

The study of the infrared spectra of complexes of the bipyridines was not very helpful in understanding the nature of these complexes. However, this study does provide some further empirical information about the nature of spectral changes to be expected on complex formation. The pyridine complexes provide the best information on this question. It would appear that the changes in spectra, while profoundly affecting the appearance of the spectrum, result mostly from changes in the relative intensities of vibrations. The changes in frequency appear to be of the order of 5% for larger observed changes; changes of this small

magnitude are to be expected only if the formation of the complex does not radically change the chemical bonding in the donor molecule. The spectra of the bipyridines support these general conclusions. However, the consequence of the relative smallness of the effects in the infrared spectra is that little information on structure of these complexes can be gained until reliable normal coordinates are available so that the intensity changes can be understood.

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

Chemistry of the Metal Carbonyls. XI. Metal Complexes of 5,6-Dimethylenebicyclo[2.2.1]heptene-2¹

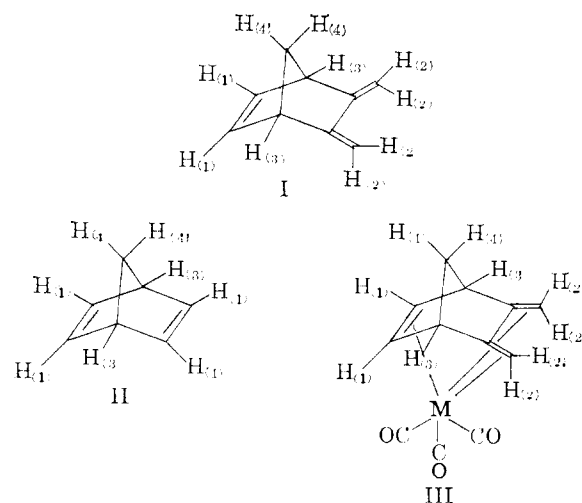
BY R. B. KING² AND F. G. A. STONE

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The bicyclic triene 5,6-dimethylenebicyclo[2.2.1]heptene-2 (I) has been found to react with chromium, molybdenum and tungsten hexacarbonyls to produce volatile red-to-orange crystalline solids of composition $C_9H_{10} \cdot M(CO)_3$ [$M = Cr, Mo$ or W]. The spectral properties of these new compounds are discussed, as well as the reactions of some related polyenes with metal carbonyls.

Recently a variety of polyolefins and aromatic hydrocarbons have been shown to react with carbonyls of Group VI metals to afford π -complexes. Compounds of the type $L \cdot M(CO)_3$ [$M = Cr, Mo$ or W] have been obtained from aromatic hydrocarbons,³ and from cycloheptatriene or substituted cycloheptatrienes,⁴ 1,3,5-cyclooctatriene⁵ and perhaps even cyclononatetraene.^{3e} In addition to complexes derived from conjugated trienes, metal complexes [$L \cdot M(CO)_4$] involving the non-conjugated dienes 1,5-cyclooctadiene⁶ and bicyclo[2.2.1]heptadiene (II)⁷ have been reported, as well as compounds of composition $L_2Mo(CO)_2$ derived from 1,3,6-cyclooctatriene^{5a} and 1,3-cyclohexadiene.⁸ In view of the existence of these various Group VI metal complexes having a variety of trienes and dienes as ligands, it seemed worthwhile to investigate reactions between 5,6-dimethylene-

bicyclo[2.2.1]heptene-2 (C_9H_{10}) (I)⁹ and the carbonyls of chromium, molybdenum and tungsten, in order to determine the role Compound I would play as a ligand to a Group VI metal. In Com-



(1) Previous paper in this series, P. M. Treichel, E. Pitcher, R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

(2) National Science Foundation Predoctoral Research Fellow, 1958-1961.

(3) (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); (b) E. O. Fischer, K. Üfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, *Ber.*, **91**, 2763 (1958); (c) G. Natta, R. Ercoli and F. Calderazzo, *Chem. e Ind. Milano*, **40**, 287 (1958); (d) E. O. Fischer, N. Kriebitzsch and R. D. Fischer, *Ber.*, **92**, 3214 (1959); (e) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960).

(4) (a) E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958); (b) T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 231 (1960).

(5) (a) E. O. Fischer, C. Palm and H. P. Fritz, *Ber.*, **92**, 2645 (1959); (b) E. O. Fischer and C. Palm, *Z. Naturforsch.*, **14b**, 598 (1959).

