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Oxidations of Hydrocarbons by Manganese(III) Tris(hexafluoroacetylacetonate)

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$Mn(hfacac)_3$ is an easily prepared and reactive oxidant (hfacac = hexafluoroacetylacetonate). It forms stable solutions in benzene and methylene chloride but is rapidly reduced in acetonitrile, DMSO, acetone, and ethers. It is reduced by ferrocene to give the Mn(II) complex $[Cp_2Fe][Mn(hfacac)_3]$, which has been structurally characterized. $Mn(hfacac)_3$ also rapidly oxidizes 1-acetylferrocene, 1,1′-diacetylferrocene, and tris(4-bromophenyl)amine. Based on an equilibrium established with tris(2,4-dibromophenyl)amine, a redox potential of 0.9 ± 0.1 V vs $Cp_2Fe^{+/0}$ is calculated. $Mn(hfacac)_3$ oxidizes 9,10-dihydroanthracene (DHA) cleanly to anthracene, with a bimolecular rate constant of 6.8×10^{-4} M^{-1} s^{-1} at 25 °C in benzene solution. In the presence of small amounts of water, the manganese(II) product is isolated as *cis*-$Mn(hfacac)_2(H_2O)_2$, which has also been structurally characterized. $Mn(hfacac)_3$ also oxidizes xanthene to 9,9′-bixanthene, 1,4-cyclohexadiene to benzene, and 2,4-di-*tert*-butylphenol to the phenol dimer. Toluene and substituted toluenes are oxidized to tolylphenylmethanes. Product analyses and relative rates—for instance that *p*-methoxytoluene reacts much faster than toluene—indicate that the more electron rich substrates react by initial electron transfer to manganese. For the less electron rich substrates, such as 1,4-cyclohexadiene, a mechanism of initial hydrogen atom transfer to $Mn(hfacac)_3$ is suggested. The ability of $Mn(hfacac)_3$ to abstract $H^{\bullet}$ is reasonable given its high redox potential and the basicity of $[Mn(hfacac)_3]^-$. In CH_2Cl_2 solution, oxidation of DHA is catalyzed by chloride ion.

Introduction

Oxidations of organic compounds by manganese(III) complexes have long been of interest because Mn^{III} is used as a stoichiometric oxidant in lab-scale syntheses and as a catalyst in industrial processes.[1−3] For instance, Mn(III) is a component of the catalyst for *p*-xylene oxidation to terephthalic acid in the Amoco-Mid Century process.[2] Further interest derives from reports that a low molecular weight manganese(III) complex is responsible for the biological degradation of lignin in woody material.[4] The heme-iron enzyme manganese peroxidase catalyzes the oxidation of Mn(II) to Mn(III), which is stabilized by organic acid chelates such as oxalate, lactate, and malonate.[5] The resulting freely diffusible low molecular weight manganese complex can oxidize alkyl aromatic and phenolic substrates with weak C−H and O−H bonds, including lignin model compounds.[6]

Previous work on Mn(III) oxidants has focused on manganese acetate, manganese pyrophosphates, manganese sulfate, manganese fluoride, and manganese acetylacetonate ($Mn(acac)_3$).[1,7] Understanding these oxidations has been complicated by the difficulty in determining the speciation of the manganese, especially the ligand environment of the

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(1) (a) De Klein, W. J. In *Organic Syntheses By Oxidation With Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 261−314. (b) Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, 1981; pp 1−25.

(2) (a) Olah, G. A.; Molnár, Á. *Hydrocarbon Chemistry*; Wiley: New York, 1995; pp 375 ff. (b) Partenheimer, W. *Catal. Today* **1995**, *23*, 69. (c) For a recent leading reference, see: Jiao, X. D.; Metelski, P. D.; Espenson, J. H. *Inorg. Chem.* **2001**, *40*, 3228−3233.

(3) Chiswell, B.; McKensie, E. D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 1, pp 88−90.

(4) (a) Joshi, D. K.; Gold, M. H. *Biochemistry* **1994**, *33*, 10969−10976. (b) Wariishi, H.; Valli, K.; Gold, M. H. *Biochemistry* **1989**, *28*, 6017−6023. (c) Banci, L.; Ciofi-Baffoni, S.; Tien, M. *Biochemistry* **1999**, *38*, 3205−3210. (d) Wariishi, H.; Akileswaran, L.; Gold, M. H. *Biochemistry* **1988**, *27*, 5365−5370. (e) Kishi, K.; Wariishi, H.; Marquez, L.; Dunford, H. B.; Gold, M. H. *Biochemistry* **1994**, *33*, 8694−8701.

(5) Kishi, K.; Wariishi, H.; Marquez, L.; Dunford, H. B.; Gold, M. H. *Biochemistry* **1994**, *33*, 8694−8701.

(6) See, for example: (a) Valli, K.; Gold, M. H. *J. Bacteriol.* **1991**, *173*, 345−352. (b) Reddy, G. V. B.; Gelpke, M. D. S.; Gold, M. H. *J. Bacteriol.* **1998**, *180*, 5159−5164. (c) See also refs 4b,c above.

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reactive material. For example, manganese(III) acetate in acetic acid has been used to oxidize alcohols, phenols, aromatic ethers, and especially hydrocarbons (as in the Mid Century process), but the manganese speciation under these conditions is complex.[2c,3]

Presented here are chemical properties and oxidation reactions of manganese(III) hexafluoroacetylacetonate, Mn(hfacac)$_3$.[8] This complex is readily prepared from Mn_2O_3 and H-hfacac. It is soluble and reactive as a well-defined molecular species in low-polarity solvents. Previous studies of Mn(III) oxidations have indicated mechanisms of initial electron transfer or formation of dissociated ligand radicals. This study indicates that Mn(hfacac)$_3$ reacts either by electron transfer or by hydrogen atom abstraction. These are reasonable pathways because Mn(hfacac)$_3$ is a strong outer-sphere oxidant (being reduced to Mn(II)) and the reduced form [Mn(hfacac)$_3$]$^-$ can be protonated at a hfacac$^-$ ligand. We have previously shown that a variety of compounds which contain an oxidizing metal center and a basic ligand site can abstract hydrogen atoms from organic substrates.[7,9]

Experimental Section

General Considerations. All experiments were performed under an N_2 atmosphere using standard techniques unless otherwise noted. Solvents (including deuterated solvents from Cambridge Isotope) were degassed and dried according to standard procedures.[10] Dihydroanthracene (DHA) was recrystallized twice from absolute EtOH, 2,4-di-*tert*-butylphenol was sublimed, and toluene was dried over Na and vacuum transferred prior to use. Other reagents were purchased from Aldrich and used as received unless otherwise noted. 1-(4-Methoxyphenyl)-2,2-dimethyl-1-propanol[11] and 9,9′-bixanthene[12] were synthesized according to literature methods.

