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Organometallic Chemistry of the Transition Metals. VII. Cyclopentadienylmetal Nitrosyl Derivatives of Chromium and Manganese with Bridging Nitrosyl Groups[1,2]

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The compounds $[C_5H_5Cr(NO)_2]_2$ and $[C_5H_5MnCONO]_2$ have been obtained by sodium borohydride reduction of $C_5H_5Cr(NO)_2Cl$ and $[C_5H_5Mn(CO)_2NO][PF_6]$, respectively, in aqueous media. Infrared spectra of these new nitrosyl derivatives indicate the presence of bridging nitrosyl groups. Ultraviolet irradiation of the manganese derivative $[C_5H_5MnCONO]_2$ in benzene solution converts it to the black hexanuclear derivative $(C_5H_5)_6Mn_6(NO)_8$.

Introduction

A variety of metal nitrosyl derivatives are known with terminal nitrosyl groups. However, the only reported metal nitrosyl derivative claimed to have bridging nitrosyl groups on the basis of a band in the infrared spectrum at 1510 $cm.^{-1}$ is the peculiar compound $(C_5H_5)_3Mn_2(NO)_3$ prepared by Piper and Wilkinson[3] several years ago. If the suggestion of bridging nitrosyl groups in $(C_5H_5)_3Mn_2(NO)_3$ is indeed correct, it seemed very likely that metal nitrosyl derivatives with bridging nitrosyl groups could also be prepared isoelectronic with known metal carbonyl derivatives with bridging carbonyl groups. In this paper we describe the preparation and properties of the compounds $[C_5H_5MnCONO]_2$ and $[C_5H_5Cr(NO)_2]_2$ isoelectronic with the well-known stable compound $[C_5H_5Fe(CO)_2]_2$.[4]

Experimental

Infrared spectra were generally taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl and nitrosyl regions of the infrared spectra of certain compounds were investigated in more detail in halocarbon oil mulls on a Beckman IR-9 spectrometer. Proton n.m.r. spectra were taken in carbon disulfide, chloroform, benzene, or acetone solutions with hexamethyldisiloxane as an internal standard and recorded on a Varian A-60 spectrometer. Ultraviolet spectra were taken in cyclohexane solution and recorded on a Cary Model 14 spectrometer. Microanalyses and molecular weight determinations (Mechrolab osmometer in benzene solution) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Materials.—Cyclopentadienylmanganese tricarbonyl was purchased from the Ethyl Corporation, New York, New York. Ammonium hexafluorophosphate was purchased from Ozark Mahoning Company, Tulsa, Oklahoma. Anhydrous chromium(III) chloride was obtained from the Diamond Alkali Company, Painesville, Ohio. Sodium borohydride was purchased from Metal Hydrides, Beverly, Massachusetts. Molybdenum and tungsten hexacarbonyls were purchased from the Climax Molybdenum Company, New York, New York.

Cyclopentadienylchromium dinitrosyl chloride, first reported by Piper and Wilkinson,[3] was prepared by a more recently described procedure of Fischer and Kuzel.[5] The product from the crude reaction mixture was extracted with dichloromethane rather than hexane in order to permit milder extraction conditions. The $C_5H_5Cr(NO)_2Cl$ thus obtained was identified by its n.m.r. and infrared spectra.

Cyclopentadienylchromium Dinitrosyl Dimer. (A) **From $C_5H_5Cr(NO)_2Cl$.**—A mixture of 8.50 g. (40 mmoles) of $C_5H_5Cr(NO)_2Cl$, 150 ml. of water, and 150 ml. of thiophene-free benzene was treated dropwise under nitrogen with 3.0 g. (79 mmoles) of sodium borohydride dissolved in 50 ml. of water. After stirring for 16 hr. at room temperature the reaction mixture was filtered by suction. The benzene layer was separated, combined with a benzene extract of the aqueous layer, and then filtered by gravity. Solvent was removed from the filtrate at ~30 mm. The remaining black residue was dissolved in ~100 ml. of benzene and the filtered dark red-brown solution chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with benzene. A single large red-violet band appeared which was eluted with benzene, the eluate being collected under nitrogen. Solvent was removed from the filtered eluate at ~30 mm., leaving red-violet crystals which were washed with two 20-ml. portions of pentane and dried to give 0.70 g. (5% yield) of $[C_5H_5Cr(NO)_2]_2$, m.p. 158–159° dec.

(B) **From Chromium(III) Chloride.**—A solution of sodium cyclopentadienide was prepared under nitrogen by the usual procedure by adding dropwise 125 ml. (100 g., 1510 mmoles) of freshly cracked cyclopentadiene to a mixture of 47.0 g. (1020 mg.-atoms of sodium) of 50% sodium dispersion in mineral oil and 1000 ml. of tetrahydrofuran freshly distilled over lithium aluminum hydride. The resulting pink solution was treated with 80 g. (500 mmoles) of anhydrous chromium(III) chloride. An exothermic reaction occurred and the reaction mixture became deep green. To ensure complete reaction the reaction mixture was refluxed for 2.5 hr.

After standing overnight the reaction mixture was treated with ~30 g. (1000 mmoles) of nitric oxide purified by prior passage through a −78° trap charged with Linde Type 4A Molecular Sieves. The amount of nitric oxide added was estimated by the pressure drop in a tank of known size. After the nitric oxide treatment was complete, the reaction mixture was stirred for an additional hour. Solvent was then removed at 30 mm.

