as in spectrum of $C_9H_{10}\cdot Mo(CO)_3$, with two outer peaks too weak to be observed), and 1.13 p.p.m.

Because of the low reactivity of tungsten hexacarbonyl, reaction with I was carried out in *n*-decane (b.p. 174°) rather than ethylcyclohexane (b.p. 135°). The compound $C_9H_{10}\cdot W(CO)_3$ (m.p. of 113–114°, sublimes at 80° (0.1 mm.)) was obtained in 13% yield.

Anal. Calcd. for $C_{12}H_{10}O_3W$: C, 37.3; H, 2.6; W, 47.7. Found: C, 37.4; H, 2.7; W, 47.3.

The n.m.r. spectrum of the tungsten compound showed resonances at 4.23, 4.11 (doublet, separation 15 cycles), 2.30 (probably a quadruplet) and 1.68 p.p.m. In the infrared spectrum of the complex, carbonyl stretches (C_2Cl_4 solution) occur at 2000, 1932 and 1905 cm.$^{-1}$. In CS_2 solution, C–H stretches appear from 2940 to 3055 cm.$^{-1}$. Other major bands are at 1510(w) cm.$^{-1}$ (C_2Cl_4 solution), and at 1392(m), 1284(m), 1178(m), 1042(vw), 870(w) 800(vw) and 754(w) cm.$^{-1}$ (CS_2 solution). The ultraviolet spectrum has maxima at 214 mμ (ε 36,100) and at 321 mμ (ε 13,100).

Vinylcycloheptatriene.—A solution of vinylmagnesium bromide in tetrahydrofuran was prepared from 14.6 g. (0.6 g. atom) of magnesium and 75 g. (0.7 mole) of purified[16] vinyl bromide. A suspension of tropylium bromide (85.5 g., 0.5 mole) in 200 ml. of tetrahydrofuran was added over a period of 5 hr. The mixture then was stirred at room temperature for 14 hr., and subsequently hydrolyzed with saturated ammonium chloride solution and filtered. Solvent was distilled from the filtrate at 30° (250 mm.), and 33 g. (56% yield) of a colorless liquid ($n^{22.5}D$ 1.5185) collected at 75° (80 mm.).

Anal. Calcd. for C_9H_{10}: C, 91.5; H, 8.5. Found: C, 91.6; H, 8.5.

The n.m.r. spectrum of vinylcycloheptatriene shows resonances at 6.72 (triplet, separation 3 cycles), 6.26 (complex group of peaks), 5.26 (complex group of peaks) and 2.24 (doublet, separation 5 cycles) p.p.m. Relative intensities were 2:4:3:1, respectively, in accord with the vinylcycloheptatriene being the structural isomer VI, as expected from the method of preparation.

Principal bands in the infrared spectrum (liquid film) of vinylcycloheptatriene occur at 3098(sh), 3050(s), 2865(m), 1842(w), 1778(w), 1738(vw), 1695(w), 1645(m), 1600(m), 1439(w), 1418(m), 1392(m), 1348(w), 1288(w), 1250(m), 1193(w), 1130(vw), 1053(vw), 992(s), 949(m), 914(vs), 800(vw), 792(sh), 740(vs), 700(vvs), and 663(s) cm.$^{-1}$.

Reaction between Iron Pentacarbonyl and Vinylcycloheptatriene.—A mixture of iron pentacarbonyl (10 g., 50 mmoles) and VI (1.8 g., 15 mmoles) in 40 ml. of ethylcyclohexane was refluxed for 14 hr. under nitrogen, an iron mirror being deposited during the later stages of the heating. After cooling the mixture to room temperature and filtering, solvent was removed at 0.1 mm., yellow crystals separating out during this process. The residue was sublimed at 50–70° (0.1 mm.) to drive off oily impurities. Further sublimation (95–105° (0.1 mm.) afforded a dirty orange sublimate. The latter was washed with 25 ml. of isohexane at −78° and the yellow crystals (1.8 g., 30% yield) removed by filtration. The analytical sample was obtained by resublimation. In a repeat preparation final purification was effected by chromatography on alumina. Samples from the two independent preparations were analyzed.

Anal. Calcd. for $C_{15}H_{10}O_6Fe_2$: C, 45.3; H, 2.51; Fe, 28.1; mol. wt., 398. Found: C, 45.9, 45.3; H, 2.50, 2.53; Fe, 27.8, 27.7; mol. wt. (isopiestic), 411.

The complex $C_9H_{10}\cdot Fe_2(CO)_6$ is yellow solid, m.p. 126–127°. The infrared spectrum in the carbonyl region (CaF_2 optics, C_2Cl_4 solution) showed bands at 2051(w), 2037(s), 1979(s) and 1966(s) cm.$^{-1}$.