NMR spectra were recorded on Bruker AC-200 (^{1}H, ^{19}F), AF-300 (^{1}H, ^{19}F), and AM-500 (^{1}H) spectrometers at ambient temperatures and are reported in ppm relative to TMS (^{1}H) or external $CFCl_3$ (^{19}F). UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer and are reported as λ_{max} (nm) (ϵ, M^{-1} cm^{-1}). GC/MS spectra were obtained on a Hewlett-Packard 5971 instrument equipped with a nonpolar capillary column and a mass spectral analyzer. GC/FID spectra were obtained on a Hewlett-Packard 5890 instrument equipped with a similar column. Mass spectrometric analysis for [Cp_2Fe][Mn(hfacac)$_3$] was performed on an Esquire-LC electrospray ion trap mass spectrometer (Bruker/Hewlett-Packard). The sample was dissolved in acetonitrile and infused at a flow rate of 1 μL/min. Mn(hfacac)$_3$ was analyzed on a double-focusing mass spectrometer with reverse geometry (JEOL HX-110). A solid sample was introduced by a direct insertion probe (at room temperature) and ionized by electron impact (70 eV). CV data were collected on a BAS CV-27.

Synthesis of Mn^{III}(hfacac)$_3$. In a modification of the literature preparation,[8] a slurry of Mn_2O_3 (1.80 g, 11.4 mmol), H-hfacac (10.5 mL, 74.1 mmol, 6.5 equiv), and 25 mL of dry *n*-hexane was heated at reflux under N_2 for 24 h. The reaction mixture was cooled to −78 °C, and the liquid was decanted to isolate the dark green solid, which was further dried under dynamic vacuum. The crude product was sublimed twice under vacuum at ∼65−70 °C to give 3.5 g (45%) of black-green Mn(hfacac)$_3$. UV−vis (CH_2Cl_2): 276 (17000), 550 (200). ^{1}H NMR (CD_2Cl_2): 10.7 (s, 3 H). ^{19}F NMR (CD_2Cl_2): −47 ppm (s). Anal. Calcd for $C_{15}H_3F_{18}MnO_6$: C, 26.65; H, 0.44; N, 0. Found: C, 26.52; H, 0.49; N, 0. ESI-MS: *m*/*z* 676 (M^+), 469, 400, 262, 212, 139, 69.

Synthesis of [Cp_2Fe][Mn(hfacac)$_3$]. A solution of Mn(hfacac)$_3$ (0.1 g, 0.15 mmol), Cp_2Fe (20 mg, 0.11 mmol), and 10 mL of pentane was stirred at room temperature for 20 min. The blue solid was filtered and washed with additional pentane (0.05 g, 53%). X-ray quality crystals were obtained by slow diffusion of pentane into a saturated solution in CH_2Cl_2. ^{1}H NMR (CD_2Cl_2): 38 (br, Cp_2Fe^+; shifts upfield on addition of Cp_2Fe). UV−vis (CH_2Cl_2): 309 (660), 622 (255). ESI-MS: *m*/*z* 676, 207 (in the negative mode), 187, 186, 184, 155 (in the positive mode, displaying a characteristic iron isotope pattern). Anal. Calcd for $C_{25}H_{13}F_{18}FeMnO_6$: C, 34.83; H, 1.52; N, 0. Found: C, 34.87; H, 1.53; N, 0. **[^{n}Pr$_4$N][Mn(hfacac)$_3$]** was prepared similarly from Mn(hfacac)$_3$ (0.2 g, 0.3 mmol), ^{n}Pr$_4$NI (90 mg, 0.29 mmol), and 20 mL of CH_2Cl_2. After stirring for 20 min, the CH_2Cl_2 was removed under dynamic vacuum and the yellow solid washed with pentane (0.18 g, 72%). Anal. Calcd for $C_{27}H_{31}F_{18}MnNO_6$: C, 37.60; H, 3.62; N, 1.62. Found: C, 37.78; H, 3.60; N, 1.62. UV−vis (CH_2Cl_2): 314 (∼20000).

X-ray Structure Determinations of Mn(hfacac)$_2$(H$_2$O)$_2$ and [Cp_2Fe][Mn(hfacac)$_3$]. A yellow plate of Mn(hfacac)$_2$(H$_2$O)$_2$ and a blue plate of [Cp_2Fe][Mn(hfacac)$_3$] were mounted on glass capillaries with epoxy. Data were collected at 23 °C on a Nonius Kappa CCD diffractometer. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Disorder in the CF_3 groups was indicated by large anisotropic displacement parameters for the F atoms. All hydrogen atoms were located from difference maps and were refined with a riding model. Data were refined using SHELXL-97 and corrected by scaling and averaging using the program SCALEPACK.

Typical Procedure for Organic Oxidations. A solution of **xanthene** (16 mg, 90 μmol) and Mn(hfacac)$_3$ (9 μmol) in 3 mL of C_6H_6 turned yellow within 15 min. Bixanthene was observed by GC/MS *m*/*z* 181, M^+ (at twice the retention time of xanthene), 152, 69, 39 and confirmed by comparison with an authentic sample. In an alternative procedure, a J. Young sealable NMR tube was charged with **1,4-cyclohexadiene** (0.3 μL, 3.2 μmol), C_6D_6 (1 mL), and $(Me_3Si)_2O$ (1 μL) as an internal standard. An initial ^{1}H NMR spectrum was acquired. The tube was brought back into the drybox, Mn(hfacac)$_3$ (4 mg, 6.4 μmol) was added, and the reaction was monitored by ^{1}H NMR. Reactions of **1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol** were performed in a similar manner in both C_6D_6 and CD_2Cl_2; GC/MS showed (*m*/*z*) 136 (4-methoxybenzaldehyde) and 194 (starting material). Oxidations of DHA were monitored by GC/MS and ^{1}H NMR (as in the above procedures), and by UV−vis spectroscopy, where anthracene production was evident from its characteristic spectrum in CH_2Cl_2: 359 (8800), 378 (8200). Yellow crystals of **Mn(hfacac)$_2$(H$_2$O)$_2$** deposited (0.033 g, 60% yield from 0.07 g of Mn(hfacac)$_3$ and 0.093 g of DHA in

(7) We have also examined hydrocarbon oxidations by manganese μ-oxo dimers: (a) Wang, K.; Mayer, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 1470−1471. (b) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T. J.; Lovell, S.; Sadílek, M.; Tureek, F.; Mayer, J. M. Submitted.

(8) Evans, S.; Hamnett, A.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 227−250.

(9) (a) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441−450. (b) Roth, J. P.; Mayer, J. M. *Inorg. Chem.* **1999**, *38*, 2760−2761. (c) Lockwood, M. A.; Blubaugh, T. J.; Collier, A. M.; Lovell, S.; Mayer, J. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 225−227.

(10) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(11) (a) Baciocchi, E.; Bietti, M.; Putignani, L.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 5952−5960. (b) Baciocchi, E.; Bietti, M.; Lanzalunga, O. *Acc. Chem. Res.* **2000**, *33*, 243−251.

(12) Coellen, M.; Rüchardt, C. *Chem. Eur. J.* **1995**, *1*, 564−567.

CH_2Cl_2) upon exposure of the DHA reaction mix to air or degassed water.