The resulting green-black residue was treated with 500 ml. of benzene and 500 ml. of water. The mixture was stirred thoroughly in order to dissolve as much of the residue as possible in the solvents. A solution of 19.0 g. (500 mmoles) of sodium borohydride in 100 ml. of water was added dropwise and the reaction mixture then stirred for an additional hour. The reaction mixture was then filtered by suction. The benzene layer was combined with a benzene extract (three 150-ml. portions) of the aqueous layer and dried for 1 hr. over anhydrous sodium sulfate. The benzene solution was then filtered by gravity to remove the drying agent, the filtrate being collected under nitrogen. Benzene was removed from the filtrate at ~30 mm.,

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[1] For part VI of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[2] For a preliminary communication on some of this work see R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **85**, 2527 (1963).

[3] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

[4] O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

[5] E. O. Fischer and P. Kuzel, *Z. anorg. allgem. Chem.*, **317**, 226 (1962).

leaving a purple residue which was washed with four 40-ml. portions of pentane to remove liquid impurities. The crude purple crystals consisting mostly of $[C_5H_5Cr(NO)_2]_2$ were purified by chromatography as in the first preparation to give finally 1.66 g. (1.9% yield) of $[C_5H_5Cr(NO)_2]_2$, m.p. 154–156°.

Anal. Calcd. for $C_{10}H_{10}N_4Cr_2O_4$: C, 33.9; H, 2.8; N, 15.8; Cr, 29.4; O, 18.1; mol. wt., 354. Found (two independent preparations): C, 34.0, 34.4; H, 2.8, 3.4; N, 16.1, 16.1; Cr, 28.2, 28.7; O, 18.1, 18.1; mol. wt., 347.

Infrared Spectrum.—C–H band at 3100 (vw) cm.$^{-1}$; terminal nitrosyl band[6] at 1672 (vs) cm.$^{-1}$; bridging nitrosyl band[6] at 1505 (vs) cm.$^{-1}$; other bands at 1430 (w), 1355 (w), 1057 (w), 1015 (w), 1005 (w), 845 (w), 836 (w), 815 (s), 716 (w, br), and 698 (m) cm.$^{-1}$.

Ultraviolet Spectrum.—Maximum at 271 mμ (ϵ 33,700).

Visible Spectrum.—No maxima. Gradual decrease in absorption at varying rates from 400 to 700 mμ.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 4.82 (chloroform solution) due to the ten equivalent π-cyclopentadienyl protons.

Reaction between $[C_5H_5Cr(NO)_2]_2$ and Iodine.—A 0.35-g. (1 mmole) sample of $[C_5H_5Cr(NO)_2]_2$ was treated with 25 ml. of a 0.06 *M* solution of iodine in chloroform (1.5 mmoles of I_2). The purple color of the iodine immediately became yellow-brown, indicating rapid reaction. To ensure complete reaction the reaction mixture was allowed to stand for 3.5 hr. Excess iodine was removed by shaking with two 25-ml. portions of a 4% aqueous solution of sodium thiosulfate 5-hydrate. To facilitate separation the chloroform layer was diluted with dichloromethane as necessary. The washed chloroform–dichloromethane solution of $C_5H_5Cr(NO)_2I$ was dried briefly over anhydrous magnesium sulfate. After filtration from the drying agent solvent was removed from the brown solution at ~30 mm. The resulting green-black crystals were washed with three 15-ml. portions of pentane and dried to give 0.14 g. (23% yield) of $C_5H_5Cr(NO)_2I$, m.p. 143–147°, identical with material obtained from $C_5H_5Cr(NO)_2Cl$, $AgNO_3$, and NaI by the procedure of Piper and Wilkinson.[3] Mechanical losses during the sodium thiosulfate washing were partially responsible for the rather low yield.

Anal. Calcd. for $C_5H_5N_2ICrO_2$: C, 19.7; H, 1.7. Found: C, 19.1; H, 1.9.

Infrared Spectrum.—C–H band at 3075 (w) cm.$^{-1}$; metal nitrosyl bands at 1810 (s), 1695 (s, sh), and 1685 (s) cm.$^{-1}$; no bridging metal nitrosyl bands; other bands at 1422 (w), 1008 (vw), and 829 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 4.24 due to the five equivalent π-cyclopentadienyl protons.

$[C_5H_5Mn(CO)_2NO][PF_6]$.—The hexachloroplatinate(IV) salt of the $[C_5H_5Mn(CO)_2NO]^+$ cation was reported by Piper, Cotton, and Wilkinson.[7] For our work we used the much less expensive hexafluorophosphate salt of this cation prepared by the procedure given below.

A mixture of 180 g. (882 mmoles) of cyclopentadienylmanganese tricarbonyl, 2700 ml. of 95% ethanol, and 540 ml. of concentrated (~35%) hydrochloric acid was heated under nitrogen to the boiling point in a 5-l. flask, and a solution of 63 g. (914 mmoles) of sodium nitrite in ~200 ml. of water was added dropwise. The reaction mixture was filtered while hot. The filtrate was treated with a solution of 180 g. (1105 mmoles) of ammonium hexafluorophosphate in 600 ml. of water. A yellow precipitate of $[C_5H_5Mn(CO)_2NO][PF_6]$ formed immediately. After the reaction mixture had cooled to room temperature, the yellow precipitate was filtered, washed with dichloromethane to ensure removal of any unchanged $C_5H_5Mn(CO)_3$, and dried finally in a vacuum desiccator. The yield of yellow $[C_5H_5Mn(CO)_2NO][PF_6]$ was 40 to 50% based on $C_5H_5Mn(CO)_3$.