(6) (a) T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 1349 (1959); (b) E. O. Fischer and W. Fröhlich, *Ber.*, **92**, 2995 (1959); (c) M. A. Bennett and G. Wilkinson, *Chemistry & Industry*, 1516 (1959).

(7) (a) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959); (b) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry & Industry*, 1592 (1958).

(8) E. O. Fischer and W. Fröhlich, *Z. Naturforsch.*, **15b**, 266 (1960).

pound I the isolated double bond and the two conjugated double bonds are in a similar relationship to one another as the two double bonds of bicycloheptadiene (II). It seemed quite probable, therefore, that when Compound I was heated with a Group VI metal carbonyl, such as molybdenum hexacarbonyl, all three double bonds of the triene, because of their favorable steric disposition, would displace carbonyl groups from the hexacarbonyl to form a tricarbonyl complex, e.g., $C_9H_{10} \cdot Mo(CO)_3$. However, if only two of the

(9) (a) K. Alder, S. Hartung and O. Netz, *Ber.*, **90**, 1 (1957); (b) M. A. P. Bowe, R. G. J. Miller, J. B. Rose and D. G. M. Wood, *J. Chem. Soc.*, 1541 (1960).

three double bonds of I were to bond to molybdenum, the resultant complex might either have a formula $C_9H_{10}Mo(CO)_4$ analogous to bicycloheptadiene-molybdenum tetracarbonyl,⁷ or have a formula $(C_9H_{10})_2Mo(CO)_2$ analogous to the 1,3-cyclohexadiene and 1,3,6-cyclooctatriene complexes of molybdenum.^{5a,8}

When Compound I was heated with molybdenum hexacarbonyl in refluxing ethylcyclohexane, an orange solution was produced after several hours, from which an orange crystalline solid was obtained in yields of up to 50%. The composition of the solid was $C_9H_{10}Mo(CO)_3$, and no evidence for formation of other compounds of composition $(C_9H_{10})_2Mo(CO)_2$ or $C_9H_{10}Mo(CO)_4$ was obtained. Analogous reactions between chromium or tungsten hexacarbonyls and I, in ethylcyclohexane and *n*-decane, respectively, afforded the crystalline complexes $C_9H_{10}Cr(CO)_3$ and $C_9H_{10}W(CO)_3$, but in much lower yield.

The three 5,6-dimethylenebicyclo[2.2.1]heptene-2 metal tricarbonyl complexes range in color from orange in the case of the molybdenum derivative to red in the case of the chromium derivative. They are more volatile than the isomeric compounds $C_9H_{10}Mo(CO)_3$ [$M = Mo, W$] obtained from 8,9-dihydroindene,^{3e} and they are also much more resistant to oxidation. The dimethylenebicycloheptene complexes can be stored for months at room temperature without observable decomposition, and are readily soluble in organic solvents. However, the solutions begin to decompose after exposure to air for several hours.

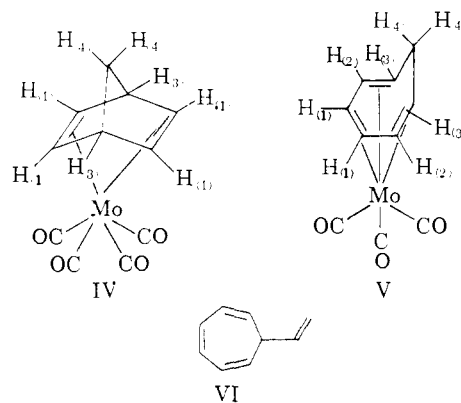
The ultraviolet, infrared and proton magnetic resonance spectra of the complexes III are very similar, showing only minor variations. Infrared spectra of the complexes in the carbonyl region each show three absorptions, entirely analogous to the behavior of cycloheptatriene-metal tricarbonyl complexes.^{4a} This might be expected, since in both classes of compound the metal-tricarbonyl groups would have the same local symmetry. Arene-metal tricarbonyl compounds, due to their higher symmetry, display only two carbonyl absorptions.³

The proton magnetic resonance spectra of III show two complex groups of resonances, one group of relative intensity corresponding to six hydrogen atoms and the other group of relative intensity corresponding to four hydrogen atoms. In the molybdenum-dimethylenebicycloheptene complex these resonances occur at 3.43, 3.35 (complex doublet, separation 18 cycles), 1.97 (apparent quadruplet) and 1.62 p.p.m.,¹⁰ with relative intensities 2:4:2:2, respectively. The resonances at 3.43 and 3.35 p.p.m., corresponding to six protons, are probably due to hydrogen atoms $H_{(1)}$ and $H_{(2)}$ in III. The groups of peaks centered at 1.97 p.p.m. and the resonance at 1.62 p.p.m. would then be due to protons $H_{(3)}$ and $H_{(4)}$ in III.

