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.]

Acknowledgment. We thank the National Science Foundation (Grant CHE 89-17586) and the Office of Naval Research under their Young Investigator Award Program for support of this research and Lubrizol and Quantum Chemicals for fellowships to R.J.M. We particularly thank Dr. Scott Wilson and Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determinations. G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990) and a Henry and Camille Dreyfus Teacher-Scholar Award (1988–1993).

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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Received July 9, 1990

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

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Table I. Physical and Microanalytical Data for the New Manganese Aryls

				anal.[a]			
compd	color	mp, °C	μ_{eff}, μ_B	C	H	Mn	X
$[Li(tmed)_2]_2[Mn(o\text{-}C_6H_4Me)_4]$ (**1**)	golden		5.7	69.6 (69.5)	9.58 (10.3)	6.7 (6.12)	*b*
$Mn(Mes)Cl_2(PMe_3)_2$ (**2a**)	red-orange	114 dec	4.8	45.6 (45.4)	7.40 (7.38)	13.6 (13.8)	17.6 (17.9)[c]
$Mn(Mes)Br_2(PMe_3)_2$ (**2b**)	red	110 dec	4.8	36.3 (37.1)	5.92 (6.01)	11.3 (11.3)	34.0 (32.9)[c]
$Mn(Mes)I_2(PMe_3)_2$ (**2c**)	dark red	117 dec	4.8	30.6 (31.1)	5.19 (5.00)	10.3 (9.47)	43.4 (43.8)[c]
$Mn(Mes)_2(PMe_3)_2$ (**4**)	off-white		5.7	62.3 (64.7)	8.86 (9.05)		

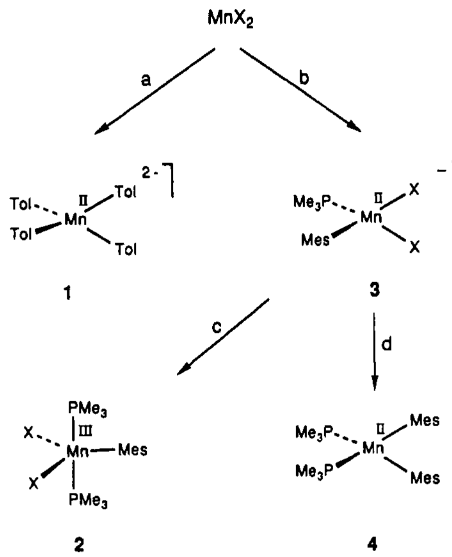
[a] Calculated values are in parentheses. [b] N, 11.4 (12.5); Li, 1.62 (1.55). [c] X = halogen.

$Mn(acac)_3$ or $MnMe_4(PMe_3)_2$. However, this approach has not proven to be as useful for the preparation of high-valent manganese aryls.

There are other ways to prepare Mn^{III} and Mn^{IV} complexes, and in particular, the oxidation of divalent manganese complexes by O_2 is a popular method to prepare higher valent inorganic manganese species.[3] For example, several manganese(II) phosphine complexes have been reported to bind O_2 reversibly to give manganese(III) superoxo species.[4-7] Although the O_2 adducts can be prepared in cold solutions, in matrices, or in the solid state, attempts to obtain them as pure materials have thus far resulted in the isolation of Mn^{II} or Mn^{III} products that lack O_2 ligands. Notably, the reaction of MnX_2 with O_2 in the presence of PMe_3 gives the Mn^{III} halo complexes $MnX_3(PMe_3)_2$.[8] Evidently, the manganese–dioxygen complexes are unstable and undergo one of three reactions: the dioxygen ligand dissociates to regenerate the Mn^{II} starting material, the Mn^{III} complex is irreversibly destroyed by oxidizing the phosphine ligands to phosphine oxides, or halide exchange occurs to give a stable Mn^{III} product that lacks an O_2 ligand. The reactions of manganese centers with O_2, and the reverse process in which oxomanganese species evolve O_2, continue to be of interest owing to their relevance to the oxygen-evolving manganese complex in the photosynthetic apparatus of green plants and cyanobacteria.[9-14]

