# Non-oxo Chemistry of Manganese in High Oxidation States. Part 1. Mononuclear *tert*-Butylimido Compounds of Manganese-(VII) and -(VI)†

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The interaction of manganese(III) chloride in acetonitrile with $NHR(SiMe_3)$ (R = $Bu^t$ or $CMe_2CH_2Me$) gave the manganese(VII) species $Mn(NR)_3Cl$ as thermally and air-stable green crystals. The chlorine atom in $Mn(NBu^t)_3Cl$ **1** has been substituted by Br, OC(O)R (R = Me or $CF_3$), $OC_6X_5$ (X = F or Cl), $OCH(CF_3)_2$, $SC_6F_5$, $C_6F_5$ or $NHBu^t$ by use of $SiMe_3Br$ and the silver, thallium or lithium salts of other reagents. Interaction of compound **1** with $Ag(O_3SCF_3)$ or $AgPF_6$ and $NH_2Bu^t$ gave the salts of the cation $[Mn(NBu^t)_3(NH_2Bu^t)]^+$, with $Li(NHBu^t)$ under selected conditions gave the paramagnetic manganese(VI) analogues of the manganate(VI) anion, $[LiL]_2[Mn(NBu^t)_4]$ [L = 1,2-dimethoxyethane (dme) or *N,N,N',N'*-tetramethylethylenediamine (tmen)], and with HCl gave $Mn(NBu^t)_2(NHBu^t)Cl_2$, the reaction being reversed by addition of pyridine. Unstable compounds, *e.g.* $Mn(NBu^t)_3(C_6F_5)$ and $Mn(NBu^t)_3(NHBu^t)$, were characterised spectroscopically. The mechanism of the formation of **1** is discussed together with a mechanism accounting for the instability of compounds where the X-group has β-H atoms as in $Mn(NBu^t)_3[OCH(CF_3)_2]$. β-Hydrogen transfer to a $NBu^t$ group to give a manganese(V) dimer $[Mn(NBu^t)_2(NHBu^t)]_2$ occurs with the formation of ketones from alkoxides; for alkyls decomposition appears to involve homolysis of the Mn–C bond and a radical pathway. The crystal structures of the compounds $Mn(NBu^t)_3X$, X = OC(O)Me, $OC_6F_5$, $SC_6F_5$, $[Mn(NBu^t)_3(NH_2Bu^t)]Y$, Y = $CF_3SO_3$ or $PF_6$ and $[Li(dme)]_2[Mn(NBu^t)_4]$ have been determined. In all the compounds the manganese atom has distorted tetrahedral geometry. In the first three the Mn–N(imido) bond lengths are 1.664(3)–1.673(9) Å and the Mn–N–C angles 139.9(2) to 144.6(3)°, indicating partial multiple-bond character. The Mn–X distances, 1.91(3), 1.896(2) and 2.289(1) Å respectively indicate single bonds. In the cationic compounds the Mn–N(imido) distances are 1.531(8)–1.655(8) Å, with Mn–N–C angles of 135.8(6)–170.2(9)°, suggesting more uneven distribution of the Mn–N multiple bonding, although these structures were less precisely determined due to disorder. In the manganate(VI) anion the Mn–N(imido) lengths are longer, 1.746(3)–1.749(3) Å, as expected.

The history of manganese compounds in the oxidation states VI and VII is long and recondite.[1a] The manganate, $MnO_4^{2-}$, and permanganate, $MnO_4^-$, ions were first observed by Glauber[1b] in 1659, by Pott in 1740 and Scheele[1b] in 1775 after fusion of pyrolusite ($MnO_2$) with alkali in air or with $KNO_3$ and dissolution of the melt in water. However, the isolation and characterisation of crystalline salts was not achieved until after *ca.* 1830 by Mitscherlich,[1b] Aschoff and others. During this period, the oxide $Mn_2O_7$[1a,2] and the oxohalides $MnO_3X$, X = F (Wöhler,[1b] 1827) or Cl (Aschoff, 1860) were made though probably in impure states. The fluoride[3] and chloride[4] were fully characterised only quite recently; both are explosive when pure, as is $Mn_2O_7$.

Of interest is the statement by Collins *et al.*[5] that 'Although there are over 120,000 entries in the *Chemical Abstracts Formula Index* for manganese, fewer than ten, unique, fully characterized species of manganese-(V), -(VI) and -(VII) are stable under normal conditions'. Reviews are available.[6]

The first compounds of $Mn^{VII}$ and $Mn^{VI}$ without Mn=O bonds, $Mn(NBu^t)_3Cl$ **1** and $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$, have been briefly described and the crystal structure of **1** reported.[7] This paper describes the synthesis and some reactions of mononuclear *tert*-butylimido species of $Mn^{VI}$ and $Mn^{VII}$; the dimeric and other manganese species in oxidation states V, VI and VI–VII will be described subsequently. Analytical and physical data for the new compounds are given in Table 1, NMR data in Table 2. The principal reactions are shown in Scheme 1.

## Results and Discussion

*Syntheses.*—The synthesis of $Mn(NBu^t)_3Cl$ **1** involves the interaction at *ca.* −40 °C between the purple solution of $MnCl_3$ in acetonitrile that was obtained on reaction of $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ with $SiMe_3Cl$ in MeCN[8a] and an excess of $NHBu^t(SiMe_3)$. It appears that the stoichiometry of the bulk oxoacetate may vary; an analytical sample was found[8b] to be $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot MeCO_2H\cdot 3H_2O$. The yields of **1** can be given only approximately (18–20%) since the oxoacetate was made on a 300 g scale and some loss of water or acetic acid could have occurred with time on storage.

The addition of $NHBu^t(SiMe_3)$ to the purple solution should be carried out at low temperatures, *ca.* −40 °C, with stirring especially in large-scale preparations, in order to avoid local heating caused by the exothermic reaction of the silylamine with the $MnCl_3$ solution. The use of excess of silylamine is required (*a*) to neutralise acidic compounds produced by the reaction of water and acetic acid with $SiMe_3Cl$, (*b*) to remove HCl produced in the synthesis of compound **1** (see proposed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
*Non-SI unit employed:* G = $10^{-4}$ T.

**Table 1** Analytical and physical data for new manganese compounds

| Compound | Colour | M.p.[a]/°C | Analysis (%)[b] C | H | N |
|---|---|---|---|---|---|
| **1** $Mn(NBu^t)_3Cl$ | Dark green | 94–95 | 47.3 (47.4) | 8.8 (8.9) | 13.4 (13.8) |
| **2** $Mn(NCMe_2CH_2Me)_3Cl$ | Green | 63–65 | 51.8 (52.1) | 10.1 (9.6) | 12.1 (12.1) |
| **3** $Mn(NBu^t)_3Br$ | Green | 105–107 | 51.8 (52.1) | 10.1 (9.6) | 12.1 (12.1) |
| **4** $Mn(NBu^t)_3(O_2CMe)$ | Green | 49–59 | 51.4 (51.4) | 9.3 (9.2) | 12.8 (12.8) |
| **5** $Mn(NBu^t)_3(O_2CCF_3)$ | Green | 69–72 | 43.8 (44.1) | 6.4 (7.0) | 10.5 (11.0) |
| **6** $Mn(NBu^t)_3(OC_6F_5)$ | Green | 95–97 | 48.4 (47.9) | 6.1 (6.0) | 9.8 (9.3) |
| **7** $Mn(NBu^t)_3(OC_6Cl_5)$ | Green | 111–112 | 40.5 (41.7) | 4.8 (5.2) | 7.7 (8.1) |
| **8** $Mn(NBu^t)_3[OCH(CF_3)_2]$ | Green | Oil[c] | — | — | — |
| **9** $Mn(NBu^t)_3(SC_6F_5)$ | Green | 121–122 | 46.6 (46.2) | 5.9 (5.8) | 9.4 (9.0) |
| **10** $Mn(NBu^t)_3(C_6F_5)$ | Green | Oil[c,d] | — | — | — |
| **11** $Mn(NBu^t)_3(NHBu^t)$ | Green-brown | Oil[d] | — | — | — |
| **12** $Mn(NBu^t)_3[OC(O)NHBu^t]$ | Green | *d* | — | — | — |
| **13** $[Mn(NBu^t)_3(NH_2Bu^t)]CF_3SO_3$ | Green | 127–129 | 41.8 (41.6) | 6.9 (5.9) | 11.5 (11.4) |
| **14** $[Mn(NBu^t)_3(NH_2Bu^t)]PF_6$ | Green | 120–125 (decomp.) | — | — | — |
| **15** $[Li(dme)]_2[Mn(NBu^t)_4]$ | Brown | 170–180 (decomp.) | 51.0 (54.0) | 10.2 (10.5) | 9.9 (10.5) |
| **16** $[Li(tmen)]_2[Mn(NBu^t)_4]$ | Red-brown | 173–175 (decomp.) | 57.4 (57.4) | 12.1 (11.6) | — |

[a] Compounds **1**–**7** tend to decompose partially at or slightly below the m.p. [b] For mass spectra see Experimental section. [c] For accurate mass spectrum see Experimental section. [d] Unstable, see text.

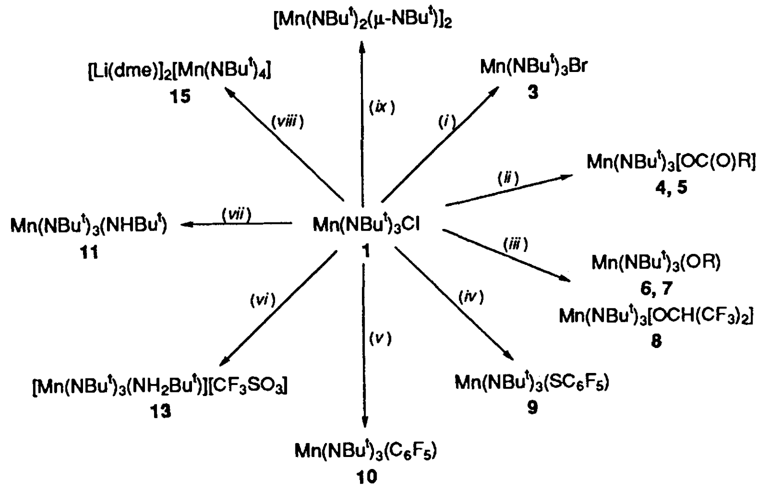
**Table 2** NMR data for manganese(VII) compounds[a]

| | $^1H$ | | $^{13}C-\{^1H\}$ | | | | $^{19}F$ |
|---|---|---|---|---|---|---|---|
| Compound | $CH_3C$ | Other | $C_\alpha$[b] | $C_\beta$[b] | $\Delta\delta$ | Other | |
| **1** | 1.38 | | | | | | |
| | 1.56[c] | | 80.5[c] | 30.7[c] | 49.8 | | |
| **2** | 1.38 | 0.95 (t), 1.80 (q)<br>$(CH_3CH_2, CH_2)$<br>$J$ = 7.25 Hz | 83.6 | 28.8<br>37.2<br>$(CH_2Me)$ | 54.8<br>46.4 | 10.5<br>$(CH_2CH_3)$ | |
| **3** | 1.40 | | *d* | 30.6 | | | |
| **4** | 1.55 | 1.96 $(CH_3CO_2)$ | | | | | |
| | 1.51[c] | 1.84[c] | 79.7[c] | 30.5[c] | 49.2 | 22.9 $(CH_3CO_2)$,<br>174.8 $(CO_2)$ | |
| **5** | 1.57 | | 80.8 | 30.4 | 50.4 | 115.6 $(CF_3CO_2)$,<br>$J_{CF}$ = 289.5 Hz;<br>160.7 $(CF_3CO_2)$ | −74.3 |
| **6** | 1.29 | | 80.4 | 30.8 | 49.6 | *e* | −158.8 (d),<br>−168.1 (t),<br>−173.7 (m) |
| **7** | 1.24 | | 81.9 | 30.9 | 51.0 | 122.7, 131.6,<br>163.6 (aromatic) | |
| **8** | 1.29 | 4.33 $[(CF_3)_2CHO]$ | 79.6 | 30.5 | 49.1 | *d* | −74.9 |
| **9** | 1.29 | | 79.5 | 30.7 | 48.8 | *e* | −129.9 (d),<br>−159.5 (d),<br>−165.1 (m) |
| **10** | 1.39 | | | | | | −107.5 (d),<br>−157.8 (d),<br>−162.8 (t) |
| **11** | 1.45 | 1.22 $[(CH_3)_3CNH]$,<br>3.05 $(Bu^tNH)$ | 78.2,<br>53.5 | 31.4,<br>33.8 $(Bu^tNH)$ | 46.8 | | |
| **12** | 1.48 | 1.19 $[OC(O)NHBu^t]$,<br>4.4 $[OC(O)NHBu^t]$ | 78.9 | 31.2 | 47.7 | 50.1 $[Me_3CNHC(O)O]$,<br>30.0 $[(CH_3)_3CNHC(O)O]$,<br>160.0 $[OC(O)]$ | |
| **13** | 1.38 | 1.23 $[(CH_3)_3CNH_2]$ | 82.1 | 31.0 | 51.1 | 52.2 $(Me_3CNH_2)$,<br>30.2 $[(CH_3)_3CNH_2]$ | −78.1 |
| **14**[f] | 1.28 | 1.01 $[(CH_3)_3CNH_2]$,<br>3.9 $(Me_3CNH_2)$ | 82.0 | 31.0 | 51.0 | 52.1 $(Me_3CNH_2)$,<br>30.1 $[(CH_3)_3CNH_2]$ | |

[a] In $C_6D_6$. [b] For $C_\beta H_3C_\alpha$ of $Bu^tN$ imido groups; $\Delta\delta = \delta_\alpha - \delta_\beta$ [see ref. 11(*a*), Table 14–4, p. 133). [c] In $CD_2Cl_2$. [d] Not observed. [e] Aryl C not observed. [f] $^{31}P-\{^1H\}$: δ −142.3 (spt, $J_{PF}$ = 712 Hz).

mechanism below). After addition of $NHBu^t(SiMe_3)$ the solution becomes orange-brown but on stirring at room temperature for several hours it turns dark green. The work-up is described below and in the Experimental section.

