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tert-Butylimido Compounds of Manganese-(VII), -(VI), -(V) and -(II); Nitrido, Amido, Alkyl, Zinc and Aluminium Compounds†

Andreas A. Danopoulos,[a] Geoffrey Wilkinson,*[,a] Tracy K. N. Sweet[b] and Michael B. Hursthouse*[,b]
[a] *Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

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The interaction of $Mn(NBu^t)_3Cl$ with $Li(NHBu^t)$ under prescribed conditions leads to the manganese(VI) dimer, $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **1** and lithium salts **2**, **3** of the manganese(VII) nitrido anion $[Mn(N)(NBu^t)_3]^{2-}$, but the interaction with $Li(NHC_6H_3Me_2\text{-}2,6)$ gives the paramagnetic, tetrahedral, spiro manganese(II) complex $Mn[N(Bu^t)=C(H)C_6H_3(Me)NH]_2$ **4**. The interaction of $Mn(NBu^t)_3Cl$ with methyllithium or dimethylzinc gives the dimeric methyl compound $[MnMe(NBu^t)(\mu\text{-}NBu^t)]_2$ **5**, while interaction with ZnR_2 (R = Et, CH_2Bu^t, CH_2CMe_2Ph, CH_2SiMe_3 or CH_2Ph) gives similar alkyls **6**–**10** respectively. The interaction of **1** with ZnR_2 produces $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4ZnR$ (R = Me **11** or CH_2Bu^t **12**), and with Al_2Me_6, $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4AlMe_2$ **13**. The interaction of $[Li(dme)]_2[Mn(NBu^t)_4]$ (dme = 1,2-dimethoxyethane) and Al_2Me_6 gives $Mn[(\mu\text{-}NBu^t)_2AlMe_2]_2$ **14**. The structures of compounds **1**, **2**, **3**, **4**, **7**, **10** and **11** have been determined by X-ray crystallography. Compound **1** has been shown to be isostructural with its rhenium analogue, although twinning or disorder problems precluded accurate analysis. The nitrido compounds **2** and **3** have a common tetrahedral co-ordination sphere of manganese bonded to one nitride and three imido groups. The lithium cations are bonded to the imido nitrogen atoms, chloride ions and ether oxygen atoms. Compound **4** has a molecular structure which comprises a four-co-ordinate tetrahedral 'spiro' manganese atom chelated by two $N(Bu^t)=C(H)C_6H_3(Me)NH^-$ ligands. The six-membered chelate ring formed is approximately planar and the spiro rings (one generated from the other by the two-fold axis through Mn) are almost perpendicular, with a dihedral angle of 91.5° at the Mn^{II} centre. The two formally single Mn–N bonds are slightly different at 2.036 and 2.135 Å. The alkyl dimers **7** and **10** have closely analogous symmetrical structures, comprising two tetrahedral manganese atoms bridged by two imido groups and each bonded to one terminal imido and one alkyl ligand. With respect to the central Mn_2N_2 unit the two alkyls and the two imides adopt *cis* or *Z* arrangements. The geometry of the planar Mn_2N_2 unit in each structure has acute Mn–N–Mn (average 83.6°) and obtuse N–Mn–N (average 96.3°) angles consistent with the presence of direct Mn–Mn interaction, which formally has double bond character. Compound **11** has a molecular structure which contains a two-fold axis passing through the methyl and the Zn and Mn atoms. There is an unusual trigonal-planar Zn^{II} atom bonded to a methyl group and two bridging imido groups; Mn(1), in oxidation state V, is bonded to four bridging imido ligands, and Mn(2), oxidation state VI, is bonded to two bridging and two terminal imido ligands.

The synthesis of $Mn(NBu^t)_3Cl$ and a number of complexes derived by substitution of Cl with other anionic ligands has been described.[1] The syntheses and spectroscopic data and crystal structures of further new compounds derived from $Mn(NBu^t)_3Cl$ are now described. The main reactions are shown in Scheme 1; analytical and physical data for the new compounds are listed in Table 1.

Results and Discussion

Interaction of $Mn(NBu^t)_3Cl$ *with* $Li(NHBu^t)$.—The products from these reactions are critically dependent upon the conditions. The amido compound $Mn(NBu^t)_3(NHBu^t)$, which is thermally unstable, was characterised only spectroscopically,[1] but lithium salts of the *tert*-butylimido analogue of the manganate(2−) anion were studied by X-ray crystallography. Table 2 lists the conditions for the synthesis of these and the new compounds. The neutral manganese(VI) dimer $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **1** is obtained from the reaction in Et_2O. After warming to room temperature the solutions are blue to blue-green and are extremely air and moisture sensitive; no crystalline compounds could be isolated. After removal of Et_2O the ^1H NMR spectrum of the oily residue showed broad Et_2O resonances plus bridging (δ *ca.* 1.65–1.75) and terminal (δ *ca.* 1.30–1.40) *tert*-butylimido groups, these NBu^t groups being in a 1:2 ratio. These bands can be attributed to mixtures of $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ and the reduced species $[Li_x(OEt_2)_y][Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ (x = 1 or 2, y = 1–3). The admission of dry oxygen to a light petroleum solution of the oil causes an instantaneous colour change from green-brown to brown and on work-up essentially quantitative yields of **1** are obtained. Although compound **1** was obtained in other ways by reduction of $Mn(NBu^t)_3Cl$, *e.g.* by Na–Hg in tetrahydrofuran (thf),[1] the present method is the most convenient and gives the highest yield.

The brown dimer **1** is air-stable and diamagnetic like its rhenium analogue,[2] which was the first homoleptic imido compound to be made. It is extremely soluble in hydrocarbon solvents and crystals can be obtained only in low yields. However, the bulk product is sufficiently pure to be used as a starting material. The ^1H NMR spectrum has sharp singlets in a

† Non-oxo Chemistry of Manganese in High Oxidation States. Part 2.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: G = 10^{-4} T, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1} mmHg ≈ 133 Pa.

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Table 1 Analytical and physical data for new compounds

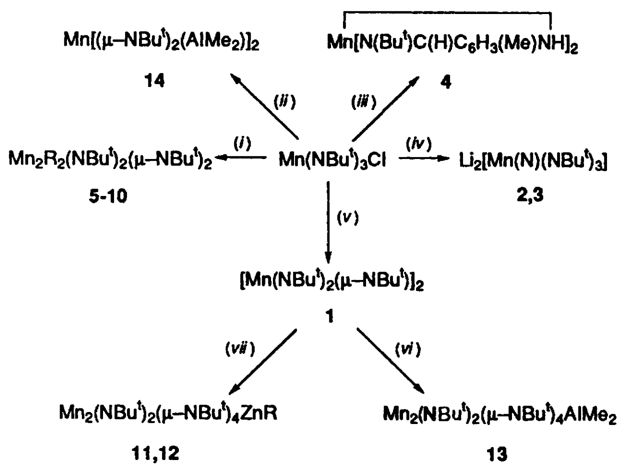
Compound	Colour	M.p./°C	Analysis (%)* C	H	N
1 [Mn(NBu^t)$_2$(μ-NBu^t)]$_2$	Red-brown	145 (decomp.)	53.0 (53.7)	9.7 (10.1)	15.1 (15.7)
2 [Li(OEt$_2$)]$_2$[Mn(N)(NBu^t)$_3$]·LiCl	Green	> 240	48.8 (49.3)	8.9 (9.6)	11.2 (11.5)
3 [Li(thf)]$_2$[Mn(N)(NBu^t)$_3$]·LiCl	Green	192–194	51.9 (49.8)	7.8 (8.9)	11.9 (11.6)
4 Mn[N(Bu^t)=C(H)C$_6$H$_3$(Me)NH]$_2$	Red-orange	230–233	65.8 (66.5)	7.0 (7.8)	12.5 (12.9)
5 Mn$_2$Me$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Red-purple	120–122	50.5 (50.9)	9.2 (9.2)	13.2 (13.2)
6 Mn$_2$Et$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Red-purple	Oil	MS only (see Experimental section)		
7 Mn$_2$(CH$_2$CMe$_3$)$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Red-purple	139–142	58.0 (58.2)	9.5 (10.8)	10.6 (10.5)
8 Mn$_2$(CH$_2$CMe$_2$Ph)$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Purple	182–184	64.6 (64.5)	9.1 (9.2)	8.5 (8.8)
9 Mn$_2$(CH$_2$SiMe$_3$)$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Brown-red	165–166	49.9 (50.7)	10.1 (10.2)	9.2 (9.9)
10 Mn$_2$(CH$_2$Ph)$_2$(NBu^t)$_2$(μ-NBu^t)$_2$	Brown	89–90	62.0 (62.5)	8.5 (8.7)	9.3 (9.7)
11 Mn$_2$(NBu^t)$_2$(μ-NBu^t)$_4$ZnMe	Red-purple	206–208 (decomp.)	46.5 (46.7)	8.6 (9.2)	13.4 (13.6)
12 Mn$_2$(NBu^t)$_2$(μ-NBu^t)$_4$ZnCH$_2$CMe$_3$	Purple	Oil	MS only (see Experimental section)		
13 Mn$_2$(NBu^t)$_2$(μ-NBu^t)$_4$AlMe$_2$	Purple	205–208	51.8 (52.6)	9.9 (10.1)	13.5 (14.6)
14 Mn[(μ-NBu^t)$_2$AlMe$_2$]$_2$	Purple	202–206	51.1 (53.0)	9.2 (9.3)	11.5 (12.4)

* Calculated values in parentheses.

Table 2 Conditions for reactions of Mn(NBu^t)$_3$Cl with Li(NHBu^t) and the products

Product	Solvent	Temp. regime/°C	Li(NHBu^t)–Mn ratio
Mn(NHBu^t)(NBu^t)$_3$ [a]	thf	−78 to −40	1.3
[Mn(NBu^t)$_2$(μ-NBu^t)]$_2$ **1**	Et$_2$O	−78 to +20 then O$_2$	2.3
[Li(thf)]$_2$[Mn(N)(NBu^t)$_3$]·LiCl **3**	thf, *dilute*	−90 to +20 *very* slowly	3.85
[Li(OEt$_2$)]$_2$[Mn(N)(NBu^t)$_3$]·LiCl [b] **2**	dme–toluene (3:1)	−78 to +10 over 12 h	5
[Li(dme)]$_2$ [Mn(NBu^t)$_4$] [a]	dme–toluene (3:1)	−78 to +20 slowly	5

[a] See ref. 1. [b] Crystallised from Et$_2$O.