Three organometallic complexes of high-valent manganese have been prepared by the addition of O_2 to lower valent precursors. The tetraalkyls MnR_4, where R = 1-norbornyl, neopentyl, and (trimethylsilyl)methyl, are made by exposure of solutions of divalent MnR_2 species to O_2,[15,16] and of these, only the norbornyl derivative is stable at room temperature. We now describe the preparation of several stable manganese(III) aryl complexes by this method. The intermediates present just prior to oxidation have been investigated, and attempts to characterize the previously reported[17] manganese(III) cyclopentadienyl complex "$NaMnCp_4$" are described. Some of this work has appeared in preliminary form.[18]

Scheme I



[a] Li(*o*-Tol) and tmed in Et_2O. [b] $^1/_2MgMes_2$ and PMe_3 in Et_2O. [c] O_2 and PMe_3 in Et_2O. [d] $^1/_2$ $MgMes_2$ and PMe_3 in Et_2O.

Table II. ^1H NMR Data for the $Mn(Mes)X_2(PMe_3)_2$ Species[a]

compd	*p*-Me	*m*-H	PMe_3
$Mn(Mes)Cl_2(PMe_3)_2$ (**2a**)	110.8 (830)	−53.4 (540)	−70.1 (1200)
$Mn(Mes)Br_2(PMe_3)_2$ (**2b**)	114.5 (1600)	−53.1 (920)	−70.8 (1600)
$Mn(Mes)I_2(PMe_3)_2$ (**2c**)	118.9 (2600)	−50.3 (580)	−72.6 (1400)

[a] Chemical shifts in ppm (fwhm in Hz).

Results and Discussion

Synthesis and Properties of Manganese(III) Aryls. We have shown in the previous paper that manganese(III) alkyls can be prepared by alkylation of $Mn(acac)_3$.[2] In contrast, treatment of $Mn(acac)_3$ with aryl-containing reagents gives only divalent products: for example, the addition of diphenylmagnesium in the presence of PMe_3 gives Mn^{II} products and biphenyl. A similar reaction of $Mn(acac)_3$ with excess *o*-tolyllithium followed by the addition of *N,N,N',N'*-tetramethylethylenediamine (tmed) gave only the manganese(II) product $[Li(tmed)_2]_2[Mn(o\text{-}C_6H_4Me)_4]$ in good yield; this species can also be obtained from $Li(o\text{-}C_6H_4Me)$ and $MnCl_2$. The EPR spectrum of this complex is very similar to that of the tetraphenylmanganate complex $[Li(tmed)]_2[MnPh_4]$, which we have described previously.[19]

$$Mn(acac)_3 + 5Li(o\text{-}C_6H_4Me) + 4\,tmed \rightarrow \underset{\mathbf{1}}{[Li(tmed)_2]_2[Mn(o\text{-}C_6H_4Me)_4]} + {}^1/_2\,o,o'\text{-}C_{12}H_8Me_2 + 3Li(acac)$$

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(3) Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Chapter 41.

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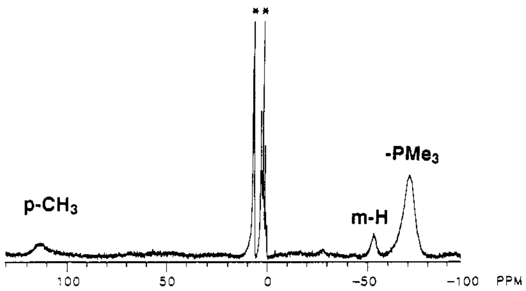

Figure 1. 300-MHz ^{1}H NMR spectrum of $Mn(Mes)Br_2(PMe_3)_2$ (**2b**) at 25 °C in C_6D_6. A base-line-corrected spectrum is shown.

See Table I for physical and microanalytical data for the new compounds isolated and Scheme I for a summary of the reactions described herein.

Whereas Mn^{III} aryls cannot be prepared directly from Mn^{III} starting materials, oxidation of divalent manganese(II) aryls has proven to be more successful. Treatment of manganese(II) halides with $^1/_2$ equiv of the mesityl (2,4,6-trimethylphenyl) reagent $Mg(Mes)_2(thf)_2$ and excess PMe_3 gives yellow Mn^{II} monomesityl species (see below). Solutions of the Mn^{II} monomesityl intermediates turn bright red upon exposure to dry dioxygen, and from these solutions may be isolated low yields of the new Mn^{III} aryl complexes $Mn(Mes)X_2(PMe_3)_2$ (**2**), where X is Cl, Br, or I.

