Synthesis and X-Ray Crystal Structure of Chloro Tris(*tert*-butylimido)manganese

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Interaction of a solution of manganese(III) chloride in acetonitrile with trimethylchlorosilane and trimethylsilyl(*tert*-butyl)amide produces the green, thermally stable, manganese(VII) compound, $MnCl(NBu^t)_3$, which has a tetrahedral structure (X-ray).

Compounds without oxo groups are unknown for manganese in the VI and VII oxidation states;[1a,b] there are also only nitridoporphyrinates such as that of the tetra-*p*-tolylporphyrinato(2−) anion (L), Mn(N)L,[1c] for Mn^V although oxo species are known.[1d] Some of these oxo compounds, especially the oxohalides, $MnXO_3$, X = Cl,[1a,b] F,[1e] are unstable and may be highly explosive when pure.

In view of the syntheses[2] of $ReCl(NBu^t)_3$ and Li(tmed)-$[Re(NBu^t)_4]$, (tmed = tetramethylethylenediamine), by the sequence shown in eqn. (1), we attempted to obtain analogues but were hampered by the lack of suitable manganese starting

$$Re(OSiMe_3)(NBu^t)_3 \rightarrow ReCl(NBu^t)_3 \rightarrow Re(NBu^t)_3(NHBu^t) \rightarrow Li(tmed)Re(NBu^t)_4 \quad (1)$$

materials. It now appears that the interaction of the purple solutions of $MnCl_3$ in acetonitrile, obtained[3] from an oxoacetate and Me_3SiCl, with $Bu^tNH(SiMe_3)$ at *ca.* −35 °C gives initially an unisolable, orange intermediate which slowly becomes green. Evaporation of the solution followed by addition of hexane and water, separation of the hexane phase, reduction of this in volume and crystallisation at −20 °C gives green, dichroic crystals of $MnCl(NBu^t)_3$ **1**.† Although the yield is only *ca.* 25%, gram quantities of **1** are readily obtained. The compound is stable towards air and water and thermal stability is remarkably different from that of MnO_3Cl which detonates above 0 °C—it melts sharply at 94–95 °C and sublimes in vacuum.

The ^1H NMR spectrum shows only a sharp singlet for NBu^t while the $^{13}C\{^1H\}$ spectrum gives a separation, $\Delta\delta = 49.8$, for the shifts of C_α and C_β that is characteristic for *tert*-butylimido species;[4] *cf.* for $ReCl(NBu^t)_3$,[2] $\Delta\delta = 37.8$.

The molecular structure is shown in Fig. 1 (50% probability ellipsoids).‡ The coordination geometry is essentially tetrahedral and the molecule has an approximate threefold rotation axis along the Cl–Mn bond. The Cl–Mn–N and N–Mn–N angles lie in the narrow ranges 106.8(2) to 108.0(2) and 111.1(2) to 112.2(3)°, respectively. The Mn–N–C angles are also very similar, and lie in the range 138.5(3) to 141.8(3)°. The bending is consistent with a delocalisation of the 2 × 4e + 1 × 2e bonding contributions required from the three imido functions for an 18e manganese configuration. The Mn–N bonds are still quite short [1.655(5) to 1.656(5) Å], however, and compare with values of 1.60–1.61(1)Å found for the Mn–O bonds in permanganate ion.[5] It is pertinent to note that no peaks at all were found in the vicinity of the N atoms, whereas all the methyl hydrogens on the Bu^t groups were experimentally located. The possibility of having $NHBu^t$ groups and formally Mn^{IV} is conclusively confirmed by the absence of appropriate bands for NH in both the NMR and IR spectra, the latter having only CH_3 bands and a $Mn{=}NBu^t$ band at 1187 cm^{-1}.

The mechanism of formation of **1** is as yet unclear but oxidation of an intermediate amido species by molecular oxygen as in the synthesis of $Ru(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(PMe_3)_2$[6] does not appear to be involved. Although **1** can be obtained also by interaction of $(Bu^n_4N)MnO_4$ with Me_3SiCl and $Me_3SiNHBu^t$, the green product is oily and difficult to purify from siloxanes; the ^1H NMR spectrum is the same as for **1**.