Scheme 1 Main reactions of Mn(NBu^t)$_3$Cl. (*i*) LiMe, dme; ZnR$_2$, thf, R = Me, Et, CH$_2$Bu^t, CH$_2$CMe$_2$Ph, CH$_2$SiMe$_3$, CH$_2$Ph; (*ii*) Li(NHBu^t), dme, to give [Li(dme)]$_2$[Mn(NBu^t)$_4$] (ref. 1), then Al$_2$Me$_6$ in light petroleum; (*iii*) excess Li(NHC$_6$H$_3$Me$_2$-2,6), dme; (*iv*) excess Li(NHBu^t), dme–light petroleum or thf; (*v*) Li(NHBu^t), Et$_2$O, then O$_2$; (*vi*) Al$_2$Me$_6$ toluene; (*vii*) ZnR$_2$, R = Me, CH$_2$Bu^t, thf

2:1 ratio for the terminal and bridging NBu^t groups, respectively, at the same δ value as the rhenium analogue. The ^{13}C-{^{1}H} NMR spectrum gives chemical shift difference $\Delta\delta_{C\alpha-C\beta}$ values[3] of 41.4 and 33.6 for the terminal and bridging groups that are smaller than those for the Mn^{VII} compound (45–50)[1] indicating a less π-acidic metal centre. The diamagnetism can be attributed to spin pairing of the d^1, Mn^{VI} electrons *via* the bridges or a metal–metal bond.

X-Ray data were collected on a small, rather poor quality crystal, and confirmed analogy with the previously studied Re$_2$(NBu^t)$_6$ species.[2] However, as a result of gross disorder or, as we now suspect, twinning, it was only possible to locate the manganese and nitrogen atoms with any confidence. Similar problems had occurred with the Re complex but they were considerably more severe in the case of the present study.

It is of interest that the technetium and rhenium arylimido compounds [M(NR′)$_3$]$_2$ R′ = 2,6-Pr$^i_2$C$_6$H$_3$, have an ethane-like structure with no bridging groups while the R′ = 2,6-Me$_2$C$_6$H$_3$ compounds have bridges;[4a] attempts to make the technetium *tert*-butyl analogue were unsuccessful.[4b]

The formation of **1** probably involves initial conversion of Mn(NBu^t)$_3$Cl to Mn(NBu^t)$_3$(NHBu^t) and homolysis (*cf.* ref. 1 for thermal decomposition products) to give Mn(NBu^t)$_3$$^•$ which then dimerizes. In the presence of excess Li(NHBu^t) reduction to dimeric anionic Mn^{V,VI} or Mn^{V,V} species could occur, these species then being re-oxidised by O$_2$ to give **1**. The green V,V dianion has been obtained by reduction of **1** using stoichiometric amounts of Li powder in 1,2-dimethoxyethane (dme) and will be described in a later paper along with other anionic and cationic species.

The nitrido anion of manganese(VII), [Mn(N)(NBu^t)$_3$]$^{2-}$, was obtained as noted in Table 2 but only when low manganese concentrations in thf or dme–toluene were used and the temperature allowed to reach room temperature *very slowly* otherwise reduction as above occurs. There is evidently competition between reduction and nitrido complex formation. When the reaction is carried out in toluene–dme, the light petroleum extracts are purple and contain additionally the compound [Li(dme)]$_2$[Mn(NBu^t)$_4$] that was isolated and identified. Two nitrido salts, **2** and **3**, with [Li(OEt$_2$)]$^+$ and [Li(thf)]$^+$ as counter ions respectively have been obtained; both

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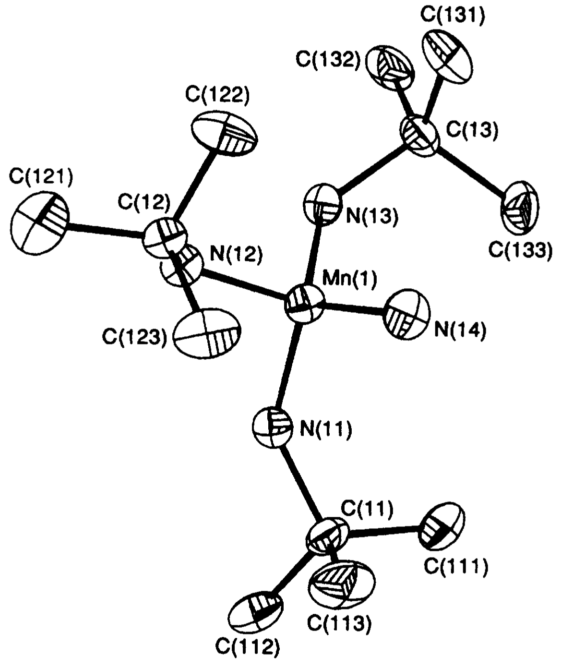

Fig. 1 Structure of $[Mn(N)(NBu^t)_3]^{2-}$ in $[Li(OEt_2)]_2[Mn(N)(NBu^t)_3]$·LiCl **2**

Table 3 Selected bond lengths (Å) and angles (°) for compounds **2** and **3**

	2	**3a**	**3b**
Mn(1)–N(11)	1.770(4)	1.786(8)	1.747(9)
Mn(1)–N(12)	1.766(4)	1.758(8)	1.756(8)
Mn(1)–N(13)	1.753(4)	1.791(8)	1.752(8)
Mn(1)–N(14)	1.545(5)	1.562(8)	1.553(9)
N(11)–C(11)	1.467(7)	1.462(13)	1.482(13)
N(12)–C(12)	1.476(6)	1.472(13)	1.499(13)
N(13)–C(13)	1.485(7)	1.485(14)	1.485(14)
N(11)–Mn(1)–N(12)	105.0(2)	105.0(4)	105.7(4)
N(11)–Mn(1)–N(13)	105.1(2)	105.8(4)	104.0(4)
N(11)–Mn(1)–N(14)	113.8(2)	114.4(5)	114.3(5)
N(12)–Mn(1)–N(13)	105.2(2)	104.3(4)	104.7(4)
N(12)–Mn(1)–N(14)	114.3(2)	114.6(5)	114.3(5)
N(13)–Mn(1)–N(14)	112.5(2)	111.8(4)	112.9(5)
C(11)–N(11)–Mn(1)	131.6(4)	129.3(8)	131.7(8)
C(12)–N(12)–Mn(1)	128.8(4)	132.1(7)	131.0(7)
C(13)–N(13)–Mn(1)	130.5(4)	129.7(7)	131.5(8)

For compound **3**, **a** refers to molecule 1 and **b** refers to molecule 2 in the asymmetric unit (consistent labelling exists between the two molecules, although the numbering is given in terms of molecule **3a**).

contain LiCl in the lattice. A crystal structure determination confirms that compound **2** in the solid state has the formula $[Li(OEt_2)]_2[Mn(N)(NBu^t)_3]$·LiCl. A diagram of the manganese-containing anion is shown in Fig. 1 and selected bond lengths and angles are given in Table 3.

In the anion, the Mn–NBu^t bond lengths are similar and all consistent with the imido formulation (rather than, say, an amido possibility) and this, together with the overall formulation of the compound identifies the metal as an Mn^{VII} centre. The Mn–N(imido) bond lengths are also somewhat longer than those in the neutral $Mn(NBu^t)_3X$ species[1] and this feature, together with the Mn–N–C angles of 130° is consistent with the behaviour of all three imido ligands as 4e bent Mn=N–R rather than linear Mn≛NR donors. An 18e configuration for the Mn atom thus derives from the 6e nitride, plus three 4e imides. The lithium ions are normal, four-co-ordinate, with bonds to two Cl^- ions plus two imido nitrogens [Li(1)] or to one Cl^-, one O(ether) and two imido nitrogens [Li(2) and Li(3)]. Each imido function makes links to two lithiums.

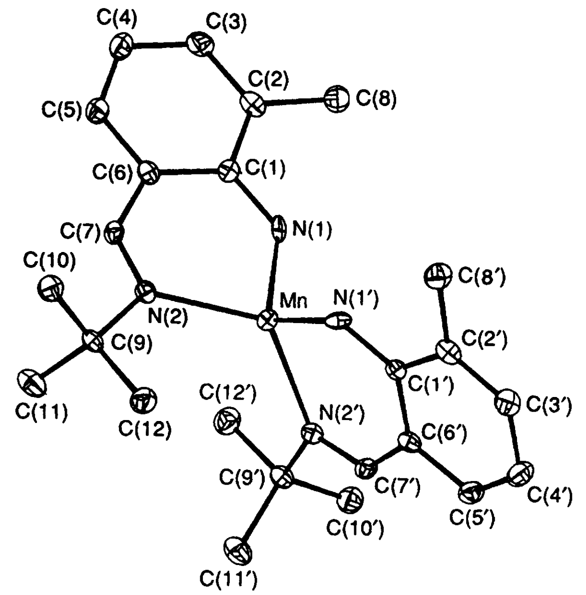

Fig. 2 Structure of $Mn[N(Bu^t)=C(H)C_6H_3(Me)NH]_2$ **4**

The crystallographic asymmetric unit for compound **3** has the formula $Li_6(thf)_4Cl_2[Mn(N)(NBu^t)_3]_2$ making it analogous to **2**. Selected bond lengths and angles for the manganate ions are listed in Table 3. Geometric parameters in the two $[Mn(N)(NBu^t)_3]^{2-}$ ions are very similar to those in compound **2**.

The co-ordination environments of the lithium atoms vary in this structure. Thus Li(1), Li(3) and Li(4) have distorted four-fold co-ordination to one Cl, one ether oxygen and two imido nitrogens, but Li(5) and Li(6) make short contacts only to three atoms, one Cl and two imido nitrogens, and Li(2) has only one short contact to an ether oxygen, but longer contacts (*ca.* 3.0 Å) to methyl carbons or more likely the associated hydrogen atoms.

The only other compounds with Mn≡N bonds are the porphyrinato species Mn^V(N)(porph), porph(2–) = *p*-methoxyphenyl-,[5] dimethyloctaethyl-[6] and tetra-*p*-tolyl-porphyrinate,[7] and the phthalocyaninato (pc) complex, Mn^V(N)(pc);[8] synthetic methods and reactions of nitrido compounds have been reviewed.[9]

Compounds **2** and **3** are moisture but not oxygen sensitive and they are diamagnetic. The IR spectra have a band at 1044 cm^{-1}, assignable to Mn≡N[10] in addition to NBu^t and solvent bands.

A reasonable mechanism for the formation of the anion is shown in Scheme 2. The initial formation of $Mn(NBu^t)_3(NHBu^t)$ is followed by deprotonation of the NHBu^t group, then a second deprotonation of a CH_3 group by the strongly basic Li(NHBu^t) leads to elimination of isobutylene (2-methylprop-1-ene). A similar elimination of isobutylene was proposed for the synthesis of the nitrido anion $[Ru(N)\{Bu^tNC(O)NBu^t\}]^-$ and was detected by its reaction with bromine.[11] A thermal elimination reaction from the *tert*-butoxide of $[W_2(OBu^t)_7]^-$ to yield a hydrido-oxo species has been recently reported.[12]

Interaction of $Mn(NBu^t)_3Cl$ *with* $Li(NHC_6H_3Me_2$-2,6).—The interaction of this lithium amide and $Mn(NBu^t)_3Cl$ under conditions similar to those used in the reaction of Li(NHBu^t) leads to only one isolable product in *ca.* 18% yield. This is the neutral manganese(II) species $Mn[N(Bu^t)=C(H)C_6H_3(Me)NH]_2$ **4**.

