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Thirteen-Electron Manganese(II) Tetraalkyls. Synthesis, Characterization, and X-ray Crystal Structures of $[Li(tmed)]_2[MnMe_4]$ and the "β-Unstable" Species $[Li(tmed)]_2[MnEt_4]$ and $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$

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Alkylation of diethyl ether solutions of $MnCl_2$ with 4 equiv of LiR (R = Me, Et, *n*-Bu, *t*-Bu, CH_2SiMe_3, or Ph) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmed) gives pale-colored divalent tetraalkylmanganates of stoichiometry $[Li(tmed)]_2[MnR_4]$ in good yields. In the case of Li(*t*-Bu), a side reaction with diethyl ether leads to the formation of ethylene and the eventual isolation of the insertion product $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$; the *tert*-butyl complex $[Li(tmed)]_2[Mn(t\text{-}Bu)_4]$ could not be prepared even in other solvents. These 13-electron peralkyl species are stable at room temperature and are among the few well-characterized compounds of their type. The alkyls that contain β-hydrogen atoms are remarkably resistant to β-elimination. The single-crystal X-ray structures of $[Li(tmed)]_2[MnMe_4]$ (**1**), $[Li(tmed)]_2[MnEt_4]$ (**2**), and $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$ (**3**) have been determined, and compounds **2** and **3** are the first structurally characterized transition-metal peralkyls that contain β-hydrogen atoms. The coordination geometries around the manganese centers are essentially tetrahedral, and there are no agostic Mn···H–C interactions. The Li cations each interact with two α-carbon atoms of the alkyl ligands and bridge opposite edges of the tetrahedron to give nearly linear Li···Mn···Li arrays. Crystallographic data (Mo K$\bar{\alpha}$, $\lambda = 0.71073$ Å): **1**, space group $P2_1/c$ with $a = 13.591$ (2) Å, $b = 15.190$ (3) Å, $c = 12.007$ (2) Å, $\beta = 94.27$ (1)°, $V = 2472$ (1) Å^3, $Z = 4$, $T = 223$ K, $R_F = 0.062$, $R_{wF} = 0.068$ on 179 variables and 1812 data; **2**, space group $C2/c$ with $a = 14.766$ (5) Å, $b = 10.442$ (2) Å, $c = 18.696$ (3) Å, $\beta = 109.37$ (2)°, $V = 2720$ (2) Å^3, $Z = 4$, $T = 248$ K, $R_F = 0.045$, $R_{wF} = 0.048$ on 227 variables and 1631 data; **3**, space group $C2/c$ with $a = 10.846$ (3) Å, $b = 19.972$ (4) Å, $c = 21.435$ (4) Å, $\beta = 99.25$ (2)°, $V = 4583$ (4) Å^3, $Z = 4$, $T = 248$ K, $R_F = 0.053$, $R_{wF} = 0.063$ on 196 variables and 1109 data.

Introduction

The formation of manganese(II) alkyls by the interaction of manganous halides with alkylating reagents was first reported by Gilman, but the organometallic products were neither isolated nor characterized.[1,2] Later, Tamura and Kochi compared the rates of decomposition of manganese(II) alkyls prepared in situ by the action of Grignard reagents on manganese dichloride in tetrahydrofuran.[3] They obtained some of the first evidence that β-elimination followed by alkene dissociation was the principal decomposition route for alkyls that contain β-hydrogen atoms. Shortly thereafter, the synthesis and characterization of several β-stabilized organomanganese species of the type $[MnR_2]_n$ appeared in the literature. Currently known dialkylmanganese species include monomeric $Mn[C(SiMe_3)_3]_2$,[4] dimeric $[Mn(CH_2CMe_2Ph)_2]_2$[5] (which is monomeric[6] in the gas phase), trimeric $[Mn(2,4,6\text{-}C_6H_2Me_3)_2]_3$,[7] tetrameric $[Mn(CH_2CMe_3)_2]_4$,[5] and polymeric $[Mn(CH_2SiMe_3)_2]_n$.[5] All of these species have been structurally characterized. Several Lewis base adducts of dialkylmanganese species[5,8-15] as well as an unusual ylide complex[16] have also been reported.

In addition to the electrically neutral manganese(II) alkyls described above, several anionic species are known. Early workers described lithium salts of stoichiometry $Li[MnR_3]$ (R = Me, Et, *n*-Bu, etc.) that were incompletely characterized.[17,18] Kochi also studied the decomposition rates of alkylmanganates prepared by addition of alkyllithium reagents to $MnCl_2$ in tetrahydrofuran, although again the products were not isolated;[3] two β-stabilized tetraalkyl manganates, $Li_2[MnR_4]$, were later prepared and characterized by EPR spectroscopy.[5] Interestingly, three authentic triarylmanganates, $[Li(Et_2O)_2]_2[Mn_2Ph_6]$, $[Li(thf)_4]_2[Mn_2Ph_6]$, and $[Li(thf)_4][Mn(2,4,6\text{-}C_6H_2Me_3)_3]$, have recently been structurally characterized.[19,20]

We have recently described the Mn^{III} and Mn^{IV} alkyl anions $[MnMe_5{}^{2-}]$,[21] $[MnOMe_3{}^{2-}]$,[22] and $[MnMe_6{}^{2-}]$.[21] In related work, we now describe the preparation and characterization of a series of Mn^{II} tetraalkyls, $[MnR_4{}^{2-}]$, which have been crystallized as their $[Li(tmed)^+]$ salts. These

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Table I. Physical and Microanalytical Data for the Divalent Manganese Compounds

				anal.[a]				
compd	color	mp, °C	μ_{eff}, μ_B	C	H	N	Li	Mn
$[Li(tmed)]_2[MnMe_4]$ (1)	pale orange	148 dec	5.6	53.2 (53.2)	12.3 (12.3)	15.7 (15.5)	4.03 (3.84)	15.0 (15.2)
$[Li(tmed)]_2[MnEt_4]$ (2)	peach	110 dec	5.8	57.6 (57.5)	12.6 (12.6)	13.2 (13.4)	3.50 (3.33)	13.1 (13.2)
$[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$ (3)	off-white	140 dec	5.9	66.7 (67.4)	13.7 (13.2)	8.66 (8.72)	1.79 (2.16)	9.04 (8.56)
$[Li(tmed)]_2[Mn(n\text{-}Bu)_4]$ (4)	off-white	132 dec	5.8	63.0 (63.5)	13.1 (12.9)	10.6 (10.6)	2.77 (2.62)	11.0 (10.4)
$[Li(tmed)]_2[Mn(CH_2SiMe_3)_4]$ (5)	off-white	168 dec	5.6	51.6 (51.7)	11.9 (11.8)	8.29 (8.61)	2.03 (2.14)	8.34 (8.45)
$[Li(tmed)]_2[MnPh_4]$ (6)	yellow	176 dec	5.8	70.8 (70.9)	8.71 (8.60)	9.32 (9.20)	2.42 (2.28)	9.32 (9.01)

[a] Calculated values are in parentheses.

