Volume 3
Number 6
June 1, 1964

Inorganic Chemistry

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH 13, PENNSYLVANIA

Organometallic Chemistry of the Transition Metals. VI. Some Cycloheptatrienyl Derivatives of Chromium, Molybdenum, and Cobalt[1,2]

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Received November 6, 1963

Reduction of chromium(III) chloride with certain alkylmagnesium halides in the presence of a mixture of cyclopentadiene and cycloheptatriene gives a low yield of green crystalline volatile $C_5H_5CrC_7H_7$. Treatment of $C_7H_7Mo(CO)_2I$ with $NaMn(CO)_5$ gives dark green volatile $C_7H_7Mo(CO)_2Mn(CO)_5$. Treatment of $C_7H_7Mo(CO)_2I$ with sodium cyclopentadienide in tetrahydrofuran gives orange crystalline volatile $C_5H_5Mo(CO)_2C_7H_7$. Irradiation of dicobalt octacarbonyl with excess cycloheptatriene in toluene solution gives a low yield of the dark red volatile liquid $C_7H_7Co(CO)_3$. The structures of these compounds are discussed.

Introduction

Hundreds of transition metal complexes containing π-bonded cyclopentadienyl rings have been prepared during the past 12 years.[3] More recently, a variety of transition metal complexes containing π-bonded six-membered carbocyclic aromatic rings such as benzene have been prepared.[3] At the time the work described in this paper was begun (fall, 1962) very few π-cycloheptatrienylmetal complexes had been reported in the literature. The reported complexes included the two vanadium compounds $C_7H_7V(CO)_3$[4,5] and $C_5H_5VC_7H_7$[6] and the chromium[7] and molybdenum[8,9] derivatives of general formulas $[C_7H_7M(CO)_3]^+$ and $C_7H_7Mo(CO)_2X$ (X = Cl, Br, or I). These few known π-cycloheptatrienyl metal derivatives did not permit an accurate assessment of the chemical and physical properties of this class of compounds. It therefore seemed desirable to synthesize additional examples of complexes containing this type of bonding in order to be able to compare the chemistry of the π-cycloheptatrienyl metal derivatives with that of the more thoroughly studied π-benzene and π-cyclopentadienyl derivatives.

Certain gaps appeared to be present in the chemistry of the "mixed" π-cyclopentadienyl–π-cycloheptatrienyl derivatives. The vanadium compound $C_5H_5VC_7H_7$ which has one electron less that the favored inert gas configuration is readily obtainable by heating a mixture of cyclopentadienylvanadium tetracarbonyl and cycloheptatriene and has been known for several years.[6] The chromium, molybdenum, and tungsten compounds $C_5H_5MC_7H_7$ (M = Cr, Mo, or W) which would have the inert gas configurations had not been reported when this work was begun. Occasional attempts by R. B. K. during the past few years to prepare these derivatives by heating or irradiating certain cyclopentadienyl metal carbonyl derivatives of chromium molybdenum, and tungsten with cycloheptatriene always led to negative results. Apparently the carbonyl groups in these cyclopentadienylmetal carbonyl derivatives are too firmly bonded to be replaced completely by cycloheptatriene.

Somewhat more recently Fischer and Müller reported the synthesis of the iron complex $C_6H_6FeC_6H_8$ by reduction of a mixture of iron(III) chloride and 1,3-cyclohexadiene with an ethereal solution of an alkylmagnesium halide, preferably one with a branched-chain alkyl group such as isopropyl.[10] It immediately appeared promising to extend this reaction to the preparation of $C_5H_5CrC_7H_7$ by reduction of a mixture of chromium(III) chloride, cyclopentadiene, and cycloheptatriene with a secondary or tertiary alkylmagnesium halide. Our preliminary communication[2] briefly described the successful synthesis of $C_5H_5CrC_7H_7$ by this method.

While our work on the synthesis of $C_5H_5CrC_7H_7$

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(1) For part V of this series see R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

(2) For a preliminary communication of some of this work see R. B. King and M. B. Bisnette, *Tetrahedron Letters*, 1137 (1963).

(3) See, for example, E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 56 (1959), and G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

(4) R. P. M. Werner and S. A. Manastyrskyj, *J. Am. Chem. Soc.*, **83**, 2023 (1961).

(5) F. Calderazzo and P. L. Calvi, *Chim. Ind.* (Milan), **44**, 1217 (1962).

(6) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 5263 (1959).

(7) J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3475 (1961).

(8) H. J. Dauben, Jr., and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

(9) D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961 (Prof. H. J. Dauben, Jr., research adviser).