Acknowledgment.—We are indebted to the Union Carbide Metals Co. for a gift of chromium hexacarbonyl, and to the Climax Molybdenum Co. for a gift of molybdenum and tungsten hexacarbonyls. We wish to thank Dr. T. D. Coyle for helpful discussions concerning the interpretation of n.m.r. spectra.

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[16] B. Bartocha, H. D. Kaesz and F. G. A. Stone, *Z. Naturforsch.*, **14b**, 352 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Chemistry of the Metal Carbonyls. XII. New Complexes Derived from Cyclopentadienylcobalt Dicarbonyl[1]

BY R. B. KING,[2] P. M. TREICHEL[2] AND F. G. A. STONE

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Stable volatile complexes of the type C_5H_5Co(diene) are described, being prepared by treating cyclopentadienylcobalt dicarbonyl with 1,5-cycloöctadiene, bicyclo[2.2.1]heptadiene and 1,3-cyclohexadiene. The nature of the complex $C_5H_5CoC_8H_{10}$ obtained from 1,3,5-cycloöctatriene and cyclopentadienylcobalt dicarbonyl is discussed. Reaction between cyclopentadienylcobalt dicarbonyl and perfluoroalkyl iodides (R_FI) affords black volatile solids of the general formula $C_5H_5Co(CO)(R_F)I$.

A variety of cyclopentadienyl metal carbonyls are now known,[3] having many properties similar to those of the parent carbonyls. However, an even closer relationship may be found between specific metal carbonyls and cyclopentadienyl metal carbonyls of the next higher periodic group. Thus both $[Co(CO)_4]_2$ and $[C_5H_5NiCO]_2$ form complexes with acetylene bridges, $(CO)_6Co_2\cdot RC{\equiv}CR$[4a] and $[C_5H_5Ni]_2RC{\equiv}CR$,[4b] respectively, and the metal–metal bonds in $Mn_2(CO)_{10}$ and $(C_5H_5)_2Fe_2(CO)_4$ are cleaved readily by sodium amalgam to form salts $NaMn(CO)_5$[5a,b] and $NaFe(CO)_2C_5H_5$.[5c]

A search for similar relationships is aided by considerations based on formal oxidation states. For this purpose it is a convenient formalism to treat the cyclopentadienyl group as an anion, so that the formal oxidation state of the metal atom

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[1] Previous paper in this series, R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961).

[2] National Science Foundation Predoctoral Research Fellow.

[3] For reviews of these compounds see: (a) E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Editors, Emeléus and Sharpe, Academic Press, Inc., New York, N. Y., 1959, p. 56; (b) G. Wilkinson and F. A. Cotton, "Progress in Inorganic Chemistry," Vol. I, editor, Cotton, Interscience Publishers, Inc., New York, N. Y., 1959, p. 1; (c) J. Chatt, P. L. Pauson and L. M. Venanzi, Chapter 10, "Organometallic Chemistry," A.C.S. Monograph, Editor, Zeiss, Reinhold Publ. Corp., New York, N. Y., 1960.

[4] (a) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954); **78**, 120 (1956); (b) J. F. Tilney-Bassett and O. S. Mills, *ibid.*, **81**, 4757 (1959).

[5] (a) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957); (b) W. Hieber and G. Wagner, *Z. Naturforsch.*, **12b**, 478 (1957); (c) E. O. Fischer and R. Böttcher, *ibid.*, **10b**, 600 (1955).

in the usual cyclopentadienyl carbonyls which contain one cyclopentadienyl group per metal atom may be regarded as +1, compared with a formal oxidation state of 0 for the metal atom in a pure metal carbonyl. In this way it is seen that the number of electrons furnished by the metal atoms in such pairs as $[Co^0(CO)_4]_2$ and $[C_5H_5Ni^{+1}CO]_2$, or $[C_5H_5Fe^{+1}(CO)_2]_2$ and $[Mn^0(CO)_5]_2$ is the same. In this paper new complexes derived from cyclopentadienylcobalt dicarbonyl are described, illustrating resemblances between the chemistry of cyclopentadienylcobalt dicarbonyl and iron pentacarbonyl. In both of these carbonyls the metal can be regarded as contributing eight electrons toward the total needed to complete the valence shells of cobalt and iron.[6]

