

Pentamercuration of Cyclopentadienylmanganese Tricarbonyl and Cyclopentadienylrhenium Tricarbonyl. Crystal Structure of (Pentaiodocyclopentadienyl)manganese Tricarbonyl

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Treatment of cyclopentadienylmanganese tricarbonyl and cyclopentadienylrhenium tricarbonyl with mercuric acetate (5 equiv) in refluxing 1,2-dichloroethane for 4 h afforded (pentakis(acetoxymercuro)cyclopentadienyl)manganese tricarbonyl (73%) and (pentakis(acetoxymercuro)cyclopentadienyl)rhenium tricarbonyl (90%) as pale yellow powders. These new complexes were characterized by ¹H NMR, infrared spectroscopy, and microanalysis. Reaction of (pentakis(acetoxymercuro)cyclopentadienyl)manganese tricarbonyl with cupric chloride in refluxing acetone, cupric bromide in refluxing acetone, and potassium triiodide in water afforded (pentachlorocyclopentadienyl)manganese tricarbonyl (45%), (pentabromocyclopentadienyl)manganese tricarbonyl (44%), and (pentaiodocyclopentadienyl)manganese tricarbonyl (19%). Treatment of (pentakis(acetoxymercuro)cyclopentadienyl)rhenium tricarbonyl with the above halogenating agents afforded only unidentified decomposition products. The structure of (pentaiodocyclopentadienyl)manganese tricarbonyl was determined, showing that this compound crystallized in the triclinic space group *P* $\bar{1}$, with cell dimensions *a* = 13.547(4) Å, *b* = 14.360(3) Å, *c* = 16.729(4) Å, α = 90.95(2)°, β = 89.91(2)°, γ = 103.77(2)°, *V* = 3160(1) Å³, and *Z* = 8.

Introduction

The mercuration of cyclopentadienylmanganese tricarbonyl and cyclopentadienylrhenium tricarbonyl has been the subject of several studies.¹⁻⁴ The first direct mercuration of cyclopentadienylmanganese tricarbonyl afforded a 37% yield of the ((chloromercuro)cyclopentadienyl)manganese tricarbonyl in the presence of alcoholic calcium chloride, while a mixture of the mono- and dimercurated products was isolated if the reaction was conducted in ethanol and the calcium chloride was omitted.^{1a} ((Chloromercuro)cyclopentadienyl)manganese tricarbonyl was later obtained in 53% yield by treatment of cyclopentadienylmanganese tricarbonyl with mercuric acetate in the presence of perchloric acid, followed by treatment with lithium chloride.^{1b} Treatment of cyclopentadienylmanganese tricarbonyl with mercuric trifluoroacetate (5 equiv) in dichloromethane at 20 °C leads to replacement of all five hydrogens to afford (pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl)manganese tricarbonyl.^{2a} Recently, (pentaiodocyclopentadienyl)manganese tricarbonyl was prepared by treatment of cyclopentadienylmanganese tricarbonyl with mercuric acetate (5 equiv), followed by treatment with sodium triiodide.^{2b} The presumed pen-

tamercurated intermediate, (pentakis(acetoxymercuro)cyclopentadienyl)manganese tricarbonyl, was neither isolated nor characterized. Treatment of cyclopentadienylrhenium tricarbonyl with mercuric acetate in ethanol leads to a mixture of the mono- and dimercurated complexes.³ Both ((chloromercuro)cyclopentadienyl)manganese tricarbonyl and ((chloromercuro)cyclopentadienyl)rhenium tricarbonyl have also been prepared by indirect routes from the lithium and sulfinate derivatives.⁴

Recently, we have disclosed that the cyclopentadienyl ligands in ruthenocene,^{5a} ferrocene,^{5a} and pentamethylruthenocene^{5b} can be pentamercurated in either dichloroethane or ethanol/diethyl ether to afford the permercurated complexes in nearly quantitative yields. Treatment of these permercurated species with chlorinating, brominating, and iodinating agents afforded moderate to good yield of the perhalometallocenes. In view of the potential utility of permercurated cyclopentadienyl complexes in preparing persubstituted species, we have been exploring the mercuration of non-metallocene cyclopentadienyl complexes. Herein we report that treatment of cyclopentadienylmanganese tricarbonyl and cyclopentadienylrhenium tricarbonyl with mercuric acetate in refluxing dichloroethane affords high yields of the pentamercurated cyclopentadienyl complexes. The characterization of these species is presented. (Pentakis(acetoxymercuro)cyclopentadienyl)manganese tricarbonyl serves as a useful precursor to perhalocyclopentadienyl complexes. The crystal structure of (pentaiodocyclopentadienyl)manganese tricarbonyl is also described.

