvent resonances unless stated otherwise, EI mass spectra on solid samples were obtained using a Kratos MS80RF spectrometer. Melting points were determined under argon in sealed capillary tubes using an electrothermal apparatus and are uncorrected.

Syntheses

[1,7-Bis(trimethylsilyl)hepta-1,3,5,7-tetraaza-1,4,6-trienyllithium]$_3$ 4. Triazine **1** (1.62 g, 20.0 mmol) was added in portions to a stirred solution of $[LiNR_2]_3$ (3.39 g, 6.8 mmol) in benzene (30 cm^3) with cooling (waterbath at ambient temperature). After stirring for 2½ h at ambient temperature, volatiles were evaporated *in vacuo* and the residue was "stripped" with pentane and carefully dried *in vacuo*. Pentane (30 cm^3) was added and the solution was kept at −20 °C. This yielded analytically pure, colourless crystals (1.66 g); a second and a third fraction gave another 1.96 g to give a total for **4** of 3.62 g (70%). In a typical procedure for molecular weight determination, a sample of **4** (0.3854 g) was dissolved in benzene (20.0 cm^3) resulting in a decrease of 0.176 K for the melting point: $M_w = 641$. Recrystallisation from pentane yielded colourless single crystals of **4**, suitable for X-ray analysis, mp 188 °C (with decomp.) (Found: C, 44.4; H, 8.64; N, 22.2. $C_{27}H_{63}Li_3N_{12}Si_6$ requires C, 43.5; H, 8.52; N, 22.55%). ^1H NMR: δ 8.24 (s, 6H), 7.85 (s, 3H), 0.37 (s, 54H, SiMe$_3$). $^7Li\{^1H\}$ NMR: δ 3.13 (1Li), 1.94 (2Li). $^{13}C\{^1H\}$ NMR: δ 177.8 [N*C*(H)N], 170.5 [RN*C*(H)], 0.85 (SiMe$_3$). Mass spectrum (EI): *m*/*z* 503 ([*M* − L]$^+$, 18), 255 ([*M* − L$_2$Li]$^+$, 10), 242 ([L + H]$^+$, 8).

[1,7,7-Tris(trimethylsilyl)hepta-1,3,5-triaza-1,4,6-trienyllithium]$_2$(μ-thf) 5. Triazine **1** (0.70 g, 8.6 mmol) was added in portions to a stirred solution of $[Li(thf)_4][Li(CR_3)_4]_2$ (3.33 g, 4.2 mmol) in benzene (30 cm^3) with cooling (waterbath at ambient temperature). After stirring for 48 h at ambient temperature, volatiles were evaporated *in vacuo* and the pale yellow residue was "stripped" with pentane. Crystallisation from pentane at −20 °C afforded analytically pure yellow crystals of compound **5** (1.17 g, 38%). Recrystallisation from pentane yielded colourless, single crystals, suitable for X-ray analysis, mp 111–113 °C (Found: C, 48.8; H, 9.45; N, 12.7. $C_{26}H_{60}Li_2N_6Si_6$ requires C, 48.9; H, 9.46; N, 13.15%). ^1H NMR: δ 8.20 [s, 2H, RNC(*H*)N], 7.89 [br s, 2H, C(H)NC(*H*)NC(H)], 7.47 [s, 2H, NC(*H*)CR$_2$], 3.59 (ddd, 4H, thf), 1.41 (ddd, 4H, thf), 0.36 (s, 18H, SiMe$_3$), 0.33 (s, 18H, SiMe$_3$), 0.17 (s, 18H, SiMe$_3$). $^7Li\{^1H\}$ NMR: δ 1.40. $^{13}C\{^1H\}$ NMR: δ 171.5, 169.95, 159.8, 121.7 (*ipso*), 68.1 (thf), 25.65 (thf), 2.7 (SiMe$_3$), 1.2 (SiMe$_3$), 0.3 (SiMe$_3$). Mass spectrum (EI): *m*/*z* 638 ([*M* − thf]$^+$, 13), 565 ([*M* − thf − SiMe$_3$]$^+$, 12), 326 ([*M* − L − thf]$^+$, 38).

