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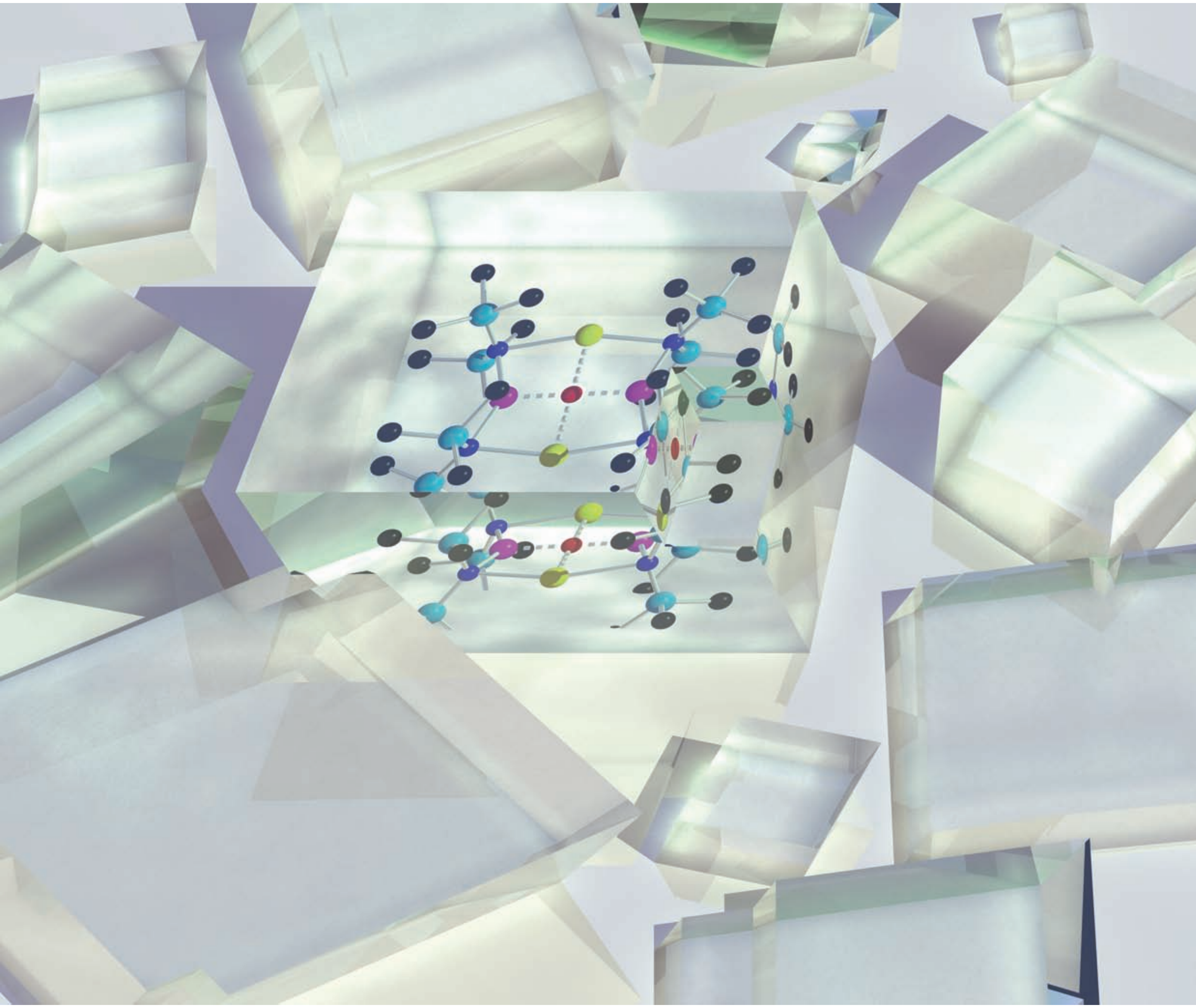

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Manganese(II)–lithium and –sodium inverse crown ether (ICE) complexes†

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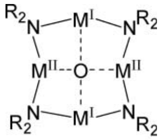
Extending to transition metals, the class of compounds known as inverse crown ethers, two mixed alkali metal–manganese(II) amide ring compounds with oxo cores have been synthesised and crystallographically characterised, together with an oxo-free alkyl-amido precursor.

