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The synthesis of alkylmanganese(III) complexes. Crystal structure of $MnMe(2\text{-}Me_2NCH_2C_6H_4)_2$

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Abstract

Treatment of bis(3-*N*,*N*-dimethylaminopropyl)manganese(II) with methyllithium and subsequently with silver tetrafluoroborate gives bis(3-*N*,*N*-dimethylaminopropyl)methylmanganese(III) (**1**). The related complex bis(2-*N*,*N*-dimethylaminomethylphenyl)methylmanganese(III) (**2**) was prepared similarly. The structure of **2** was established by single-crystal X-ray crystallography. The molecule is trigonal bipyramidal, with aryl *ipso* carbon atoms in the axial positions and the two nitrogen atoms plus the methyl carbon forming the equatorial plane.

Introduction

There is a continuing need to assess various classes of organomanganese compounds as possible feedstocks for the chemical vapour deposition (CVD) of diluted magnetic semiconductors [1]. It would be useful to have a range of compounds differing in volatility and thermal stability. We have extended our previous investigations [2,3] in this area to include the chemistry of some high-valent manganese compounds. Such compounds offer the opportunity to avoid carbon monoxide ligands which some workers believe are potential sources of metal oxides. Moreover, in contrast to most non-ionic manganese (II) compounds, the higher valent compounds are not likely to be oligomeric. The two routes used for the preparation of high-valent manganese organometallics have been by alkylation of $Mn(acac)_3$ [4,5] sometimes with concommitant disproportionation to Mn^{II} and Mn^{IV} products [6], and air oxidation of Mn^{II} intermediates, either deliberately [7,8] or presumably inadvertently [9]. We report here the controlled oxidation of two manganese(II) complexes to produce the first organomanganese compound

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containing two different alkyl groups. We have also further investigated the reaction between manganocene and diethylcadmium, which was reported [10] to give the manganese(IV) alkyl (η-C_5H_5)MnEt$_3$.

Experimental

All experiments were carried out under argon by standard Schlenk techniques, since all the starting materials and products are very air-sensitive. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone, toluene from sodium, and hexane from sodium–potassium alloy. Methyllithium in diethyl ether (low halide) (Aldrich) was standardized prior to use [11]. Bis(2-*N*,*N*-dimethylaminomethylphenyl)manganese(II) was prepared from anhydrous manganese dichloride and 2-*N*,*N*-dimethylaminomethylphenyllithium [12] by the reported method [13]. 3-*N*,*N*-Dimethylaminopropyllithium was prepared by the published procedure [14]; it should be noted, however, that the lithium sand used in this synthesis must contain some sodium. Manganocene was prepared from $MnI_2(thf)_3$ [15] by the published procedure [16]. Elemental analyses were carried out by the Australian Microanalytical Service, Melbourne. IR spectra were recorded on a Perkin–Elmer 1600 Series FTIR spectrometer and mass spectra on a VG Micromass 7070F mass spectrometer. Magnetic moments were determined at room temperature by use of a Johnson Matthey Magnetic Susceptibility Balance calibrated with $[Ni(en)_3]S_2O_3$.

Preparation and thermal decomposition of η-cyclopentadienyltriethylmanganese(IV)

This is a modification of a previously reported synthesis [10]. A mixture of manganocene (6.16 g, 33.3 mmol) and diethylcadmium (8.75 g, 51.3 mmol) in hexane (20 ml) was stirred at room temperature for 4 days. A metal mirror gradually formed on the walls of the reaction flask. Filtration of the thick yellow–orange suspension and subsequent extraction of the residue with hexane (3 × 20 ml) gave a yellow filtrate. Hexane was distilled from the filtrate at atmospheric pressure, and the remaining liquid was vacuum distilled (68°C, 0.1 mm). The orange distillate was treated with dry degassed methanol to destroy any unchanged diethylcadmium. Removal of methanol by distillation and subsequent vacuum distillation (34–38°C, 0.05 mm) gave (η-C_5H_5)Mn(C_2H_5)$_3$ as an orange liquid (4.73 g, 69%). MS, *m/z* 207 [M^+].

A stream of nitrogen was passed over (η-C_5H_5)Mn(C_2H_5)$_3$ (0.20 g) in a flask kept at 45°C. The vapour was passed into a heated Pyrex tube containing several alumina substrates. The first section of the pyrolysis tube was maintained at 60°C and the middle section at 200°C. Inspection of the tube after all the manganese compound had been transferred revealed a metallic deposit throughout the length of the tube. XPS analysis of the deposit on the substrates indicated that manganese was the only metal present.

