CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

Organometallic Chemistry of the Transition Metals. XVI. Polynuclear Cyclopentadienylmetal Carbonyls of Iron and Cobalt[1,2]

BY R. B. KING[3]

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Prolonged heating of $[C_5H_5Fe(CO)_2]_2$ in boiling xylene solution gives dark green, very stable, crystalline tetrameric $[C_5H_5FeCO]_4$. Ultraviolet irradiation of $C_5H_5Co(CO)_2$ in hexane solution gives black, crystalline trimeric $[C_5H_5CoCO]_3$. Evidence is presented for the existence of two forms of the cobalt complex at least partially separable by crystallization.

Introduction

Pyrolysis or photolysis of many of the known mononuclear or binuclear pure metal carbonyls has been well established to give other metal carbonyls containing more metal atoms and a lower ratio of carbonyl groups per metal atom by condensation of 2 or more moles of metal carbonyl fragments with elimination of carbon monoxide. Pentacarbonyliron, $Fe(CO)_5$, can thus be converted to enneacarbonyldiiron, $Fe_2(CO)_9$, and finally to dodecacarbonyltriiron, $Fe_3(CO)_{12}$.[4] Similarly octacarbonyldicobalt, $Co_2(CO)_8$, can be converted to dodecacarbonyltetracobalt, $Co_4(CO)_{12}$.[5] Similar formation of polynuclear derivatives by such condensation reactions have been observed for the carbonyls of the heavier congeners of iron and cobalt: ruthenium,[6] osmium,[7] rhodium,[8] and iridium.[9] Particularly unusual is the formation of the octahedral[10] hexanuclear hexadecacarbonylhexarhodium, $Rh_6(CO)_{16}$, in this manner.

A few similar reactions have been observed for the cyclopentadienylmetal carbonyls although the reported examples of these reactions are considerably more limited. Pyrolysis of $[C_5H_5NiCO]_2$ was found by Fischer and Palm[11] to give the unusual green paramagnetic trinuclear derivative $(C_5H_5)_3Ni_3(CO)_2$ which was demonstrated by Hock and Mills[12] to contain carbonyl groups bridging three metal atoms. Photolysis of $C_5H_5Rh(CO)_2$ was shown by Fischer and Bittler[13] to give a binuclear derivative demonstrated to be $(C_5H_5)_2Rh_2(CO)_3$ by Mills[14] using X-ray diffraction.

In the course of the work on transition metal organometallic chemistry carried out at the Mellon Institute large quantities of $[C_5H_5Fe(CO)_2]_2$ and of $C_5H_5Co(CO)_2$ have been prepared for an extensive study of their reactions. This led to the serendipitous discovery[15] of the tetranuclear $[C_5H_5FeCO]_4$ as well as the successful planned synthesis of the trinuclear $[C_5H_5CoCO]_3$. This paper describes the preparation and properties of these new compounds.[16]

Experimental Section

The same infrared, ultraviolet, and proton nmr spectrometers used in previous work from this laboratory were used for this work. Mass spectra were taken at 70-ev electron energies using an Associated Electrical Industries MS-9 mass spectrometer. Magnetic susceptibility measurements were carried out by the Faraday method. Microanalyses were performed by Pascher Microanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were performed at the Mellon Institute (F. J. Michalek) using the Mechrolab vapor pressure osmometer in benzene solution at three or more different concentrations. Melting points were taken in capillaries and are uncorrected.

The preparations of $[C_5H_5Fe(CO)_2]_2$ and $C_5H_5Co(CO)_2$ required in large quantities for this work were recently described in detail[17] and therefore will not be repeated here.

Cyclopentadienylcarbonyliron Tetramer.—A mixture of 28.4 g (80 mmoles) of $[C_5H_5Fe(CO)_2]_2$ and 260 ml of CP xylene was refluxed vigorously under nitrogen with stirring for 12 days (~284 hr). After allowing the green-black reaction mixture to cool to room temperature over a period of several hours, the black precipitate was filtered and washed with three 20-ml portions of xylene and 20 ml of benzene. When still slightly moist with benzene[18] this black solid was transferred to the thimble of a Soxhlet extraction apparatus and extracted continuously for 1 week (~160 hr) with ~250 ml of boiling diethyl ether.[19] The deep green diethyl ether extracts, containing precipitated, well-formed, dark green crystals of $[C_5H_5FeCO]_4$ were cooled to room temperature. The crystals were filtered, washed with diethyl ether and/or pentane, and dried to give 3.4 g (14% yield)

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(1) For Part XV of this series see R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(2) Some of this work was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p 22-O.