Oxidation of Toluene and Substituted Toluenes. In a typical reaction, a thick-walled glass bomb was charged with 19 mg (28 μmol) of Mn(hfacac)$_3$ and 2.8 mmol of toluene, *p*-methoxytoluene, methylbenzotrifluoride, or *p*-nitrotoluene (100 equiv) in 5 mL of benzene. The solution sat at room temperature for several weeks. Periodically, the flask was brought into the drybox and an aliquot was removed and analyzed by GC/MS. The *p*-methoxytoluene solution had turned yellow in 14 days, and GC/MS revealed the methoxy-substituted tolylphenylmethane isomers (*m*/*z* 242) as well as an unidentified product (*m*/*z* 448 (M^+), 351, 331, 316, 301, 280, 165, 135, 105, 69). After 50 days at room temperature, the toluene and *p*-nitrotoluene flasks were heated to 100 °C for ~67 h, until the reaction mixtures had turned yellow. GC/MS analysis revealed the presence of tolylphenylmethane isomers (*m*/*z* 182) in the toluene reaction, but no product was observed in the *p*-nitrotoluene reaction mixture. The competition reactions were run under similar conditions with mixtures of toluenes. GC/MS of the methylbenzotrifluoride reaction mixture revealed 4-trifluorodiphenylmethane (*m*/*z* 236, *m*/*z* 241 from reaction in C_6D_6).

Kinetics Studies of the Oxidation of DHA. Kinetics studies were carried out under air-free conditions in sealable quartz cuvettes with pseudo-first-order conditions of excess DHA: typically 3 mM Mn(hfacac)$_3$ and 120 or 240 mM DHA in CH_2Cl_2 or C_6H_6. Kinetic data were typically gathered at 550 nm every 10−30 s over 4000−70000 s. All solutions were made up and mixed in a nitrogen-filled drybox, sealed, and then transported to the spectrophotometer. Rate constants were determined at four temperatures in the range 16−59 °C. At least four kinetics traces were acquired at each temperature. **Product autocatalysis** was observed in both benzene and CH_2Cl_2: A typical kinetics run with a large excess of DHA was set up in C_6H_6 or CH_2Cl_2 as above. After approximately 3 half-lives (20000 s for C_6H_6, 750 s for CH_2Cl_2) an additional 1 equiv of Mn(hfacac)$_3$ was added to the cuvette and the kinetics continued. The reaction of the second aliquot of Mn(hfacac)$_3$ was faster than the first.

Estimation of Redox Potential of Mn(hfacac)$_3$. UV−vis spectra were recorded for CD_2Cl_2 solutions containing 3 mM Mn(hfacac)$_3$ and either Cp_2Fe, acetylferrocene,[13] 1,1′-diacetylferrocene,[14] (4-$BrC_6H_4)_3N$, or (2,4-$Br_2C_6H_3)_3N$.[15] It was assumed that (2,4-$Br_2C_6H_3)_3N$ has the same ϵ as (4-$BrC_6H_4)_3N$ (λ_{max} = 720 nm, $\epsilon = 3 \times 10^4$).[16] Cyclic voltammograms of the amines were acquired from +2.0 to −1.7 V, with scan rates of 0.1 and 1.0 V/s, in CH_2Cl_2 with 0.1 M $^nBu_4NPF_6$ with a Ag/Ag^+ reference electrode and Cp_2Fe as an internal standard: (4-$BrC_6H_4)_3N$, 0.7 V, (2,4-$Br_2C_6H_3)_3N$, 1.2 V (both vs $Cp_2Fe^{+/0}$); peak separations were comparable to that of Cp_2Fe.

Results

Synthesis, Characterization, and Properties of Mn(hfacac)$_3$. Preparation of Mn(hfacac)$_3$ from Mn_2O_3 and 6 equiv of hexafluoroacetylacetone[8,17] requires water-free solvent in order to avoid the addition of water to the fluorinated pentanedione.[18] Mn(hfacac)$_3$ is quite volatile and is readily purified by sublimation. While its X-ray structure has been reported,[17] there is little published spectroscopic data for this complex. Mass spectrometry gives the correct *m*/*z*, and the fragmentation pattern matches those described in the literature for similar complexes.[19] ^{1}H NMR and ^{19}F NMR spectra in CD_2Cl_2 consist of single broad peaks at δ 10.7 ppm (^{1}H) and −47 ppm (^{19}F). The UV−vis spectrum contains a well-defined d → d transition at 550 nm (ϵ = 200 M^{-1} cm^{-1}). Mn(hfacac)$_3$ is soluble and stable in hydrocarbon and chlorinated solvents, but decomposes rapidly in acetonitrile, DMSO, THF, acetone, and ethers. Decomposition is indicated by a rapid color change from green-brown to light yellow. Since the Mn(II) compounds in this system are yellow, decomposition is most likely a result of reduction of Mn(hfacac)$_3$ by the solvent. As a result, all oxidation reactions have been carried out in methylene chloride, hydrocarbon solvents, or neat substrate. Mn(hfacac)$_3$ reacts with acetylacetone to give a mixture of products, including free H-hfacac (by NMR).

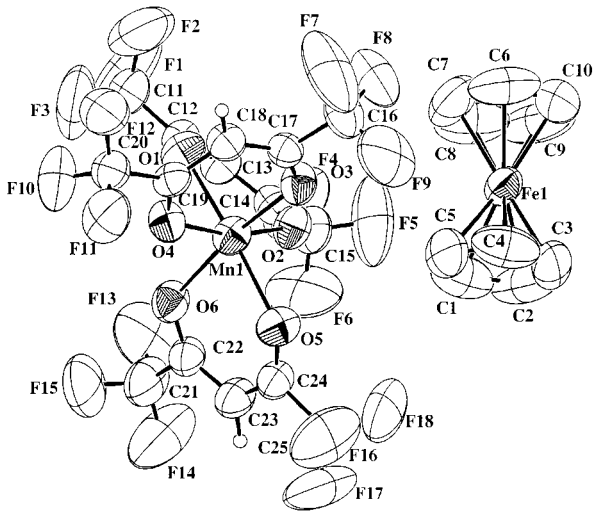


Figure 1. ORTEP drawing of [Cp_2Fe][Mn(hfacac)$_3$].

Ferrocene rapidly reduces Mn(hfacac)$_3$, forming the blue ferrocenium salt [Cp_2Fe][Mn^{II}(hfacac)$_3$]. ^{1}H NMR and UV−vis spectra of the product show the presence of Cp_2Fe^+. Electrospray ionization mass spectrometry in the negative ion mode reveals a parent ion for [Mn^{II}(hfacac)$_3$]$^-$ (*m*/*z* 676) and in the positive mode shows the characteristic pattern for Cp_2Fe^+(centered at *m*/*z* 186). Mn(hfacac)$_3$ is also reduced by $^nPr_4NI$, giving [$^nPr_4N$][Mn^{II}(hfacac)$_3$] and iodine. The X-ray structure of [Cp_2Fe][Mn^{II}(hfacac)$_3$] (Figure 1, Tables 1 and 2) shows a regular octahedral manganese complex, in contrast to the Jahn−Teller distorted d^4 Mn(hfacac)$_3$. The Mn^{II}−O bond lengths in the d^5 anion (2.158 ± 0.019 Å) are comparable to the longer distances in the distorted manganese(III) compound (two at 2.144 ± 0.003 Å and four at 1.922 ± 0.016 Å).[17]

(13) Mayo, D. W.; Pike, R. M.; Butcher, S. S. *Microscale Organic Laboratory*, 2nd ed.; Wiley: New York, 1989; pp 291−295.
(14) Schwink, L.; Knochel, P. *Chem. Eur. J.* **1998**, *4*, 950−968.
(15) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577−585.
(16) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, *19*, 2719−2720.
(17) Bouwman, E.; Caulton, K. G.; Christou, G.; Folting, K.; Gasser, C.; Hendrickson, D. N.; Huffman, J. C.; Lobkovsky, E. B.; Martin, J. D.; Michel, P.; Tsai, H.; Xue, Z. *Inorg. Chem.* **1993**, *32*, 3463−3470.
(18) H_2O + H-hfacac gives the bis(*gem*-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol.[17]
(19) Reichert, C.; Bancroft, G. M.; Westmore, J. B. *Can. J. Chem.* **1970**, *48*, 1362−1370.