$$MnX_2 + \tfrac{1}{2}Mg(Mes)_2(thf)_2 + 2PMe_3 + \tfrac{1}{2}O_2 \rightarrow Mn(Mes)X_2(PMe_3)_2 + \tfrac{1}{2}[MgO] + thf$$

2a, X = Cl
2b, X = Br
2c, X = I

The red crystalline compounds are high spin in solution ($\mu = 4.8\ \mu_B$) and are EPR silent. The ^{1}H NMR spectra of these species (Table II) show shifted and broadened peaks, as expected from the paramagnetism; a representative spectrum of $Mn(Mes)Br_2(PMe_3)_2$ is shown in Figure 1.

There are only three other manganese(III) phosphine complexes of any kind: $MnI_3(PMe_3)_2$,[14] $MnH_3(dmpe)_2$,[20] and $[MnCl_2(dmpb)_2^+]$,[21] where dmpb is 1,2-bis(dimethylphosphino)benzene. We have attempted, without success, to prepare complexes of stoichiometry $Mn(R)X_2(PR_3)_2$ with other alkyl or aryl groups or with other trialkylphosphines. For example, attempts to prepare the *o*-tolyl analogues $Mn(o\text{-}C_6H_4Me)X_2(PMe_3)_2$ by the procedure for compound **2** quickly led to decomposition of all manganese(III) products even at low temperatures. Evidently, the mesityl ligand is sufficiently sterically demanding to lend the manganese(III) product considerable kinetic stability but the *o*-tolyl ligand is not. Similar differences in the stability of rhenium aryls upon treatment with O_2 have been noted by Wilkinson.[22]

X-ray Structure of $Mn(Mes)Br_2(PMe_3)_2$. Single crystals of **2b** were grown by cooling saturated diethyl ether solutions to −20 °C. Crystal data are given in Table III, 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 IV.

Table III. Crystallographic Data for $Mn(Mes)Br_2(PMe_3)_2$ (2b) at 26 °C

$C_{15}H_{29}Br_2P_2Mn$
space group: $P2_1/n$
a = 8.956 (3) Å
b = 25.228 (8) Å
c = 9.472 (3) Å
β = 100.29 (2)°

V = 2106 (1) Å^3
Z = 4
mol wt: 486.09
d_{calcd} = 1.533 g cm^{-3}
μ_{calcd} = 45.04 cm^{-1}
size: 0.3 × 0.3 × 0.4 mm

diffractometer: Syntex $P2_1$
radiatn: Mo K$\bar{\alpha}$, λ = 0.71073 Å
monochromator: graphite cryst, 2θ = 12°
scan range: 3° ≤ 2θ ≤ 53°
scan speed, type: 3–20° min^{-1}, $\omega/2\theta$
rflns: 4931, 4387 unique, 1835 with $I > 2.58\sigma(I)$
internal consistency: R_i = 0.036

R_F = 0.036
R_{wF} = 0.048

no. of variables: 182
p factor: 0.020

Table IV. Selected Bond Distances and Angles for $Mn(Mes)Br_2(PMe_3)_2$ (2b)

	Distances (Å)		
Mn–C1	2.089 (8)	C1–C2	1.39 (1)
Mn–Br1	2.505 (1)	C2–C3	1.38 (1)
Mn–Br2	2.490 (2)	C3–C4	1.38 (1)
Mn–P1	2.424 (3)	C4–C5	1.37 (1)
Mn–P2	2.427 (3)	C5–C6	1.40 (1)
		C1–C6	1.41 (1)
	Angles (deg)		
P1–Mn–P2	171.6 (1)	P2–Mn–C1	85.9 (2)
Br1–Mn–Br2	101.68 (6)	P1–Mn–Br1	93.38 (7)
Br1–Mn–C1	128.6 (2)	P1–Mn–Br2	90.54 (8)
Br2–Mn–C1	129.8 (2)	P2–Mn–Br1	93.36 (7)
P1–Mn–C1	86.0 (2)	P2–Mn–Br2	92.99 (8)