An analytical sample of $[C_5H_5Mn(CO)_2NO][PF_6]$ was obtained by dissolving a small portion of the crude product in a minimum of reagent grade acetone and reprecipitating the product from the filtered dark yellow solution with diethyl ether.

As thus obtained $[C_5H_5Mn(CO)_2NO][PF_6]$ is a yellow solid deeper in color than the isoelectronic $[C_5H_5Fe(CO)_3][PF_6]$.[8] On heating it blackens gradually above ~230° without melting. Treatment of $[C_5H_5Mn(CO)_2NO][PF_6]$ with dimethylformamide gives an unstable deep blue solution with gas evolution. An n.m.r. spectrum could not be obtained of this solution, apparently due to the presence of paramagnetic materials. Similar treatment of $[C_5H_5Fe(CO)_3][PF_6]$ with dimethylformamide gives a red solution.

Anal. Calcd. for $C_7H_5F_6NPMnO_3$: C, 23.9; H, 1.4; N, 4.0; P, 8.8; F, 32.5. Found: C, 24.1; H, 1.4; N, 4.1; P, 8.5; F, 31.1.

Infrared Spectrum.—C–H band at 3100 (w) cm.$^{-1}$; metal carbonyl bands at 2125 (s) and 2075 (s) cm.$^{-1}$; metal nitrosyl band at 1840 (s) cm.$^{-1}$; P–F band at 834 (vs, br) cm.$^{-1}$; other bands at 1425 (w), 1112 (vw), 1010 (vw, br), and 870 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 3.86 (acetone solution) due to the five equivalent π-cyclopentadienyl protons.

Conductivity.—The molar conductances of acetone solutions ranged from 190 ohm^{-1} cm.^{2} mole^{-1} in a 1.415×10^{-3} *M* solution to 149 ohm^{-1} cm.^{2} mole^{-1} in a 6.45×10^{-3} *M* solution.

Cyclopentadienylmanganese Carbonyl Nitrosyl Dimer.—A mixture of 70 g. (200 mmoles) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 200 ml. of water, and 400 ml. of thiophene-free benzene was treated under nitrogen at 0° (ice bath) with stirring with a solution of 10 g. (336 mmoles) of sodium borohydride in 100 ml. of water over a period of 30 min. Gas evolution occurred and the reaction mixture gradually became a dark red-brown. After all of the sodium borohydride solution had been added, the reaction mixture was stirred for ~1 hr. while gradually allowing it to warm to room temperature. The reaction mixture was then filtered by suction, and the solid residue washed with four 30-ml. portions of benzene. The benzene solutions were washed with ~100 ml. of water, and the combined aqueous solution was extracted with three 100-ml. portions of benzene to ensure removal of all the $[C_5H_5MnCONO]_2$. The combined benzene solutions of $[C_5H_5MnCONO]_2$ were dried for ~20 min. under nitrogen over anhydrous sodium sulfate. The drying agent was then removed by gravity filtration, and the solvent was removed from the filtrate at ~30 mm., leaving dark purple-brown crystals. Pentane washing (three 50-ml. portions) and drying gave ~21 g. (59% yield) of crude product. Recrystallization from a mixture of dichloromethane (~400 ml.) and hexane (~70 ml.) gave 16 g. (45% yield) of pure $[C_5H_5MnCONO]_2$.

Storage of $[C_5H_5MnCONO]_2$ at room temperature in a bottle flushed out with nitrogen led to gradual decomposition to an insoluble brown solid. After several months this decomposition was complete. Storage in a freezer is therefore recommended. On heating $[C_5H_5MnCONO]_2$ in a capillary, decomposition without melting, sometimes vigorous, occurred around 200°. On heating in a sublimer at ~0.1 mm. decomposition without sublimation occurred around 100°.

Anal. Calcd. for $C_{12}H_{10}N_2Mn_2O_4$: C, 40.4; H, 2.8; N, 7.9; Mn, 30.9; O, 18.0. Found (three independent preparations): C, 39.6, 39.3, 40.3; H, 2.9, 2.8, 2.7; N, 8.0, 8.1; Mn, 31.2, 31.7, 31.1; O, 17.9, 18.1.

Infrared Spectrum.—C–H band at 3080 (vw) cm.$^{-1}$; terminal metal carbonyl band[6] at 1956 (vs) cm.$^{-1}$; bridging metal carbonyl band[6] at 1781 (vs) cm.$^{-1}$; band[6] at 1742 (w) cm.$^{-1}$ probably due to bridging carbonyls or terminal nitrosyls; terminal metal nitrosyl band[6] at 1707 (vs) cm.$^{-1}$; bridging metal nitrosyl band[6] at 1509 (vs) cm.$^{-1}$; other bands at 1415 (m), 1355 (w), 1305 (w), 1257 (vw), 1115 (vw), 1055 (vw), 1012 (w), 1000 (w), 838 (sh), 822 (s), 732 (w, sh), and 710 (vs) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Due to the weak paramagnetism

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[6] This region of these infrared spectra was investigated in halocarbon oil mulls on a Beckman IR-9 machine with grating optics.

[7] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[8] (a) E. O. Fischer and K. Fichtel, *Ber.*, **94**, 1200 (1961); (b) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961); (c) R. B. King, *Inorg. Chem.*, **1**, 964 (1962).

of the compound (~0.7 B.M.),[9] only very poor spectra were obtained. In these spectra a weak broad resonance was observed at τ ~5.0 (chloroform solution) or τ ~5.6 (benzene solution)[10] due to the ten π-cyclopentadienyl protons.