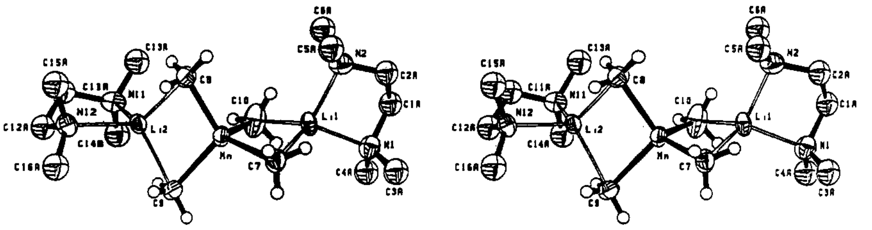

Figure 1. Stereoview of the molecular structure of $[Li(tmed)]_2[MnMe_4]$ (1). Only the α-hydrogen atoms have been included for clarity.

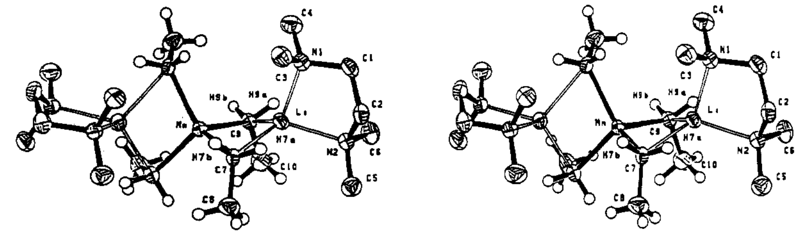

Figure 2. Stereoview of the molecular structure of $[Li(tmed)]_2[MnEt_4]$ (2). Only the alkyl hydrogen atoms have been included for clarity.

13-electron species are remarkably stable thermally both in the solid state and in solution. Although $[MnR_4^{2-}]$ species with "β-stable" alkyls such as methyl or CH_2SiMe_3 have been reported previously,[5] we have found that even alkyl groups possessing β-hydrogen atoms, such as ethyl and n-butyl, form stable Mn^{II} complexes. Transition-metal peralkyl complexes that contain β-hydrogen atoms are rare,[18,23,24] and the compounds described herein are the first of this class to be structurally characterized.[25-31]

Results

Synthesis and Properties. In 1976, Wilkinson reported that the interaction of diethyl ether suspensions of anhydrous manganese dichloride with 4 equiv of methyllithium followed by the addition of N,N,N',N'-tetramethylethylenediamine (tmed) gives the tetramethylmanganate salt $Li_2MnMe_4{\cdot}2tmed$.[5] A similar (trimethylsilyl)methyl complex, $Li_2Mn(CH_2SiMe_3)_4$, was also prepared, and the EPR spectra of both complexes were described. This synthetic method can be modified to give a entire series of stable 13-electron tetraalkylmanganate(II) complexes, 1–6. The syntheses of compounds 3 and 4

$$MnCl_2 + 4LiR + 2tmed \rightarrow [Li(tmed)]_2[MnR_4] + 2LiCl$$
$$\begin{gathered} 1, R = Me \\ 2, R = Et \\ 3, R = CH_2CH_2\text{-}t\text{-}Bu \\ 4, R = n\text{-}Bu \\ 5, R = CH_2SiMe_3 \\ 6, R = Ph \end{gathered}$$

differ slightly in that they are successful only if tmed is present before addition of the alkyllithium reagent. Attempts to prepare a tetra-*tert*-butylmanganate complex from $MnCl_2$ and *tert*-butyllithium in diethyl ether led instead to the isolation of the neohexyl complex $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$. A side reaction of $Li(t\text{-}Bu)$ with diethyl ether is known to yield ethylene; reaction of ethylene with a second equivalent of $Li(t\text{-}Bu)$ gives $Li(CH_2CH_2\text{-}t\text{-}Bu)$ as the active alkylating species.[32]

$$Li(t\text{-}Bu) + Et_2O \rightarrow i\text{-}C_4H_{10} + LiOEt + CH_2CH_2$$

$$Li(t\text{-}Bu) + CH_2CH_2 \rightarrow Li(CH_2CH_2\text{-}t\text{-}Bu)$$

We have been unable to prepare pure samples of the *tert*-butyl compound $[Li(tmed)]_2[Mn(t\text{-}Bu)_4]$ under any conditions; for example, reaction of *tert*-butyllithium with $MnCl_2$ in pentane in the presence of tmed gave an oily impure product.

Table I contains physical and microanalytical data for compounds 1–6. The divalent tetraalkyl manganates range in color from off-white to yellow and are air- and moisture-sensitive. Room-temperature magnetic susceptibility measurements in benzene showed that the complexes adopt high-spin d^5 configurations with μ_{eff} = 5.6–5.9 μ_B.

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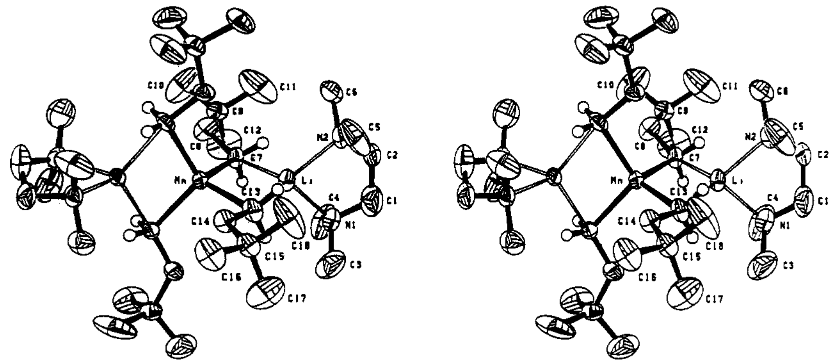

Figure 3. Stereoview of the molecular structure of $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$ (3). Only the α-hydrogen atoms have been included for clarity.