(3) Department of Chemistry, University of Georgia, Athens, Ga.

(4) J. Dewar and H. O. Jones, *Proc. Roy. Soc.* (London), **B76**, 564 (1905); E. Speyer and H. Wolf, *Ber.*, **60**, 1424 (1927); H. G. Cutforth and P. W. Selwood, *J. Am. Chem. Soc.*, **65**, 2414 (1943).

(5) L. Mond, H. Hirtz, and M. D. Cowap, *J. Chem. Soc.*, **97**, 798 (1910).

(6) M. Manchot and W. J. Manchot, *Z. Anorg. Allgem. Chem.*, **226**, 385 (1936).

(7) W. Hieber and H. Stallman, *Z. Elektrochem.*, **49**, 288 (1943).

(8) W. Hieber and H. Lagally, *Z. Anorg. Allgem. Chem.*, **251**, 96 (1943).

(9) W. Hieber and H. Lagally, *ibid.*, **245**, 321 (1940).

(10) E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

(11) E. O. Fischer and C. Palm, *Ber.*, **91**, 1725 (1958).

(12) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," Proceedings of the Sixth International Conference on Coordination Chemistry, Detroit, Mich., 1961, S. Kirschner, Ed., p 640.

(13) E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 835 (1961).

(14) O. S. Mills, Proceedings of the Eighth International Conference on Coordination Chemistry, Vienna, 1964, p 257, and further unpublished results.

(15) Tetranuclear $[C_5H_5FeCO]_4$ was first discovered accidentally in the mixture obtained by heating $[C_5H_5Fe(CO)_2]_2$ with tetramethyltetrazene in boiling toluene in an unsuccessful attempt to prepare new organonitrogen derivatives of iron.

(16) An X-ray diffraction study on $[C_5H_5FeCO]_4$ has been carried out in the laboratory of Professor L. F. Dahl (University of Wisconsin). A separate publication on this structural study is contemplated.

(17) R. B. King, "Organometallic Synthesis," Vol. I, Academic Press Inc., New York, N. Y., 1965.

(18) When completely dry, this residue may be pyrophoric.

(19) The diethyl ether is boiled by means of an oil bath rather than a heating mantle to minimize the danger of boiling away all of the ether and overheating the dry residue.

of deep green $[C_5H_5FeCO]_4$. The product was air stable not only in the solid state but even in dichloromethane solution. Upon heating it decomposed at ~220° without melting to give volatile orange crystals of ferrocene.

Anal. Calcd for $C_{24}H_{20}Fe_4O_4$: C, 48.3; H, 3.3; O, 10.7; Fe, 37.6; mol wt, 596. Found: C, 48.8; H, 3.5; O, 10.6; Fe, 37.0; mol wt, 574 (osmometer), 596 (mass spectrometer).

Infrared Spectrum.[20,21]—ν_{CH} at 3060 (vw) cm^{-1}; ν_{CO} at 1620 cm^{-1}; other bands at 1420 (w), 1355 (vw), 1112 (vw), 1024 (vw), 1017 (w), 1010 (w), 920 (vw), 862 (m), 858 (m), 835 (s), and 825 (s) cm^{-1}.

Proton Nmr Spectrum.—There was a single sharp resonance at τ 5.16 ($CHCl_3$ solution) or τ 4.91 (CF_3COOH solution) due to the 20 equivalent π-cyclopentadienyl protons. The proton nmr spectrum of the deep green trifluoroacetic acid solution exhibited no resonances in the τ 10–200 region characteristic of hydrogen directly bonded to an iron atom. The signal-to-noise ratio of the π-cyclopentadienyl resonance was sufficiently high that even one Fe–H proton relative to the 20 equivalent π-cyclopentadienyl protons would easily have been observed.