Conversion of $[C_5H_5MnCONO]_2$ to $(C_5H_5)_6Mn_6(NO)_8$.—A red-brown solution of 2.0 g. (5.62 mmoles) of $[C_5H_5MnCONO]_2$ in 25 ml. of benzene was irradiated with magnetic stirring under nitrogen in a quartz tube for 18 hr. approximately 30 cm. from a 1000-watt mercury ultraviolet lamp. The resulting reaction mixture was poured down a 2 × 50 cm. alumina column and the resulting chromatogram developed with benzene. A red-violet band appeared followed by a widely separated black band. Elution of the red-violet band with benzene gave a red-brown solution. After filtration under nitrogen, this eluate was evaporated at ~30 mm. to give 0.30 g. (15% recovery) of unchanged $[C_5H_5MnCONO]_2$ which was purified by washing with pentane (three 20-ml. portions) and identified by its infrared spectrum. The black band was eluted with dichloromethane to give a black solution with a yellow-green tinge. After filtration under nitrogen this solution was evaporated at ~30 mm. to give 0.45 g. (33.4% conversion, 39.3% yield) of black crystalline $(C_5H_5)_6Mn_6(NO)_8$ which was washed with pentane and sucked dry. On heating in a capillary $(C_5H_5)_6Mn_6(NO)_8$ decomposed at 220–225°.

Anal. Calcd. for $C_{30}H_{30}N_8Mn_6O_8$: C, 37.6; H, 3.1; N, 11.7; Mn, 34.4; O, 13.3; mol. wt., 960. Found (three independent preparations): C, 37.7, 38.1, 37.5; H, 3.1, 3.3, 3.8; N, 11.5, 11.3, 11.7; Mn, 35.2, 32.8, 34.6; O, 11.9, 12.8; mol. wt., 905, 1140.

Infrared Spectrum.—C–H band at 3080 (w) cm.$^{-1}$; no terminal nitrosyl bands; bridging metal nitrosyl bands at 1520 (s) and 1475 (s) cm.$^{-1}$; band at 1313 (s) cm.$^{-1}$ possibly due to nitrosyl groups bridging between three manganese atoms; other bands at 1425 (m), 1348 (w), 1257 (m), 1114 (vw), 1055 (w), 1014 (m), 1007 (m), 936 (vw), 856 (m), 833 (m), 812 (s), and 717 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 4.94 (chloroform solution) due to the thirty equivalent π-cyclopentadienyl protons.

Conductivity.—The conductivity of a 1.06×10^{-4} *M* solution of $(C_5H_5)_6Mn_6(NO)_8$ in acetone was no higher than the conductivity of pure acetone, indicating $(C_5H_5)_6Mn_6(NO)_8$ to be a nonelectrolyte.

Preparation of the Piper and Wilkinson Compound $(C_5H_5)_3Mn_2(NO)_3$.—Piper and Wilkinson[3] prepared $(C_5H_5)_3Mn_2(NO)_3$ by the treatment of tetrahydrofuran solutions of manganese(II) cyclopentadienide with the stoichiometric quantity of nitric oxide. In order to avoid handling of the air-sensitive manganese(II) cyclopentadienide, we refluxed manganese(II) bromide with sodium cyclopentadienide and treated the resulting mixture with nitric oxide without isolation of the intermediate manganese(II) cyclopentadienide. A procedure for obtaining $(C_5H_5)_3Mn_2(NO)_3$ from manganese metal without isolating any intermediates is described below.

A suspension of 27.5 g. (500 mg.-atoms) of powdered manganese metal in 300 ml. of 1,2-dimethoxyethane[11] freshly distilled over lithium aluminum hydride was treated dropwise with 80 g. (500 mmoles) of bromine. The resulting white suspension of manganese(II) bromide (or an etherate) was treated with a solution of sodium cyclopentadienide prepared by the usual procedure from 46.0 g. (1000 mg.-atoms of sodium) of a 50% sodium dispersion in mineral oil and 125 ml. (100 g., 1510 mmoles) of freshly cracked cyclopentadiene in 450 ml. of redistilled tetrahydrofuran. The reaction mixture was refluxed for 3.5 hr.

The next day the yellow reaction mixture was treated at room temperature with ~75 g. (2400 mmoles) of nitric oxide purified by passage through a −78° trap charged with molecular sieves. The amount of nitric oxide was estimated by the decrease in the pressure of the gas in the tank. After the nitric oxide treatment was complete, solvent was removed from the black reaction mixture at ~30 mm.

The resulting brown residue was extracted with 1600 ml. of dichloromethane in several portions. The extracts were first filtered by suction through chromatography grade alumina and then by gravity, collecting the final filtrate under nitrogen. Solvent was removed from the filtrate at ~30 mm. leaving a sticky black crystalline residue. Washing this material on a filter with six 400-ml. portions of pentane removed the oily impurities, leaving a black solid with a reddish tinge. The yield of crude $(C_5H_5)_3Mn_2(NO)_3$ was 8.4 g. (8.5% based on manganese metal).

In order to obtain a pure sample of $(C_5H_5)_3Mn_2(NO)_3$ chromatography was used, although with considerable loss of material. A 2.5-g. sample of the crude $(C_5H_5)_3Mn_2(NO)_3$ was dissolved in ~100 ml. of benzene and the filtered solution chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with benzene. The large brown band of $(C_5H_5)_3Mn_2(NO)_3$ was eluted with benzene, the red-brown eluate being collected under nitrogen. Solvent was removed from the filtered eluate at ~30 mm., leaving a red-brown crystalline residue. Purification by recrystallization from a mixture of dichloromethane and hexane gave 0.54 g. (21.6% recovery) of red-black crystals of $(C_5H_5)_3Mn_2(NO)_3$ which were washed with pentane and dried.

