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High-Valent Organomanganese Chemistry. 1. Synthesis and Characterization of Manganese(III) and -(IV) Alkyls

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A new manganese(IV) alkyl, the hexamethylmanganate salt $[Li(tmed)]_2[MnMe_6]$, has been prepared by treatment of $MnMe_4(PMe_3)_2$ with methyllithium followed by addition of *N,N,N',N'*-tetramethylethylenediamine (tmed). The X-ray structure of the hexamethyl complex reveals an octahedral geometry for this d^3 ion with the lithium atoms capping opposite faces in an asymmetric fashion: Mn–C = 2.12 (1) Å, Li–C = 2.20 (1), 2.35 (2), 2.53 (2) Å. Addition of excess methyllithium to $Mn(acac)_3$ followed by treatment with tmed gives the pentamethylmanganate $[Li(tmed)]_2[MnMe_5]$. This trivalent species can also be obtained by a comproportionation reaction of the manganese(IV) complex $[Li(tmed)]_2[MnMe_6]$ with 1 equiv of the manganese(II) complex $[Li(tmed)]_2[MnMe_4]$ in diethyl ether. Interestingly, conducting the same comproportionation reaction in toluene leads to a different trivalent product, the tetramethylmanganate $[Li(tmed)_2][MnMe_4]$. The X-ray crystal structure of $[Li(tmed)_2][MnMe_4]$ reveals a square-planar geometry about manganese that is slightly distorted tetrahedrally: Mn–C = 2.078 (5) Å, C–Mn–C(trans) = 161.3 (2)°, C–Mn–C(cis) = 91.5 (2)°. Crystal data (Mo K$\bar{\alpha}$, λ = 0.71073 Å): $[Li(tmed)]_2[MnMe_6]$, space group *Pbca*, with a = 12.386 (4) Å, b = 13.358 (7) Å, c = 15.349 (7) Å, V = 2540 (4) Å^3, Z = 4, T = 173 K, R_F = 0.051, and R_{wF} = 0.058 for 115 variables and 909 data; $[Li(tmed)_2][MnMe_4]$, space group $P2_1/n$, with a = 9.818 (2) Å, b = 15.573 (2) Å, c = 15.245 (9) Å, β = 98.24 (4)°, V = 2307 (3) Å^3, Z = 4, T = 198 K, R_F = 0.044, and R_{wF} = 0.044 for 321 variables and 2491 data. The nonexistence of the quadruply bonded dimanganese(III) complex $[Mn_2Me_8{}^{2-}]$ is also discussed.

Introduction

The chemistry of manganese in its trivalent and tetravalent oxidation states is of interest due to the role of Mn^{III} and Mn^{IV} in biological redox reactions,[1-12] particularly in photosystem II of the photosynthetic electron-transfer pathway, in acid phototases, and in the bacterial enzyme superoxide dismutase.[11,12] Inorganic complexes of manganese(III) and manganese(IV) are often potent oxidants; for example, manganic acetate, "$Mn(O_2CMe)_3$", is able to oxidize olefins to lactones, and aromatic hydrocarbons to esters under relatively mild conditions.[13,14] In addition, the recently demonstrated ability of high-valent manganese porphyrin complexes to oxidize alkanes has stimulated substantial efforts to determine the mechanistic details of manganese-mediated organic oxidation processes.[15-20]

In contrast to the importance of high-valent inorganic complexes of manganese, the organometallic chemistry of manganese is almost entirely limited to the 0, +1, and +2 oxidation states.[21] High-valent organomanganese complexes were unknown until the discovery of $Mn(nor)_4$ (nor = 1-norbornyl) by Bower and Tennent in 1972.[22] The analogous but thermally unstable complexes $Mn(CH_2SiMe_3)_4$ and $Mn(CH_2CMe_3)_4$ were prepared subsequently,[23,24] and the only other high-valent organomanganese species known are the octahedral Mn^{IV} complexes $MnMe_4(PMe_3)_2$ and $MnMe_4(dmpe)$[24] and the cyclopentadienyl species "$NaMnCp_4$"[25] and $CpMnMe_3$.[26,27]

The rarity of high-valent organomanganese complexes is largely due to the lack of suitable Mn^{III} and Mn^{IV} starting materials, since the binary halides are generally unstable or nonexistent. While MnF_3 and Lewis base adducts of $MnCl_3$ such as $MnCl_3(OPR_3)_3$ are known,[28-30]

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Table I. Physical and Microanalytical Data for the High-Valent Manganese Compounds

				anal.[a]				
compd	color	mp, °C	μ_{eff}, μ_B	C	H	N	Mn	Li
$[Li(tmed)]_2[MnMe_6]$ (1)	yellow-orange	132 dec	3.9	54.9 (55.2)	12.8 (12.9)	14.4 (14.3)	14.1 (14.0)	3.71 (3.55)
$[Li(tmed)]_2[MnMe_5]$ (2)	red	119 dec	4.9	54.1 (54.2)	12.4 (12.6)	14.9 (14.9)	14.7 (14.9)	3.81 (3.69)
$[Li(tmed)_2][MnMe_4]$ (3)	dark red	124 dec	4.8	53.4 (54.2)	12.5 (12.5)	15.8 (15.8)	16.2 (15.5)	2.08 (1.96)

[a] Calculated values are in parentheses.

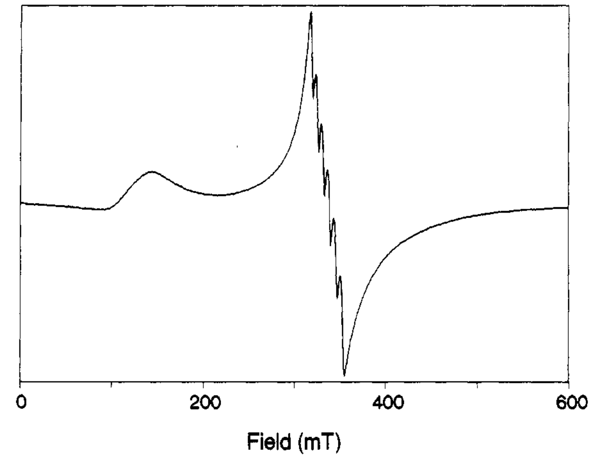


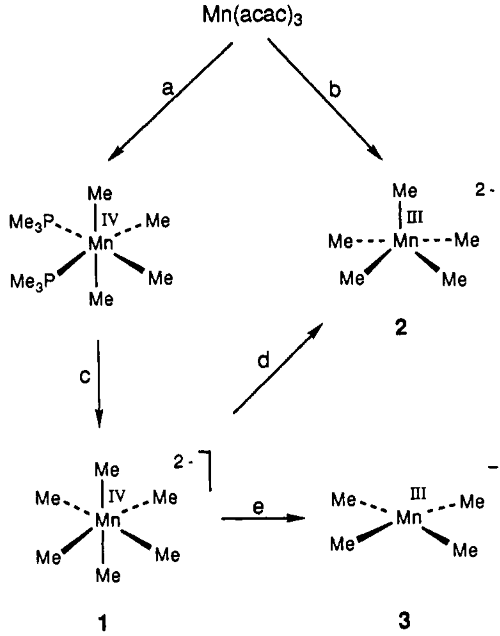
Figure 1. X-Band EPR spectrum of $[Li(tmed)]_2[MnMe_6]$ (1) in toluene at −100 °C.

they either do not react with alkylating agents or are reduced by them. More recently, the 1,4,7-trimethyl-1,4,7-triazacyclononane complex $MnCl_3(Me_3TACN)$ has been prepared;[31] this complex is very stable toward reduction to manganese(II), but its reactions with alkylating agents have not been investigated. Other species[32,33] such as K_2MnCl_5, "$Mn(O_2CMe)_3$", K_2MnCl_6, and MnO_2 are rather insoluble in organic solvents and are essentially unreactive toward organolithium and organomagnesium reagents.