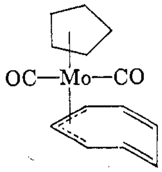
(10) E. O. Fischer and J. Müller, *Z. Naturforsch.*, **17b**, 776 (1962).

was in progress, a brief communication appeared by Fischer and Breitschaft[11] disclosing the synthesis of $C_5H_5CrC_7H_7$ by the entirely different method of displacement of the benzene ring in $C_5H_5CrC_6H_6$[12] with cycloheptatriene in the presence of aluminum chloride followed by reduction of the intermediate $[C_5H_5CrC_7H_7]^+$ cation. Later Fischer and Breitschaft[13] described the preparation of the closely related derivatives $C_5H_5CrC_7H_6R$ (R = methyl or phenyl) by ring expansion of the benzene ring in $C_5H_5CrC_6H_6$ with acetyl or benzoyl chloride in the presence of aluminum chloride and reduction of the intermediate $[C_5H_5CrC_7H_6R]^+$ cation. A similar ring expansion could be effected with the manganese derivative $C_5H_5MnC_6H_6$[14] to give the cations $[C_5H_5MnC_7H_6R]^+$.

Both of these syntheses by Fischer and Breitschaft of $C_5H_5MC_7H_7$ derivatives, although very interesting, suffer from the disadvantage that the rather difficultly prepared mixed cyclopentadienylarenemetal derivatives $C_5H_5MC_6H_6$[12,14] are required as starting materials. It therefore seemed desirable to investigate further our synthesis of $C_5H_5MC_7H_7$ derivatives by reduction of a mixture of anhydrous metal halides, cyclopentadiene, and cycloheptatriene with isopropylmagnesium bromide. In this paper additional details of the synthesis of $C_5H_5CrC_7H_7$ by this method are described as well as attempts to extend this synthesis to metals other than chromium.

We also explored other routes to the synthesis of π-cyclopentadienyl-π-cycloheptatrienylmetal derivatives. A promising route for the synthesis of $C_5H_5MoC_7H_7$ appeared to be the reaction between $C_7H_7Mo(CO)_2I$[9] and sodium cyclopentadienide. Instead of the anticipated product, a *dicarbonyl* derivative $C_5H_5Mo(CO)_2C_7H_7$ was obtained for which the novel structure I was proposed.[2] The characteristic feature of this structure (I) is the presence of an "allylic" π-cycloheptatrienyl ring (II) with only three of the seven carbon atoms bonded to the metal atom rather than the more usual "planar" π-cycloheptatrienyl ring (III) with all seven carbon atoms bonded to the metal atom.

This paper describes further the properties of $C_5H_5Mo(CO)_2C_7H_7$ and the preparation of a cobalt carbonyl derivative $C_7H_7Co(CO)_3$ in which the cycloheptatrienyl ring is bonded to the metal atom in a manner similar to the proposed cycloheptatrienyl-metal bond in $C_5H_5Mo(CO)_2C_7H_7$.



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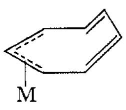

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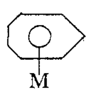

III

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double beam spectrometer with sodium chloride optics. In addition, the metal carbonyl regions of some of the compounds were taken in halocarbon oil mulls and recorded on a Beckman IR-9 spectrometer with grating optics. Proton n.m.r. spectra were taken in carbon disulfide, chloroform, or benzene solution on a Varian Associates Model A-60 spectrometer. Hexamethyldisiloxane was used as an internal standard. Ultraviolet and visible spectra were taken in Fisher spectro grade cyclohexane solutions and recorded on a Cary Model 14 spectrometer. 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; Pascher Mikroanalytisches Laboratorium, Bonn, Germany; and Schwarzkopf Microanalytical Laboratory, Woodside, New York. Melting points were taken in capillaries and are uncorrected.

Materials.—Chromium trichloride was obtained from Diamond Alkali Corp., Painesville, Ohio. Vanadium trichloride was purchased from Anderson Chemical Corp., Weston, Michigan. Molybdenum hexacarbonyl was purchased from the Climax Molybdenum Company, New York, New York. Dicobalt octacarbonyl was purchased in a ~14% toluene solution from Union Carbide Olefins, South Charleston, West Virginia.

π-Cycloheptatrienyl molybdenum dicarbonyl iodide was prepared by the procedure of Bertelli.[9] The procedure was easily scaled up to give 27.7 g. (75% yield from $C_7H_8Mo(CO)_3$) in a single run.

The large quantities of cycloheptatriene required for this work were obtained as generous research samples from Shell Chemical Company, New York, New York.

π-Cyclopentadienyl-π-cycloheptatrienylchromium.—A mixture of 15.8 g. (100 mmoles) of anhydrous chromium(III) chloride, 10 ml. (8.0 g., 121 mmoles) of freshly cracked cyclopentadiene, 25 ml. (22.8 g., 250 mmoles) of 91.3% cycloheptatriene, and 200 ml. of anhydrous diethyl ether was treated at −78° with a solution of isopropylmagnesium bromide prepared from 12.1 g. (500 mg.-atoms) of magnesium turnings, 57 ml. (74.7 g., 607 mmoles) of 2-bromopropane, and 300 ml. of anhydrous diethyl ether. After all of the isopropylmagnesium bromide solution had been added, the reaction mixture was allowed to warm slowly to room temperature by the gradual evaporation of the Dry Ice from the metal pan serving as the cooling bath.