Several complexes $L{\cdot}Fe(CO)_3$ are known where L is a conjugated diene.[7] It seemed of interest, therefore, to investigate reactions between cyclopentadienylcobalt dicarbonyl and conjugated dienes in an attempt to obtain complexes $L{\cdot}CoC_5H_5$. It seemed likely that such reactions would afford new cobalt complexes, in view of the preparation of cyclopentadienylcobalt-cyclopentadiene (I)[8] by an indirect route involving reduction of bis-(cyclopentadienyl)-cobalt(III) salts. Accordingly, the reaction between cyclopentadienylcobalt dicarbonyl and 1,3-cyclohexadiene was investigated and found to give a red-orange crystalline solid (II). Butadiene and alloöcimene also react with cyclopentadienylcobalt dicarbonyl to give cyclopentadienylcobalt-diene complexes, the crude products being orange and deep-red liquids, respectively. However, it proved impossible to obtain pure crystalline products. The only reported example of an iron complex $L{\cdot}Fe(CO)_3$, where L is a non-conjugated diene, is the highly unstable compound 1,5-cycloöctadiene-iron tricarbonyl.[7b] Apparently, the tendency of non-conjugated diolefins to function as ligands to iron forming complexes of the metal-olefin type is quite low.[7] However, in view of the fact that rhodium, in the same subgroup as cobalt, is known to form complexes with non-conjugated dienes, *e.g.*, $C_5H_5RhC_8H_{12}$,[9] it appeared likely that cobalt would do so also, yielding a complex more stable than $C_8H_{12}{\cdot}Fe(CO)_3$. Thus from the reaction between cyclopentadienylcobalt dicarbonyl and 1,5-cycloöctadiene, III was obtained, which was moderately soluble in organic solvents, but less soluble than the other cobalt diene complexes described here. Unlike $C_8H_{12}{\cdot}Fe(CO)_3$, III can be kept at room temperature under nitrogen for at least several months without decomposition. A related complex is cyclopentadienylcobalt-cycloöctatetraene (IV).[10] In contrast to cycloöctatetraene-iron tricarbonyl,[11] which shows a single resonance in its proton n.m.r. spectrum, the spectrum of IV shows two resonances of equal intensity due to the C_8H_8 moiety,[10] as expected if cycloöctatetraene retains in IV its normal tub-like configuration. It is interesting to compare the reported n.m.r. spectrum of IV with that observed by us for III.[12] The spectrum of III shows resonances at 4.45, 3.37, 2.32 and 1.62 p.p.m., with relative intensity 5:4:4:4. The peak at 4.45 p.p.m., because of its relative intensity and sharpness, may be ascribed to the five protons of the cyclopentadienyl ring, leaving the remaining three peaks of equal intensity assignable to the three groups of four equivalent protons ($H_{(2)}$, $H_{(3)}$ and $H_{(4)}$ in III) in the cycloöctadiene moiety. The spectrum of IV has resonances at 5.57, 4.67 and 3.65 p.p.m., relative intensity 4:5:4.[10,12] On the basis of its relative intensity the resonance at 4.67 p.p.m. was assigned to protons of the cyclopentadienyl ring, leaving the resonances at 5.57 and 3.65 p.p.m. as being due to the protons of the chelate bonded cycloöctatetraene ring. Because the chemical shift is in the region for olefinic protons, it is reasonable to assign the resonance at 5.57 p.p.m. to the hydrogen atoms $H_{(1)}$ in IV. The resonance at 3.65 p.p.m. may then be ascribed to the protons $H_{(2)}$. These assignments are supported by the fact that in the spectrum of III there is no resonance near 5.57 p.p.m., since III has no protons on carbon atoms of uncomplexed double bonds. Furthermore, assignment of the resonance at 3.65 p.p.m. in IV to the $H_{(2)}$ protons makes it reasonable to assign the corresponding resonance at 3.37 p.p.m. in III to the olefinic protons $H_{(2)}$, leaving the resonances at 2.32 and 1.62 p.p.m. as arising from one or other of the two sets of protons $H_{(3)}$ and $H_{(4)}$, magnetically distinguishable by their different proximities to the cobalt atom.

In view of the existence of the chelate metal-olefin complexes III and IV it seemed worthwhile to investigate the reaction between cyclopentadienylcobalt dicarbonyl and 1,3,5-cycloöctatriene, in order to determine whether this hydrocarbon would also form a complex (V) involving coördination of a pair of 1,5-double bonds to cobalt. It also seemed possible however, that cyclopentadienylcobalt dicarbonyl might react with 1,3,5-cycloöctatriene to form a complex (VI) involving the bicyclo[4.2.0]-octa-2,4-diene moiety, since in a study of iron carbonyl complexes derived from 1,3,5-cycloöctatriene it has been shown that the $C_8H_{10}{\cdot}Fe(CO)_3$ complex obtained in greatest yield is bicyclo[4.2.0]octa-2,4-diene-iron tricarbonyl, a compound containing no free double bond.[13] A second complex also of composition $C_8H_{10}{\cdot}Fe(CO)_3$, formed under mild

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(6) Certain chemical resemblances between the carbonyls $Fe(CO)_5$ and $C_5H_5Co(CO)_2$ are already recognizable. Thus both carbonyls form complexes with cyclopentadienone derivatives of the type (cyclopentadienone)$Fe(CO)_3$ and C_5H_5Co(cyclopentadienone). See G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959), and R. Markby, H. W. Sternberg and I. Wender, *Chemistry & Industry*, 1381 (1959).