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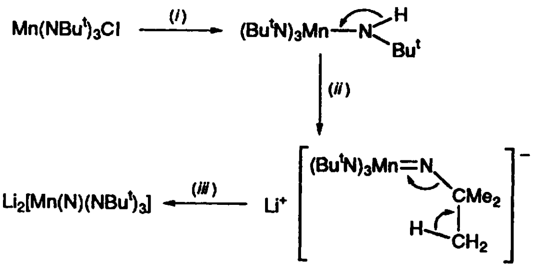
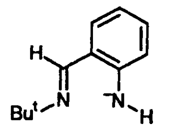


Scheme 2 Formation of Mn≡N species by deprotonation reactions and elimination of $Me_2C{=}CH_2$. (*i*) +Li(NHBu^t) − LiCl; (*ii*) +Li(NHBu^t) − Bu^{t}NH$_2$; (*iii*) +Li(NHBu^t) − Bu^{t}NH$_2$ − $Me_2C{=}CH_2$



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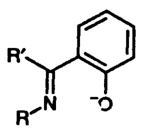

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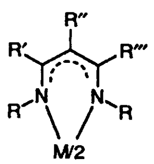
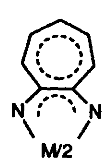
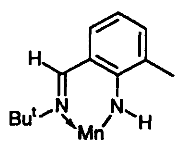


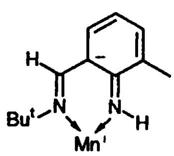
III



IV



Va



Vb

The structure of **4** is shown in Fig. 2; important bond lengths and angles are given in Table 4. The molecule lies on a two-fold axis of symmetry in the unit cell with a dihedral angle of 91.5° between the two almost planar chelate rings. All hydrogen atoms were experimentally located.

The ligand **I** is the amino analogue of the well known salicylaldimino ligands **II**[13] and is comparable to the large family of β-difunctional ligands typified by Schiff bases and acetylacetonates as well as N,N′ ligands such as β-diketimines **III**[14] and aminotroponiminates **IV**.[15] In **4**, as well as in Schiff-base complexes the presence of the aromatic ring affects the π-electron delocalisation in the chelate ring compared to that in acetylacetonates or complexes of type **III**. This is consistent with the bond lengths in **4**; C(7)–N(2) at 1.287 Å is clearly a double bond. However, the C(1)–N(1) distance of 1.343 Å implies some conjugation with the benzene ring, *cf.* **Va**,**Vb**. Of further interest are the Mn–N distances of 2.036(3) and 2.135(3) Å, which are on average similar to those in a high-spin, square-planar manganese(II) porphyrin[16a] [2.083(2) Å]; both are larger than the distances in the comparable phthalocyaninato complex[16b] where Mn^{II} has an intermediate spin state ascribed to the small size of the ligand cavity which would prefer the small Mn radius associated with spin pairing.

Compound **4** is paramagnetic with a moment *ca.* 2.7 μ_B in solution by Evans' NMR method. It has no NMR spectrum and is EPR silent in toluene from 77 to 293 K. In thf solution there is a temperature-dependent spectrum characteristic for Mn^{II}, $g = 1.958$, $\alpha_{Mn} = 70$ G. Weak EPR spectra of other Mn^{II} compounds have been rationalized.[17] The compound is very air-sensitive but surprisingly stable thermally, melting without decomposition at *ca.* 230 °C. The mode of formation of **4** is uncertain: this requires the loss of two H atoms from one *o*-Me group on each arene ring, the formation of a Bu^{t}N=C(H)– moiety that can only come from the Bu^{t}N groups of Mn(NBu^t)$_3$Cl, as well as Mn^{VII}–Mn^{II} reduction.

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**

Mn–N(1)	2.036(3)	C(1)–C(2)	1.445(5)
Mn–N(2)	2.135(3)	C(2)–C(3)	1.366(5)
N(1)–C(1)	1.343(4)	C(3)–C(4)	1.406(5)
N(2)–C(7)	1.287(4)	C(4)–C(5)	1.364(5)
N(2)–C(9)	1.512(4)	C(5)–C(6)	1.414(5)
C(1)–C(6)	1.437(5)	C(6)–C(7)	1.441(5)
N(1)–Mn–N(2)	89.59(12)	C(3)–C(2)–C(1)	120.5(3)
N(2′)–Mn–N(2)	124.8(2)	C(3)–C(2)–C(8)	120.5(3)
N(1′)–Mn–N(2)	119.12(12)	C(1)–C(2)–C(8)	119.0(3)
N(1′)–Mn–N(1)	117.7(2)	C(2)–C(3)–C(4)	122.5(4)
C(1)–N(1)–Mn	130.7(3)	C(5)–C(4)–C(3)	118.0(4)
C(1)–N(1)–H(1)	110(3)	C(4)–C(5)–C(6)	122.9(4)
Mn–N(1)–H(1)	118(3)	C(5)–C(6)–C(1)	119.1(3)
C(7)–N(2)–C(9)	116.6(3)	C(5)–C(6)–C(7)	115.7(3)
C(7)–N(2)–Mn	122.0(2)	C(1)–C(6)–C(7)	125.2(3)
C(9)–N(2)–Mn	121.5(2)	N(2)–C(7)–C(6)	130.6(3)
N(1)–C(1)–C(6)	120.9(3)	N(2)–C(7)–H(7)	120(2)
N(1)–C(1)–C(2)	122.0(3)	C(6)–C(7)–H(7)	109(2)
C(6)–C(1)–C(2)	117.0(3)		

The atoms marked X′ are equivalent to atoms X, generated by the symmetry transformation *y*, *x*, −*z*.

Table 5 Selected bond lengths (Å) and angles (°) for compounds **7** and **10**

	7	10
Mn(1)–Mn(2)	2.391(2)	2.392(1)
Mn(1)–N(1)	1.624(4)	1.630(3)
Mn(1)–N(2)	1.791(4)	1.785(3)
Mn(1)–N(4)	1.782(4)	1.799(3)
Mn(1)–C(6)	2.041(5)	2.045(4)
Mn(2)–N(2)	1.799(4)	1.811(3)
Mn(2)–N(3)	1.606(4)	1.629(3)
Mn(2)–N(4)	1.797(4)	1.782(3)
Mn(2)–C(5)	2.062(5)	2.041(4)
N(1)–C(1)	1.458(6)	1.452(5)
N(2)–C(2)	1.470(5)	1.468(4)
N(3)–C(3)	1.479(6)	1.454(5)
N(4)–C(4)	1.482(6)	1.480(4)
C(5)–C(51)	1.500(7)	1.479(5)
C(6)–C(61)	1.515(7)	1.466(5)
Mn(1)–N(2)–Mn(2)	83.5(2)	83.4(1)
Mn(1)–N(4)–Mn(2)	83.8(2)	83.8(1)
N(4)–Mn(1)–N(2)	96.7(2)	96.5(1)
N(2)–Mn(2)–N(4)	95.9(2)	96.2(1)
Mn(1)–N(1)–C(1)	158.3(4)	160.1(3)
Mn(1)–N(2)–C(2)	136.7(3)	138.8(2)
Mn(1)–N(4)–C(4)	138.7(3)	135.0(2)
Mn(1)–C(6)–C(61)	125.8(4)	113.7(3)
Mn(2)–N(2)–C(2)	137.4(3)	135.6(2)
Mn(2)–N(4)–C(4)	136.5(3)	138.6(2)
Mn(2)–N(3)–C(3)	160.3(4)	161.8(3)
Mn(2)–C(5)–C(51)	124.2(4)	119.2(3)

A recent chelate, Mn[N(C$_6$H$_3$Pr$^i_2$-2,6)CH$_2$CH$_2$N(H)(C$_6$H$_3$Pr$^i_2$-2,6)]$_2$, might have appeared to be similar to other N,N′ species but it has two short Mn–N interactions (2.394 Å) so that Mn^{II} is quasi-two-co-ordinate.[18a] It may be noted finally that salicylaldiminato compounds of Mn^{II} are known but their structures are uncertain, some appearing to be dimers or polymers.[18b]

Alkylation Reactions of Mn(NBu^t)$_3$Cl.—The reaction of Mn(NBu^t)$_3$Cl with lithium alkyls or Grignard reagents in most cases led to reduction or decomposition, but interaction with Ag(C$_6$F$_5$) allowed the isolation of the reasonably stable green

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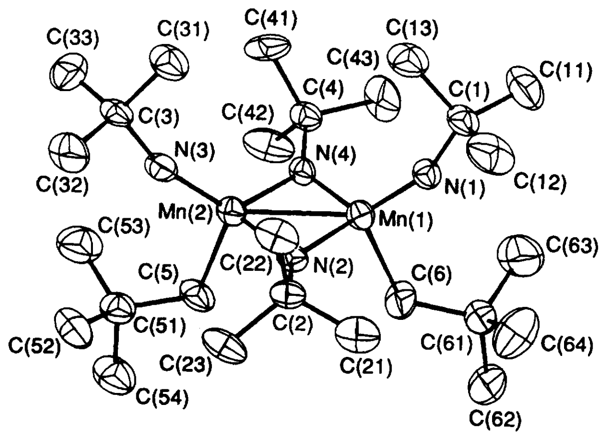


Fig. 3 Structure of $[Mn(CH_2CMe_3)(NBu^t)(\mu\text{-}NBu^t)]_2$ **7**

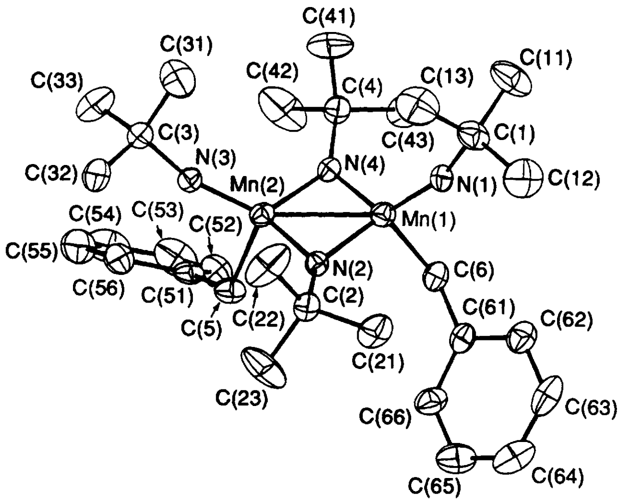
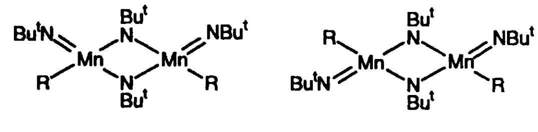


Fig. 4 Structure of the benzyl complex **10**

oil $Mn(NBu^t)_3(C_6F_5)$ that was characterised only spectroscopically.[1] We have now obtained a series of manganese(V) alkyls of formula $[MnR(NBu^t)(\mu\text{-}NBu^t)]_2$ (R = Me **5**, Et **6**, CH_2Bu^t **7**, CH_2CMe_2Ph **8**, CH_2SiMe_3 **9** or CH_2Ph **10**). We have been unable to synthesise similar compounds having aryl, allyl or alkynyl groups.