Results

Mercuration Studies. Treatment of cyclopentadienylmanganese tricarbonyl with mercuric acetate (5 equiv)

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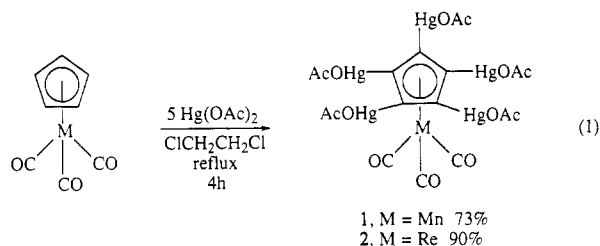
(2) (a) Kuzmina, L. G.; Ginzburg, A. G.; Struchkov, Y. T.; Kusanov, D. N. *J. Organomet. Chem.* 1983, 253, 329. (b) Bunz, U. H. F.; Enkelmann, V.; Räder, J. *Organometallics* 1993, 12, 4745.

(3) Nesmeyanov, A. N.; Kolobova, N. E.; Anisimov, K. N.; Baryshnikov, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1964, 1057.

(4) Nesmeyanov, A. N.; Korol'kov, V. V.; Bryukhova, E. V.; Kuznetsov, S. I.; Tolstaya, T. P.; Semin, G. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1977, 1899. Nesmeyanov, A. N.; Kolobova, N. E.; Anisimov, K. N.; Makarov, Y. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1969, 357. Nesmeyanov, A. N.; Kolobova, N. E.; Makarov, Y. V.; Anisimov, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1969, 1992. Cais, M.; Kozikowski, J. J. *Am. Chem. Soc.* 1960, 82, 5667.

(5) (a) Winter, C. H.; Han, Y.-H.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 1161. (b) Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* 1992, 11, 3169.

in refluxing 1,2-dichloroethane for 4 h afforded (pentakis(acetoxymercurio)cyclopentadienyl)manganese tricarbonyl (**1**, 73%) as a yellow powder (eq 1). This compound

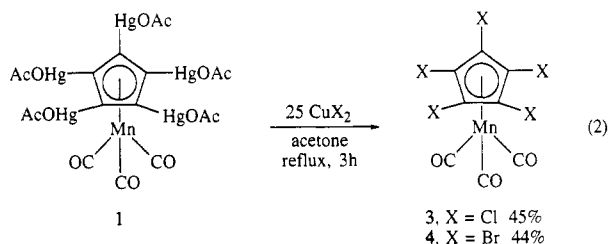


was slightly soluble in dichloromethane and could be obtained as an analytically pure powder by filtration and removal of the solvent. Complex **1** was characterized by ^1H NMR and infrared spectroscopy and gave microanalytical results consistent with the proposed formulation. The molar solubility of **1** was too low to allow collection of its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The ^1H NMR of **1** showed no resonances between δ 3 and 6 that could be attributed to a partially mercurated complex, which indicates that **1** is $\geq 98\%$ pentamercurated. An experiment was conducted in which cyclopentadienylmanganese tricarbonyl was treated with mercuric acetate (1 equiv) under conditions otherwise identical with the above preparation of **1**. Workup afforded **1** (6%) and unreacted cyclopentadienylmanganese tricarbonyl (78%). This experiment indicates that the first mercuration step is the slowest. Analogous mercuration of cyclopentadienylrhenium tricarbonyl afforded (pentakis(acetoxymercurio)cyclopentadienyl)rhenium tricarbonyl (**2**, 90%) as a pale yellow powder (eq 1). Spectral and analytical data were consistent with the proposed formulation. Complex **2** was sufficiently soluble in dichloromethane- d_2 to allow collection of its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Resonances were observed at 196.40 (s, Mn-CO), 178.88 (broad s, HgOCOCH_3), 50.98 (s, C-Hg), and 22.52 (broad s, HgOCOCH_3) ppm. The signal to noise ratio was not high enough to resolve ^{13}C - ^{199}Hg coupling. The ^1H NMR of **2** showed no resonances between δ 3 and 6, indicating $\geq 98\%$ pentamercuration. Treatment of cyclopentadienylrhenium tricarbonyl with mercuric acetate (1 equiv) as above afforded **2** (10%) and unreacted cyclopentadienylrhenium tricarbonyl (81%). Again, the first mercuration is the slowest.