(7) (a) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958); (b) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

(8) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

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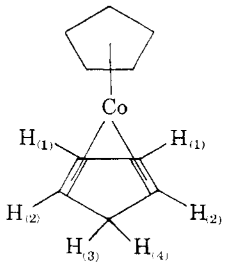
(10) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **33**, 425 (1960).

(11) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

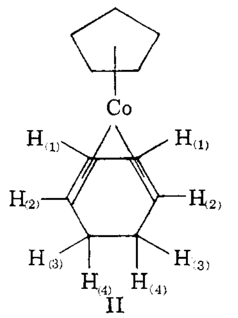
(12) The n.m.r. spectra of the new cobalt-diene complexes described in this paper were obtained at 60 mc. by a Varian model 4300B high resolution spectrometer fitted with a superstabilizer. Concentrated solutions in carbon disulfide were employed, and chemical shifts are in p.p.m., downfield from tetramethylsilane. The proton n.m.r. spectrum of IV was obtained at 40 mc., relative to cyclohexane (see ref. 10). For the sake of easy comparison the results for IV have been converted to p.p.m. downfield from tetramethylsilane, to correspond to other spectra reported in this paper.

(13) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6240 (1960).

reaction conditions, was shown spectroscopically to contain a free double bond.



I



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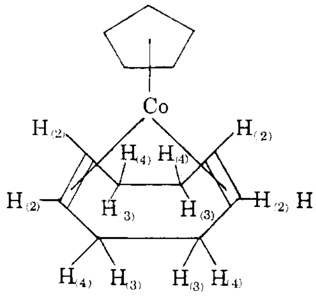

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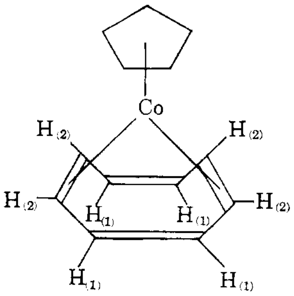

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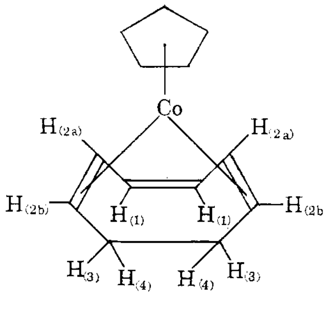
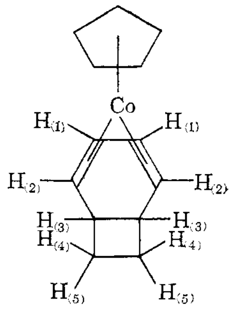


V



VI

It was found that cyclopentadienylcobalt dicarbonyl and 1,3,5-cycloöctatriene react to give a complex of composition $C_5H_5CoC_8H_{10}$. The latter showed no band in the carbon–carbon double bond region of the spectrum, making structure V or any other structure involving coördination of two of the three double bonds of 1,3,5-cycloöctatriene to the cobalt atom very improbable. This suggests that the new cobalt compound C_5H_5Co-C_8H_{10} is cyclopentadienylcobalt-bicyclo[4.2.0]octa-2,4-diene (VI). The proton n.m.r. spectrum of $C_5H_5CoC_8H_{10}$ is also consistent with structure VI. Resonances of relative intensities 2:5:2:2:2:2 occur at 5.04, 4.62, 3.13, 2.29, 1.56 and 0.86 p.p.m. The sharp resonance at 4.62 p.p.m. is due to the cyclopentadienyl group in VI, and may be compared with similar resonances which occur in the spectrum of I at 4.60 p.p.m.,[8] and in the spectrum of II at 4.63 p.p.m. The remaining five resonances in the spectrum of $C_5H_5CoC_8H_{10}$ are the number expected if the bicyclo[4.2.0]octa-2,4-diene moiety is present. Unfortunately, fine structure of these resonances was not determined due to experimental difficulties. However, if the cobalt compound were the cyclooctatriene derivative V, with the free double bond, it would be expected to have a resonance corresponding to two protons near 5.57 p.p.m. due to the two uncomplexed olefinic protons ($H_{(1)}$ in V), similar to the corresponding protons $H_{(1)}$ in IV. Instead, the spectrum of $C_5H_5CoC_8H_{10}$ shows a resonance at 5.04 p.p.m. which compares favorably with the presence of a resonance at 5.25 p.p.m. in the spectrum of I and assigned[8] to the analogous protons $H_{(1)}$, and a resonance at 4.80 p.p.m. observed by us in the spectrum of II. Furthermore, if V were the correct structure, the n.m.r. spectrum would be expected to show resonances near 3.65 p.p.m. due to protons $H_{(2a)}$ and $H_{(2b)}$, similar to the corresponding protons $H_{(2)}$ in IV.