It is interesting to compare the n.m.r. spectrum of III with that of the ligand I and with that of

bicycloheptadiene (II). A complete analysis has been made of the spectrum of the latter compound,¹¹ while the n.m.r. spectrum of I has been recorded in this Laboratory. In the spectrum of II, resonances occur at 6.64, 3.48 and 1.95 p.p.m., and have been assigned to protons $H_{(1)}$, $H_{(3)}$ and $H_{(4)}$, respectively.¹¹ The spectrum of I displays resonances at 5.92, 4.97 (doublet, $J = 13$ cycles), 3.24 and 1.67 (complex doublet, separation 6 cycles) p.p.m., with relative intensities 2:4:2:2, respectively. Relative intensities, as well as analysis of the spectrum of II, make it reasonable to assign the spectrum of I as follows: 5.92 p.p.m. resonance, olefinic protons ($H_{(1)}$); 4.97 (doublet) p.p.m., methylene protons ($H_{(2)}$); 3.24 p.p.m. resonance, bridgehead protons ($H_{(3)}$); 1.67 p.p.m. resonance, bridge protons ($H_{(4)}$).

The n.m.r. spectra of bicycloheptadiene-molybdenum tetracarbonyl (IV) and cycloheptatriene-molybdenum tricarbonyl (V) were also examined during the course of the work described in this paper. The spectrum of IV consists of resonances at 4.97 (triplet, $J = 2$ cycles), 3.82 and 1.35 (tri-



plet, separations about 2 cycles) p.p.m. On the basis of relative intensity, as well as position, the resonance at 4.97 p.p.m. may be assigned to the olefinic protons $H_{(1)}$ in IV. Comparison of the spectrum of IV with that of II¹¹ suggests that the resonance at 3.82 p.p.m. in the metal complex is due to the bridgehead protons $H_{(3)}$, and that the resonance at 1.35 p.p.m. is due to the bridge protons $H_{(4)}$. It will be noted that the protons [$H_{(1)}$] on the olefinic carbon atoms in III [$M = Mo$] are more shielded than the analogous protons [$H_{(1)}$] in IV.

In the n.m.r. spectrum of V resonances occur at 6.04, 4.88, 3.56 and 2.56 p.p.m., all of equal intensity, corresponding to two protons apiece. It appears that the three sets of olefinic protons in V [$H_{(1)}$, $H_{(2)}$, and $H_{(3)}$] have very different chemical shifts, suggesting that the idea^{4a} of *pseudo*-aromaticity in the C_4 -ring of V may not be correct.^{11a}

During the course of our work the reaction between molybdenum hexacarbonyl and vinylcycloheptatriene (VI), an isomer of I, was studied. None of the four possible isomers of vinylcyclo-

(10) Proton magnetic resonance spectra discussed in this paper were obtained at 60 mc. by a Varian model 4300B high resolution spectrometer fitted with a super stabilizer. Concentrated solutions in carbon disulfide were employed, and chemical shifts are in p.p.m., downfield from tetramethylsilane as standard.

(11) F. S. Mortimer, *J. Molec. Spec.*, **3**, 528 (1959).

(11a) NOTE ADDED IN PROOF.—An X-ray crystallographic study has now confirmed that in the C_4H_3 part of V a pattern of C-C single and double bonds occurs. See J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

heptatriene has been described in the literature. However, a simple method for synthesis of the vinylcycloheptatriene (VI) was suggested by the fact that tropylium bromide reacts with Grignard reagents to produce alkylcycloheptatrienes.¹² Extension of this reaction to vinylmagnesium bromide with tetrahydrofuran as solvent afforded vinylcycloheptatriene in 56% yield. Treatment of VI with molybdenum hexacarbonyl under a variety of conditions gave red solutions. However, attempts to isolate products yielded only very air-sensitive deep red oils, too unstable for characterization.

