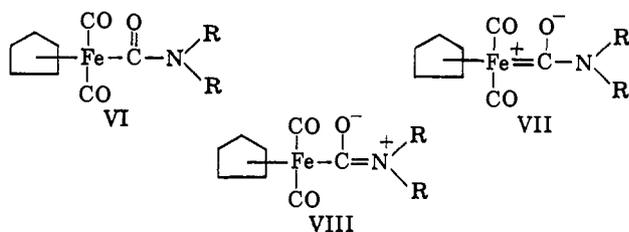


contains the free amine R_2NH identified by precipitation of the amine as the tetraphenylborate and comparison of this precipitate with an authentic sample of the amine tetraphenylborate. The iron appeared to be present in a brown insoluble material which was not further investigated. The compounds $C_5H_5Fe(CO)_2CONR_2$ are therefore unusual among cyclopentadienyliron dicarbonyl derivatives in being decomposed by water at room temperature. This sensitivity to water may account for the difficulty in obtaining reproducible infrared spectra in potassium bromide pellets (which are extremely difficult to have absolutely dry) and possibly for the presence of a band of variable intensity at $\sim 1760\text{ cm}^{-1}$ in such infrared spectra arising from the bridging carbonyl group in $[C_5H_5Fe(CO)_2]_2$ produced in decomposition.



It is of interest that in the compounds $C_5H_5Fe(CO)_2CONR_2$ the carbamyl carbonyl group appears at extremely low wave numbers ($1535 \pm 10\text{ cm}^{-1}$). This is much lower than even the acyl carbonyl group in the compounds $RCOFe(CO)_2C_5H_5$ ($\sim 1650\text{ cm}^{-1}$). This suggests that not only is the carbon-oxygen bond order reduced by resonance contributions of structures with partial iron-carbon double bonding (VII) similar to that postulated above for the acyl derivatives (II) but also by resonance contributions of structures with partial nitrogen-carbon double bonding (VIII) as in other amide derivatives.

C. Cyclopentadienyliron Dicarbonyl Thiolbenzoate.—Cyclopentadienyliron dicarbonyl dimer and thiolbenzoic acid were found to react at $\sim 100^\circ$ in an inert solvent to give the brown-orange compound $C_6H_5C(O)SFe(CO)_2C_5H_5$. This compound appears to be a covalent derivative similar to the recently reported covalent trifluoroacetates $CF_3CO_2W(CO)_3C_5H_5$, $CF_3CO_2Mo(CO)_3C_5H_5$ and $CF_3CO_2Re(CO)_5$.¹² The presence of thiolbenzoate carbonyl bands at 1590 and 1568 cm^{-1} suggests that there is a carbon-oxygen double bond in the molecule and therefore that the iron atom is bonded to the sulfur atom rather than to the oxygen atom. It will be noted that this organosulfur derivative of cyclopentadienyliron carbonyl is of a different type from the recently prepared compounds $[C_5H_5FeCOSR]_2$ ($R = \text{methyl}^{13}$ and $t\text{-butyl}^{14}$) with bridging sulfur atoms.

Other reactions of thiolacids and metal carbonyl derivatives have been investigated, but in most cases the reaction mixtures have been found to be more complex. In certain reactions involving iron pentacarbonyl or triiron dodecacarbonyl and thiolacids compounds of the type $[Fe(CO)_3SR]_2$ ¹⁵ have been isolated in low yield. Molybdenum hexacarbonyl and cyclopentadienylmolybdenum tricarbonyl dimer appear to react with thiolacids with complete loss of carbonyl and cyclopentadienyl groups to form black crystalline products of as yet uncertain composition. Some of these materials are being investigated further.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance in carrying out the reactions described in this paper and for taking most of the infrared spectra.

(12) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(13) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(14) R. B. King, unpublished results.

(15) See R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962), and references given there.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PENNA.]

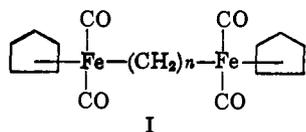
Reactions of Alkali Metal Derivatives of Metal Carbonyls. III. Reaction between Sodium Pentacarbonylmanganate(−I) and Certain Organic Polyhalides¹

BY R. B. KING

RECEIVED DECEMBER 21, 1962

The yellow crystalline manganese derivative $(CH_2)_3[Mn(CO)_5]_2$ has been prepared by the reaction between $NaMn(CO)_5$ and 1,3-dibromopropane or $ClCH_2CH_2CH_2COCl$. The reaction between $NaMn(CO)_5$ and 1,3-dibromobutane yields a similar yellow compound $CH_3C_3H_5[Mn(CO)_5]_2$. Proton n.m.r. studies suggest an unusual structure for these compounds. Reaction between $NaMn(CO)_5$ and perfluoroglutaryl dichloride yields the pale yellow diacyl derivative $(CO)_5MnCOCF_2CF_2CF_2COMn(CO)_5$ which undergoes facile decarbonylation on heating to give white $(CO)_5MnCF_2CF_2CF_2Mn(CO)_5$. Reaction between $NaMn(CO)_5$ and cyanuric chloride yields white crystalline $C_3N_3Cl[Mn(CO)_5]_2$.