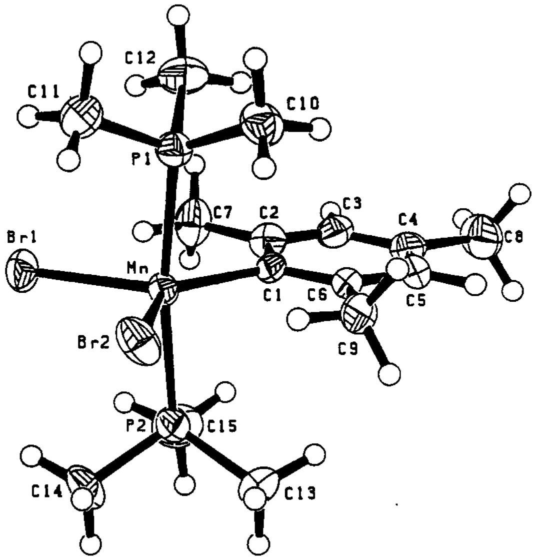

Figure 2. Molecular structure of $Mn(Mes)Br_2(PMe_3)_2$ (**2b**). The 35% probability density surfaces are shown.

The structural analysis shows that crystals of **2b** are composed of discrete monomers of $Mn(Mes)Br_2(PMe_3)_2$; a perspective view of **2b** is shown in Figure 2. The molecular geometry of **2b** is best described as a distorted trigonal bipyramid with the phosphine ligands occupying the axial sites. The overall geometry is similar to that described for the mmanganese(III) complex $MnI_3(PMe_3)_2$[14] and the rhenium(III) species $RePh_3(PEt_2Ph)_2$.[23] The Mn–P distances of 2.424 (3) and 2.427 (3) Å are essentially identical with those of 2.43 (1) Å reported for $MnI_3(PMe_3)_2$ and are longer than the 2.344 Å Mn–P distance in the

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low-spin octahedral manganese(III) complex $[\mathrm{MnCl_2(dmpb)_2}^+]$.[21] The Mn–Br distances of 2.490 (2) and 2.505 (1) Å are shorter than that of 2.666 (3) Å in the high-spin manganese(II) complex $\mathrm{MnBr_2(dmpe)_2}$,[24] as expected from the differences in the ionic radii of $\mathrm{Mn^{III}}$ and high-spin $\mathrm{Mn^{II}}$.

The trimethylphosphine ligands are bent toward the mesityl group and away from the bromide ligands, and the closing of the P–Mn–P angle to 171.6 (1)° is most likely attributable to the relative sizes of C and Br. The equatorial plane is occupied by the mesityl group and the two bromine atoms; the Br–Mn–Br angle of 101.68 (6)° is smaller than the ideal 120°, evidently to allow room for the *o*-methyl groups of the mesityl ligand. The orientation of the mesityl ring in the equatorial plane minimizes nonbonded repulsions, so that the *o*-methyl group fit into the "notch" formed by the axial phosphine ligands.

The $\mathrm{Mn^{III}}$–C(sp^2) distance of 2.089 (8) Å is statistically equal to the $\mathrm{Mn^{II}}$–C(sp^2) contacts of 2.11 (1) Å reported for the $\mathrm{Mn^{II}}$ mesityl complex $[\mathrm{Mn(C_6H_2Me_3)_2}]_3$[25] and to the $\mathrm{Mn^{III}}$–C(sp^3) contacts of 2.041 (5)–2.122 (4) Å reported for the $\mathrm{Mn^{III}}$ alkyls $[\mathrm{MnOMe_3}^{2-}]$[26] and $[\mathrm{MnMe_4}^-]$.[2] Normally, M–C(sp^2) distances are shorter than corresponding M–C(sp^3) distances, but this trend is not observed here. Evidently, the steric crowding of the *o*-methyl groups of the mesityl ligand in **2b** lengthens the Mn–C bond slightly and accounts for the similarity of the $\mathrm{Mn^{III}}$–C(sp^2) and $\mathrm{Mn^{III}}$–C(sp^3) distances.