Table II. Crystal Data for $[Li(tmed)]_2[MnMe_4]$ (1), $[Li(tmed)]_2[MnEt_4]$ (2), and $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$ (3)

	1	2	3
space group	$P2_1/c$	$C2/c$	$C2/c$
T, °C	−50	−25	−25
a, Å	13.591 (2)	14.766 (5)	10.846 (3)
b, Å	15.190 (3)	10.442 (2)	19.972 (4)
c, Å	12.007 (2)	18.696 (3)	21.435 (4)
β, deg	94.27 (1)	109.37 (2)	99.25 (2)
V, Å^3	2472 (1)	2720 (2)	4583 (4)
Z	4	4	4
mol wt	361.37	417.48	641.92
d_{calcd}, g cm^{-3}	0.971	1.019	0.930
μ_{calcd}, cm^{-1}	5.15	4.75	2.98
size, mm	0.3 × 0.3 × 0.5	0.4 × 0.4 × 0.4	0.3 × 0.4 × 0.4
diffractometer	Enraf-Nonius CAD4		
radiatn	Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.71073 Å		
monochromator	graphite crystal, $2\theta = 12°$		
scan range, type	$2.0 \le 2\theta \le 52.0°$, ω/θ		
scan speed, width	3–16° min^{-1}, $\Delta\omega = 1.50[1.00 + 0.35 \tan\theta]°$		
rflctns, total	4909	2998	1819
rflctns, unique	4344	2664	1583
rflctns, $I > 2.58\sigma(I)$	1812	1631	1109
R_i	0.014	0.016	0.014
R_F	0.062	0.045	0.053
R_{wF}	0.068	0.048	0.063
variables	179	227	196
p factor	0.020	0.020	0.030

Table III. Selected Bond Distances and Angles for the Peralkylmanganates, $[Li(tmed)]_2[MnR_4]$

	1, R = Me	2, R = Et	3, R = $CH_2CH_2\text{-}t\text{-}Bu$
		Distances (Å)	
Mn–C	2.223 (7)–2.228 (6)	2.249 (4)	2.27 (1), 2.28 (1)
Mn···Li	2.59 (1)	2.572 (6)	2.58 (2)
Li–C	2.25 (1)–2.27 (1)	2.236 (7)–2.315 (6)	2.20 (2), 2.24 (2)
Li–N	2.09 (1)–2.11 (1)	2.118 (6)–2.146 (6)	2.15 (2)
C_α–C_β		1.519 (7), 1.525 (6)	1.51 (2), 1.53 (2)
		Angles (deg)	
C–Mn–C^a	107.3 (2), 108.4 (3)	106.9 (1)	107.6 (4)
C–Mn–C^b	108.7 (2)–113.2 (3)	108.6 (1)–116.4 (1)	110.1 (4)–110.6 (4)
Mn–C–Li	70.4 (3)–70.7 (3)	68.6 (20), 70.0 (2)	69.8 (6), 70.4 (6)
Mn–C_α–C_β		110.3 (3), 112.5 (3)	100.7 (8), 104.5 (8)
N–Li–N	86.8 (5)–86.4 (4)	87.5 (2)	86.6 (5)
C–Li–C	105.3 (5)–106.0 (5)	105.1 (3)	110.2 (5)
Li···Mn···Li	162.2 (3)	158.4 (2)	172.7 (4)

[a] Bridged by Li. [b] Unbridged by Li.

The high-spin nature of these compounds suggests that they adopt tetrahedral geometries; this is supported in the solid state by single-crystal X-ray analyses of 1, 2, and 3 and by the near cubic symmetry observed by EPR.

Crystallographic Studies. Single crystals of 1 and 2 were grown by cooling saturated diethyl ether solutions to −20 °C; 3 was obtained similarly from a saturated pentane solution. Crystal data are given in Table II while final atomic coordinates and anisotropic thermal parameters with estimated standard deviations are deposited in the supplementary material. Bond distances and angles are presented with estimated standard deviations in Table III.

The structural analyses show that crystals of 1, 2, and 3 are composed of discrete monomers of $[Li(tmed)]_2[MnMe_4]$, $[Li(tmed)]_2[MnEt_4]$, and $[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$, respectively; stereoviews of these molecules are shown in Figures 1–3. Although no crystallographically imposed symmetry occurs in 1, both 2 and 3 contain a C_2 axis that bisects two C–Mn–C angles and renders the [Li(tmed)] units symmetry equivalent. Overall, the molecular structures closely resemble that of the tetramethylmagnesium salt $[Li(tmed)]_2[MgMe_4]$,[33] which is crystallographically isomorphous with 1. In fact, all the bond distances and angles in 1 and the tetramethylmagnesium anion are essentially identical except the average Mg–C distance of 2.263 (8) Å is slightly longer than the average Mn–C distance in 1 of 2.225 (7) Å. This is somewhat surprising since the ionic radius of Mg^{II} is ca. 0.09 Å smaller than that of Mn^{II}.[34]

In all three compounds, the manganese center adopts a distorted tetrahedral geometry. The C–Mn–C angles may be divided into two classes: those that are bridged by a [Li(tmed)] unit and those that are not. The bridged C–Mn–C angles are slightly smaller at 106.9 (1)–108.4 (3)° than the unbridged angles of 108.6 (1)–116.4 (1)°. The net result of the interactions with the [Li(tmed)] cations is to distort the $[MnR_4{}^{2-}]$ anion away from perfect tetrahedral symmetry, although the magnitude of the distortion is relatively small. Presumably, the interactions of the α-carbons with the $[Li(tmed)^+]$ groups cause the bridged C–Mn–C angles to decrease slightly in order to form the best possible tetrahedron around the Li atoms. Indeed, the C_α–Li–C_α angles are near the tetrahedral value of 109.5° and range from 105.1 (3)° to 110.2 (5)°. The Li···Mn···Li angles in 1, 2, and 3 of 162.2 (3)°, 158.4 (2)°, and 172.7 (4)°, respectively, all deviate from linearity. The differences are most likely attributable to crystal packing forces.

The Mn–C bond lengths in 1, 2, and 3, which range from 2.223 (7) to 2.28 (1) Å, are somewhat longer than reported Mn–C bond lengths of 2.111 (3)–2.19 (3) Å in other high-spin tetrahedral Mn^{II} species.[8,9] The relatively longer Mn–C bonds in the anions are doubtlessly attributable to the bridging of the alkyl groups between the manganese and lithium centers. In fact, the Mn–C distances in 1–3 closely resemble those in dimeric Mn^{II} species which contain alkyl groups that bridge between two manganese

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Table IV. Bond Distances and Angles Involving α-Hydrogen Atoms in [Li(tmed)]$_2$[MnEt$_4$] (2)

	Distances (Å)		
Mn···H7A	2.94 (3)	Li···H7A	2.05 (3)
Mn···H9A	2.90 (3)	Li···H9A	2.01 (3)
Mn···H7B	2.55 (4)	Li···H7B	2.98 (4)
Mn···H9B	2.60 (3)	Li···H9B	3.12 (4)
	Angles (deg)		
Mn-C7-H7A	128 (2)	Li···C7-H7A	62 (2)
Mn-C9-H9A	123 (2)	Li···C9-H9A	64 (2)
Mn-C7-H7B	97 (2)	Li···C7-H7B	125 (2)
Mn-C9-H9B	99 (2)	Li···C9-H9B	148 (2)

centers; the corresponding Mn–C distances in these dimers are 2.208 (3)–2.245 (2) Å.[5,9]

The Mn···Li contacts of 2.572 (6) Å indicate that there are no significant interactions between the manganese and lithium atoms. The Li–N[35] and C_α–C_β[36] single bond distances are well within the normal ranges.