The structures of compounds **7** and **10** have been determined. Both dimers have closely analogous structures (Figs. 3, 4 and Table 5) comprising two tetrahedral manganese atoms bridged by two imido groups and each bonded to one terminal imide and one alkyl. With respect to the central Mn_2N_2 unit the two alkyls and the two imides adopt *cis* or *Z* arrangements. This is different to the situation found in the related Tc^{VI} dimer,[19] $[TcMe_2(NR')(\mu\text{-}NR')]_2$ (R' = $C_6H_3Me_2$-2,6), where the two terminal imides adopt a *trans* or *E* structure (erroneously described as *Z* by the authors), but analogous to the *cis* arrangement of the terminal oxo functions in $[TcMe_2(O)(\mu\text{-}O)]_2$.[20] The geometry of the planar Mn_2N_2 unit in each structure, with acute Mn–N–Mn (average 83.5°) and obtuse N–Mn–N (average 96.3°) angles is consistent with the presence of direct Mn–Mn interaction, which formally has double bond character in this Mn^V–Mn^V dimer. Other geometry parameters are as expected. The terminal imido groups are approaching linearity (Mn–N–C ≈ 160°) with Mn–N bond lengths in the range 1.61–1.63 Å, consistent with normal 6e character, and the bridges are close to being symmetrical. The Mn–C–C angles on the neopentyls are 124.2 and 125.8°, slightly enlarged as a result of the steric bulk of the ligand. A small difference in the corresponding angles in the benzyl compound, 113.7 and 119.2° probably reflects different steric environments. The Mn–C



VIa **VIb**

distances, 2.041 and 2.062 Å are shorter than those in the Mn^{IV} species $MnMe_4$(dmpe) [dmpe = 1,2-bis(dimethylphosphino)-ethane][21a] and $[MnMe_6]^{2-}$[21b] although the latter distances are likely to be affected by Li^+–H_3C interactions. It is also relevant to compare present distances with those in Mn^{II} alkyls.[17,22]

The methyl compound **5** was obtained using $ZnMe_2$ or by interaction with 4 equivalents of LiMe in dme at very low temperatures. The other compounds **6–10** were obtained only using zinc dialkyls and even then only in low to moderate (neopentyl) yields. All these compounds are diamagnetic and surprisingly thermally stable; they sublime at 80–100 °C in vacuum to a solid CO_2 probe. The mass spectra (electron impact, EI) show the molecular ions but for **5** and **7** the highest mass fragments are $(M + 14)^+$. Accurate mass measurements indicate that these fragments are due to $M + CH_2$ ions probably formed during the ionization process. Chemical ionization (isobutane) suppresses this fragmentation pathway.

The ^1H NMR spectra of **5–10** are basically similar. The peak at δ *ca.* 1.9 can be assigned to μ-NBu^t and the one at δ *ca.* 1.1 to terminal NBu^t groups, the remainder of the spectra being due to alkyls. In the ^{13}C-{^1H} NMR spectra the chemical shift difference $\Delta\delta_{C_\alpha - C_\beta}$ is *ca.* 39–40 for terminal and 34–36 for μ-NBu^t groups.

Assuming that the pairs of NBu^t groups are related by symmetry in both '*cis*' (**VIa**, as found in the solid state, see above) and '*trans*' **VIb** isomers, the presence of only one peak for the bridging and terminal NBu^t groups implies the presence of only one isomer in solution. However, after *ca.* 2 weeks at room temperature compound **5** showed broadened ^1H NMR spectra while **7** had additional peaks in the two imido regions. The spectra of **5** sharpened on heating in $[^2H_8]$toluene and remained so on cooling. The temperature dependence of the spectrum of **7** is more complicated.

The mechanism of formation of **5–10** which involves loss of NBu^t groups is not clear. We have been unable to detect any soluble NBu^t zinc species or to stop the reaction at the Mn^{VI} oxidation state.

Alkylations of $[Tc(NR')_3]_2$ (R' = $C_6H_3Me_2$-2,6) with MgMeCl result in replacement of one or two arylimido groups per Tc atom with two or four Me groups respectively,[19] without accompanying reduction of the metal. A similar reaction with **1** gives only intractable solids. Reduction has also been observed in the reaction of $SnMe_4$ with Tc_2O_7 to give $[TcMe_2(O)(\mu\text{-}O)]_2$.[20]

The formation of such thermally stable Mn^V compounds with alkyls having β-H atoms is unusual but similar *tert*-butylimido compounds of both Re^V and Re^{VII} have been made.[23] A simple explanation for the thermal stability is that the metal atoms are co-ordinatively saturated and pathways for decomposition involving β-H transfer are not available.[24]

Interaction of **1** *with* ZnR_2 (R = Me, CH_2Bu^t) *or* Al_2Me_6.—In an attempt to clarify the formation mechanism of the alkyls from $Mn(NBu^t)_3Cl$ we studied the interaction of **1** with ZnR_2 (R = Me or CH_2Bu^t), the idea being that this might show whether it was an intermediate in the formation of the alkyls. In thf, the interaction of **1** with $ZnMe_2$ even in excess yields only the purple mixed-valence $Mn^{VI}Mn^V$ dimer, $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4ZnMe$ **11**, in the form of very air-sensitive but thermally robust crystals. The compound is paramagnetic and has the complicated EPR spectrum shown in Fig. 5. The interaction of $Zn(CH_2Bu^t)_2$ with **1** gave a purple-blue oil **12** that is similar

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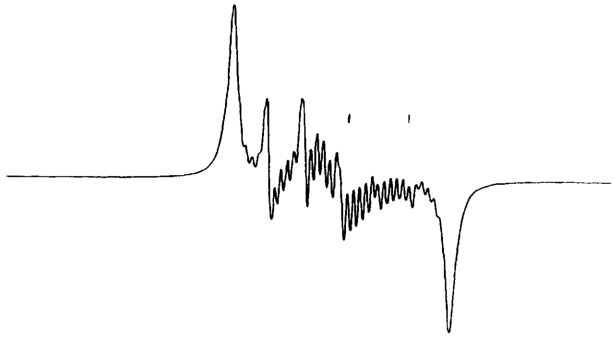


Fig. 5 X-Band EPR spectrum of the mixed-valence $Mn^{VI}Mn^{V}$ complex $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4ZnMe$ **11** in toluene at 293 K; scale indicates 100 G

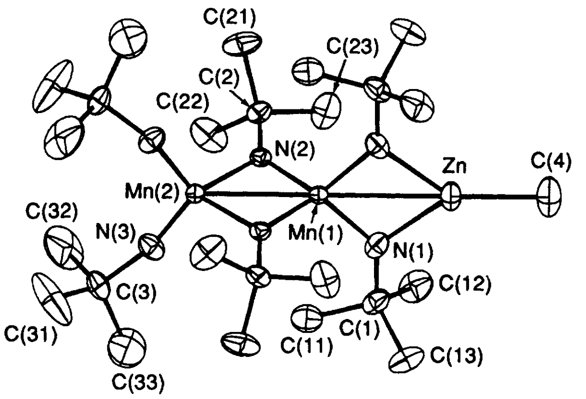


Fig. 6 The structure of the zinc complex **11**

to **11**. The molecular structure of compound **11** is shown in Fig. 6, selected bond lengths and angles are given in Table 6. The molecule lies on a two-fold axis of symmetry and so the trimetallic unit is linear. With an oxidation state of 2 for Zn the manganese centres are formally 5+ and 6+. Inspection of the Mn–N bond lengths shows that whilst those around the central manganese, Mn(1), are very similar, the bridges between Mn(1) and Mn(2) are quite unsymmetrical, with distances involving Mn(2) some 0.1 Å longer than for Mn(1). The terminal Mn(2)-N(3) imido bond length [1.624(2) Å] and near linear Mn–N–C angle [164.5(2)°] are consistent with 6e donor character $Mn \equiv NBu^t$. The representation of the structure as a resonance between the two related forms **VIIa**, **VIIb** describes the structure as Zn^{2+}–Mn^{6+}–Mn^{5+} and accounts quite simply for the bond length distribution.

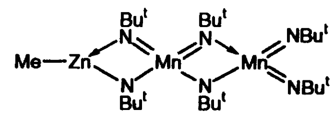
The reaction of Al_2Me_6 and **1** in toluene also leads to reduction to a $Mn^{V}Mn^{VI}$ compound **13** similar to **11** but with the ZnMe moiety replaced by $AlMe_2$. This compound is also very air sensitive, incapable of being reduced further even with excess Al_2Me_6 and paramagnetic with an EPR spectrum similar to that of **11**.

Finally, since $[Li(dme)]_2[Mn(NBu^t)_4]$[1] is similar to the species $Li_2[M(NBu^t)_4]$ (M = W, Mo[25a] or Cr[25b]), a reaction similar to that described[25a] with Al_2Me_6 is expected and indeed the purple, air-sensitive manganese(VI) compound $Mn[(\mu\text{-}NBu^t)_2AlMe_2]_2$ **14** is obtained. It is similar to the structurally characterised tungsten complex, is thermally stable, melting without decomposition at *ca.* 200 °C and sublimes in vacuum to a cold probe at *ca.* 100 °C. The compound is paramagnetic (d^1) with an EPR spectrum characteristic for Mn^{VI} tetrahedral monomers, $g = 2.022$, $a_{Mn} = 102.9$ G.

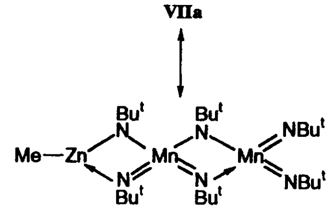
By contrast with $[Li(dme)]_2[Mn(NBu^t)_4]$, compound **14** is easily reduced in thf by Na–Hg giving extremely air-sensitive, turquoise solutions. After evaporation and extraction into light petroleum, cooling and attempted crystallisation gave only an oil, probably $[Li(thf)]_3[Mn(NBu^t)_4]$, whose EPR spectra shows reduction of Mn^{VI} to Mn^{V}. Careful treatment of the light petroleum solution with dry oxygen results in oxidation to the purple Mn^{VI} solutions of **14** as shown by comparison of the EPR spectra.