Inverse crown ethers (ICEs) of general structural type **I**, a special category of heterobimetallic compound,[1] are known for their mixed alkali metal–magnesium (M$^{\rm I}$ = Li or Na, M$^{\rm II}$ = Mg, NR$_2$ = TMP or HMDS; M$^{\rm I}$ = K, M$^{\rm II}$ = Mg, NR$_2$ = HMDS)[2] and alkali metal–zinc (M$^{\rm I}$ = Na or K, M$^{\rm II}$ = Zn, NR$_2$ = HMDS)[3] combinations (TMP = 2,2,6,6-tetramethylpiperidide; HMDS = 1,1,3,3-hexamethyldisilazide).



I

Strictly, these are mixed metal, mixed ligand oxo-amido or peroxo-amido compounds, not organic ethers, but are loosely labelled inverse crown 'ethers' due to their topological similarity (but with interchanged Lewis acidic/Lewis basic positions) to conventional crown ether complexes (alternatively these complexes can be called mixed metal amide crowns or MMACs). Recently, we have developed[4,5] mixed alkali metal–manganese(II) reagents that closely resemble mixed alkali metal–magnesium and –zinc reagents in their structural constitutions and behaviour in deprotonative metallation reactions (in general, referred to as alkali–metal-mediated metallation). The possibility of extending this similarity to ICEs of Mn(II) through the moisture or oxygen exposure of suitable reagents (the methodology used to prepare Mg and Zn ICEs) seemed remote, as Wilkinson *et al.* had previously noted[6] that bis(trimethylsilylmethyl)manganese, Mn(CH$_2$SiMe$_3$)$_2$ (the Mn bis(alkyl) compound employed successfully in our previous mixed metal work), suffers oxidation to Mn(IV) under such exposure. However, such pessimism discounted the special properties that can be conferred on other metals when they are combined with alkali metals. Thus, as reported herein, in practice, we find that lithium– and sodium–manganese(II) ICEs can be readily synthesised. Furthermore, we present compelling evidence that these first transition metal (d-block) additions to the ICE family are formed through a redox reaction, in which molecular oxygen is reduced to oxide and the alkyl Me$_3$SiCH$_2^-$ (R$^-$) ligand is oxidatively coupled to give R–R.

Serendipity was at play in the synthesis of the first Mn(II) ICE complex, [Li$_2$Mn$_2$(TMP)$_4$(O)] (**1**).‡ When re-preparing the heteroleptic Mn(II) reagent [(TMEDA)Li(TMP)(R)Mn(R)] (**2**), which we designed previously[4] to effect the direct manganation of ferrocene, we noted that the usual pale yellow toluene solution turned purple, then reverted back to pale yellow upon standing, before finally depositing colourless needle-like crystals. From experience, we know that **2** must be prepared under stringent inert atmosphere conditions, and that the appearance of a purple colour signifies the unintentional intrusion of air into the solution. The surprising discovery, revealed by X-ray crystallography,§ that the crystals were of **1** strongly implies that the adventitious air (oxygen) had been consumed in the reaction, consistent with the disappearance of the purple colouration, to ultimately produce the oxo core of the new ICE. Its molecular structure (Fig. 1) is centrosymmetric, comprising a near-square of TMP N atoms, the N···N edges of which are bisected by metal atoms to give overall a (LiNMnN)$_2$ eight-membered ring that surrounds an oxide (O^{2-}) core. Without the core anion, the structure resembles the tetrameric arrangement

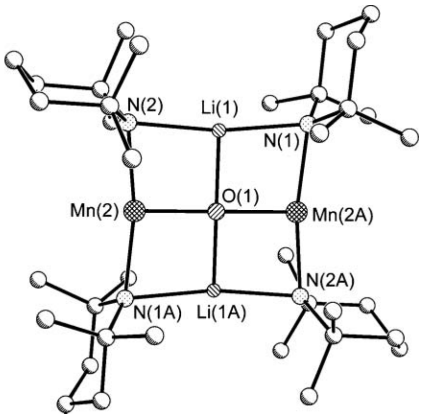


Fig. 1 Molecular structure of **1** with hydrogen atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and bond angles (°): Li(1)–O(1) 1.9334(6), Mn(2)–O(1) 1.9368(5), Li(1)–N(1) 2.1311(17), Li(1)–N(2) 2.1344(17), Mn(2)–N(1) 2.1266(18), Mn(2)–N(2) 2.0995(17); Li(1)–O(1)–Mn(2) 90.26(5), Mn(2)–O(1)–Mn(2A) 180.00(2), O(1)–Li(1)–N(1) 94.73(5), O(1)–Li(1)–N(2) 94.47(5). Symmetry operator A: $-x$, ½ $-y$, $1-z$.