After eluting the $(C_5H_5)_3Mn_2(NO)_3$ with benzene, a black band remained at the top of the column. Elution of this band with dichloromethane gave a yellow-black eluate. Evaporation of the filtered eluate at 30 mm. gave 0.02 g. of black crystals identified as $(C_5H_5)_6Mn_6(NO)_8$ from the infrared spectrum.

The composition of the $(C_5H_5)_3Mn_2(NO)_3$ was checked by a complete analysis.

Anal. Calcd. for $C_{15}H_{15}N_3Mn_2O_3$: C, 45.6; H, 3.8; N, 10.6; Mn, 27.8; O, 12.1. Found: C, 46.0; H, 4.3; N, 10.5; Mn, 27.9; O, 12.2.

Infrared Spectrum.—The infrared spectrum corresponded within the errors of the spectrometer to that reported by Piper and Wilkinson[3]: C–H band at 3050 (vvw) cm.$^{-1}$; terminal metal nitrosyl band at 1720 (s) cm.$^{-1}$; bridging metal nitrosyl band at 1497 (s) cm.$^{-1}$; other bands at 1430 (w), 1365 (vw), 1078 (vw), 1015 (vw), 935 (vw), 846 (w), 832 (w), 822 (w), 754 (m), 716 (sh), and 704 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Only a poor spectrum of $(C_5H_5)_3Mn_2(NO)_3$ was obtained. Complex rather broad resonances at τ ~4.7 and 5.6 of relative intensity ~2:1 were observed, indicating two cyclopentadienyl rings of one type and one cyclopentadienyl ring of another type.

Discussion

(A) Chromium Derivatives.—In their preparation of alkyl derivatives of cyclopentadienylchromium dinitrosyl of general formula $C_5H_5Cr(NO)_2R$ in diethyl ether as solvent Piper and Wilkinson[12] failed to isolate any $[C_5H_5Cr(NO)_2]_2$. In the present study, the use of a two-phase water–benzene system, with the desired product $[C_5H_5Cr(NO)_2]_2$ going into the benzene phase as it is produced, reduces the possibility of further attack by the reducing agent permitting successful isolation of the $[C_5H_5Cr(NO)_2]_2$.

This new chromium nitrosyl derivative [C5H5Cr-

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[9] We are indebted to Dr. L. Vaska of this Institute for this measurement carried out by the Faraday method.

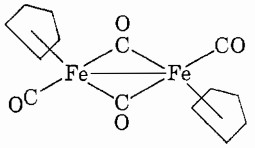
[10] Similar large changes in the apparent chemical shifts of π-cyclopentadienyl protons in going from chloroform or carbon disulfide solutions to benzene solutions with hexamethyldisiloxane as an internal standard have been noted for many cyclopentadienylmetal carbonyl derivatives in this laboratory.

[11] Tetrahydrofuran cannot be used for a solvent in the reaction between manganese and bromine due to the vigorous reaction between tetrahydrofuran and bromine. After the manganese(II) bromide has been prepared, tetrahydrofuran can be used for a later stage of the reaction.

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

$(NO)_2]_2$ is a red-purple crystalline solid bearing a remarkable resemblance to the isoelectronic $[C_5H_5Fe(CO)_2]_2$. The chromium derivative $[C_5H_5Cr(NO)_2]_2$ is apparently stable in air in the solid state for at least a few days, but oxidizes appreciably when exposed to air in solution for 1 hr. Storage in a closed vial flushed with nitrogen leads to slight decomposition at room temperature during several weeks as evidenced by a lowering of the melting point from 158–159° to 150°. The proton n.m.r. spectrum of $[C_5H_5Cr(NO)_2]_2$ exhibits a single sharp resonance, demonstrating the equivalence of the two π-cyclopentadienyl rings and also demonstrating the diamagnetism of the compound.

Of particular interest is the infrared spectrum of $[C_5H_5Cr(NO)_2]_2$. The related compound $[C_5H_5Fe(CO)_2]_2$ for which structure I with two bridging carbonyl groups and two terminal carbonyl groups is well established[4] exhibits bands in its infrared spectrum[13] at 1940 and 1955 cm.$^{-1}$ due to the terminal carbonyl groups and a band at 1756 cm.$^{-1}$ due to the bridging carbonyl groups. The frequency of the bridging carbonyl groups is thus ~90% of the frequency of the terminal carbonyl groups. The chromium nitrosyl derivative $[C_5H_5Cr(NO)_2]_2$ exhibits a band at 1672 cm.$^{-1}$ which may be attributed to the terminal nitrosyl groups and a band at 1505 cm.$^{-1}$ due to the *bridging* nitrosyl groups. As in the case of $[C_5H_5Fe(CO)_2]_2$ the frequency of the bridging groups is ~90% of the frequency of the terminal groups. This infrared evidence clearly indicates $[C_5H_5Cr(NO)_2]_2$ to have structure II, analogous to the structure of $[C_5H_5Fe(CO)_2]_2$ (I) but with chromium atoms replacing iron atoms and nitrosyl groups replacing carbonyl groups rather than the possible alternative structure III where the two halves of the molecule are linked solely with a chromium–chromium bond.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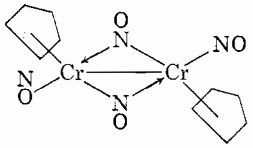
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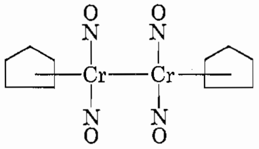