Table 6 Selected bond lengths (Å) and angles (°) for compound **11**

Mn(1)–Mn(2)	2.544(1)	Mn(2)–N(2)	1.869(2)
Mn(1)–Zn	2.727(1)	Mn(2)–N(3)	1.624(2)
Zn–C(4)	1.983(5)	N(1)–C(1)	1.452(4)
Zn–N(1)	1.985(3)	N(2)–C(2)	1.477(3)
Mn(1)–N(1)	1.766(2)	N(3)–C(3)	1.446(4)
Mn(1)–N(2)	1.767(2)		
C(4)–Zn–Mn(1)	180.0	N(2′)–Mn(1)–Zn	132.71(7)
Mn(2)–Mn(1)–Zn	180.0	N(3′)–Mn(2)–N(3)	113.0(2)
Mn(1)–N(1)–Zn	93.1(1)	N(3)–Mn(2)–N(2)	113.6(1)
Mn(1)–N(2)–Mn(2)	88.73(8)	N(3)–Mn(2)–N(2′)	113.2(1)
N(1)–Zn–C(4)	139.71(7)	N(2′)–Mn(2)–N(2)	88.0(1)
Zn–N(1)–C(1)	130.7(2)	N(3)–Mn(2)–Mn(1)	123.5(1)
N(1′)–Mn(1)–N(1)	93.3(2)	N(2)–Mn(2)–Mn(1)	43.98(6)
N(1′)–Mn(1)–N(2′)	117.2(1)	N(1′)–Zn–N(1)	80.6(1)
N(1)–Mn(1)–N(2′)	118.3(1)	N(1′)–Zn–Mn(1)	40.29(7)
N(2′)–Mn(1)–N(2)	94.6(1)	Mn(1)–N(1)–C(1)	136.2(2)
N(1′)–Mn(1)–Mn(2)	133.36(8)	Mn(1)–N(2)–C(2)	138.6(2)
N(2′)–Mn(1)–Mn(2)	47.29(7)	Mn(2)–N(2)–C(2)	132.6(2)
N(1′)–Mn(1)–Zn	46.64(8)	Mn(2)–N(3)–C(3)	164.5(2)



VIIa



VIIb

Experimental

Analyses were by the Imperial College microanalytical laboratory. General techniques have been described.[1] Mass spectra were recorded on a VG7070-E spectrometer; IR spectra were in Nujol mulls; NMR spectra were taken on a JEOL-ES-270 spectrometer in C_6D_6 unless otherwise specified. Commercial chemicals were from Aldrich, Jannsen Chimica and Avocado Research Chemicals. The light petroleum used had b.p. 40–60 °C.

The compound $Mn(NBu^t)_3Cl$ was prepared as described;[1] $Li(NHBu^t)$ and $Li(NHC_6H_3Me_2\text{-}2,6)$ were made by interaction of the amine with $LiBu^n$ in light petroleum. For ZnR_2 the procedures used for R = Me, CH_2Bu^t, CH_2CMe_2Ph, CH_2SiMe_3 and CH_2Ph were as in refs. 26*a*–*e*, respectively. Solvents were dried and degassed by standard methods; all operations were carried out under purified N_2 or Ar, in vacuum or in a Vacuum Atmospheres box.

*Di-μ-*tert*-butylimido-bis[bis(*tert*-butylimido)manganese(*VI*)]* **1**.—To a solution of $Mn(NBu^t)_3Cl$ (1.0 g, 3.3 mmol) in Et_2O (50 cm^3) at −78 °C was added *via* a cannula, a solution of $Li(NHBu^t)$ (0.6 g, 7.6 mmol) in Et_2O (30 cm^3). After completion of addition, the reaction mixture was allowed to warm to room temperature over *ca.* 0.5 h, when the colour changed from green to brown then to green-blue. After stirring (1 h) the volatiles were removed under vacuum and the residue extracted with

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light petroleum (3 × 30 cm^3). The combined extracts were exposed to dry oxygen for 5 min when the solution became brown. Filtration and evaporation left **1** as a brown, microcrystalline solid that can be handled in air for periods of up to *ca.* 2 h. Yield: 0.85 g, 96%; this product can be used without further purification. Mass spectrum (EI): *m*/*z* 536 (M^+), 521 (M^+ − Me), 450 (M^+ − NBu^t − Me), 394 (M^+ − 2NBu^t). IR: 1200 (Mn=NBu^t), 1016 cm^{-1} (Mn–μ–NBu^t). NMR: ^1H δ 1.35 [s, 36 H, $(CH_3)_3CN$], 1.72 [s, 18 H, μ-$(CH_3)_3CN$]; in $CDCl_3$, δ 1.30, 1.45; ^{13}C-{^1H} δ 32.13 [$(CH_3)_3CN$], 34.16 [μ-$(CH_3)_3CN$], 67.80 [μ-$(CH_3)_3CN$], 73.53 [$(CH_3)_3CN$].

Bis[*(diethyl ether)lithium*] [*Tris*(tert-*butylimido*)(*nitrido*)-*manganate*(VII)]–*Lithium Chloride* (1/1) **2**.—To a solution of Mn(NBu^t)$_3$Cl (0.3 g, *ca.* 1 mmol) in dme–toluene (3:1, 60 cm^3) at −78 °C was added Li(NHBu^t) (0.385 g, 4.9 mmol) in the same solvent (40 cm^3). The green solution on warming to 10 °C over 12 h became purple-red, then purple {this colour is due to Li_2[Mn(NBu^t)$_4$]}. After evaporation the residue was washed with light petroleum until the washings were colourless. The green residue was dissolved in Et_2O (30 cm^3), filtered, reduced to 20 cm^3 and cooled (−20 °C) to give green, air-sensitive plates. Yield: 0.17 g, *ca.* 35%. IR: 1190 (Mn=NBu^t), 1044 cm^{-1} (Mn≡N). ^1H NMR: δ 3.3 [q, 8 H, $(CH_3CH_2)_2O$], 1.47 [s, 27 H, $(CH_3)_3CN$], 1.2 [t, 12 H, $(CH_3CH_2)_2O$].

Bis[*(tetrahydrofuran)lithium*] [*Tris*(tert-*butylimido*)(*nitrido*)-*manganate*(VII)]–*Lithium Chloride* (1/1) **3**.—To a solution of Mn(NBu^t)$_3$Cl (0.25 g, 0.87 mmol) in thf (60 cm^3) at −90 °C was added *via* cannula over 5 min a pre-cooled (−78 °C) solution of Li(NHBu^t) (0.25 g, 3.16 mmol) in thf (50 cm^3). Toward the end of the addition, the initial green colour changed to green-brown, and the solution was allowed to reach room temperature over a period of *ca.* 12 h. After this stage the solution was usually green-brown but on occasion it was purple (see above). Removal of solvent in vacuum and extraction of the residue with light petroleum (3 × 80 cm^3), filtration, concentration to *ca.* 40 cm^3, and slow cooling to −20 °C gave green, rhomboidal prisms. Yield: 0.15 g, *ca.* 38%. IR: 1188 (Mn=NBu^t), 1044 cm^{-1} (Mn≡N). ^1H NMR: δ 3.63 (br m, 8 H, thf), 1.58 (br m, 8 H, thf), 1.80 [br s, 27 H, $(CH_3)_3CN$].

Bis(6-tert-*butyliminomethyl*-o-*tolylamido*)*manganese*(II) **4**.—To a solution of Mn(NBu^t)$_3$Cl (0.3 g, *ca.* 1 mmol) in dme–toluene (3:1, 50 cm^3) at −78 °C was added Li(NHC$_6$H$_3$Me$_2$-2,6) (0.64 g, 5 mmol) in dme (20 cm^3). The green-brown solution was allowed to reach room temperature over 8 h with stirring. The orange-brown solution was evaporated, the residue extracted with light petroleum (4 × 30 cm^3) and the extracts concentrated to *ca.* 20 cm^3. After standing at room temperature until crystallisation started (2–3 d) and subsequent cooling (−20 °C, 7 d), red-orange prisms of **4** were obtained. Yield: 0.08 g, *ca.* 18%. Mass spectrum (EI): *m*/*z* 433 (M^+), 189 [N(H)C$_6$H$_3$MeCHNBu^t]. IR: 3369 (N–H), 1605 cm^{-1} (C=N).

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)*methylmanganese*-(V)] **5**.—*Method* 1. To a solution of Mn(NBu^t)$_3$Cl (1 g, 3.3 mmol) in dme–toluene (4:1, 100 cm^3) at −90 °C (ethanol + solid CO_2 + liquid nitrogen) was added a pre-cooled (−78 °C) solution of methyllithium [13.2 mmol: 14.5 cm^3 of LiMe in Et_2O (0.9 mol dm^{-3}) added to dme–toluene 4:1 (*ca.* 26 cm^3)] dropwise over 10 min. The resulting brown-green solution was allowed to warm to room temperature over 18 h when it was brown and stirred for an additional 10 h when it was red-purple. Removal of the volatiles in vacuum and extraction of the residue with light petroleum (2 × 50 cm^3), filtration and evaporation left a residue which was dissolved in hot acetonitrile. Filtration and cooling (−20 °C) gave red-purple needles or plates. Yield: 0.3 g, 46% in two crops.

Method 2. To Mn(NBu^t)$_3$Cl in thf (0.3 g, 1 mmol in 40 cm^3) at −78 °C was added $ZnMe_2$ (0.48 g, 5 mmol in 20 cm^3 light petroleum) dropwise. The solution was allowed to warm with stirring for *ca.* 2 d when it was red-purple. Work-up as above gave 0.07 g, 35% yield. Mass spectra: (EI), *m*/*z* 438 (M^+ + 14), 424 (M^+), 409 (M^+ − Me), 394 (M^+ − 2 Me), 379 (M^+ − 3 Me), 364 (M^+ − 4 Me); chemical ionization (CI) (isobutane), *m*/*z* (438, low intensity), 424 (M^+), 409 (M^+ − Me), 394 (M^+ − 2 Me), 379 (M^+ − 3 Me), 364 (M^+ − 4 Me); high resolution, *m*/*z* 424.217, $C_{18}H_{42}Mn_2N_4$ requires 424.217. NMR: ^1H δ 1.89 [s, 18 H, μ-$(CH_3)_3CN$], 1.19 [s, 18 H, $(CH_3)_3CN$], 0.56 (s, 6 H, CH_3); ^{13}C-{^1H} δ 13.78 (CH_3), 32.35 [$(CH_3)_3CN$)], 35.82 [μ-$(CH_3)_3CN$], 72.96 [$(CH_3)_3CN$], 72.20 [μ-$(CH_3)_3CN$].

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)*ethylmanganese*(V)] **6**.—To a solution of Mn(NBu^t)$_3$Cl (0.3 g, 1 mmol in 40 cm^3 thf) at −78 °C was added $ZnEt_2$ (5 cm^3 of 1 mol dm^{-3} solution in hexanes) and the mixture allowed to warm to room temperature over 1 h. After stirring for 12 h, the solution was evaporated and the residue extracted with light petroleum (2 × 10 cm^3). After filtration the purple-red solution was concentrated to *ca.* 2 cm^3 and chromatographed on neutral Al_2O_3 (deactivated with thf) eluting with light petroleum. After evaporation of the purple fraction the purple oil was distilled and collected on a solid CO_2 cooled probe. Yield: 0.06 g, *ca.* 25%. The oil was pure according to ^1H NMR spectra. Mass spectrum (EI): *m*/*z* 452 (M^+), 423 (M^+ − Et), 408 (M^+ − Et − Me), 393 (M^+ − Et − 2 Me). NMR: ^1H δ 1.93 [s, 18 H, μ-$(CH_3)_3CN$], 1.73 (t, 6 H, CH_2CH_3), 1.65 (q, 4 H, CH_2CH_3), 1.16 [s, 18 H, $(CH_3)_3CN$]; ^{13}C-{^1H} δ 25.66 (CH_3CH_2), 32.52 [$(CH_3)_3CN$], 35.57 (CH_3CH_2), 36.35 [μ-$(CH_3)_3CN$], 70.49 (μ-Me_3CN), 72.05 (Me_3CN).