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† Electronic supplementary information (ESI) available: Molecular structures and crystal data of **1**, **4** and **5**; NMR spectroscopic and GC/MS characterisation of Me$_3$SiCH$_2$CH$_2$SiMe$_3$. See DOI: 10.1039/b714880a

of homometallic LiTMP,[7] but including the core anion, it is essentially identical to the structure of the aforementioned lithium–magnesium ICE $[Li_2Mg_2(TMP)_4(O)]$ (**3**).[8] Mutual substitution disorder of the Li and Mn atoms, a problem also in **3** for Li/Mg, renders invalid any discussion of the dimensions within **1**. An interesting synthetic point is that TMEDA chelation of Li in **2** does not interfere with, and is destroyed during, the reaction producing **1**.

To circumvent the metal disorder problems, we next attempted to synthesise a sodium analogue of **1**. However, subjecting mixtures of NaTMP, MnR_2 and TMPH (in keeping with the monoalkyl-bisamido composition of known sodium TMP-manganates[5]) to air, introduced *via* a drying tube, failed to yield a solid product, but instead gave an intractable purple oil, yet to be identified. Switching the amide from TMP to the less reactive HMDS proved more successful. Thus, a 1 : 1 : 1 mixture of NaHMDS, MnR_2 and HMDS(H), which initially afforded a colourless precipitate, was deliberately exposed to dry air for one hour, as described above. This exposure was accompanied by a colour change from a colourless to a dark green solution. Heating the hexane solution and re-cooling produced two distinct sets of crystals: colourless needles and light green parallelogram-shaped blocks, easily distinguishable from each other by eye. X-Ray crystallography§ revealed these crystals to be the oxygen-free monoalkyl-bisamido manganate $[\{Na(HMDS)_2Mn(R)\}_\infty]$ (**4**) and the sodium–manganese ICE $[Na_2Mn_2(HMDS)_4(O)]$ (**5**), respectively (Scheme 1).

Manganate **4**, which could be prepared rationally on its own under stringent anaerobic conditions, exists in the crystal as a zig-zag chain polymer (Fig. 2) of dinuclear $Na(\mu\text{-}HMDS)_2MnR$ units (Fig. 3) linked in a head-to-head fashion through intermolecular $Na\cdots Me(HMDS)$ interactions [Na1–C13A 2.886(2) Å; Na1–C7B 3.121(2) Å]. Alkyl R groups, terminally bound to Mn, run along opposite edges of the chain in a staggered fashion, while the polar $(metal\text{-}N)_2$ rings occupy the two central strands of the chain, again in a staggered (zig-zag) formation relative to each other. Bonding within the dinuclear ring is unsymmetrical (mean Na–N 2.457 Å; mean Mn–N 2.132 Å). In contrast to its bridging role in the TMP-manganate $[(TMEDA)Na(\mu\text{-}TMP)(\mu\text{-}R)Mn(TMP)]$,[5] "R" binds terminally to Mn in **4** [2.117(2) Å] to complete a distorted trigonal planar coordination (mean angle at Mn 119.25°), with the distortion most pronounced at N2–Mn1–N1 [103.73(5)°]. This narrowing to form the $Mn(\mu\text{-}N)_2Na$ bridge sets up intramolecular $Na\cdots Me$ [Na1–C10 2.768(2) Å; Na1–C16 2.734(2) Å] interactions to coordinatively saturate Na, significantly shorter than the propagating intermolecular examples. Interestingly, one polymorph of NaHMDS[9] also adopts an infinite chain structure (mean Na–N bond length 2.355 Å), though the repeating unit is a simple NaHMDS monomer. There is only one previously reported sodium HMDS-manganate structure, namely $[\{Na(12\text{-}crown\text{-}4)_2\}^+\ \{Mn(HMDS)_3\}^-]$,[10] the crown ether-separated nature of which leads to modestly shorter Mn–N bonds (mean, 2.070 Å) than in **4**. Ion-contacted $[(THF)Li(\mu\text{-}HMDS)_2Mn(HMDS)]$[11] provides a closer analogy, with mean Mn–N bridge bonds of 2.143 Å.