Recently the reactions between $NaFe(CO)_2C_5H_5$ and various polymethylene dibromides of general formula $Br(CH_2)_nBr$ ($n = 3, 4, 5, 6$) were investigated and found to yield stable crystalline products of the general formula $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ with the expected properties for materials with iron-carbon σ -bonds and the obvious structure I.² Another sodium



derivative capable of reacting with certain organic halogen derivatives to form compounds with stable transition metal-carbon σ -bonds is the manganese derivative $NaMn(CO)_5$.³ It therefore seemed of interest to investigate the reactions between $NaMn(CO)_5$ and various organic polyhalogen derivatives in order to compare the properties of the resulting products with those of the previously prepared iron compounds.^{1,2}

(2) R. B. King, *Inorg. Chem.*, **2**, 531 (1963).

(3) (a) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957); (b) W. Hieber and G. Wagner, *Ann.*, **618**, 24 (1958); (c) W. Hieber, G. Braun and W. Beck, *Ber.*, **93**, 901 (1960); (d) H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960); (e) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

(1) For part II see R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer model 21 double-beam machine with NaCl optics. In addition, the metal carbonyl regions of the infrared spectrum of selected compounds (Table I) were taken in halocarbon oil mulls and recorded on a Perkin-Elmer model 112 single-beam machine with CaF₂ optics. Proton n.m.r. spectra were taken in carbon disulfide or chloroform solutions on a Varian Associates model A-60 machine. Hexamethyldisiloxane was used as an internal standard. F¹⁹ n.m.r. spectra were taken in tetrahydrofuran solution on a Varian Associates machine using CFCl₃ as an internal standard. Chemical shifts are given in p.p.m. upfield from CFCl₃. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; and Huffman Microanalytical Laboratory, Wheatridge, Colo. Melting points were taken in capillaries and are uncorrected.

Materials.—Dimanganese decacarbonyl was purchased from the Ethyl Corporation, New York, N. Y. The organic polyhalogen derivatives were commercial samples. Tetrahydrofuran was redistilled over lithium aluminum hydride. All reactions were carried out under nitrogen.

Reaction between NaMn(CO)₅ and 1,3-Dibromopropane.—A solution of 25 mmoles of NaMn(CO)₅ in 100 ml. of redistilled tetrahydrofuran was prepared from Mn₂(CO)₁₀ and excess ~1% sodium amalgam by the usual procedure. After removing the excess amalgam this solution was treated with 2.5 g. (12.5 mmoles) of 1,3-dibromopropane. After stirring overnight (~16 hr.) at room temperature the reaction mixture was heated 2 hr. at the boiling point. After cooling to room temperature solvent was removed at ~30 mm. The residue was extracted with four 50-ml. portions of pentane. This residue from the pentane extraction on sublimation at 60–90° (0.1 mm.) gave 0.57 g. of (CH₂)₃[Mn(CO)₅]₂, m.p. 64.5–65.5°.

The yellow pentane extracts were filtered by gravity. Solvent was removed from the filtrate at ~30 mm. leaving a yellow crystalline residue. A portion of this residue was sublimed at 70–80° (0.1 mm.) to give an additional 0.60 g. of yellow crystalline (CH₂)₃[Mn(CO)₅]₂, m.p. 67–68°. The remainder of this residue was chromatographed on a 2 × 60 cm. alumina column. After developing the chromatogram with pentane, two yellow bands were observed which were eluted with pentane. The eluate from the first yellow band which was extremely weakly colored yielded 0.05 g. of dimanganese decacarbonyl after evaporation and recrystallization from pentane. The eluate from the second yellow band possessed a much stronger yellow color. It was evaporated at ~30 mm. The resulting crystals were recrystallized by dissolving in pentane at room temperature and cooling the filtered yellow solution in a −78° bath. From the recrystallized material 0.40 g. of (CH₂)₃[Mn(CO)₅]₂, m.p. 64–65°, was isolated by sublimation at 80° (0.1 mm.).

The total amount of (CH₂)₃[Mn(CO)₅]₂ obtained from these three fractions was 1.57 g. (28% yield); infrared spectrum: C–H bands at 2975(sh) and 2875(w) cm.^{−1}; see Table I for metal carbonyl bands; other bands at 1478(w), 1455(w), 1404(w), 1375(m), 1282(w), 1198(s), 1185(s), 1054(m), 1030(m), 980(m), 942(vw), 894(w), 870(w), 833(w) and 778(w) cm.^{−1}; proton n.m.r. spectrum (see Fig. 1): triplet at τ = 5.14; triplet at τ = 6.32; quintet at τ = 8.04; all separations 8 cycles; relative intensities 2:2:2.

Anal. Calcd. for C₁₃H₆Mn₂O₁₀: C, 36.1; H, 1.4; Mn, 25.5; O, 37.0; mol. wt., 432. Found: C, 36.3, 36.2; H, 1.4, 1.4; Mn, 25.6; O, 37.1, 36.7; mol. wt., 431.

Reaction between NaMn(CO)₅ and 1,3-Dibromobutane.—The reaction between NaMn(CO)₅ and 1,3-dibromobutane was carried out in a manner analogous to the reaction between NaMn(CO)₅ and 1,3-dibromopropane described above. From 5.0 g. of dimanganese decacarbonyl 1.55 g. (27% yield) of CH₃C₃H₆[Mn(CO)₅]₂, m.p. 69–71°, was isolated; infrared spectrum: C–H at 2960(vw) and 2900(vw) cm.^{−1}; see Table I for metal carbonyl bands; other bands at 1455(vw), 1447(sh), 1400(w), 1380(w), 1355(m), 1300(vw), 1275(vw), 1215(m), 1195(w), 1180(w), 1135(vw), 1064(vw), 1013(m), 970(w), 940(vw), 787(w), 785(sh), 783(sh) and 757(w) cm.^{−1}; proton n.m.r. spectrum (see Fig. 1): complex asymmetric multiplet (seven discernible peaks) centered at τ = ~4.9; complex asymmetric multiplet (eight discernible peaks) centered at τ = ~6.3; broad resonance centered at τ = 7.9; sharp doublet due to the three methyl protons at τ = 8.44, J = 7 cycles; approximate relative intensities 1:2:2:3.