In each compound, the Li cations interact with the α-carbons of the alkyl groups; this undoubtedly arises from electrostatic attractions with the partial negative charge on these carbon atoms. Similar behavior is also observed in many arylmetalates, in which the Li cations interact with the ipso carbon atoms of the aromatic rings.[19,37–39] The Li–C distances of 2.20 (2)–2.27 (1) Å in 1 and 3 are normal for Li–C(sp^3) contacts.[33,40–43] However, 2 contains two significantly different Li–C_α distances of 2.236 (7) and 2.315 (6) Å. This asymmetry is not reflected in any of the other bond distances and angles and is probably a crystal packing effect.

Dispositions of the α-Hydrogen Atoms. The alkyl hydrogen atoms in [Li(tmed)]$_2$[MnEt$_4$] (2) were located and independently refined, and this affords an opportunity to determine whether Li···H and Mn···H interactions are present. The methylene units of the ethyl groups are oriented so that one of the α-hydrogen atoms of each alkyl ligand points toward a lithium cation (H7A, H9A) while the other does not (H7B, H9B) (see Table IV). The Li···H contacts of 2.05 (3) and 2.01 (3) Å are shorter than those of 2.112 (9)–2.265 (3) Å reported for the tetramethylborate salt LiB(CH$_3$)$_4$,[43] and the associated Li···C_α–H angles in 2 are quite acute at 62 (2)° and 64 (2)°. We do not believe that the Li···H contacts are chemically significant since the 2.0 Å distances are well outside the 1.55 Å sum of the covalent radii. Additionally, the orientation of the neohexyl groups in [Li(tmed)]$_2$[Mn(CH$_2$CH$_2$-*t*-Bu)$_4$] (3) gives calculated positions for the α-hydrogen atoms that are even further from the lithium centers. The lack of an orientational preference for the α-methylene groups in 2 and 3 indicates that the Li···H interactions are weak at best.

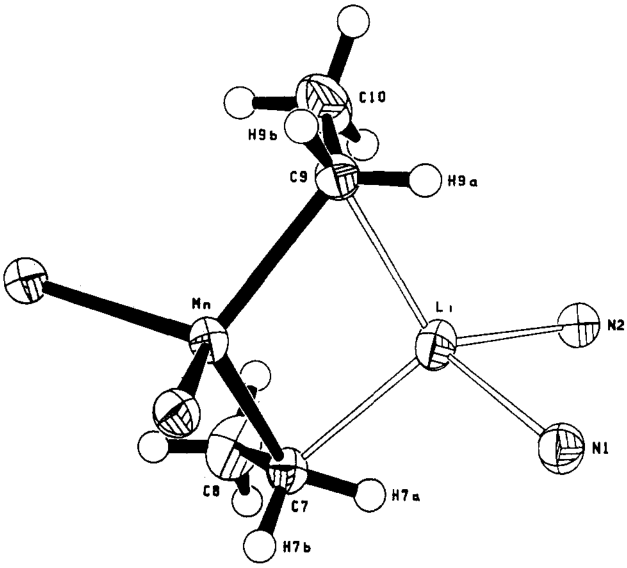

Figure 4. Geometry of the Mn(μ-Et)$_2$Li interaction in 2.

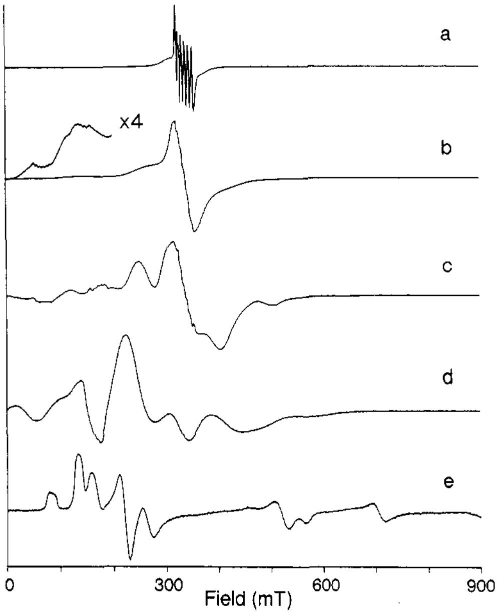

Figure 5. X-Band EPR spectra of manganese alkyls as frozen toluene solutions at 100 K: (a) [Li(tmed)]$_2$[Mn(CH$_2$SiMe$_3$)$_4$] (5), (b) [Li(tmed)]$_2$[MnMe$_4$] (1), (c) [Li(tmed)]$_2$[MnEt$_4$] (2), (d) [Li(tmed)]$_2$[MnPh$_4$] (6), (e) Mn(CH$_2$CMe$_3$)$_2$(tmed) (7).

Instead, the primary interactions are probably between lithium and the α-carbon atoms. These Li···C interactions are correlated with the presence of low-energy vibrations in the infrared spectrum of 2 at 2701, 2663, and 2630 cm^{-1}. Similarly low C–H stretching frequencies were noted by Wilkinson in the IR spectrum of Li$_2$MnMe$_4$·2tmed and were first proposed in that study to arise from Li···H–C interactions between solvated Li cations and the [MnMe$_4$$^{2-}$] anion.[5]

The Mn–C7–H7A and Mn–C9–H9A angles in 2 of ca. 125° are larger than the idealized tetrahedral value of 109°. The opening up of these angles evidently allows closer approach of the Li cations to the α-carbon centers (see Figure 4).

The α-hydrogen atoms that do not point toward the lithium cations are located 2.55 (4)–2.60 (3) Å from the manganese center. These distances are much longer than reported agostic Mn–H distances of 2.15 (6)–2.29 (6) Å in alkyl-bridged manganese(II) dimers such as Mn$_2$(CH$_2$SiMe$_3$)$_4$(PMe$_2$Ph)$_2$, Mn$_2$(CH$_2$Ph)$_4$(PMe$_3$)$_2$, and Mn$_2$(CH$_2$SiMe$_3$)$_4$(PMe$_3$)$_2$.[8] The corresponding Mn–C_α–H angles of 97 (2)° and 99 (2)° in 2 are also well outside the range expected for agostic Mn···H–C interactions; thus,

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there are no significant Mn···H interactions in the tetraalkylmanganate complexes.

Electron Paramagnetic Resonance Spectra. The X-band EPR spectra of compounds 1–6 were measured in toluene glasses at liquid-nitrogen temperatures (see Figure 5). All of the spectra except that of $[Li(tmed)]_2[MnPh_4]$ contain a strong signal at ca. 335 mT along with weaker features at varying field strengths. The presence of hyperfine structure, with $A = 0.0060$ cm^{-1}, due to ^{55}Mn ($I = {}^5/_2$, 100% abundant) is most pronounced in the 335 mT signal. However, fine structure is also evident on some of the lower field resonances. The spectra of compounds **1**–**6** exhibit varying degrees of rhombic distortion from cubic symmetry.