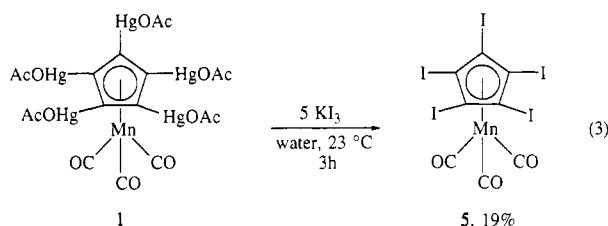
The infrared spectra of **1** (ν_{CO} 2000 (vs), 1919 (vs) cm^{-1} ; $\nu_{\text{HgO}_2\text{CCH}_3}$ 1586 (s), 1461 (m) cm^{-1}) and **2** (ν_{CO} 1999 (vs), 1897 (vs) cm^{-1} ; $\nu_{\text{HgO}_2\text{CCH}_3}$ 1572 (s), 1499 (m) cm^{-1}) revealed strong absorptions due to the manganese-carbonyl and mercury acetate groups. The ^1H NMR spectra of **1** and **2** in chloroform- d at 23 $^\circ\text{C}$ showed slightly broad singlets at δ 1.93 and 1.94, respectively, for the acetate methyls. We have previously reported that the complex $(\text{C}_5(\text{Hg}(\text{OAc})_5)(\text{C}_5\text{Me}_5)\text{Ru}$ exists as a mixture of eight isomers in solution due to acetate isomerism (i.e., the acetate methyl points either toward the C_5Me_5 ligand or away from it) and slow acetate rotation on the NMR time scale.^{5b} In order to probe for analogous processes in **1** (eight isomers are possible), the ^1H NMR spectra were recorded between +20 and -80 $^\circ\text{C}$ in dichloromethane- d_2 . Surprisingly, the spectra between these temperatures were essentially static and showed a broad singlet whose chemical shift varied between δ 1.88 at -80 $^\circ\text{C}$ and δ 1.95 at +20 $^\circ\text{C}$. The ^1H NMR spectra between +20 and -80 $^\circ\text{C}$ in toluene- d_8 were invariant and showed a broad singlet at δ 1.62. Hence, acetate rotation is probably fast on the NMR time scale,

even at -80 $^\circ\text{C}$. Such behavior is consistent with much lower steric congestion about the manganese center than is present around the ruthenium center in $(\text{C}_5(\text{Hg}(\text{OAc})_5)(\text{C}_5\text{Me}_5)\text{Ru}$. Alternatively, the possible isomers of **1** may have very little difference in chemical shifts for the methyl resonances, which could lead to the observed broad peak.

Halogenation. Treatment of **1** with excess cupric chloride (25 equiv) in refluxing acetone for 3 h afforded (pentachlorocyclopentadienyl)manganese tricarbonyl (**3**, 45%) as a yellow crystalline solid (eq 2). Analogous



treatment of **1** with cupric bromide afforded (pentabromocyclopentadienyl)manganese tricarbonyl (**4**, 44%) as a yellow crystalline solid. Complexes **3** and **4** have been previously prepared by treatment of tetrachlorodiazocyclopentadiene and tetrabromodiazocyclopentadiene with pentacarbonylmanganese chloride or pentacarbonylmanganese bromide.^{6,7} The spectral data of **3** and **4** are consistent with the literature values. Complex **1** was also halogenated using potassium triiodide (prepared from I_2 and KI at 25 $^\circ\text{C}$) in water to afford (pentaiodocyclopentadienyl)manganese tricarbonyl (**5**, 19%) as an orange crystalline powder, after workup (eq 3). The structure of **5**^{2b} was established from spectral and analytical data from an X-ray crystal structure determination (vide infra).



Surprisingly, treatment of **2** with the above halogenating reagents did not afford the pentahalocomplexes. For each of the halogenating agents ($\text{CuCl}_2/\text{acetone}$, $\text{CuBr}_2/\text{acetone}$, $\text{KI}_3/\text{H}_2\text{O}$), low yields ($\leq 10\%$) of impure compounds were isolated. The infrared spectra showed carbonyl stretches consistent with those expected for (pentahalocyclopentadienyl)rhenium tricarbonyl, but the compounds could not be obtained in analytically pure form. The poor reactivity of **2** toward halogenation is surprising, compared to the successful reactions of **1**, since cyclopentadienylrhenium tricarbonyl derivatives are generally more robust than analogous cyclopentadienylmanganese tricarbonyl complexes.