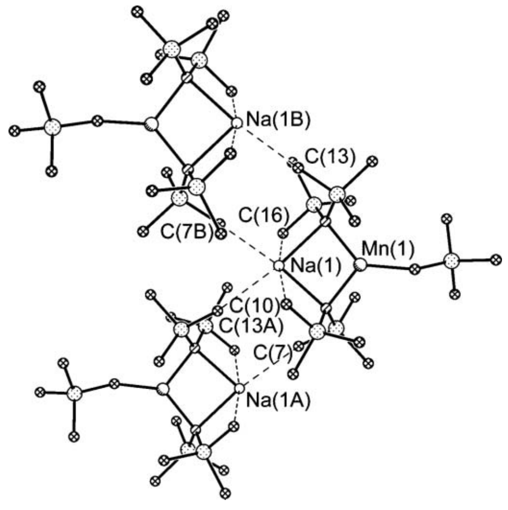


Fig. 2 Section of the polymeric chain structure of **4**, showing intramolecular and intermolecular $Na\cdots Me$ contacts as broken lines.

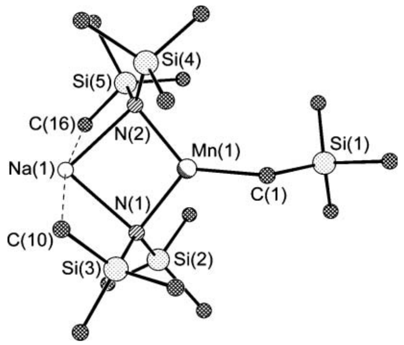
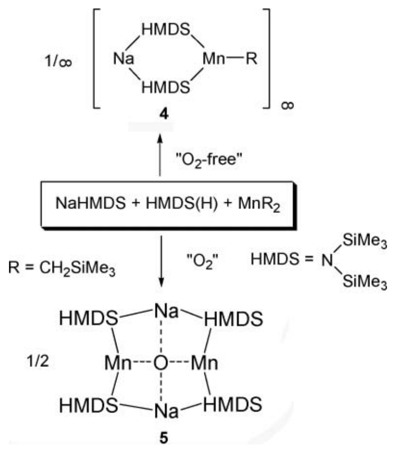


Fig. 3 Dinuclear unit of **4** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mn(1)–C(1) 2.117(2), Mn(1)–N(1) 2.1291(14), Mn(1)–N(2) 2.1345(14), Na(1)–N(1) 2.4493(15), Na(1)–N(2) 2.4655(15), Na(1)–C(10) 2.768(2), Na(1)–C(16) 2.734(2); N(1)–Mn(1)–N(2) 103.73(5), C(1)–Mn(1)–N(2) 122.66(10), C(1)–Mn(1)–N(2) 131.38(10), N(1)–Na(1)–N(2) 86.05(5).



Scheme 1 Different outcomes of the reaction, depending on whether anaerobic (top) or aerobic (bottom) conditions are employed.

The molecular structure of **5** (Fig. 4) displays the classical centrosymmetric ICE motif with alternating Na and Mn atoms, linked through N bridges in a $(NaNMnN)_2$ octagonal ring, supporting an oxide core. The smaller Mn atoms approach the core O more closely [Mn1–O1, 1.9272(2) Å] than the Na atoms [Na1–O1, 2.3262(6) Å] in the strictly planar Na_2Mn_2O

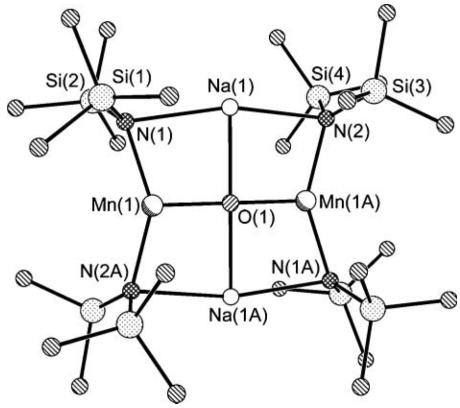
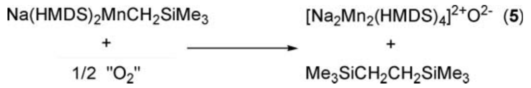