III

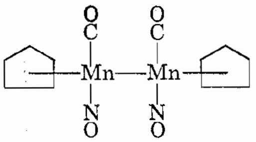
Only relatively small quantities of $[C_5H_5Cr(NO)_2]_2$ were available due to the 5% yield in its preparation from $C_5H_5Cr(NO)_2Cl$. Therefore, an extensive study of its reactions could not be made. The presence of $C_5H_5Cr(NO)_2$ groups in $[C_5H_5Cr(NO)_2]_2$ is demonstrated chemically by its facile cleavage with iodine in chloroform solution to give brown-black $C_5H_5Cr(NO)_2I$ identified by analysis, infrared spectrum, and comparison with an authentic sample prepared according to Piper and Wilkinson[3] from $C_5H_5Cr(NO)_2Cl$. As expected, the band at 1505 cm.$^{-1}$ in the infrared spectrum of $[C_5H_5Cr(NO)_2]_2$ assigned above to bridging nitrosyl groups disappeared on conversion to $C_5H_5Cr(NO)_2I$, which, of course, has only terminal nitrosyl groups.

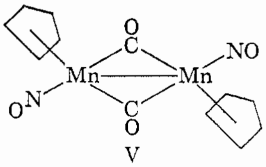
(B) $[C_5H_5MnCONO]_2$.—The sodium borohydride reduction of $[C_5H_5Mn(CO)_2NO]^+$ is undoubtedly very similar to the sodium borohydride reduction of the isoelectronic $[C_5H_5Fe(CO)_3]^+$ which gives $[C_5H_5Fe(CO)_2]_2$ in good yield *via* the unstable intermediates $C_5H_6Fe(CO)_3$ and $C_5H_5Fe(CO)_2H$.[8b] Attempts to carry out the sodium borohydride reduction of $[C_5H_5Mn(CO)_2NO]^+$ in tetrahydrofuran solution as in the analogous reduction of $[C_5H_5Fe(CO)_3]^+$ gave a complex brown reaction mixture from which only very small quantities of $[C_5H_5MnCONO]_2$ could be isolated with difficulty. However, a 60% yield of $[C_5H_5MnCONO]_2$ was obtained if the sodium borohydride reduction of $[C_5H_5Mn(CO)_2NO][PF_6]$ was carried out in a two-phase water–benzene system like the preparation of $[C_5H_5Cr(NO)_2]_2$.

The cyclopentadienylmanganese carbonyl nitrosyl derivative $[C_5H_5MnCONO]_2$ is a red-violet to brown-violet crystalline solid resembling the isoelectronic compounds $[C_5H_5Cr(NO)_2]_2$ and $[C_5H_5Fe(CO)_2]_2$ in appearance. The manganese derivative $[C_5H_5MnCONO]_2$ is much less stable than either $[C_5H_5Cr(NO)_2]_2$ or $[C_5H_5Fe(CO)_2]_2$, decomposing completely on storage during several weeks in a closed bottle flushed with nitrogen at room temperature. Solutions of $[C_5H_5MnCONO]_2$ in organic solvents were unstable, preventing molecular weight determinations and interfering with observation of the n.m.r. spectrum. Preliminary magnetic susceptibility measurements[9] on solid $[C_5H_5MnCONO]_2$ show weak paramagnetism with a magnetic moment of only ~0.7 B.M., which is far too low for even one unpaired electron for each manganese atom.

Several structures are possible for $[C_5H_5MnCONO]_2$. These include IV with no bridging groups, V with two bridging carbonyl groups, VI with two bridging nitrosyl groups, and possibly even VII with one bridging carbonyl group and one bridging nitrosyl group. The infrared spectrum of $[C_5H_5MnCONO]_2$ exhibits strong bands at 1956, 1781, 1707, and 1509 cm.$^{-1}$ which on the basis of the positions of the bands in $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Cr(NO)_2]_2$ may be assigned to terminal carbonyl groups, bridging carbonyl groups, terminal nitrosyl groups, and bridging nitrosyl groups, respectively. In addition a much weaker band, possibly attributable to either bridging carbonyl groups or terminal nitrosyl groups, was observed at 1742 cm.$^{-1}$.

These infrared spectral data suggest that $[C_5H_5MnCONO]_2$ either has structure VII, is a mixture of


IV


V

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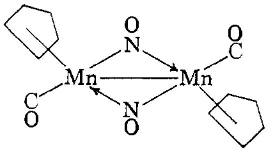
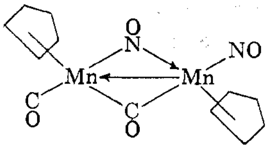
(13) K. Noack, *J. Inorg. Nucl. Chem.*, **25**, 1383 (1963).

isomers with structures V and VI, or is a mixture of V and/or VI with VII. Attempts to separate $[C_5H_5MnCONO]_2$ into two or more isomers by chromatography on alumina in benzene solution were unsuccessful. It is possible that V, VI, and VII might be rapidly interconvertible in solution and that the product always isolated might be an equilibrium mixture of the three compounds.



VI



VII

An attempt was made to prepare the iodide $C_5H_5MnCONOI$ by cleavage of $[C_5H_5MnCONO]_2$ with iodine in chloroform or dichloromethane, a reaction successful for the preparation of $C_5H_5Cr(NO)_2I$ or $C_5H_5Fe(CO)_2I$ from $[C_5H_5Cr(NO)_2]_2$ or $[C_5H_5Fe(CO)_2]_2$, respectively. Instead of the expected $C_5H_5MnCONOI$ a black complex carbonyl-free material was obtained which was not studied in detail. This failure of $[C_5H_5MnCONO]_2$ to give $C_5H_5MnCONOI$ on cleavage with iodine further demonstrates its instability.