*Preparation of bis(3-*N,N*-dimethylaminopropyl)manganese(II)*

This is a modification of a previously reported synthesis [17] using the Jonas methodology [18]. 3-*N*,*N*-Dimethylaminopropyllithium (2.82 g, 30.3 mmol) was added to a solution of manganocene (2.78 g, 15.0 mmol) in THF (20 ml). The yellow suspension was stirred for one hour at room temperature and then evaporated to dryness under vacuum. The residue was extracted with boiling hexane until the extracts were colourless. After filtration of the extract the filtrate was evaporated under reduced pressure to incipient crystallization and then reheated to dissolve any solid which had deposited. Slow cooling to −20°C gave long pale yellow crystals, which were isolated by decanting the mother liquor at −20°C, washing with hexane at −20°C, and drying under vacuum. Yield: 2.85 g, 12.6 mmol, 84%.

*Preparation of bis(3-*N,N*-dimethylaminopropyl)methylmanganese(III) (1)*

Methyllithium (0.75 M, 15.0 ml, 11.3 mmol) was added to a solution of bis(3-*N*,*N*-dimethylaminopropyl)manganese(II) (1.20 g, 5.27 mmol) in toluene (10 ml). The pale yellow suspension was cooled in a bath at −60 to −70°C. Silver tetrafluoroborate (2.24 g, 11.5 mmol) in warm toluene (10 ml) was then added dropwise to the cold organomanganese solution over 20 min. The black suspension was allowed to warm slowly to room temperature and was stirred at room temperature for 30 min. The suspension was evaporated to dryness under a vacuum. The residue was extracted with hot hexane until the extracts were colourless. After filtration, the orange filtrate was evaporated to small volume, and was cooled slowly to −20°C and subsequently to −80°C. The orange needles which separated were isolated by decanting the mother liquor at −80°C and then washed with a minimum of cold hexane at −80°C and dried under vacuum at 0°C for 1 h. Subsequent warming to 30°C for 5 min (the orange solid was observed to melt) and drying at room temperature for 1 h gave the final product (**1**) as a red oil (0.89 g, 3.7 mmol, 69%). Anal. Found: C, 55.3; H, 11.4; N, 11.4. Calc. $C_{11}H_{27}MnN_2$: C, 54.5; H, 11.2; N, 11.6%. Calc. $C_{12}H_{30}MnN_2$: C, 56.0; H, 11.8; N, 10.9%. μ_{eff} 4.5 B.M. MS, m/z 242 [M^+].

*Preparation of bis(2-*N,N*-dimethylaminomethylphenyl)methylmanganese(III)*

Methyllithium (1.59 M, 2.0 ml, 3.2 mmol) was added to a solution of bis(2-*N*,*N*-dimethylaminomethylphenyl)manganese(II) (0.94 g, 2.9 mmol) in toluene (10 ml). The dark orange suspension was cooled in a bath at −60 to −70°C. Silver tetrafluoroborate (0.59 g, 3.0 mmol) was dissolved in warm toluene (10 ml) and the solution added dropwise to the cold organomanganese solution during 15 min. The black suspension was allowed to warm slowly to room temperature and stirred at room temperature for 30 min. The suspension was evaporated to dryness under a vacuum. The residue was extracted with boiling hexane the extract filtered and the yellow filtrate cooled slowly to −20°C. Yellow crystals of **2** separated on standing. These were isolated by decanting the mother liquor at −20°C, washing with a minimum of hexane at −20°C, and drying under vacuum. A second crop was obtained by concentration of the mother liquor. A second recrystallization from boiling hexane afforded fine yellow-green crystals (0.61 g, 1.8 mmol, 62%). Found: C, 67.9; H, 8.3; N, 8.0. Calc. $C_{19}M_{27}MnN_2$: C, 67.4; H, 8.0; N, 7.9%. μ_{eff} 4.8 B.M. MS, m/z 338 [M^+]. Repetition of the synthesis with a mole ratio of 1:2:2 of the above reagents gave **2** (28%).