Table 1. Crystallographic Data for *cis*-$Mn(hfacac)_2(H_2O)_2$ and $[Cp_2Fe][Mn^{II}(hfacac)_3]$

empirical formula	$C_{10}H_6F_{12}MnO_6$	$C_{25}H_{13}F_{18}FeMnO_6$
fw	505.09	862.14
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
unit cell dimens		
a (Å)	21.760(3)	8.5403(3)
b (Å)	8.2466(13)	20.3938(9)
c (Å)	9.8746(7)	18.3572(7)
β (deg)	96.346(8)	100.187(2)
vol ($Å^3$)	1761.1(4)	3146.9(2)
Z	4	4
density (calcd, Mg/m^3)	1.905	1.820
abs coeff (mm^{-1})	0.898	1.008
λ (Å)	0.71070	0.71070
cryst size (mm)	0.21 × 0.08 × 0.04	0.35 × 0.28 × 0.20
temp (K)	296(2)	296(2)
θ range (deg)	2.64−29.35	2.25−30.51
index ranges	$-26 \le h \le 26$	$-11 \le h \le 11$
	$-10 \le k \le 10$	$-26 \le k \le 28$
	$-10 \le l \le 10$	$-25 \le l \le 25$
reflns/unique	18762/1880	58116/8084
R_{int}	0.0661	0.0480
R1, wR2	0.0439, 0.1107	0.0742, 0.2599
GOF on F^2	0.933	0.954

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Mn(hfacac)_3$, $[FeCp_2][Mn(hfacac)_3]$, and $Mn(hfacac)_2(H_2O)_2$

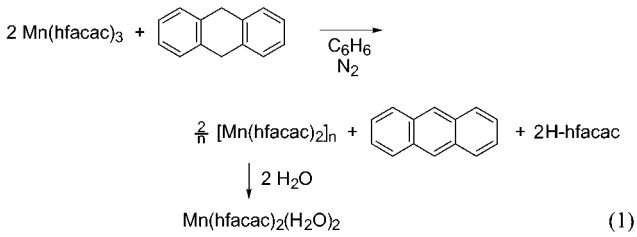
	$Mn(hfacac)_3$[a]	$[Mn(hfacac)_3]$-$[FeCp_2]$	$Mn(hfacac)_2$-$(H_2O)_2$
Mn−O(1)	1.9121(25)	2.169(4)	2.162(2)
Mn−O(2)	2.1410(25)	2.168(4)	2.1400(18)
Mn−O(3)	1.9063(24)	2.144(4)	2.162(2)
Mn−O(4)	2.1469(25)	2.139(4)	2.1401(18)
Mn−O(5)	1.9372(25)	2.157(4)	2.167(2)[b]
Mn−O(6)	1.9327(24)	2.170(4)	2.167(2)[b]
O(1)−Mn−O(2)	82.23(14)	87.71(10)	82.61(7)
O(2)−Mn−O(4)	167.11(15)	177.62(10)	171.39(11)
O(3)−Mn−O(6)	171.28(15)	179.03(11)	170.06(8)[b]
O(4)−Mn−O(3)	82.89(13)	88.39(10)	82.61(7)
O(5)−Mn−O(1)	169.96(14)	178.58(10)	170.06(8)[b]
O(6)−Mn−O(5)	82.35(15)	90.26(10)	83.78(11)[b]

[a] Reference 17. [b] O(5) and O(6) in this structure are part of water molecules, not hfacac ligands.

A redox potential has not been reported for $Mn(hfacac)_3$, but its free energy of electron attachment in the gas phase has been estimated to be −109 kcal mol^{-1} at 350 K.[20] Our attempts at electrochemical measurements have been frustrated by reactions with solvent (MeCN, DMSO) or apparently with supporting electrolyte ($^nBu_4NPF_6$ in CH_2Cl_2). The potential has therefore been estimated using reactions with ferrocene derivatives and bromoarylamines. In CH_2Cl_2, $Mn(hfacac)_3$ oxidizes ferrocene, 1-acetylferrocene (+0.27 V), 1,1′-diacetylferrocene (+0.49 V), and tris(4-bromophenyl)amine (+0.7 V). The quoted potentials are for methylene chloride, vs $Cp_2Fe^{+/0}$.[21] $Mn(hfacac)_3$ does not fully oxidize tris(2,4-dibromophenyl)amine, but an equilibrium is established, with $K_{eq} \cong 3 \times 10^{-5}$ by UV−vis spectroscopy. The potential for tris(2,4-dibromophenyl)amine in CH_2Cl_2 is measured at +1.2 V vs $Cp_2Fe^{+/0}$, close to the reported value of +1.14 V vs $Cp_2Fe^{+/0}$ in acetonitrile.[21b] Combining this potential with the observed K_{eq} gives the $Mn(hfacac)_3$ potential as 0.9 ± 0.1 V vs $Cp_2Fe^{+/0}$ in CH_2Cl_2.

The basicity of the manganese(II) anion, $[^nPr_4N][Mn(hfacac)_3]$, has been probed in a similar manner by reaction with standard acids. No reaction is observed with lutidinium perchlorate, which has a pK_a of 14.0 in acetonitrile, but protonation is observed with *p*-toluenesulfonic acid (pK_a of 8.01 in MeCN)[22] to give H-hfacac.

Oxidations of Organic Compounds. $Mn(hfacac)_3$ reacts with 9,10-dihydroanthracene (DHA) in benzene solution to produce anthracene in 98% yield in a matter of hours at room temperature (eq 1). Following the reaction by ^1H NMR



(1)

spectroscopy shows the disappearance of both DHA and $Mn(hfacac)_3$ and shows the appearance of anthracene and free hexafluoroacetylacetone (H-hfacac, the protonated ligand). ^{19}F NMR spectroscopy confirms the conversion of bound $hfacac^-$ (−47 ppm) to unbound H-hfacac (−75 ppm). The H-hfacac peak has ca. 28% of the integrated intensity of the starting $Mn(hfacac)_3$. Considering the 3:1 hfacac stoichiometry in eq 1, the integration corresponds to an 85% yield of H-hfacac. The inorganic product of the reaction has no apparent NMR signal. UV−vis spectroscopy similarly shows the conversion of brown-green $Mn(hfacac)_3$ to yellow manganese(II) complex(es), and the characteristic anthracene bands are readily apparent. Although no spectroscopic method allows observation of all the products, the data indicate that the bulk of the reaction follows the balanced equation written in eq 1.

