

and angles, torsion angles, and least-squares planes (11 pages); a listing of experimental and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Isolation and Characterization of the First σ -Organomanganese(III) Complex. Crystal and Molecular Structure of (2,4,6-Trimethylphenyl)-dibromobis(trimethylphosphine)manganese(III)

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Received March 23, 1987

Summary: Alkylation of MnBr_2 with the mesityl (2,4,6-trimethylphenyl) reagent $\text{Mg}(\text{C}_6\text{H}_2\text{Me}_3)_2(\text{THF})_2$ in the presence of trimethylphosphine followed by reaction with 1 equiv of oxygen yields dark red crystals of $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$, which is the first isolated example of a σ -organomanganese(III) complex. This high-spin ($\mu = 4.8 \mu_B$) complex adopts a distorted trigonal-bipyramidal structure of approximate C_{2v} symmetry with the phosphine ligands occupying the axial sites. The metal-ligand distances are consistent with a trivalent oxidation state, while the orientation of the mesityl ring in the equatorial plane and the interligand angles can be rationalized on steric grounds.

The chemistry of manganese in its trivalent oxidation state is of interest due to the role of Mn^{III} in biological redox reactions¹⁻¹² and as inorganic oxidants;¹³⁻¹⁵ the recently demonstrated ability of high-valent manganese porphyrin complexes to oxidize alkanes has stimulated substantial efforts to determine the mechanistic details of manganese-mediated organic oxidation processes.¹⁶⁻²¹ Despite these studies, in no case has a manganese(III)

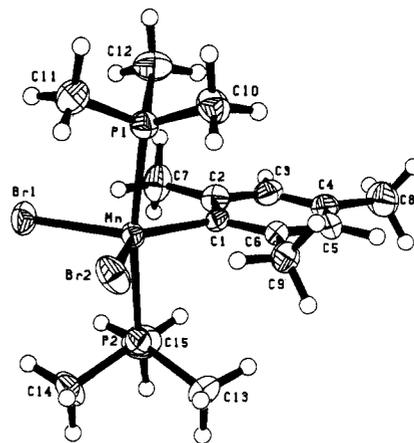


Figure 1. Molecular structure of $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$. Important bond distances (Å) and angles (deg): $\text{Mn}-\text{C}1 = 2.089$ (8), $\text{Mn}-\text{P}1 = 2.424$ (3), $\text{Mn}-\text{P}2 = 2.427$ (3), $\text{Mn}-\text{Br}1 = 2.505$ (1), $\text{Mn}-\text{Br}2 = 2.490$ (2), $\text{C}1-\text{Mn}-\text{Br}1 = 128.6$ (2), $\text{C}1-\text{Mn}-\text{Br}2 = 129.8$ (2), $\text{C}1-\text{Mn}-\text{P}1 = 86.0$ (2), $\text{C}1-\text{Mn}-\text{P}2 = 85.9$ (2), $\text{P}1-\text{Mn}-\text{P}2 = 171.6$ (1), $\text{Br}1-\text{Mn}-\text{Br}2 = 101.68$ (6).

compound been prepared that contains a metal-carbon σ -bond. We now report the synthesis and characterization of an organomanganese(III) complex derived from a divalent starting material and molecular oxygen.

Interaction of MnBr_2 in diethyl ether with trimethylphosphine²²⁻²⁶ and $1/2$ equiv of the mesityl (2,4,6-trimethylphenyl) reagent $\text{Mg}(\text{C}_6\text{H}_2\text{Me}_3)_2(\text{THF})_2$ ²⁷ generates pale yellow solutions of a monomesityl intermediate that is assigned a monomeric, 13-electron manganese(II) structure of stoichiometry $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}(\text{PMe}_3)_2$ or $[\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2]^-$, on the basis of previous studies of the reactions of manganese dihalides with alkylmagnesium reagents and phosphines.²⁸⁻³¹ Although the monomesityl intermediate has not yet been obtained as a pure material, addition of an additional $1/2$ equiv of dimesitylmagnesium generates $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)_2(\text{PMe}_3)_2$,³² which may be isolated as air-sensitive, pale yellow prisms by crystallization from diethyl ether. This 13-electron complex possesses an EPR spectrum essentially identical with those of other rhombically distorted $S = 5/2$ complexes such as $\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2(\text{PMe}_3)_2$ ²⁸ and $\text{Mn}(t\text{-Bu})_2(\text{dmpe})$,²⁹ where dmpe is 1,2-bis(dimethylphosphino)ethane. Interestingly, these manganese(II) dialkyl species have been reported to give brightly colored solutions upon reaction with oxygen, but no organometallic products could be isolated;^{28,31} identical behavior is observed upon oxidation of $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)_2(\text{PMe}_3)_2$.