X-Ray crystal structure determination of $MnMe(2\text{-}Me_2NCH_2C_6H_4)_2$ (2)

An orange crystal with dimensions 0.08 × 0.14 × 0.11 mm was mounted under nitrogen in a capillary. Intensity data were measured at room temperature on an

Table 1

Fractional atomic coordinates ($\times 10^5$ for Mn, $\times 10^4$ for remaining atoms) for complex **2**

Atom	x	y	z
Mn	43579(5)	19701(3)	9565(5)
N(1)	4923(3)	1780(2)	−844(2)
N(2)	5194(3)	3270(2)	1341(3)
C(1)	6186(3)	1349(2)	1187(3)
C(2)	6925(3)	1235(2)	195(3)
C(3)	8191(4)	845(3)	214(5)
C(4)	8752(4)	591(3)	1218(5)
C(5)	8071(5)	698(3)	2204(5)
C(6)	6791(4)	1058(2)	2190(4)
C(7)	6398(4)	1614(3)	−887(3)
C(8)	4180(5)	1004(3)	−1145(4)
C(9)	4551(5)	2451(3)	−1652(3)
C(10)	2642(3)	2699(3)	677(3)
C(11)	2844(4)	3576(2)	735(3)
C(12)	1756(5)	4132(3)	635(4)
C(13)	471(5)	3838(4)	413(4)
C(14)	258(4)	2989(3)	311(3)
C(15)	1316(3)	2426(3)	458(3)
C(16)	4275(4)	3911(3)	857(4)
C(17)	6614(4)	3462(3)	1044(4)
C(18)	5089(5)	3269(3)	2599(3)
C(19)	3353(5)	1198(3)	2068(4)

Enraf–Nonius CAD4F diffractometer with graphite monochromatized Mo-K_α radiation ($\lambda = 0.7107$ Å) using the $\omega:2\theta$ scan technique. A total of 3217 reflections ($\theta_{\max}$ 22.5°) were measured, of which 2885 were unique and 1615 absorption

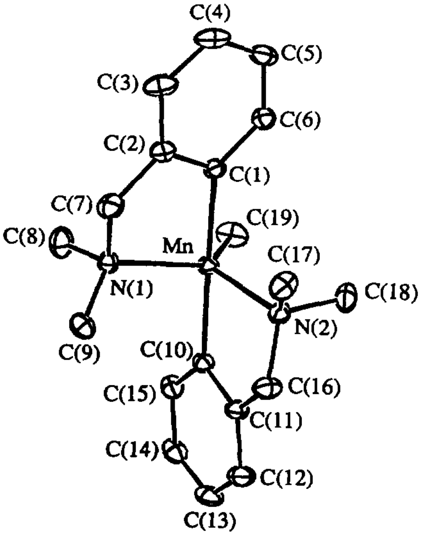

Fig. 1. Molecular structure of complex **2**, hydrogen atoms omitted.

Table 2

Selected bond lengths and angles for complex **2**

Bond lengths (Å)		*Bond angles (deg)*	
N(1)–Mn	2.218(3)	N(2)–Mn–N(1)	102.9(1)
N(2)–Mn	2.259(3)	C(1)–Mn–N(1)	80.8(1)
C(1)–Mn	2.068(3)	C(1)–Mn–N(2)	95.5(1)
C(10)–Mn	2.072(3)	C(10)–Mn–N(1)	97.5(1)
C(19)–Mn	2.050(4)	C(10)–Mn–N(2)	79.8(1)
		C(10)–Mn–C(1)	174.2(1)
		C(19)–Mn–N(1)	131.0(2)
		C(19)–Mn–N(2)	126.2(2)
		C(19)–Mn–C(1)	93.2(2)
		C(19)–Mn–C(10)	92.1(2)

corrected data satisfied the $I \geq 2.5\sigma(I)$ criterion. Crystal data for $C_{19}H_{27}MnN_2$, mol. wt. = 338.4, monoclinic, space group $P2_1/n$, $a = 9.855(3)$, $b = 15.808(3)$, $c = 11.794(3)$ Å, $\beta = 90.23(2)°$, $V = 1837.4$ Å^3, $d_{calc} = 1.223$ g cm^{-3}, $F(000) = 720$, $\mu = 6.64$ cm^{-1}. The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure based on F (SHELX-76) [19]. All non-H atoms were refined anisotropically and H-atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence; $R = 0.032$, $k = 1.23$, $g = 0.0004$, $R_w = 0.034$. Final positional parameters are given in Table 1. Figure 1 shows the atomic labelling scheme (drawn with ORTEP [20] at 15% probability ellipsoids), and selected bond lengths and angles are listed in Table 2. Scattering factors for neutral Mn (corrected for f' and f'') were from ref. 21 and those for the remaining atoms were as incorporated in the SHELX-76 program [19]. Lists of thermal parameters, all bond distances and angles, and observed and calculated structure factors are available from E.R.T.T.