In an effort to expand the known chemistry of high-valent organomanganese species, we have explored the alkylation of soluble Mn^{III} and Mn^{IV} starting materials such as $Mn(acac)_3$ (acac = 2,4-pentanedionato). We now report the synthesis of a series of Mn^{III} and Mn^{IV} alkyls that can be prepared either by oxidation of lower valent complexes or directly from Mn^{III} and Mn^{IV} starting materials. One interesting point that will be addressed is the stability of the hypothetical quadruply bonded Mn^{III}–Mn^{III} dimer $[Mn_2Me_8^{2-}]$. Some of this work has appeared in preliminary form.[34]

Results and Discussion

Scheme I



[a] LiMe and PMe_3 in Et_2O. [b] LiMe and tmed in Et_2O. [c] LiMe and tmed in Et_2O. [d] $[Li(tmed)]_2[MnMe_4]$ in Et_2O. [e] $[Li(tmed)]_2[MnMe_4]$ in PhMe.

Synthesis and Properties of Manganese(IV) Alkyls. The previously reported octahedral manganese(IV) alkyl $MnMe_4(PMe_3)_2$ is readily synthesized in a disproportionation reaction from $Mn(acac)_3$, LiMe, and PMe_3,[24] and we have found that it can serve as a starting material for other organomanganese(IV) compounds. Alkylation of $MnMe_4(PMe_3)_2$ with 2 equiv of LiMe followed by the addition of 2 equiv of *N,N,N′,N′*-tetramethylethylenediamine (tmed) gives an orange solution from which the new peralkylmanganate(IV) complex $[Li(tmed)]_2[MnMe_6]$ (1) may

$$MnMe_4(PMe_3)_2 + 2LiMe + 2\,tmed \rightarrow \underset{1}{[Li(tmed)]_2[MnMe_6]} + 2PMe_3$$

be isolated; see Table I for physical and analytical data for the new high-valent organomanganese compounds and Scheme I for a summary of the reactions described herein. The hexamethylmanganate complex is thermally robust but air-sensitive. The +4 oxidation state of 1 is confirmed by its magnetic moment of 3.9 μ_B and its EPR spectrum (Figure 1), which shows a strong sextet at 340 mT ($A_{Mn} = 0.0060$ cm^{-1}) and a relatively weak half-field transition at 145 mT that are consistent with the presence of a nearly cubic ($D = \lambda = 0$) $S = {}^3/_2$ ion.[35,36] The presence of the half-field transition ($\Delta M_s = 2$) indicates that the cubic symmetry is broken slightly, and this symmetry breaking undoubtedly is a result of close contacts between the $[MnMe_6^{2-}]$ anion and the $[Li(tmed)^+]$ cations (see below). Attempts to observe ^1H NMR resonances for the $[MnMe_6^{2-}]$ methyl groups were unsuccessful.

Although the preparation of 1 from $MnMe_4(PMe_3)_2$ is clean and straightforward, 1 can also be synthesized from Mn^{III} precursors. Alkylation of diethyl ether solutions of $Mn(acac)_3$ at 0 °C with excess methyllithium results in the formation of an orange solution. Removal of the solvent gives an orange solid that contains a pentane-soluble

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Table II. Crystallographic Data for $[Li(tmed)]_2[MnMe_6]$ (1) and $[Li(tmed)_2][MnMe_4]$ (3)

	1	3
space group	*Pbca*	$P2_1/n$
T, °C	−100	−75
a, Å	12.386 (4)	9.818 (2)
b, Å	13.358 (7)	15.573 (5)
c, Å	15.349 (7)	15.245 (9)
β, deg	90	98.24 (4)
V, $Å^3$	2540 (4)	2307 (3)
Z	4	4
mol wt	391.44	354.43
d_{calcd}, g cm^{-3}	1.024	1.020
μ_{calcd}, cm^{-1}	5.05	5.51
size, mm	0.3 × 0.4 × 0.5	0.4 × 0.5 × 0.5
diffractometer	Enraf-Nonius CAD4	
radiation	Mo $K\bar{\alpha}$, $\bar{\lambda} = 0.71073$ Å	
monochromator	graphite cryst, $2\theta = 12°$	
scan range, deg	$2 < 2\theta < 50$	
scan type	ω/θ	
scan speed, deg min^{-1}; scan width, deg	3–20; $\Delta\omega = 1.50[1.00 + 0.35 \tan \theta]$	
no. of rflns, total	3891	4095
no. of rflns, unique	2230	3610
no. of rflns, $I > 2.58\sigma(I)$	909	2491
R_i	0.016	0.033
R_F	0.051	0.044
R_{wF}	0.058	0.044
no. of variables	115	321
p factor	0.020	0.010

Table III. Atomic Coordinates for $[Li(tmed)]_2[MnMe_6]$ (1)

	x/a	*y/b*	*z/c*
Mn	0.0	0.0	0.0
Li	0.0719 (9)	−0.1569 (7)	0.0941 (8)
C7A	0.038 (1)	0.0248 (9)	0.1325 (8)
C8A	−0.0956 (9)	−0.1272 (8)	0.0270 (8)
C9A	0.142 (1)	−0.0871 (9)	−0.0233 (8)
C7B	0.043 (1)	0.141 (1)	0.054 (1)
C8B	−0.167 (1)	0.039 (1)	−0.0149 (10)
C9B	0.044 (1)	0.047 (1)	−0.1285 (9)
N1	0.1819 (5)	−0.1844 (4)	0.2060 (5)
N2	0.0533 (6)	−0.3197 (4)	0.0981 (5)
C1	0.1611 (8)	−0.2884 (7)	0.2276 (7)
C2	0.138 (1)	−0.3502 (6)	0.1606 (8)
C3	0.2927 (7)	−0.1681 (6)	0.1801 (5)
C4	0.1607 (9)	−0.1261 (7)	0.2838 (6)
C5	−0.0544 (8)	−0.3519 (6)	0.1248 (8)
C6	0.0799 (6)	−0.3683 (5)	0.0163 (6)

fraction and a pentane-insoluble fraction. From the pentane extract may be isolated a yellow crystalline material of stoichiometry $[Li(Et_2O)_x]_2[MnMe_6]$; this compound is extremely pyrophoric in the solid state and thus is difficult to characterize fully. Addition of tmed to $[Li(Et_2O)_x]_2[MnMe_6]$ produces orange solutions from which crystalline 1 may be isolated as orange prisms; the yield of this material based on $Mn(acac)_3$ is modest (<10%). How Mn^{IV} species are generated upon alkylation of $Mn(acac)_3$ with LiMe is unclear; while trace oxidation could produce Mn^{IV} species, the product could also result from partial disproportionation of Mn^{III} to Mn^{II} and Mn^{IV}. In fact, we have evidence that such redox equilibria are established in solution (see below).