After stirring ~15 hr. at room temperature the brown reaction mixture was cooled again to −78° and treated dropwise with 200 ml. of methanol. The reaction mixture was allowed to warm to room temperature and then filtered with exclusion of air. The residue was washed with diethyl ether until the washings were no longer colored. Solvent was removed from the combined filtrate and washings in a water-pump vacuum at ~30 mm., leaving a brown-green residue. After admitting nitrogen to the evacuated flask the residue was transferred to a sublimation apparatus and the crude $C_5H_5CrC_7H_7$ driven out as sticky brown crystals by sublimation at 100–150° (0.1 mm.) for 5 hr. The crude product was washed rapidly with ~50 ml. of pentane and the washed crystals resublimed at 80–100° (0.1 mm.) to give 0.45 g. (2.2% yield) of dark green crystalline $C_5H_5CrC_7H_7$, m.p. ~225° dec. (lit.[11] m.p. 230°).

In a similar reaction using *t*-butylmagnesium chloride rather than isopropylmagnesium bromide as the reducing agent, a 1.2% yield of twice sublimed $C_5H_5CrC_7H_7$ was obtained.

Anal. Calcd. for $C_{12}H_{12}Cr$: C, 69.2; H, 5.8; Cr, 25.0; mol. wt., 208. Found: C, 69.4; H, 5.9; Cr, 24.8; mol. wt., 218.

Infrared Spectrum.—C–H band at 2980 (vw, br) cm.$^{-1}$; other bands at 1878 (w), 1835 (w), 1765 (w), 1703 (w), 1672 (vw), 1620 (w), 1507 (w), 1467 (vw), 1415 (s), 1257 (w), 1241 (m), 1173 (vw), 1120 (w), 1107 (s), 1101 (sh), 1056 (w), 1045 (vw),

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[11] E. O. Fischer and S. Breitschaft, *Angew. Chem.*, **75**, 94 (1963).

[12] E. O. Fischer and H. P. Kögler, *Z. Naturforsch.*, **13b**, 197 (1958).

[13] E. O. Fischer and S. Breitschaft, *Angew. Chem.*, **75**, 167 (1963).

[14] S. Breitschaft, Diplomarbeit, University of Munich, 1962; see also T. H. Coffield, V. Sandel, and R. D. Closson, *J. Am. Chem. Soc.*, **79**, 5826 (1957).

1010 (s), 1001 (s), 965 (m), 930 (sh), 905 (m, br), 893 (m, br), 857 (s), 830–800 (vs, br), and 727 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Cycloheptatrienyl resonance at τ 4.59 (benzene solution) or τ 4.45 (carbon disulfide solution). Cyclopentadienyl resonance at τ 6.38 (benzene solution) or τ 6.28 (carbon disulfide solution). The n.m.r. spectrum could not be taken in chloroform due to decomposition.

The Salt [$C_5H_5CrC_7H_7$][PF_6]. Method A.—The reduction of 100 mmoles of anhydrous chromium(III) chloride in the presence of 250 mmoles of cycloheptatriene and 121 mmoles of cyclopentadiene was carried out with isopropylmagnesium bromide in diethyl ether solution as described in the above preparation of the neutral $C_5H_5CrC_7H_7$. Instead of decomposing the reaction mixture with methanol at −78°, the reaction mixture was decomposed at 0° by the dropwise addition of a mixture of 50 ml. of concentrated hydrochloric acid, 10 ml. of 30% aqueous hydrogen peroxide, and 200 ml. of water. After stirring for 1 hr. the reaction mixture was filtered and the aqueous layer of the filtrate treated with a solution of 20 g. (123 mmoles) of ammonium hexafluorophosphate in 30 ml. of water. After standing for 1 hr. the resulting mossy green precipitate was filtered, washed with two 10-ml. portions of water, and sucked dry. The crude product was purified by dissolving in a minimum quantity of acetone and reprecipitating with diethyl ether to give 0.47 g. (1.3% yield) of dirty yellow crystals of [$C_5H_5CrC_7H_7$][PF_6], dec. ~250°.

Method B.—Blue solutions were obtained by washing samples of crude $C_5H_5CrC_7H_7$ with pentane. Sucking air through these blue solutions caused complete decolorization after a few minutes, forming a yellow sludge. This yellow sludge was dissolved in water and treated with excess ammonium hexafluorophosphate. The yellow precipitate which formed was filtered, washed with two 10-ml. portions of water, and dried in the air for several days. The product was purified by dissolving in a minimum quantity of acetone and reprecipitating with diethyl ether to give yellow solid [$C_5H_5CrC_7H_7$][PF_6] exhibiting an infrared spectrum identical with that of the material obtained by method A.

Anal. Calcd. for $C_{12}H_{12}F_6PCr$: C, 40.8; H, 3.4. Found (method A): C, 41.6; H, 3.5. Found (method B): C, 40.2; H, 3.4.

Infrared Spectrum.—C–H bands at 3100 (w) and 3070 (vw, sh) cm.$^{-1}$; P–F band at 823 (vs)$^{-1}$; other bands at 1425 (w), 1380 (vw), 1010 (w), 965 (vw), 875 (s, sh), 850 (vs), and 798 (m) cm.$^{-1}$.