Results and discussion

There has been a report [10] that volatile manganese(IV) compounds $(\eta\text{-}C_5H_5)MnR_3$ (R = Me, Et, ^{n}Pr, ^{n}Bu, ^{i}Bu) can be prepared from manganocene and cadmium dialkyls. We have confirmed this unusual reaction for R = Et.

$$(\eta\text{-}C_5H_5)_2Mn + 2CdEt_2 \rightarrow (\eta\text{-}C_5H_5)MnEt_3 + 2Cd + CpEt \qquad (1)$$

The product is volatile, but we found that it decomposes at 60°C under a hydrogen atmosphere, a temperature too low for conventional CVD applications. Similar behaviour is expected for the other compounds $(\eta\text{-}C_5H_5)MnR_3$.

Manganese(II) compounds readily form manganates on reaction with alkylating agents, as exemplified by the formation of $Li_2[MnMe_4] \cdot 0.5Et_2O$ from methyllithium and manganese dichloride [7]. We have found that treatment of a toluene solution of $Mn(CH_2CH_2CH_2NMe_2)_2$ [22] with methyllithium (mole ratio 1:1) results in a colour change from yellow to deep red, and this is attributed to formation of a methylmanganate(II) anion.

$$Mn(CH_2CH_2CH_2NMe_2)_2 + MeLi \rightarrow Li[MnMe(CH_2CH_2CH_2NMe_2)_2] \qquad (2)$$

Addition of a further mole equivalent of methyllithium gives a yellow solution, which we consider to contain a dimethylmanganate(II) species.

$$Li[MnMe(CH_2CH_2CH_2NMe_2)_2] + MeLi \rightarrow Li_2[MnMe_2(CH_2CH_2CH_2NMe_2)_2] \quad (3)$$

Treatment of this complex with silver tetrafluoroborate (mole ratio 1:2) results in precipitation of silver metal as a black powder. Extraction of the mixture with hexane and evaporation of the solvent yields a volatile red oil **1**. This distils at 64°C/0.1 mm, but there is substantial decomposition and some manganese metal is formed. The red oil crystallizes from hexane at −78°C, but melts at room temperature. Microanalytical data are acceptable for $MnMe_n(CH_2CH_2CH_2NMe_2)_2$ ($n = 1$ or 2), whereas the mass spectrum of **1** shows a parent ion at m/z 242 attributable to $n = 1$ and no higher mass peaks. Thus, **1** is considered to be the manganese(III) compound $[MnMe(CH_2CH_2CH_2NMe_2)_2]$, formed according to eq. 4, where $R{=}CH_2CH_2CH_2NMe_2$.

$$Li_2[MnR_2Me_2] + 2AgBF_4 \rightarrow MnR_2Me + 2Ag + 1/2Me\text{–}Me + 2LiBF_4 \quad (4)$$

The demethylation accompanying oxidation can be considered to involve electrophilic attack by Ag^+ to give methylsilver, which decomposes into ethane and silver at ambient temperature [23]. Confirmation of the identity of **1** is provided by formation of one mole of methane per mole of complex on protolysis with trifluoroacetic acid.

$$[MnMe(CH_2CH_2CH_2NMe_2)_2] + 5H^+ \rightarrow Mn^{3+} + MeH + 2MeCH_2CH_2NMe_2H^+ \quad (5)$$

In addition, the magnetic moment ($\mu_{eff} = 4.5$ B.M.) is consistent with high-spin manganese(III) (expected spin-only value 4.9 B.M.).

To support the formulation of **1** as a manganese(III) complex and to provide evidence as to its structure, we prepared a crystalline analogue suitable for X-ray examination. Reaction of bis(2-*N*,*N*-dimethylaminomethylphenyl)manganese(II) [24] with methyllithium and then silver tetrafluoroborate (mole ratio 1:2:2) gave the yellow crystalline complex $MnMe(2\text{-}Me_2NCH_2C_6H_4)_2$, (**2**), (eq. 4, $R{=}2\text{-}Me_2NCH_2C_6H_4$). The yield was low (28%) but was increased substantially (62%) when equimolar amounts of the three reagents were used. The latter reaction presumably involves formation and oxidation of a monomethylmanganate(II) complex.