The only other compound similar to **1** that has been obtained by this route is the *tert*-pentyl, $Mn(NCMe_2CH_2Me)_3Cl$ **2**, obtained using $NH(CMe_2CH_2Me)(SiMe_3)$ obtained from $NH_2(CMe_2CH_2Me)$ and $SiMe_3Cl$. No product could be isolated using $NHPr^i(SiMe_3)$; with cyclohexylsilylamine a blue-green coloration was observed which exists for *ca.* 10 min at room temperature fading to a colourless paramagnetic ($Mn^{II}$) solution and a white precipitate. Most persistent blue-green colorations are observed using $NMe(SiMe_3)_2$ or $NH(SiMe_3)_2$, but these again fade after *ca.* 10 min. The monosilyl derivatives



**Scheme 1** Principal reactions of Mn(NBu$^t$)$_3$Cl. (*i*) SiMe$_3$Br, toluene; (*ii*) R = Me **4** or CF$_3$ **5**, silver salts, CH$_2$Cl$_2$; (*iii*) R = C$_6$X$_5$, X = F **6**, Cl **7** and CH(CF$_3$)$_2$ **8**, Tl(OR), toluene; (*iv*) Tl(SC$_6$F$_5$), toluene; (*v*) Ag(C$_6$F$_5$), Et$_2$O; (*vi*) Ag(O$_3$SCF$_3$), NH$_2$Bu$^t$, CH$_2$Cl$_2$; (*vii*) Li(NHBu$^t$), thf, −40 °C; (*viii*) Li(NHBu$^t$) (5 equivalents) dme, −78 °C, slow warming; (*ix*) Na–Hg, thf

of aromatic amines (PhNH$_2$, 2,6-Me$_2$C$_6$H$_3$NH$_2$ and 2,6-Pr$^i_2$C$_6$H$_3$NH$_2$), or the amines themselves, react with MnCl$_3$ in MeCN only to give intractable materials. The exception is C$_6$F$_5$NH$_2$ which gives initially a green solution that fades to yellow and finally yellow-orange. Yellow-orange crystals isolated from this solution after evaporation, extraction with hexane and cooling were identified by spectroscopic (mass, NMR) and analytical data and m.p. 137–138 (lit., 138 °C) as decafluoroazobenzene[9] that is evidently formed by coupling of C$_6$F$_5$N groups.

The yield of compound **1** never exceeds *ca.* 20% based on Mn when the solvent is MeCN; lower yields are obtained when CH$_2$Cl$_2$ or tetrahydrofuran is used as solvent. There is no significant variation in the yield of **1** when the reaction mixture in MeCN is exposed to dry oxygen or when oxidants such as FeCl$_3$, [NH$_3$Bu$^t$][MnO$_4$] or [Hpy]$_2$[CeCl$_6$] (py = pyridine) are added. However, exposure to moisture has to be avoided before the green solution is evaporated under vacuum to remove all volatiles [*e.g.* SiMe$_3$Cl, MeCO$_2$SiMe$_3$, (Me$_3$Si)$_2$O, NHBu$^t$(SiMe$_3$) and MeCN]. The presence of water evidently leads to hydrolysis of excess of SiMe$_3$Cl and reduced yields of **1**. The dry residue can then be treated with water and **1** extracted with hexane. The aqueous phase contains various salts such as NH$_3$Bu$^t$Cl and the yellow-green [MnCl$_4$]$^{2-}$ ion that has been isolated and characterised by X-ray diffraction as the mixed salt [NH$_3$Bu$^{t+}$]$_3$[MnCl$_4$]$^{2-}$Cl$^-$. Solutions containing **1** should not be heated above *ca.* 50 °C when decomposition begins (see below).

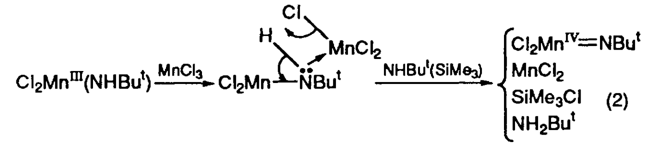
The compound **1** can also be obtained by interaction of the purple MeCN solution of MnCl$_3$ with NH$_2$Bu$^t$ when NHBu$^t$(SiMe$_3$) is formed *in situ* from the excess of SiMe$_3$Cl used for conversion of the oxoacetate into MnCl$_3$. It is also possible to react MnCl$_3$ made in CH$_2$Cl$_2$ as solvent with NBu$^t$Cl$_2$ [10a] or NBu$^t$Cl(SiMe$_3$) [10b] but the yields are low and there is the hazard of using the toxic chloroamines. Finally, **1** can be formed in low yield by interaction of [NBu$^n_4$][MnO$_4$] in MeCN with SiMe$_3$Cl and NHBu$^t$(SiMe$_3$) but polysiloxane by-products lead to difficulties in separation of **1**.

It has not been possible to isolate any manganese intermediates in the initial reaction mixture in MeCN, which of course contains also a variety of silicon compounds. As no obvious oxidant other than MnCl$_3$ is present, the formal 4e oxidation Mn$^{\text{III}}$ $\longrightarrow$ Mn$^{\text{VII}}$ to give **1** presumably depends on MnCl$_3$ acting as a Lewis acid, leading to dehydrochlorination of amido intermediates. Oxidations of compounds with N–H (and C–H) bonds leading to an increase in the oxidation state of the metal are known,[11a] while oxidations by O$_2$ of amido species to imido complexes of ruthenium have been reported.[8b,c]

Presumably, the initial reaction is the interaction of MnCl$_3$(MeCN)$_3$ with NHBu$^t$(SiMe$_3$) as in equation (1)

$$\mathrm{MnCl_3 + NHBu^t(SiMe_3) \longrightarrow MnCl_2(NHBu^t) + SiMe_3Cl} \quad (1)$$

(omitting co-ordinated MeCN). This reaction could then be followed by that in equation (2) which leads to the oxidation



(2)

Mn$^{\text{III}}$ $\longrightarrow$ Mn$^{\text{IV}}$. Repetition of this sequence would lead to Mn$^{\text{VI}}$(NBu$^t$)$_3$ which could finally be chlorinated by MnCl$_3$ to give compound **1** and the overall stoichiometry of equation (3).

$$\mathrm{5MnCl_3 + 6NHBu^t(SiMe_3) \longrightarrow MnCl(NBu^t)_3 + 4MnCl_2 + 6SiMe_3Cl + 3NH_2Bu^t} \quad (3)$$

This would suggest a maximum yield of 20% based on manganese comparable to those observed. Since HCl would be liberated on the addition of SiMe$_3$Cl to the hydrated oxoacetate, [NH$_3$Bu$^t$]Cl will be present in the reaction mixture as well as siloxanes. The end result is that after evaporation of the mixture and addition of water the manganese products are MnCl(NBu$^t$)$_3$ and [NH$_3$Bu$^t$]$_2$[MnCl$_4$]. This scheme is doubtless oversimplified and species with the amines co-ordinated to MnCl$_3$ and MnCl$_2$ are likely to be involved also.

*Properties of* Mn(NBu$^t$)$_3$Cl.—The compound is unaffected by air and water under ambient conditions. It melts (*ca.* 94 °C) with some decomposition and sublimes in vacuum at *ca.* 70 °C; in solution in organic solvents, decomposition begins at around 60 °C (see later). Whether the imido groups are formally considered as 4e or 6e donors,[12] the chemical reactivity of **1** suggests that the metal centre is electronically saturated: thus **1** does not add or react with Lewis bases, *e.g.* pyridine, and is unaffected by methanol and acetic acid when diluted in organic solvents. By comparison its rhenium analogue Re(NBu$^t$)$_3$Cl[13] is attacked by both water and alcohols.

The $^{13}$C NMR chemical shift difference, Δδ, between the C$_\alpha$ and C$_\beta$ atoms of the *tert*-butylimido groups in compound **1** (Table 2) is indicative of the degree of π donation from the nitrogen atom to the metal [see ref. 11(*a*), p. 133]. The value of

$\Delta\delta = 49.8$ is higher than that for the rhenium analogue ($\Delta\delta = 37.8$), and comparable to values found for compounds having strong π-electron-accepting metal centres, *e.g.* $\mathrm{Re(NBu^t)_2Cl_3}$ [11a] (50), $\mathrm{Os(NBu^t)O_3}$ [11a] (55) and $\mathrm{Cr(NBu^t)_2Cl_2}$ [14] (52.1).

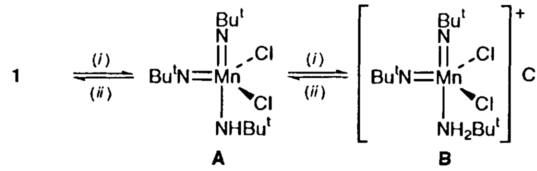
The mass spectrum of compound **1** shows that there is facile sequential loss of methyl groups from the *tert*-butyl groups; this is a feature also of the other $\mathrm{Mn(NBu^t)_3X}$ compounds discussed below and suggests a low-energy, unimolecular decomposition pathway in the gas phase.

In cyclohexane, benzene, $\mathrm{CHCl_3}$ and other similar solvents decomposition of compound **1** is complete within *ca.* 3 h at 60 °C. The green solution becomes red-brown and is paramagnetic; in cyclohexane a brown precipitate is formed. After collection of volatiles in a cold-trap under vacuum the main species identified by gas chromatography–mass spectrometry (GC–MS) are $\mathrm{Me_2C{=}CH_2}$, $\mathrm{Me_2C{=}NMe}$, $\mathrm{NH_2Bu^t}$, $\mathrm{Me_3CN{=}CMe_2}$ [15a] and a smaller amount of $\mathrm{Me_2C{=}NH}$. A further major component [$m/z = 115$, $^1$H NMR δ 1.34(3) and 1.92(1)] is tentatively assigned as $\mathrm{Me_2(NHMe)CCHMe_2}$. Thermogravimetric study of the thermal decomposition of **1** under $\mathrm{N_2}$ showed a weight loss of *ca.* 35% of the initial mass occurring exothermically beginning at 82.3 °C; this initial loss could be $\mathrm{Me_3CN{=}CMe_2}$ (*cf.* mass spectrum). The residue after heating to 1000 °C corresponds to 23% of the initial mass and is probably a manganese carbide–nitride mixture.

The decomposition mechanism in solutions probably involves radical transfer of H or Me to N, carbonium-ion rearrangements,[15b] *etc.* The presence of $\mathrm{NH_2Bu^t}$ can be ascribed to H abstraction from the solvent by radicals. The *tert*-pentyl, $\mathrm{Mn(NCMe_2CH_2Me)_3Cl}$, begins to decompose in solutions at *ca.* 40 °C.