Another diene which has been shown to react with iron pentacarbonyl to form a complex L·Fe(CO)$_3$ is bicyclo[2.2.1]heptadiene.[14] Other known bicycloheptadiene complexes are $C_7H_8Co_2(CO)_6$, $(C_7H_8)_2$-$Co_2(CO)_4$[15] and $C_7H_8{\cdot}Mo(CO)_4$.[16] We have found that bicycloheptadiene reacts with cyclopentadienylcobalt dicarbonyl to give orange crystalline cyclopentadienylcobalt-bicyclo[2.2.1]heptadiene.

Another reaction characteristic of iron pentacarbonyl is the formation of perfluoroalkyliron tetracarbonyl iodides on treatment with perfluoroalkyl iodides.[17] It thus seemed reasonable that cyclopentadienylcobalt dicarbonyl would also react with perfluoroalkyl iodides to give compounds of the general formula $C_5H_5Co(CO)(R_F)I$, complexes with four different groups bonded to a single cobalt atom. Treatment of cyclopentadienylcobalt dicarbonyl with perfluoropropyl iodide in benzene at 45° afforded a black crystalline complex C_5H_5-$Co(CO)(C_3F_7)I$.[18] The C_2F_5 and CF_3 compounds were made in an analogous manner.

The infrared spectra of the new perfluoroalkylcobalt compounds show a single carbonyl stretch, as well as bands due to the cyclopentadienyl and perfluoroalkyl groups. The proton n.m.r. spectra each show the single expected sharp resonance due to protons on the cyclopentadienyl ring. The resonance is shifted downfield (*e.g.*, at 5.65 p.p.m. for $C_5H_5Co(CO)(C_3F_7)I$ in chloroform solution) from the corresponding resonance at 4.92 p.p.m. for the cyclopentadienyl protons in cyclopentadienylcobalt dicarbonyl. It appears that the observed downfield shift is due to the electronegativity of the fluorocarbon group. A similar shift of the cyclopentadienyl-proton resonance occurs in the compound $HCF_2CF_2Mo(CO)_3C_5H_5$.[18] The F^{19} n.m.r. spectra of the new cobalt compounds have also been recorded and will be described in detail elsewhere.[19]

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

(15) G. Winkhaus and G. Wilkinson, *Chemistry & Industry*, 1083 (1960).

(16) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

(17) T. A. Manuel, S. L. Stafford and F. G. A. Stone, *ibid.*, **83**, 249 (1961); R. B. King, S. L. Stafford, P. M. Treichel and F. G. A. Stone, *ibid.*, **83**, 3604 (1961).

(18) For a preliminary mention of this reaction and of fluorocarbon derivatives of other transition metals, see R. B. King, P. M. Treichel and F. G. A. Stone, *Proc. Chem. Soc.*, 69 (1961).

(19) E. Pitcher, A. D. Buckingham and F. G. A. Stone, *J. Chem. Phys.*, in press.

Experimental[20]

Infrared spectra were recorded using a Perkin–Elmer model 21 double-beam spectrophotometer fitted with sodium chloride optics.

We are indebted to the Antara Division of General Aniline and Film Co. for a gift of cycloöctatetraene. 1,3,5-Cycloöctatriene was obtained by reduction of the cyclooctatetraene with zinc dust in the presence of excess of potassium hydroxide in ethanol at 80°.[21] Perfluoroalkyl iodides were obtained from Columbia Organic Chemicals Co.

Two entirely different methods have been reported for the synthesis of cyclopentadienylcobalt dicarbonyl, one based on treatment of bis-(cyclopentadienyl)-cobalt with carbon monoxide under pressure[22a] and one based on reaction of cobalt carbonyl with cyclopentadiene.[22b] We have found that reaction of bis-(cyclopentadienyl)-cobalt with carbon monoxide under pressure is the most satisfactory method for making relatively large quantities of cyclopentadienylcobalt dicarbonyl. The preparation described below permits preparation of the cyclopentadienyl carbonyl in quantities of about 40 g. at a time and, unlike the previous method,[22a] avoids isolation in the pure state of pyrophoric bis-(cyclopentadienyl)-cobalt.