Conductivity.—The molar conductances of acetone solutions ranged from 256 ohm^{-1} cm.^{2} mole^{-1} in a 1.13×10^{-4} M solution to 176 ohm^{-1} cm.^{2} mole^{-1} in a 3.71×10^{-3} M solution.

π-Cycloheptatrienylmolybdenum Dicarbonyl Manganese Pentacarbonyl.—A solution of 10 mmoles of $NaMn(CO)_5$ in 50 ml. of redistilled tetrahydrofuran was prepared under nitrogen by the usual procedure[15] from 2.0 g. (~5 mmoles) of dimanganese decacarbonyl (Ethyl Corporation) and an excess (~26 mg.-atoms) of sodium as ~1% amalgam. After removing the excess amalgam this solution was treated with 3.70 g. (10 mmoles) of π-cycloheptatrienylmolybdenum dicarbonyl iodide and the reaction mixture stirred for 18 hr. at room temperature. Solvent was then removed from the reaction mixture at ~30 mm., leaving a deep green residue. After admitting nitrogen the green residue was extracted with three 50-ml. portions of dichloromethane. The dichloromethane extracts were filtered by gravity, collecting the dark green filtrate under nitrogen. Solvent was removed from this filtrate at ~30 mm., leaving a dark green residue. This residue was dissolved in benzene and purified by chromatography on a 2 × 50 cm. alumina column. A single deep green band appeared which was eluted with pentane or preferably benzene. Evaporation of this eluate at ~30 mm. left dark green crystals which were purified with appreciable losses by sublimation at 90–110° (0.1 mm.) to give a total of 0.28 g. (6.4% yield) of dark green $C_7H_7Mo(CO)_2Mn(CO)_5$, m.p. 123° dec.

Anal. Calcd. for $C_{14}H_7MnMoO_7$: C, 38.3; H, 1.6; Mn, 12.6; Mo, 21.9; mol. wt., 438. Found: C, 38.4; H, 1.8; Mn, 12.7; Mo, 22.1; mol. wt., 450.

Infrared Spectrum.—C–H bands too weak to be observed; metal carbonyl bands at 2058 (s), 1985 (s), 1960 (s), and 1935–1908 (s, broad unresolved) cm.$^{-1}$ (Beckman IR-9); other bands at 1480 (vw), 1435 (w), 1245 (w), 930 (w), 868 (w), 864 (vw), 854 (vw), and 800 (m) cm.$^{-1}$.

Ultraviolet Spectrum.—Maximum at 279 mμ (ϵ 22,800).

Visible Spectrum.—Maxima at 452 mμ (ϵ 3060) and 622 mμ (ϵ 505).

Proton N.m.r. Spectrum.—Single peak at τ 4.61 due to the seven π-cycloheptatrienyl protons.

π-Cyclopentadienyl-π-cycloheptatrienylmolybdenum Dicarbonyl.—A solution of ~104 mmoles of sodium cyclopentadienide was prepared under nitrogen from 8.0 g. of 30% sodium dispersion in xylene and 15 ml. of freshly cracked cyclopentadiene in 500 ml. of redistilled tetrahydrofuran. After adding 11.2 g. (30.2 mmoles) of π-cycloheptatrienylmolybdenum dicarbonyl iodide, the dark orange reaction mixture was stirred 18 hr. at room temperature. Solvent was then removed from the reaction mixture at ~30 mm., leaving a semisolid orange residue.

After admitting nitrogen this residue was extracted with three 100-ml. portions of dichloromethane. The extracts were filtered by suction through ~40 g. of alumina (chromatography grade). Solvent was removed from the orange filtrate at ~30 mm., leaving orange crystals which were washed with ~100 ml. of pentane at −78° in several portions to give 5.6 g. (60% yield) of crude $C_5H_5Mo(CO)_2C_7H_7$ used for preparative purposes.

For the analytical sample the crude product was chromatographed in benzene solution on a 5 × 50 cm. alumina column. The chromatogram was developed with benzene. A single orange band appeared which was eluted with benzene. Solvent was removed from the orange eluate leaving orange crystals which were washed with pentane and sucked dry. A portion of this product was sublimed at 90° (0.1 mm.) to give the analytical sample, m.p. 111–112°. The chromatography and sublimation were quite wasteful, the final sublimed product representing only ~10% of the crude product.

Anal. Calcd. for $C_{14}H_{12}MoO_2$: C, 54.5; H, 3.9; Mo, 31.2; O, 10.4; mol. wt., 308. Found: C, 54.8; H, 3.9; Mo, 31.3; O, 10.5; mol. wt., 318.

Infrared Spectrum.—C–H bands at 3100 (vw) and 3010 (vw) cm.$^{-1}$; metal carbonyl bands at 1933 (s) and 1893 (s) cm.$^{-1}$ (Beckman IR-9; halocarbon oil mull); other bands at 1425 (w), 1400 (vw), 1146 (w), 1060 (w), 1015 (w), 997 (w), 935 (vw), 846 (m), 828 (w), 812 (s), and 704 (s) cm.$^{-1}$.