Interaction of **1** with Na/Hg or lithium reagents such as $LiNHBu^t$ in Et_2O leads to reduction to the brown dimer, $[(Bu^tN)_2Mn(\mu\text{-}NBu^t)]_2$, whose ^1H NMR spectrum is almost identical to that of its rhenium analogue.[2] The reactions involving removal of the Cl atom from **1** are slow, even with $AgOSO_2CF_3$ in MeCN, possibly because of the strength of the Mn–Cl bond consistent with the short distance, Mn–Cl = 2.222(3) Å. The interaction with $AgCR_3CO_2$, R = H or F, in CH_2Cl_2, produces the corresponding green carboxylate substitution products.

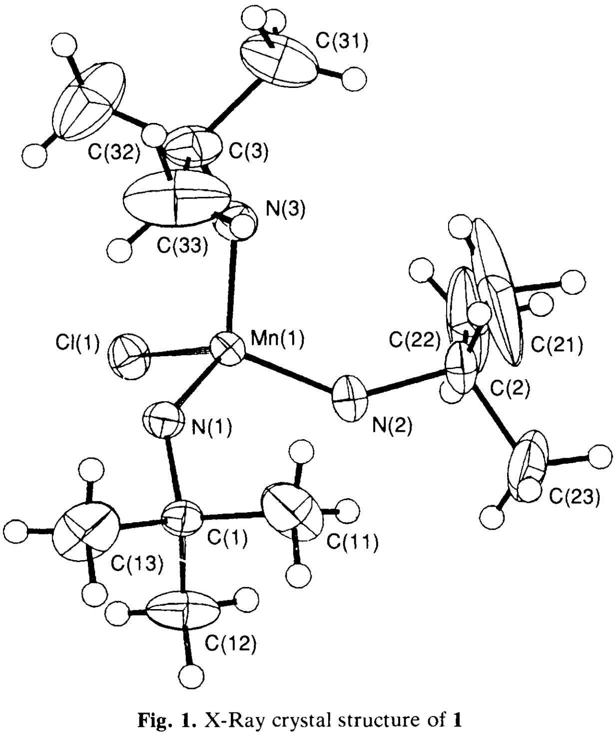

Fig. 1. X-Ray crystal structure of **1**

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† *Selected spectroscopic data*: satisfactory elemental analysis were obtained. MS (EI): *m/z* = 303 (M^+), 288 (M–Me), 273 (M 2Me). IR (Nujol or hexachlorobutadiene mull) ν/cm^{-1}: *no* N–H str, 1187 ($Mn = NBu^t$). ^1H NMR: δ 1.38 s (C_6D_6), 1.52 s (CD_2Cl_2), NBu^t. $^{13}C\{^1H\}(CD_2Cl_2)$: δ 30.7, 80.5, C_α and C_β of Bu^t. The compound contains a very minor paramagnetic impurity that is evident only in X-band EPR spectra. We have been unable to remove (or positively identify) this by crystallisation or sublimation of **1**; it has no effect on the shift or line width of the NMR bands.

‡ *Crystal data* for $C_{12}H_{27}N_3ClMn$: M_r = 303.757, monoclinic, a = 8.028(1), b = 11.615(2), c = 18.356(1)Å, β = 94.005(5)°, V = 1707.56Å^3, space group $P2_1/n$, Z = 4, D_c = 1.1816 g cm^{-3}, $F(000)$ = 648, μ(Mo-Kα) = 8.881 cm^{-1}. Data were collected on a FAST TV Area detector diffractometer following previously described procedures.[7] From the ranges scanned, 13 102 data were recorded and merged to give 4172 unique (R_{int} = 0.04) and 2196 observed [$F_0 > 3\sigma(F_0)$]. The structure was solved *via* direct methods and refined by least-squares analysis. A correction for absorption was made using DIFABS.[8] The final R, R_w values were 0.0383, 0.0423 for 190 parameters (hydrogen atoms were fixed in calculated positions, C–H = 0.96 Å). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The syntheses of isoelectronic analogues of **1** and reactivity studies are in progress.

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