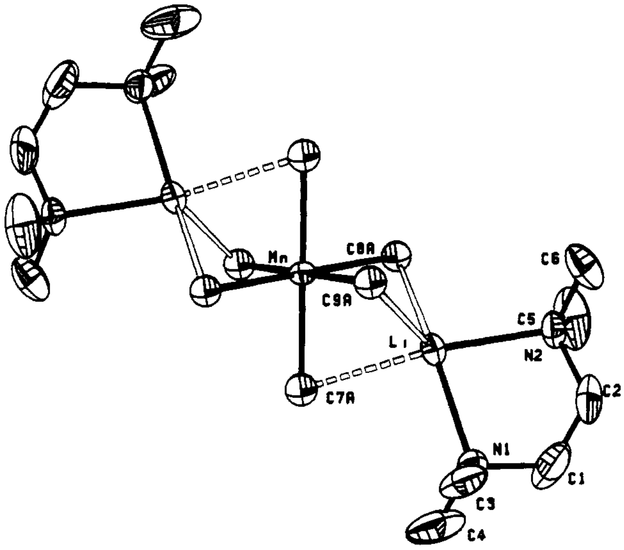

Figure 2. Molecular structure of orientation A of $[Li(tmed)_2][MnMe_6]$ (1; site occupancy of Mn–Me atoms 56.3%).

Crystal Structure of $[Li(tmed)]_2[MnMe_6]$. Single crystals of 1 were grown by cooling saturated diethyl ether solutions to −20 °C. Crystal data are given in Table II, final atomic coordinates are given in Table III, and bond distances and angles are presented with estimated standard deviations in Table IV.

The structural analysis reveals that 1 forms discrete monomers of $[Li(tmed)]_2[MnMe_6]$ in which the $[MnMe_6^{2-}]$ core is disordered in two orientations about the crystallographic inversion center. The disorder does not affect the positions of the Mn, Li, or tmed atoms but involves only the methyl carbon atoms bound to manganese. Three of the manganese-bound methyl groups (and their inversion-related partners) have site occupancies of 56.3 (8)%, and a view of the molecule including only these six major carbon atom positions is shown in Figure 2. The bond distances and angles between the central $[MnMe_6^{2-}]$ core and the $[Li(tmed)^+]$ units are similar in the two orientations, and accordingly the following discussion will refer to the orientation described by the carbon partial atoms with the larger site occupancies.

The $[MnMe_6^{2-}]$ anion is a nearly ideal octahedron in which all of the cis C–Mn–C angles lie between 86 and 94°, and all three trans C–Mn–C angles are 180° as required

Table IV. Selected Bond Distances and Angles for $[Li(tmed)]_2[MnMe_6]$ (1)

	molecule A	molecule B		molecule A	molecule B
		Distances (Å)			
Mn–C7	2.11 (1)	2.13 (2)	Li–C8	2.35 (2)	2.31 (2)
Mn–C8	2.11 (1)	2.14 (1)	Li–C9	2.20 (2)	2.12 (2)
Mn–C9	2.13 (1)	2.14 (1)	Li–N1	2.22 (1)[a]	2.22 (1)[a]
Li–C7	2.53 (2)	2.70 (2)	Li–N2	2.19 (1)[a]	2.19 (1)[a]
		Angles (deg)			
C7–Mn–C8	93.5 (5)	94.0 (6)	C8–Mn–C9	86.8 (4)	86.0 (6)
C7–Mn–C9	93.8 (5)	92.2 (6)			
C8–Mn–C9	93.2 (4)	94.4 (6)	C7–Li–C8	78.0 (5)	76.7 (6)
C7–Mn–C8′	86.5 (5)	87.8 (6)	C7–Li–C9	81.4 (5)	78.4 (6)
C7–Mn–C9′	86.2 (5)	87.8 (6)	C8–Li–C9	85.2 (6)	90.2 (7)
C8–Mn–C9′	86.8 (4)	85.6 (6)	N1–Li–N2	83.0 (4)[a]	83.0 (4)[a]

[a] The Li–N distances and the N–Li–N angles are unaffected by the disorder.

by the inversion symmetry. The Mn–C distances of 2.11 (1)–2.13 (1) Å in **1** are similar to those of 2.08–2.12 Å in the related octahedral manganese(IV) complex $\mathrm{MnMe_4(dmpe)}$.[24] No other $\mathrm{Mn^{IV}}$–C distances have been determined.

The coordination geometries around the lithium atoms are distorted trigonal bipyramids with atoms C7 and N2 in the axial positions. There is one long Li–C distance of 2.53 (2) Å and two shorter Li–C distances of 2.20 (2) and 2.35 (2) Å. The presence of three Li–C contacts to the $\mathrm{[Li(tmed)^+]}$ cation is unusual: in other alkylmanganate salts there are normally only two Li–C contacts to each $\mathrm{[Li(tmed)^+]}$ cation.[37] Evidently, the Li atom interacts with the $\mathrm{[MnMe_6{}^{2-}]}$ anion in this manner to maximize the number of contacts with the partial negative charges that reside on the methyl groups. The shortest of the Li–C distances (2.20 Å) is comparable with the Li–C contacts in alkyllithium reagents.[38] The Li–N distances of 2.19 (1) and 2.22 (1) Å are well within the normal range, and the N–Li–N angle of 83.0 (4)° is characteristic of Li(tmed) units.[38]

Synthesis and Properties of Manganese(III) Alkyls. The pentane-washed orange residue from the reaction of $\mathrm{Mn(acac)_3}$ and excess LiMe (see above) can be extracted with diethyl ether to give a dark orange solution; filtration and addition of tmed yields a red solution from which red crystals of the trivalent pentamethylmanganate complex $\mathrm{[Li(tmed)]_2[MnMe_5]}$ (**2**) may be isolated in

$$\mathrm{Mn(acac)_3 + 5LiMe + 2\,tmed \rightarrow \underset{\mathbf{2}}{[Li(tmed)]_2[MnMe_5]} + 3Li(acac)}$$

moderate yield. This EPR-silent $\mathrm{Mn^{III}}$ product exhibits a solution magnetic moment of 4.9 μ_B that is consistent with the presence of four unpaired electrons. Compound **2** shows no observable ^{1}H NMR resonances for the metal-bound methyl groups.

An alternative preparation of **2** involves oxidation of the known[37] divalent tetramethylmanganate salt $\mathrm{[Li(tmed)]_2[MnMe_4]}$. Exposure of solutions of $\mathrm{[Li(tmed)]_2[MnMe_4]}$ to air in the presence of excess LiMe gives low yields of **2**.

$$\mathrm{[Li(tmed)]_2[MnMe_4] + O_2 + LiMe \rightarrow \underset{\mathbf{2}}{[Li(tmed)]_2[MnMe_5]} + Li^+ + [O_2{}^-]}$$

Similarly, exposure of solutions of $\mathrm{[Li(tmed)]_2[MnMe_5]}$ to air in the presence of excess LiMe gives low yields of the tetravalent alkyl $\mathrm{[Li(tmed)]_2[MnMe_6]}$ (**1**). Complex **2** can also be prepared via comproportionation of a manganese(II) and a manganese(IV) alkyl (see below).