The data can be analyzed in terms of the spin-Hamiltonian given below,

$$H = \beta BgS + D[S_z^2 - \tfrac{1}{3}S(S + 1) + \lambda(S_x^2 - S_y^2)] + SAI$$

where D is a zero-field splitting parameter and λ ($= E/D$) is a symmetry parameter which can have a minimum of zero for axial geometries and a maximum of $^1/_3$ for the most rhombically distorted geometries.[44,45] The values of D and λ were estimated by using the D–B plot method,[44,45] assuming that g is isotropic and equal to 2.0 (normal for $^6S_{5/2}$ ground states), for external fields parallel to the principal axes (x, y, z) of the zero-field splitting tensor.

$[Li(tmed)]_2[Mn(CH_2SiMe_3)_4]$. Spectroscopic results in toluene for this species largely agree with those obtained previously by Wilkinson for the tmed-free complex in petroleum ether.[5] The EPR spectrum of the tetrakis((trimethylsilyl)methyl)manganate ion (**5**) exhibited the least rhombic distortion from cubic symmetry of all the tetraalkylmanganates. The ^{55}Mn hyperfine splitting of 0.0060 cm^{-1} was best resolved in this spectrum; presumably, this is due to the high degree of symmetry resulting in a narrow line width. Although the solid-state structure of this compound has not been determined, the EPR spectrum of **5** provides some structural information regarding the interaction of the Li cations with the $[Mn(CH_2SiMe_3)_4{}^{2-}]$ unit. The small distortion from cubic symmetry indicates that the rotationally averaged C–Si axes of the (trimethylsilyl)methyl ligands coincide with the C_3 axes of the MnC_4 tetrahedron. Furthermore, the near cubic symmetry suggests that the lithium cations are interacting only weakly with the α-carbon atoms of the (trimethylsilyl)methyl ligands. Evidently the sterically demanding CH_2SiMe_3 groups prevent close approach of the [Li(tmed)] units to the MnC_4 core.[5] The largely ionic bonding in **5** contrasts with the structures of the other tetraalkylmanganates described above, in which Li···C$_\alpha$ interactions give contact ion clusters. The weak interactions of the lithium cations and the manganese centers in **5** is also reflected in its decreased solubility; this compound is far less soluble in nonpolar solvents such as pentane and diethyl ether than are the other tetraalkylmanganates we have studied.

$[Li(tmed)]_2[MnR_4]$ (R = Me, Et, *n*-Bu, CH_2CH_2-*t*-Bu). The EPR spectra of the methyl, ethyl, *n*-butyl, and neohexyl species indicate that the symmetries of these molecules are lower than that of the (trimethylsilyl)methyl compound (see Figure 5), i.e. more rhombically distorted from cubic symmetry. This is reflected in the broadening of the signal at ca. 335 mT and the more poorly resolved hyperfine structure. The coordination of lithium cations to the α-carbon atoms of the alkyl groups renders the x and y axes inequivalent and lowers the symmetry. Also, the appearance of peaks outside of the $g = 2$ region indicates that there is a larger zero-field splitting.[44,45] This is reflected in the larger D values deduced from the D–B plots (see Table V). Estimation of the exact value of λ is difficult when the zero-field splitting parameter D is small; however, taking λ to be nonzero but less than 0.03 is consistent with the available data.

Table V. Hamiltonian Parameters *D* and λ for Manganese(II) Alkyls[a]

compd	D, cm^{-1}	λ
$[Li(tmed)]_2[Mn(CH_2SiMe_3)_4]$	0.010	<0.03
$[Li(tmed)]_2[MnMe_4]$	0.015	<0.03
$[Li(tmed)]_2[MnEt_4]$	0.035	<0.03
$[Li(tmed)]_2[Mn(n\text{-}Bu)_4]$	0.025	<0.03
$[Li(tmed)]_2[Mn(CH_2CH_2\text{-}t\text{-}Bu)_4]$	0.035	<0.03
$[Li(tmed)]_2[MnPh_4]$	0.050	<0.03
$Mn(CH_2CMe_3)_2(tmed)$	0.350	0.27

[a] Estimated standard deviation for D ±0.005 cm^{-1}.

Our spectra of $[Li(tmed)]_2[MnMe_4]$ are much better resolved than those previously reported for frozen tetrahydrofuran solutions of this complex.[5] Specifically, manganese hyperfine was not discernible in the earlier study but in our hands was readily apparent. The hyperfine splitting values of 0.0060 cm^{-1} in **1**–**5** are consistent with the values reported for other high-spin Mn^{II} species.[9,21]

$[Li(tmed)]_2[MnPh_4]$ and $Mn(CH_2CMe_3)_2(tmed)$. The EPR spectrum of the tetraphenylmanganate complex also exhibits rhombic distortion from cubic symmetry as was noted for the other tetraalkylmanganates. However, the phenyl ligands possess local C_2 axes that are incompatible with the C_3 axes of the tetrahedron, and a larger rhombic distortion is observed. Consistent with this, the resonances in the spectrum are the broadest of the series, and hyperfine structure due to ^{55}Mn is completely absent (see Figure 5). Although this spectrum was the most difficult of the series to interpret, the estimated zero-field splitting parameter D was larger than those of the other alkyls (see Table V).

The known[5] manganese alkyl $Mn(CH_2CMe_3)_2(tmed)$ (**7**) was isolated in attempts to prepare the still unknown neopentyl complex $[Li(tmed)]_2[Mn(CH_2CMe_3)_4]$. Compound **7** exhibits a severely rhombically distorted EPR spectrum as shown by the magnitudes of the associated Hamiltonian parameters, $D = 0.35$ cm^{-1} and $\lambda = 0.27$. The spectrum presented here (see Figure 5) is much better resolved than the one reported previously,[5] but the derived values of D and λ are quite similar. This molecule is geometrically similar to its phosphine analogue, $Mn(CH_2CMe_3)_2(dmpe)$, which possesses larger Hamiltonian parameters of $D = 0.555$ cm^{-1} and $\lambda = 0.279$.[9] The larger zero-field splitting parameter for this latter compound is consistent with the increased ligand field strength of phosphines vs amines.[45]

Discussion

Kochi noted that manganese(II) alkyls prepared from $MnCl_2$ and an excess of a "β-unstable" alkyllithium reagent decomposed readily at room temperature but exhibited slower β-elimination rates than manganese(II) alkyls prepared from the analogous Grignard reagent.[3] Presumably, different species were formed in the two reactions: anionic $Li_2[MnR_4]$ salts in the first case and neutral $MnR_2(thf)_x$ or $MnRCl(thf)_x$ complexes in the second.