Aerobic reactions of $Mn(hfacac)_3$ and DHA in undried solvents give anthraquinone and anthrone (presumably by an autoxidation pathway) and precipitate yellow crystals. An X-ray crystal structure showed the yellow product to be *cis*-$Mn(hfacac)_2(H_2O)_2$ (Figure 2, Tables 1 and 2). This structure differs from the previously reported structure of *trans*-$[Mn(hfacac)_2(H_2O)_2]H_2O$[23] in both the number and the stereochemistry of water molecules. No precipitate is observed when the reaction is run under air/water-free conditions, even after extended periods of time. Addition of degassed water to yellow reaction solutions yields *cis*-$Mn(hfacac)_2(H_2O)_2$. The inorganic product of reaction 1 in the absence of water is most likely an oligomeric Mn(II) complex, $[Mn(hfacac)_2]_n$, by analogy with trimeric $[Mn(acac)_2]_3$.[24]

(20) Sharpe, P.; Eyler, J. R.; Richardson, D. E. *Inorg. Chem*. **1990**, *29*, 2779−2787.
(21) (a) Geiger, W. E. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier Science Pub.: Amsterdam, 1990; pp 142−172. (b) Connelly, N. G.; Geiger, W. E. *Chem. Rev*. **1996**, *96*, 877−910.
(22) Izutsu, K. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, 1990; Vol. 21, p 28
(23) Dickman, M. H. *Acta Crystallogr*. **1997**, *C53*, 402−404.
(24) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; pp 479−482.

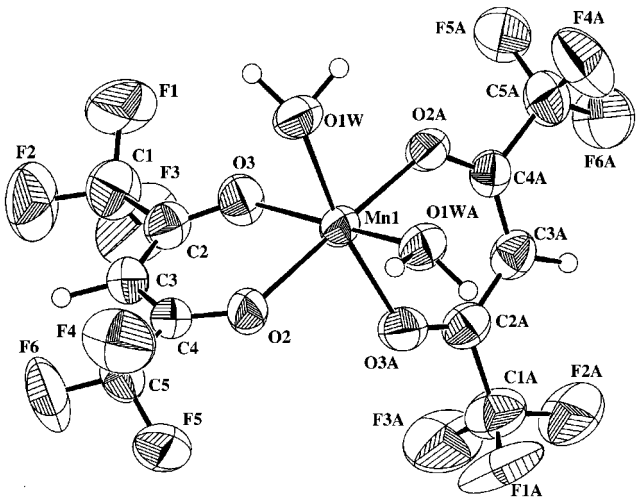
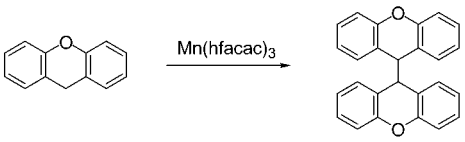


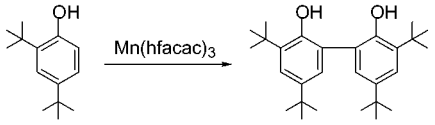
Figure 2. ORTEP drawing of Mn(hfacac)$_2$(H$_2$O)$_2$.

Reactions of Mn(hfacac)$_3$ with other organic substrates are similar to the DHA reaction, with conversion of green-brown Mn(III) to yellow Mn(II). In benzene solution, xanthene is converted within minutes to 9,9′-bixanthene in 30(±10)% yield by GC/FID (using 9,9′-bifluorene as an integration standard; eq 2). The identity of 9,9′-bixanthene was indicated



(2)

by GC/MS (retention time twice that of xanthene, a small M^+ and large $0.5M^+$ in the MS) and was confirmed by independent synthesis.[12] 1,4-Cyclohexadiene is oxidized to benzene in 82% yield over a period of days (by ^{1}H NMR in C_6D_6). Both reactions are considerably faster in methylene chloride (vide infra). 2,4-Di-*tert*-butyl phenol is oxidized to the bis(phenol) in essentially quantitative yield (by NMR) after a few minutes in C_6H_6 and 78% yield (by NMR) in CD_2Cl_2 (eq 3). No other products were identified; presumably

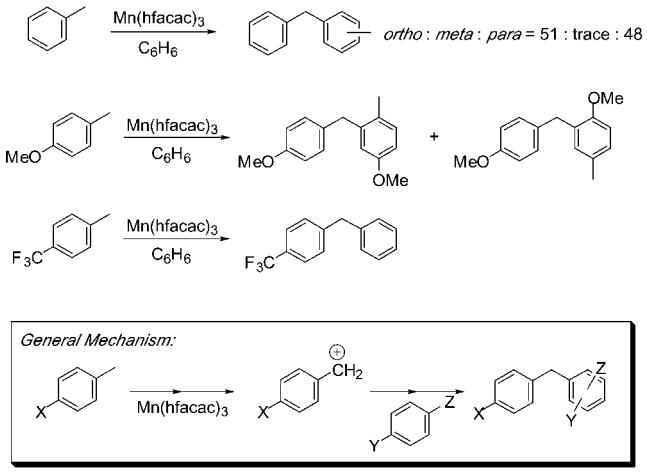


(3)

the limited overoxidation (to the quinone) is a result of using a 2- to 10-fold excess of the phenol. Bixanthene and the bis(phenol) result from coupling of xanthenyl and phenoxyl radicals, respectively.

Mn(hfacac)$_3$ oxidizes toluene (as a 5% solution in benzene) very slowly at ambient temperatures and over a few days at 100 °C. The organic products are tolylphenylmethanes, with ortho:meta:para = 51:trace:48 (by GC/MS, Scheme 1). No bibenzyl, the product of radical coupling, is observed. Methyldiphenylmethanes are the result of Friedel−Crafts addition of benzyl cation to toluene,[25] as shown at the bottom of Scheme 1. These products are often observed in metal-mediated oxidations of methylaromatics, including by Mn-