Nature of the Intermediates Present before Oxidation. Treatment of diethyl ether suspensions of $\mathrm{MnX_2}$ (X = Cl, Br, I) with $^1/_2$ equiv of $\mathrm{Mg(Mes)_2(thf)_2}$ and 2 equiv of $\mathrm{PMe_3}$ yields pale yellow solutions of new monomesitylmanganese(II) species.

$$\mathrm{MnX_2 + {}^1\!/\!_2Mg(Mes)_2(thf)_2 + 2PMe_3 \rightarrow Mn(Mes)X(PMe_3)_2 + {}^1\!/\!_2MgX_2 + thf}$$

3a, X = Cl
3b, X = Br
3c, X = I

Although we have been unable to isolate these monomesityl complexes, they have been assigned monomeric, 13-electron manganese(II) structures of stoichiometry $\mathrm{Mn(Mes)X(PMe_3)_2}$ or $[\mathrm{Mn(Mes)X_2(PMe_3)}^-]$ on the basis of the known chemistry of alkylmanganese(II) species.[20,27] The X-band EPR spectra of solutions of the monomesityl intermediates were measured in diethyl ether glasses at liquid-nitrogen temperatures (see Figure 3). All of the spectra contain a strong signal at ca. 170 mT but also contain other absorptions that are halide-dependent. As the halide is changed from Cl to Br to I, the feature near 60 mT increases in relative intensity while the feature near 340 mT diminishes in relative intensity. The EPR spectra show that the monomesityl complexes are rhombically distorted high-spin $\mathrm{Mn^{II}}$ species that contain halide.[28,29] The stoichiometries $\mathrm{Mn(Mes)X(PMe_3)_2}$ and $[\mathrm{Mn(Mes)X_2(PMe_3)}^-]$ are both consistent with these observations. We were unable to determine the number of phosphine ligands bound to these intermediates since, as is usual for high-spin $\mathrm{Mn^{II}}$ complexes, the phosphorus hyperfine coupling is too small to be resolved.[20,27]

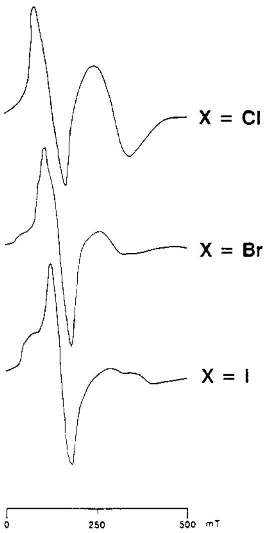

Figure 3. X-Band EPR spectra of the monomesityl intermediates **3a–c** in diethyl ether at −100 °C.

Addition of another $^1/_2$ equiv of dimesitylmagnesium to solutions of the monomesityl intermediates generates the manganese(II) diaryl $\mathrm{Mn(Mes)_2(PMe_3)_2}$ (**4**), which may be isolated as air-sensitive beige prisms from diethyl ether.

$$\mathrm{MnCl_2 + Mg(Mes)_2(thf)_2 + 2PMe_3 \rightarrow \underset{\textbf{4}}{Mn(Mes)_2(PMe_3)_2} + MgCl_2 + 2\,thf}$$

Complex **4** may also be prepared directly from $\mathrm{MnCl_2}$ in higher yield. This high-spin ($S = {}^5/_2$) manganese(II) complex is NMR silent and exhibits a typical rhombically distorted EPR spectrum that is similar to those of known $\mathrm{MnR_2L_2}$ species.[20,27] Interestingly, addition of $\mathrm{O_2}$ to $\mathrm{Mn(Mes)_2(PMe_3)_2}$ quickly leads to the formation of brown intractable solids from which no organomanganese species could be isolated.

Attempts To Prepare Manganese(III) Cyclopentadienyl Complexes. Thiele has recently reported that addition of 3 equiv of sodium cyclopentadienide to $\mathrm{Mn(acac)_3}$ in tetrahydrofuran gives a red-violet solution from which the manganese(III) salt $\mathrm{NaMnCp_4}$ could be obtained as a purple microcrystalline solid upon removal of the solvent.[17] We have been unable to reproduce this result. Addition of 1–4 equiv of NaCp to $\mathrm{Mn(acac)_3}$ in thf results in immediate decolorization of the solution and formation of a colorless precipitate; evidently, sodium cyclopentadienide reduces $\mathrm{Mn^{III}}$ to $\mathrm{Mn^{II}}$. We have been able to obtain red-violet solutions only if $\mathrm{O_2}$ is added to the reaction flask. After the addition of $\mathrm{O_2}$, a purple microcrystalline solid can be isolated by following Thiele's procedure, but in our hands this product contains no manganese (<1%). Microanalytical data have given a stoichiometry near $\mathrm{NaC_5H_5{\cdot}2thf}$, and infrared spectroscopy shows the presence of C=C functional groups. In summary, we have been unable to isolate any organomanganese(III) species by the reaction of $\mathrm{Mn(acac)_3}$ with NaCp; reduction to $\mathrm{Mn^{II}}$ occurs under anaerobic conditions, and only organic oxidation products are obtained upon addition of $\mathrm{O_2}$.