A solution of sodium cyclopentadienide (1.7 moles) in 1000 ml. of redistilled tetrahydrofuran was prepared in a 2-liter 3-necked flask under nitrogen, from commercial 50% sodium dispersion in mineral oil and an excess of freshly cracked cyclopentadiene. About 110 g. (0.84 mole) of anhydrous cobalt(II) chloride (prepared by dehydrating reagent grade material at 160–180° (4 mm.) for several hours) was added to the sodium cyclopentadienide solution, and the deep purple reaction mixture was stirred for several hours at room temperature. Solvent then was removed (25° (20 mm.)) leaving a sticky residue. The latter was dissolved in about 400 ml. of reagent-grade benzene and transferred to a 1-liter autoclave, avoiding exposure to air by using protective atmospheres of nitrogen and carbon dioxide in the transfer. After pressurizing with 2450 p.s.i. C.P. carbon monoxide, the autoclave was heated with rocking to 130° for about 10 hr. A considerable pressure drop occurred initially. After the reaction period was over, the autoclave was cooled to 35°, flushed with 1000 p.s.i. nitrogen, and then opened. The resulting benzene solution of the product was filtered, and the residue washed with a total of about 300 ml. of benzene. The latter then was removed through a column at about 30° (reduced pressure), and the remaining liquid distilled at 37–38.5° (2 mm.), cooling the distillate at −10°. A yield of 39.1 g. (25.5%) of the deep red liquid cyclopentadienylcobalt dicarbonyl was obtained and stored under nitrogen in the refrigerator.

General Procedure for the Preparation of Cyclopentadienylcobalt-diene Complexes.—A mixture of 1 ml. (1.3 g., 7 mmoles) of cyclopentadienylcobalt dicarbonyl, excess of the olefin (1–2 ml.) and 5 ml. of ethylcyclohexane was refluxed for several hours at the boiling point of the solvent (~135°) in a 50-ml. flask. The entire reaction mixture was then chromatographed on a 2 × 40 cm. column of Merck alumina. The chromatogram was developed with pentane. In the cases of the olefins discussed in this paper the only band that was observed on the column was that of the diene complex, usually some shade of orange in color. Unreacted cyclopentadienylcobalt dicarbonyl was not observed. The product was eluted from the column with pentane, and the resulting eluate evaporated immediately at 25–40° (20 mm.) usually leaving an oil. The further workup of the products after this stage varied from one compound to another and is described below for each compound.

(a) **Cyclopentadienylcobalt-1,3-cyclohexadiene (II).**—The red-orange liquid obtained after chromatography crystallized slightly below room temperature. Yield of crude material was about 30%. To obtain II pure, the red oil was dissolved in 10 ml. of pentane and cooled to −78°, orange crystals separating. The product was filtered through a sintered glass funnel cooled to −78°. The analytical sample (m.p. 40–42°) was purified by sublimation (50° (0.1 mm.)).

Anal. Calcd. for $C_{11}H_{13}Co$: C, 64.7; H, 6.4; Co, 28.9. Found: C, 64.6; H, 6.2; Co, 28.7.

Compound II is very soluble in organic solvents, but in solution decomposes in air after several hours. The infrared spectrum of II (carbon disulfide solution) has bands at 3067(w), 3005(w), 2960(m), 2890(m), 2840(m), 2800(m), 1325(w), 1254(w), 1165(m), 1108(m), 1002(m), 909(w), 836-829(w, unresolved) and 801(s) cm.$^{-1}$. The n.m.r. spectrum of II shows resonances at 4.79, 4.63, 3.00, 1.24, 0.71 p.p.m., of relative intensities 2:5:2:2:2.

(b) **Cyclopentadienylcobalt-1,5-cycloöctadiene (III).**—The orange solution eluted from the chromatography column on evaporation deposited light orange crystals. The yield of crude product was 800 mg. (48%). Analytically pure material (650 mg., 39% yield), m.p. 103–105°, was obtained by sublimation (50–70°(0.1 mm.)); infrared spectrum of III (tetrachloroethylene solution) has bands at 2960(m), 2900(m), 2847(m), 2800(m), 1515(m), 1450(m), 1425(w), 1320(m), 1012(m) and 991(m) cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{17}Co$: C. 67.2; H, 7.3; Co, 25.5; mol. wt., 232. Found: C, 67.4; H, 7.3; Co, 25.7; mol. wt., 241.

(c) **Cyclopentadienylcobalt-bicyclo[4.2.0]octadiene (VI).**—The deep red liquid obtained by chromatography was treated with 5 ml. of pentane and chilled to −78° for 1 hr., deep red crystals separating. After filtering and drying, the crystals were purified by sublimation (70° (0.1 mm.)), affording 280 mg. (17% yield) of VI (m.p. 45–46°).