Ultraviolet Spectrum.—Maximum at 306 mμ (ϵ 11,600).

Visible Spectrum.—Maximum at 758 mμ (ϵ 315).

Proton N.m.r. Spectrum.—Sharp cycloheptatrienyl resonance at τ 4.93 and sharp cyclopentadienyl resonance at τ 5.21 of relative intensity ~7:5 (carbon disulfide solution).

π-Cycloheptatrienylcobalt Tricarbonyl.—A mixture of 100 ml. of the commercial ~14% solution of dicobalt octacarbonyl in toluene (~40 mmoles of $Co_2(CO)_8$) and 100 ml. of 91.3% cycloheptatriene was irradiated 16 hr. in a quartz vessel under nitrogen with a ~1000-watt mercury ultraviolet lamp placed 30–60 cm. from the reaction vessel. The resulting reaction mixture was filtered and the orange filtrate collected under nitrogen. Excess toluene and cycloheptatriene was removed from the resulting reaction mixture at ~1 mm. After admitting nitrogen the resulting dark colored partially liquid residue was extracted with 100 ml. of pentane in three portions. The extracts were filtered by gravity, the dark red-brown filtrate being collected under nitrogen. This filtrate was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with pentane. A large red band followed by much smaller yellow and black bands appeared. The latter two bands because of weakness and instability were not further investigated. The red band was eluted with pentane, the red eluate being collected under nitrogen. Solvent was removed from the filtered eluate at ~30 mm., leaving ~1.5 g. (8% yield) of dark red impure C_7H_7-

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(15) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957); W. Hieber and G. Wagner, *Ann.*, **618**, 24 (1958).

$Co(CO)_3$ containing impurities richer in carbon as indicated by analyses.

In order to obtain a pure product the crude chromatographed dark red liquid was diluted with 20–40 ml. of pentane and the dark red solution filtered by gravity, collecting the filtrate under nitrogen. Cooling this filtrate to −78° for several hours precipitated dark red crystals. The supernatant liquid was removed with a syringe, and final traces of pentane were removed by drying in a stream of nitrogen. Upon reaching room temperature the red crystals melted to a dark red liquid. The yield of pure $C_7H_7Co(CO)_3$ was 10–30% of the crude material.

π-Cycloheptatrienylcobalt tricarbonyl is a dark red air-sensitive malodorous liquid. When pure it solidifies in a freezer at −20°. Although readily volatile at 40° (0.5 mm.), π-cycloheptatrienylcobalt tricarbonyl was not successfully separated from impurities by sublimation alone.

Anal. Calcd. for $C_{10}H_7CoO_3$: C, 51.3; H, 3.0; Co, 25.2; O, 20.5; mol. wt., 234. Found: C, 51.6; H, 3.3; Co, 24.9; O, 20.5; mol. wt., 233.

Infrared Spectrum.—C–H band at 3030 (m) cm.$^{-1}$; metal carbonyl bands at 2050 (vs) and 1970 (vs, br) cm.$^{-1}$; other bands at 1700 (m), 1600 (m), 1470 (m), 1435 (w), 1416 (m), 1250 (m), 1170 (m), 928 (m), 910 (w), 889 (m), 872 (m), 838 (s), 815 (w), 742 (w), and 705 (vs) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Single sharp resonance at τ 4.49 (carbon disulfide solution) or τ 4.93 (benzene solution).

Discussion

(A) $C_5H_5CrC_7H_7$ and Related Compounds.—The synthesis of $C_5H_5CrC_7H_7$ in one step from chromium(III) chloride, cycloheptatriene, cyclopentadiene, and an isopropyl- or *t*-butylmagnesium halide in diethyl ether described in this paper is more convenient than the method of Fischer and Breitschaft[11] which requires the prior rather difficult preparation of cyclopentadienylbenzenechromium. Unfortunately, the yields in our method of preparation of $C_5H_5CrC_7H_7$ were never greater than ~2% based on chromium(III) chloride.

In agreement with Fischer and Breitschaft we find $C_5H_5CrC_7H_7$ to be a volatile dark green solid resembling $[C_5H_5Cr(CO)_3]_2$[16] very much in color. The melting point and infrared spectrum obtained by us and by Fischer and Breitschaft are in reasonable agreement, indicating the two compounds to be identical. Proton n.m.r. spectra of the deep blue solutions of $C_5H_5CrC_7H_7$ in benzene and carbon disulfide as expected exhibited two resonances of approximately 7:5 relative intensity due to the π-cycloheptatrienyl and the π-cyclopentadienyl rings, respectively.

Fischer and Breitschaft reported $C_5H_5CrC_7H_7$ to be very air-sensitive ("sehr luftempfindlich"). We found the deep blue pentane solutions of $C_5H_5CrC_7H_7$ to be readily oxidized by air to give a yellow water-soluble slimy precipitate. The presence of the $[C_5H_5CrC_7H_7]^+$ cation in this precipitate was demonstrated by precipitation of $[C_5H_5CrC_7H_7][PF_6]$ by treatment of its aqueous solution with ammonium hexafluorophosphate. The same $[C_5H_5CrC_7H_7]^+$ ion was also isolated as the hexafluorophosphate from the dirty yellow aqueous solution obtained by decomposition with acidic hydrogen peroxide of the crude mixture obtained in the isopropylmagnesium bromide reduction of chromium(III) chloride, cyclopentadiene, and cycloheptatriene.