Scheme 1. Oxidations of Toluenes by Mn(hfacac)$_3$



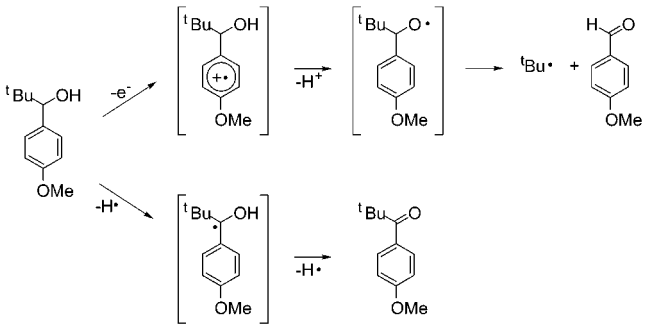
(III).[26] Oxidation of *p*-methylbenzotrifluoride (*p*-$CF_3C_6H_4CH_3$) at 100 °C in benzene gives only a singly CF_3 substituted diarylmethane, *p*-$CF_3C_6H_4CH_2C_6H_5$ (Scheme 1). This is the product of *p*-$CF_3C_6H_4CH_2^+$ addition to the benzene solvent, as confirmed by obtaining the d_5-substituted diarylmethane when the reaction was run in C_6D_6. *p*-Methoxytoluene is oxidized to coupled diarylmethane products (Scheme 1), analogous to toluene but much faster, being complete in 2 weeks at ambient temperatures. Reacting Mn(hfacac)$_3$ with a mixture of toluene and *p*-methoxytoluene in benzene yielded only products from *p*-methoxytoluene. GC/MS of this reaction also shows a product in which a hfacac fragment is coupled to a *p*-methoxytoluene diarylmethane, possibly from further oxidation of the diarylmethane.[41] A similar competition reaction between toluene and *p*-$CF_3C_6H_4CH_3$ gave 10 times more toluene oxidation products than *p*-$CF_3C_6H_4CH_3$-derived products. Treatment of Mn(hfacac)$_3$ with *p*-nitrotoluene causes a color change to yellow, indicative of reduction to Mn(II), faster than in the reaction with toluene, but no products are observed by GC/MS or ^{1}H NMR. Oxidations of *p*-nitrotoluene and *p*-methylbenzotrifluoride in CH_2Cl_2 show similar bleaching of Mn(hfacac)$_3$, but again, no products are observed by GC/MS. Heating Mn(hfacac)$_3$ in neat cyclooctane causes a color change over 4 days at 100 °C. Cyclooctane appears to be oxidized under these conditions, as a number of unidentified products are observed by GC/MS. No color change is observed on heating Mn(hfacac)$_3$ under similar conditions in benzene solution.

Oxidation of 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol by Mn(hfacac)$_3$ yields 4-methoxybenzaldehyde as the only product observed by GC/MS. Baciocchi and co-workers

(25) (a) Uemura, S.; Ikeda, T.; Tanaka, S.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 2574−2576. (b) Darbeau, R. W.; White, E. H.; Song, F.; Darbeau, N. R.; Chou J. *J. Org. Chem.* **1999**, *64*, 5966−5978.

(26) (a) Andrulis, P. J., Jr.; Dewar, M. J. S.; Dietz, R.; Hunt, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5473−5478. (b) Uemura, S.; Tanaka, S.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1966−1969. (c) Uemura, S.; Ikeda, T.; Tanaka, S.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2574−2576. (d) McKillop, A.; Turrell, A. G.; Young, D. W.; Taylor, E. C. *J. Am. Chem. Soc.* **1980**, *102*, 6504−6512. (e) Necsoiu, I.; Ghenciulescu, A.; Rentea, M.; Rentea, C. N.; Nenitzescu, C. D. *Rev. Roum. Chim.* **1967**, *12*, 1503−1510. (f) King, S. T. *J. Catal.* **1991**, *131*, 215−225. (g) Lockwood, M. A.; Wang, K.; Mayer, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 11894−11895.

Scheme 2. Pathways for Oxidation of 1-(4-Methoxyphenyl)-2,2-dimethyl-1-propanol



have shown that this substrate can be used as a mechanistic probe:[11] electron transfer gives the arene radical cation, which deprotonates and fragments to the benzaldehyde, while hydrogen atom abstraction leads to the ketone (Scheme 2). The observation of the benzaldehyde product implicates an electron transfer pathway for this alkoxyaromatic compound. The analogous substrate without the methoxy group, 1-phenyl-2,2-dimethyl-1-propanol, which has not been examined as a mechanistic probe, is similarly oxidized to benzaldehyde.

The kinetics of $Mn(hfacac)_3$ oxidizing DHA in methylene chloride were examined in some detail. In the presence of a large excess of DHA (>100 equiv), the decay of [$Mn(hfacac)_3$] followed first-order kinetics, but the rate constants were irreproducible. The addition of 2,6-di-*tert*-butylpyridine, a proton scavenger, caused a marked decrease in the reaction rate, as did washing the CH_2Cl_2 solvent through basic alumina prior to use. As these observations suggested acid catalysis, a small amount of triflic acid was added to the reaction. This, unexpectedly, also resulted in a decreased rate.

We believe that the origin of the irreproducibility is the presence of differing amounts of trace chloride in CH_2Cl_2 solutions.[27] Addition of chloride sources such as $^nBu_4NCl$, 2,6-di-*tert*-butylpyridinium chloride, or [PPN]Cl results in bleaching of $Mn(hfacac)_3$ in CH_2Cl_2, both in the presence and in the absence of oxidizable substrates. This contrasts with the lack of reaction of $Mn(hfacac)_3$ with 2,6-di-*tert*-butylpyridine. Some reaction is observed, however, with $^nBu_4NPF_6$ and $[PPN]PF_6$, showing that the cations are not innocent in this system. To test for catalysis by chloride, a solution containing $Mn(hfacac)_3$ and DHA was divided into two parts, $^nBu_4NCl$ added to one, and both reactions quenched after 3 min. Essentially quantitative conversion to anthracene and Mn(II) was observed for the chloride-added reaction, while very little change was observed without chloride. Under these conditions, an ~1% yield of 9-chloroanthracene is also observed (detected by GC/MS and confirmed by addition of an authentic sample). The origin of the catalysis and quenching by chloride salts is not clear. This is of particular interest given the use of bromide as a cocatalyst in the Amoco-Mid Century process. Perhaps a chlorine atom or some species with reactivity like a chlorine atom is formed, analogous to the formation of Br_2^- in the Mid Century process.[2c] However, this is difficult to rationalize with the selectivity observed, for instance that DHA is oxidized in preference to $^nBu_4N^+$ and that cyclohexane is not oxidized by $Mn(hfacac)_3/Cl^-$. It appears more likely that catalysis is due to chloride binding to $Mn(hfacac)_3$.[28]

(27) We thank Professor Ronny Neumann for this suggestion (personal communication, 2000).

Table 3. Relative Rate Constants for Oxidation by $Mn(hfacac)_3$, Ionization Energies, and Bond Dissociation Energies for Organic Substrates

	rel rate constant[a]	ionization energy[b]	BDE[c]
xanthene	3×10^2	7.65	75.5
DHA	1	8.54	78
1,4-cyclohexadiene	4×10^{-1}	8.82	77
p-$MeOC_6H_4CH_3$	3×10^{-3}	7.90	~89[g]
$C_6H_5CH_3$	$\sim 10^{-7}$ [d]	8.83	90
p-$CF_3C_6H_4CH_3$	$\sim 10^{-8}$ [e]	~9.3[f]	~90.5 [h]
C_6H_6	no reaction	9.24	111

[a] Relative to *k*(DHA) at 298 K, 6.8×10^{-4} M^{-1} s^{-1}. [b] In eV, from ref 33; errors ±0.05 V or less. [c] C−H bond dissociation energies, in kcal mol^{-1}, from refs 35. [d] Estimated from 19% reaction after 2 months in 120 mM toluene. [e] Estimated as 10 times smaller than *k*(toluene) on the basis of a competition experiment. [f] Estimated from the IP for $C_6H_4CF_3$ [9.685 (± 0.005) eV][33] and the fact that addition of a methyl group to a benzene derivative consistently lowers the IP by ~0.4 eV.[33] [g] Estimated on the basis of DFT calculations as 1 kcal/mol lower than toluene, see ref 35e. [h] Based on DFT calculations as 0.5 kcal/mol higher than toluene, from ref 35f.