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)*neopentylmanganese*(V)] **7**.—This procedure serves also for compounds **8**–**10**. To Mn(NBu^t)$_3$Cl (0.6 g, 2 mmol in 60 cm^3 thf) at −78 °C was added Zn(CH$_2$Bu^t)$_2$ (2.1 g, 10 mmol in light petroleum, 10 cm^3). After warming to room temperature over 1 h and stirring (16 h) removal of volatiles, extraction of the residue with light petroleum (3 × 20 cm^3) and filtration gave a purple solution which was concentrated to *ca.* 5 cm^3, chromatographed on Al_2O_3 with the work-up as above for **5**. Yield: 0.21 g, *ca.* 38%. X-Ray quality crystals were obtained by slow cooling to −20 °C of dilute acetonitrile solutions.

Mass spectra: (EI), *m*/*z* 550 (M^+ + 14), 536 (M^+), 478 (M^+ − isobutylene), 465 (M^+ − Me − isobutylene), 450 (M^+ − 2 Me − isobutylene); high resolution, *m*/*z* 536.338, $C_{26}H_{58}Mn_2N_4$ requires 536.342. NMR: ^1H δ 1.96 [s, 18 H, μ-$(CH_3)_3CN$], 1.93 [s, br, 4 H, CH_2CMe_3], 1.43 [s, 18 H, $(CH_3)_3CH_2$], 1.12 [s, 18 H, $(CH_3)_3CN$]; ^{13}C-{^1H} δ 32.73 [$(CH_3)_3CN$], 34.09 [$(CH_3)_3CH_2$], 36.26 [μ-$(CH_3)_3CN$], 57.59 [$(CH_3)_3CH_2$], 70.50 [μ-$(CH_3)_3CN$], 72.00 [$(CH_3)_3CN$].

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)(*2-methyl-2-phenylpropyl*)*manganese*(V)] **8**.—As for **1** from Mn(NBu^t)$_3$Cl (0.3 g, 1 mmol) and Zn(CH$_2$CMe$_2$Ph)$_2$ (1.65 g, 5 mmol). Final crystallisation from light petroleum. Yield: 0.05 g, 15%. Mass spectrum (EI): *m*/*z* 660 (M^+), 527 (M^+ − CH_2CMe_2Ph), 456 (M^+ − NBu^t − CH_2CMe_2). NMR: ^1H δ 7.42–7.20 (m, 10 H, $CH_2CMe_2C_6H_5$), 2.01 (s, 4 H, CH_2CMe_2Ph), 1.83 [s, 18 H, μ-NC$(CH_3)_3$], 1.44 [s, 12 H, $CH_2C(CH_3)_2Ph$], 1.02 [s, 18 H, NC$(CH_3)_3$]; ^{13}C-{^1H} δ 153.20 [*ipso* (C_6H_5)C(Me)$_2$CH$_2$], 129.06, 126.88, 126.12 [other aromatic (C_6H_5)C(Me)$_2$CH$_2$], 71.90 (NCMe_3), 70.91 (μ-NCMe_3), 56.98 [$CH_2C(Me)_2CH_2$], 41.76 [$CH_2C(Me)_2Ph$], 36.25 [μ-$(CH_3)_3CN$], 33.95 [CH_2C-$(CH_3)_2Ph$], 32.47 [$(CH_3)_3CN$].

Di-μ-tert-*butylimido*-*bis*[(tert-*butylimido*)(*trimethylsilylmethyl*)*manganese*(V)] **9**.—As for **7** from Mn(NBu^t)$_3$Cl (0.3 g) and Zn(CH$_2$SiMe$_3$)$_2$ (1.2 g). Yield: 0.04 g, 15%. Mass spectrum (EI): *m*/*z* 568 (M^+), 495 (M^+ − SiMe$_3$), 481[M^+ −

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Table 7 Details of data collection and refinement for compounds **2**, **3**, **4**, **7**, **10** and **11**

	2	**3**	**4**	**7**	**10**	**11**
Formula	$C_{20}H_{47}ClLi_3MnN_4O_2$	$C_{40}H_{86}Cl_2Li_6Mn_2N_8O_4$	$C_{24}H_{34}MnN_4$	$C_{26}H_{58}Mn_2N_4$	$C_{30}H_{50}Mn_2N_4$	$C_{25}H_{57}Mn_2N_6Zn$
M_r	486.83	965.59	433.49	536.64	576.62	617.02
T/K	120	140	120	120	160	150
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/n$	$P2_1/c$	$P4_12_12$	$P2_1/n$	$P2_1/n$	$I\bar{4}2d$
a/Å	10.593(3)	15.252(2)	8.106(1)	12.131(5)	11.165(1)	13.988(6)
b/Å	19.183(6)	19.083(2)	8.106(1)	16.312(4)	16.555(3)	13.988(6)
c/Å	14.382(1)	20.281(2)	34.81(2)	15.982(3)	17.439(2)	33.674(2)
α/°	90	90	90	90	90	90
β/°	94.98(2)	104.10(3)	90	91.87(3)	94.88(1)	90
γ/°	90	90	90	90	90	90
U/Å^3	2911.5(12)	5725.0(11)	2287.3(14)	3161(2)	3211.7(7)	6589(4)
Z	4	4	4	4	4	8
D_c/g cm^{-3}	1.111	1.120	1.259	1.128	1.193	1.244
F(000)	1036	2040	924	1168	1232	2632
μ(Mo-Kα)/mm^{-1}	0.563	0.573	0.594	0.817	0.809	1.498
Crystal size/mm	0.6 × 0.15 × 0.1	0.12 × 0.1 × 0.05	0.25 × 0.20 × 0.15	1.00 × 0.09 × 0.06	0.22 × 0.14 × 0.11	0.68 × 0.43 × 0.32
θ Range for data/°	1.77 to 25.04	1.85 to 25.09	2.34 to 22.72	1.78 to 25.15	2.09 to 25.07	2.33 to 25.10
hkl Ranges	−9 to 11 −22 to 22 −16 to 17	−18 to 18 −21 to 21 −23 to 21	−6 to 8 −8 to 6 −34 to 35	−14 to 14 −18 to 17 −14 to 19	−13 to 13 −17 to 18 −20 to 17	−11 to 16 −15 to 14 −37 to 37
Reflections collected	11802	16401	5629	11837	12759	11356
Independent reflections	4401	8177	1418	4658	4943	2667
R_{int}	0.0953	0.1054	0.0673	0.0591	0.0668	0.0434
Data/restraints/parameters	4399/8/295	8176/0/588	1415/0/200	4652/0/313	4942/0/337	2666/0/167
Maximum, minimum absorption correction factors	—	—	1.051, 0.928	1.149, 0.696	1.065, 0.878	1.217, 0.899
Maximum peak and hole/e Å^{-3}	1.075, −0.528	0.348, −0.229	0.165, −0.189	0.744, −0.339	0.465, −0.280	2.604, −0.288
Goodness of fit on F^2	0.865	0.511	0.411	0.775	0.758	1.083
$R1$	0.0650	0.0663	0.0259	0.0527	0.0390	0.0393
$wR2$ (all data)	0.1754	0.2703	0.0801	0.1246	0.0841	0.0940

Goodness of fit = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$, where n = number of reflections and p = total number of parameters. $R1 = \Sigma|F_o - F_c|/\Sigma(F_o)$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (gP)^2]$. Weighting parameters, g, were 0.0810, 0.0001, 0, 0.0519, 0.0206 and 0.0684 for compounds **2**, **3**, **4**, **7**, **10** and **11** respectively; where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

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Table 8 Fractional atomic coordinates ($\times 10^4$) for compound **2**

Atom	x	y	z
Li(1)	594(9)	5250(5)	5885(6)
Li(2)	-1664(9)	5285(5)	6967(6)
Li(3)	-958(9)	6520(5)	5854(6)
Cl	-1648(1)	5376(1)	5201(1)
Mn(1)	353(1)	6020(1)	7297(1)
O(1)	-3179(4)	4853(2)	7367(3)
O(2)	-1769(4)	7234(2)	5063(3)
N(11)	243(4)	5100(2)	7248(3)
N(12)	-1230(4)	6315(2)	7252(3)
N(13)	895(4)	6268(2)	6229(3)
N(14)	1210(5)	6294(3)	8143(3)
C(11)	862(6)	4554(3)	7838(4)
C(12)	-1813(6)	6804(3)	7883(4)
C(13)	2042(5)	6666(3)	6023(4)
C(111)	2287(6)	4561(4)	7756(5)
C(112)	305(6)	3862(3)	7492(5)
C(113)	631(7)	4650(4)	8862(4)
C(121)	-3225(6)	6827(4)	7601(4)
C(122)	-1259(7)	7526(3)	7807(4)
C(123)	-1595(7)	6544(3)	8902(4)
C(131)	2026(6)	7407(3)	6411(4)
C(132)	2055(6)	6691(3)	4965(4)
C(133)	3248(5)	6279(4)	6422(4)
C(1)	-3905(9)	4837(4)	8914(5)
C(2)	-3296(8)	4500(4)	8215(5)
C(3)	-4310(6)	4978(5)	6802(5)
C(4)	-4765(8)	4472(5)	6165(7)
C(5)	-3969(11)	7302(10)	5046(8)
C(6)	-2946(8)	7076(5)	4577(9)
C(7)	-1409(10)	7936(4)	5002(8)
C(8)	-783(8)	8233(5)	4289(6)

$Me_3Si(CH_2)$], 466 ($M^+ - Me_3SiCH_2 - Me$), 451 ($M^+ - Me_3SiCH_2 - 2$ Me). NMR: ^{1}H δ 1.92 [s, 18 H, μ-$(CH_3)_3CN$], 1.03 [s, 18 H, $(CH_3)_3CN$], 0.51 [s, 18 H, $CH_2Si(CH_3)_3$], 0.47 [s, 4 H, CH_2SiMe_3]; ^{13}C-{^{1}H} δ 2.78 [$CH_2Si(CH_3)_3$], 23.66 [CH_2SiMe_3], 32.96 [$(CH_3)_3CN$], 35.83 [μ-$(CH_3)_3CN$)], 71.31 (μ-Me_3CN), 72.53 (Me_3CN).