In attempting to make a more stable metal derivative of vinylcycloheptatriene, an interesting new iron compound was prepared. Cycloheptatriene itself appears to react with iron pentacarbonyl to form cycloheptatriene-iron tricarbonyl,¹³ with one of the double bonds in the ligand not bonded to iron. In view of this, it appeared likely that the 8π -electron system vinylcycloheptatriene would form a binuclear complex $C_7H_{10}[Fe(CO)_3]_2$, with one of the iron tricarbonyl groups bonded to two adjacent double bonds in the ring, and the other one bonded to one double bond in the ring and to the double bond of the vinyl group. Treatment of VI with iron pentacarbonyl in refluxing ethylcyclohexane did indeed give a yellow air-stable solid of composition $C_9H_{10}Fe_2(CO)_6$, in yields of about 30%. Unfortunately, it has not yet proved possible to determine from which isomer of vinylcycloheptatriene this new iron compound is derived, or whether the vinylcycloheptatriene has undergone rearrangement involving more than simple shift of double bonds. However, the stability of the complex suggests that it is derived from a system in which both iron tricarbonyl residues are bonded to conjugated diene systems. Work described elsewhere¹⁴ has demonstrated that iron carbonyls are capable of effecting the rearrangement of two isolated double bonds to a structure in which the double bonds become conjugated.

It was found previously^{4b} that dimethyldivinylsilane reacts with molybdenum and tungsten hexacarbonyls to form dimethyldivinylsilane-metal tetracarbonyl complexes. This result led us to investigate the reaction between methyltrivinylsilane and molybdenum and tungsten hexacarbonyls to determine whether three vinyl groups bonded to a silicon atom were suitably disposed to complex with a Group VI metal. Air-sensitive yellow solids were obtained in low yield. Quantity and purity of the products were too low for adequate characterization, but the infrared spectrum of the tungsten compound in the carbonyl region was similar to that of dimethyldivinylsilane-tungsten tetracarbonyl, suggesting that only two double bonds of the trivinylsilane were bonded to the metal.

Experimental¹⁵

Infrared spectra were recorded using a Perkin-Elmer model 21 double-beam spectrophotometer fitted with

(12) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 681 (1956).

(13) See J. Chatt, P. L. Pauson and L. M. Venanzi, Chapter 10, *Am. Chem. Soc. Monograph*, "Organometallic Chemistry" (Editor, H. Zeiss), Reinhold Publ. Corp., New York, N. Y., 1960.

(14) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

sodium chloride optics except as otherwise stated. A Cary model 11M recording spectrophotometer was used to take the ultraviolet spectra.

Since the discovery^{9a} of 5,6-dimethylenebicyclo[2.2.1]-heptene-2, an improved method of synthesis has been described.^{9b} Samples of I needed for the work described in this paper were prepared by the improved method^{9b} with two further modifications introduced to simplify the procedure even further. A mixture of 1,4-dichlorobutene-2 (200 g., 1.6 moles), dicyclopentadiene (53 g., 0.4 mole) and hydroquinone (0.1 g.) was heated at 160° for 20 hr. After cooling to room temperature, excess of 1,4-dichlorobutene was removed by distillation, leading to recovery of 156 g. of material, b.p. 75–110° (50 mm.). The residue was heated for 68 hr. at 80° with potassium hydroxide (70 g., 1.2 moles) and absolute ethanol (250 ml.). After cooling to room temperature the mixture was diluted with 500 ml. of water and extracted with pentane (400 ml.). The extracts were dried over calcium chloride, and the pentane removed at 25 mm. through a Vigreux column. The product then was distilled (60° (45 mm.)) through a 40-cm. Vigreux column, giving 9.6 g. of 5,6-dimethylenebicyclo[2.2.1]heptene-2 (yield 21% based on 1,4-dichlorobutene-2 consumed), a colorless liquid, n_D^{25} 1.5143.

Anal. Calcd. for C_9H_{10} : C, 91.5; H, 8.5. Found: C, 91.4; H, 8.6.

Dimethylenebicycloheptene polymerizes readily and is best stored under nitrogen in a refrigerator with hydroquinone added as an inhibitor.

