

Permethyl Manganates. Synthesis and Characterization of Divalent $[\text{MnMe}_4^{2-}]$, Trivalent $[\text{MnMe}_5^{2-}]$, and Tetravalent $[\text{MnMe}_6^{2-}]$

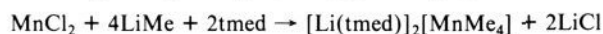
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The organometallic chemistry of manganese is almost entirely limited to the 0, +1, and +2 oxidation states.¹ The paucity of high-valent organomanganese compounds is most certainly due to the lack of good Mn^{III} and Mn^{IV} starting materials; the binary halides are generally unstable or nonexistent,² and other species such as K_3MnCl_6 , " $\text{Mn}(\text{O}_2\text{CMe})_3$ ", K_2MnCl_6 , and MnO_2 are essentially unreactive toward organolithium or -magnesium reagents. The potential use of alkyl manganates in organic alkylation reactions and the need for high-valent organomanganese species to model the oxidation of organic substrates by high-valent manganese porphyrins³ has prompted us to study a series of permethyl manganates. We now report the synthesis and characterization of the $[\text{Li}(\text{tmed})^+]$ salts of $[\text{MnMe}_4^{2-}]$, $[\text{MnMe}_5^{2-}]$, and $[\text{MnMe}_6^{2-}]$.

Alkylation of MnCl_2 with 4 equiv of methylolithium in diethyl ether followed by filtration and addition of N,N,N',N' -tetramethylethylenediamine (tmed) gives pale orange crystals of the tetramethyl manganate $[\text{Li}(\text{tmed})_2][\text{MnMe}_4]$ (**1**).⁴



This high-spin ($\mu_{\text{eff}} = 5.7 \mu_B$) Mn^{II} species possesses an X-band ESR spectrum in frozen toluene that consists of a strong signal at 335 mT with a ^{55}Mn hyperfine coupling of 0.0060 cm^{-1} , and weaker features at 70, 135, and 260 mT. This spectrum yields the Hamiltonian parameters $D < 0.05$ and $\lambda < 0.03$ and is consistent with nearly ideal tetrahedral symmetry;⁵ this conclusion is confirmed by the X-ray crystal structure (Figure 1a).⁶ Despite the presence of close interactions with the $\text{Li}(\text{tmed})$ cations, the C–Mn–C angles are all within 4° of the ideal tetrahedral value. The average Mn–C bond length of $2.26(1) \text{ \AA}$ is much longer than the $2.149(8) \text{ \AA}$ distance in the high-spin Mn^{II} alkyl $\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2(\text{PMe}_3)_2$ ⁷ presumably as a result of the $\text{Li}\cdots\text{C}$ interactions. The $\text{Li}(\text{tmed})$ cations bridge opposite edges of the $[\text{MnMe}_4^{2-}]$ tetrahedron with an average $\text{Li}\cdots\text{C}$ contact of 2.26

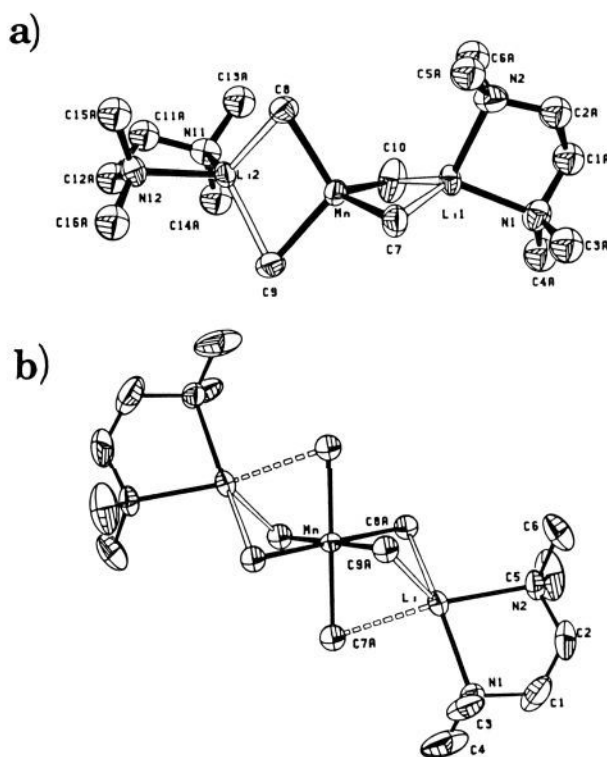
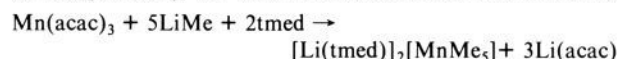