Anal. Calcd. for C₁₄H₈Mn₂O₁₀: C, 37.7; H, 1.8; Mn, 24.7; O, 35.8; mol. wt., 446. Found: C, 37.7; H, 2.0; Mn, 25.2; O, 35.6; mol. wt., 442.

Reaction between NaMn(CO)₅ and ClCH₂CH₂CH₂COCl.—A solution of 25 mmoles of NaMn(CO)₅ in 75 ml. of redistilled tetrahydrofuran was prepared by the usual procedure from Mn₂(CO)₁₀ and excess ~1% sodium amalgam. After removing the excess amalgam the NaMn(CO)₅ solution was treated with 1.76 g. (12.5 mmoles) of ClCH₂CH₂CH₂COCl. The reaction mixture was stirred for 16 hr. at room temperature. Solvent was removed at ~30 mm. leaving a yellow-orange semisolid residue. This residue was extracted with three 50-ml. portions of dichloromethane and the yellow extract filtered by gravity. Solvent was removed from the filtrate at ~30 mm. The resulting residue was dissolved in ~100 ml. of pentane and chromatographed on a 2 × 60 cm. alumina column. The chromatogram was developed with pentane. Two yellow bands appeared, the second band being stronger than the first. They were eluted with pentane and solvent removed from the eluates at ~30 mm. The yellow crystalline residue from the first eluate after recrystallization from pentane yielded 0.40 g. (8% recovery) of Mn₂(CO)₁₀, m.p. 152–153°. The yellow crystalline residue from the second band was also recrystallized from pentane to give 0.75 g. (14% conversion) of (CH₂)₃[Mn(CO)₅]₂, m.p. 67–68°. The infrared and proton n.m.r. spectra of this material were identical with those of the material obtained from NaMn(CO)₅ and 1,3-dibromopropane.

TABLE I
INFRARED SPECTRA OF −Mn(CO)₅ DERIVATIVES IN THE METAL CARBONYL REGION^a

Compound	Metal carbonyl bands, cm. ^{−1}
Mn ₂ (CO) ₁₀	1942, 1963, 1976, 1984, 2011, 2027, 2041
Mn(CO) ₅ Br	1956, 1991, 2046, 2062, 2078, 2139
(CH ₂) ₃ [Mn(CO) ₅] ₂	1959, 1972, 1989, 1995, 2022, 2088
CH ₃ C ₃ H ₆ [Mn(CO) ₅] ₂	1953, 1971, 1989, 1998, 2021, 2089
(CF ₂) ₃ (CO) ₂ [Mn(CO) ₅] ₂	1967, 1994, 1999, 2017, 2040, 2078, 2084, 2131
(CF ₂) ₃ [Mn(CO) ₅] ₂	2003, 2012, 2021, 2028, 2040, 2052 (sh), 2070; 2074, 2085, 2133
C ₃ N ₂ Cl[Mn(CO) ₅] ₂	2011, 2020, 2035, 2051, 2069, 2121, 2128

^a CaF₂ optics, halocarbon oil mulls.

(CO)₁₀ and excess ~1% sodium amalgam. After removing the excess amalgam the NaMn(CO)₅ solution was treated with 1.76 g. (12.5 mmoles) of ClCH₂CH₂CH₂COCl. The reaction mixture was stirred for 16 hr. at room temperature. Solvent was removed at ~30 mm. leaving a yellow-orange semisolid residue. This residue was extracted with three 50-ml. portions of dichloromethane and the yellow extract filtered by gravity. Solvent was removed from the filtrate at ~30 mm. The resulting residue was dissolved in ~100 ml. of pentane and chromatographed on a 2 × 60 cm. alumina column. The chromatogram was developed with pentane. Two yellow bands appeared, the second band being stronger than the first. They were eluted with pentane and solvent removed from the eluates at ~30 mm. The yellow crystalline residue from the first eluate after recrystallization from pentane yielded 0.40 g. (8% recovery) of Mn₂(CO)₁₀, m.p. 152–153°. The yellow crystalline residue from the second band was also recrystallized from pentane to give 0.75 g. (14% conversion) of (CH₂)₃[Mn(CO)₅]₂, m.p. 67–68°. The infrared and proton n.m.r. spectra of this material were identical with those of the material obtained from NaMn(CO)₅ and 1,3-dibromopropane.

Anal. Calcd. for C₁₃H₆Mn₂O₁₀: C, 36.1; H, 1.4; O, 37.0. Found: C, 35.7; H, 1.5; O, 36.5.