$$\begin{aligned}&[Mn(2\text{-}Me_2NCH_2C_6H_4)_2] + MeLi \rightarrow Li[MnMe(2\text{-}Me_2NCH_2C_6H_4)_2]\\&Li[MnMe(2\text{-}Me_2NCH_2C_6H_4)_2] + AgBF_4 \rightarrow \mathbf{2} + LiBF_4 + Ag\end{aligned} \quad (6)$$

By contrast with the preparation of **1**, the markedly lower yield of **2** with a 1:2:2 mole ratio of reagents may indicate attack of Ag^+ on the 2-dimethylaminomethylphenyl ligand in competition with the required demethylation (eq. 4, $R{=}2\text{-}Me_2NCH_2C_6H_4$). Support for the identification of **2** is provided by a parent ion in the mass spectrum and the magnetic moment (4.8 B.M.).

The structure of **2** was determined by an X-ray diffraction study, and the atomic coordinates and selected bond distances and angles are listed in Tables 1 and 2, respectively. The structure (Fig. 1) reveals trigonal bipyramidal stereochemistry for manganese, with the aryl carbons C(1) and C(10) occupying apical positions and the nitrogen atoms and the methyl carbon C(19) in equatorial positions. The C(1)–Mn–C(10) angle (174.2(1)°) deviates slightly from linearity, and the sum of the equatorial angles is 360°. Manganese is virtually coplanar with N(1), N(2), and C(19), and lies 0.0067(5) Å above the trigonal plane in the direction of the C(10) atom. Distortions from ideal geometry appear related to the steric influence of the methyl group. Thus, the angles C(1)–Mn–C(19) and C(10)–Mn–C(19) are opened beyond 90° (Table 2) leading to closure of C(1)–Mn–C(19) from linearity. The steric effect of the methyl group is more marked in the equatorial plane, with considerable opening of the angles C(19)–Mn–N(1) and C(19)–Mn–N(2) from 120° and consequent closure of N(1)–Mn–N(2) to 102.9(1)°. Each of the five membered chelate rings $\overline{\text{Mn–NCCC}}$ is puckered owing to the presence of the methylene group. Consequently, significant distortions from the least squares plane passing through the ligand are observed for C(7) (−0.210(4) Å) and N(1) (0.093(3) Å) of one ligand, and C(16) (−0.234(5) Å) and N(2) (0.120(3) Å) of the other. The dihedral angle between the least squares plane through each of the ligands is 87.8°.

Trigonal bipyramidal stereochemistry is also observed [8] in the organomanganese(III) complex $MnBr_2(2,4,6\text{-}C_6H_2Me_3)(PMe_3)_2$ (**3**), whilst $[K(py)_2][Mn(C_4H_8)_2py]$, (**4**), is described [25] as distorted square pyramidal. The manganese–carbon bond lengths in **2** lie in the range expected for Mn(III)–C σ-bonds [4,5,7,9]; for example, this distance is 2.089(8) Å for the mesityl–manganese bond of **3**. There appear to be no crystal structures of organomanganese(III) complexes with amine ligands, but the Mn–N bond lengths seem unremarkable; they are shorter than those in **4**, presumably owing to the different nature of the nitrogen donor atoms. In contrast to the equatorial location of the nitrogen atoms in **2**, the nitrogens of the ψ-trigonal bipyramidal stannylene $Sn(2\text{-}Me_2NCH_2C_6H_4)_2$, (**5**) are apical [26]. However, the arrangement in **5** is significantly distorted owing to close contacts between the methyl(−N) groups and adjacent aryl groups. In **2**, the manganese bound methyl group provides an additional steric constraint which has a greater effect than the electronic repulsion associated with the lone pair of **5**. This, together with the significantly smaller radius of Mn^{3+} compared with Sn^{4+}, probably leads to the different stereochemistry of **2**. It is likely that **1** has a structure similar to that of **2**.

We have thus, by controlled oxidation of an alkylmanganate, succeeded in forming the first organomanganese(III) compound containing two different alkyl ligands, and the first triorganomanganese(III) complexes. Our route offers the possibility of a much wider range of substitution patterns around manganese than were available from previous routes to high-valent organomanganese complexes. That two equivalents of $AgBF_4$ did not give manganese(IV) compounds indicates either that stronger oxidants are required, or more likely, that chelating σ-alkyls favour manganese(III). We plan to extend the range of alkylmanganese(III) compounds prepared in this way, and to test selected compounds for CVD applications. Of the present two compounds, **1** appears to have insufficient thermal stability and **2** to be insufficiently volatile for use as CVD feedstocks.

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