In an attempt to prepare the vanadium derivative $C_5H_5VC_7H_7$[6] a mixture of vanadium(III) chloride, cycloheptatriene, and cyclopentadiene was reduced with ethereal isopropylmagnesium bromide analogous to the preparation of $C_5H_5CrC_7H_7$. Only traces (<0.1% yield) of purple, volatile, crystalline $C_5H_5VC_7H_7$ identified by its infrared spectrum were obtained by this reaction. The inferior results obtained by this method in the synthesis of $C_5H_5VC_7H_7$ as compared with the chromium analog may be related to the fact that the vanadium compound unlike the chromium compound has one electron less than the inert gas configuration and is therefore more reactive, being subject to decomposition possibly by further reduction with the excess of isopropylmagnesium bromide necessary to carry out the synthesis.

In an attempt to prepare the iron derivative $C_5H_5FeC_7H_7$ isoelectronic with $(C_5H_5)_2Ni$[17] and $[C_6(CH_3)_6]_2Fe$,[18] a mixture of iron(III) chloride, cycloheptatriene, and cyclopentadiene was reduced with ethereal isopropylmagnesium bromide. A red diamagnetic volatile liquid was obtained which failed to crystallize even at −78°. Although the analytical data were fair for formulation as a π-cyclopentadienyl-π-diisopropylcycloheptadienyliron compound, the reluctance of this material to crystallize and the rather complex n.m.r. spectrum create doubts as to whether this red liquid is a single pure compound despite purification by chromatography and volatilization under high vacuum. The presence of methyl groups in this red liquid as demonstrated by the presence of methyl resonances in its n.m.r. spectrum indicates that isopropyl groups from this isopropylmagnesium bromide have been incorporated into the product. A similar but not identical red liquid of somewhat greater air sensitivity was obtained by reduction of iron(III) chloride in the presence of cyclopentadiene and cycloheptatriene with *t*-butylmagnesium chloride in diethyl ether. Attempts to prepare the unsubstituted π-cyclopentadienyl-π-cycloheptadienyliron $C_5H_5FeC_7H_9$ (IV) by obvious extensions of the preparative techniques described in this paper such as ethereal lithium aluminum hydride reduction of a mixture of iron(III) chloride, cyclopentadiene, and cycloheptatriene or ethereal isopropylmagnesium bromide reduction of a mixture of iron(III) chloride, cyclopentadiene, and cycloheptadiene gave negative results.

An attempt to prepare $C_5H_5WC_7H_7$ by reduction of tungsten(VI) chloride, cyclopentadiene, and cycloheptatriene with isopropylmagnesium bromide gave a brown solid which on the basis of its n.m.r. spectrum and analytical data clearly contained no $C_5H_5WC_7H_7$. This product, apparently complex and containing isopropyl groups from the isopropylmagnesium bromide, was not investigated in detail.

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[16] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 140 (1955); E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. allgem. Chem.*, **282**, 47 (1955).

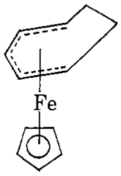
[17] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 217 (1953); G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, **76**, 1970 (1954).

[18] E. O. Fischer and F. Röhrscheid, *Z. Naturforsch.*, **17b**, 483 (1962).

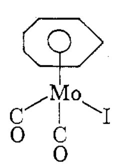
(B) Cycloheptatrienyl Derivatives of Molybdenum.—An obvious precursor to the preparation of interesting cycloheptatrienyl derivatives of molybdenum appeared to be π-cycloheptatrienylmolybdenum dicarbonyl iodide $C_7H_7Mo(CO)_2I$ (V) described in a thesis by Bertelli.[9] The preparation of $C_7H_7Mo(CO)_2I$ was readily scaled up to give 25 g. in a single preparation in 40–50% yield based on molybdenum hexacarbonyl. Small scale exploratory reactions indicated that $C_7H_7Cr(CO)_2I$ could not be prepared analogously.

The halides $C_5H_5Fe(CO)_2X$ are reported to form the cation $[C_5H_5FeC_6H_6]^+$ on refluxing with aluminum chloride in benzene solution.[19] However, similar treatment of $C_7H_7Mo(CO)_2I$ with aluminum chloride in boiling benzene solution gave a low yield of the $[C_7H_7Mo(CO)_3]^+$ cation identified by comparison of its hexafluorophosphate with an authentic sample of $[C_7H_7Mo(CO)_3][PF_6]$ obtained from $C_7H_8Mo(CO)_3$ and $[(C_6H_5)_3C][PF_6]$. The extra carbonyl group must come from decomposition of some of the $C_7H_7Mo(CO)_2I$.