*Reactions of Compound* **1** *with* HCl *and Lewis Acids*.—In solution in $\mathrm{CH_2Cl_2}$, toluene or ethers at −78 °C containing HCl, compound **1** reacts to give blood-red solutions that are stable only at low temperatures decomposing at *ca.* −35 ($\mathrm{CH_2Cl_2}$) or *ca.* −10 °C (tetrahydrofuran, thf). The reaction on addition of a deficiency of HCl solution to **1** in $\mathrm{CH_2Cl_2}$ can be followed by $^1$H NMR spectroscopy. The spectra from −78 to −35 °C show two broad peaks at δ 1.80 and 1.59 in addition to the band of **1** (δ 1.44) that is also broadened. Addition of more HCl solution results in the disappearance of the peak for **1** and an increase in those at δ 1.80 and 1.59. Addition of an excess of pyridine or 2,2′-bipyridyl causes reversion to the green colour and $^1$H NMR spectrum of **1**. When the red solution is warmed above *ca.* −35 °C the formation of brown paramagnetic species is shown by the irreversible, complete disappearance of the spectrum. In thf at −78 °C the broad new peaks are at δ 1.64 and 1.00 in addition to the broad peak of **1**; at −78 °C there is a reversible collapse to a broad singlet at δ 1.35.

The reversible reaction sequence proposed is given in Scheme 2. The species **A** and **B** are five-co-ordinate and fluxional, accounting for the broad lines. All the *tert*-butylimido environments are observed as a broad envelope, while the amido and amino groups give separate NMR peaks. The irreversible decomposition above −35 °C probably involves reductive elimination of $\mathrm{Cl_2}$ with reduction of the manganese oxidation state to V or lower; the decomposition products have not been isolated. Attempts to stabilize **A** or **B** by addition of chelate ligands of low basicity, *e.g.* 1,2-dimethoxyethane, were unsuccessful.



**Scheme 2** (*i*) HCl; (*ii*) py

The interaction of compound **1** with the Lewis acids $\mathrm{AlCl_3}$ or $\mathrm{SbCl_5}$ in $\mathrm{CH_2Cl_2}$ also gives red solutions stable up to *ca.* −10 °C. Tracking the reaction with $\mathrm{SbCl_5}$ in $\mathrm{CD_2Cl_2}$ by $^1$H NMR spectroscopy shows a broad new peak at δ 1.76, unchanged from −78 to −10 °C, which could be due to the cation in $\mathrm{[Mn(NBu^t)_3]^+SbCl_6^-}$. We have been unable to obtain crystals from these solutions at low temperatures.

*Other Reactions*.—Interaction of compound **1** with $\mathrm{PPh_3}$ leads to reduction and transfer of $\mathrm{NBu^t}$ to phosphorus giving the phosphinimine $\mathrm{Ph_3P{=}NBu^t}$. Interaction with phenol in $\mathrm{CH_2Cl_2}$ is slow giving brown solutions from which, after collection of volatiles in vacuum, $\mathrm{Bu^tN{=}NBu^t}$ and $\mathrm{PhOBu^t}$ were identified by GC–MS. No manganese-containing species could be cleanly isolated.

The interaction of compound **1** with $\mathrm{OsO_4}$ in thf for 3 d at room temperature gives brown solutions from which $\mathrm{Os(NBu^t)O_3}$ [16] can be isolated in high yield after sublimation to a cold-finger. The product was identified by comparison of its spectra with that of an authentic sample. The manganese-containing residue was intractable.

*Substitution Reactions*.—Attempts to obtain stable derivatives by substitution of the chloride in compound **1** *via* interaction with lithium, magnesium ($\mathrm{MgR_2}$ and MgRX) and zinc reagents having alkyl or aryl groups were unsuccessful, except in the case of the aryl $\mathrm{C_6F_5}$ where only use of the silver aryl was effective. Similar attempts to make alkoxides or aryl oxides also were unsuccessful except where fluorinated compounds were used. Interaction of **1** with LiX, X = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, mesityl or Ph, led to reduction to the brown manganese(VI) dimer $\mathrm{[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2}$, which is also formed on reduction of **1** with sodium amalgam in thf.

The instability of hydrocarbon alkyls and aryls and also alkoxides could be due to facile β-H transfer to $\mathrm{NBu^t}$ as proposed below for alkoxides or to homolytic cleavage of the Mn–C bond. The interaction of compound **1** with $\mathrm{LiBu^n}$ in cyclohexane at −90 °C followed by slow warming to room temperature, collection of volatiles on a probe at −196 °C and GC–MS analysis showed the formation of $\mathrm{CH_2{=}CHEt}$ as expected for β-H transfer, but also $\mathrm{NH_2Bu^t}$, *n*-octane, $\mathrm{NHBu^t(CH_2CH_2CH{=}CH_2)}$ and $\mathrm{NH(Bu^t)Bu^n}$. The $^1$H NMR spectrum of the hexane-soluble fraction of the brown, manganese-containing residue showed the presence of the manganese(VI) dimer.

A similar experiment using $\mathrm{LiBu^t}$ in pentane gave $\mathrm{Me_2C{=}CH_2}$ and $\mathrm{Me_3C{-}CMe_3}$ as the major products. Although more detailed studies are desirable, it appears that the major decomposition pathway is homolysis and radical formation with coupling, hydrogen abstraction from the solvent, *etc.*

Compound **3**, $\mathrm{Mn(NBu^t)_3Br}$, which is similar to the chloride, is readily obtained in quantitative yield by interaction of **1** with $\mathrm{SiMe_3Br}$. It has similar physical and chemical properties to those of **1** and was identified by analytical and spectroscopic data. Efforts to prepare the fluoride and iodide analogues so far have been unsuccessful. Interaction of **1** with AgF or TlF in MeCN or $\mathrm{CH_2Cl_2}$ leads to brown solutions (and precipitates of AgCl or TlCl) but no well defined manganese products could be isolated. Interaction of **1** with $\mathrm{SiMe_3I}$ in toluene or light petroleum gives iodine, $\mathrm{SiMe_3Cl}$ and intractable, manganese-containing materials.

*Carboxylates*. Interaction of compound **1** with an excess of silver acetate or trifluoroacetate in $\mathrm{CH_2Cl_2}$ gives the compounds $\mathrm{Mn(NBu^t)_3[OC(O)R]}$ (R = Me **4** or $\mathrm{CF_3}$ **5**) respectively in high yields. These compounds are very soluble in hydrocarbons and can be crystallised only at −78 °C. The carboxylate group is unidentate according to IR spectra as shown by the separation,[17] Δ, between ν(C=O) and ν(C–O), of 313 and 315 cm$^{-1}$ for **4** and **5**, respectively. The unidentate bonding is confirmed by the X-ray analysis of the acetate discussed below.

*Alkoxides and aryl oxides.* Interaction of compound **1** with lithium or sodium alkoxides, aryl oxides and siloxides [*e.g.* of OPr$^i$, $OC_6H_nR_{5-n}$ (R = Me, Pr$^i$, Bu$^t$ or Ph; *n* = 2 or 3), $OSiR_3$ (R = Me or Ph)] gave no isolable alkoxide products. However, the green, crystalline compounds Mn(NBu$^t_3$)(OR) were obtained using $Tl(OC_6X_5)$ (X = F or Cl). The $OC_6Cl_5$ compound **7** is somewhat less stable than the $OC_6F_5$ compound **6** which is stable indefinitely at room temperature.

The substitution of Cl in compound **1** also appears to compete with electron transfer to give the manganese(VI) dimer when lithium or sodium alkoxide or aryl oxides are used, even at low temperatures. For the thallium reagents at low temperatures, substitution is faster than electron transfer, but above *ca.* $-40$ °C hydrogen-transfer reactions from H-containing alkoxo groups leads to formation of a manganese(V) dimer (see below).

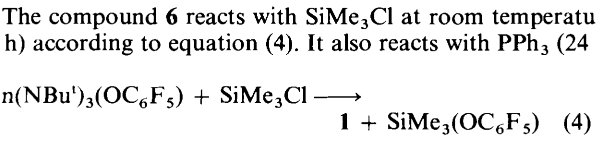
The structure of the $C_6F_5O$ compound has been confirmed by X-ray diffraction (see later) but it is convenient to mention here that the long Mn–O bond distance 1.896(2) Å and the geometry around the phenoxide oxygen atom found indicate minimum π interaction of oxygen lone pairs with the Mn atom [*cf.* the carboxylate 1.91(3) Å]. The commonly found bond angles for M–O–C in alkoxides are close to 180° and this is associated with O→M π donation.[18] The difference in the manganese compounds is evidently related to the electronic saturation noted above.

The compound **6** reacts with $SiMe_3Cl$ at room temperature (6 h) according to equation (4). It also reacts with $PPh_3$ (24 h, room temperature) giving brown, unidentified, paramagnetic species, while photolysis of benzene solutions (3 h, 125 W, medium-pressure mercury lamp) gives a brown unidentified oil.

$$Mn(NBu^t)_3(OC_6F_5) + SiMe_3Cl \longrightarrow \mathbf{1} + SiMe_3(OC_6F_5) \quad (4)$$

Thermogravimetric study of compound **6** showed an exothermic decomposition similar to that of **1** at 83.1 °C with an accompanying weight loss of *ca.* 29%; decomposition above this temperature is featureless.

In order to clarify decomposition pathways, the interactions of compound **1** with $Tl[OCH(CF_3)_2]$ and $Tl(OCHPh_2)$ were studied. The former gives $Mn(NBu^t)_3[OCH(CF_3)_2]$ **8** as a green oil characterised by IR and NMR spectra. This compound decomposes only slowly (over *ca.* 2 d) at room temperature or more rapidly in refluxing benzene (1 h). The $^{19}F$ NMR spectra of the collected volatile products confirm the presence of hexafluoroacetone, while the red, paramagnetic residual oil shows N–H bonds in the IR spectrum and FAB mass spectrometry indicates this to be $[Mn(NBu^t)(\mu\text{-}NBu^t)(NHBu^t)]_2$. Hence β-H transfer accompanied by reduction $Mn^{VII} \longrightarrow Mn^{V}$ is evident as in Scheme 3.



Scheme 3

The interaction of compound **1** and $Tl(OCHPh_2)$ (obtained from diphenylmethanol) in toluene at $-78$ °C with slow warming produced a white precipitate (TlCl) and a change in colour from green to green-brown (alkoxide); at room temperature the solution was red-brown [manganese(V) dimer]. Collection of the volatiles on a cold-finger ($-78$ °C) in vacuum allowed confirmation of the formation of benzophenone, $Ph_2CO$, as the only product by comparison of the $^1H$ NMR spectrum with that of an authentic sample. It may be noted that by contrast the isopropoxide of rhenium, $Re(NBu^t)_3(OPr^i)$ is thermally stable[19] so that the difference from Mn may be due to the unavailability of low-energy orbitals on rhenium to accept electrons. Since other alkoxides having no β-hydrogens and aryl oxides are unisolable in the manganese case [yet stable for rhenium, *e.g.* $Re(NBu^t)_3(OSiMe_3)$] different decomposition mechanisms must apply for $OSiMe_3$, OBu$^t$, OPh, *etc.*, but products from these reactions have not yet been studied; γ-H transfers are one possibility.

*Pentafluorothiophenoxide.* Use of $Tl(SC_6F_5)$ allows the synthesis from compound **1** of $Mn(NBu^t)_3(SC_6F_5)$ **9** which is more thermally stable and less chemically reactive than the analogous pentafluorophenoxide **6**. Thus **9** does not react with $SiMe_3Cl$ or $PPh_3$ and is stable to prolonged photolysis under the same conditions as used for **6**. However, it is decomposed by hydrogen [100 psi (*ca.* 689 × 10$^5$ Pa), 12 h, 20 °C] to intractable products. Thermogravimetric study shows exothermic decomposition at *ca.* 100 °C, weight loss *ca.* 22%; the residue after 1000 °C is 22% of the initial mass.