Crystal Structure of 5. The crystal structure of **5** was determined in order to characterize its molecular geometry. X-ray data were collected under the conditions summarized in Table 1. Selected bond lengths, selected bond angles, and positional parameters are summarized in

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(7) Hermann, W. A.; Huber, M. *J. Organomet. Chem.* 1977, 140, 55.

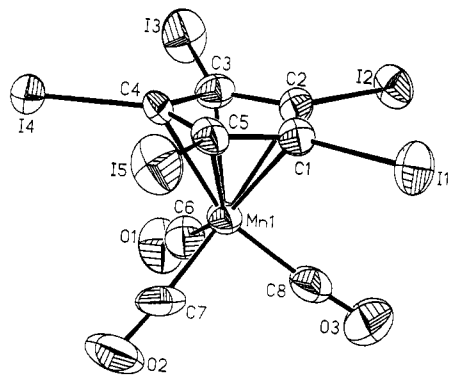


Figure 1. Perspective view of 5.

Table 1. Experimental Crystallographic Data for 5

formula	$MnC_8O_3I_5$	fw	833.55
<i>a</i>	13.547(4) Å	space group	$P\bar{1}$
<i>b</i>	14.360(3) Å	<i>T</i>	22 °C
<i>c</i>	16.729(4) Å	λ	0.710 73 Å
α	90.95(2)°	ρ (calc)	3.503 g cm ⁻³
β	89.91(2)°	μ	104.7 cm ⁻¹
γ	103.77(2)°	transmissn coeff	0.452–0.191
<i>V</i>	3160(1) Å ³	<i>Z</i>	8
<i>R</i> ^a	0.054	<i>R</i> _w ^a	0.057

$$^a R = (\sum|\Delta F|)/\sum|F_o|; R_w = [(\sum w|\Delta F|^2)/\sum wF_o^2]^{1/2}.$$

Table 2. Bond Lengths (Å) and Selected Bond Angles (deg) for 5

Mn–C(1)	2.13(1)	Mn(1)–C(2)	2.15(1)
Mn(1)–C(3)	2.12(1)	Mn(1)–C(4)	2.16(1)
Mn(1)–C(5)	2.16(1)	Mn(1)–C(6)	1.79(2)
Mn(1)–C(7)	1.81(2)	Mn(1)–C(8)	1.80(2)
Mn(1)–CP(1)	1.77(1)	I(1)–C(1)	2.08(1)
I(2)–C(2)	2.06(1)	I(3)–C(3)	2.08(1)
I(4)–C(4)	2.07(1)	I(5)–C(5)	2.07(1)
C(1)–C(2)	1.43(2)	C(1)–C(5)	1.40(2)
C(2)–C(3)	1.40(2)	C(3)–C(4)	1.45(2)
C(4)–C(5)	1.42(2)	C(6)–O(1)	1.12(2)
C(7)–O(2)	1.13(2)	C(8)–O(3)	1.15(2)
Mn(1)–C(6)–O(1)	177(1)	Mn(1)–C(7)–O(2)	177(1)
Mn(1)–C(8)–O(3)	174(1)	C(6)–Mn(1)–C(7)	90.3(8)
C(6)–Mn(1)–C(8)	93.4(7)	C(6)–Mn(1)–CP(1)	124.1(7)
C(7)–Mn(1)–C(8)	93.1(7)	C(7)–Mn(1)–CP(1)	124.4(6)
C(8)–Mn(1)–CP(1)	122.5(7)		

Table 3. Atomic Positional Parameters for 5

atom	<i>x</i>	<i>y</i>	<i>z</i>
Mn(1)	0.7123(2)	0.2560(2)	0.5590(1)
I(1)	0.46908(8)	0.09222(8)	0.63246(7)
I(2)	0.48985(8)	0.17839(8)	0.41639(7)
I(3)	0.7596(1)	0.1826(1)	0.34222(7)
I(4)	0.91564(8)	0.12479(8)	0.52077(7)
I(5)	0.73009(9)	0.04709(9)	0.69303(7)
C(1)	0.602(1)	0.123(1)	0.5649(9)
C(2)	0.608(1)	0.154(1)	0.4841(9)
C(3)	0.708(1)	0.161(1)	0.4595(9)
C(4)	0.765(1)	0.131(1)	0.5239(9)
C(5)	0.695(1)	0.107(1)	0.5882(9)
C(6)	0.786(1)	0.352(1)	0.502(1)
C(7)	0.792(1)	0.296(1)	0.646(1)
C(8)	0.621(1)	0.323(1)	0.589(1)
O(1)	0.834(1)	0.411(1)	0.4647(9)
O(2)	0.845(1)	0.319(1)	0.6979(8)
O(3)	0.557(1)	0.359(1)	0.6056(9)

Tables 2 and 3. A perspective view is shown in Figure 1. Complex 5 crystallized with four independent molecules in the unit cell. Data are presented only for the molecule containing Mn(1). The other three independent molecules of 5 were identical within experimental error; their structural data are contained in the supplementary material.