Several five-coordinate $\mathrm{Mn^{III}}$ species have been crystallographically characterized. The anions $\mathrm{[MnCl_5{}^{2-}]}$,[39] $\mathrm{[Mn(SCH_2CH_2S)_2(imidazole)^-]}$,[40] and $\mathrm{[Mn(S_2C_6H_3Me)_2(MeOH)^-]}$[41] adopt nearly ideal or slightly distorted square-pyramidal structures. In addition, complexes of stoichiometry Mn(porph)X are invariably square-pyramidal due to the constraints imposed by the porphyrin macrocycle.[42] Although we have been unable so far to obtain X-ray-quality crystals of **2**, a square-pyramidal geometry is most likely on the basis of these precedents.

We have attempted to prepare other trivalent peralkylmanganates by treatment of $\mathrm{Mn(acac)_3}$ with other alkyllithium reagents. However, alkylation of $\mathrm{Mn(acac)_3}$ with ethyllithium in the presence of tmed results in the isolation of the known[37] divalent peralkyl $\mathrm{[Li(tmed)]_2[MnEt_4]}$ in good yield, while alkylation with $\mathrm{LiCH_2SiMe_3}$ or $\mathrm{LiCH_2CMe_3}$ results in disproportionation to tetravalent $\mathrm{MnR_4}$ monomers and divalent $\mathrm{[MnR_2]_n}$ oligomers.[24]

Comproportionation Reactions. We have previously reported the synthesis of the $\mathrm{Mn^{II}}$ alkyl $\mathrm{[Li(tmed)]_2[MnMe_4]}$,[37] which adopts a high-spin tetrahedral structure, and were interested to determine whether $\mathrm{Mn^{III}}$ complexes could be made by a redox reaction between this complex and the $\mathrm{Mn^{IV}}$ alkyl **1**. When cold (0 °C) diethyl ether solutions of divalent $\mathrm{[Li(tmed)]_2[MnMe_4]}$ and tetravalent $\mathrm{[Li(tmed)_2[MnMe_6]}$ are mixed in a 1:1 ratio, comproportionation occurs to give the trivalent pentamethylmanganate salt $\mathrm{[Li(tmed)]_2[MnMe_5]}$ (**2**) in good yield. Under these conditions, the comproportionation reaction occurs relatively slowly ($t_{1/2} \approx 10$ min), presumably since methyl group transfer as well as electron transfer must take place.

$$\mathrm{[Li(tmed)]_2[MnMe_4] + \underset{\mathbf{1}}{[Li(tmed)]_2[MnMe_6]} \rightarrow 2\underset{\mathbf{2}}{[Li(tmed)]_2[MnMe_5]}}$$

Interestingly, the comproportionation occurs much more quickly in toluene at room temperature ($t_{1/2} < 10$ s), and a different trivalent product, the tetramethylmanganate(III) salt $\mathrm{[Li(tmed)_2][MnMe_4]}$ (**3**), is isolated as large red prisms in good yield.

$$\mathrm{[Li(tmed)]_2[MnMe_4] + \underset{\mathbf{1}}{[Li(tmed)]_2[MnMe_6]} \rightarrow 2\underset{\mathbf{3}}{[Li(tmed)_2][MnMe_4]} + 2LiMe}$$

(Note: care must be taken in distinguishing the very similar formulas of the dianionic $\mathrm{Mn^{II}}$ species $\mathrm{[Li(tmed)]_2[MnMe_4]}$ and the monoanionic $\mathrm{Mn^{III}}$ species $\mathrm{[Li(tmed)_2][MnMe_4]}$.) Compound **3** is an EPR-silent 12-electron species that exhibits a solution magnetic moment of 4.8 μ_B as expected for four unpaired electrons. The 1:2 Li:tmed ratio in the $\mathrm{[Li(tmed)_2{}^+]}$ cation differs from the 1:1 ratio observed for the $\mathrm{[Li(tmed)^+]}$ cations of the $\mathrm{[MnMe_5{}^{2-}]}$ and $\mathrm{[MnMe_6{}^{2-}]}$ salts. Evidently, the lower negative charge of the $\mathrm{[MnMe_4{}^-]}$ monoanion reduces the electrostatic attraction of the $\mathrm{Li^+}$ cation, and the ion-separated lithium center completes its coordination environment by binding two tmed ligands.

The stoichiometry of the manganate salt that crystallizes from solution is a function of the solvent employed: the contact ion pentamethylmanganate salt crystallizes from diethyl ether, while the ion-separated tetramethylmanganate salt crystallizes from toluene. This observation implies that there is a solvent-dependent equilibrium between the two trivalent permethylmanganates in solution.

$$\mathrm{\underset{\mathbf{2}}{[Li(tmed)]_2[MnMe_5]} \rightleftharpoons \underset{\mathbf{3}}{[Li(tmed)_2][MnMe_4]} + LiMe}$$

Since the trivalent peralkylmanganates are related to divalent and tetravalent species via disproportionation equilibria, it is possible that methylation of a manganese starting material could result in the isolation of any one of four peralkylmanganate species: $\mathrm{[MnMe_6{}^{2-}]}$, $\mathrm{[MnMe_5{}^{2-}]}$, $\mathrm{[MnMe_4{}^-]}$, or $\mathrm{[MnMe_4{}^{2-}]}$. Accordingly, it would very useful to develop a set of simple spectroscopic criteria to distinguish the various peralkylmanganates. We have found that while the series of permethylmanganates $\mathrm{[Li(tmed)]_2[MnMe_6]}$ (**1**), $\mathrm{[Li(tmed)]_2[MnMe_5]}$, (**2**), $\mathrm{[Li(tmed)_2]}$-

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Table V. Atomic Coordinates for $[Li(tmed)_2][MnMe_4]$ (3)