*Pentafluorophenyl.* The compound $Mn(NBu^t)_3(C_6F_5)$ **10**, which is the only relatively stable compound so far obtained with a Mn–C bond, is obtained by interaction of **1** and $Ag(C_6F_5)$ as a green-brown oil that begins to decompose slowly at room temperature. It was characterised by high-resolution MS and NMR spectroscopy. The GC–MS study of the decomposition products showed $NHBu^t(C_6F_5)$ and $Me_2(NHMe)CPr^i$. By contrast, a variety of stable rhenium aryls, *e.g.* $Re(NBu^t)_3(C_6H_4Me\text{-}o)$, are known.[20]

tert-*Butylamido.* The compound $Mn(NBu^t)_3(NHBu^t)$ **11** characterised only by $^1H$ NMR spectroscopy is obtained on interaction of **1** with $Li(NHBu^t)$ in tetrahydrofuran at *ca.* $-35$ °C; it is unstable above this temperature decomposing completely within 2 h at room temperature to give $Me_2C{=}CH_2$, $NH_2Bu^t$ and $Bu^tN(H)N(H)Bu^t$ identified by GC–MS, together with other unidentified species. The rhenium analogue is stable.[13]

At $-78$ °C in hexane, compound **11** undergoes an insertion reaction with $CO_2$ to give the green crystalline carbamate $Mn(NBu^t)_3[OC(O)NHBu^t]$ **12**. Since only low-quality crystals, thermally unstable at room temperature, could be obtained it was characterised only by $^1H$ and $^{13}C$ NMR and IR spectra.[21] The $^1H$ spectrum shows two types of Bu$^t$ groups in a ratio 3:1 at δ 1.48 and 1.19 assignable to the *tert*-butylimido and unidentate carbamato groups respectively with the NH resonance at δ 4.4. The $^{13}C$ spectrum shows the C of the carbamato group at δ 160. The IR spectrum has characteristic bands at 3285 (NH) and 1636, 1582 and 1263 cm$^{-1}$ for the symmetric and asymmetric C=O stretch respectively. The interaction of **11** with Bu$^t$NCO under similar conditions gives, as the only isolable solid, $(Bu^tNH)_2CO$[22] ($^1H$ NMR, $C_6D_6$, δ 1.29).

tert-*Butylamine.* The interaction of compound **1** in $CH_2Cl_2$ with silver trifluoromethanesulfonate in the presence of an excess of $NH_2Bu^t$ gives the cationic complex $[Mn(NBu^t)_3(NH_2Bu^t)][CF_3SO_3]$ **13**. The same cation is obtained in low yield as the $PF_6$ salt **14** by interaction with $TlPF_6$ and an excess of Bu$^t$CN; no evidence for a co-ordinated nitrile has been found. The spectra of **13** and **14** are in accord with the X-ray diffraction results discussed below.

Bis[(1,2-*dimethoxyethane*)*lithium*] *tetrakis*(tert-*butylimido*)*manganate*(VI). This extremely air-sensitive compound **15** was obtained by interaction of **1** with 5 equivalents of $Li(NHBu^t)$ in 1,2-dimethoxyethane (dme). Crystals of X-ray quality were obtained after evaporation, extraction of the residue with light petroleum and cooling. This compound is the first one of manganese to have four Bu$^t$N groups and is formally a *tert*-butylimido analogue of the manganate(2−) ion, $MnO_4^{2-}$. It can be compared with the chromium,[14] molybdenum[23] and tungsten(VI) compounds,[23] $Li_2M(NBu^t)_4$, that are dimeric[24] with bridging N$\cdots$Li$\cdots$N interactions, and to the rhenium(VII) compound [Li(tmen)][Re(NBu$^t$)$_4$][13,24] (tmen = *N,N,N′,N′*-tetramethylethylenediamine) which is the analogue of the perrhenate. The manganese analogue corresponding to permanganate, *i.e.* LiMn(NBu$^t$)$_4$, has so far not been obtained, nor has the rhenium(VI) analogue of **15**, Li$_2$Re(NBu$^t$)$_4$, although it ought to be possible to synthesise both.

A similar reaction of compound **1** in presence of tmen gives [Li(tmen)]$_2$[Mn(NBu$^t$)$_4$] **16**. Both **15** and **16** are paramagnetic. The X-band EPR spectrum of **15** in toluene at room temperature is shown in Fig. 1 as having a six-line pattern, $I = \frac{5}{2}$, $g = 2.015$; hyperfine couplings $\alpha_{\text{Mn}} = 60$ and $\alpha_{\text{N}} = 4.56$ G were observed. For **16**, $g = 2.004$, $\alpha_{\text{Mn}} = 59$ G but no nitrogen hyperfine splitting was observed.

*X-Ray Crystallography*.—The three molecules **4**, **6** and **9** have analogous, slightly distorted-tetrahedral structures as previously found[7] for Mn(NBu$^t$)$_3$Cl **1**. The gross geometrical features are similar although there are small but significant differences that are related to the character of the X ligand in Mn(NBu$^t$)$_3$X. Selected bond lengths and angles for **1**, **4**, **6** and **9** are given in Table 3. Diagrams of the acetate **4**, pentafluorophenoxide **6** and pentafluorothiophenoxide **9** are given in Figs. 2–4, respectively.

The Mn–N imido distances in the four molecules lie in the range 1.644(3)–1.673(9) Å and the N–Mn–N and X–Mn–N angles are 110.9(1)–113.1(1)° and 103.7(1)–110.6(1)°, respectively. The Mn–N–C angles vary from 139.9(2) to 144.6(3)°. These data are consistent with the model previously considered[7] in which only two of the three imido groups are able to act as 6e (RN$^{2-}$) donors (*i.e.* RN$\rightleftarrows$Mn) in a formal 18e configuration, but are averaged over all three such ligands. The Mn–X distances in the four compounds are comparable in terms of accepted values of covalent radii, indicating similar bonding character with little or no $\pi$ bonding, as discussed earlier. However, there is a significant difference between the Mn–O–C (both *ca.* 120°) and Mn–S–C (*ca.* 99°) angles. The origin of the latter angle is uncertain, but it is pertinent to point out that the bend of the ligand places the C$_6$F$_5$ group nearer to the imido ligands defined by N(1) and N(3) for which the S–Mn–N angles [106.4(1) and 107.3(1)°] are some 3° greater than S–Mn–N(2) at 103.7(1)°. At the same time, one rather close contact of 3.11 Å occurs between N(1) and F(1). Recent studies[25] have shown that in some arenethiolato complexes of zinc the M–S–C angles are generally larger.

The identity of the cationic complex [Mn(NBu$^t$)$_3$(NH$_2$Bu$^t$)][CF$_3$SO$_3$] **13** was confirmed by X-ray study, but the poor quality of the crystals and related severe disorder prevented accurate determination. Study of the analogous PF$_6^-$ salt **14** gave similar problems when the structure refinement was made. Nevertheless, in both structures the main features are clear. A diagram of the cation in **14** is shown in Fig. 5 and selected bond lengths and angles are given in Table 4. A packing diagram of the unit-cell contents of the structure of **13** is shown in Fig. 6. Both the Mn–N bond lengths and Mn–N–C angles clearly show the presence of three imido NBu$^t$ groups and one different

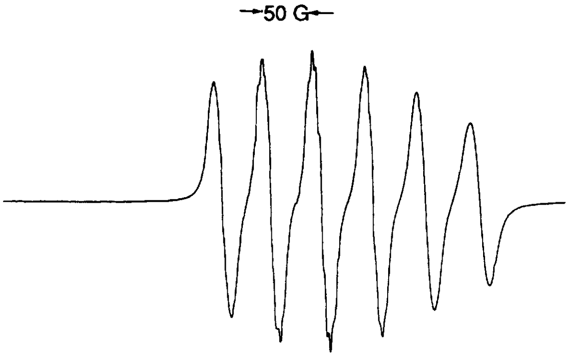


**Fig. 1** X-Band EPR spectrum of [Li(dme)]$_2$[Mn(NBu$^t$)$_4$] **15** in toluene at 293 K

**Table 3** Selected bond lengths (Å) and angles (°) for compounds **1**, **4**, **6** and **9**, with estimated standard deviations (e.s.d.s) in parentheses

| | **1** | **4** | **6** | **9** |
|---|---|---|---|---|
| Mn–N(1) | 1.656(5) | 1.656(5) | 1.661(2) | 1.644(3) |
| Mn–N(2) | 1.655(5) | 1.673(9) | 1.658(2) | 1.658(3) |
| Mn–N(3) | 1.656(5) | 1.65(2) | 1.652(2) | 1.651(3) |
| Mn–X | 2.222(3) | 1.91(3) | 1.896(2) | 2.289(1) |
| N(1)–C(11) | 1.466(5) | 1.454(9) | 1.457(3) | 1.449(4) |
| N(2)–C(21) | 1.457(6) | 1.48(2) | 1.466(3) | 1.464(4) |
| N(3)–C(31) | 1.463(6) | 1.46(2) | 1.461(4) | 1.459(4) |
| N(1)–Mn–X | 108.0(2) | 105.8(8) | 109.1(1) | 106.4(1) |
| N(2)–Mn–X | 107.0(2) | 104.0(3) | 105.2(1) | 103.7(1) |
| N(3)–Mn–X | 106.8(2) | 110.6(11) | 108.7(1) | 107.3(1) |
| N(2)–Mn–N(1) | 111.1(2) | 112.8(3) | 111.7(1) | 113.0(1) |
| N(3)–Mn–N(1) | 112.2(3) | 111.9(3) | 110.9(1) | 112.6(1) |
| N(3)–Mn–N(2) | 111.6(3) | 111.3(7) | 110.9(1) | 113.1(1) |
| C(11)–N(1)–Mn | 138.5(3) | 144.6(3) | 141.9(2) | 143.1(2) |
| C(21)–N(2)–Mn | 141.8(3) | 140.1(5) | 139.9(2) | 142.0(2) |
| C(31)–N(3)–Mn | 140.6(3) | 142.2(5) | 140.7(2) | 142.2(2) |
| C(*n*)–X–Mn | — | 119.3(3) | 120.4(2) | 99.2(1) |

$n = 1$, X = Cl **1**, OC(O)Me **4**, $n = 6$, X = OC$_6$F$_5$ **6** or SC$_6$F$_5$ **9**. Numbering for complex **1** as previously reported has been changed to be compatible with that for the new structures.

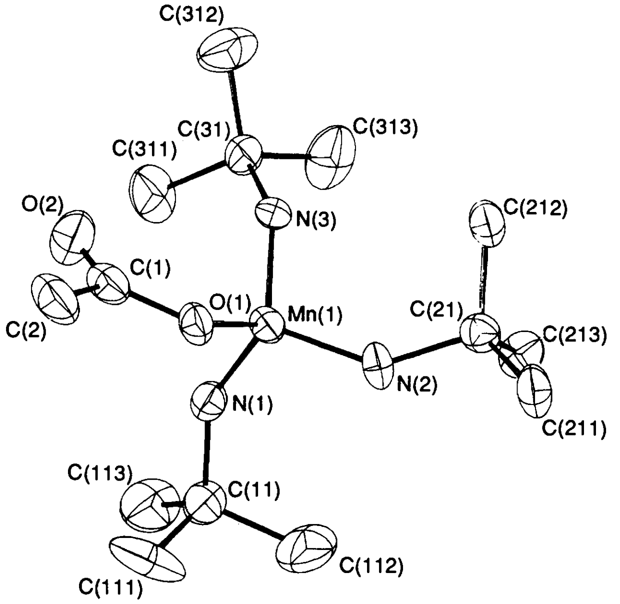


**Fig. 2** The structure of Mn(NBu$^t$)$_3$[OC(O)Me] **4**

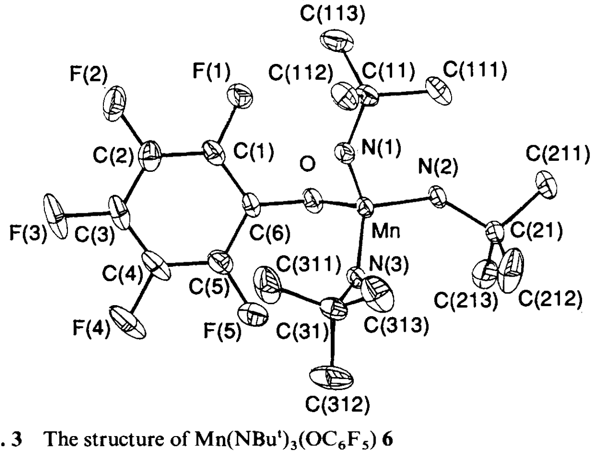


**Fig. 3** The structure of Mn(NBu$^t$)$_3$(OC$_6$F$_5$) **6**

**Table 4** Selected bond lengths (Å) and angles (°) for the analogous cation of compounds **13** and **14**, $[Mn(NBu^t)_3(NH_2Bu^t)]^+$, with e.s.d.s in parentheses

| | **13** | **14** | | **13** | **14** |
|---|---|---|---|---|---|
| Mn(1)–N(1) | 1.592(8) | 1.655(7) | N(1)–C(1) | 1.595(9) | 1.460(10) |
| Mn(1)–N(2) | 1.626(8) | 1.653(7) | N(2)–C(2) | 1.488(9) | 1.465(12) |
| Mn(1)–N(3) | 1.647(6) | 1.655(8) | N(3)–C(3) | 1.518(7) | 1.469(11) |
| Mn(1)–N(4) | 2.036(3) | 2.028(9) | N(4)–C(4) | 1.536(5) | 1.517(10) |
| Mn(2)–N(5) | 1.621(4) | — | N(5)–C(5) | 1.484(6) | — |
| Mn(2)–N(6) | 1.621(4) | — | N(6)–C(6) | 1.475(7) | — |
| Mn(2)–N(7) | 1.531(8) | — | N(7)–C(7) | 1.45(1) | — |
| Mn(2)–N(8) | 1.938(4) | — | N(8)–C(8) | 1.485(6) | — |
| N(1)–Mn(1)–N(2) | 111.8(4) | 110.4(4) | N(6)–Mn(2)–N(8) | 102.2(2) | — |
| N(1)–Mn(1)–N(3) | 142.2(4) | 111.6(4) | N(7)–Mn(2)–N(8) | 116.3(4) | — |
| N(1)–Mn(1)–N(4) | 111.1(3) | 103.5(3) | C(1)–N(1)–Mn(1) | 135.8(6) | 141.0(6) |
| N(2)–Mn(1)–N(3) | 75.5(4) | 112.9(4) | C(2)–N(2)–Mn(1) | 140.5(7) | 141.4(6) |
| N(2)–Mn(1)–N(4) | 99.5(3) | 111.9(4) | C(3)–N(3)–Mn(1) | 136.2(4) | 146.5(6) |
| N(3)–Mn(1)–N(4) | 103.7(2) | 106.1(4) | C(4)–N(4)–Mn(1) | 121.8(2) | 124.5(6) |
| N(5)–Mn(2)–N(6) | 110.4(2) | — | C(5)–N(5)–Mn(2) | 143.4(4) | — |
| N(5)–Mn(2)–N(7) | 118.5(4) | — | C(6)–N(6)–Mn(2) | 147.5(4) | — |
| N(5)–Mn(2)–N(8) | 112.0(2) | — | C(7)–N(7)–Mn(2) | 170.2(9) | — |
| N(6)–Mn(2)–N(7) | 94.2(5) | — | C(8)–N(8)–Mn(2) | 128.3(3) | — |