Mass Spectrum.—The following ions, *m/e* ratios, and relative intensities, respectively, were observed: $(C_5H_5)_4Fe_4(CO)_4^+$, 596, 225; $(C_5H_5)_4Fe_4(CO)_3^+$, 568, 7; $(C_5H_5)_4Fe_2(CO)_2C^+$, 552, 7; $(C_5H_5)_4Fe_4(CO)_2^+$, 540, 9; $(C_5H_5)_3Fe_3(CO)_2^+$, 419, 610; $(C_5H_5)_3Fe_3CO^+$, 391, 118; $(C_5H_5)_3Fe_3^+$, 363, 1090; $(C_5H_5)_3Fe_2^+$, 307, 710; $(C_5H_5)_2Fe_2(CO)_2^+$, 298, 400; $(C_5H_5)_2Fe_2CO^+$, 270, 300; $(C_5H_5)_2Fe_2^+$, 242, 450; $(C_5H_5)_2Fe^+$ 186, ~17,500; $C_5H_5Fe(CO)_2^+$, 177, 1170; $C_5H_5FeCO^+$, 149, 375; $C_5H_5Fe^+$ 121, ~17,500.

Reaction between Bromine and $[C_5H_5FeCO]_4$.—Excess bromine (0.5 ml, 1.46 g, 9.1 mmoles as Br_2) was added to 0.289 g (0.485 mmole) of $[C_5H_5FeCO]_4$ in ~50 ml of dichloromethane. Immediate formation of a finely divided black precipitate without gas evolution occurred. After standing overnight to assure complete reaction, the precipitate was filtered, washed with dichloromethane and/or diethyl ether, and dried to give 0.383 g (95% yield) of $[C_5H_5FeCO]_4Br_3$, a sparingly soluble, air-stable black powder.

Anal. Calcd for $C_{24}H_{20}Br_3Fe_4O_4$: C, 34.5; H, 2.4; Br, 28.7. Found: C, 35.2; H, 2.7; Br, 28.0.

Infrared Spectrum.[20]—ν_{CH} at 3080 (vw) cm^{-1}; ν_{CO} at 1675 (s) cm^{-1}; other bands at 1425 (m), 1415 (m), 1350 (vvw), 1064 (m), 1015 (w), 1003 (w), 934 (w), 881 (m), 868 (m), 836 (s), 833 (sh), and 825 (sh) cm^{-1}.

Magnetic Susceptibility.—$\chi_{\text{mole}}^{23°} = +1623 \times 10^{-6}$ cm^3/mole (sample I) and $+1465 \times 10^{-6}$ cm^3/mole (sample II) corresponding to magnetic moments of 2.13 BM (sample I) and 2.03 BM (sample II).

Cyclopentadienylcarbonylcobalt Trimer.—A solution of 1.5 ml (2.1 g, 11.7 mmoles) of $C_5H_5Co(CO)_2$ in 50 ml of hexane was irradiated under nitrogen in a quartz tube with a 450-w ultraviolet source about 45 cm distant. A black precipitate gradually formed. After 5 days (~115 hr) the irradiation was discontinued, and the black crystals were filtered, washed with three 15-ml portions of pentane, and dried.

This crude black solid was extracted with a total of ~75 ml of diethyl ether in four portions. The filtered black extracts were concentrated to ~50 ml in a stream of nitrogen and then cooled in a −78° bath. After 16 hr the precipitated black crystals (hereafter designated as fraction A) were filtered and dried to give 0.074 g (4.2% yield) of $[C_5H_5CoCO]_3$.

The residue from the diethyl ether extraction was extracted with a total of ~50 ml of dichloromethane in three portions. These extracts were filtered collecting the filtrate under nitrogen. After treating the filtrate with 20 ml of hexane, solvent was removed from the filtrate at 20° (25 mm). The resulting black crystals were washed on a filter with several portions of pentane, and then the resulting black crystals (hereafter designated as fraction B) were recrystallized again from dichloromethane–hexane in the same manner to give 0.371 g (21% yield) of black, crystalline $[C_5H_5CoCO]_3$.