1,7,7-Tris(trimethylsilyl)hepta-1,3,5-triaza-1,4,6-trienyllithium. The procedure followed was similar to that for **5**, but with triazine **1** (0.21 g, 2.6 mmol) and $[LiCR_3]_2$ (0.62 g, 1.3 mmol) in benzene (15 cm^3). The title compound (0.41 g, 49%) was obtained as a yellow powder from pentane, mp 101–104 °C. ^1H NMR ($C_6D_5CD_3$, 343 K): δ 8.24 (s, 1H), 7.90 (br s, 1H), 7.28 (s, 1H), 0.17 (s, 18H), 0.07 (s, 9H). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 323 K): δ 170.6, 170.2, 158.7, 123.5 (*ipso*), 2.7 (SiMe$_3$), 1.1 (SiMe$_3$), 0.2 (SiMe$_3$).

1,7,7-Tris(trimethylsilyl)hepta-1,3,5-triaza-1,4,6-trienyllithium(pmdien) 6. Pmdien (160 mm^3, 0.77 mmol) was added to a solution of the 1,3,5-triazaheptatrienyllithium **5** (0.27 g, 0.4 mmol) in pentane (1 cm^3) at ambient temperature. After 20 min, volatiles were removed *in vacuo*. Recrystallisation from pentane yielded colourless single crystals of **6** (0.25 g, 66%), suitable for X-ray analysis, mp 122 °C (Found: C, 53.6; H, 10.7; N, 17.4. $C_{22}H_{53}LiN_6Si_3$ requires C, 53.6; H, 10.8; N, 17.0%). ^1H NMR: δ 8.57 (br s, 1H), 8.36 (s, 1H), 7.87 (s, 1H), 2.11 (s, 3H), 2.07 (s, 12H), 1.8 (br s, 8H), 0.60 (s, 9H), 0.40 (s, 9H), 0.17 (s, 9H). $^7Li\{^1H\}$ NMR: δ 0.91. $^{13}C\{^1H\}$ NMR: δ 173, 172.5, 166.3, 117 (*ipso*), 56.3 (pmdien), 53.8 (pmdien), 45.1 (pmdien), 43.9 (pmdien), 2.4 (SiMe$_3$), 1.5 (SiMe$_3$), 0.8 (SiMe$_3$).

[1,7-Bis(trimethylsilyl)hepta-1,3,5-triaza-1,4,6-trienyllithium]$_4$ 7. Triazine **1** (0.69 g, 8.5 mmol) was added in portions to a stirred solution of $[LiCHR_2]_\infty$ (1.41 g, 8.5 mmol) in benzene (25 cm^3) with cooling (waterbath at ambient temperature). Stirring was continued for 12 h; volatiles were removed *in vacuo*. The resulting green/white powder (2.05 g) was heated to 140 °C under reduced pressure (*ca.* 10^{-3} mbar) for *ca.* 5 min. Crystallisation of the brown/yellow residue from diethyl ether and recrystallisation from hexane at ambient temperature yielded colourless single crystals of compound **7** (1.44 g, 70%), suitable for X-ray analysis, mp 188–191 °C (with decomp.) (Found: C, 48.3; H, 8.94; N, 16.8. $C_{40}H_{88}Li_4N_{12}Si_8$ requires C, 48.55; H, 8.96; N, 17.0%). ^{1}H NMR (348 K): δ 8.21 [s, 4H, RNC(*H*)N], 7.80 [s, 4H, C(H)NC(*H*)N], 6.79 [d, $^3J = 15.9$ Hz, 4H, C(H)C*H*R], 5.63 [d, 4H, C(*H*)CHR], 0.31 (s, 36H), 0.26 (s, 36H). ^{13}C{^{1}H} NMR (333 K): δ 171.5 (br), 171.3 (br), 151.7, 114 (br, *C*HR), 0.3 ($SiMe_3$), −0.6 ($SiMe_3$). ^{7}Li{^{1}H} NMR (333 K): δ 1.49. Mass spectrum (EI): *m*/*z* 221 (18), 168 (6), 148 (80), 82 (85), 70 (88), 28 (100).