**Table 5** Selected bond lengths (Å) and angles (°) for compound **15**, $[Li(dme)]_2[Mn(NBu^t)_4]$, with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Mn–N(1) | 1.749(3) | O(1)–C(4) | 1.394(6) |
| Mn–N(1a) | 1.749(3) | O(2)–C(5) | 1.395(6) |
| Mn–N(2) | 1.746(3) | O(2)–C(6) | 1.422(6) |
| Mn–N(2a) | 1.746(3) | Li–N(1a) | 1.928(4) |
| N(1)–C(1) | 1.464(5) | Li–N(2) | 1.944(4) |
| N(2)–C(2) | 1.457(5) | Li–O(1) | 2.072(5) |
| O(1)–C(3) | 1.431(6) | Li–O(2) | 2.057(5) |
| N(1a)–Mn–N(2) | 97.7(2) | C(2)–N(2)–Mn | 135.8(3) |
| N(1)–Mn–N(2a) | 97.7(2) | O(1)–Li–O(2) | 78.9(4) |
| N(1)–Mn–N(2) | 115.6(2) | O(1)–Li–N(1a) | 127.2(4) |
| N(2a)–Mn–N(1a) | 115.6(2) | O(2)–Li–N(1a) | 125.8(4) |
| N(2)–Mn–N(2a) | 115.0(2) | O(1)–Li–N(2) | 121.9(4) |
| N(1)–Mn–N(1a) | 116.3(2) | O(2)–Li–N(2) | 122.8(4) |
| C(1)–N(1)–Mn | 134.8(3) | N(1a)–Li–N(2) | 85.7(4) |

Symmetry transformation used to generate equivalent atoms: (a) $-x, y, \frac{1}{2} - z$.

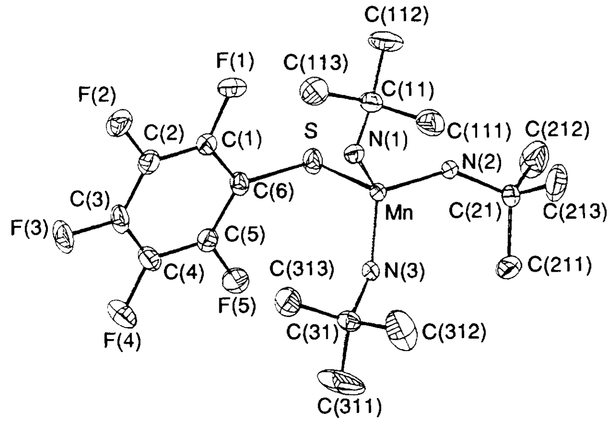


**Fig. 4** The structure of $Mn(NBu^t)_3(SC_6F_5)$ **9**

ligand, assigned as $NH_2Bu^t$ on the cations in each structure. The Mn–N imido bond lengths of 1.531(8)–1.655(8) Å and Mn–N–C angles of 135.8(6)–170.2(9)°, especially those in structure **14** are close to values in the more accurately determined structures of the neutral molecules described above, whilst the unique amino ligands give Mn–N bond lengths of 1.938(4)–2.036(3) Å and Mn–N–C angles of 121.8–128.3(3)°.

The structure of $[Li(dme)]_2[Mn(NBu^t)_4]$ **15** is shown in Fig. 7 and selected bond lengths and angles are given in Table 5. The molecule has approximate $D_2$ symmetry and lies in the unit cell with one of its molecular two-fold axes coincident with a crystallographic two-fold axis. As expected, the manganese centre has approximate tetrahedral geometry but with the lithium-bridged angles narrowed to 97.2(2)° and the non-bridged angles increased to 115.0(2)–116.3(2)°. The bridged angle is very similar in value to that of the equivalent fragment in the structure[24] of $[Li(tmen)][Re(NBu^t)_4]$, 98.8(8)°.[13] The Mn–N distances of 1.746(3)–1.749(3) Å are longer than those in the manganese(VII) species described above, a combined result of the change in oxidation state, the averaging out of the 2 × 4e (Mn=NR) and 2 × 6e (Mn≡NR) interactions required for an 18e configuration, and possibly the effect of the lithium bridging. In the rhenium complex mentioned above the Re–N distances were 1.77 and 1.78(2) Å to non-bridging and 1.80 and 1.87(3) Å to the bridging ligands.

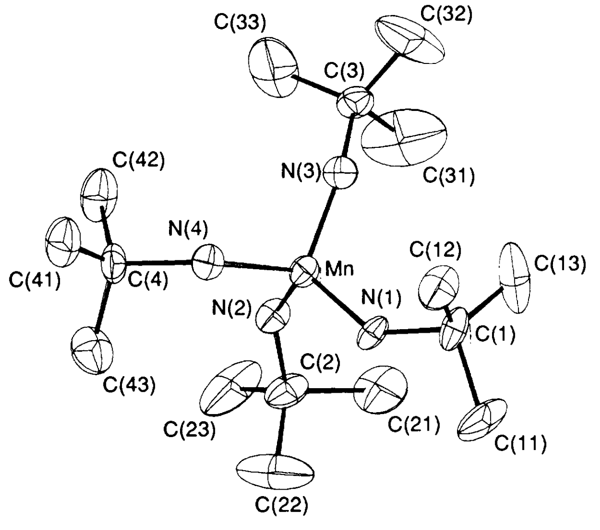


**Fig. 5** The structure of the cation in $[Mn(NBu^t)_3(NH_2Bu^t)]PF_6$ **14**

## Experimental

Analyses were by the laboratories of Imperial College, University College, London, Medac plc and Pascher, Remagen. The instrumentation and general procedures were as described.[26] The GC–MS and high-resolution MS spectra were recorded by the University of London instrument service at King's College and the School of Pharmacy, respectively, IR

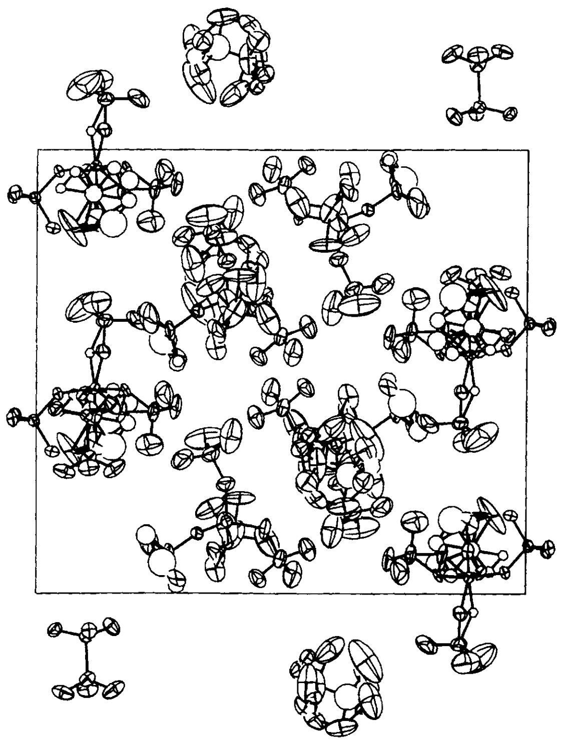


**Fig. 6** A packing diagram of the unit cell contents of the structure $[Mn(NBu^t)_3(NH_2Bu^t)]CF_3SO_3$ **13**

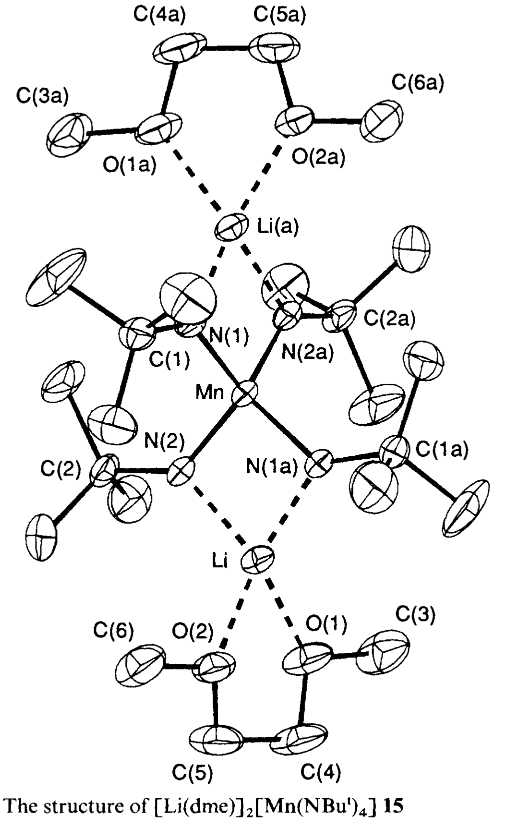


**Fig. 7** The structure of $[Li(dme)]_2[Mn(NBu^t)_4]$ **15**

spectra in Nujol unless otherwise stated and NMR spectra on a JEOL-ES-270 spectrometer (δ *vs.* $SiMe_4$).

Commercial chemicals were from Aldrich. *tert*-Butylsilylamine and *tert*-pentylsilylamine were prepared by interaction of the primary amines and $SiMe_3Cl$ in $Et_2O$.[27] The solution of $MnCl_3$ in MeCN was obtained as described[8a] from $[Mn_{12}O_{12}(O_2CMe)_{16}](H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$.[8b] The thallium compounds Tl(OR) [R = $C_6F_5$, $C_6Cl_5$, $SC_6F_5$ or $CH(CF_3)_2$] were made by interaction of Tl(OEt) and the appropriate phenol, thiophenol or alcohol in benzene with exclusion of light. The white crystalline solids were isolated after addition of hexane, washed with hexane and dried *in vacuo*. They were held at *ca.* −20 °C in the dark. The compound $Ag(C_6F_5)$ was prepared as described.[28] **CAUTION**: thallium compounds are highly toxic and careful handling and disposal of residues is required.

Solvents were dried and degassed by standard methods and all operations were carried out under purified argon or $N_2$ or *in vacuo* unless otherwise specified. The light petroleum used had b.p. 40–60 °C.