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- (32) Yield: 61%. Anal. Calcd: C, 64.7; H, 9.05. Found: C, 63.2; H, 8.86. The carbon analyses are low evidently due to the air-sensitive nature of the complex and the volatility of the phosphine ligand.

Similarly, the pale yellow solutions of the manganese(II) monomesityl intermediate instantly turn bright red upon addition of 1 mol of dry oxygen/mol of manganese(II). Unlike previous studies, however, the color is persistent, and removal of the solvent followed by crystallization from diethyl ether gives deep red prisms of the new manganese(III) aryl complex $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$.³³ This 14-electron compound is high-spin in solution ($\mu = 4.8 \mu_B$) and is EPR silent; the ^1H NMR spectrum shows shifted and broadened peaks, as expected from the paramagnetism. The complex is unique in being the only σ -organomanganese(III) complex prepared to date, and there are only three other manganese(III) phosphine complexes of any kind: $\text{MnI}_3(\text{PMe}_3)_2$,²⁶ $\text{MnH}_3(\text{dmpe})_2$,²⁹ and $[\text{MnCl}_2(\text{dmpb})_2]^+$,³⁴ where dmpb is 1,2-bis(dimethylphosphino)benzene.

The X-ray crystal structure³⁵ reveals that the $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$ molecule (Figure 1) possesses a distorted trigonal-bipyramidal structure with the phosphine ligands occupying the axial sites; the overall coordination geometry is similar to that described for the manganese complex $\text{MnI}_3(\text{PMe}_3)_2$ ²⁷ and the rhenium species $\text{RePh}_3(\text{PEt}_2\text{Ph})_2$.^{36,37} The phosphines are bent toward the mesityl group and away from the bromide ligands, $\text{P-Mn-P} = 171.61 (10)^\circ$, evidently due to the relative sizes of C and Br. 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 $\text{MnI}_3(\text{PMe}_3)_2$ ²⁷ and longer than the 2.344 Å distance in the low-spin octahedral manganese(III) complex, $[\text{MnCl}_2(\text{dmpb})_2]^+$.³⁴ 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 $\text{MnBr}_2(\text{dmpe})_2$.³⁰

The mesityl group and the bromide ligands occupy the molecular equatorial plane, with the ortho methyl groups of the aryl ring fitting into the "notch" formed by the axial phosphines. The Mn-C(sp²) distance of 2.089 (8) Å is somewhat short relative to the Mn-C(sp²) contact of 2.11 (1) Å reported for the Mn^{II} mesityl complex³⁸ $[\text{Mn}$

$(\text{C}_6\text{H}_2\text{Me}_3)_2]_3$ and the 2.10–2.20 Å range reported for other Mn^{II} aryl complexes^{28–31} but is comparable to the 2.06–2.12 Å distances observed in the Mn^{IV} aryl $\text{MnMe}_4(\text{dmpe})$.³⁹ These trends are fully explicable in terms of the decreasing size of the metal center with increasing oxidation state⁴⁰ and the differences in the covalent radii of sp² vs. sp³ carbon atoms.⁴¹

The isolation of an organomanganese(III) complex is somewhat surprising in view of the tendency of Mn^{III} either to reduce to Mn^{II} or disproportionate to Mn^{II} and Mn^{IV}.¹³ For example, alkylation of the trivalent β -diketonate complex $\text{Mn}(\text{acac})_3$ with methyllithium and dmpe rapidly gives the disproportionation products $\text{MnMe}_2(\text{dmpe})_2$ and $\text{MnMe}_4(\text{dmpe})$ without any Mn^{III} intermediates being observable even at -78°C .³⁹ The isolation of the present compound suggests that while the high-valent manganese species studied to date invariably react with organic substrates via electron transfer, i.e., radical pathways,^{16–20} there may in fact be a significant chemistry of organic groups bound directly to a tri- or tetravalent manganese center. Such chemistry may lead to further advances in the regioselectivity possible in the oxidation of alkanes and other organic substrates by high-valent manganese reagents.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program (Contract N00014-86-K-0638) for support of this research and Lubrizol for a fellowship (R.J.M.). We particularly thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination.