Anal. Calcd for $C_{18}H_{15}Co_3O_3$: C, 47.4; H, 3.3; O, 10.5; Co, 38.8; mol wt, 456. Found (fraction A): C, 47.3, 47.3; H, 3.6, 3.5; O, 11.3, 11.9; Co, 37.9, 37.6; mol wt, 491, 410 (osmometer). Found (fraction B): C, 46.9, 46.7; H, 3.6, 3.6; O, 11.6, 12.2; Co, 38.2, 37.9; mol wt, 507, 480 (osmometer).

Infrared Spectra.[20] **Fraction A.**—ν_{CH} at 3050 (vw) cm^{-1}; ν_{CO} at 1940 (w), 1820 (s), 1765 (s), and 1665 (s) cm^{-1}; other bands at 1423 (sh), 1408 (w), 1342 (w), 1105 (vw), 1050 (vw), 1010 (vw), 997 (w), 848 (w), 828 (m), 815 (m), 811 (m), and 804 (m) cm^{-1}.

Fraction B.—ν_{CH} at 3070 (vw) cm^{-1}; ν_{CO} at 1940 (w), 1825 (s), 1800 (s), 1760 (s), 1740 (s), 1675 (sh), and 1670 (s) cm^{-1}; other bands at 1430 (vw), 1406 (w), 1344 (w), 1110 (vw), 1050 (vw), 1012 (w), 997 (vw), 829 (m), and 804 (m) cm^{-1}.

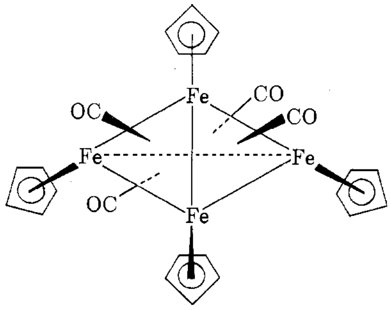
Proton Nmr Spectra.—The proton nmr spectra of fractions A and B were identical. In benzene solutions both compounds exhibited a singlet resonance at τ 5.44 due to the 15 equivalent π-cyclopentadienyl protons.

Discussion

A. $[C_5H_5FeCO]_4$.—The spectroscopic properties of $[C_5H_5FeCO]_4$ are in accord with a symmetrical tetrahedral structure (I). The 1620-cm^{-1} frequency of the single strong metal carbonyl band in the infrared spectrum is the lowest metal carbonyl frequency known to the author. Since bridging is well established to lower metal carbonyl frequencies,[22] the abnormally low value of this sole carbonyl frequency in $[C_5H_5FeCO]_4$ suggests that each of the four carbonyl groups is acting as a bridge between three iron atoms similar to the two carbonyl groups in $(C_5H_5)_3Ni_3(CO)_2$.[12] Such bridging can readily be accommodated if the iron atoms form a tetrahedron with a bridging carbonyl group above each of the four faces of the tetrahedron.

The proton nmr spectrum, besides indicating $[C_5H_5FeCO]_4$ to be diamagnetic, exhibits a single, sharp resonance indicating all of the π-cyclopentadienyl rings to be equivalent. This is again in agreement with the tetrahedral structure I with one π-cyclopentadienyl ring bonded to each of the four equivalent iron atoms at each apex of the tetrahedron.

The usual relationship (designated hereafter for brevity and clarity as trichoric[23]) between the cyclopentadienylmetal carbonyls and the pure metal car-



I

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[20] This spectrum was taken in a KBr pellet and recorded on a Perkin-Elmer Model 21 spectrometer.

[21] Dr. W. G. Fateley of the Mellon Institute has made a detailed analysis of this infrared spectrum and will report his results elsewhere.

[22] J. Chatt, P. L. Pauson, and L. M. Venanzi in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp 477–479.