*Tris*(tert-*butylimido*)*chloromanganese*(VII) **1**.—To the oxo-acetate (12.5 g, 6.5 mmol) and acetonitrile (450 $cm^3$) in a three-neck, 1 l flask cooled at −35 to −40 °C was added an excess of $SiMe_3Cl$ (40 $cm^3$) and the mixture stirred until it was a deep red-purple, when an excess of $NHBu^t(SiMe_3)$ (60 $cm^3$) was added dropwise over *ca.* 15 min. The reaction mixture became orange-brown but after allowing to warm to room temperature with stirring overnight it was dark green; if moisture is present at this stage lower yields of compound **1** result. The green solution was filtered and evaporated under vacuum using a rotary evaporator at *ca.* 45–50 °C; the residual green solid can be handled in air. The addition of light petroleum (200 $cm^3$) and water (200 $cm^3$) followed by vigorous stirring gave a green organic phase and a yellow-green aqueous phase (see below). The latter was extracted with more light petroleum (3 x 100 $cm^3$) and the combined extracts dried over anhydrous $Na_2SO_4$ (2 h). Filtration and evaporation of the solution gave a green solid which was recrystallised from light petroleum at −20 °C. Yield (two crops): 1.6–1.9 g, *ca.* 20% based on manganese. The compound readily sublimes in *in vacuo* at *ca.* 70 °C to a chilled probe. High-resolution mass spectrum: molecular ion at *m*/*z* 303.1289; calc. for $C_{12}H_{27}MnN_3$, 303.12. Electron-impact (EI) mass spectrum: *m*/*z* 303 ($M^+$), 288 ($M^+$ − Me), 273 ($M^+$ − 2Me), 232 ($M^+$ − $Bu^tN$), 217 ($M^+$ − $Bu^tN$ − Me), 202 ($M^+$ − $Bu^tN$ − 2Me), 187 ($M^+$ − $Bu^tN$ − 3Me), 161 ($M^+$ − $2Bu^tN$) and 131 ($M^+$ − $2Bu^tN$ − 2Me). IR (Nujol or hexachlorobutadiene mulls): no NH str.; 1187 ($Mn{=}NBu^t$) and 395 $cm^{-1}$ (Mn–Cl).

The yellow-green aqueous phase above was reduced in volume and allowed to crystallise. X-Ray study showed this to be a tetrachloromanganese(II) dianion with *tert*-butylammonium cations. While the crystal size and quality precluded the recording of a good data set, the structure was solved and refined with reasonable ease and stable refinement achieved. The precision is therefore not high, but is adequate to show *via* Mn–Cl bond lengths that the anion is $[MnCl_4]^{2-}$; examples of salts of this tetrahedral ion are well known.[29] Data have been deposited.

*Chlorotris*(tert-*pentylimido*)*manganese*(VII) **2**.—To a solution of $MnCl_3$ made as above from the oxoacetate (2 g, *ca.* 1 mmol) and $SiMe_3Cl$ (2.8 $cm^3$, *ca.* 30 mmol) in MeCN (40 $cm^3$) was added at −30 °C *tert*-pentylsilylamine (5.6 g, 35 mmol) and the brown solution allowed to warm over 8 h when work-up as above and crystallisation at −78 °C from light petroleum gave green needles. Yield: 0.35 g, *ca.* 9%. EI mass spectrum ($^{35}Cl$): *m*/*z* 345 ($M^+$), 316 ($M^+$ − Et), 281 ($M^+$ − Et − Cl) and 175 [$M^+$ − $2N(CMe_2CH_2Me)$]. IR: 1177 [$Mn{=}N(CMe_2CH_2Me)$] and 386 $cm^{-1}$ (Mn–Cl).

*Bromotris*(tert-*butylimido*)*manganese*(VII) **3**.—To a solution of compound **1** (0.3 g, *ca.* 1 mmol) in toluene (30 $cm^3$) was added freshly distilled $SiMe_3Br$ (0.5 g, excess) and the green solution stirred for 12 h. Evaporation *in vacuo*, extraction of the residue with light petroleum followed by filtration, concentration to *ca.* 3 $cm^3$ and cooling to −20 °C gave green crystals. Yield: 0.27 g, 80%. Mass spectrum ($^{79}Br$): *m*/*z* 347 ($M^+$), 332 ($M^+$ − Me), 317 ($M^+$ − 2Me), 276 ($M^+$ − $Bu^tN$), 261 ($M^+$ − $Bu^tN$ − Me), 246 ($M^+$ − $Bu^tN$ − 2Me) and 205 ($M^+$ − $2Bu^tN$) and 58 ($Me_2C{=}CH_2^+$).

**Table 6** Details of data collection and refinement for compounds **4**, **6**, **9** and **13**–**15**

| | **4** | **6** | **9** | **13** | **14** | **15** |
|---|---|---|---|---|---|---|
| Formula | $C_{14}H_{30}MnN_3O_2$ | $C_{18}H_{27}F_5MnN_3O$ | $C_{18}H_{27}F_5MnN_3S$ | $C_{34}H_{72}F_6Mn_2$-$N_8O_6S_2$ | $C_{16}H_{38}F_6MnN_4P$ | $C_{24}H_{56}Li_2$-$MnN_4O_4$ |
| $M_r$ | 327.35 | 451.36 | 467.43 | 976.995 | 486.41 | 533.55 |
| Crystal system | Orthorhombic | Triclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *Pnma* | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $C/c$ |
| $a$/Å | 17.75(12) | 8.072(2) | 8.369(5) | 21.099 | 12.62(4) | 14.572(7) |
| $b$/Å | 32.35(1) | 11.468(4) | 10.831(5) | 12.801 | 9.318(11) | 13.862(1) |
| $c$/Å | 10.0(2) | 12.318(2) | 12.742(3) | 19.016 | 21.26(6) | 16.451(3) |
| $\alpha$/° | 90 | 103.396(5) | 82.12(3) | 90 | 90 | 90 |
| $\beta$/° | 90 | 91.57(1) | 88.77(2) | 90.47 | 91.4(2) | 102.24(4) |
| $\gamma$/° | 90 | 103.29(2) | 74.09(2) | 90 | 90 | 90 |
| $U$/Å$^3$ | 5742.12 | 1075.6 | 1100.1 | 5135.8 | 2499 | 3248 |
| $Z$ | 12 | 2 | 2 | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.136 | 1.394 | 1.411 | 1.2635 | 1.293 | 1.091 |
| $F$(000) | 2112 | 468 | 484 | 2064 | 1024 | 1156 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.667 | 0.642 | 0.715 | 0.6133 | 0.644 | 0.436 |
| Crystal size/mm | 0.5 × 0.2 × 0.13 | 0.35 × 0.2 × 0.15 | 0.4 × 0.35 × 0.2 | 0.5 × 0.4 × 0.2 | 0.54 × 0.09 × 0.06 | 0.36 × 0.3 × 0.1 |
| $\theta$ Range for data/° | 2.14–23.96 | 2.21–30.08 | 2.37–30.18 | 2.14–25.51 | 1.92–25.06 | 2.05–25.10 |
| *hkl* Ranges | −13 to 18,<br>−33 to 20,<br>−10 to 10 | −10 to 9,<br>−12 to 16,<br>−16 to 17 | −5 to 11,<br>−11 to 14,<br>−16 to 16 | −11 to 25,<br>−14 to 12,<br>−22 to 20 | −8 to 14,<br>−8 to 10,<br>−23 to 23 | −16 to 13,<br>−16 to 10,<br>−15 to 19 |
| Reflections collected | 12 637 | 7939 | 5835 | 15 787 | 6833 | 4997 |
| Independent reflections | 3807 | 5061 | 5118 | 8065 | 3737 | 2518 |
| $R_{int}$ | 0.0977 | 0.0523 | 0.0654 | 0.0560 | 0.0652 | 0.1275 |
| Data/parameters | 3799/321 | 504/264 | 5028/264 | 8042/646 | 3717/267 | 2514/173 |
| Maximum, minimum transmission | | 0.766, 0.593 | 1.253, 0.742 | — | 1.162, 0.858 | — |
| Maximum peak and hole/e Å$^{-3}$ | 0.317, −0.226 | 0.285, −0.350 | 0.545, −0.300 | 0.956, −0.533 | 0.687, −0.522 | 0.578, −0.638 |
| Goodness of fit on $F^2$ | 0.521 | 0.421 | 0.449 | 0.718 | 0.808 | 0.472 |
| $R1$ | 0.0426 | 0.0367 | 0.0448 | 0.0654 | 0.1063 | 0.0559 |
| $wR2$ (all data) | 0.1776 | 0.1103 | 0.1317 | 0.1810 | 0.3186 | 0.1840 |

Goodness of fit = $S = [\Sigma w(F_o^2 - F_c^2)/(n - p)]^{\frac{1}{2}}$ where $n$ = number of reflections and $p$ = total number of parameters. $R1 = \Sigma|F_o - F_c|/F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (gP)^2$ where $p = [\max.(F_o^2, O) + 2F_c^2]/3$, values of $g$ were 0.0, 0.1, 0.1, 0.08, 0.1, 0.1 for compounds **4**, **6**, **9**, **13**, **14** and **15** respectively.

*Acetatotris*(tert-*butylimido*)*manganese*(VII) **4**.—To a suspension of Ag($O_2$CMe) (0.7 g, 4.2 mmol) in $CH_2Cl_2$ (50 cm$^3$) was added a solution of **1** (1.0 g, 3.3 mmol) in $CH_2Cl_2$ (30 cm$^3$). The reaction mixture was stirred in the dark at room temperature (8 h), filtered, and evaporated. The green residue was extracted with light petroleum (2 × 30 cm$^3$), the extracts filtered, concentrated to *ca.* 15 cm$^3$ and cooled (−78 °C) for 5 h to give green needles. Yield: 0.7 g, 65%. X-Ray-quality crystals were obtained by slow cooling of light petroleum solutions at *ca.* −40 °C. EI mass spectrum: *m*/*z* 327 ($M^+$), 312 ($M^+$ − Me), 268 ($M^+$ − MeCO$_2$) and 256 ($M^+$ − Bu$^t$N). IR: 1662 (C=O), 1355 (C–O) and 1190 cm$^{-1}$ (Mn=NBu$^t$).

*Tris*(tert-*butylimido*)(*trifluoroacetato*)*manganese*(VII) **5**.—This compound was made as for **4** using **1** (0.3 g, 1 mmol) and Ag($O_2CCF_3$) (0.29 g, 1.3 mmol). Yield: 0.17 g, 45%. EI mass spectrum: *m*/*z* 381 ($M^+$), 366 ($M^+$ − Me), 351 ($M^+$ − 2Me), 239 ($M^+$ − 2Bu$^t$N), 224 ($M^+$ − 2Bu$^t$N − Me), 209 ($M^+$ − 2Bu$^t$N − 2Me), and 113 ($CF_3CO_2^+$). IR: 1713 (C=O), 1394 (C–O) and 1185 cm$^{-1}$ (Mn=NBu$^t$).

*Tris*(tert-*butylimido*)(*pentafluorophenoxo*)*manganese*(VII) **6**.—To a solution of compound **1** (0.3 g, 1 mmol) in toluene (20 cm$^3$) at −78 °C was added a solution of Tl($OC_6F_5$) (0.43 g, 1.1 mmol in 10 cm$^3$ toluene) and the mixture allowed to warm during which time TlCl began to precipitate. After stirring for 2 h the mixture was filtered and evaporated. Extraction of the green residue with light petroleum (2 × 20 cm$^3$), filtration and concentration until crystallisation started followed by cooling to −20 °C gave green needles. Yield: 0.35 g, 80%, in two crops. X-Ray-quality crystals were obtained by slow cooling of concentrated MeCN solution at *ca.* −20 °C. EI mass spectrum: *m*/*z* 451 ($M^+$), 380 ($M^+$ − Bu$^t$N), 365 ($M^+$ − Bu$^t$N − Me), and 268 ($M^+$ − OC$_6$F$_5$). IR: 1230 (Mn=NBu$^t$) and 1167 cm$^{-1}$ (C–F).

*Tris*(tert-*butylimido*)(*pentachlorophenoxo*)*manganese*(VII) **7**.—This compound was prepared as for **6** from **1** (0.3 g, 1 mmol) and Tl($OC_6Cl_5$) (0.51 g, 1.1 mmol) with crystallisation from hexane at −78 °C. Yield: 0.35 g, 65%. It decomposes at room temperature within 36 h but is stable indefinitely in the dark at −20 °C. IR: 1185 (Mn=Bu$^t$) and 991 cm$^{-1}$ (C–Cl).

*Bis*(*trifluoromethyl*)*methoxotris*(tert-*butylimido*)*manganese*(VII) **8**.—To a solution of compound **1** (0.15 g, 0.5 mmol) in toluene (20 cm$^3$), cooled to −78 °C, was added a solution of Tl[OCH($CF_3$)$_2$] in toluene (0.23 g, 0.62 mmol in 10 cm$^3$). The reaction mixture was allowed to warm to room temperature and stirred for 0.5 h. After filtering off the white precipitate (TlCl), evaporating the green solution to dryness, extracting the residue with light petroleum (2 × 20 cm$^3$), filtering again and evaporating the filtrate compound **8** was obtained as a green oil, pure according to NMR spectroscopy. It can be stored for a few hours at −78 °C without decomposition. Analytical data could not be obtained due to the thermal instability. Yield: 0.11 g, *ca.* 55%. EI mass spectrum: *m*/*z* 435 ($M^+$), 420 ($M^+$ − Me), 364 ($M^+$ − NBu$^t$), 349 ($M^+$ − NBu$^t$ − Me) and 334 ($M^+$ − NBu$^t$ −2Me).