In contrast to the results in CH_2Cl_2, kinetics runs in benzene are well-behaved and reproducible. Roughly first-order decay of $Mn(hfacac)_3$ is observed in the presence of excess DHA, and the pseudo-first-order rate constants are linearly related to the DHA concentration, suggesting second-order kinetics with $k = 6.8(\pm 1.5) \times 10^{-4}$ M^{-1} s^{-1}. Rate constants measured from 289 to 332 K yield the activation parameters $\Delta H^{\ddagger} = 14.8 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24 \pm 5$ cal mol^{-1} K^{-1}. For each of the other substrates, one or two kinetic runs (3 mM Mn:120 mM substrate in benzene) showed first-order decay of $Mn(hfacac)_3$ and a second-order rate law was assumed. The relative rate constants are given in Table 3.

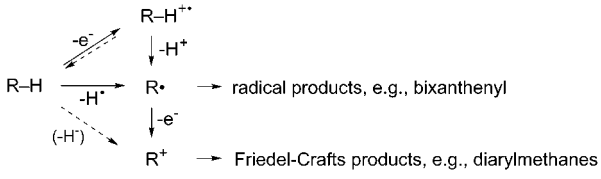
In both benzene and CH_2Cl_2 solutions, there is evidence for catalysis of the reactions by the manganese product. To show this, a reaction of $Mn(hfacac)_3$ and excess DHA was run to completion and a second equivalent of $Mn(hfacac)_3$ was added. The rate of consumption of the second equivalent of $Mn(hfacac)_3$ was 2−3 times that of the initial reaction. Such autocatalysis would normally cause substantial deviations from pseudo-first-order behavior, but this was not observed; perhaps the nature of the resulting manganese products varies with time. The complexities observed and the high reactivity of $Mn(hfacac)_3$ with added reagents have prevented a more in depth kinetic study.

Discussion

$Mn(hfacac)_3$ is a potent oxidant, with a redox potential estimated to be $+0.9 \pm 0.1$ V vs $Cp_2Fe^{+/0}$ in CH_2Cl_2,

(28) Precedent for chloride binding to an oxidizing manganese center is found in the chlorination of alkenes by manganese acetate in the presence of chloride species. See, for example: (a) Donnelly, K. D.; Fristad, W. E.; Gellerman, B. J.; Peterson, J. R.; Selle, B. J. *Tetrahedron Lett.* **1984**, *25*, 607−610. (b) Yonemura, H.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3153−3159.

Scheme 3. Pathways for C−H Bond Oxidation by Mn(hfacac)$_3$



equivalent to ca. +1.5 V vs NHE. This is a very high potential for a neutral oxidant.[21b,29] Mn(hfacac)$_3$ could be a useful oxidizing reagent because of its ease of preparation and its solubility in nonpolar media such as hydrocarbons. We have used this solubility to study oxidations of organic compounds in benzene under conditions where the structure and speciation of the manganese oxidant is not in question. Mn(hfacac)$_3$ undoubtedly has a distorted octahedral structure in benzene solution similar to that found in the solid state.[17] The second-order kinetics for 9,10-dihydroanthracene (DHA) oxidation in this solvent implies that this molecular species is the reactive oxidant. This conclusion contrasts with the situation for "manganese(III) acetate" in acetic acid, for instance, where monomers and oligomers coexist and have different reactivities.[2c] Similarly, little is known about the structure of the organic-acid stabilized Mn(III) complex produced by white-rot fungi to oxidize benzylic and phenolic bonds in lignin. Mn(hfacac)$_3$ thus provides a simplified model system for stoichiometric and catalytic oxidations by Mn(III).

The organic reactions described here all involve the oxidation of two X−H bonds (X = C, O) with the hydrogen being transferred to a ligand to form free H-hfacac. In the process, 2 equiv of Mn(hfacac)$_3$ are reduced, apparently to [Mn(hfacac)$_2$]$_n$. The formation of bixanthene from xanthene indicates the presence of xanthenyl radicals, and the diarylmethane products from toluenes indicate the intermediacy of benzylic carbocations.[25] As shown in Scheme 3, these intermediates could be made directly, by hydrogen atom abstraction[7,9] or hydride abstraction,[26g] or by stepwise electron and proton transfers.[26] One-step hydride transfer is very unlikely in this system, as it would require two-electron reduction of the manganese center to an unfavorable Mn(I) complex. Initial proton transfer is also not possible since Mn(hfacac)$_3$ is not a strong base and the hydrocarbons have very low acidity. Thus the first step in these reactions is either electron transfer or hydrogen atom transfer.[30]

A pathway of initial electron transfer is indicated by the oxidation of Baciocchi's mechanistic probe, and by *p*-methoxytoluene being oxidized much faster than toluene.[31] Hydrogen atom abstractions from toluenes are not dramatically affected by substituents,[32] while the gas phase ionization energy (IE) of *p*-methoxytoluene is 0.93 eV below that of toluene (Table 3). Electron transfer from *p*-methoxytoluene to Mn(hfacac)$_3$ is approximately 0.5 V uphill.[34]

The rate constants in Table 3, however, do not simply correlate with the IEs, as would be expected for a rate-limiting electron transfer pathway. 1,4-Cyclohexadiene (CHD), for instance, has an IE similar to that of toluene and ∼0.9 V higher than that of *p*-methoxytoluene, yet it reacts orders of magnitude faster than both (Table 3). *p*-$CF_3C_6H_4CH_3$ reacts only a factor of 10 slower than toluene despite an almost 0.5 eV difference in IEs (this difference in IEs corresponds to roughly a 10^8 difference in equilibrium constants for electron transfer). It is possible that some of these reactions proceed by pre-equilibrium electron transfer followed by rate-limiting deprotonation, but since all of the radical cations are strong acids, it is difficult to see how this would account for the, for instance, 10^5 faster rate for CHD than toluene. Pre-equilibrium electron transfer should result in an inverse-first-order rate dependence on [Mn(II)], but addition of Mn(II) (as [^{n}Pr$_4$N][Mn(hfacac)$_3$]) had no appreciable effect on the reaction rate with DHA in either benzene or CH_2Cl_2. This result is, however, complicated by the tight ion pairing in these solvents. The apparent oxidation of cyclooctane also supports a hydrogen atom transfer pathway, as outer-sphere electron transfer from an alkane is unlikely.

The relative rate results suggest that the hydrocarbons with weak C−H bonds and high IEs most likely react by initial hydrogen atom transfer. Mn(hfacac)$_3$ could accept H$^\bullet$ to give [Mn^{II}(H-hfacac)(hfacac)$_2$], which would dissociate to the observed products [Mn(hfacac)$_2$]$_n$ and H-hfacac. It is reasonable that Mn(hfacac)$_3$ has a high affinity for H$^\bullet$, since it has a high redox potential and the reduced form, [Mn(hfacac)$_3$]$^-$, has some basicity. Our related studies of oxidizing man-

(29) Carborane radicals are more potent one-electron oxidants: King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902−10903.