Reaction of $C_7H_7Mo(CO)_2I$ with $NaMn(CO)_5$ gives the deep green $C_7H_7Mo(CO)_2Mn(CO)_5$ (VI), the first metal carbonyl derivative containing both molybdenum and manganese to be described. Related metal carbonyl derivatives containing two different transition metals are known such as $C_5H_5Mo(CO)_3$–$W(CO)_3C_5H_5$,[20] $C_5H_5Fe(CO)_2Mn(CO)_5$,[21] $C_5H_5Fe(CO)_2Mo(CO)_3C_5H_5$,[21] $C_5H_5Fe(CO)_2Co(CO)_4$,[22] $(CO)_5MnCo(CO)_4$,[22] and $(CO)_5MnRe(CO)_5$.[23] The infrared spectrum of $C_7H_7Mo(CO)_2Mn(CO)_5$ clearly demonstrates the absence of bridging carbonyl groups, indicating that the two halves of the molecule are held together solely by the molybdenum–manganese bond. The n.m.r. spectrum exhibits a single sharp resonance at τ 4.61 due to the seven equivalent π-cycloheptatrienyl protons. The thermal stability of $C_7H_7Mo(CO)_2Mn(CO)_5$ permits purification by sublimation at ~100° (0.1 mm.) but with considerable loss due to decomposition. The green color of $C_7H_7Mo(CO)_2Mn(CO)_5$ is unprecedented among the "mixed" metal carbonyl derivatives mentioned above. However, the related neutral planar[24] π-cycloheptatrienylmetal derivatives $C_7H_7V(CO)_3$,[4,5] $C_7H_7Mo(CO)_2X$,[9] and $C_5H_5CrC_7H_7$ are green, blue-green, or green-black. It thus appears that neutral planar π-cycloheptatrienyl derivatives with the inert gas configuration are green or some closely related color.



IV



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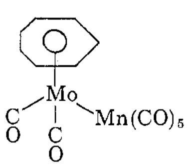
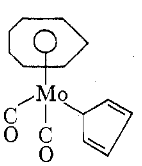


VI



VII

In an attempt to prepare $C_7H_7Mo(CO)_2CH_3$ analogous to the iron compound $C_5H_5Fe(CO)_2CH_3$,[25] the iodide $C_7H_7Mo(CO)_2I$ was treated with methylmagnesium iodide in diethyl ether. No organomolybdenum compound of interest could be isolated from this reaction mixture. Sodium amalgam reduction of $C_7H_7Mo(CO)_2I$ followed by methyl iodide treatment of the resulting solution also failed to give any $C_7H_7Mo(CO)_2CH_3$.

Treatment of $C_7H_7Mo(CO)_2I$ with sodium cyclopentadienide in an attempt to prepare $C_5H_5MoC_7H_7$ gave instead the *orange* diamagnetic derivative $C_5H_5Mo(CO)_2C_7H_7$.[2] The fact that the neutral diamagnetic cycloheptatrienyl derivative is orange rather than green already suggests that it is not the planar π-cycloheptatrienyl derivative VII. Moreover, the position of the cyclopentadienyl resonance of $C_5H_5Mo(CO)_2C_7H_7$ at τ 4.94 is greatly different from the position of the resonance of the σ-cyclopentadienyl protons of the closely analogous σ-cyclopentadienyl-π-cyclopentadienyliron dicarbonyl[25] at τ ~3.5. In view of these considerations, the most probable structure for $C_5H_5Mo(CO)_2C_7H_7$ is that of π-cyclopentadienyl-π-cycloheptatrienylmolybdenum dicarbonyl (I). In this structure the molybdenum atom receives three electrons from the allylic[24] π-cycloheptatrienyl ring, five electrons from the π-cyclopentadienyl ring, and four electrons from the two carbonyl groups, giving it the desired inert gas configuration.

The apparent presence of two uncomplexed double bonds in the allylic π-cycloheptatrienyl ring of $C_5H_5Mo(CO)_2C_7H_7$ suggested the possibility of addition reactions. Attempts to hydrogenate $C_5H_5Mo(CO)_2C_7H_7$ at atmospheric pressure using palladium or rhodium on charcoal as catalysts were unsuccessful, little or no absorption of hydrogen taking place and unchanged $C_5H_5Mo(CO)_2C_7H_7$ being recovered. Irradiation of $C_5H_5Mo(CO)_2C_7H_7$ with iron pentacarbonyl failed to give the diene–iron tricarbonyl complex $C_5H_5Mo(CO)_2C_7H_7Fe(CO)_3$. The orange solutions of $C_5H_5Mo(CO)_2C_7H_7$ in benzene turned yellow instantly on treatment with benzene solutions of tetracyanoethylene. A yellow precipitate separated but was not obtained pure. These observations indicate that the two uncomplexed double bonds in $C_5H_5Mo(CO)_2C_7H_7$ are very unreactive.