*Tris*(tert-*butylimido*)(*pentafluorothiophenolato*)*manganese*(VII) **9**.—To a solution of compound **1** (0.3 g, 1 mmol) in toluene (10 cm$^3$) at −78 °C was added a solution of $Tl(SC_6F_5)$ (0.44 g, 1.1 mol in 10 cm$^3$ toluene) and the mixture allowed to warm; precipitation of TlCl started after *ca.* 15 min. After stirring for 2 h, work-up as for **6** with extraction of the residue using light petroleum (40 cm$^3$), concentration to *ca.* 10 cm$^3$ and cooling at −20 °C (1 d) gave green prisms. Yield: 0.21 g, 45%. EI mass spectrum: *m*/*z* 467 ($M^+$), 452 ($M^+$ − Me), 437 ($M^+$ − 2Me), 396 ($M^+$ − NBu$^t$), 381 ($M^+$ − NBu$^t$ − Me), 366 ($M^+$ − NBu$^t$ − 2Me), 325 ($M^+$ − 2NBu$^t$), 295 ($M^+$ − 2NBu$^t$ − 2Me) and 200 ($C_6F_5SH^+$). IR: 1232 (Mn=NBu$^t$) and 1165 cm$^{-1}$ (C–F).

*Tris*(tert-*butylimido*)(*pentafluorophenyl*)*manganese*(VII) **10**.—To a solution of compound **1** in $Et_2O$ (0.15 g, 0.5 mmol in 20 cm$^3$) cooled to −78 °C was added a precooled (−78 °C) solution of $Ag(C_6F_5)$ in $Et_2O$ (0.17 g, 0.625 mmol in 10 cm$^3$) and the mixture allowed to warm to room temperature and stirred for 1 h. After filtering off AgCl and evaporating volatiles under vacuum, the green-brown oily residue was extracted with light petroleum (20 cm$^3$) and filtered quickly; removal of the solvent left a brown-green oil which is pure (> 95%) according to NMR spectroscopy. The compound decomposes at room temperature but can be stored for at least 3 h at −78 °C. High-resolution mass spectrum: molecular ion at *m*/*z* 435.147; calc. for $C_{18}H_{27}F_5MnN_3$ 435.150. EI mass spectrum: *m*/*z* 435 ($M^+$), 420 ($M^+$ − Me), 405 ($M^+$ − 2Me), 364 ($M^+$ − NBu$^t$), 349 ($M^+$ − NBu$^t$ − Me) and 334 ($M^+$ − NBu$^t$ − 2Me).

tert-*Butylamidotris*(tert-*butylimido*)*manganese*(VII) **11**.—To a solution of compound **1** in thf cooled to −78 °C (0.3 g, 0.98 mmol in 30 cm$^3$) was added a solution of Li(NHBu$^t$) (prepared from $NH_2Bu^t$ and $LiBu^n$ in light petroleum; 0.10 g, 1.28 mmol, 1.3 equivalents in 30 cm$^3$) precooled to −78 °C. The reaction mixture was allowed to reach −40 to −35 °C and stirred at this temperature for 16 h. After removing volatiles at −20 to −30 °C in vacuum, the residue was extracted with precooled light petroleum (30 cm$^3$, −30 °C) and filtered quickly. Evaporation of the volatiles at low temperature afforded a green-brown oil pure (>98%) according to $^1H$ NMR spectroscopy. The compound is stable at −78 °C for several hours but decomposes slowly at above *ca.* −20 °C.

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

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn(1) | 1379(1) | 695(1) | 1732(1) |
| Mn(2) | 1688(1) | 7500* | 2388(1) |
| N(1) | 1563(2) | 1179(1) | 1299(4) |
| N(2) | 2158(2) | 413(1) | 1965(4) |
| N(3) | 816(2) | 671(1) | 3051(4) |
| N(4) | 1614(4) | 6994(2) | 1965(9) |
| N(4′) | 1006(4) | 7232(3) | 1711(8) |
| N(5) | 2531(4) | 7328(2) | 2025(7) |
| O(1) | 911(2) | 449(1) | 206(3) |
| O(2) | −168(2) | 803(1) | 516(4) |
| O(3) | 1617(2) | 7500* | 4293(4) |
| O(4) | 440(4) | 7278(3) | 4386(7) |
| C(1) | 226(3) | 570(2) | −150(5) |
| C(2) | −36(3) | 382(2) | −1474(5) |
| C(3) | 1002(4) | 7500* | 6399(7) |
| C(4) | 991(5) | 7500* | 4918(9) |
| C(11) | 2135(3) | 1455(2) | 764(9) |
| C(21) | 2507(3) | 140(2) | 2982(5) |
| C(31) | 402(3) | 930(2) | 4000(5) |
| C(41) | 1031(4) | 6750(2) | 1158(7) |
| C(51) | 3277(4) | 7500* | 1432(8) |
| C(211) | 3060(3) | −148(2) | 2288(5) |
| C(212) | 1904(3) | −124(2) | 3690(5) |
| C(213) | 2921(3) | 422(2) | 3972(5) |
| C(311) | 181(3) | 1348(2) | 3411(6) |
| C(312) | −304(3) | 686(2) | 4404(6) |
| C(313) | 913(4) | 986(2) | 5220(6) |
| C(111) | 2090(4) | 1403(2) | −759(7) |
| C(112) | 2924(3) | 1336(2) | 1243(8) |
| C(113) | 1938(3) | 1894(2) | 1125(7) |
| C(411) | 1555(4) | 6537(4) | 444(12) |
| C(412) | 590(5) | 6534(3) | 2237(9) |
| C(413) | 417(7) | 6899(3) | 185(11) |
| C(511) | 3398(5) | 7135(3) | 621(10) |
| C(512) | 3795(5) | 7500* | 2637(10) |

* Invariant parameter.

**Table 8** Fractional atomic coordinates (× 10$^4$) for compound **6**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 2 713(1) | 7 705(1) | 6 964(1) |
| F(1) | 458(2) | 7 728(2) | 9 604(1) |
| F(2) | 1 204(2) | 7 034(2) | 11 456(1) |
| F(3) | 2 736(3) | 5 136(2) | 11 327(2) |
| F(4) | 3 488(3) | 3 932(2) | 9 292(2) |
| F(5) | 2 790(2) | 4 642(2) | 7 430(2) |
| O | 1 144(2) | 6 536(2) | 7 534(2) |
| N(1) | 3 311(3) | 9 019(2) | 7 948(2) |
| N(2) | 1 653(3) | 7 878(2) | 5 864(2) |
| N(3) | 4 374(3) | 7 138(2) | 6 588(2) |
| C(1) | 1 214(4) | 6 787(3) | 9 506(2) |
| C(2) | 1 587(4) | 6 435(3) | 10 455(2) |
| C(3) | 2 369(4) | 5 484(3) | 10 398(3) |
| C(4) | 2 747(4) | 4 884(3) | 9 367(3) |
| C(5) | 2 375(4) | 5 243(3) | 8 417(2) |
| C(6) | 1 590(3) | 6 213(2) | 8 444(2) |
| C(11) | 3 175(4) | 10 297(2) | 8 216(2) |
| C(21) | 1 640(4) | 7 598(3) | 4 640(2) |
| C(31) | 6 203(4) | 7 366(3) | 6 889(2) |
| C(111) | 2 746(5) | 10 707(3) | 7 175(3) |
| C(112) | 4 888(4) | 11 095(3) | 8 807(3) |
| C(113) | 1 757(4) | 10 369(3) | 9 009(3) |
| C(211) | 495(6) | 8 308(4) | 4 218(3) |
| C(212) | 3 424(5) | 7 953(4) | 4 291(3) |
| C(213) | 898(5) | 6 219(3) | 4 206(3) |
| C(311) | 6 518(5) | 7 532(4) | 8 152(3) |
| C(312) | 6 795(5) | 6 246(4) | 6 263(4) |
| C(313) | 7 119(4) | 8 538(3) | 6 560(3) |

**Table 9** Fractional atomic coordinates (× 10$^4$) for compound **9**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 2986(1) | 2619(1) | 3000(1) |
| F(1) | 4424(3) | 3104(2) | 183(2) |
| F(2) | 2678(3) | 3060(2) | −1538(2) |
| F(3) | 1264(3) | 1100(2) | −1648(2) |
| F(4) | 1673(3) | −846(2) | −9(2) |
| F(5) | 3363(3) | −802(2) | 1735(2) |
| S | 5035(1) | 1217(1) | 2189(1) |
| N(1) | 2405(3) | 3962(3) | 2161(2) |
| N(2) | 3920(3) | 2802(3) | 4080(2) |
| N(3) | 1471(3) | 1923(2) | 3265(2) |
| C(1) | 3733(4) | 2129(3) | 172(3) |
| C(2) | 2848(4) | 2104(3) | −719(2) |
| C(3) | 2134(4) | 1119(3) | −787(3) |
| C(4) | 2350(4) | 126(3) | 55(3) |
| C(5) | 3213(4) | 178(3) | 940(2) |
| C(6) | 3926(4) | 1165(3) | 1044(2) |
| C(11) | 2481(5) | 5295(3) | 1968(3) |
| C(21) | 3897(4) | 2548(3) | 5237(2) |
| C(31) | −263(4) | 2062(3) | 3003(3) |
| C(111) | 1456(6) | 6028(3) | 2807(3) |
| C(112) | 4308(5) | 5315(4) | 2040(4) |
| C(113) | 1767(6) | 5868(4) | 859(3) |
| C(211) | 2873(7) | 1625(5) | 5628(3) |
| C(212) | 5659(6) | 2050(5) | 5635(3) |
| C(213) | 3100(8) | 3845(4) | 5612(3) |
| C(311) | −572(6) | 751(5) | 3361(4) |
| C(312) | −1290(5) | 3052(5) | 3637(4) |
| C(313) | −615(5) | 2486(4) | 1838(3) |