We have shown that tetraalkylmanganates of stoichiometry $[Li(tmed)]_2[MnR_4]$ are in fact thermally stable *even if* the alkyl groups possess β-hydrogen atoms. For

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example, crystalline samples of $[Li(tmed)]_2[MnEt_4]$ are remarkably robust and may be heated under argon to 110 °C before noticeable decomposition occurs. The β-elimination rates of the tmed adducts are significantly slower than those of the "$Li_2[MnR_4]$" species prepared in situ by Kochi in tetrahydrofuran. Our success in preparing stable alkylmanganates that contain β-hydrogen atoms may arise in part from a shift in the $[MnR_4^{2-}] \rightleftarrows [MnR_3^-]$ equilibrium to the left by the complexation of the lithium counterions by tmed. One principal effect of tmed is to reduce the Lewis acidity of the lithium cations. This would inhibit the dissociation of LiR from the $Li_2[MnR_4]$ ion clusters and prevent formation of the coordinately unsaturated (and presumably less stable) $[MnR_3^-]$ species. Other factors, such as steric effects, are doubtlessly important also in stabilizing the tetraalkylmanganate salts.

The EPR data have shown that interactions of the Li cations with the $[MnR_4^{2-}]$ anions affect the magnitude of the rhombic distortion away from perfect tetrahedral symmetry. The (trimethylsilyl)methyl species **5** evidently has weaker C···Li interactions than the analogous methyl, ethyl, *n*-butyl, and neohexyl complex **1**–**4**. It is possible that the large steric bulk of the CH_2SiMe_3 ligands prevents the lithium cations from approaching as closely to the α-carbon atoms. The γ-carbon and γ-hydrogen atoms are probably not involved in short contacts with the cations, since little negative charge density resides on the methyl substituents of the CH_2SiMe_3 groups.

Although the tetraphenylmanganate complex **6** shows the largest rhombic distortion by EPR spectroscopy, it is difficult to assess the origin of this result. The larger rhombic distortion may be due to the presence of strong C···Li interactions with the ipso carbon atoms (which is well-known to occur)[19,37–39] or to the incompatibility of the local C_2 and C_3 symmetry axes of the phenyl groups and MnC_4 tetrahedron, respectively.

Previous studies reported red to red-brown colors for Li_2MnR_4 complexes[5] which contrast with the pale to colorless appearance of the $[Li(tmed)]_2[MnR_4]$ salts we have isolated and the pale colors expected for high-spin d^5 manganese(II) species. We have reported elsewhere that air oxidation of $[Li(tmed)]_2[MnMe_4]$ in the presence of excess methyllithium gives *red* solutions, from which the red manganese(III) complex $[Li(tmed)]_2[MnMe_5]$ may be isolated.[22] Since the spectroscopic studies reported previously agree in all details with our results, we suspect that the presence of trace amounts of manganese(III) impurities led to the darker colors previously noted.

Finally, the discovery of high-yield synthetic routes to stable alkylmanganates may be useful in organic synthesis. It has been noted that species thought to be of stoichiometry $LiMnR_3$ (but more probably Li_2MnR_4) are able to alkylate organic substrates such as halocarbons and ketones.[46,47] The manganese reagents are slightly more reactive than the analogous organocuprates and in some cases may better serve to effect high-yield conversions of organic molecules to alkylated derivatives.

Experimental Section

All operations were carried out in vacuum or under argon. Pentane, diethyl ether, and tetrahydrofuran were distilled under nitrogen from sodium–benzophenone immediately before use. Anhydrous $MnCl_2$ was prepared by heating manganese dichloride hydrate with thionyl chloride followed by drying under vacuum at 200 °C. Methyllithium (Aldrich) was filtered before use, while *n*-butyllithium (Aldrich) and *tert*-butyllithium (Aldrich) were used as received. Ethyllithium,[49] neopentyllithium,[50] ((trimethylsilyl)methyl)lithium,[51] and phenyllithium[52] were prepared by literature routes and *N,N,N′,N′*-tetramethylethylenediamine (Aldrich) was distilled from and stored over sodium.

Microanalyses were performed by Mr. Josef Nemeth and Mr. Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B infrared spectrometer as Nujol mulls. The ^1H NMR data were obtained on a General Electric QE-300 spectrometer at 300 MHz. The X-band EPR experiments were performed on a Bruker 220D-SRC spectrometer; the data were obtained from frozen toluene solutions at −173 °C. Magnetic moments were determined by a modification of Evans' method. Melting points were measured on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Tetramethylmanganate(II) (1). To a suspension of $MnCl_2$ (1.36 g, 10.8 mmol) in diethyl ether at 0 °C (50 mL) was added methyllithium (27 mL of a 1.63 M solution in diethyl ether, 44 mmol). After being stirred for 10 min at 0 °C, the reaction mixture was warmed to room temperature and stirred for 3 h to give an orange solution and a large amount of white precipitate. To the filtered solution was added *N,N,N′,N′*-tetramethylethylenediamine (6.6 mL, 44 mmol) which caused the immediate formation of pale orange needles. Cooling the solution to −20 °C gave additional pale orange needles that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. Yield: 3.6 g (92%). The product may be recrystallized from diethyl ether (ca. 50 mL/g) by cooling to −20 °C; recovery 90%. IR (cm^{-1}, CsI): 2333 vw, 2193 vw, 2013 vw, 1693 vw, 1355 s, 1291 s, 1272 sh, 1253 m, 1249 sh, 1181 m, 1160 s, 1131 s, 1118 sh, 1103 m, 1169 s, 1035 s, 1018 s, 951 s, 947 sh, 941 sh, 839 w, 771 m, 585 s, 539 vs, 463 vs, 393 vs, 363 vs, 308 sh.

Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Tetraethylmanganate(II) (2). To a cold (−78 °C) suspension of $MnCl_2$ (0.70 g, 5.6 mmol) in diethyl ether (50 mL) was added ethyllithium (61 mL of a 0.37 M benzene solution was taken to dryness and the white solid was redissolved in 30 mL of diethyl ether (22.6 mmol)). The reaction mixture developed a slight brown color. After being stirred at −78 °C for 1 h, the reaction mixture was warmed to 0 °C and stirred for 2 h to give a dark orange solution and a large amount of white precipitate. To the cold (0 °C) filtered solution was added *N,N,N′,N′*-tetramethylethylenediamine (3.4 mL, 22.4 mmol) resulting in the immediate formation of small white prisms. Cooling the solution to −20 °C gave additional crystals that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. Yield: 1.6 g (68%). The product may be recrystallized from diethyl ether (ca. 40 mL/g) by cooling to −20 °C; recovery 80%. IR (cm^{-1}, CsI): 2701 s, 2663 m, 2630 m, 2489 w, 2040 w, 1418 m, 1405 m, 1385 m, 1360 sh, 1351 s, 1388 s, 1385 sh, 1249 m, 1209 m, 1176 s, 1153 s, 1123 s, 1093 m, 1061 s, 1042 m, 1029 s, 1013 s, 941 vs, 912 s, 869 m, 783 s, 762 m, 714 w, 580 m, 450 vs, 380 vs, 302 s, 249 s.