Fig. 4 Molecular structure of **5** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Na(1)–O(1) 2.3262(6), Mn(1)–O(1) 1.9272(2), Na(1)–N(1) 2.5269(13), Na(1)–N(2) 2.5627(14), Mn(1)–N(1) 2.0909(12), Mn(1)–N(2) 2.0884(12); Na(1)–O(1)–Mn(1) 91.273(16), O(1)–Na(1)–N(1) 83.54(3), O(1)–Na(1)–N(2) 81.46(3), O(1)–Mn(1)–N(1) 107.23(3), O(1)–Mn(2)–N(2) 105.36(3). Symmetry operator A: $-x$, $-y$, $1 - z$.



$$\mathrm{Na(HMDS)_2MnCH_2SiMe_3} + 1/2\ \text{"}\mathrm{O_2}\text{"} \longrightarrow [\mathrm{Na_2Mn_2(HMDS)_4}]^{2+}\mathrm{O}^{2-}\ (\mathbf{5}) + \mathrm{Me_3SiCH_2CH_2SiMe_3}$$

Scheme 2 Proposed redox reaction for the formation of ICE complex **5**.

cross-section, while the N atoms lie only 0.214 Å (for N1) or 0.266 Å (for N2) above and below this plane. Interestingly, the Na–N bonds (mean 2.545 Å) are slightly elongated and the Mn–N bonds (mean, 2.089 Å) slightly contracted in comparison to those in **4** (by 0.088 and 0.043 Å, respectively). In part, this reflects the replacement of weak Na···Me interactions by a stronger Na–O bond in the former case, and the preference of Mn for bonding to C over O in the latter case. With respect to the N atoms, the Na atoms project outwards [endocyclic N1–Na1–N2 angle 161.97(5)°] and the Mn atoms project inwards [exocyclic N1–Mn1–N2A angle 147.42(5)°] from/towards the ring. The same pattern exists in the magnesium analogue $[\mathrm{Na_2Mg_2(HMDS)_4(O)_{0.68}(O_2)_{0.32}}]$, with corresponding angles of 159.84(2) and 141.60(5)°.[8]

To gain more information on the nature of the reaction producing **5**, the synthesis was repeated, but now dry air was introduced for a longer time (2 h).‡ Subsequently, the solvent was removed under vacuum and distilled into a second Schlenk tube. Examination of this solution by ^{1}H NMR spectroscopy† showed that the major component was not the ether $(\mathrm{Me_3SiCH_2})_2\mathrm{O}$, as anticipated, but the substituted ethane $\mathrm{Me_3SiCH_2CH_2SiMe_3}$. GC-MS studies† confirmed the latter was the major product in solution. This observation of an R–R coupled product strongly suggests that ICE **5** originates from a redox process (Scheme 2).

In conclusion, the first transition metal ICE complexes have been synthesised and crystallographically characterised. While the classical filled octagonal motif of alkali metal–magnesium and –zinc ICEs is maintained in these Mn(II)-based complexes, the accessibility of several oxidation states for the latter, inaccessible to the former, should open the way to new inverse crown chemistry.

We thank the EPSRC for their generous sponsorship of this research.

Notes and references

‡ All reactions were carried out under a protective argon atmosphere unless otherwise stated.

Synthesis of $\mathit{Na(HMDS)_2Mn(CH_2SiMe_3)}$ (**4**): To a suspension of Na*n*Bu (0.16 g, 2.0 mmol) in 20 ml *n*-hexane were added two equivalents of HMDS(H) (0.84 mL, 4.0 mmol) to form a 1 : 1 mixture of NaHMDS and HMDS(H). Next, $\mathrm{Mn(CH_2SiMe_3)_2}$ (0.46 g, 2.0 mmol) was added, and the colour of the suspension changed from orange to colourless. Heating afforded a transparent, colourless solution. On cooling at 0 °C, pale pink crystals were obtained (0.72 g, 74.1%). Elemental analysis: Found: C, 39.25; H, 10.2; N, 5.7. Calc. for $\mathrm{C_{16}H_{47}MnN_2NaSi_5}$: C, 39.55; H, 9.75; N, 5.8%.