Reaction between NaMn(CO)₅ and Perfluoroglutaryl Dichloride.—A solution of 25 mmoles of NaMn(CO)₅ in 100 ml. of redistilled tetrahydrofuran was prepared by the usual procedure from Mn₂(CO)₁₀ and excess ~1% sodium amalgam. After removing the excess amalgam, the NaMn(CO)₅ solution was treated with 3.88 g. (13.7 mmoles) of perfluoroglutaryl dichloride. The reaction mixture was stirred for ~40 hr. at room temperature. Solvent was then removed at ~30 mm. After admitting nitrogen the residue was extracted with three 50-ml. portions of dichloromethane. The extracts were filtered by gravity and solvent was removed from the filtrate at ~30 mm. The resulting pale yellow crystalline residue was recrystallized from a hexane-dichloromethane mixture to give 3.58 g. (47% yield) of very pale yellow crystals of (CO)₅MnCO(CF₂)₃COMn(CO)₅, m.p. 105–106°; infrared spectrum: see Table I for metal carbonyl bands; acyl carbonyl band at 1635(s) cm.^{−1}; C–F bands at 1256(m), 1150(s), 1135(s), 1075(w) and 972(m) cm.^{−1}; other bands at 708(m) and 702(s) cm.^{−1}; F¹⁹ n.m.r. spectrum: resonances at 109 p.p.m. and 121 p.p.m. upfield from CFCl₃ of approximate relative intensities 2:1; no fine structure of these resonances could be discerned.

Anal. Calcd. for C₁₅F₆Mn₂O₁₂: C, 30.2; H, 0.0; F, 19.1; Mn, 18.5. Found: C, 30.2; H, 0.5; F, 19.0; Mn, 18.0.

Preparation of (CF₂)₃[Mn(CO)₅]₂.—A sample of 1.0 g. (1.68 mmoles) of the perfluoroglutaryl derivative (CO)₅MnCO(CF₂)₃COMn(CO)₅ was heated at 105° (~200 mm.) for 90 minutes. Carbon monoxide was evolved. The residue was sublimed at 105° (0.25 mm.) for 16 hr., collecting the sublimate on a water-cooled probe to give 0.43 g. (47% yield) of pure white crystals of (CF₂)₃[Mn(CO)₅]₂, m.p. 161°; infrared spectrum: see Table I for metal carbonyl bands; C–F bands at 1185(w), 1110(s), 1054(s), 1025(s), 997(m), 985(m) and 913(m) cm.^{−1}; other band at 732(m) cm.^{−1}; F¹⁹ n.m.r. spectrum: resonances at 55 p.p.m. (triplet, J = ~2 cycles) and 99 p.p.m. (quintet, J = ~2 cycles) upfield from CFCl₃ of approximate relative intensities 2:1.

Anal. Calcd. for C₁₃F₆Mn₂O₁₀: C, 28.9; H, 0.0; F, 21.2; Mn, 20.3; mol. wt., 540. Found: C, 29.0; H, 0.3; F, 20.8; Mn, 20.6; mol. wt., 575.

Reaction between NaMn(CO)₅ and Cyanuric Chloride.—A solution containing ~10 mmoles of NaMn(CO)₅ in ~50 ml. of tetrahydrofuran was prepared in the usual manner from ~1% sodium amalgam and Mn₂(CO)₁₀. This was treated at room temperature with 0.62 g. (3.3 mmoles) of cyanuric chloride. After stirring for 12 hr. at ~25°, solvent was removed. The yellowish residue was extracted with two 30-ml. portions of dichloromethane and the extract filtered. Solvent was removed

(4) Most of the work on C₃N₂Cl[Mn(CO)₅]₂ described in this paper was carried out in 1960 at Harvard University. The author is indebted to Prof. F. G. A. Stone there for helpful discussions and to Dr. Paul Treichel for the isopiestic molecular weight determination on this compound.

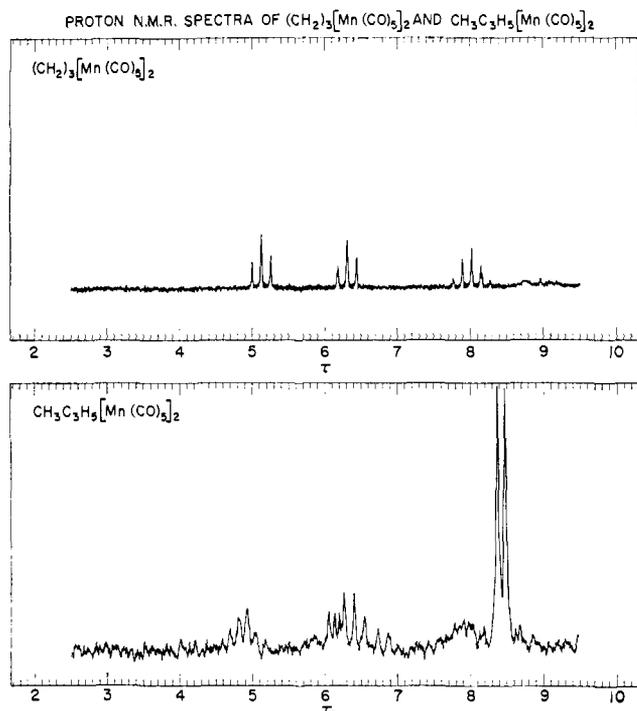


Figure 1.

from the filtrate at ~ 25 mm. The resulting yellowish residue was purified by sublimation at 0.1 mm. After collecting and removing $\text{Mn}_2(\text{CO})_{10}$ which sublimed at $50\text{--}80^\circ$, the sublimation was continued at $100\text{--}120^\circ$ for 16 hr. The resulting white sublimate was purified by two additional sublimations giving 200 mg. (11% yield) of pure white crystals of $\text{C}_3\text{N}_3\text{Cl}[\text{Mn}(\text{CO})_5]_2$. Each sublimation left significant amounts of a brownish residue.