Supplementary Material Available: Tables of final atomic parameters and bond lengths and angles for $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$ (5 pages); a listing of observed and calculated structure factors for $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$ (8 pages). Ordering information is given on any current masthead page.

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(33) To a suspension of MnBr_2 (0.42 g, 2.00 mmol) in diethyl ether (25 mL) at 25°C was added trimethylphosphine (0.40 mL, 3.90 mmol) and $\text{Mg}(\text{C}_6\text{H}_2\text{Me}_3)_2(\text{THF})_2$ (0.46 g, 1.15 mmol) suspended in diethyl ether (25 mL), giving a clear yellow-orange solution. After the solution was stirred for 15 min, dry oxygen (45 mL, 2.00 mmol) was injected by syringe, immediately causing the solution to turn dark red. After the solution was stirred for 3 h, the solvent was removed under vacuum. The residue was washed with pentane (50 mL) and extracted with diethyl ether (75 mL), and the filtered solution was concentrated to ca. 50 mL. Cooling to -20°C resulted in the formation of large clusters of small dark red prisms. Two additional crops of crystals were obtained from the supernatant. Yield: 0.11 g (11%). Anal. Calcd: C, 37.1; H, 6.01; Br, 32.9; Mn, 11.3. Found: C, 36.3; H, 5.92; Br, 34.0; Mn, 11.3. Mp. 110°C , dec.

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(35) Dark red single crystals of $\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3)\text{Br}_2(\text{PMe}_3)_2$ grown from diethyl ether are monoclinic, space group $P2_1/n$, with $a = 8.956 (3) \text{ \AA}$, $b = 25.228 (8) \text{ \AA}$, $c = 9.472 (3) \text{ \AA}$, $\beta = 100.29 (2)^\circ$, $V = 2106 (1) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 1.533 \text{ g cm}^{-3}$, $\mu_{\text{calcd}} = 45.04 \text{ cm}^{-1}$. X-ray diffraction data were collected on a $0.3 \times 0.3 \times 0.4 \text{ mm}$ crystal for 4387 independent reflections having $2\theta < 53^\circ$ and for $\pm h, \pm k, \pm l$ on a Syntex $P2_1$ automated diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, and ω/θ scans. The space group was unambiguously determined from the systematic absences. Refinement proceeded after averaging of nonunique data and correcting for Lorentz, polarization, crystal decay ($<10\%$), anomalous dispersion, and absorption effects; for the last, the maximum and minimum transmission factors were 0.324 and 0.276, respectively. The structure was solved by direct methods, followed by least-squares difference Fourier syntheses. The final residuals for 182 variables refined against the 1835 data for which $I > 2.58\sigma(I)$ were $R_F = 0.050$ and $R_{wF} = 0.048$. All non-hydrogen atoms were refined with anisotropic thermal coefficients, while a group isotropic thermal parameter was varied for the hydrogen atoms, which were included as fixed contributors in idealized positions with C-H = 0.96 Å; the hydrogen atoms of the mesityl methyl groups were placed in arbitrary rotational conformations about the C-CH₃ bonds.

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Ligand Rearrangements in Dinuclear Iron Carbonyl Complexes. A Novel Delocalized Bridging Vinylcarbene Complex

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Received March 30, 1987

Summary: Reaction of $[\text{Li}][(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]$ salts with ethoxyacetylene followed by reaction of the anionic intermediate with an electrophile yields bridging vinylcarbene or bridging α,β -unsaturated acyl products resulting from unusual intramolecular rearrangement chemistry involving vinyl and carbonyl ligands.

Recently, we reported the synthesis of unusual dinuclear (σ,π -vinyl thioketal)- and (σ,π -vinyl thio ester)iron carbonyl