[23] The terms "dichoric" and "trichoric" are derived from the Greek word χῶρος, meaning "a place." They refer to the number of carbonyl groups replaced by a single π-cyclopentadienyl ligand in the analogous series of compounds under investigation.

bonyls emphasizes the parallel between a metal carbonyl derivative and an isoelectronic cyclopentadienylmetal carbonyl where the cyclopentadienyl ring has replaced three carbonyl groups with an increase of 1 in the atomic number of the metal to retain the same charge and electronic configuration. The similarities between the chemistry of the pairs $[C_5H_5Cr(CO)_3]_2$, $V(CO)_6$; $C_5H_5Mn(CO)_3$, $Cr(CO)_6$; $[C_5H_5Fe(CO)_2]_2$, $Mn_2(CO)_{10}$; $C_5H_5Co(CO)_2$, $Fe(CO)_5$; and $[C_5H_5NiCO]_2$, $Co_2(CO)_8$ are thus emphasized. According to this trichoric analogy, $[C_5H_5Fe(CO)_2]_2$ should behave in an analogous manner to $Mn_2(CO)_{10}$ on pyrolysis or photolysis.

A tetranuclear derivative $Mn_4(CO)_{16}$ has never been obtained by pyrolysis or photolysis of $Mn_2(CO)_{10}$. However, the tetranuclear derivative $Co_4(CO)_{12}$ is readily obtained from $Co_2(CO)_8$.[5] It thus appears that the formation of $[C_5H_5FeCO]_4$ by pyrolysis of $[C_5H_5Fe(CO)_2]_2$ is a further example of a second type of analogy (designated hereafter as dichoric[23]) between the cyclopentadienylmetal carbonyls and the pure metal carbonyls. This dichoric relationship emphasizes the parallel between a metal carbonyl derivative and an isoelectronic cyclopentadienylmetal carbonyl where the cyclopentadienyl ring has replaced only two carbonyl groups with a decrease of 1 in the atomic number of the metal atom. The dichoric analogy relates the pairs $C_5H_5V(CO)_4$, $Cr(CO)_6$; $[C_5H_5Cr(CO)_3]_2$, $Mn_2(CO)_{10}$; $C_5H_5Mn(CO)_3$, $Fe(CO)_5$; $[C_5H_5Fe(CO)_2]_2$, $Co_2(CO)_8$; and $C_5H_5Co(CO)_2$, $Ni(CO)_4$. Other examples of the significance of the dichoric relationship as compared with the trichoric relationship cited above include the facile carbon monoxide exchange in both $C_5H_5Co(CO)_2$ and $Ni(CO)_4$ but the slow carbon monoxide exchange in $Fe(CO)_5$[24] and the presence of bridging carbonyl groups in $[C_5H_5Fe(CO)_2]_2$ and $Co_2(CO)_8$ but the absence of bridging carbonyl groups in $Mn_2(CO)_{10}$.[25] The comparative chemistry of metal carbonyls and cyclopentadienyl carbonyls, too extensive to be cited in this paper, suggests that the trichoric relationship is more relevant for comparisons involving electronic factors and the dichoric relationship is more relevant for comparisons involving steric factors although many cases are somewhat equivocal. The implication of this suggestion, of course, is that a π-cyclopentadienyl ligand electronically corresponds to three carbonyl groups but sterically only to two carbonyl groups.

As noted in the Experimental Section, $[C_5H_5FeCO]_4$ is remarkably stable to atmospheric oxidation since dichloromethane solutions can be evaporated in the air over 5 days without any signs of the normally ubiquitous formation of brown insoluble Fe_2O_3.[26] However, treatment of $[C_5H_5FeCO]_4$ with powerful oxidizing agents such as bromine, antimony pentachloride, or the free radical tri-*p*-tolylaminium hexafluorophosphate, $[(p\text{-}CH_3C_6H_4)_3N][PF_6]$, gives insoluble black materials without carbon monoxide evolution. In the infrared spectra of substances obtained from each of these three oxidizing agents, ν_{CO} at 1620 cm^{-1} in $[C_5H_5FeCO]_4$ changes to 1675 cm^{-1} suggesting formation of a new iron carbonyl derivative. The reconversion of these insoluble black materials to $[C_5H_5FeCO]_4$ by bases or reducing agents suggests retention of the tetrahedral system of four iron atoms. The insolubility of these materials has impeded their purification and detailed characterization. Analyses on the compound obtained from $[C_5H_5FeCO]_4$ and bromine are in reasonable agreement with the formula $[C_5H_5FeCO]_4Br_3$ which may be the tribromide salt of the $[C_5H_5FeCO]_4{}^+$ cation. In accord with this possibility, solid samples of $[C_5H_5FeCO]_4Br_3$ were found to be paramagnetic to the approximate extent expected for one unpaired electron in each $[C_5H_5FeCO]_4{}^+$ cluster.