5,6-Dimethylenebicyclo[2.2.1]heptene-2-Molybdenum Tricarbonyl.—A mixture of molybdenum hexacarbonyl (1.32 g., 5 mmoles) and I (0.6 g., 5 mmoles) in 40 ml. of ethylcyclohexane was refluxed under nitrogen for 3.5 hr., the reaction mixture becoming a bright orange. After cooling to ambient temperature, solvent was removed at 0.1 mm. The residue was transferred to a sublimator and excess of molybdenum hexacarbonyl and oily impurities removed at 40–60° (0.1 mm.). After cleaning the probe of the sublimator, product was isolated by sublimation for several hours at 90° (0.1 mm.). In this manner bright orange crystals (m.p. 105–107°), 0.75 g. (50% yield), were obtained.

Anal. Calcd. for $C_{12}H_{10}O_3Mo$: C, 48.3; H, 3.3; Mo, 32.2; mol. wt., 298. Found: C, 48.5; H, 3.3; Mo, 31.8; mol. wt. (isopiestic), 304.

In a representative analysis for CO groups, 298.7 mg. (1.00 mmole) of $C_9H_{10}Mo(CO)_3$ was heated in an evacuated Pyrex bulb at 220° for 15 hr. with excess of iodine. This treatment gave 67.7 cc. (S.T.P.) (3.02 mmoles) of carbon monoxide, corresponding to quantitative cleavage of CO groups from $C_9H_{10}Mo(CO)_3$.

The ultraviolet spectrum of $C_9H_{10}Mo(CO)_3$ shows maxima at 214 $m\mu$ (ϵ 33,500) and at 328 $m\mu$ (ϵ 12,000). The infrared spectrum of the complex shows carbonyl bands at 2000, 1932 and 1903 cm^{-1} (C_2Cl_4 solution). Other bands in the spectrum occur at 3040, 2960(b.sh), 1510(m), 1420(m), 1397(m), 1287(m), 1180(m), 1077(w) and 1050(w) cm^{-1} (C_2Cl_4 solution); and at 870(w), 797(w) and 747(w) cm^{-1} (CS_2 solution).

Reactions between Chromium or Tungsten Hexacarbonyl and I.—Preparation of the chromium tricarbonyl derivative of I was analogous to that of the molybdenum derivative except that a much longer reaction time (24 hr.) was used due to the lower reactivity of chromium hexacarbonyl. Yield of the desired red crystalline $C_9H_{10}Cr(CO)_3$ (m.p. 96–98°, sublimes at 70–80° (0.1 mm.)) was 18%.

Anal. Calcd. for $C_{12}H_{10}O_3Cr$: C, 56.7; H, 3.9; CO groups, 3. Found: C, 56.7; H, 4.0; CO groups, 2.7.

The ultraviolet spectrum of $C_9H_{10}Cr(CO)_3$ shows maxima at 215 $m\mu$ (ϵ 30,900) and at 344 $m\mu$ (ϵ 7400). The infrared spectrum has carbonyl stretching bands (C_2Cl_4 solution) at 1992, 1933 and 1905 cm^{-1} . Unresolved C–H stretching bands (CS_2 solution) occur from 2940 to 3040 cm^{-1} . Other absorptions occur at 1520(s) cm^{-1} (C_2Cl_4 solution), and at 1398(m), 1287(m), 1183(m), 1048(w) and 660(s) cm^{-1} (CS_2 solution). The n.m.r. spectrum of $C_9H_{10}Cr(CO)_3$ is qualitatively similar to the molybdenum analog. Resonances occur at 3.13, 3.23 (doublet, separation 13 cycles), 2.08 (doublet, separation 11 cycles; could be quadruplet,

(15) Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute für Kohlenforschung, Mülheim, Germany.

as in spectrum of $C_9H_{10}Mo(CO)_8$, 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 $C_9H_{10}W(CO)_8$ (m.p. of 113–114°, sublimes at 80° (0.1 mm.)) was obtained in 13% yield.

Anal. Calcd. for $C_{12}H_{10}O_8W$: 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 $m\mu$ (ϵ 36,100) and at 321 $m\mu$ (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 purified¹⁶ 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_D^{25} 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 $C_{15}H_{10}O_5Fe_2$: 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 $C_9H_{10}Fe_2(CO)_8$ 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.

(16) B. Bartocha, H. D. Kesz 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 Dicarbonyl¹

BY R. B. KING,² P. M. TREICHEL² 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-cyclooctadiene, bicyclo[2.2.1]heptadiene and 1,3-cyclohexadiene. The nature of the complex $C_5H_5CoC_8H_{10}$ obtained from 1,3,5-cyclooctatriene 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, $(CO)_6Co_2RC\equiv CR$ ^{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

(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).