Concluding Remarks. The new manganese(III) aryl complexes $\mathrm{Mn(Mes)X_2(PMe_3)_2}$, where Mes = 2,4,6-trimethylphenyl, can be prepared by addition of $\mathrm{O_2}$ to suitable manganese(II) aryl intermediates. Unlike most 5-coordinate manganese(III) species, which adopt square-pyramidal structures, the aryl complexes are trigonal-bipyramidal like the chemically related iodo complex $\mathrm{MnI_3(PMe_3)_2}$.[8] The relationship between square-pyramidal

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and trigonal-bipyramidal geometries has been much discussed,[30-32] especially for low-spin complexes.[32] It is interesting that, despite a wide range ligands and d-electron configurations, all monomeric MX_3L_2 complexes of which we are aware are trigonal bipyramidal with the neutral Lewis bases in the axial sites. Among the first-row transition metals, examples are known for Ti,[33] V,[34-36] Cr,[33] Mn,[8] Fe,[37,38] Co,[39] Ni,[40-43] and Cu.[43] The preference for trigonal-bipyramidal structures has been rationalized on both steric[31] and electronic[32] grounds, and doubtlessly both effects are important.

The reaction chemistry of the high-valent aryl complexes and of the $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$ alkyls discussed in the previous paper is of interest and will be described separately.

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. Trimethylphosphine,[44] dimesitylmagnesium–bis(tetrahydrofuran),[45] *o*-tolyllithium,[46] and tris(acetylacetonato)manganese(III)[47] were prepared by literature routes. *N,N,N′,N′*-Tetramethylethylenediamine (tmed) was purchased from Aldrich and was distilled from and stored over sodium. Anhydrous $MnCl_2$ was prepared by heating manganese dichloride with thionyl chloride, followed by drying under vacuum at 200 °C. Anhydrous $MnBr_2$ and MnI_2[48] were prepared in diethyl ether from manganese powder and anhydrous HBr or I_2, respectively.

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 or frozen diethyl ether solutions at −100 °C. Magnetic moments were measured by a modification of Evans's method.[49] Melting points were determined on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

Bis[bis(*N,N,N′,N′*-tetramethylethylenediamine)lithium] Tetrakis(2-methylphenyl)manganate(II) (1). Method A. To a cold (−78 °C) suspension of $Mn(acac)_3$ (0.26 g, 0.74 mmol) in diethyl ether (50 mL) was added *o*-tolyllithium (12.5 mL of a 0.47 M solution in diethyl ether, 5.9 mmol); a yellow precipitate and a colorless solution formed immediately. The reaction mixture was warmed to room temperature to give a yellow solution and a white precipitate. To the filtered solution was added *N,N,N′,N′*-tetramethylethylenediamine (1 mL, 6.6 mmol), and the solution was concentrated to ca. 20 mL. The solution was cooled to −20 °C to give large golden prisms of the product, yield 0.33 g (68%).

Method B. To a cold (0 °C) suspension of $MnCl_2$ (0.34 g, 2.7 mmol) in diethyl ether (60 mL) was added *o*-tolyllithium (22.8 mL of a 0.47 M solution in diethyl ether, 10.7 mmol); a pale orange solution and a white precipitate formed immediately. To the filtered solution was added *N,N,N′,N′*-tetramethylethylenediamine (1 mL, 6.6 mmol), and the solution was concentrated to ca. 30 mL. The solution was cooled to −20 °C to yield large golden prisms, yield 1.34 g (56%). IR (cm^{-1}, KBr): 3087 w, 3011 s, 2789 s, 2705 w, 1562 w, 1371 m, 1358 s, 1289 s, 1270 m, 1247 m, 1236 s, 1176 m, 1161 s, 1129 s, 1097 s, 1071 s, 1033 s, 1014 s, 947 s, 859 vw, 787 s, 773 m, 742 s, 731 s, 709 m, 624 w, 589 m, 536 m, 494 m, 464 m, 442 m, 426 s, 382 s.