The complex is a mononuclear, molecular species with three-legged piano-stool geometry. The manganese–carbon distances averaged 2.14 Å for the pentachlorocyclopentadienyl ligand, while the manganese–carbon distances for the carbonyls averaged 1.80 Å. The manganese–cyclopentadienyl (centroid) distance was 1.77 Å. The carbon–iodine bond lengths averaged 2.07 Å, while the carbon–carbon distances averaged 1.42 Å. The average carbon–oxygen distance was 1.13 Å. The manganese–carbon–oxygen angles were linear and varied between 174 and 177°. The carbonyl carbon–manganese–cyclopentadienyl (centroid) angles ranged from 122 to 124°. The iodine atoms were displaced out of the plane of the C₅ core, away from the manganese atom, by an average of 0.152 Å (I(1), 0.109(1) Å; I(2), 0.153(1) Å; I(3), 0.319(2) Å; I(4), –0.009(1) Å; I(5), 0.186(1) Å). The structure parameters of 5 are very similar to other structures of cyclopentadienylmanganese tricarbonyl derivatives.^{8,9}

Discussion

Treatment of cyclopentadienylmanganese tricarbonyl and cyclopentadienylrhodium tricarbonyl with mercuric acetate (5 equiv) in refluxing dichloroethane affords the pentamercurated complexes 1 and 2 in 73% and 90% yields, respectively. The high reactivity of the starting complexes toward pentamercuration was evidenced by the exclusive isolation of 1 and 2, rather than monomercurated species, when only 1 equiv of mercuric acetate was used. These experiments reveal that the first mercuration is the slowest step in the pentamercuration process. It has been previously demonstrated that cyclopentadienylmanganese tricarbonyl can be pentamercurated by treatment with mercuric trifluoroacetate,^{2a} although no yield was presented and no reactions were described. We have found that decakis(trifluoroacetoxy)mercurioferrocene^{10b} reacts with cupric chloride in acetone to afford mixtures of partially chlorinated ferrocenes, while decakis(acetoxymercurio)ferrocene affords only decachloroferrocene under similar conditions.¹¹ For this reason, permercurated complexes derived from mercuric acetate are likely to be more useful synthetically than those derived from mercuric trifluoroacetate. The isolation of 1 and its subsequent transformation to 5 confirm the intermediacy of 1 in a preparation of 5 recently reported by Bunz.^{2b}

Conflicting reports have suggested that the HgOAc group is a strong electron-withdrawing substituent on an arene ring ($\sigma_p = 0.40$)¹² and also that the HgX group possesses a negligible electronic effect as an aromatic

(8) (a) Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* 1963, 16, 118. (b) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* 1969, 8, 1950. (c) Khotsyanova, T. L.; Kuznetsov, S. I.; Bryukhova, E. V.; Makarov, Y. V. *J. Organomet. Chem.* 1975, 88, 351. (d) Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. G. *J. Organomet. Chem.* 1979, 179, 403.

(9) For crystal structure determinations of complexes containing pentachlorocyclopentadienyl and pentabromocyclopentadienyl ligands, see: (a) Day, V. W.; Reimer, K. J.; Shaver, A. J. *Chem. Soc., Chem. Commun.* 1975, 403. (b) Brown, G. M.; Hedberg, F. L.; Rosenberg, H. *J. Chem. Soc., Chem. Commun.* 1972, 5. (c) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* 1988, 110, 6130. (d) Priebisch, W.; Hoch, M.; Rehder, D. *Chem. Ber.* 1988, 121, 1971.

(10) For leading references, see: (a) Deacon, G. B.; Farquharson, G. *J. J. Organomet. Chem.* 1974, 67, C1. *Aust. J. Chem.* 1976, 29, 627. (b) See also: Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* 1977, 47, 727. *Izv. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1977, 20, 1789.