Figure 1. (a) Crystal structure of $[\text{Li}(\text{tmed})_2][\text{MnMe}_4]$. Important bond lengths and angles: Mn–C = $2.227(4) \text{ \AA}$; C \cdots Li = $2.26(1) \text{ \AA}$; Li–N = $2.10(1) \text{ \AA}$; C–Mn–C(bridged) = $107.8(3)^\circ$; C–Mn–C(unbridged) = $110.3(3)^\circ$; C–Li–C = $105.7(5)^\circ$; N–Li–N = $86.6(5)^\circ$. (b) Crystal structure of $[\text{Li}(\text{tmed})_2][\text{MnMe}_5]$. Important bond distances (\AA) and angles (deg): Mn–C = $2.12(1) \text{ \AA}$; C \cdots Li = $2.20(2)$, $2.35(2)$, $2.53(2) \text{ \AA}$; Li–N = $2.20(1) \text{ \AA}$; C–Mn–C(bridged) = $93.5(5)^\circ$; C–Mn–C(unbridged) = $86.5(5)^\circ$; C–Li–C = $78.0(5)$ – $85.2(5)^\circ$; N–Li–N = $83.0(4)^\circ$.

$(1) \text{ \AA}$; these interactions are associated with low-energy C–H stretches near 2700 cm^{-1} in the infrared spectrum.

The previously reported⁸ description of $\text{Li}_2\text{MnMe}_4 \cdot 2\text{tmed}$ as a red crystalline material may have been due to trace oxidation. Indeed, we have found that air oxidation of $[\text{MnMe}_4^{2-}]$ solutions in the presence of excess LiMe yields a red crystalline product upon addition of tmed. This red species can be prepared by another route in higher yield by treatment of $\text{Mn}(\text{acac})_3$ with 8 equiv of LiMe in diethyl ether followed by filtration and addition of tmed. Dark red crystals of the pentamethyl manganate $[\text{Li}(\text{tmed})_2][\text{MnMe}_5]$ (**2**)⁹ may be obtained from these solutions.



This ESR-silent Mn^{III} product is only the second σ -organomanganese(III) complex known,¹⁰ and the first to contain more than one Mn–C bond. Its magnetic moment of $4.9 \mu_B$ indicates the presence of 4 unpaired electrons. We have been unable so far to obtain X-ray quality crystals of **2**, but a square-pyramidal geometry is most likely.²

Exposure of solutions of $[\text{MnMe}_5^{2-}]$ to air gives rise to a new yellow-orange species in low yield; this further-oxidized product may be obtained nearly quantitatively by addition of 2 equiv of LiMe and tmed to the manganese(IV) methyl species, $\text{MnMe}_4(\text{PMe}_3)_2$.¹¹ The product of this reaction is the yellow-orange $\text{MnMe}_4(\text{PMe}_3)_2 + 2\text{LiMe} + 2\text{tmed} \rightarrow$



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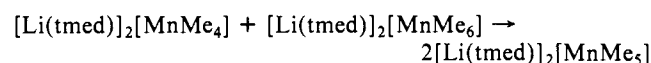
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(6) Crystal data for **1** ($T = 223 \text{ K}$): space group $P2_1/c$, with $a = 13.591(2) \text{ \AA}$, $b = 15.190(3) \text{ \AA}$, $c = 12.007(2) \text{ \AA}$, $\beta = 94.27(1)^\circ$, $V = 2472(1) \text{ \AA}^3$; $Z = 4$; $R_F = 0.062$, $R_{wF} = 0.068$ for 179 variables and 1812 unique data for which $I > 2.58\sigma(I)$. Hydrogen atoms were included as fixed contributors in "idealized" positions, and the carbon atoms of the tmed ligands were each disordered over two sites with relative occupancies of 0.65 (1) and 0.35 (1).

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hexamethyl manganese $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$ (**3**).¹² The +4 oxidation state of this species is confirmed by a magnetic moment of $3.9 \mu_B$ and by the ESR spectrum, which shows a strong sextet at 340 mT ($A_{\text{Mn}} = 0.0060 \text{ cm}^{-1}$) and a moderately intense "spin-forbidden" transition at 145 mT that are consistent with the presence of a nearly cubic ($D = \lambda = 0$) $S = 3/2$ ion.¹³ The X-ray crystal structure¹⁴ (Figure 1b) reveals an octahedral $[\text{MnMe}_6]^{2-}$ core that is capped by two "semi-face-bridging" Li-(tmed) cations; the molecular unit resides on a crystallographic inversion center. The average Mn-C distance of 2.12 Å is similar to those in $\text{MnMe}_4(\text{dmpe})$ of 2.08–2.12 Å, while the Li...H₃C-Mn contacts are divided into two short distances of 2.20–2.35 Å and one longer distance of 2.53 (2) Å. The coordination geometry about lithium may be best described as a distorted trigonal bipyramid, with C(7A) and N(2) in the axial positions.