**Table 10** Fractional atomic coordinates ( $\times 10^4$) for compound **13***

| Atom | *x* | *y* | *z* | occ. |
|---|---|---|---|---|
| Mn(1) | 8 843(1) | 2 302(1) | 9 630(1) | |
| Mn(2) | 6 127(1) | −2 812(1) | 6 631(1) | |
| F(11) | 8 955(1) | −2 426(2) | 2 852(1) | |
| F(12) | 9 448(2) | −959(2) | 2 774(1) | |
| F(13) | 8 434(2) | −992(2) | 2 828(2) | |
| F(21a) | 3 279(4) | 7 898(7) | 3 250(5) | 0.4 |
| F(21b) | 3 159(5) | 7 874(8) | 2 894(5) | 0.3 |
| F(21c) | 3 329(6) | 7 778(10) | 2 548(7) | 0.3 |
| F(22) | 3 261(3) | 9 305(5) | 3 485(4) | |
| F(23) | 3 156(2) | 9 167(4) | 2 585(3) | |
| S(1) | 8 999(1) | −1 360(1) | 4 026(1) | |
| S(2) | 4 259(1) | 8 833(1) | 2 948(1) | |
| O(11) | 9 618(1) | −1 770(2) | 4 180(2) | |
| O(12) | 8 932(1) | −259(2) | 4 161(2) | |
| O(13) | 8 483(2) | −1 996(2) | 4 247(2) | |
| O(21a) | 4 472(5) | 8 102(8) | 2 529(5) | 0.5 |
| O(21b) | 4 295(4) | 8 240(6) | 2 165(4) | 0.5 |
| O(22a) | 4 455(3) | 9 870(5) | 3 003(5) | 0.6 |
| O(22b) | 4 307(4) | 9 947(7) | 2 682(5) | 0.4 |
| O(23a) | 4 623(6) | 8 194(9) | 3 290(7) | 0.3 |
| O(23b) | 4 452(6) | 8 459(9) | 3 567(7) | 0.3 |
| O(23c) | 3 993(7) | 8 440(11) | 3 731(7) | 0.4 |
| N(1a) | 9 071(4) | 1 129(6) | 9 518(4) | 0.4 |
| N(1b) | 8 822(3) | 1 365(4) | 9 031(3) | 0.6 |
| N(2a) | 8 671(4) | 2 536(7) | 10 447(4) | 0.5 |
| N(2b) | 8 941(3) | 1 796(5) | 10 418(3) | 0.5 |
| N(3a) | 8 210(3) | 3 054(4) | 9 589(3) | 0.5 |
| N(3b) | 8 296(3) | 2 704(6) | 9 102(4) | 0.5 |
| N(4) | 9 575(1) | 3 321(2) | 9 510(2) | |
| N(5) | 6 736(2) | −2 162(3) | 6 357(2) | |
| N(6) | 6 147(2) | −2 919(4) | 7 480(2) | |
| N(7a) | 6 107(5) | −3 993(7) | 6 505(6) | 0.5 |
| N(7b) | 6 086(4) | −3 918(7) | 6 134(4) | 0.5 |
| N(8) | 5 341(2) | −2 060(3) | 6 473(2) | |
| C(11) | 8 884(3) | 194(4) | 9 002(3) | |
| C(21) | 8 648(2) | 2 001(4) | 11 140(2) | |
| C(31) | 7 643(2) | 3 173(4) | 9 099(3) | |
| C(41) | 10 052(2) | 3 212(3) | 8 908(2) | |
| C(51) | 7 310(2) | −2 236(5) | 5 913(3) | |
| C(61) | 6 456(3) | −2 618(4) | 8 148(3) | |
| C(71) | 5 985(3) | −5 076(4) | 6 327(4) | |
| C(81) | 5 027(2) | −1 803(3) | 5 793(3) | |
| C(11a) | 9 302(9) | 98(15) | 8 222(12) | 0.4 |
| C(11b) | 9 070(13) | 109(23) | 8 175(10) | 0.3 |
| C(11c) | 8 799(12) | 411(15) | 8 401(14) | 0.3 |
| C(11d) | 9 538(6) | −452(9) | 9 122(6) | 0.3 |
| C(11e) | 9 251(5) | −343(7) | 9 499(5) | 0.4 |
| C(11f) | 8 474(7) | −405(11) | 9 584(8) | 0.3 |
| C(11g) | 8 164(10) | −196(15) | 9 301(11) | 0.3 |
| C(11h) | 8 489(16) | 271(26) | 8 323(19) | 0.3 |
| C(11i) | 8 171(6) | −152(9) | 8 845(7) | 0.4 |
| C(211) | 8 796(4) | 2 954(5) | 11 546(3) | |
| C(212) | 9 071(5) | 1 205(7) | 11 448(5) | |
| C(213) | 7 986(3) | 1 664(7) | 11 151(4) | |
| C(311) | 7 429(3) | 4 140(5) | 9 486(4) | |
| C(312) | 7 187(2) | 2 266(4) | 9 217(3) | |
| C(313) | 7 723(4) | 3 438(5) | 8 365(3) | |
| C(411) | 9 686(2) | 3 202(3) | 8 222(2) | |
| C(412) | 10 438(2) | 2 216(3) | 9 022(2) | |
| C(413) | 10 484(2) | 4 186(3) | 8 949(2) | |
| C(51a) | 7 739(4) | −3 065(9) | 6 203(5) | 1.0 |
| C(51b) | 7 158(8) | −1 313(15) | 5 343(7) | 0.4 |
| C(51c) | 7 164(8) | −2 333(13) | 5 191(9) | 0.3 |
| C(51d) | 7 146(8) | −2 971(10) | 5 229(7) | 0.3 |
| C(51e) | 7 791(6) | −1 387(9) | 6 319(6) | 0.5 |
| C(51f) | 7 458(10) | −1 206(15) | 5 698(11) | 0.5 |
| C(611) | 6 041(4) | −1 892(6) | 8 568(5) | |
| C(612) | 7 044(3) | −1 987(6) | 8 031(4) | |
| C(613) | 6 566(5) | −3 591(5) | 8 501(4) | |
| C(71a) | 5 299(3) | −5 262(6) | 6 194(4) | 1.0 |
| C(71b) | 6 479(7) | −5 353(9) | 6 927(7) | 0.5 |
| C(71c) | 5 879(8) | −5 512(9) | 7 164(6) | 0.5 |
| C(71d) | 6 349(6) | −5 778(11) | 5 905(7) | 0.5 |
| C(71e) | 6 364(7) | −5 428(9) | 5 544(7) | 0.5 |
| C(811) | 4 468(2) | −1 099(4) | 6 010(3) | |
| C(812) | 4 772(3) | −2 788(4) | 5 441(4) | |
| C(813) | 5 488(2) | −1 205(4) | 5 348(3) | |
| C(100) | 8 959(2) | −1 441(3) | 3 074(2) | |
| C(20a) | 3 625(10) | 8 753(14) | 2 684(10) | 0.5 |
| C(20b) | 3 740(9) | 9 100(9) | 1 989(7) | 0.5 |

* occ. = Occupancy of partially occupied sites resulting from disorder.

(tert-*Butylcarbamato*)*tris*(tert-*butylimido*)*manganese*(VII) **12**.—Through a solution of compound **11** (0.2 g, 0.6 mmol) in light petroleum (40 cm$^3$) at −78 °C was bubbled $CO_2$ for 5 min; the brown-green colour changed to dark green within 30 s. After warming to ambient temperature under $CO_2$ and evaporation under vacuum the residue was washed with hexamethyldisiloxane (2 × 2 cm$^3$) and crystallised from light petroleum at −20 °C as green needles. Yield: 0.06 g, *ca.* 25%.

tert-*Butylaminetris*(tert-*butylimido*)*manganese*(VI) *Trifluoromethanesulfonate* **13** *and Hexafluorophosphate* **14**.—To a solution of compound **1** (0.3 g, 1 mmol) in $CH_2Cl_2$ (30 cm$^3$) was added a solution of $Ag(O_3SCF_3)$ (0.27 g, 1.05 mmol) in $CH_2Cl_2$ (30 cm$^3$) containing $NH_2Bu^t$ (1 cm$^3$, excess). Separation of AgCl began in *ca.* 10 min and after stirring (3 h), evaporation and washing the residue with light petroleum (2 × 10 cm$^3$), the green solid was extracted with $Et_2O$ until the extracts were colourless (5 × 20 cm$^3$). Filtration, concentration to *ca.* 20 cm$^3$ and cooling (−20 °C) gave green needles. Yield: 0.25 g, 50%. X-Ray-quality crystals were obtained by slow crystallisation at −20 °C from toluene. IR: 3201, 3118 (N–H), 1230 ($Mn{=}NBu^t$) and 1253 cm$^{-1}$ ($CF_3SO_3$).

As above but $TlPF_6$ (0.38 g, 1.1 mmol) and $Bu^tCN$ (0.2 cm$^3$) were added with stirring for 12 h, filtering and evaporation. Extraction of the residue with $Et_2O$ (*ca.* 20 cm$^3$) and cooling yielded green rod-like crystals of compound **14**. Yield: 0.1 g *ca.* 20%.

*Bis*[(1,2-*dimethoxyethane*)*lithium*] *Tetrakis*(tert-*butylimido*)-*manganate*(VI) **15**.—To a solution of compound **1** (0.3 g, *ca.* 1 mmol) in 1,2-dimethoxyethane–toluene (3:1, 40 cm$^3$) cooled at −78 °C was added dropwise *via* a cannula a precooled (−78 °C) solution of $Li(NHBu^t)$ (0.36 g, 5 mmol) in dme–toluene (2:1). The colour of the reaction mixture changed at −78 °C from green to brown. The mixture was allowed to reach room temperature *very slowly* over 12 h. At this point it was red-brown. Removal of volatiles under vacuum, extraction of the brown residue with light petroleum (3 × 30 cm$^3$), filtration, concentration of the combined filtrates to *ca.* 10 cm$^3$ and cooling (−20 °C) for 24 h gave red-brown diamond-like crystals. A second crop can be obtained by concentration and cooling of the supernatant solution in solid $CO_2$. Yield: *ca.* 60%. EPR spectrum: see text.

*Bis*[(*N,N,N',N'-tetramethylethylenediamine*)*lithium*] *Tetrakis*(tert-*butylimido*)*manganate*(VI) **16**.—To a solution of compound **1** (0.3 g, *ca.* 1 mmol) in toluene (30 cm$^3$) containing tmen (2 cm$^3$) cooled at −78 °C was added dropwise *via* cannula a precooled (−78 °C) solution of $Li(NHBu^t)$ (0.36 g, 5 mmol) in toluene (20 cm$^3$) containing tmen (2 cm$^3$, excess). The colour of the reaction mixture changed at −78 °C from green to brown. It was allowed to reach room temperature *very slowly* over 12 h, when the colour was purple. Work-up as before gave red-brown diamond-like crystals in two crops. Yield: 0.35 g, *ca.* 60%.

**Table 11** Fractional atomic coordinates ( × $10^4$) for compound **14**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 2657(1) | 1563(1) | 1167(1) |
| F(1) | 9504(5) | 2696(7) | 974(4) |
| F(2) | 7900(5) | 2436(7) | 537(4) |
| F(3) | 8102(8) | 2034(9) | 1561(4) |
| F(4) | 7803(5) | 203(7) | 912(4) |
| F(5) | 9397(5) | 477(7) | 1362(4) |
| F(6) | 9187(7) | 850(8) | 346(3) |
| P | 8641(2) | 1487(3) | 962(1) |
| N(1) | 2950(6) | −166(7) | 1133(3) |
| N(2) | 3751(5) | 2539(7) | 1164(3) |
| N(3) | 1897(6) | 1929(8) | 1770(3) |
| N(4) | 1743(6) | 1890(7) | 382(3) |
| C(1) | 2701(8) | −1530(8) | 1434(5) |
| C(2) | 4906(7) | 2397(10) | 1147(5) |
| C(3) | 1737(7) | 2834(10) | 2325(4) |
| C(4) | 1800(8) | 3211(9) | −33(4) |
| C(11) | 3522(9) | −2589(10) | 1211(7) |
| C(12) | 1605(8) | −1938(11) | 1192(5) |
| C(13) | 2738(13) | −1361(13) | 2139(5) |
| C(21) | 5254(9) | 1558(14) | 1752(6) |
| C(22) | 5181(10) | 1393(16) | 580(7) |
| C(23) | 5392(8) | 3818(12) | 1129(9) |
| C(31) | 2761(13) | 2789(21) | 2731(8) |
| C(32) | 860(13) | 2163(17) | 2690(7) |
| C(33) | 1478(16) | 4295(13) | 2112(6) |
| C(41) | 886(9) | 3133(11) | −510(5) |
| C(42) | 1683(10) | 4523(10) | 383(5) |
| C(43) | 2848(8) | 3201(12) | −350(5) |

**Table 12** Fractional atomic coordinates ( × $10^4$) for compound **15**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 0* | 2247(1) | 2500* |
| Li | 1705(5) | 2238(5) | 2309(4) |
| O(1) | 2569(2) | 1503(2) | 1668(2) |
| O(2) | 2981(2) | 2867(2) | 2794(2) |
| N(1) | −557(2) | 2913(3) | 3159(2) |
| N(2) | 970(2) | 1571(2) | 2993(2) |
| C(1) | −260(3) | 3665(3) | 3784(3) |
| C(2) | 1144(3) | 816(3) | 3623(2) |
| C(3) | 2274(4) | 1083(4) | 861(3) |
| C(4) | 3460(4) | 1915(4) | 1786(4) |
| C(5) | 3716(4) | 2289(4) | 2653(4) |
| C(6) | 3196(4) | 3338(4) | 3580(3) |
| C(11) | −638(5) | 3380(5) | 4563(4) |
| C(12) | −730(4) | 4618(4) | 3449(4) |
| C(13) | 777(3) | 3816(4) | 4017(3) |
| C(21) | 1334(4) | −127(4) | 3220(3) |
| C(22) | 320(4) | 675(4) | 4047(4) |
| C(23) | 2033(4) | 1094(4) | 4264(3) |

* Invariant parameter.

*X-Ray Crystallography*.—X-Ray data for all compounds were recorded at 150 K using a FAST TV area detector diffractometer as previously described.[30] Details of the crystal data and refinement results are given in Table 6. The structures of compounds **6**, **9**, **13** and **15** were solved *via* applications of direct methods in SHELXS 86[31] whilst **4** and **14** were solved using the PATT facility in the same program. Refinement was by full-matrix least squares on $F^2$ using the program SHELXL 92.[32] Crystals of compounds **4**, **13** and **14** were of poor quality, the latter two generally being twinned or otherwise defective (for example, crystals of **13** often grew as tubes, with amorphous cores), and the data obtained were not of good quality. In addition each showed disorder in some of the components.

The structure of compound **4** contains 1.5 independent molecules in the asymmetric unit, with one in a general position and one on the mirror plane showing considerable disorder. The atoms of the molecule in a general position were defined quite reasonably and refined acceptably. Only data pertaining to this are given in Table 3. In structures **13** and **14** the anions show the most disorder but the cations were reasonably well defined. In all cases the non-hydrogen atoms of these species were successfully refined with anisotropic thermal parameters and hydrogens were included in idealised positions. The data for **6**, **9** and **14** were corrected for absorption using DIFABS,[33] but the method failed for **4**, **13** and **15** and data for these structures were not corrected. Lists of final atomic coordinates are given in Tables 7–12.

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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