(11) Han, Y.-H.; Heeg, M. J.; Winter, C. H., manuscript in preparation. (12) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 439–540. See also: Yagupolskii, L. M.; Popov, V. I.; Kondratenko, N. V.; Konovalov, E. V. *Russ. J. Org. Chem. (Engl. Transl.)* 1974, 10, 278. Kravtsov, D. N.; Kvasov, B. A.; Golovchenko, L. S.; Fedin, E. I. *J. Organomet. Chem.* 1972, 36, 227.

substituent.¹³ If the HgOAc group is electron withdrawing, then a possible rationale for the observed permercuration could be the strong σ, π -hyperconjugation associated with a carbon–mercury bond,¹⁴ which would stabilize the adjacent positive charge involved in each mercuration step. The carbonyl stretching values for **1** (ν_{CO} 2000, 1919 cm^{-1}) indicate that the pentakis(acetoxymercurio)cyclopentadienyl ligand is electron donating relative to the cyclopentadienyl ligand in cyclopentadienylmanganese tricarbonyl (ν_{CO} 2014, 1936 cm^{-1}). The permercuration of aromatic organic molecules, while not commonly observed, has been documented in a small number of cases.¹⁰

The halogenation of **1** to afford the perhalocyclopentadienyl complexes **3–5** demonstrates that the pentamercured cyclopentadienyl ligand represents a useful precursor to other pentasubstituted cyclopentadienyl ligands. Complexes **3** and **4** have been previously prepared in 76% and 83% yields, respectively, by reaction of the diazotetrahalocyclopentadienes with pentacarbonylmanganese chloride and pentacarbonylmanganese bromide.^{6,7} While the present yields of **3** and **4** are slightly lower than those from the diazotetracyclopentadienes, our methodology uses commercially available starting materials and avoids having to prepare and handle the noxious compounds hexachlorocyclopentadiene, hexabromocyclopentadiene, diazotetrachlorocyclopentadiene, and diazotetrabromocyclopentadiene. Additionally, complex **1** represents a common starting material for **3–5**. The infrared carbonyl stretches illustrate the electron-withdrawing nature of the pentahalocyclopentadienyl ligands in **3** (ν_{CO} 2033, 1954 cm^{-1}), **4** (ν_{CO} 2026, 1958 cm^{-1}), and **5** (ν_{CO} 2029, 1957 cm^{-1}), relative to cyclopentadienylmanganese tricarbonyl (ν_{CO} 2014, 1936 cm^{-1}).

Treatment of **2** with halogenating agents that were successful with **1** did not constitute a route to (pentahalocyclopentadienyl)rhenium tricarbonyl complexes. Cyclopentadienylrhenium tricarbonyl is well known to undergo reaction with halogens to afford complexes of the formula $[\text{CpRe}(\text{CO})_2\text{X}_2]$.¹⁵ It is possible that the desired compounds $(\text{C}_5\text{X}_5)\text{Re}(\text{CO})_5$ are formed in the reaction medium but react further to form $(\text{C}_5\text{X}_5)\text{Re}(\text{CO})_2\text{X}_2$ or decompose under the reaction conditions. However, we were unable to detect or isolate $(\text{C}_5\text{X}_5)\text{Re}(\text{CO})_2\text{X}_2$ in the halogenation reactions, even though the complex $\text{CpRe}(\text{CO})_2\text{Br}_2$ is reported to be a robust material.¹⁵ We are continuing to explore conditions for the halogenation of **2**.

The structural parameters of **5** are similar to those of related complexes whose structures have been determined. The average manganese–carbon distances in the C_5I_5 ligand (2.14 Å) and carbonyl ligands (1.80 Å) compare well with the corresponding distances in cyclopentadienylmanganese tricarbonyl (2.151, 1.797 Å),^{8a} (η^5 -cyclohexadienyl)manganese tricarbonyl (2.171, 1.788 Å),^{8b} (1-bromoindenyl)manganese tricarbonyl (2.162, 1.793 Å),^{8c} and (acetyl)cyclopentadienyl)manganese tricarbonyl (2.14, 1.80 Å).^{8d} The

angles about the manganese atom of **5** are also very similar to the values in the above previously reported structures. It is clear that the presence of the five iodines does not perturb the major structural features of the cyclopentadienylmanganese tricarbonyl skeleton. Complex **5** is the second reported crystal structure of a complex bearing a pentaiodocyclopentadienyl ligand.^{5b}