On heating, $\text{C}_3\text{N}_3\text{Cl}[\text{Mn}(\text{CO})_5]_2$ began to turn black at $\sim 170^\circ$.

Anal. Calcd. for $\text{C}_3\text{N}_3\text{O}_{10}\text{ClMn}_2$: C, 31.0; H, 0.0; N, 8.3; Cl, 7.1; Mn, 21.9; mol. wt., 503. Found: C, 31.4; H, 0.0; N, 8.1; Cl, 6.8; Mn, 21.3; mol. wt., 514 (isopiestic in dichloromethane).⁴

Discussion

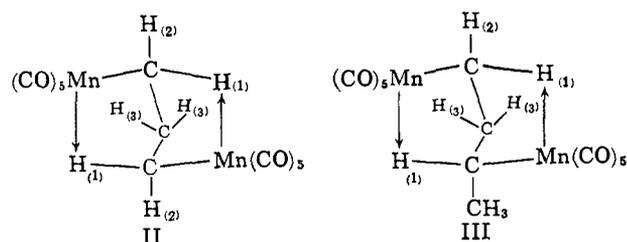
A. $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ and $\text{CH}_3\text{C}_3\text{H}_5[\text{Mn}(\text{CO})_5]_2$.—The compound $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ does not appear to be the same type of compound as $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ (I, $n = 3$).² The primary difference between these two compounds is the portion of the proton n.m.r. spectrum attributable to the protons of the three methylene groups. The proton n.m.r. spectrum of the iron compound $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ exhibits a single sharp resonance at $\tau = 8.5$ due to all six methylene protons besides the resonance due to the cyclopentadienyl group. The proton n.m.r. spectrum of the manganese compound $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ (see Fig. 1) exhibits three widely separated resonances of relative intensities 1:1:1 indicating the six methylene protons to be present as pairs of three chemically distinct types. The manganese compound and the iron compound also differ in their colors as compared with the colors of the methyl derivatives. Thus both $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ and $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ ⁵ are orange, whereas $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ is bright yellow (very similar to $\text{Mn}_2(\text{CO})_{10}$ in color) but $\text{CH}_3\text{Mn}(\text{CO})_5$ ^{3a} is pure white. These color differences suggest that whereas the structure of $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ is very similar to that of $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ except that the former contains two iron-carbon σ -bonds, the structure of $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ contains features not present in $\text{CH}_3\text{Mn}(\text{CO})_5$.

Upon consideration of the unusual proton n.m.r. spectrum of $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ it is apparent that the compound must contain some unprecedented structural feature. This proton n.m.r. spectrum exhibited the

(5) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

same three resonances in the same 1:1:1 ratio on spectra run in carbon disulfide, chloroform or trichlorofluoromethane; on samples obtained from $\text{NaMn}(\text{CO})_5$ and 1,3-dibromopropane and from $\text{NaMn}(\text{CO})_5$ and $\text{ClCH}_2\text{CH}_2\text{COCl}$; and on three fractions all melting between 64 and 68° isolated in different manners from the same reaction mixture (see Experimental section). This would make highly improbable any interpretation of this n.m.r. spectrum based on the presence of two isomers present in equal quantity since the relative quantities in a mixture of isomers sufficiently different to exhibit methylene chemical shifts greater than 1 p.p.m. should be noticeably altered by either a change in the solvent, a change in the method of preparation, or a change in the method of isolation of the product. Moreover, the extensive analytical data eliminate alternative compositions such as $(\text{CH}_2)_3\text{Mn}_2(\text{CO})_9$. The infrared spectrum, in addition, shows no band in the range $1550\text{--}1900\text{ cm.}^{-1}$, eliminating the possibility of the presence of a bridging or acyl carbonyl group. From all of these data it is apparent that the structure of $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ must consist of two $-\text{Mn}(\text{CO})_5$ residues σ -bonded to each end of a three-carbon saturated aliphatic chain.⁶ There are no double bonds to form π -bonds with manganese atoms, possibly creating in this manner three different types of protons among the three methylene groups.

The only structure for $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ in agreement with all of the data appears to be II which contains a novel type of manganese-hydrogen bond. The observed n.m.r. spectra of $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ are in excellent agreement with structure II provided $J_{13} = J_{23} = 8$ cycles and $J_{12} = \sim 0$.⁷ Such coupling constants are not unreasonable since $\text{H}_{(1)}$ and $\text{H}_{(2)}$ would both be coupled to $\text{H}_{(3)}$ across a carbon-carbon single bond and 8 cycles is similar to the observed coupling



constant of 7 cycles for the similar coupling in 1,3-dibromopropane. Since there is no precedent for the type of manganese-hydrogen bond postulated in II, there is no known reason to expect J_{12} not to be zero or nearly so. On this basis the quintet at $\tau = 8.04$ may be assigned to the center methylene protons $\text{H}_{(3)}$ split into the quintet by the four equivalently coupled protons $\text{H}_{(1)}$ and $\text{H}_{(2)}$. The triplets at $\tau = 5.14$ and $\tau = 6.32$ would then be assigned to $\text{H}_{(1)}$ and $\text{H}_{(2)}$, each split into the triplet by the two protons $\text{H}_{(3)}$. Merely on the basis of this spectrum, however, it is impossible to decide which triplet to assign to $\text{H}_{(1)}$ and which triplet to $\text{H}_{(2)}$.