Synthesis of $\mathit{Na_2Mn_2(HMDS)_4O}$ (**5**): A suspension of **4** was prepared, as explained above. With stirring, air was allowed to enter for 1 h through a drying tube filled with $\mathrm{CaCl_2}$. The colour changed slowly to a dark green. When the stirring was stopped, a precipitate could be observed that dissolved when the solution was heated. After cooling the solution, pale pink crystals of **4** and pale green crystals of **5** were obtained.

§ Crystal data for **1**: $\mathrm{C_{36}H_{72}Li_2Mn_2N_4O}$, $M_r = 700.74$, monoclinic, space group $C2/c$, $a = 16.9678(6)$, $b = 17.0135(6)$, $c = 15.7137(5)$ Å, $\beta = 118.803(2)°$, $V = 3975.0(2)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.666$ mm^{-1}, $T = 173$ K; 28348 reflections, 3894 unique, R_{int} 0.080; final refinement to convergence on F^2 gave $R = 0.0437$ (F, 2648 obs. data only) and $R_{\mathrm{w}} = 0.0993$ (F^2, all unique data), GOF = 1.040. CCDC 662468.

Crystal data for **4**: $\mathrm{C_{16}H_{47}MnN_2NaSi_5}$, $M_r = 485.94$, triclinic, space group $P\bar{1}$, $a = 10.2226(3)$, $b = 11.9296(3)$, $c = 12.0857(3)$ Å, $\alpha = 97.180(1)$, $\beta = 100.700(1)$, $\gamma = 93.377(1)°$, $V = 1431.78(7)$ Å^3, $Z = 2$, $\lambda = 0.71073$ Å, $\mu = 0.690$ mm^{-1}, $T = 150$ K; 32095 reflections, 6576 unique, R_{int} 0.051; final refinement to convergence on F^2 gave $R = 0.0329$ (F, 5179 obs. data only) and $R_{\mathrm{w}} = 0.0774$ (F^2, all unique data), GOF = 1.021. CCDC 662469.

Crystal data for **5**: $\mathrm{C_{24}H_{72}Mn_2N_4Na_2OSi_8}$, $M_r = 813.44$, triclinic, space group $P\bar{1}$, $a = 8.8889(2)$, $b = 10.8003(3)$, $c = 12.7193(4)$ Å, $\alpha = 95.656(1)$, $\beta = 108.382(1)$, $\gamma = 98.832(1)°$, $V = 1130.89(5)$ Å^3, $Z = 1$, $\lambda = 0.71073$ Å, $\mu = 0.812$ mm^{-1}, $T = 150$ K; 29980 reflections, 7145 unique, R_{int} 0.042; final refinement to convergence on F^2 gave $R = 0.0315$ (F, 5578 obs. data only) and $R_{\mathrm{w}} = 0.0745$ (F^2, all data), GOF = 1.029. CCDC 662470.

Note that the unit cells of **1** and **5** are isomorphic with their respective Mg counterparts. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714880a

1 For a recent review of organic heterobimetallic compounds of Group 2, see: M. Westerhausen, *Dalton Trans.*, 2006, 4755.
2 For an early Feature Article, see: R. E. Mulvey, *Chem. Commun.*, 2001, 1049.
3 For a recent review, see: R. E. Mulvey, *Organometallics*, 2006, **25**, 1060.
4 J. Garcia-Álvarez, A. R. Kennedy, J. Klett and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2007, **46**, 6548.
5 L. M. Carella, W. Clegg, D. V. Graham, L. M. Hogg, A. R. Kennedy, J. Klett, R. E. Mulvey, E. Rentschler and L. Russo, *Angew. Chem., Int. Ed.*, 2007, **46**, 4662.
6 R. A. Andersen, E. Carmona-Guzman, J. F. Gibson and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 2204.
7 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Roger and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.
8 A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *Angew. Chem., Int. Ed.*, 1998, **37**, 3180.
9 R. Grüning and J. L. Atwood, *J. Organomet. Chem.*, 1977, **137**, 101.
10 M. A. Putzer, B. Neumüller, K. Dehnicke and J. Magull, *Chem. Ber.*, 1996, **129**, 715.
11 B. D. Murray and P. P. Power, *Inorg. Chem.*, 1984, **23**, 4584.