	x/a	*y/b*	*z/c*
Mn	0.21180 (5)	0.07387 (3)	0.28978 (3)
N1	0.6774 (3)	0.1894 (2)	0.4150 (2)
N2	0.4662 (3)	0.3229 (2)	0.3970 (2)
C1	0.5446 (4)	0.1801 (3)	0.4489 (3)
C2	0.4828 (5)	0.2574 (3)	0.4685 (3)
C3	0.6936 (6)	0.1132 (3)	0.3606 (3)
C4	0.7927 (5)	0.1897 (3)	0.4869 (3)
C5	0.3467 (5)	0.3053 (4)	0.3326 (4)
C6	0.4496 (7)	0.4051 (4)	0.4393 (4)
N3	0.8154 (3)	0.4022 (2)	0.3636 (2)
N4	0.6606 (3)	0.3162 (2)	0.2071 (2)
C7	0.8129 (4)	0.4332 (3)	0.2716 (2)
C8	0.7923 (4)	0.3616 (3	0.2048 (3)
C9	0.9491 (5)	0.3623 (3)	0.3944 (3)
C10	0.7977 (5)	0.4768 (3)	0.4205 (3)
C11	0.6585 (5)	0.2387 (3)	0.1533 (3)
C12	0.5450 (5)	0.3717 (3)	0.1689 (3)
C13	0.3042 (5)	0.0928 (3)	0.1764 (3)
C14	0.1587 (6)	0.0882 (4)	0.4166 (3)
C15	0.3425 (5)	−0.0266 (3)	0.3322 (3)
C16	0.0380 (6)	0.1405 (4)	0.2334 (4)
Li	0.6547 (5)	0.3067 (3)	0.3454 (3)
H1a[a]	0.5601	0.1466	0.5022
H1b[a]	0.4822	0.1502	0.4051
H2a[a]	0.3929	0.2442	0.4826
H2b[a]	0.5376	0.2822	0.5194
H3a	0.696 (4)	0.060 (3)	0.395 (3)
H3b	0.787 (5)	0.122 (3)	0.337 (3)
H3c	0.623 (5)	0.113 (3)	0.312 (3)
H4a	0.794 (4)	0.133 (3)	0.520 (3)
H4b	0.882 (4)	0.189 (3)	0.455 (3)
H4c	0.775 (4)	0.237 (3)	0.524 (3)
H5a	0.334 (4)	0.360 (3)	0.294 (3)
H5b	0.367 (5)	0.252 (3)	0.302 (3)
H5c	0.271 (5)	0.296 (3)	0.365 (3)
H6a	0.371 (5)	0.400 (3)	0.470 (3)
H6b	0.447 (5)	0.448 (3)	0.392 (3)
H6c	0.528 (5)	0.417 (3)	0.482 (3)
H7a	0.743 (4)	0.476 (3)	0.258 (3)
H7b	0.905 (4)	0.465 (3)	0.263 (3)
H8a	0.795 (4)	0.383 (3)	0.147 (3)
H8b	0.867 (4)	0.316 (3)	0.221 (3)
H9a	0.956 (4)	0.346 (3)	0.455 (3)
H9b	1.025 (5)	0.404 (3)	0.391 (3)
H9c	0.962 (4)	0.314 (3)	0.357 (3)
H10a	0.802 (4)	0.455 (3)	0.486 (3)
H10b	0.708 (4)	0.506 (3)	0.396 (3)
H10c	0.867 (5)	0.519 (3)	0.416 (3)
H11a	0.576 (5)	0.206 (3)	0.156 (3)
H11b	0.666 (4)	0.251 (3)	0.091 (3)
H11c	0.732 (5)	0.201 (3)	0.172 (3)
H12a	0.562 (4)	0.395 (3)	0.105 (3)
H12b	0.536 (5)	0.422 (3)	0.202 (3)
H12c	0.463 (5)	0.334 (3)	0.164 (3)
H13a	0.295 (4)	0.145 (3)	0.150 (3)
H13b	0.400 (5)	0.082 (3)	0.178 (3)
H13c	0.280 (5)	0.055 (3)	0.138 (3)
H14a	0.128 (5)	0.144 (3)	0.428 (3)
H14b	0.079 (5)	0.052 (3)	0.426 (3)
H14c	0.229 (5)	0.069 (3)	0.454 (3)
H15a	0.291 (5)	−0.078 (3)	0.352 (3)
H15b	0.368 (5)	−0.052 (3)	0.288 (3)
H15c	0.401 (5)	−0.008 (3)	0.377 (3)
H16a	0.072 (5)	0.197 (3)	0.226 (3)
H16b	−0.014 (5)	0.148 (3)	0.269 (3)
H16c	0.008 (5)	0.127 (3)	0.175 (3)

[a] Hydrogen atom positions "idealized".

$[MnMe_4]$ (**3**), and $[Li(tmed)]_2[MnMe_4]$ exhibit quite similar IR spectra, they each have characteristic absorption bands that are not exhibited by the others: **1**, 640 cm^{-1}; **2**, 1113, 1076 cm^{-1}; **3**, 560 cm^{-1}, and $[Li(tmed)]_2[MnMe_4]$, 539, 463 cm^{-1}.

Table VI. Selected Bond Distances and Angles for $[Li(tmed)_2][MnMe_4]$ (3)

Distances (Å)			
Mn–C13	2.084 (5)	Li–N1	2.108 (6)
Mn–C14	2.085 (5)	Li–N2	2.128 (6)
Mn–C15	2.067 (5)	Li–N3	2.157 (6)
Mn–C16	2.075 (6)	Li–N4	2.122 (6)
Angles (deg)			
C13–Mn–C14	161.8 (2)	N1–Li–N2	87.2 (2)
C13–Mn–C15	92.4 (2)	N1–Li–N3	120.7 (3)
C13–Mn–C16	90.9 (2)	N1–Li–N4	123.0 (3)
C14–Mn–C15	91.0 (2)	N2–Li–N3	122.0 (3)
C14–Mn–C16	91.7 (2)	N2–Li–N4	120.6 (3)
C15–Mn–C16	160.8 (2)	N3–Li–N4	87.5 (2)

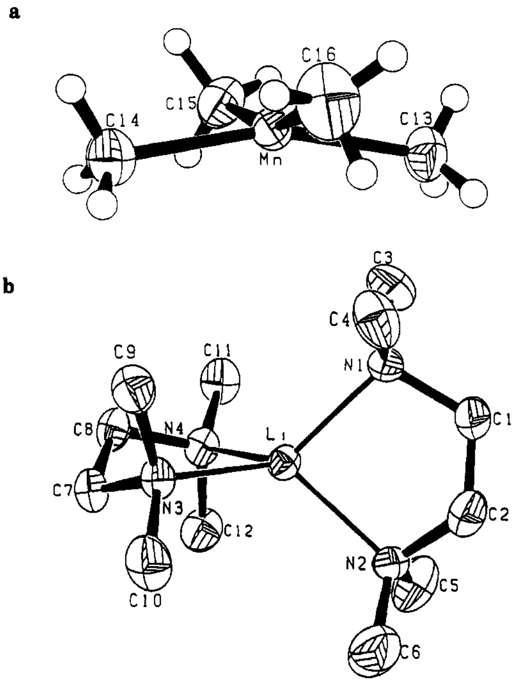

Figure 3. Molecular structure of (a) the $[MnMe_4^-]$ anion of **3** and (b) the $[Li(tmed)_2^+]$ cation of **3**.

Crystal Structure of $[Li(tmed)_2][MnMe_4]$. Single crystals of **3** were grown by cooling saturated toluene solutions to −20 °C. Crystal data are given in Table II, final atomic coordinates are given in Table V, and bond distances and angles are presented with estimated standard deviations in Table VI.

