Transition-Metal Methylene Complexes. 57.[1] The Unusual Structure and Reactivity of the Paramagnetic Trinuclear Cluster Compound (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$Co$_2$(η^5-C$_5$H$_5$)$_2$[†]

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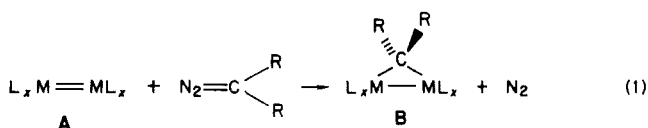
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The trinuclear cluster compound of composition (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$Co$_2$(η^5-C$_5$H$_5$)$_2$ (3, Me = CH$_3$) has been synthesized in high yield by treatment of the unsaturated dinuclear precursor (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$Co(η^5-C$_5$H$_5$) (1) with the mononuclear bis(ethylene) complex (η^5-C$_5$H$_5$)Co(π-C$_2$H$_4$)$_2$ (2). The bis(ethylene) complex acts as a convenient source of the (η^5-C$_5$H$_5$)Co fragment by virtue of the extreme lability of both ethylene ligands. The molecular structure of the paramagnetic complex 3, as established by X-ray diffraction techniques, may be broken down formally into the planar Ir(μ-CO)$_2$Co core of the precursor molecule 1 to which a (η^5-C$_5$H$_5$)Co fragment has been added. One intriguing structural feature of the cluster ensemble Co$_2$Ir(μ-CO)$_2$ is the coordination mode of the two carbonyl ligands that occupy primarily edge-bridging geometries along the cobalt–iridium bond of the original precursor building block 1; the addition of the extremely electron-deficient (η^5-C$_5$H$_5$)Co fragment to the electronically and coordinatively unsaturated complex 1 causes only a minor out-of-plane distortion of the Co(μ-CO)$_2$Ir moiety in the solid state with the interplanar angle between the Co(1),C(1),Ir and Co(1),C(2),Ir planes amounting to 169.8°. The triangular Co$_2$Ir framework exhibits two ordinary metal–metal bonds (d[Co(1)–Co(2)] = 2.359 (1) Å and d[Co(1)–Ir] = 2.527 (1) Å) and one fairly short, unbridged metal–metal bond (d[Co(2)–Ir] = 2.473 (1) Å). The distances between the added (η^5-C$_5$H$_5$)Co fragment and the carbonyl carbon atoms are considerably longer (2.435 (6) and 2.393 (5) Å) than expected for conventional CO bridges (e.g., d[Co(1)–C(1)] = 1.896 (5) Å and d[Co(1)–C(2)] = 1.901 (5) Å). The paramagnetism of the 46-electron molecule 3 corresponds to a triplet ground state as proven by an ^{1}H NMR study in the temperature range –93 to +100 °C. Structural degradation of the unsaturated 46-electron cluster occurs when 3 is exposed to oxygen, ethylene, or (η^5-C$_5$Me$_5$)Ir(CO)$_2$ under mild conditions; the dinuclear precursor molecule (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$Co(η^5-C$_5$H$_5$) (1) is cleanly formed in these cases. In contrast, two-electron ligands such as CO and the CH$_2$ fragment are incorporated into the trinuclear cluster assembly without degradation of the latter. When 3 is treated with carbon monoxide or diazomethane, respectively, the 48-electron complexes (η^5-C$_5$Me$_5$)Ir(CO)[Co(μ-CO)(η^5-C$_5$H$_5$)]$_2$ (4) and (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$(μ-CH$_2$)[Co(η^5-C$_5$H$_5$)]$_2$ (5) are obtained in quantitative yields. In these latter reactions, the Co$_2$Ir core remains intact, with the added ligands assuming either terminal (CO, 4) or edge-bridging (CH$_2$, 5) geometries.

Introduction

Organometallic compounds exhibiting metal–metal multiple bonds are of current interest not only with respect to their structural chemistry[4] but also because of manyfold reactivity patterns that are now being discovered by synthetic chemists who employ multiply metal–metal bonded species as preparative building blocks for the purpose of systematic functionalization reactions.[4,5] While di- or polynuclear metal cores sometimes undergo degradation to smaller fragments, an ever growing number of examples are being discovered that proceed in the opposite direction, e.g., addition of small organic fragments to intact polynuclear organometallic species. One such case, schematically represented in eq 1, is the transfer of alkylidene

$$L_xM = ML_x + N_2 = C\begin{matrix}R\\R\end{matrix} \longrightarrow L_xM \underset{\begin{matrix}\overset{R}{\diagup}C\diagdown R\end{matrix}}{-} ML_x + N_2 \quad (1)$$

A   **B**

groups from the respective diazoalkane precursor molecules onto metal–metal double bonds.[6] This cyclopropanation reaction enjoys a very broad scope of applicability in that it is not confined to doubly bonded transition-metal systems but also works with analogous compounds that exhibit multiple bonds between a main-group element (e.g., germanium, selenium, tellurium) and a transition metal.[7] The chemistry of dimetallacyclopropanes **B** easily obtained

by this method is closely related to carbon–carbon coupling processes occurring on metal surfaces, thus revealing a possible connection to Fischer–Tropsch and CO reduction chemistry.[8]

In order to more fully understand how the chemical behavior of bridging alkylidene ligands depends upon the attendant metals, we set out to prepare reactive heterodinuclear precursor compounds of type **A**.[9] In this con-

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(1) Communication 56: Herrmann, W. A.; Flöel, M.; Weber, C.; Hubbard, J. L.; Schäfer, A. *J. Organomet. Chem.*, in press.