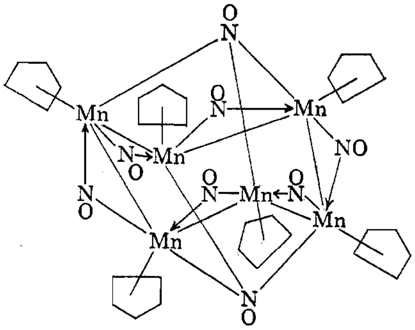
(C) $\mathbf{(C_5H_5)_6Mn_6(NO)_8}$.—A reaction characteristic of certain nitrosyl carbonyl derivatives is disproportionation on heating to form a derivative with more nitrosyl groups per metal atom and a derivative with only carbonyl groups. For example, heating $Hg[Fe(CO)_3NO]_2$ gives a mixture of $[HgFe(CO)_4]_n$ and $Fe(CO)_2(NO)_2$,[14] apparently according to the equation

$$Hg[Fe(CO)_3NO]_2 \longrightarrow \frac{1}{n}[HgFe(CO)_4]_n + Fe(CO)_2(NO)_2$$

Similarly, $Mn(CO)_4NO$[15] appears to be somewhat unstable with respect to $MnCO(NO)_3$ and $Mn_2(CO)_{10}$. However, heating $[C_5H_5MnCONO]_2$ under vacuum up to 100° only caused decomposition into brown insoluble nonvolatile materials. On the other hand, ultraviolet irradiation of $[C_5H_5MnCONO]_2$ in benzene solution gave a reaction mixture indicated by chromatography to contain two soluble materials: unchanged $[C_5H_5MnCONO]_2$ and a new black solid identified as the new compound $(C_5H_5)_6Mn_6(NO)_8$ by analyses and molecular weight determinations on several preparations. Neither $C_5H_5Mn(CO)_3$, $C_5H_5Mn(NO)_2$, nor less likely possibilities such as $C_5H_5MnC_6H_6$ were formed in this reaction.

This new, rather unusual cyclopentadienylmanganese nitrosyl derivative $(C_5H_5)_6Mn_6(NO)_8$ isolated from a reproducible distinct black band on the chromatography column forms black crystals giving green-black solutions in benzene, chloroform, or acetone. When heated in an open capillary, $(C_5H_5)_6Mn_6(NO)_8$ decomposes with partial melting at 220± 5°. In general, the stability of $(C_5H_5)_6Mn_6(NO)_8$ appears to be greater than that of any other of the neutral nitrosyl derivatives discussed in this paper. Acetone solutions of $(C_5H_5)_6Mn_6(NO)_8$ have a conductance no higher than that of pure acetone, eliminating possible ionic formulations for this compound. The proton n.m.r. spectrum of $(C_5H_5)_6Mn_6(NO)_8$ taken in chloroform or acetone solution exhibits a single sharp resonance at τ 4.94 indicating all the six cyclopentadienyl rings to be equivalent and the compound to be diamagnetic. The quality of the n.m.r. spectrum of $(C_5H_5)_6Mn_6(NO)_8$ was better than that of the less complex nitrosyl derivatives $[C_5H_5Cr(NO)_2]_2$, $[C_5H_5MnCONO]_2$, or $(C_5H_5)_3Mn_2(NO)_3$. The infrared spectrum of $(C_5H_5)_6Mn_6(NO)_8$ in either a KBr pellet, halocarbon oil mull, or chloroform solution exhibited no bands in the region associated with terminal metal nitrosyl groups, but three strong bands at 1520, 1475, and 1313 cm.$^{-1}$ apparently due to bridging nitrosyl groups.

A structure for $(C_5H_5)_6Mn_6(NO)_8$ in agreement with its spectral properties and diamagnetism is VIII.[16-18] Here the six manganese atoms form a six-membered, not necessarily planar, ring. Each manganese atom has the inert gas configuration and is equivalent, being bonded to one cyclopentadienyl ring, one-half each of two-way bridging nitrosyl groups (like those in $[C_5H_5Cr(NO)_2]_2$), and one-third of a three-way bridging nitrosyl group. Since all six manganese atoms are equivalent, the cyclopentadienyl rings to which they are bonded are also equivalent in accord with the single sharp cyclopentadienyl resonance in the n.m.r. spectrum.



VIII

The infrared spectrum also supports structure VIII. Thus the strong bands at 1520 and 1475 cm.$^{-1}$ may be assigned to the six two-way bridging nitrosyl groups. These bands are in the same region as the band at 1505 cm.$^{-1}$ in $[C_5H_5Cr(NO)_2]_2$ assigned to bridging nitrosyl groups. In addition, the strong band at 1313 cm.$^{-1}$ in $(C_5H_5)_6Mn_6(NO)_8$ may be assigned to the two three-way bridging nitrosyl groups. As a first approximation the nitrogen–oxygen bond in a three-way bridging

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[14] W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **320**, 101 (1963).

[15] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961), and further unpublished observations.

[16] The six manganese atoms in $(C_5H_5)_6Mn_6(NO)_8$ could be in the same plane rather than in a configuration corresponding to the "chair" configuration of cyclohexane as in XIV; however, the corresponding structure of $(C_5H_5)_6Mn_6(NO)_8$ with the manganese atoms in the same plane is more difficult to depict in two dimensions.