(30) (a) It is interesting that xanthene is oxidized to bixanthene but toluene does not give bibenzyl even though (i) xanthyl and benzyl radicals must be intermediates and (ii) it is much easier to oxidize xanthyl radical to xanthyl carbocation than $PhCH_2^\bullet$ to $PhCH_2^+$.[30b] Presumably radical coupling is favored for xanthene by the much higher steady-state concentration of the xanthyl radical. If Mn(hfacac)$_3$ + RH ⇄ Mn(H-hfacac)(hfacac)$_3$ + R$^\bullet$ were at equilibrium, the concentration of R$^\bullet$ would be ∼10^{10} times higher for xanthene than for toluene because of its weaker C−H bond strength. While equilibrium is unlikely, this indicates that the xanthyl radical concentration is likely to be much higher. (b) Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655−2660. Handoo, K. L.; Cheng, J.-P.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 5067−5072.

(31) For leading references to other electron transfer oxidations of *p*-methoxytoluene, see: (a) Eberson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192−3199. (b) Schlesener, C. J.; Kochi, J. K. *J. Org. Chem.* **1984**, *49*, 3142−3150.

(32) Howard, J. A.; Chenier, J. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 3054−3055: ^{t}BuO$^\bullet$ abstracts H$^\bullet$ from *p*-$MeOC_6H_4Me$ 2.7 times faster than from toluene.

(33) Http://webbook.nist.gov/chemistry accessed 14 May 2001.

(34) Ionization potentials for the organic compounds have been used as surrogates for redox potentials, in part due to the lack of consistency in the reported electrochemical potentials. Some reported redox potentials can be found in these references: For xanthene, DHA, and *p*-methoxytoluene: (a) Salah, N. B.; Mhalla, F. M. *J. Electroanal. Chem.* **2000**, *485*, 42−48. For 1,4-CHD, toluene, and benzene: (b) Kochi, J. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 7, pp 849−889. Other values for benzene, toluene, and *p*-methoxytoluene: Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987; p 44.

(35) For xanthene: (a) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218−2221. For DHA: (b) Bordwell, F. G.; Cheng, J. P.; Ji, G.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795. For 1,4-CHD: (c) Laarhoven, L. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342−349. For toluene: (d) Bierbaum, V.; DePuy, C.; Davico, G.; Ellison, B. *Int. J. Mass Spectrom. Ion Phys.* **1996**, *156*, 109−131. For *p*-$MeOC_6H_4CH_3$: (e) Fox, T.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 2950−2956. For *p*-$CF_3C_6H_4CH_3$: (f) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877−4882. For benzene: (g) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765

ganese,[7,9a,36] iron,[9b] copper,[9c] and chromium complexes[9a] indicate the viability of hydrogen atom abstraction by basic ligands bound to oxidizing metal centers. An X−H bond strength can, in favorable cases, be determined from redox potential and pK_a values,[9,37] but the needed thermochemical data is not available for methylene chloride solutions, and this system is complicated by the dissociation of H-hfacac.

In comparison to other Mn(III) oxidants, $Mn(hfacac)_3$ is more reactive and is capable of oxidations under milder conditions. Its redox potential (+0.9 V vs $Cp_2Fe^{+/0}$ in CH_2Cl_2) appears to be higher than that of $Mn(acac)_3$, ca. +0.7 V vs $Cp_2Fe^{+/0}$ in MeCN.[38] Oxidations of *p*-methoxytoluene by "$Mn(OAc)_3$" in acetic acid are typically run at 70−100 °C.[26] Several studies of Mn(III) reactions indicate that substrates with low IEs (≤8.0) are oxidized by electron transfer, but invoke alternative mechanisms for substrates with higher values.[39] Thermolysis of acidic solutions of manganese(III) acetate to ≥80 °C results in formation of carboxylmethyl radicals, $^{\bullet}CH_2CO_2H$, which are hydrogen atom abstracting agents. Malonyl radicals are formed similarly from "$Mn(OAc)_3$" and diethyl malonate. There is no evidence for the formation of hfacac$^{\bullet}$ radicals in reactions of $Mn(hfacac)_3$, and the high thermal stability of the oxidant makes this unlikely. Oxidation of hfacac$^-$ to the radical would seem much more unfavorable than for nonfluorinated ligands, yet $Mn(hfacac)_3$ appears more reactive. Carboxylmethyl, malonyl, and related radicals all add to aromatic rings and olefins competitively with hydrogen atom abstraction (a useful process[40]), but hfacac-substituted products are not, in general, observed in this system.[41] We suggest that a reasonable alternative pathway is direct hydrogen atom transfer from a weak C−H bond to a manganese-bound hfacac oxygen, giving $[Mn^{II}(hfacac)_2(H\text{-}hfacac)]$, which then dissociates H-hfacac.

Conclusions

$Mn(hfacac)_3$ is an easily synthesized, hydrocarbon soluble, strong neutral oxidant (0.9 ± 0.1 V vs $Cp_2Fe^{+/0}$). Its reactions serve as a model for the oxidations of organic compounds by various manganese(III) complexes. In contrast to other Mn(III) oxidations, the speciation of the manganese is well defined under the reaction conditions. $Mn(hfacac)_3$ oxidizes organic compounds that either have a low redox potential or a weak C−H or O−H bond, including 9,10-dihydroanthracene (DHA), 2,4-di-*tert*-butyl phenol, toluene, and *p*-methoxytoluene. Most of these oxidations can be performed at room temperature in benzene solution. Mechanistic studies indicate that alkoxy-aromatic compounds are oxidized by initial electron transfer, but less electron rich substrates, such as 1,4-cyclohexadiene, appear to react by initial hydrogen atom transfer to a manganese-bound hfacac oxygen.

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Supporting Information Available: Representative kinetics traces and overlay plots for the oxidation of DHA and xanthene. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. *Inorg. Chem.* **1997**, *36*, 2069−2078.
(37) Mayer, J. M. In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000.
(38) Yamaguchi, K.; Sawyer, D. T. *Inorg. Chem.* **1985**, *24*, 971−976. Our electrochemistry experiments and other references indicate that redox potentials in CH_3CN and CH_2Cl_2 are similar when reported vs $Cp_2Fe^{+/0}$.
(39) (a) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138−145. (b) Citterio, A.; Santi, R.; Fiorani, T.; Strologo, S. *J. Org. Chem.* **1989**, *54*, 2703−2712. (c) Fristad, W. E.; Peterson, J. R.; Ernst, A. B.; Urbi, G. B. *Tetrahedron* **1986**, *42*, 3429−3442. (d) van der Ploeg, R. E.; de Korte, R. W.; Kooyman, E. C. *J. Catal.* **1968**, *10*, 52−59.
(40) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339−363. See also refs 39.
(41) The oxidation of *p*-methoxytoluene gave a product with mass corresponding to the coupling of a hfacac ligand to the aromatic ring of the substituted diphenylmethane. It is unclear if the ligand is bound through an oxygen or a carbon. See Experimental Section for fragmentation pattern.