The structural analysis shows that crystals of **3** are composed of charge-separated $[Li(tmed)_2^+]$ and $[MnMe_4^-]$ ions (Figure 3). The $[MnMe_4^-]$ unit exhibits a slight tetrahedral distortion from a square plane, as shown by the trans C–Mn–C angles of 160.8 (2) and 161.8 (2)° and the dihedral angle between the two cis C–Mn–C planes of 26.2°. This dihedral angle is similar to those of 28.4 and 15.8° reported for the isoelectronic chromium(II) alkyls CrR_2(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane) for R = neopentyl and (trimethylsilyl)methyl, respectively.[43] The overall geometry of the $[MnMe_4^-]$ anion is similar to that of the previously described oxo alkyl $[MnOMe_3^{2-}]$.[44] The oxo alkyl also adopts a tetrahedrally distorted square-planar structure with trans C–Mn–C and C–Mn–O angles of 149.0 (2) and 152.5 (2)°. The Mn–C distances of 2.067 (5)–2.085 (5) Å for **3** are similar to those of 2.041 (5)–2.122 (4) Å reported for the oxo alkyl.

Square-planar manganese(III) complexes are exceedingly rare: besides the oxo alkyl $[MnOMe_3^{2-}]$, the only other

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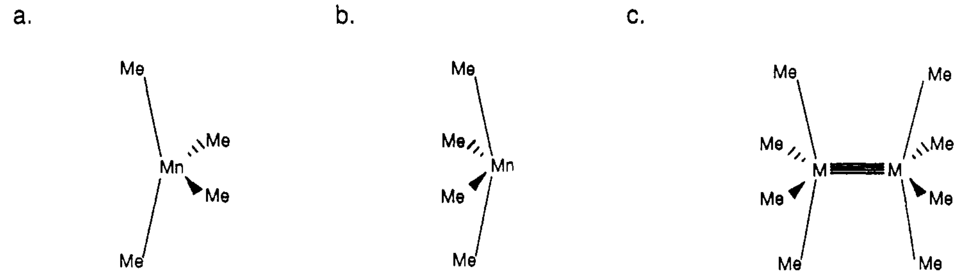

Figure 4. Schematic disposition of methyl groups in (a) [$MnMe_4^-$], (b) hypothetical pyramidal [$MnMe_4^-$], (c) hypothetical [$Mn_2Me_8^{2-}$].

structurally characterized four-coordinate Mn^{III} monomer is [$Mn(S_2C_6H_3Me)_2^-$], which exhibits an essentially flat square plane.[41,45,46] The planarity of this species is probably due to the reduced steric demand of the chelating dithiolate ligands in comparison to the methyl groups of **3**. Although square-planar coordination geometries are rare for manganese(III), they are often observed for isoelectronic chromium(II). The d^4 electronic configuration half-fills the four low-lying d orbitals characteristic of square-planar ligand arrays.

The cations in **3** are [$Li(tmed)_2^+$] units in which the lithium atom possesses a distorted-tetrahedral coordination geometry. The Li–N distances range from 2.108 (6) to 2.157 (6) Å, and the N–Li–N angles range from 87.2 (2) to 123.0 (3)°. The distortions from perfect tetrahedral geometry are most certainly a result of the chelating nature of tmed and are similar to those in the [$Li(tmed)_2^+$] cation in [$Li(tmed)_2$][$CH_3Ni(C_2H_4)_2$].[47]

Why Does [$Mn_2Me_8^{2-}$] Not Exist? Apart from being the first structurally characterized Mn^{III} peralkyl, the trivalent tetramethylmanganate anion [$MnMe_4^-$] is of interest in another context. Specifically, [$MnMe_4^-$] shows no tendency to dimerize to give the octamethyldimanganate dianion, [$Mn_2Me_8^{2-}$], which would be isoelectronic with the known quadruply bonded dimers [$Cr_2Me_8^{4-}$],[48,49] [$Mo_2Me_8^{4-}$],[50,51] [$W_2Me_8^{4-}$],[52] and [$Re_2Me_8^{2-}$].[53] Interestingly, ab initio calculations have suggested that [$Mn_2Me_8^{2-}$] should be stable and should possess a diamagnetic $\sigma^2\pi^4\delta^2$ ground state.[54]

Several alternative explanations could account for the monomeric nature of [$MnMe_4^-$]. First, the octamethyldimetalates of Cr^{II}, Mo^{II}, W^{II}, and Re^{III} invariably exhibit close contacts with their lithium counterions: the [$Li(thf)^+$] cations bridge the metal–metal bond by interacting with two methyl groups on each metal center. It is possible that such bridging interactions contribute substantially to the stabilities of the dimers relative to d^4 [MMe_4^{n-}] monomers and that [$MnMe_4^-$] is stable as a monomer because the lithium atom forms a charge-separated [$Li(tmed)_2^+$] cation. Despite several attempts, we have been unable to crystallize solvates of $LiMnMe_4$ with unidentate Lewis bases such as tetrahydrofuran, so we cannot rule out the possibility that [$Li(thf)$]$_2$[Mn_2Me_8] would be stable. Conversely, it would be interesting to determine whether known quadruply bonded dimers such as [$Cr_2Me_8^{4-}$] remain intact upon complexation of the lithium cations by tmed.

Second, [$MnMe_4^-$] may be intrinsically incapable of forming a dimer, irrespective of the nature of the cation. This situation could arise electronically if the manganese d orbitals are too low in energy to engage in strong metal–metal bonding. Certainly, the high +3 oxidation state will contract the d orbitals and reduce the amount of direct overlap between orbitals on adjacent metal centers. In this view, only d^4 metals in lower oxidation states (Cr^{II}, Mo^{II}, W^{II}) and those in the second and third rows (Mo^{II}, W^{II}, Re^{III}) have d orbitals that are sufficiently high in energy to form strong quadruple metal–metal bonds.

Third, steric factors could also contribute to the stability of the [$MnMe_4^-$] monomer. The structure of [$MnMe_4^-$] shows that the methyl groups are not all coplanar but that instead the anion is tetrahedrally distorted (Figure 4a). Such distortions have been attributed in analogous square-planar d^4 Cr^{II} complexes to steric crowding.[43] Of the d^4 metal ions Cr^{II}, Mo^{II}, W^{II}, Mn^{III}, and Re^{III}, the trivalent manganese ion is by far the smallest and steric crowding should be most severe. Therefore, steric repulsions between the methyl groups may prevent the four methyl groups from adopting a pyramidal arrangement (Figure 4b) as they do in the [$Me_4MMMe_4^{n-}$] complexes of Cr, Mo, W, and Re (Figure 4c). Steric effects are likely to be quite severe for a quadruply bonded dimanganese center, since the Mn–Mn distance would be very short: the Mn–Mn distance of 1.980 Å used in the MO calculation is a reasonable guess in view of the known doubly bonded Mn–Mn distance of 2.393 (2) Å in $Cp_2Mn_2[NN(SiMe_3)_2]_2$[55] and the triply bonded Mn–Mn distance of 2.170 (1) Å in $(C_5Me_5)Mn_2(CO)_3$.[56] It is possible that the MO calculation, which predicted that [$Mn_2Me_8^{2-}$] should be stable, is in error because this anion is in fact prohibitively crowded.[57,58]

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(45) The manganese(III) thiolate [$Mn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4^-$] is crystallographically isomorphous with the tetrahedrally distorted square-planar cobalt(III) analogue (trans S–Co–S angle = 161.3°). Although a distorted square-planar structure for the Mn^{III} complex is not guaranteed by the isomorphous relationship, such a structure is likely: Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311–3312.