Anal. Calcd. for $C_{13}H_{15}Co$: C, 67.8; H, 6.5; Co, 25.7; mol. wt., 230. Found: C, 67.7; H, 6.5; Co, 25.2; mol. wt., 225.

The infrared spectrum of VI (carbon disulfide solution) showed bands at 3075(w), 3010(w), 2950(m), 2905(m), 2825(w), 1333(w), 1277(w), 1213(w), 1128(m), 1108(m), 1008(m), 999(m), 930(w), 895(w), 825(m) and 801(s) cm.$^{-1}$. Using tetrachloroethylene as solvent no band was observed in the carbon–carbon double bond stretching region of spectrum. However a weak band was observed at 1516 cm.$^{-1}$. Such a band is characteristic of a C=C group coördinated to a metal.[23] In the infrared spectrum of IV, first reported by Nakamura and Hagihara,[10] we have observed in tetrachloroethylene solution a sharp band at 1640 cm.$^{-1}$ in the carbon–carbon double bond stretching region.

(d) **Cyclopentadienylcobalt-bicyclo[2.2.1]heptadiene.**—The orange liquid obtained after chromatography was sublimed at 50–70° (0.1 mm.) onto a probe cooled to −78°. After warming the probe to 0° the sublimate was removed, giving 300 mg. (19% yield) of an oil which crystallized completely after an hour. The pure compound melts at 60–61°. The infrared spectrum of cyclopentadienylcobalt-bicyclo-[2.2.1]heptadiene (carbon disulfide solution) shows bands at 3075(w), 3028(m), 2978(m), 2924(m), 2890(m), 2827 (w), 1370(m), 1295(m), 1164(m), 1155(w, sh), 1109(m), 1052(w), 1008(m), 995(m), 891(m), 837(w), 830(w), 798(s), 766(w), 740(w) and 732(vw) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{13}Co$: C, 66.6; H, 6.0; Co, 27.3; mol. wt., 216. Found: C, 66.4; H, 6.1; Co, 27.0; mol. wt., 215.

Reactions between Cyclopentadienylcobalt Dicarbonyl and Perfluoroalkyl Iodides. (a) Perfluoropropyl Iodide.—A mixture of 2.0 g. (11 mmoles) of cyclopentadienylcobalt dicarbonyl, 4.9 g. (16.6 mmoles) of heptafluoropropyl iodide, and 50 ml. of benzene was heated at 45° under nitrogen for 16 hr. Solvent was removed at 20 mm., leaving a black residue which on sublimation (100–105°(0.1 mm.)) gave 3.06 g. (62% yield) of $C_5H_5Co(CO)(C_3F_7)I$. The analytical sample was resublimed (85°(0.1 mm.)). The product formed black crystals melting at 120–122°, in appearance resembling cyclopentadienyliron dicarbonyl iodide. The infrared spectrum of the compound (carbon disulfide solution) shows a strong carbonyl band at 2080 cm.$^{-1}$. Other bands occur at 1317(m), 1230(s), 1193(s), 1168(vw), 1158(m), 1090(m), 1086(m), 1061(w), 1041(m), 1012(w, broad), 841(m), 830(m), 802(m), 720(s) and 661(m) cm.$^{-1}$.

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Anal. Calcd. for $C_9H_5F_7OCoI$: C, 24.1; H, 1.1; F, 29.7; Co, 13.2; I, 28.4; mol. wt., 448. Found: C, 24.0, 24.2; H, 1.2, 1.7; F, 29.3, 29.5; Co, 12.9, 12.8; I, 28.0, 28.4; mol. wt., 445.

(b) **Pentafluoroethyl Iodide.**—To a mixture of cyclopentadienylcobalt dicarbonyl (3.0 g., 17 mmoles) and 50 ml. of benzene was added pentafluoroethyl iodide (10 g., 40.6 mmoles) and the reaction mixture was maintained at 45° for 17 hr., a Dry-Ice cooled condenser being used to prevent escape of the pentafluoroethyl iodide. Removal of solvent at 20 mm. (25°) and sublimation of the residue at 85° (0.1 mm.) for 12 hr. gave 4.77 g. (72% yield) of black crystalline $C_5H_5Co(CO)(C_2F_5)I$, m.p. 138°. The analytical sample was resublimed at 75° (0.1 mm.). The infrared spectrum of the compound (carbon disulfide solution) showed a strong carbonyl band at 2080 cm.$^{-1}$. Other bands occur at 1286(m), 1186(s), 1065(s), 1055(s), 1028(s), 905(w), 896(m), 842(w), 831(w) and 729(m) cm.$^{-1}$.