B. $[C_5H_5CoCO]_3$.—The most unusual feature of $[C_5H_5CoCO]_3$ is its reproducible isolation in two different forms with different infrared spectra in the metal carbonyl region. Material obtained by crystallization from diethyl ether solution (fraction A) as described in the Experimental Section is characterized by three strong bands at 1830, 1770, and 1670 cm^{-1} in a region associated with bridging carbonyl groups between two or three metal atoms. However, in material (fraction B) obtained by crystallization from a mixture of dichloromethane and hexane the three strong bands in this region are split into doublets resulting in absorptions at 1825, 1800, 1760, 1740, 1675, and 1670 cm^{-1}. The relative simplicity of the carbonyl region of the infrared spectrum of fraction A suggests it to consist of essentially a single pure isomer. After considering the experimental errors in frequency determination, fraction B may be a mixture of the isomer contained in fraction A and a second different isomer. If this is the case, the process of elimination assigns the strong bands at 1800, 1740, and 1675 cm^{-1} to the second isomer present in fraction B but not in fraction A.

The proton nmr spectrum of $[C_5H_5CoCO]_3$, besides indicating it to be diamagnetic, exhibited a single, sharp cyclopentadienyl resonance. The chemical shifts of this resonance in fractions A and B were identical making nmr useless as a technique for the analysis of isomer mixtures. However, the identity of the chemical shifts of the protons of all three π-cyclopentadienyl rings eliminates linear structures for $[C_5H_5CoCO]_3$ where the center cobalt atom which is bonded to two other cobalt atoms would be expected to be very different from the two outer cobalt atoms which are bonded to only one other cobalt atom. The cobalt atoms in $[C_5H_5CoCO]_3$ thus appear to be in a triangle as already established for other systems by X-ray crystallographic studies on $(C_5H_5)_3Ni_3(CO)_2$,[12]

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[24] F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

[25] X-Ray diffraction studies of all three of these binuclear carbonyl derivatives have been reported. See the following references: (a) $Co_2(CO)_8$: G. Sumner and H. P. Klug, *Acta Cryst.*, **17**, 732 (1964); (b) $Mn_2(CO)_{10}$: L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957); L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963); (c) $[C_5H_5Fe(CO)_2]_2$: O. S. Mills, *ibid.*, **11**, 620 (1958).

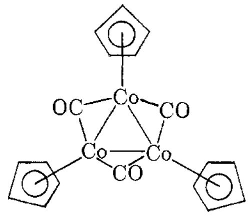
[26] Large dark green crystals suitable for purposes such as X-ray diffraction can be grown by slow, spontaneous evaporation of solutions of $[C_5H_5FeCO]_4$ in solvents such as dichloromethane.

$Ru_3(CO)_{12}$,[27] $[(C_2H_5)_3NH][HFe_3(CO)_{11}]$,[28] and $Fe_3(CO)_{12}$.[29]

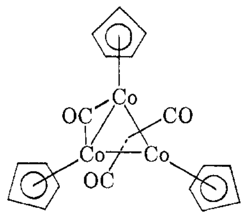
The locations of the carbonyl groups in $[C_5H_5CoCO]_3$ are somewhat uncertain, especially since the lability of bridging carbonyl groups[30] may rapidly interchange certain structures creating unexpectedly simple nmr spectra. Thus the apparent equivalence of all three π-cyclopentadienyl rings in the proton nmr spectrum may be consistent with any structure with a triangular arrangement of cobalt atoms and exactly one π-cyclopentadienyl ring bonded to each cobalt atom regardless of the arrangement of terminal, two-way-bridging, and three-way-bridging metal carbonyl groups.