(46) One Zintl phase, $Ca_{14}MnBi_{11}$, is known that contains a distorted-tetrahedral Mn^{III} center: Kauzlarich, S. M.; Kuromoto, T. Y.; Olmstead, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8041–8042. Kuromoto, T. Y.; Kauzlarich, S. M.; Webb, D. J. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 349–357.

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(57) We note that the geometry assumed in the molecular orbital calculation[52] for the hypothetical [$Mn_2Me_8^{2-}$] anion would greatly underestimate the steric repulsions in this dimer, since the Mn–C distances were fixed at 2.199 Å, a value that was arbitrarily set equal to the observed Cr–C distances in [$Cr_2Me_8^{4-}$]. However, the present results clearly show that this Mn–C distance is unrealistically long, since the Mn–C distances in [$MnMe_4^-$] are only 2.078 (5) Å.

(58) Sterically bulky ligands can prevent formation of quadruply bonded dimers in Cr^{II} chemistry: Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 2142–2147.

Concluding Remarks. We have prepared several new high-valent organomanganese complexes, including square-planar [$MnMe_4^-$], square-pyramidal [$MnMe_5^{2-}$], and octahedral [$MnMe_6^{2-}$]. Along with the oxo alkyl [$MnOMe_3^{2-}$],[44] the phosphine complexes $MnMe_4(PMe_3)_4$ and $MnMe_4$(dmpe),[24] the MnR_4 tetraalkyls,[22,23] and the Mn^{III} aryls described in the following paper,[59] these molecules demonstrate that several classes of high-valent organomanganese complexes exist. Although the high-valent inorganic manganese complexes that have been studied to date invariably react with organic substrates via radical pathways and usually are relatively unselective oxidants,[60] it is possible that high-valent organomanganese species will prove useful for the *selective* functionalization of organic molecules. Clearly, there is a rich and varied chemistry of high-valent manganese complexes that possess organic ligands.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium (toluene) or sodium–benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. Tris(acetylacetonato)manganese(III)[61] was prepared by a literature route. Methyllithium and *N,N,N′,N′*-tetramethylethylenediamine (tmed) were purchased from Aldrich; methyllithium was filtered before use, and tmed was distilled from and stored over sodium. The manganese(II) alkyl [$Li(tmed)]_2[MnMe_4]$[37] and the manganese(IV) alkyl $MnMe_4(PMe_3)_2$[24] were prepared as previously described.

Microanalyses were performed by Mr. Josef Nemeth and Mr. Tom McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer as Nujol mulls, and ^1H NMR spectra were obtained on a General Electric QE-300 instrument at 300 MHz; chemical shifts are uncorrected for the paramagnetic shift of the reference. The X-band EPR experiments were performed with a Bruker 220D-SRC or a Bruker ESP300 spectrometer on frozen toluene solutions at −100 °C. Magnetic moments were measured by a modification of Evans' method.[62] Melting points were determined on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Hexamethylmanganate(IV) (1). Method A. To a cold (−78 °C) solution of $MnMe_4(PMe_3)_2$ (0.40 g, 1.5 mmol) in diethyl ether (40 mL) was added methyllithium (3.4 mL of a 1.4 M solution in diethyl ether, 4.8 mmol), which caused the dark orange solution to turn light yellow-orange. The solution was warmed to room temperature and stirred for 3 h. The solvent was then removed under vacuum, and the yellow-orange solid was extracted with diethyl ether (40 mL). To the filtered yellow-orange solution was added *N,N,N′,N′*-tetramethylethylenediamine (0.70 mL, 4.6 mmol), which caused the solution to turn dark orange. The solution was refiltered and cooled to −20 °C to give dark orange crystals. Additional crops of crystals were obtained by concentration and cooling of the supernatant; yield 0.49 g (87%). IR (cm^{-1}, KBr): 2775 vs, 2695 m, 2180 vw, 1453 vw, 1383 m, 1350 s, 1282 s, 1240 m, 1170 m, 1149 s, 1121 s, 1100 m, 1090 s, 1065 s, 1039 m, 1025 s, 1008 s, 937 s, 820 w, 780 s, 765 m, 710 w, 640 m, 582 m, 440 vw, 368 vs.

Method B. To a cold (0 °C) suspension of $Mn(acac)_3$ (1.14 g, 3.2 mmol) in diethyl ether (60 mL) was added methyllithium (19.6 mL of a 1.63 M solution in diethyl ether, 32 mmol), which caused the solution to turn orange. After it was warmed to room temperature, the solution was stirred for 2 h. The solvent was removed under vacuum, and the orange solid was extracted with pentane (4 × 40 mL). The filtered extracts were taken to dryness to give a yellow solid (*Caution!* pyrophoric), which was then extracted with diethyl ether (50 mL). To the filtered ether solution was added *N,N,N′,N′*-tetramethylethylenediamine (1 mL, 6.6 mmol) to give an orange solution. The solution was filtered, concentrated to ca. 30 mL, and cooled to −20 °C to give orange prisms. Additional crops of crystals were obtained by concentration and cooling of the supernatant; yield 0.10 g (8%).

Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Pentamethylmanganate(III) (2). Method A. To a cold (0 °C) mixture of the Mn^{II} alkyl [$Li(tmed)]_2[MnMe_4]$ (0.127 g, 0.35 mmol) and the Mn^{IV} alkyl [$Li(tmed)]_2[MnMe_6]$ (0.137 g, 0.35 mmol) was added cold (0 °C) diethyl ether (30 mL). The two orange solids dissolved to give an orange solution, which turned deep red within 15 min upon being warmed to room temperature. After being stirred for an additional 1 h, the solution was filtered, concentrated to ca. 10 mL, and cooled to −20 °C to give dark red needles, yield 0.128 g (49%). IR (cm^{-1}, KBr): 1360 s, 1293 s, 1253 m, 1186 m, 1160 s, 1131 s, 1113 m, 1100 m, 1076 m, 1068 m, 1038 s, 1020 s, 951 s, 796 s, 777 m, 728 w, 594 m, 448 vs.

Method B. To a cold (0 °C) suspension of $Mn(acac)_3$ (1.14 g, 3.2 mmol) in diethyl ether (60 mL) was added methyllithium (19.6 mL of a 1.63 M solution in diethyl ether, 32 mmol) to give an orange solution. After it was warmed to room temperature, the solution was stirred for 2 h. The solvent was removed under vacuum, and the orange solid was washed well with pentane (4 × 40 mL) and then extracted with diethyl ether (50 mL). To the filtered diethyl ether solution was added *N,N,N′,N′*-tetramethylethylenediamine (1 mL, 6.6 mmol), and the orange solution turned orange-red. After it was filtered, the solution was concentrated to ca. 30 mL and cooled to −20 °C to give red needles. Further crops of crystals were obtained by concentration and cooling of the supernatant; yield 0.45 g (39%).