Dichloro(2,4,6-trimethylphenyl)bis(trimethylphosphine)manganese(III) (2a). To a mixture of $MnCl_2$ (0.90 g, 7.15 mmol) and dimesitylmagnesium–bis(tetrahydrofuran) (2.2 g, 5.4 mmol) was added diethyl ether (100 mL) and trimethylphosphine (1.45 mL, 14.3 mmol). After being stirred at room temperature for 6 h, the light yellow-orange solution was treated with dry O_2 (180 mL, 8.00 mmol) via a syringe to a balloon and a deep red color developed over 5 min. The balloon was removed, and the solution was stirred for an additional 3 h. The filtered solution was concentrated to 70 mL and cooled to −20 °C to give dark red prisms. Two additional crops were obtained by concentration and cooling of the supernatant; yield 0.41 g (14%). IR (cm^{-1}, KBr): 2992 s, 2839 s, 2014 w, 1709 w, 1539 w, 1414 s, 1400 m, 1298 m, 1283 s, 994 m, 949 vs, 844 s, 749 s, 744 s, 702 m, 672 w, 581 w, 544 w.

Dibromo(2,4,6-trimethylphenyl)bis(trimethylphosphine)manganese(III) (2b). To a cold (0 °C) suspension of $MnBr_2$ (0.42 g, 2.00 mmol) in diethyl ether (25 mL) was added trimethylphosphine (0.40 mL, 3.90 mmol) and a suspension of $Mg(Mes)_2(thf)_2$ (0.46 g, 1.15 mmol) in diethyl ether (25 mL). After being warmed to room temperature, the solution was clear yellow-orange. After the solution had been stirred for 30 min, dry oxygen (45 mL, 2.00 mmol) was injected by syringe, which immediately caused the solution to turn dark red. The solution was stirred for 3 h, and then the solvent was removed under vacuum. The residue was washed with pentane (50 mL) and extracted with diethyl ether (75 mL); the filtered solution was concentrated to ca. 50 mL and cooled to −20 °C to give large clusters of small dark red prisms. Additional crops of crystals were obtained by concentration and cooling of the supernatant; yield 0.11 g (11%). IR (cm^{-1}): 1582 w, 1408 m, 1289 w, 1271 m, 980 w, 931 s, 830 m, 730 m, 689 w, 654 w.

Diiodo(2,4,6-trimethylphenyl)bis(trimethylphosphine)manganese(III) (2c). To a cold (−78 °C) suspension of MnI_2 (0.42 g, 1.4 mmol) in diethyl ether (25 mL) was added trimethylphosphine (0.28 mL, 2.8 mmol) and a suspension of $Mg(Mes)_2(thf)_2$ (0.43 g, 1.1 mmol) in diethyl ether (25 mL). A reaction occurred immediately to give a colorless solution, which turned pale yellow-orange upon being warmed to room temperature. The solution was exposed to dry O_2 (45 mL, 2.00 mmol) via a syringe to a balloon, and a deep red color developed. After the solution had been stirred for 15 min, the solvent was removed under vacuum. The residue was washed with pentane (50 mL) and extracted with diethyl ether (80 mL); the filtered solution was concentrated to ca. 50 mL and cooled to −20 °C to give small dark red prisms. One additional crop of crystals was obtained by concentration and cooling of the supernatant; yield 76 mg (9%). IR (cm^{-1}): 1718 w, 1601 w, 1581 w, 1533 w, 1424 sh, 1412 s, 1392 sh, 1301 sh, 1295 m, 1276 s, 1261 sh, 1226 w, 1165 w, 985 m, 943 br, s, 883 w, 844 s, 741 s, 696 m, 667 m, 543 w.

Preparation of the Monomesityl Intermediates 3a (X = Cl), 3b (X = Br), and 3c (X = I). Solutions of the manganese monomesityl intermediates were prepared by interaction of the appropriate $\mathrm{Mn^{II}}$ halide with $^1/_2$ equiv of $Mn(Mes)_2(thf)_2$ and ca. 3 equiv of PMe_3 in diethyl ether at 25 °C. The solutions were stirred for 1 h, and aliquots of the clear supernatant were transferred to EPR tubes for study.