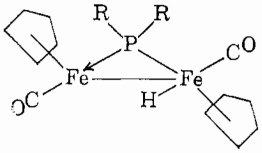
[17] Attempts to formulate $(C_5H_5)_6Mn_6(NO)_8$ with an octahedron of six manganese atoms analogous to the octahedral configuration of the six rhodium atoms in $Rh_6(CO)_{16}$ (ref. 18) meet with the difficulty of the manganese atoms attaining the greatly preferred inert gas electronic configuration.

[18] E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

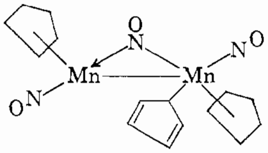
nitrosyl group would be expected to be similar to the nitrogen–oxygen bond in an amine oxide, R_3NO. It is of interest that Bellamy[19] reports amine oxides to absorb at 1200–1300 cm.$^{-1}$ in the infrared spectrum, in reasonable agreement with the band at 1313 cm.$^{-1}$ in $(C_5H_5)_6Mn_6(NO)_8$ assigned to the three-way bridging nitrosyl groups.

It is thus apparent that the chemical and spectroscopic properties of $(C_5H_5)_6Mn_6(NO)_8$ are in accord with structure VIII. However, X-ray studies currently in progress in another laboratory should provide more definite information regarding the structure of $(C_5H_5)_6Mn_6(NO)_8$.

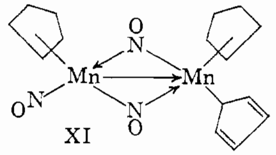
(D) **$(C_5H_5)_3Mn_2(NO)_3$.**—The synthesis of several new nitrosyl derivatives with bridging nitrosyl groups in this work made of interest a further study of the compound $(C_5H_5)_3Mn_2(NO)_3$ prepared several years ago by Piper and Wilkinson[3] from manganese(II) cyclopentadienide and nitric oxide. We have confirmed the preparation of $(C_5H_5)_3Mn_2(NO)_3$ and our analyses on chromatographed material for all elements, including a direct oxygen analysis, confirm the composition suggested by Piper and Wilkinson. A proton n.m.r. spectrum of $(C_5H_5)_3Mn_2(NO)_3$ exhibits two broad cyclopentadienyl resonances at $\tau \sim 4.7$ and ~ 5.6 of relative intensity $\sim 2:1$, supporting the postulation of Piper and Wilkinson of two different types of cyclopentadienyl rings in $(C_5H_5)_3Mn_2(NO)_3$. Recent syntheses of compounds such as IX by Hayter[20] make the related structure X for $(C_5H_5)_3Mn_2(NO)_3$ with only one bridging nitrosyl group and two terminal nitrosyl groups as probable as the structure XI[21] suggested by Piper and Wilkinson[3] with two bridging nitrosyl groups and one terminal nitrosyl group. At this stage we are unable to provide definite evidence for either structure, but hope that X-ray studies currently in progress in another laboratory will provide a solution to this problem.



IX



X



XI

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[19] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, pp. 307–308.

[20] R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

[21] A manganese–manganese bond has been added to the structure of $(C_5H_5)_3Mn_2(NO)_3$ proposed by Piper and Wilkinson (ref. 3) in accord with more recent views on the structure of polynuclear transition metal derivatives.

Contribution from the Mellon Institute,
Pittsburgh 13, Pennsylvania

Organometallic Chemistry of the Transition Metals. VIII. π-Cyclopentadienyl-π-pyrrolyliron and π-Cyclopentadienyl-π-indenyliron[1,2]

By R. B. KING and M. B. BISNETTE

Received November 6, 1963

Ferrous chloride reacts with a mixture of sodium cyclopentadienide and sodium pyrrolide in tetrahydrofuran to give red, very volatile, crystalline $C_5H_5FeC_4H_4N$ in very low yield. Ferrous chloride reacts with a mixture of sodium cyclopentadienide and sodium indenide to give red-violet crystalline $C_5H_5FeC_9H_7$. Hydrogenation of $C_5H_5FeC_9H_7$ gives orange volatile $C_5H_5FeC_9H_{11}$.

Although cyclopentadienyl derivatives of transition metals have been known for over 12 years and hundreds of such compounds have been prepared, little is known of the corresponding pyrrolyl transition metal derivatives despite the analogy between the relationship of the pyrrolide anion (I)[3] to the cyclopentadienide anion and the relationship of pyridine to benzene. Occasionally during the past several years R. B. K. as well as other workers in the field[4] attempted to prepare π-pyrrolylmetal complexes by a variety of methods but always without success. In view of these negative results it appeared for a long time that π-pyrrolyl derivatives would not be stable. However, finally in late 1962 Joshi and Pauson[5] reported the synthesis of π-pyrrolylmanganese tricarbonyl (II) by heating dimanganese decacarbonyl with pyrrole. These positive results indicating that π-pyrrolyl derivatives had appreciable stability led us to investigate more thoroughly the synthesis of other π-pyrrolyl derivatives in order to permit comparison of these π-

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[1] For part VII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

[2] For a preliminary communication on some of this work see R. B. King and M. B. Bisnette, *Angew. Chem.*, **75**, 642 (1963).

[3] By analogy with "cyclopentadienyl" we prefer the term "pyrrolyl" rather than "pyrryl" for the C_4H_4N derivatives discussed in this paper.

[4] (a) Work in the research group of G. Wilkinson, Harvard University, 1952–1956 (L. T. Reynolds, private communication, June, 1959); (b) E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

[5] K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc.*, 326 (1962).