Anal. Calcd. for $C_8H_5F_5OCoI$: C, 24.1; H, 1.3; F, 23.8; Co, 14.8; I, 31.9; mol. wt., 398. Found: C, 24.4; H, 1.4; F, 23.4; Co, 14.9; I, 32.0; mol. wt., 378.

(c) **Trifluoromethyl Iodide.**—The preparation of $C_5H_5Co(CO)(CF_3)I$ was entirely analogous to the preparation of the C_2F_5 derivative described above. The yield was much lower, due probably to loss of trifluoromethyl iodide past the −78° condenser. Thus cyclopentadienylcobalt dicarbonyl (2.0 g., 11 mmoles) and trifluoromethyl iodide (13.4 mmoles, measured as gas) in 50 ml. of benzene gave only 0.3 g. (7.5% yield) of black crystalline $C_5H_5Co(CO)(CF_3)I$, decomp. without melting at ~145°, subliming at 100° (0.1 mm.). The infrared spectrum of the compound (carbon disulfide solution) shows a strong carbonyl stretch at 2073 cm.$^{-1}$. Other bands occur at 1067(s), 1053(s), 1019(s), 838(m), 830(m) and 709(w) cm.$^{-1}$.

Anal. Calcd. for $C_7H_5F_3OCoI$: C, 24.1; H, 1.5; F, 16.4; Co, 17.0; I, 36.5. Found: C, 24.2; H, 1.5; F, 16.2; Co, 17.2; I, 36.0.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. XIII. Iron Complexes of Divinylbenzenes[1]

BY T. A. MANUEL,[2] S. L. STAFFORD[3] AND F. G. A. STONE

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Diiron hexacarbonyl complexes of *meta*- and *para*-divinylbenzenes are described, representing the first reported examples of substances wherein iron carbonyl groups are bonded to benzene rings. The diene complex 1,4-diphenylbutadiene-iron tricarbonyl and the arene complex 1,4-diphenylbutadiene-chromium tricarbonyl have been prepared. The latter compound reacts with triiron dodecacarbonyl to afford a complex in which 1,4-diphenylbutadiene is bonded both to chromium tricarbonyl and iron tricarbonyl groups.

Many aromatic hydrocarbons react with the hexacarbonyls of the sub-group VI metals to give arene-metal tricarbonyl complexes.[4] In contrast arene-iron dicarbonyl complexes have never been reported as products of reactions between aromatic hydrocarbons and iron carbonyls, even though π-complexes of iron of many types have been obtained by treating olefinic hydrocarbons with iron carbonyls.[5]

Although arene-iron dicarbonyl complexes have not been reported, benzene and other aromatic hydrocarbons can be bonded to iron atoms under certain circumstances, for example, in the complexes cyclopentadienebenzene-iron,[6] acenaphthylene-diiron hexacarbonyl,[4e] azulene-diiron pentacarbonyl[7] and the cyclopentadienylmesitylene iron (I) cation.[8] In view of the existence of these iron complexes there would appear at present to be no valid reason why suitably chosen substituents should not be able to activate a benzene ring so that it could form π-complexes of one type or another with iron carbonyl groups. Accordingly, reactions between triiron dodecacarbonyl and alkylbenzenes, mesitylene, hexamethylbenzene, naphthalene, anthracene, styrene, 2,4-dimethylstyrene, vinyltoluene and 2,4,6-trimethylstyrene were studied. No π-complexes of iron were isolated from any of these reactions. However, reaction between *p*-divinylbenzene and triiron dodecacarbonyl in refluxing benzene afforded the compound *p*-divinylbenzene-diiron hexacarbonyl (I), a yellow solid melting with decomposition at 110°.

The reaction between triiron dodecacarbonyl and an excess of a commercial mixture of *meta*- and *para*-divinylbenzenes was next investigated. An orange crystalline complex (m.p. 135–136° with decomp.) was obtained. This complex (II) was isomeric with I and shown to be *m*-divinylbenzene-diiron hexacarbonyl by partial oxidation to isophthalic acid. The results of the competitive reaction between triiron dodecacarbonyl and excess of the two divinylbenzene isomers indicate that the *m*-divinylbenzene-diiron hexacarbonyl (II) is more stable than its *para*-isomer (I). Both iron complexes are stable in air and soluble in organic solvents.

The divinylbenzenes are ten π-electron systems. Because of this, and from a consideration of the "inert gas configuration" formalism, it was possible that the divinylbenzenes would form complexes of type divinylbenzene–diiron pentacarbonyl rather than divinylbenzene–diiron hexacarbonyl. Nevertheless, it was found that the divinylbenzene–iron carbonyl complexes contain two $Fe(CO)_3$ groups rather than an $Fe(CO)_3$ group and an $Fe(CO)_2$ group, since reaction of the compounds

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[2] National Science Foundation predoctoral fellow, 1958–1961.

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