X-Ray crystallography

Details are given in Table 5. Unique datasets for compounds **4**–**7** were collected on an Enraf-Nonius CAD4 diffractometer at 173(2) K. The structures were solved *via* direct methods using SHELXS 86,[32] and refined by full-matrix least squares on all F^2 using SHELXL 93[33] with all non-H atoms anisotropic; H's were included in riding mode with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C)$ for methyl groups.

CCDC reference number 186/1687.

See http://www.rsc.org/suppdata/dt/1999/4041/ for crystallographic files in .cif format.

Acknowledgements

We thank Dr A. G. Avent for the variable temperature NMR spectroscopic experiments, Dr A. Abdul-Sada for the mass spectra, the European Community for a Human Capital and Mobility grant (category 20) for W. M. B. and EPSRC for other support.

References

1 C. Grundmann, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 309; A. Kreutzberger, *Fortschr. Chem. Forsch.*, 1963, **4**, 273.

2 A. Kreutzberger, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 940.

3 F. C. Schaefer, *J. Org. Chem.*, 1962, **27**, 3608.

4 D. R. Armstrong, W. Clegg, M. MacGregor, R. E. Mulvey and P. A. O'Neil, *J. Chem. Soc., Chem. Commun.*, 1993, 608; D. R. Armstrong, K. W. Henderson, M. MacGregor, R. E. Mulvey, M. J. Ross, W. Clegg and P. A. O'Neil, *J. Organomet. Chem.*, 1995, **486**, 79; W. Clegg, M. R. J. Elsegood, L. Horsburgh, R. E. Mulvey and M. J. Ross, *Chem. Ber.*, 1997, **130**, 621.

5 A. W. Cordes, C. D. Bryan, W. M. Davis, R. H. de Laat, S. H. Glarum, J. D. Goddard, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, S. R. Scott and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1993, **115**, 7232.

6 M. F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 1995, **500**, 203.

7 L. S. Cook, G. Prudhoe, N. D. Venayak and B. J. Wakefield, *J. Chem. Res. (S)*, 1982, 113.

8 A. L. Weis, *Adv. Heterocycl. Chem.*, 1985, **38**, 91.

9 W. M. Boesveld, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1997, 2091.

10 B. J. Wakefield, *Best Synthetic Methods: Organolithium Methods*, Academic Press, London, 1988; L. Brandsma and H. Verkuijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin, 1987.

11 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, in *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980.

12 W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353; K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167.

13 F. E. Romesberg and D. B. Collum, *J. Am. Chem. Soc.*, 1992, **114**, 2112; D. B. Collum, *Acc. Chem. Res.*, 1993, **26**, 227; B. L. Lucht, M. P. Bernstein, J. F. Remenar and D. B. Collum, *J. Am. Chem. Soc.*, 1996, **118**, 10707; T. Koizumi, K. Morihashi and O. Kikuchi, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 305 and references cited therein.

14 J. Arnold, *J. Chem. Soc., Chem. Commun.*, 1990, 976; J. Arnold, D. Y. Dawson and C. G. Hoffman, *J. Am. Chem. Soc.*, 1993, **115**, 2707; U. Piarulli, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1996, **118**, 3634.

15 H. Homborg and C. L. Teske, *Z. Anorg. Allg. Chem.*, 1985, **527**, 45; H. Sugimoto, M. Mori, H. Masuda and T. Taga, *J. Chem. Soc., Chem. Commun.*, 1986, 962; B. Assmann, A. Franken and H. Homborg, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1715; B. Latte, B. Assmann and H. Homborg, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1281.