Experimental Section

General Considerations. The mercuration reactions were performed under an atmosphere of nitrogen using Schlenk techniques. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Reagent grade 1,2-dichloromethane and acetone were used as received. Chloroform-*d* was purified by vacuum transfer from 4-Å molecular sieves. Cyclopentadienylrhenium tricarbonyl was prepared by a literature procedure.¹⁶ Cyclopentadienylmanganese tricarbonyl was used as received from Strem Chemicals. Mercuric acetate, cupric chloride, cupric bromide, sodium thiosulfate, potassium iodide, and iodine were used as received from Aldrich Chemical Co. Complexes **3**⁶ and **4**⁷ have been previously prepared by treatment of the pentacarbonylmanganese halide with tetrahalodiazocyclopentadiene.

¹H NMR and ¹³C{¹H} NMR spectra were obtained at 300 and 75 MHz in chloroform-*d*, unless otherwise noted. Infrared spectra were obtained using potassium bromide as the medium. Mass spectra were obtained in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital point apparatus and are uncorrected.

(Pentakis(acetoxymercurio)cyclopentadienyl)manganese Tricarbonyl (1). A 50-mL Schlenk flask was charged with cyclopentadienylmanganese tricarbonyl (0.498 g, 2.44 mmol), mercuric acetate (3.89 g, 12.2 mmol), dichloromethane (20 mL), and a stirbar and was fitted with a reflux condenser. The mixture was refluxed for 4 h. After the mixture was cooled to ambient temperature, the solvent was removed under reduced pressure to afford a yellow solid. The solid was dissolved in acetone (50 mL), and the resultant solution was filtered through a 1-cm pad of Celite on a coarse glass frit to remove mercury impurities. Removal of the solvent under reduced pressure afforded **1** as an analytically pure yellow powder (2.68 g, 73%): dec range 165–181 °C; IR (KBr, cm^{-1}) $\nu_{\text{Mn-CO}}$ 2000 (vs), 1919 (vs), $\nu_{\text{HgO}_2\text{CCH}_3}$ 1586 (s), 1461 (m); ¹H NMR (CDCl_3 , δ) 1.93 (s, HgOCOCH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{MnO}_3$: C, 14.44; H, 1.01. Found, C, 14.57; H, 1.20.

Reaction of Cyclopentadienylmanganese Tricarbonyl with 1 Equiv of Mercuric Acetate. In analogy with the above preparation of **1**, cyclopentadienylmanganese tricarbonyl (0.539 g, 2.64 mmol) and mercuric acetate (0.842 g, 2.64 mmol) were reacted to afford cyclopentadienylmanganese tricarbonyl (0.375 g, 78%) and **1** (0.023 g, 6%).

(Pentakis(acetoxymercurio)cyclopentadienyl)rhenium Tricarbonyl (2). In a fashion similar to the preparation of **1**, cyclopentadienylrhenium tricarbonyl (0.253 g, 0.754 mmol) and mercuric acetate (1.19 g, 3.77 mmol) were reacted to afford **2** as a pale yellow powder (1.09 g, 90%): dec range 213–237 °C; IR (KBr, cm^{-1}) ν_{CO} 1999 (s), 1897 (s), $\nu_{\text{HgO}_2\text{CCH}_3}$ 1572 (m), 1499 (m); ¹H NMR (CDCl_3 , δ) 1.94 (s, HgOCOCH_3); ¹³C{¹H} NMR (CD_2Cl_2 , ppm) 196.40 (s, Mn–CO), 178.88 (broad s, HgOCOCH_3), 50.98 (s, C–Hg), 22.52 (broad s, HgOCOCH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{Re}$: Re, 13.28; H, 0.93. Found: C, 13.41; H, 1.03.

Reaction of Cyclopentadienylrhenium Tricarbonyl with 1 Equiv of Mercuric Acetate. In analogy with the above preparation of **2**, cyclopentadienylrhenium tricarbonyl (0.254 g, 0.757 mmol) and mercuric acetate (0.232 g, 0.728 mmol) were reacted to afford cyclopentadienylrhenium tricarbonyl (0.125 g, 81%) and **2** (0.049 g, 10%).