Bis[(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Tetrakis(3,3-dimethylbutyl)manganate(II) (3). To a suspension of $MnCl_2$ (1.99 g, 15.8 mmol) in diethyl ether (100 mL) at 0 °C was added *N,N,N′,N′*-tetramethylethylenediamine (9.5 mL, 63 mmol). To the resulting brown slurry was added *tert*-butyllithium (37.1 mL of a 1.7 M solution in hexane, 63 mmol). After being stirred at 0 °C for 2 h, warmed to room temperature, and stirred for an additional 2 h, the solution was dark orange and there was a large amount of dark gray precipitate. The filtered solution was concentrated to ca. 50 mL and cooled to −20 °C to give off-white prisms that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. The product was recrystallized from pentane (ca. 30 mL/g) by cooling to −20 °C; recovery 85%. Yield: 2.21 g (22%). IR (cm^{-1}, KBr): 3000 s, 2708 m, 1382 s, 1355 s, 1309 w, 1292 s, 1286 m, 1253 m, 1231 m, 1200 m, 1182 m, 1159 m, 1129

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s, 1100 m, 1064 m, 1038 s, 1020 s, 992 s, 950 s, 920 m, 876 w, 823 w, 789 m, 770 m, 727 w, 578 m, 530 s, 460 m, 423 m, 400 s.

Bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium] Tetra-*n*-butylmanganate(II) (4). To a suspension of $MnCl_2$ (1.66 g, 13.2 mmol) in diethyl ether (80 mL) at 0 °C was added *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (8.0 mL, 52.8 mmol). To the resulting brown slurry was added *n*-butyllithium (33 mL of a 1.6 M solution in hexane, 52.8 mmol) to give an orange solution and a white precipitate. After being stirred for 20 min, the reaction mixture was warmed to room temperature and stirred for 2 h and the solvent was removed under vacuum. The solid was extracted with pentane (2 × 40 mL), and the combined filtrates were concentrated to ca. 20 mL. Cooling to −20 °C gave off-white prisms that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. The product was recrystallized from pentane (ca. 20 mL/g) by cooling to −20 °C; recovery 40%. Yield: 1.69 g (28%). IR (cm^{-1}, KBr): 1406 m, 1381 sh, 1362 s, 1350 s, 1325 m, 1303 m, 1285 s, 1263 s, 1248 s, 1173 s, 1153 s, 1123 s, 1095 m, 1063 s, 1030 s, 1014 s, 963 s, 941 s, 848 m, 828 m, 782 s, 764 s, 713 w, 579 s, 505 vs, 444 vs.

Bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium] Tetrakis((trimethylsilyl)methyl)manganate(II) (5). To a suspension of $MnCl_2$ (1.0 g, 7.9 mmol) in diethyl ether (50 mL) was added ((trimethylsilyl)methyl)lithium (58 mL of a 0.62 M solution in hexane was taken to dryness and the white solid was dissolved in 40 mL of diethyl ether (36 mmol)). After being stirred for 5 h, the solution was dark orange and there was a large amount of an off-white precipitate. To the filtered solution was added *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (5.5 mL, 36 mmol) which resulted in immediate precipitation of small off-white crystals. Cooling the solution to −20 °C gave additional crystals that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. Yield: 4.8 g (94%). The product may be recrystallized from a 5:1 v/v mixture of THF/Et_2O (ca. 25 mL/g) by cooling to −20 °C; recovery 90%. IR (cm^{-1}, CsI): 2693 m, 1950 vw, 1897 vw, 1834 vw, 1356 m, 1288 s, 1244 s, 1230 s, 1183 m, 1161 s, 1127 s, 1087 m, 1071 s, 1034 s, 1019 s, 993 sh, 947 s, 835 vs, 787 s, 745 vs, 665 s, 592 m, 465 s, 444 s, 375 s, 335 s, 257 m.

Bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium] Tetraphenylmanganate(II) (6). To a suspension of $MnCl_2$ (0.65 g, 5.2 mmol) in diethyl ether (30 mL) at 25 °C was added phenyllithium (49 mL of a 0.45 M solution in diethyl ether, 22 mmol). The solution immediately developed an orange color and after being stirred for 3 h was light orange with a large amount of off-white precipitate. To the filtered solution was added *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (3.2 mL, 22 mmol) resulting in a color change to dark yellow. The solution was concentrated to ca. 25 mL, and pentane (25 mL) was added. Cooling to −20 °C gave large opaque yellow blocks that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. Yield: 2.7 g (85%). The product may be recrystallized from diethyl ether (ca. 50 mL/g) by cooling to −20 °C; recovery 80%. IR (cm^{-1}, KBr): 3115 w, 3097 m, 3025 s, 2785 s, 2686 w, 2555 vw, 2545 vw, 1973 sh, 1957 w, 1953 w, 1943 sh, 1878 w, 1840 sh, 1827 w, 1768 vw, 1607 w, 1570 sh, 1559 w, 1547 sh, 1410 s, 1383 sh, 1375 s, 1283 s, 1244 s, 1223 s, 1177 s, 1155 s, 1134 m, 1122 s, 1094 m, 1057 s, 1039 s, 1028 s, 1009 s, 976 m, 937 s, 891 w, 848 vw, 781 s, 764 m, 697 vs, 663 w, 615 s, 576 m, 455 s, 423 vs.

Bis(2,2-dimethylpropyl)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)manganese(II) (7). To a suspension of $MnCl_2$ (0.21 g, 1.7 mmol) in diethyl ether (25 mL) at 0 °C was added *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (1.1 mL, 7.3 mmol). To the resulting brown slurry was added neopentyllithium (0.57 g of freshly sublimed neopentyllithium in 25 mL of ether, 73 mmol) to give a dark orange solution and a white precipitate. After the solution was warmed to room temperature and stirred for 2 h, the solvent was removed under vacuum and the residue was extracted with pentane (2 × 30 mL). The filtered orange solution was concentrated to ca. 10 mL and cooled to −20 °C to give off-white prisms that were isolated by filtration and dried under vacuum. Additional crops of crystals were obtained from the supernatant. Yield: 0.31 g (60%). The product may be recrystallized from pentane (ca. 40 mL/g) by cooling to −20 °C. IR (cm^{-1}, KBr): 3013 s, 2760 s, 2750 s, 2710 m, 2693 m, 1409 w, 1395 m, 1349 s, 1297 s, 1243 m, 1227 s, 1200 s, 1177 m, 1155 s, 1123 s, 1094 m, 1072 m, 1066 s, 1039 w, 1024 s, 1013 s, 995 s, 985 w, 950 s, 924 m, 899 m, 787 s, 767 s, 735 m, 574 m, 554 s, 527 s, 465 m, 437 m, 376 s.