Bis(2,4,6-trimethylphenyl)bis(trimethylphosphine)manganese(II) (4). To a mixture of $MnCl_2$ (0.22 g, 1.7 mmol) and $Mg(Mes)_2(thf)_2$ (0.71 g, 1.7 mmol) at −78 °C was added diethyl

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ether (50 mL) and trimethylphosphine (0.34 mL, 3.4 mmol). The solution was warmed to room temperature and stirred for 3 h. The solution was filtered, concentrated to ca. 30 mL, and cooled to −20 °C to afford off-white prisms of the product, yield 0.43 g (59%). IR (cm^{-1}): 2724 w, 2706 w, 1748 w, 1715 w, 1685 w, 1590 m, 1531 s, 1392 s, 1304 s, 1282 s, 1252 m, 1213 s, 1025 m, 1008 m, 946 s br, 876 w, 844 s, 728 s, 706 w, 667 w, 575 w, 535 s, 483 w. EPR (PhMe glass, −196 °C): 60, 172, 275, 355 mT.

Crystallographic Studies.[50] Single crystals of $Mn(Mes)Br_2(PMe_3)_2$ (**2b**), grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. 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 III.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) by using measurement parameters listed in Table III. Systematic absences for $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) were consistent with the 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 0.324 and 0.276, respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods, SHELX, weighted and unweighted difference Fourier syntheses, and full-matrix least-squares methods. The positions of the manganese, bromine, phosphorus, and five carbon atoms were deduced from an E map. Subsequent difference Fourier calculations revealed the positions of the remaining nonhydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 4.70/(\sigma(F_o)^2 + (pF_o)^2)$.

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. Hydrogen atoms were included as fixed contributors in "idealized" positions with C–H = 0.95 Å. In the final 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 0.042 in the last cycle. Final refinement parameters are given in Table III. 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.

Acknowledgment. We thank the National Science Foundation (Grant CHE 89-17586) and the Office of Naval Research under their Young Investigator Award Program for support of this research and Lubrizol and Quantum Chemicals for fellowships to R.J.M. We particularly thank Dr. Scott Wilson and Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination. G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990) and a Henry and Camille Dreyfus Teacher-Scholar Award (1988–1993).

Supplementary Material Available: Tables of final atomic coordinates, anisotropic thermal parameters, and calculated hydrogen atom positions for **2b** (3 pages); a listing of final observed and calculated structure factor amplitudes for **2b** (8 pages). Ordering information is given on any current masthead page.

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

Stereoselective Synthesis of Diacids by the Nickel Cyanide and Phase-Transfer-Catalyzed Carbonylation of Alkynols. Novel Dependency of Product Stereochemistry and Optimum Stirring Speed on the Nature of the Phase-Transfer Agent

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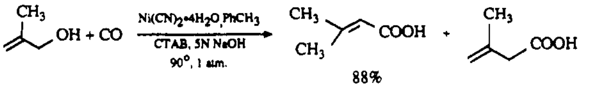
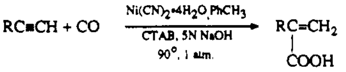
Received September 6, 1990

Alkynols react with carbon monoxide and catalytic amounts of nickel cyanide, under phase-transfer catalysis conditions [5 N NaOH, $PhCH_3$, $R_4N^+X^-$], to give unsaturated diacids in 83–95% yields. The stereoselectivity of the reaction is sensitive to the nature of the quaternary ammonium salt. Unusual stirring speed effects on the reaction rate were observed when tetrabutylammonium hydrogen sulfate or cetyltrimethylammonium bromide was used as the phase-transfer agent.

Carbonylation reactions are one of the most useful metal-catalyzed processes effected under phase-transfer conditions.[1] Recent investigations have indicated that nickel cyanide, a cheap metal catalyst, is effective for the carbonylation of a variety of organic substrates.[2-4] Of relevance to the present study are the observations that allyl alcohols can be directly carbonylated to acids (eq 1)[3] and that alkynes experience regiospecific hydrocarboxylation to unsaturated acids (eq 2).[4] It seemed



(1)



$$RC{\equiv}CH + CO \xrightarrow[\text{CTAB, 5N NaOH, 90°, 1 atm.}]{Ni(CN)_2\cdot 4H_2O,\ PhCH_3} \underset{\displaystyle COOH}{\underset{|}{RC}}{=}CH_2$$

(2)

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