16 J. Barker, D. Barr, N. D. R. Barnett, W. Clegg, I. Cragg-Hine, M. G. Davidson, R. P. Davies, S. M. Hodgson, J. A. K. Howard, M. Kilner, C. W. Lehmann, I. Lopez-Solera, R. E. Mulvey, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1997, 951; M. S. Eisen and M. Kapon, *J. Chem. Soc., Dalton Trans.*, 1994, 3507; D. Stalke, M. Wedler and F. T. Edelmann, *J. Organomet. Chem.*, 1992, **431**, C1.

17 T. Gebauer, K. Dehnicke, H. Goesmann and D. Fenske, *Z. Naturforsch., Teil B*, 1994, **49**, 1444.

18 L. M. Engelhardt, G. E. Jacobson, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 1011; D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 469; R. Kempe, A. Spannenberg and S. Brenner, *Z. Kristallogr.*, 1996, **211**, 567; M. Polamo and M. Leskelä, *J. Chem. Soc., Dalton Trans.*, 1996, 4345.

19 P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 1699; H. Gornitzka and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 693; H. Gornitzka and D. Stalke, *Organometallics*, 1994, **13**, 4398; F. S. Mair, D. Scully, A. J. Edwards, P. R. Raithby and R. Snaith, *Polyhedron*, 1995, **14**, 2397; D. G. Black, D. C. Swenson, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3539; B.-J. Deelman, M. F. Lappert, H.-K. Lee, T. C. W. Mak, W.-P. Leung and P.-R. Wei, *Organometallics*, 1997, **16**, 1247.

20 W. M. Boesveld, P. B. Hitchcock and M. F. Lappert, manuscript in preparation

21 W. M. Boesveld and M. F. Lappert, unpublished work; W. M. Boesveld, D.Phil. Thesis, University of Sussex, 1999.

22 R. T. Boeré, R. T. Oakley and R. W. Reed, *J. Organomet. Chem.*, 1987, **331**, 161; M. Wedler, F. Knösel, M. Noltemeyer and F. T. Edelmann, *J. Organomet. Chem.*, 1990, **388**, 21.

23 M. Schlosser, O. Desponds, R. Lehmann, E. Moret and G. Rauchschwalbe, *Tetrahedron*, 1993, **49**, 10175; A. Beckmann, R. Fröhlich and E.-U. Würthwein, *Tetrahedron Lett.*, 1997, **38**, 5481; M. Könemann, G. Erker, R. Fröhlich and E.-U. Würthwein, *J. Am. Chem. Soc.*, 1997, **119**, 11155; A. Krol, R. Fröhlich and E.-U. Würthwein, *Chem. Commun.*, 1998, 485.

24 Examples of μ-thf in lithium chemistry: H.-J. Gais, J. Vollhardt, H. Günther, D. Moskau, H. J. Lindner and S. Braun, *J. Am. Chem. Soc.*, 1988, **110**, 978; H. Zhang, Y. Wang, A. K. Saxena, A. R. Oki, J. A. Maguire and N. S. Hosmane, *Organometallics*, 1993, **12**, 3933; G. Boche, C. Boie, F. Bosold, K. Harms and M. Marsch, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 115; W. Clegg, L. Horsburgh, F. M. Mackenzie and R. E. Mulvey, *J. Chem. Soc., Chem. Commun.*, 1995, 2011.

25 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.

26 Recent examples: F. A. Cotton, J. H. Matonic and C. A. Murillo, *Inorg. Chem.*, 1996, **35**, 498; F. A. Cotton, S. C. Haefner, J. H. Matonic, X. Wang and C. A. Murillo, *Polyhedron*, 1997, **16**, 541.

27 M. Burke-Laing and M. Laing, *Acta Crystallogr., Sect. B*, 1976, **32**, 3216.

28 W. Hiller, M. Layh and W. Uhl, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 324.

29 C. Eaborn, P. B. Hitchcock, J. D. Smith and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1983, 827.

30 J. L. Atwood, T. Fjeldberg, M. F. Lappert, N. T. Luong-Thi, R. Shakir and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 1163.

31 D. Mootz, A. Zinnius and B. Böttcher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 378.

32 G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, p. 175.

33 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Paper 9/07375B