[Bis(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Tetramethylmanganate(III) (3). To a room-temperature mixture of the Mn^{II} alkyl [$Li(tmed)]_2[MnMe_4]$ (0.17 g, 0.47 mmol) and the Mn^{IV} alkyl [$Li(tmed)]_2[MnMe_6]$ (0.18 g, 0.47 mmol) was added toluene (40 mL); the initially orange solution quickly turned deep red. After it was stirred for 6 h, the red solution was filtered and cooled to −20 °C to give dark red prisms. Further crops of crystals were obtained by concentration and cooling of the supernatant; yield 0.127 g (38%). IR (cm^{-1}, KBr): 2780 vs, 2170 vw, 2130 vw, 2115 w, 1460 vs, 1354 s, 1284 s, 1242 s, 1180 m, 1157 s, 1095 m, 1063 s, 1040 m, 1026 s, 1008 s, 940 s, 779 s, 766 m, 711 w, 582 m, 560 s, 460 vs.

Crystallographic Studies.[63] Single crystals of [$Li(tmed)]_2[MnMe_6]$ (1), grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. [Crystals of [$Li(tmed)_2][MnMe_4]$ (3) were grown from toluene and mounted on glass fibers with Paratone-N oil. Subsequent comments in brackets will refer to this compound.] Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures followed by least-squares refinement with 25 reflections yielded the cell dimensions given in Table II.

Data were collected in one octant of reciprocal space ($-h,-k,-l$), and a complete set of intensities ($\pm h,\pm k,\pm l$) was collected over a limited 2θ range between 2 and 20° with use of measurement parameters listed in Table II. [For 3, one quadrant ($+h,+k,+l$) was collected.] Systematic absences for $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$), and $hk0$ ($h \neq 2n$) were consistent with the space group *Pbca*. [For 3, systematic absences $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) were consistent with space group $P2_1/n$.] The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.908 and 0.872, respectively. [For 3, the maximum and minimum transmission factors were 0.818 and 0.745, respectively.] Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$

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(59) Morris, R. J.; Girolami, G. S. *Organometallics*, following paper in this issue.

(60) However, see: Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801–2803.

(61) Bhattacharjee, M. N.; Chaudhuri, M. K.; Kathing, D. T. *J. Chem. Soc., Dalton Trans.* **1982**, 669–670.

(62) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931–1934.

(63) For details of the data collection and refinement procedure, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977–4982.

were used in the least-squares refinement.

The structure was solved by Patterson methods (SHELX-86), unweighted difference Fourier synthesis, and full-matrix least-squares methods (SHELX-76). [The structure of **3** was solved by Patterson methods (SHELX-86), weighted and unweighted difference Fourier syntheses, and full-matrix least squares.] The manganese atom was placed at the origin, and partial structure factor expansion gave positions for the tmed atoms. [For **3**, the position of the manganese atom was determined from a vector map and partial structure expansion gave positions for the two tmed molecules.] Subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.53/(\sigma(F_o)^2 + (pF_o)^2)$. [For **3**, $w = 1.79/(\sigma(F_o)^2 + (pF_o)^2)$.]

The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. For **1**, least-squares difference Fourier calculations revealed positions for the disordered methyl carbon atoms. A site occupancy factor for one set (group A) of three manganese-bound methyl groups (and their inversion-related partners) was refined to 0.563 (8); the corresponding site occupancy factor for the group B methyl groups was therefore 0.437. Hydrogen atoms were included as fixed contributors in "idealized" positions with C–H = 0.95 Å. In the final cycle of least squares, independent isotropic thermal coefficients were refined for the disordered carbon atoms, anisotropic thermal coefficients were refined for the remaining non-hydrogen atoms, and two separate groups of isotropic thermal parameters were varied for the tmed hydrogen atoms and the hydrogen atoms on the disordered methyl groups. [For **3**, hydrogen atoms H1a–H2b were constrained to "idealized" positions owing to a minor disorder in C1 and C2. In the final cycle of least squares, non-hydrogen atoms were refined with anisotropic thermal coefficients and a group isotropic thermal parameter was varied for the hydrogen atoms.] Successful convergence was indicated by the maximum shift/error of 0.039 [0.022 for **3**] in the last cycle. Final refinement parameters are given in Table II. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors. [For **3**, the highest peaks in the final difference Fourier map were in the vicinity of the slightly disordered C1–C2 atoms. The structure factor variances showed a slight dependence on sin θ.]

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Supplementary Material Available: Tables of anisotropic thermal parameters for **1** and **3** and calculated hydrogen atom positions for **1**, and a figure showing the relative positions of the disordered methyl groups in **1** (4 pages); listings of final observed and calculated structure factor amplitudes for **1** and **3** (15 pages). Ordering information is given on any current masthead page.

High-Valent Organomanganese Chemistry. 2. Synthesis and Characterization of Manganese(III) Aryls

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Manganese(III) aryls of stoichiometry $Mn(Mes)X_2(PMe_3)_2$ (Mes = 2,4,6-trimethylphenyl) can be prepared by the reaction of MnX_2 (X = Cl, Br, I) with $^1/_2$ equiv of $Mg(Mes)_2(thf)_2$ in the presence of PMe_3 followed by oxidation with O_2. The X-ray crystal structure of $Mn(Mes)Br_2(PMe_3)_2$ reveals a trigonal-bipyramidal geometry with the phosphines in the axial sites and the mesityl and halide ligands in the equatorial plane: Mn–C = 2.089 (8) Å, Mn–P = 2.426 (3) Å, Mn–Br = 2.497 (2) Å. The intermediates present in solution prior to oxidation with O_2 have been identified by EPR spectroscopy as manganese(II) monomesityl complexes of stoichiometry $Mn(Mes)X(PMe_3)_2$ or $[Mn(Mes)X_2(PMe_3)^-]$. Addition of a further $^1/_2$ equiv of $Mg(Mes)_2(thf)_2$ to the monomesityl intermediates gives the manganese(II) diaryl species $Mn(Mes)_2(PMe_3)_2$, which has been isolated as a crystalline material. Attempts to prepare Mn^{III} aryls directly from $Mn(acac)_3$ lead instead to Mn^{II} products such as the *o*-tolyl complex $[Li(tmed)_2]_2[Mn(o\text{-}C_6H_4Me)_4]$. Similarly, treatment of $Mn(acac)_3$ with sodium cyclopentadienide leads to the formation of Mn^{II} products and not to the manganese(III) species $NaMnCp_4$ as previously claimed. Crystal data (Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.71073 Å) for $Mn(Mes)Br_2(PMe_3)_2$: space group $P2_1/n$ with a = 8.956 (3) Å, b = 25.228 (8) Å, c = 9.472 (3) Å, β = 100.29 (3)°, V = 2106 (1) Å^3, Z = 4, T = 299 K, R_F = 0.050, and R_{wF} = 0.048 for 182 variables and 1835 data.

Introduction

Organometallic derivatives of manganese in its higher oxidation states are quite rare, and in particular, no arylmanganese species in oxidation states higher than +2 are known.[1] In the previous paper, we described the preparation and characterization of several Mn^{III} and Mn^{IV} alkyls such as $[MnMe_4^-]$, $[MnOMe_3^{2-}]$, and $[MnMe_6^{2-}]$ that open up new avenues to explore the chemistry of high-valent organomanganese centers.[2] These complexes can be prepared conveniently by the reaction of methyllithium with a suitable Mn^{III} or Mn^{IV} starting material such as

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[1] Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 29.

[2] Morris, R. J.; Girolami, G. S. *Organometallics*, preceding paper in this issue.

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