Of particular interest was the proton n.m.r. spectrum of $C_5H_5Mo(CO)_2C_7H_7$.[2] Only two sharp resonances were observed, one due to the five protons of the cyclopentadienyl ring and one due to the seven protons of the cycloheptatrienyl ring. The single sharp resonance

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[19] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

[20] E. W. Abel, A. Singh, and G. Wilkinson, *ibid.*, 1321 (1960).

[21] R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind.* (London), 747 (1961).

[22] K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, **17b**, 565 (1962).

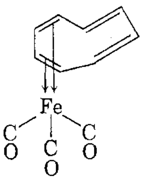
[23] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and I. S. Kolomnikov, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 194 (1963).

[24] The term "planar π-cycloheptatrienyl" will be used hereafter to refer to π-cycloheptatrienyl rings of presumed planar configuration with all seven carbon atoms bonded to the transition metal atom (III). The term "allylic π-cycloheptatrienyl" will be used to refer to π-cycloheptatrienyl rings with only three carbon atoms of the seven bonded to the transition metal atom (II). The term "dienoid cyclooctatetraene ring" will refer to cyclooctatetraene rings such as the one in $C_8H_8Fe(CO)_3$ with only four carbon atoms bonded to the metal atom.

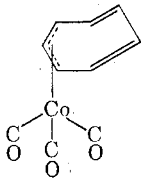
[25] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

due to all seven protons of the allylic π-cycloheptatrienyl ring is unusual since on the basis of the n.m.r. spectra of most other hydrocarbon complexes of transition metals, the three protons of the three carbon atoms of the cycloheptatrienyl ring which are bonded to the molybdenum atom and the four protons of the four carbon atoms of the two double bonds of the cycloheptatrienyl ring which are not bonded to the molybdenum atom would be expected to exhibit different chemical shifts. In addition, further complexities in the portion of the n.m.r. spectrum due to the cycloheptatrienyl ring would be expected due to such phenomena as spin–spin coupling between these different types of protons on the seven-membered ring. The presence of the single proton resonance in the proton n.m.r. spectrum due to the seven protons of the allylic π-cycloheptatrienyl ring in $C_5H_5Mo(CO)_2C_7H_7$ is, however, entirely analogous to the presence of the single proton resonance in the proton n.m.r. spectrum due to the eight protons of the cyclooctatetraene ring in $C_8H_8Fe(CO)_3$.[26] X-Ray structural studies on $C_8H_8Fe(CO)_3$[27] have shown that only four of the eight carbon atoms of the cyclooctatetraene ring are bonded to the iron atom and that the ring is not planar (VIII). A further similarity between $C_5H_5Mo(CO)_2C_7H_7$ and $C_8H_8Fe(CO)_3$[26] is the relatively low reactivity of the uncomplexed two double bonds.

(C) **π-Cycloheptatrienylcobalt Tricarbonyl.**—The cobalt compound $C_7H_7Co(CO)_3$ (IX) prepared in low yield by irradiating $Co_2(CO)_8$ with cycloheptatriene is a malodorous, volatile liquid. Like the isoelectronic $C_8H_8Fe(CO)_3$ and in contrast to the green planar π-cycloheptatrienyl derivative of similar formula $C_7H_7V(CO)_3$[4,5] the cobalt compound $C_7H_7Co(CO)_3$ is dark red. Unlike air-stable $C_8H_8Fe(CO)_3$, the cobalt derivative is air-sensitive, oxidizing completely on exposure to air for several hours. The allylic π-cycloheptatrienyl ring in $C_7H_7Co(CO)_3$ like that in $C_5H_5Mo(CO)_2C_7H_7$ exhibits a single sharp resonance in the proton n.m.r. spectrum. The position of this resonance at τ 4.49 in carbon disulfide solution clearly distinguishes it from the cyclopentadienyl resonance at τ 5.00 in carbon disulfide solution of the likewise dark red liquid $C_5H_5Co(CO)_2$. Like $C_5H_5Mo(CO)_2C_7H_7$, the dark red benzene solutions of $C_7H_7Co(CO)_3$ are immediately decolorized by tetracyanoethylene, depositing a brownish precipitate.



VIII



IX

The comparison of properties of the isoelectronic $C_7H_7Co(CO)_3$ and $C_8H_8Fe(CO)_3$ suggests that allylic π-cycloheptatrienyl derivatives are less stable than the analogous dienoid π-cyclooctatetraene derivatives, particularly to air oxidation. This may be a result of increased strain in the allylic π-cycloheptatrienyl ring system. However, in the similar series of isoelectronic compounds π-allylcobalt tricarbonyl[28] and π-butadieneiron tricarbonyl,[29] the cobalt derivative is also less stable than the iron derivative, especially to air oxidation.

Acknowledgment.—The authors are indebted to Shell Chemical Company for the generous gifts of cycloheptatriene which made this research possible. The authors are also indebted to Dr. Roy Adams of Geneva College, Beaver Falls, Pa., for suggestions concerning the terminology used in this paper.

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(26) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960); M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(27) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

(28) W. R. McClellan, H. H. Hoehn, H N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961); R. F. Heck and D. S. Breslow, *ibid.*, **82**, 750 (1960); **83**, 1097 (1961).

(29) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).