In an attempt to have a more definite basis as to which triplet in the n.m.r. spectrum of $(\text{CH}_2)_3[\text{Mn}$

(6) As a consequence of this the two terminal methylene groups must be equivalent since there is only one way in which an $-\text{Mn}(\text{CO})_5$ group can be σ -bonded to a carbon atom. Thus the presence of the three methylene resonances cannot be explained by non-equivalence of the two terminal methylene groups.

(7) A referee suggested the alternative assignment of coupling constants $J_{12} = J_{13} = J_{23} = 8$ cycles and $J_{13'} = J_{23} = 0$, where $\text{H}_{(3)}$ and $\text{H}_{(3')}$ are central methylene protons of different configurations held rigidly. However, it is difficult then to explain the quintet arising from the center methylene protons. Moreover, this assignment requires the fortuitous equivalence of more coupling constants than the assignments given above.

(CO)₅]₂ is due to H₍₁₎ and which triplet is due to H₍₂₎ as well as to have an additional example of this peculiar type of manganese compound, the reaction between 1,3-dibromobutane and NaMn(CO)₅ was investigated. A yellow crystalline solid of the expected composition CH₃C₃H₅[Mn(CO)₅]₂ was isolated. This compound possessed an infrared spectrum in the metal carbonyl region very similar to that of (CH₂)₃[Mn(CO)₅]₂ (Table I).

As would be expected, the proton n.m.r. spectrum of CH₃C₃H₅[Mn(CO)₅]₂ (III) was found to be quite complex due to the many types of splitting possible (see Fig. 1). Four main resonances were observed of relative intensities 1:2:2:3. The sharp doublet at $\tau = 8.44$ may be assigned to the three methyl protons split by H₍₁₎. The remaining resonances were either broad or complex. The broad resonance centered at $\tau = \sim 7.9$ of relative intensity 2 may be assigned to the two protons of the center methylene group (H₍₃₎ in III) on the basis of its similarity in position to the quintet at $\tau = 8.04$ in (CH₂)₃[Mn(CO)₅]₂. On the basis of relative intensities the resonance of relative intensity 1 at $\tau = \sim 4.9$ may be assigned to the single proton of the end methylene group which is not bonded to the manganese atom (H₍₂₎ in III) and the resonance of relative intensity 2 at $\tau = \sim 6.3$ may be assigned to the two protons of the end methylene groups which are bonded to the manganese atom (H₍₁₎ in III).

This interpretation of the proton n.m.r. spectrum of CH₃C₃H₅[Mn(CO)₅]₂ indicates that in the proton n.m.r. spectrum of (CH₂)₃[Mn(CO)₅]₂ the triplet at $\tau = 5.14$ may be assigned to the protons of the end methylene groups which are not bonded to the manganese atom (H₍₂₎ in II) on the basis of its similarity in position to the resonance in CH₃C₃H₅[Mn(CO)₅]₂ at $\tau = \sim 4.9$. In addition, the triplet at $\tau = 6.32$ may be assigned to the protons of the end methylene groups which are bonded to the manganese atoms (H₍₁₎ in II) on the basis of its similarity in position to the resonance in CH₃C₃H₅[Mn(CO)₅]₂ at $\tau = \sim 6.3$.

A type of metal-hydrogen bond similar to that postulated for (CH₂)₃[Mn(CO)₅]₂ but involving a hydrogen bridge between a transition metal atom and an oxygen atom rather than a hydrogen bridge between a transition metal atom and a carbon atom has been postulated for certain hydroxyl derivatives of metallocenes on the basis of a shift in the oxygen-hydrogen stretching frequency in the infrared spectrum.⁸ The weakness of the carbon-hydrogen stretching bands in (CH₂)₃[Mn(CO)₅]₂ and CH₃C₃H₅[Mn(CO)₅]₂ makes of questionable reliability any analogous deductions based on the carbon-hydrogen stretching frequencies in these compounds. Both (CH₂)₃[Mn(CO)₅]₂ and CH₃C₃H₅[Mn(CO)₅]₂ exhibit several bands in the 1480-970 cm.⁻¹ region of weak to strong relative intensities. Although at least most of these bands may be attributed to vibrations in the three-carbon system linking the two manganese atoms, it is possible that the bands at 1198(s) and 1185(s) cm.⁻¹ in (CH₂)₃[Mn(CO)₅]₂ and the bands at 1215(m), 1195(w) and 1180(w) cm.⁻¹ in CH₃C₃H₅[Mn(CO)₅]₂ which have no counterparts in (CH₂)₃[Fe(CO)₂C₃H₅]₂² may be attributed to the manganese-hydrogen bonds in structures II and III. The relative complexity of these molecules makes a definite assignment of these bands of doubtful validity.