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(Pentachlorocyclopentadienyl)manganese Tricarbonyl (3). A 250-mL round-bottomed flask was charged with **1** (0.250 g, 0.167 mmol), copper(II) chloride (0.560 g, 4.19 mmol), acetone (25 mL), and a stirbar and was fitted with a reflux condenser. The mixture was refluxed for 3 h. After it was cooled to ambient temperature, the mixture was filtered through a 1-cm pad of Celite on a coarse glass frit to afford a yellow solution. Removal of the solvent under reduced pressure afforded a brown solid. The solid was sublimed (ca. 100 °C, 0.1 mmHg) to afford **3** as a yellow crystalline solid (0.028 g, 45%): mp 76–77 °C (lit.⁶ mp 83–85 °C); IR (KBr, cm^{-1}) ν_{CO} 2033 (vs), 1954 (m) (lit.⁶ IR (cyclohexane) 2048 (s), 1982 (vs) cm^{-1}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 220.09 (s, Mn–CO), 94.61 (s, C_5Cl_5); HRMS calcd for $C_8Cl_5MnO_3$ 373.7670, found 373.7676.

(Pentabromocyclopentadienyl)manganese Tricarbonyl (4). In a fashion similar to the preparation of **3**, **1** (1.01 g, 0.671 mmol) and copper(II) bromide (3.75 g, 16.7 mmol) were reacted to afford **4** as a yellow crystalline solid (0.176 g, 44%): mp 116–117 °C (lit.⁷ mp 117 °C); IR (KBr, cm^{-1}) ν_{CO} 2026 (vs), 1958 (m) (lit.⁷ IR (CCl_4) 2045 (vs), 1963 (vs) cm^{-1}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 221.18 (s, Mn–CO), 86.66 (s, C_5Br_5); LRMS calcd for $C_8Br_5MnO_3$ 593.5, found 593.5.

(Pentaiodocyclopentadienyl)manganese Tricarbonyl (5). A 250-mL round-bottomed flask was charged with potassium iodide (0.728 g, 4.39 mmol), iodine (1.10 g, 4.33 mmol), water (50 mL), and a stirbar. The solution was stirred at ambient temperature for 0.5 h, and then **1** (1.30 g, 0.871 mmol) was added. The mixture was stirred at ambient temperature for 3 h, during which time a red precipitate formed. The crude product was collected on a medium-porosity glass frit and was washed successively with saturated aqueous sodium thiosulfate (250 mL) and saturated aqueous potassium iodide (250 mL) to remove mercury impurities. The remaining solid was dissolved in dichloromethane (50 mL), and this solution was passed through a 3-cm pad of silica gel on a coarse glass frit to afford a yellow solution. Removal of the solvent, followed by crystallization from hexane at –20 °C, afforded **5** as analytically pure yellow crystals (0.136 g, 19%): mp 141 °C dec (explodes without violence; lit.^{2b} mp 171 °C); IR (KBr, cm^{-1}) ν_{CO} 2029 (vs), 1957 (m) (lit.^{2b} IR (KBr) 2030, 1975, 1951 cm^{-1}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 207.03 (s, Mn–CO; lit.^{2b} 223.73 (s)), 68.17 (s, C_5I_5 ; lit.^{2b} 68.24 (s)); LRMS

calcd for $C_8I_5MnO_3$ 833, found 833. Anal. Calcd for $C_8I_5MnO_3$: C, 11.53; H, 0.00. Found: C, 11.11; H, 0.05.

Crystal Structure Determination of 5. The single-crystal X-ray diffraction experiment was performed on a Nicolet P2₁ automated diffractometer with Mo $K\alpha$ radiation and graphite monochromator at ambient temperature. The structure was refined in a blocked matrix with the programs of SHELX-76^{17a} and SHELXTL.^{17b} All atoms were described anisotropically. Absorption corrections were made by empirical methods. No corrections for secondary extinction were necessary. Neutral atom scattering factors and corrections for anomalous dispersions were from ref 17c. Table 1 contains experimental data. The asymmetric unit contains four independent molecules. Because of this, and the fact that the lattice angles are close to monoclinic values, the diffraction patterns were checked carefully for monoclinic symmetry. The axial photos clearly showed mirror violations along the *c* axis; therefore, a data set was collected for fully half of the complete sphere. As a check, the triclinic data were then averaged if they were monoclinic. The *R* value for averaging equivalent reflections yielded the very poor value of 35%, confirming that the unit cell is triclinic.

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Supplementary Material Available: Figures S1 and S2, showing perspective views of the four independent atoms in **5** with numbering schemes and the unit cell packing diagrams, and Tables S1–S6, listing full experimental details for data collection and refinement, thermal parameters, complete positional parameters, complete bond lengths, complete bond angles, and least-squares planes for **5** (19 pages). Ordering information is given on any current masthead page.

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