Upon mixing solutions of the Mn^{II} and Mn^{IV} compounds $[\text{Li}(\text{tmed})]_2[\text{MnMe}_4]$ and $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$ in a 1:1 ratio, comproportionation occurs to give the Mn^{III} pentamethyl man-



ganate $[\text{Li}(\text{tmed})]_2[\text{MnMe}_5]$ in nearly quantitative yield. Interestingly, however, the comproportionation reaction occurs relatively slowly ($t_{1/2} \sim 10$ min), presumably since methyl group transfer as well as electron transfer must take place. The three permethyl complexes form an unusual set of related organometallic species in three adjacent oxidation states.¹⁵

Preliminary results indicate that the tetravalent hexamethyl manganese, $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$, reacts with internal acetylenes, $\text{RC}\equiv\text{CR}$, to give low yields of methylated olefins, $\text{MeRC}=\text{CRMe}$. Such cis-alkylation reactions of acetylenes are formally similar to the cis-hydroxylation of olefins by reagents such as OsO_4 .¹⁶ The potential utility of high-valent organomanganese compounds as synthetic reagents for the specific functionalization of organic compounds is under further investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757), the Office of Naval Research under their Young Investigator Award Program, and Lubrizol for a fellowship to R.J.M. In addition, G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990). We also thank Dr. Scott Wilson, Charlotte Stern, and Connie Odle of the University of Illinois X-ray Crystallographic Laboratory for carrying out the crystal structure determinations.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **3** (11 pages); tables of final observed and calculated structure factors for **1** and **3** (12 pages). Ordering information is given on any current masthead page.

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(14) Crystal data for **3** ($T = 173$ K): space group $Pbca$, with $a = 12.386$ (4) Å, $b = 13.358$ (7) Å, $c = 15.349$ (7) Å, $V = 2540$ (4) Å³; $Z = 4$, $R_F = 0.051$, $R_{wF} = 0.058$ for 115 variables and 909 unique data for which $I > 2.58\sigma(I)$. Hydrogen atoms were included as fixed contributors in "idealized" positions, and the carbon atoms of the $[\text{MnMe}_6]^{2-}$ unit were each disordered over two sites with relative occupancies of 0.56 (1) and 0.44 (1).

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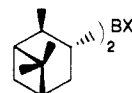
Enantioselective Ring Cleavage of *meso*-Epoxides with *B*-Halodiisopinocampheylboranes

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Asymmetric synthesis starting from *meso* compounds is an increasingly important method for the preparation of optically active compounds. Various chemical¹ and enzymatic² procedures have been utilized for such transformations. Surprisingly, not much attention has been given to the enantioselective ring cleavage of *meso*-epoxides that would lead to several classes of important compounds. We now report the synthesis of optically active 1,2-halohydrins using *B*-halodiisopinocampheylboranes, Ipc_2BX (**1a–c**).



1a: X = Cl
1b: X = Br
1c: X = I

The cleavage of carbon–oxygen bonds with boron reagents, in particular with trihaloboranes, is a well-documented and established procedure.³ However, the high Lewis acidity of trihaloboranes and their tridentate nature can result in the unwanted rupture of bonds in compounds containing other sensitive functional groups. To increase the selectivity in carbon–oxygen bond cleavage, monohaloboranes in which two of the halogens on boron are replaced by alkyl,⁴ alkoxy,⁵ thioalkyl,⁶ or nitrogen containing⁷ groups have recently been introduced. Such reagents indeed are selective and could by the proper choice of substituents cleave specific C–O bonds.⁷ Recently Guindon and co-workers reported⁴ the stereospecific ring cleavage of various cyclic ethers with *B*-bromodimethylborane. Of particular consequence in the cleavage of epoxides with these type of reagents is the fact that the halo-hydrin products are consistent with a predominantly S_N2 type mechanism proposed for such reactions.^{4,7,8} This suggests that the asymmetric version should proceed with a high degree of enantiotopic differentiation of the C–O bonds of suitable *meso*-epoxides. Recently, the enantioselective cleavage of cyclohexene oxide with thiols and azides in the presence of zinc or copper tartrates has been successfully accomplished.⁹ Except for this report, the cleavage of epoxides with chiral Lewis acids is an unexplored reaction. As part of our efforts in the field of asymmetric synthesis,¹⁰ we are currently exploring reactions involving boron based chiral Lewis acids. The present communication describes our investigations on the enantioselective ring opening of some *meso*-epoxides with *B*-halodiisopinocampheylboranes

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