*Di-μ-*tert*-butylimido-bis[benzyl(*tert*-butylimido)manganese(V)]* **10**.—As for **7** from $Mn(NBu^t)_3Cl$ (0.3 g) and $Zn(CH_2Ph)_2$ (1.23 g). After removing the volatiles in vacuum, excess $Zn(CH_2Ph)_2$ was sublimed to a solid CO_2 cooled probe at 30–40 °C (10^{-2} mmHg) and the residue chromatographed; crystallisation was from MeCN. Yield: 0.04 g, *ca.* 15%. Mass spectrum (EI): *m/z* 576 (M^+), 485 ($M^+ - CH_2Ph$), 394 ($M^+ - 2CH_2Ph$). NMR: ^{1}H δ 7.32–6.99 (s, 10 H, $CH_2C_6H_5$), 2.63 (s, 4 H, CH_2Ph), 1.72 [s, 18 H, μ-$NC(CH_3)_3$], 1.10 [s, 18 H, $NC(CH_3)_3$]; ^{13}C-{^{1}H} δ 32.3 [$(CH_3)_3CN$], 36.01 [μ-$(CH_3)_3CN$], 41.5 (CH_2Ph), 70.50 [μ-$(CH_3)_3CN$], 72.8 [$(CH_3)_3CN$], 122.8, 131.2, 151.5 (aromatic).

Interaction of **1** *with* $ZnMe_2$, *Compound* **11**.—To a solution of **1** in thf (0.2 g, 0.37 mmol in 20 cm^3) was added $ZnMe_2$ (1.48 cm^3 of 1 mol dm^{-3} solution in hexanes, 1.48 mmol). The reaction mixture was stirred at room temperature for 48 h when it was purple. After evaporation of volatiles under vacuum, extraction of the residue with light petroleum (3 × 20 cm^3), filtration, concentration to *ca.* 10 cm^3 and cooling (−20 °C), gave red-purple rhomboidal prisms. Yield: 0.15 g, *ca.* 65%. Mass spectrum (EI): *m/z* 616 (M^+), 536 (M^+ − MeZn), 521 (M^+ − MeZn − Me), 465 (M^+ − MeZn − Bu^tN − Me).

Interaction of **1** *with* $Zn(CH_2Bu^t)_2$, *Compound* **12**.—As above from **1** (0.2 g) and $Zn(CH_2Bu^t)_2$ (0.31 g, 1.48 mmol). After removing the volatiles under vacuum and condensation of high-boiling volatiles to a cold probe, the residue was extracted with light petroleum. Filtration and evaporation gave a blue-purple residue which failed to crystallise from non-polar solvent. Mass spectrum (EI): *m/z* 672 (M^+), 657 (M^+ − Me), 536 ($M^+ - CH_2Bu^tZn$).

Interaction of **1** *with* Al_2Me_6, *Compound* **13**.—To a solution of **1** in toluene (0.2 g, 0.37 mmol in 20 cm^3) was added Al_2Me_6 (0.3 cm^3 of 1.3 mol dm^{-3} solution in light petroleum, 0.39 mmol) and the mixture stirred at room temperature for 6 h when it was purple. Evaporation of the volatiles followed by extraction of the residue with light petroleum, evaporation of the blue filtrate and sublimation to a solid CO_2-cooled probe (oil-bath temperature 100–120 °C, 10^{-2} mmHg) gave a purple, air-sensitive, microcrystalline powder. Yield: 0.12 g, *ca.* 55%. Mass spectra: (EI), *m/z* 593 (M^+), 578 (M^+ − Me), 563 (M^+ − 2 Me), 548 (M^+ − 3 Me), 533 (M^+ − 4 Me); high resolution, *m/z* 593.345, $C_{26}H_{60}AlMn_2N_6$ requires 593.345.

Interaction of $[Li(dme)]_2[Mn(NBu^t)_4]$ *and* Al_2Me_6, *Compound* **14**.—To a solution of $[Li(dme)]_2[Mn(NBu^t)_4]$[1] (0.2 g, 0.37 mmol) in light petroleum (30 cm^3) was added Al_2Me_6 (1.10 cm^3 of 1.7 mol dm^{-3} solution in light petroleum, 1.87 mmol, 5 equivalents) and the purple mixture stirred for 8 h at room temperature. Removal of volatiles in vacuum, extraction of the residue in tetramethylsilane (10 cm^3), filtration, concentration to *ca.* 1 cm^3 and cooling (−20 °C), gave purple, extremely air- and moisture-sensitive rhomboidal plates of **14**. Yield: *ca.* 75%. Mass spectra: (EI), *m/z* 453 (M^+), 438 (M^+ − Me), 423 (M^+ −2 Me), 408 (M^+ − 3 Me), 393 (M^+ − 4 Me), 378 (M^+ − 5 Me); high resolution, *m/z* 453.290, $C_{20}H_{48}Al_2MnN_4$ requires 453.289.

X-Ray Crystallography.—The X-ray measurements were generally made on crystals handled under nitrogen with standard Schlenk procedures, and mounted on glass fibres using a variety of coating and adhesive media (depending on the solubility properties of the crystal being measured). Compounds **2** and **3** were handled in the dry box due to their extreme air sensitivity, and the crystals were coated with dried and degassed Nujol.

The unit-cell and intensity data for all compounds were collected using a Delft-Instruments FAST TV area detector diffractometer and graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) following previously described procedures.[27] Room-temperature (291 K) data were collected on a dark red air-stable crystal of compound **1**, using Araldite as a fixative. Most of the crystals (recrystallised from acetonitrile) were hollow plates. Although the data quality was poor, the compound was found to be isostructural with its rhenium analogue $Re_2(NBu^t)_6$.[2] The data for compound **1** were collected in the orthorhombic (body centred) crystal system with cell dimensions a = 11.045(3), b = 17.485(3) and c = 34.298(11) Å; these are almost identical to the transformed dimensions for the rhenium analogue, a = 11.193, b = 17.818, c = 35.507 Å. The data were transformed to the lower symmetry triclinic crystal system (as with the Re analogue) in an attempt to minimise the evident serious disorder which existed in all *tert*-butyl orientations. The structure was solved in the centrosymmetric space group $P\bar{1}$ and refined to an R factor of 0.12. Completion of the refinement was still not possible due to severe disorder, but the $N_2MnN_2MnN_2$ core was well defined; thus the species can be assumed to be $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$. The data collection and refinement details for the other compounds are given in Table 7, including the temperature used for each data collection. All of the structures were solved by direct methods using SHELXS 86[28] and refined using full-matrix least squares on F^2 (SHELX 93; scattering factors included in the gamma test version program).[29] The data for all of the compounds, except **2** and **3** were corrected for absorption using the program DIFABS[30] adapted for FAST geometry.[31] Compound **2** contains two disordered diethyl ether solvent molecules with high thermal parameters and large thermal ellipsoids for atoms C(4), C(5), C(6) and C(7). All of the

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Table 9 Fractional atomic coordinates ($\times 10^4$) for compound **3**

Atom	x	y	z	Atom	x	y	z
Molecule 1				Molecule 2			
Li(1)	2 293(15)	5 336(10)	364(13)	Li(1)	2 292(15)	5 334(10)	365(13)
Li(2)	11 338(12)	−5(9)	3 956(11)	Li(2)	11 336(12)	−5(9)	3 958(11)
Li(3)	13 841(12)	1 503(11)	−254(11)	Li(3)	13 836(13)	1 500(11)	−259(11)
Li(4)	12 771(12)	221(9)	−163(12)	Li(4)	12 776(13)	220(10)	−164(13)
Li(5)	14 649(13)	303(8)	538(9)	Li(5)	14 655(13)	306(9)	540(9)
Li(6)	9 628(13)	4 299(9)	150(11)	Li(6)	9 631(13)	4 293(9)	146(11)
Cl(1)	8 964(2)	5 538(1)	47(2)	Cl(1)	8 963(2)	5 538(2)	47(2)
Cl(2)	14 024(2)	341(1)	−735(2)	Cl(2)	14 024(2)	341(2)	−735(2)
Mn(1)	8 323(1)	3 745(1)	536(1)	Mn(1)	8 323(1)	3 745(1)	536(1)
Mn(2)	13 445(1)	1 061(1)	828(1)	Mn(2)	13 445(1)	1 061(1)	829(1)
O(1)	3 252(6)	4 888(5)	1 067(5)	O(1)	3 254(7)	4 888(5)	1 065(5)
O(2)	11 307(6)	685(4)	3 290(4)	O(2)	11 303(7)	683(4)	3 292(5)
O(3)	13 904(5)	2 212(4)	−926(4)	O(3)	13 902(6)	2 213(4)	−924(4)
O(4)	11 885(7)	−386(6)	−720(5)	O(4)	11 883(7)	−390(6)	−718(5)
N(11)	7 516(6)	4 412(4)	576(5)	N(11)	7 513(6)	4 416(4)	573(5)
N(12)	9 348(5)	4 050(4)	1 057(4)	N(12)	9 349(5)	4 054(4)	1 056(4)
N(13)	8 490(5)	3 787(4)	−307(4)	N(13)	8 493(6)	3 786(4)	−308(4)
N(14)	8 044(7)	2 994(4)	715(5)	N(14)	8 042(7)	2 987(5)	716(5)
N(21)	12 666(5)	1 266(4)	68(4)	N(21)	12 661(6)	1 268(4)	66(4)
N(22)	14 500(5)	1 340(4)	723(4)	N(22)	14 499(5)	1 341(5)	723(4)
N(23)	13 503(6)	144(4)	822(5)	N(23)	13 506(6)	147(4)	823(5)
N(24)	13 198(6)	1 355(5)	1 474(5)	N(24)	13 196(7)	1 357(5)	1 480(5)
C(11)	6 654(8)	4 355(7)	767(7)	C(11)	6 650(8)	4 355(7)	767(8)
C(12)	10 000(8)	3 730(6)	1 635(6)	C(12)	9 999(9)	3 727(6)	1 636(6)
C(13)	8 403(8)	3 228(6)	−828(6)	C(13)	8 405(8)	3 223(6)	−831(6)
C(21)	11 829(8)	1 692(6)	−76(7)	C(21)	11 825(8)	1 692(6)	−76(7)
C(22)	15 219(7)	1 784(6)	1 166(6)	C(22)	15 220(8)	1 782(6)	1 168(6)
C(23)	13 404(9)	−387(6)	1 334(6)	C(23)	13 408(10)	−384(7)	1 337(7)
C(101)	3 349(11)	4 150(7)	1 048(8)	C(111)	6 002(8)	3 934(6)	211(7)
C(102)	3 337(11)	3 945(7)	1 768(8)	C(112)	6 260(8)	5 108(7)	770(7)
C(103)	3 324(10)	4 605(8)	2 142(8)	C(113)	6 747(9)	4 008(7)	1 461(7)
C(104)	3 644(12)	5 123(8)	1 730(8)	C(121)	10 688(8)	4 306(7)	1 928(7)
C(121)	10 687(8)	4 303(7)	1 936(7)	C(122)	9 525(10)	3 499(8)	2 203(7)
C(111)	6 001(8)	3 936(6)	214(7)	C(123)	10 473(9)	3 110(7)	1 387(7)
C(112)	6 265(8)	5 104(7)	771(7)	C(131)	9 089(9)	2 665(6)	−561(6)
C(113)	6 755(9)	4 008(6)	1 456(6)	C(132)	8 624(9)	3 569(6)	−1 446(6)
C(122)	9 535(10)	3 500(8)	2 198(6)	C(133)	7 449(8)	2 900(6)	−1 002(7)
C(123)	10 469(8)	3 114(6)	1 390(7)	C(211)	11 136(9)	1 387(8)	286(7)
C(131)	9 085(9)	2 672(6)	−562(6)	C(212)	12 075(10)	2 459(7)	180(8)
C(132)	8 616(9)	3 570(6)	−1 444(6)	C(213)	11 437(9)	1 709(7)	−840(7)
C(133)	7 459(8)	2 902(6)	−1 001(7)	C(221)	15 579(8)	1 428(6)	1 854(6)
C(201)	11 457(12)	647(8)	2 636(7)	C(222)	15 983(7)	1 861(7)	818(7)
C(202)	11 496(10)	1 356(7)	2 371(7)	C(223)	14 827(8)	2 496(6)	1 251(6)
C(203)	11 253(16)	1 814(8)	2 869(9)	C(231)	13 628(10)	−1 096(7)	1 084(8)
C(204)	11 298(12)	1 398(8)	3 447(7)	C(232)	12 439(9)	−388(7)	1 427(7)
C(231)	13 628(10)	−1 087(7)	1 080(8)	C(233)	14 043(10)	−212(8)	2 037(7)
C(232)	12 441(8)	−392(7)	1 429(7)	C(101)	3 351(11)	4 141(7)	1 041(8)
C(233)	14 042(10)	−216(8)	2 030(7)	C(102)	3 341(11)	3 939(7)	1 764(8)
C(221)	15 576(8)	1 433(6)	1 852(6)	C(103)	3 328(10)	4 604(8)	2 143(8)
C(222)	15 982(7)	1 860(7)	815(7)	C(104)	3 652(12)	5 129(8)	1 732(8)
C(223)	14 831(8)	2 492(5)	1 252(6)	C(201)	11 456(13)	646(8)	2 632(8)
C(211)	11 133(8)	1 385(7)	286(7)	C(202)	11 493(10)	1 362(7)	2 365(7)
C(212)	12 078(9)	2 457(7)	181(8)	C(203)	11 238(17)	1 815(9)	2 866(9)
C(213)	11 441(9)	1 707(7)	−841(7)	C(204)	11 298(12)	1 397(8)	3 453(8)
C(301)	13 749(10)	2 061(7)	−1 640(6)	C(301)	13 750(11)	2 061(7)	−1 642(7)
C(302)	14 269(11)	2 560(7)	−1 942(7)	C(302)	14 272(12)	2 563(8)	−1 948(7)
C(303)	14 434(13)	3 153(9)	−1 479(8)	C(303)	14 437(13)	3 161(9)	−1 484(8)
C(304)	14 234(11)	2 909(6)	−820(8)	C(304)	14 232(12)	2 913(7)	−817(8)
C(401)	11 507(14)	−1 009(11)	−564(10)	C(401)	11 488(15)	−1 002(11)	−558(11)
C(402)	11 386(14)	−1 005(16)	−1 714(12)	C(402)	11 381(14)	−1 014(15)	−1 714(13)
C(403)	10 995(19)	−1 289(14)	−1 204(13)	C(403)	10 988(19)	−1 292(14)	−1 197(14)
C(404)	11 697(16)	−313(12)	−1 435(9)	C(404)	11 695(16)	−313(12)	−1 437(9)