It should be emphasized that the manganese-hydrogen bond postulated for (CH₂)₃[Mn(CO)₅]₂ and CH₃C₃H₅[Mn(CO)₅]₂ must not be regarded as analogous to the manganese-hydrogen bonds in Mn(CO)₅H and related compounds where the manganese atom and the hydrogen atom each contribute one electron to the bonding

and which are characterized by proton resonances at $\tau > 10$. Instead the manganese-hydrogen bond in (CH₂)₃[Mn(CO)₅]₂ may be regarded as being formed by the donation to the hydrogen atom of one of the three lone electron pairs in the three 3d-orbitals which are not involved in the d²sp³ hybridization of the octahedrally coordinated manganese atom. It is thus analogous to the hydrogen bridge bond in the HF₂⁻ ion in which one of the lone electron pairs of the fluorine atom is donated to the hydrogen atom. The ability for lone electron pairs present in non-bonding d-orbitals of transition metal atoms to form bonds with relatively positive species is indicated by recent studies on the protonation of transition metal complexes⁹ where compounds in which the transition metal already had the inert gas configuration were found to be capable of adding a proton to form protonated species in which this proton is attached to one of the lone pairs in the non-bonding d-orbitals. Such a protonation reaction may be regarded as analogous to the formation of NH₄⁺ by addition of a proton to one of the lone pairs of NH₃.

A crucial factor in the formation of the manganese-hydrogen "bridge" bond¹⁰ in (CH₂)₃[Mn(CO)₅]₂ is the fact that the formation of this bond creates a five-membered ring consisting of three carbon atoms, one hydrogen atom and one manganese atom. In order to determine whether rings of other sizes containing manganese-hydrogen bridge bonds could exist, the reactions between other dihaloalkanes and NaMn(CO)₅ were investigated. The reaction between 1,2-dibromoethane and NaMn(CO)₅ did not give a product analogous to (CH₂)₃[Mn(CO)₅]₂; the principal product of the reaction was Mn₂(CO)₁₀. Thus a four-membered ring with a manganese-hydrogen bridge bond does not seem to be especially readily formed. The reaction between 1,5-dibromopentane and NaMn(CO)₅ also did not give a product analogous to (CH₂)₃[Mn(CO)₅]₂, suggesting difficulty in forming a seven-membered ring with a manganese-hydrogen bridge bond.

Numerous attempts were made to prepare a compound (CH₂)₄[Mn(CO)₅]₂ from 1,4-dibromobutane and NaMn(CO)₅ which would contain two six-membered rings with manganese-hydrogen bridge bonding. If the reaction between 1,4-dibromobutane and NaMn(CO)₅ was carried out at the boiling point of tetrahydrofuran in a manner similar to that described in the Experimental section for the preparation of (CH₂)₃[Mn(CO)₅]₂, no (CH₂)₄[Mn(CO)₅]₂ was isolated; the principal product was Mn₂(CO)₁₀. If this reaction was carried out at 25°, mixtures of (CH₂)₄[Mn(CO)₅]₂ and Mn₂(CO)₁₀ were obtained which were not readily separated even by chromatography and the analytical data, therefore, were not entirely satisfactory. However, since Mn₂(CO)₁₀ contains no protons, it was possible to examine the proton n.m.r. spectrum of (CH₂)₄[Mn(CO)₅]₂ even though it was contaminated with Mn₂(CO)₁₀. Despite the apparent absence of paramagnetic impurities the spectrum was relatively broad. However, resonances were observed at $\tau = 5.37$ and $\tau = 6.52$ which may be attributed to the protons on the end methylene groups not bonded to the manganese atom and those bonded to the manganese atom, respectively, on the basis of their similarities in positions to the resonances of the corresponding protons in (CH₂)₃[Mn(CO)₅]₂. In addition a strong but still broad resonance

(9) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(10) In the discussion which follows the term "manganese-hydrogen bridge bond" will be used in reference to the type of manganese-hydrogen bond postulated to be present in (CH₂)₃[Mn(CO)₅]₂ where the hydrogen acts as a "bridge" between a carbon atom and a manganese atom. This term is introduced to prevent confusion between this type of bond and the manganese-hydrogen bond present in Mn(CO)₅H.

(8) D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

was observed at $\tau = \sim 8.2$ due to the remaining methylene protons and possibly due to all of the methylene protons of an isomeric $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ without any manganese-hydrogen bridge bonds and of a structure analogous to $(\text{CH}_2)_4[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2$.² The presence of this second isomer $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ without manganese-hydrogen bridge bonds in this product is suggested by the fact that the resonance at $\tau = \sim 8.2$ appears to consist of a sharper peak possibly due to the eight methylene protons of the $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ without manganese-hydrogen bridge bonds which overlaps a broader peak possibly due to the four protons of the two center methylene groups of the $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ with manganese-hydrogen bridge bonds and also by the fact that the resonance at $\tau = \sim 8.2$ is of more than twice the relative intensity of either the resonance at $\tau = 5.37$ or the resonance at $\tau = 6.52$. In $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ it thus appears that possibly an isomer with manganese-hydrogen bridge bonds and one without manganese-hydrogen bridge bonds are in equilibrium. In any case, $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ definitely appears to be much less stable than $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ with respect to decomposition to give $\text{Mn}_2(\text{CO})_{10}$.