All of the strong metal carbonyl frequencies in $[C_5H_5CoCO]_3$ fall in the range 1830–1670 cm^{-1} clearly associated with bridging metal carbonyl groups. The low frequencies around 1670 cm^{-1} may be associated with carbonyl groups bridging three metal atoms. Structure II for $[C_5H_5CoCO]_3$ with all three carbonyl groups acting as two-way bridges cannot be excluded. However, from the infrared spectrum, structure III for $[C_5H_5CoCO]_3$ with one two-way-bridging carbonyl group and two three-way-bridging carbonyl groups appears more likely. Moreover, structure III for $[C_5H_5CoCO]_3$ would be closely related to the established structure for $(C_5H_5)_3Ni_3(CO)_2$[12] with the addition of a mobile two-way-bridging carbonyl group along one of the sides of the triangle of metal atoms. X-Ray crystallography[31] appears necessary to solve this dilemma of the structure of $[C_5H_5CoCO]_3$. In any case the existence of more than one possible structure for $[C_5H_5CoCO]_3$ (*e.g.*, II[32] and III) differing mainly in the orientations of the carbonyl groups is in accord with the experimental observation of at least two isomers.

The formation of the trinuclear $[C_5H_5CoCO]_3$ on photolysis of $C_5H_5Co(CO)_2$ is of interest since photolysis of the related $C_5H_5Rh(CO)_2$ gives a binuclear derivative[13] shown to be $(C_5H_5)_2Rh_2(CO)_3$ by X-ray crystallography.[14] On the basis of the trichoric analogy defined above, the photolysis product of $C_5H_5Co(CO)_2$, *i.e.*, $[C_5H_5CoCO]_3$, is analogous to $Fe_3(CO)_{12}$, but the photolysis product of $C_5H_5Rh(CO)_2$ is $(C_5H_5)_2Rh_2(CO)_3$ analogous to the unknown $Ru_2(CO)_9$.[33] This difference in behavior of the analogous $C_5H_5M(CO)_2$ derivatives of cobalt and rhodium on photolysis is at first sight rather surprising but is probably a combined consequence of usual factors influencing metal carbonyl chemistry such as strengths of metal–carbon and metal–metal bonds, solubilities of products in the reaction medium, etc.



II



III

In a further attempt to establish the formula of $[C_5H_5CoCO]_3$, its mass spectrum was investigated. However, the observed mass spectrum corresponded to that expected for the unknown tetranuclear $(C_5H_5)_4Co_4(CO)_2$ [*m/e* (parent ion) 552] rather than that of $[C_5H_5CoCO]_3$. This anomalous mass spectrum appears to arise from pyrolysis of $[C_5H_5CoCO]_3$ in the mass spectrometer. When a sample of $[C_5H_5CoCO]_3$ was heated in a boiling 1:5 toluene–methylcyclohexane mixture, a low yield of a new black solid was obtained. Characteristic of this new material was a single, strong carbonyl stretching frequency at 1705 cm^{-1}. Unfortunately, an insufficient quantity of this new material, possibly $(C_5H_5)_4Co_4(CO)_2$, was obtained for proper characterization.

Unfortunately, the rate of production of $[C_5H_5CoCO]_3$ from $C_5H_5Co(CO)_2$ is rather slow presently limiting the availability for a detailed investigation of its chemistry.

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(27) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(28) L. F. Dahl and J. F. Blount, *ibid.*, **4**, 1373 (1965).

(29) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

(30) One indication of the lability of bridging carbonyl (and nitrosyl) groups is the work on $[C_5H_5MnCONO]_2$ by R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964). The observation of infrared spectral bands arising from all four of the possibilities (bridging and terminal carbonyl groups and bridging and terminal nitrosyl groups) of relative intensities independent of the sample and purification method suggests two or more rapidly interconverting isomers of $[C_5H_5MnCONO]_2$.

(31) A sample has been submitted to Professor L. F. Dahl for X-ray crystallographic studies.

(32) The steric requirements of the cyclopentadienyl rings and cobalt–cobalt bonds in structure II force the bridging carbonyl groups out of the plane of the ring formed by the three cobalt atoms. Two isomers of structure II are then possible depending on whether all three bridging carbonyl groups are on the same side or two on one side and one on the other side of the plane of the ring of the three cobalt atoms.

(33) The species originally reported to be $Ru_2(CO)_9$ has now been shown to be $Ru_3(CO)_{12}$.[27]