bond lengths in the diethyl ether molecules were fixed (averaged between the two molecules) giving rise to a more meaningful chemical model. Due to the small size of the crystal, compound **3** gave only a weak data set (approximately 76% of the reflections were unobserved). Therefore the value of $wR2$ for all of the data is high (0.2703). There is disorder evident in some of the thf molecules, leading to high thermal parameters for some of the carbon atoms. The bond lengths and angles are all well defined and within acceptable limits.

Compound **4** was solved in the enantiomorphic tetragonal space group $P4_12_12$(92). The structure presented gave a Flack parameter of zero [0.02(4)]. All of the hydrogen atoms for this structure were experimentally located from the difference map. The structure of compound **11** was refined

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Table 10 Fractional atomic coordinates (× 10^4) for compound **4**

Atom	x	y	z
Mn	2058(1)	2058(1)	0*
N(1)	3003(4)	2951(4)	−500(1)
N(2)	−356(3)	2746(4)	−186(1)
C(1)	2299(4)	3850(4)	−780(1)
C(2)	3257(4)	4624(4)	−1080(1)
C(3)	2502(5)	5544(5)	−1358(1)
C(4)	784(5)	5780(5)	−1368(1)
C(5)	−146(5)	5055(5)	−1089(1)
C(6)	546(4)	4110(4)	−788(1)
C(7)	−605(5)	3497(4)	−506(1)
C(8)	5102(5)	4427(6)	−1077(1)
C(9)	−1864(4)	2386(4)	56(1)
C(10)	−2859(6)	3976(5)	127(1)
C(11)	−2947(6)	1121(6)	−146(1)
C(12)	−1285(6)	1724(6)	441(1)

* Invariant parameter.

Table 11 Fractional atomic coordinates (× 10^4) for compound **7**

Atom	x	y	z
Mn(1)	1783(1)	2709(1)	6268(1)
Mn(2)	−167(1)	2492(1)	6236(1)
N(1)	2689(3)	3438(2)	6375(2)
N(2)	849(3)	2481(2)	7081(2)
N(3)	−1319(3)	2967(2)	6312(3)
N(4)	788(3)	2688(2)	5423(2)
C(1)	3118(4)	4267(3)	6485(3)
C(2)	864(4)	2523(3)	8000(3)
C(3)	−2116(4)	3644(3)	6409(3)
C(4)	715(4)	2894(3)	4520(3)
C(5)	−509(4)	1262(3)	6083(3)
C(6)	2611(4)	1631(3)	6128(4)
C(11)	3967(5)	4427(4)	5815(4)
C(12)	3604(5)	4378(4)	7361(4)
C(13)	2129(5)	4850(3)	6338(3)
C(21)	2026(5)	2328(3)	8338(3)
C(22)	565(5)	3404(3)	8259(3)
C(23)	42(5)	1922(3)	8331(3)
C(31)	−1440(5)	4432(3)	6469(4)
C(32)	−2720(5)	3499(4)	7218(3)
C(33)	−2918(5)	3661(4)	5662(4)
C(41)	−22(5)	3640(3)	4404(3)
C(42)	223(5)	2176(3)	4051(3)
C(43)	1841(4)	3101(4)	4212(3)
C(51)	−1651(5)	909(3)	6028(3)
C(52)	−2259(5)	1036(3)	6846(3)
C(53)	−2356(5)	1241(4)	5296(4)
C(54)	−1535(5)	−32(3)	5910(4)
C(61)	3852(4)	1534(3)	6109(3)
C(62)	4121(5)	616(3)	6013(4)
C(63)	4309(5)	1994(4)	5380(4)
C(64)	4420(5)	1850(4)	6897(4)

using the TWIN instruction with a batch scale factor (BASF) of 0.44.

The non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms in compounds **2**, **3**, **7**, **10** and **11** were placed in calculated positions (C–H 0.96 Å, C–C–H and H–C–H 109.5°).

Fractional atomic coordinates are given in Tables 8–13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 12 Fractional atomic coordinates (× 10^4) for compound **10**

Atom	x	y	z
Mn(1)	1049(1)	7275(1)	5323(1)
Mn(2)	1460(1)	7295(1)	6692(1)
N(1)	884(3)	7865(2)	4574(2)
N(2)	2432(2)	7217(2)	5915(1)
N(3)	1714(3)	7880(2)	7439(2)
N(4)	81(2)	7294(2)	6097(1)
C(1)	851(4)	8596(3)	4112(2)
C(2)	3725(3)	7308(3)	5841(2)
C(3)	1873(4)	8597(2)	7918(2)
C(4)	−1202(3)	7485(2)	6161(2)
C(5)	1698(3)	6175(2)	7170(2)
C(6)	660(3)	6150(2)	4884(2)
C(11)	−453(4)	8781(3)	3828(2)
C(12)	1599(4)	8460(3)	3431(2)
C(13)	1376(4)	9284(3)	4622(3)
C(21)	4000(3)	7218(3)	4999(2)
C(22)	4115(4)	8135(3)	6139(2)
C(23)	4383(4)	6660(3)	6331(2)
C(31)	1505(4)	9346(3)	7435(2)
C(32)	3178(4)	8679(3)	8233(2)
C(33)	1063(4)	8511(3)	8569(2)
C(41)	−1356(4)	8401(3)	6155(2)
C(42)	−1582(4)	7161(3)	6902(2)
C(43)	−1953(4)	7165(3)	5470(2)
C(51)	961(3)	5932(2)	7796(2)
C(52)	−2(4)	5408(3)	7667(2)
C(53)	−649(4)	5153(3)	8271(3)
C(54)	−329(4)	5414(3)	9001(3)
C(55)	621(4)	5935(3)	9143(2)
C(56)	1243(4)	6196(3)	8551(2)
C(61)	1619(3)	5805(3)	4461(2)
C(62)	1785(4)	6028(3)	3709(2)
C(63)	2700(4)	5698(3)	3318(2)
C(64)	3478(4)	5139(3)	3668(3)
C(65)	3316(4)	4912(3)	4406(3)
C(66)	2422(4)	5229(2)	4799(2)

Table 13 Fractional atomic coordinates (× 10^4) for compound **11**

Atom	x	y	z
Zn	−564(1)	2500*	1250*
Mn(1)	1386(1)	2500*	1250*
Mn(2)	3204(1)	2500*	1250*
N(1)	519(2)	2552(2)	869(1)
N(2)	2242(2)	1574(1)	1222(1)
N(3)	3844(2)	2575(2)	849(1)
C(1)	527(2)	2601(3)	439(1)
C(2)	2267(2)	519(2)	1214(1)
C(3)	4623(2)	2661(3)	569(1)
C(21)	2524(4)	169(2)	1631(1)
C(22)	3003(3)	196(3)	916(1)
C(23)	1283(3)	163(3)	1109(1)
C(11)	1549(2)	2528(3)	276(1)
C(12)	−62(3)	1769(3)	274(1)
C(13)	74(3)	3568(3)	319(1)
C(31)	5298(4)	3408(5)	720(2)
C(32)	5130(4)	1705(4)	533(2)
C(33)	4202(4)	2944(6)	174(1)
C(4)	−1982(3)	2500*	1250*

* Invariant parameter.

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