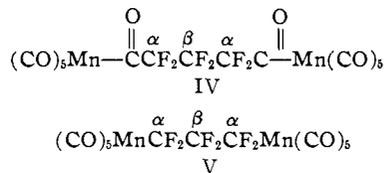
In an attempt to prepare $(\text{CH}_2)_3\text{CO}[\text{Mn}(\text{CO})_5]_2$ which might be an example of an acyl derivative with manganese-hydrogen bridge bonding, the reaction between $\text{NaMn}(\text{CO})_5$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COCl}$ was investigated. Instead of the expected acyl derivative the product was $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$, identical with the material obtained from $\text{NaMn}(\text{CO})_5$ and 1,3-dibromopropane, decarbonylation occurring even though the reaction mixture was not heated above room temperature. This extremely facile decarbonylation reaction of the as yet unisolated but presumed intermediate $(\text{CH}_2)_3\text{CO}[\text{Mn}(\text{CO})_5]_2$ ¹¹ to give $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ and the lower stability of $(\text{CH}_2)_4[\text{Mn}(\text{CO})_5]_2$ as compared with $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ both demonstrate the lower stability of six-membered rings containing manganese-hydrogen bridge bonds as compared with five-membered rings containing manganese-hydrogen bridge bonds.

B. $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$.—Attempts to prepare compounds of the type $(\text{CH}_2)_n[\text{Mn}(\text{CO})_5]_2$ exactly analogous to the iron compounds $(\text{CH}_2)_n[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2$ ² (I) have been unsuccessful due to the tendency either for the products to decompose to give $\text{Mn}_2(\text{CO})_{10}$ or to form products of the same composition $(\text{CH}_2)_n[\text{Mn}(\text{CO})_5]_2$ but with structures which are not analogous to the iron compounds I due to the greater tendency for the $-\text{Mn}(\text{CO})_5$ group to participate in transition metal-hydrogen bridge bonding than the $-\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$ group. The synthesis of the fluorine analogs of these compounds, however, of general formula $(\text{CF}_2)_n[\text{Mn}(\text{CO})_5]_2$, should meet with neither of these difficulties. As has been repeatedly shown the carbon-transition metal bonds in σ -bonded fluorocarbon derivatives are much stronger than the carbon-transition metal bonds in σ -bonded hydrocarbon derivatives. Thus the carbon-manganese bonds in the compounds $(\text{CF}_2)_n[\text{Mn}(\text{CO})_5]_2$ should not be readily broken producing $\text{Mn}_2(\text{CO})_{10}$. Moreover, with no hydrogen atoms manganese-hydrogen bridge bonding would be impossible.

The most satisfactory route to perfluoroalkyl derivatives of manganese is by the thermal decarbonylation

(11) The analogous $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CH}_2)_3\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$ has been isolated and characterized.¹

of the corresponding perfluoroacyl derivatives at temperatures around 100° .^{3d,3e} In an attempt to extend this reaction to the preparation of fluorocarbon derivatives containing two manganese atoms the reaction between perfluoroglutaryl dichloride and $\text{NaMn}(\text{CO})_5$ was investigated. The very pale yellow acyl derivative $(\text{CF}_2)_3(\text{CO})_2[\text{Mn}(\text{CO})_5]_2$ was readily isolated. This underwent facile decarbonylation at 105° to give the pure white perfluorotrimethylene derivative $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$.



The F^{19} n.m.r. spectra of these new fluorocarbon derivatives of manganese are of interest. The spectrum of the perfluoroglutaryl derivative IV exhibits a resonance at 109 p.p.m. which may be assigned to the four fluorine atoms of the α - CF_2 groups and a resonance at 121 p.p.m. which may be assigned to the two fluorine atoms of the β - CF_2 group on the basis of their relative intensities. In the spectrum of $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ (V) the resonance due to the four fluorine atoms of the α - CF_2 groups appears at 55 p.p.m. and the resonance due to the two fluorine atoms of the β - CF_2 group at 99 p.p.m. It will be noted that both resonances of $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ (V) have been shifted downfield relative to the corresponding resonances in $(\text{CF}_2)_3(\text{CO})_2[\text{Mn}(\text{CO})_5]_2$ (IV). However, as would be expected, the resonance assigned to the fluorine atoms of the α - CF_2 groups in $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ (V) which are directly bonded to a manganese atom has been shifted downfield the most and appears in the usual region for fluorine atoms on a carbon atom directly bonded to a transition metal atom.^{3d,12} It is also of interest that the resonance due to the α - CF_2 groups in $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ appears as a triplet, $J = \sim 2$ cycles, and the resonance due to the fluorine atoms of the β - CF_2 groups as a quintet, $J = \sim 2$ cycles, due to coupling between these two types of fluorine atoms. These n.m.r. data are in excellent agreement with the "normal" structure V for $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ as opposed to a completely fluorinated version of the structure II proposed for $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$. It should be noted that $(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$ besides showing two resonances in a 2:1 ratio in the F^{19} n.m.r. spectrum is pure white whereas $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ is bright yellow and exhibits three resonances in a 1:1:1 ratio in the proton n.m.r. spectrum.

C. $\text{C}_3\text{N}_3\text{Cl}[\text{Mn}(\text{CO})_5]_2$.—Recently the iron complex $\text{C}_3\text{N}_3\text{Cl}[\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5]_2$ was prepared from cyanuric chloride and $\text{NaFe}(\text{CO})_2\text{C}_6\text{H}_5$.² It seemed of interest to carry out the analogous reaction with $\text{NaMn}(\text{CO})_5$. This led to the isolation of the pure white entirely analogous $\text{C}_3\text{N}_3\text{Cl}[\text{Mn}(\text{CO})_5]_2$. It thus appears that $\text{NaMn}(\text{CO})_5$ like $\text{NaFe}(\text{CO})_2\text{C}_6\text{H}_5$ substitutes readily only two of the three chlorine atoms in cyanuric chloride.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance and for taking most of the infrared spectra.

(12) R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel and F. G. A. Stone, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 619.