Crystallographic Studies.[54] Single crystals of $[Li(tmed)]_2[MnMe_4]$ (1), grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. [Crystals of the ethyl analogue **2** and the 3,3-dimethylbutyl complex **3** were crystallized from diethyl ether and pentane, respectively. Subsequent comments in brackets will refer to these two compounds.] 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 using 25 reflections yielded the cell dimensions given in Table II.

Data were collected in one quadrant of reciprocal space ($-h,+k,\pm l$) [for **2**, ($-h,-k,\pm l$); for **3**, ($+h,+k,\pm l$)] using measurement parameters listed in Table II. [For **3**, the crystal chosen moved within the capillary and was recentered every 500 reflections. During collection of the second shell, the crystal moved out of the incident X-ray beam entirely, and data collection was discontinued so that $2.0 \leq 2\theta \leq 36°$.] Systematic absences for $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, were consistent only with space group $P2_1/c$. [For **2** and **3**, systematic absences hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, were consistent with space groups $C2/c$ and Cc. The average values of the normalized structure factors suggested the centric choice $C2/c$, which was confirmed by successful refinement of the proposed model.] 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 0.882 and 0.852, respectively. [For **2**, the maximum and minimum transmission factors were 0.871 and 0.838, respectively; for **3**, no absorption correction was applied.] Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by Patterson and weighted and unweighted difference Fourier methods. [The structure of **2** was solved by direct methods, SHELX-86; the structure of **3** was solved by Patterson methods.] The position of the manganese atom was deduced from a vector map [for **2**, from an E map], and 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 $w = 2.05/(\sigma(F_o)^2 + (pF_o)^2)$. [For **2**, $w = 1.80/(\sigma(F_o)^2 + (pF_o)^2)$; for **3**, $w = 0.94/(\sigma(F_o)^2 + (pF_o)^2)$.] 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. To compensate for high correlations between the "A" and "B" disordered carbon atom positions, chemically similar bond distances were constrained to the same variable distance. These constraints were applied to the set of methyl C–N distances and also to the set of ethylene C–C distances in the tmed ligand. No other constraints were imposed on the model. Hydrogen atoms were included as fixed contributors in "idealized" positions with C–H = 0.95Å. In the final cycle of least-squares, group isotropic thermal coefficients were varied for the hydrogen atoms and the disordered methyl and ethylene carbon atoms of the tmed ligand, while anisotropic thermal coefficients were refined for the remaining non-hydrogen atoms. [For **2**, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients. Hydrogen atoms were located in the Fourier difference maps, and their locations were independently refined with isotropic thermal parameters. For **3**, hydrogen atoms were included as fixed contributors in "idealized" positions. In the final

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cycle of least squares, anisotropic thermal coefficients were refined for the non-hydrogen atoms and a group isotropic thermal parameter was varied for the hydrogen atoms.] Successful convergence was indicated by the maximum shift/error of 0.076 [0.006 for **2** and 0.001 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 a slight dependence on sin θ. [For **2** and **3**, there were no apparent systematic errors among the final observed and calculated structure factors.]

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Supplementary Material Available: Tables of final atomic coordinates and anisotropic thermal parameters for **1**, **2**, and **3** and tables of calculated hydrogen atom positions for **1** and **3** (9 pages); listings of final observed and calculated structure factor amplitudes for **1**, **2**, and **3** (20 pages). Ordering information is given on any current masthead page.

Reduction Behavior of the Complexes $Cp'M(NO)X_2$ (Cp' = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Mo or W; X = Cl, Br, or I): Synthesis and Characterization of the $[Cp'Mo(NO)X_2]^{\bullet-}$ Radical Anions[1,2]

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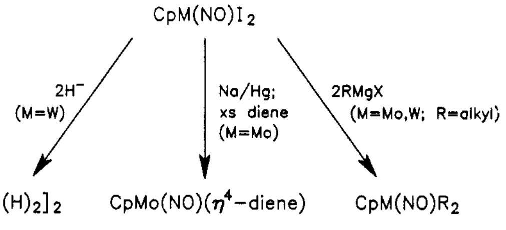
The reduction behavior of the title series of organometallic complexes has been investigated both by cyclic voltammetry and by chemical means. All the $Cp'Mo(NO)X_2$ complexes in CH_2Cl_2 undergo reversible one-electron reductions, the Cp* derivatives being more difficult to reduce by ca. 0.2 V. On a preparative scale, these reductions are best effected by utilizing Cp_2Co in THF as the reducing agent. The resulting salts $[Cp_2Co]^+[Cp'Mo(NO)X_2]^{\bullet-}$ are isolable in high yields as analytically pure, green to brown solids. The ESR spectra of solutions of these salts reveal that the extra electron density in the $[Cp'Mo(NO)X_2]^{\bullet-}$ anions is not primarily localized in their Mo–NO linkages, as might have been expected. Rather, the ESR signals due to the unpaired electrons on the anions exhibit coupling either only to the molybdenum center (X = Cl or I) or to both molybdenum and the halide (X = Br). The diiodo radical anions are relatively unstable in DMF and convert to $[Cp'Mo(NO)I]_2$ via I^- loss. The congeneric tungsten complexes $Cp'W(NO)I_2$ behave similarly upon the addition of an electron, converting to $[Cp'W(NO)I]_2$ via *EC* mechanisms. On a preparative scale, $[Cp^*W(NO)I]_2$ is most cleanly synthesized by reacting equimolar amounts of $Cp^*W(NO)I_2$ and $Cp^*W(NO)(CO)_2$ in refluxing toluene. Finally, ESR spectral evidence for the occurrence of single-electron transfer during the reactions of Grignard reagents RMgX with the $Cp'Mo(NO)X_2$ complexes has been obtained, these observations being of fundamental significance in so far as the successful syntheses of new $Cp'Mo(NO)R_2$ compounds are concerned.

Introduction

Previous work in our laboratories has resulted in the preparation and characterization of several new classes of compounds containing the CpM(NO) group (Cp = η^5-C_5H_5; M = Mo or W). Specifically, alkyl-,[3] hydride,[4] and diene-containing[5] derivatives have been synthesized by utilizing the appropriate diiodo precursors, $CpM(NO)I_2$,[6,7] as summarized in Scheme I. From a synthetic point of

Scheme I



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[6] The dihalo nitrosyl complexes $Cp'M(NO)X_2$ (Cp' = Cp or Cp*; M = Mo or W; X = Cl, Br, or I) possess either monomeric[7a] or halide-bridged[7b] dimeric molecular structures in the solid state. On the other hand, the physical and chemical properties of these compounds in solutions are most consistent with their existing as solvated monomers. Consequently, in this paper they are represented exclusively by their monomeric formulae.