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(4) Recent review articles and monographs: (a) Cotton, F. A.; Chisholm, M. H. *Chem. Eng. News* **1982**, p 40 ff. (b) "Inorganic Chemistry: Toward to the 21st Century"; Chisholm, M. H.; Ed.; American Chemical Society: Washington, D.C., 1983; *ACS Symp. Ser. No. 211*. (c) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1980.

(5) Cf.: "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC., 1981; *ACS Symp. No. 155*.

(6) For recent reviews, see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (c) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319. (d) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205.

(7) (a) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmitt, K.; Pfisterer, H.; Ziegler, M. *Angew. Chem.* **1983**, *95*, 331; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314; *Angew. Chem. Suppl.* **1983**, 363. (b) Herrmann, W. A.; Hecht, Ch.; Ziegler, M. L.; Balbach, B. *J. Chem. Soc., Chem. Commun.* **1984**, 686. (c) Brief review: Herrmann, W. A. In "Organometallic Compounds"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; Vol. 1, p 383 ff.

(8) Review: Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[†] In memoriam Earl L. Muetterties.

text, we discovered a highly reactive, paramagnetic trinuclear cobalt–iridium complex whose molecular structure and reactivity is the subject of this paper.

Experimental Section

General Data. All manipulations of the oxygen-sensitive materials described herein were conducted under a recirculating atmosphere of nitrogen in a Braun (Innovative Technology, USA) Series MB-200 inert-gas atmosphere box and automated oxygen filter equipped with a M. Braun oxygen analyzer or by employing standard Schlenk techniques. The continuously monitored oxygen content of the inert-atmosphere box was <4 ppm. The temperature within the glovebox was maintained at +25 °C by virtue of a internal automated compressor system.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 270-MHz Fourier transform instrument with Aspect 3000 (R) software. Chemical shifts are referenced to the residual proton signal of solvent: $\delta(C_6D_5H)$ 7.200, $\delta(C_7HD_7)$ 2.09 (methyl quintet), $\delta(THF\text{-}d_7)$ 3.58. Deuterated benzene, toluene, or THF were purified and degassed in the presence of benzophenone ketyl anion. Sealed NMR samples were prepared directly on a diffusion pump vacuum line. NMR tubes, fitted with NS 14.5/21 female ground-glass joints and loaded with sample in the glovebox when necessary, were put under vacuum and solvent vapor transfered directly from ketyl solution. The sample tube with frozen solvent was isolated from the vacuum line by means of a Teflon stopcock and finally sealed with a torch. Infrared (IR) spectra were recorded on either a Perkin-Elmer 283-B or a Beckman Acculab spectrometer. Electron-impact mass spectra (EIMS) were recorded on either a Varian CH5 or Varian CH7 spectrometer at Frankfurt. Field desorption mass spectra (FDMS) were recorded a Varian MAT 311-A spectrometer by Dr. K. K. Mayer at the Universität Regensburg. Technical grade n-hexane, toluene, tetrahydrofuran, and diethyl ether used for syntheses were dried and degassed over sodium/potassium alloy (30/70 wt %) by refluxing continuously under a nitrogen atmosphere for at least 2 days.

(1) Preparation of the Trinuclear Cluster Compound 3. In the above-mentioned inert-atmosphere box, 200 mg (0.4 mmol) of $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ (1)[9a] were weighed into a round-bottom flask and completely dissolved in 60 mL of diethyl ether. A 20-mL sample of n-hexane was added to the deep red-violet solution. A 5-mL sample of a separate solution of 130 mg of $(\eta^5\text{-}C_5H_5)Co(\pi\text{-}C_2H_4)_2$ (2)[10] (ca. 2 equiv) in 10 mL of the same solvent was added to the above solution with vigorous stirring. The resulting solution was stirred for 5 min where upon the solution volume was reduced at 25 °C to 60 mL by evaporation under vacuum. (Do not heat the solution!) If the resulting solution color is still red-violet, 0.5 mL of the above n-hexane solution of 2 was added and after the solution was stirred for 1–2 min, a small portion of the solution was again removed under vacuum. These additions were repeated until the solution lost its red-violet color. Once this occurred, the solution volume was reduced to 40 mL. The supernatant solution was decanted away from the microcrystalline product that was subsequently washed twice with 2 mL of n-hexane. The so formed crystalline product was dried under vacuum and used without further purification for synthetic purposes. Single crystals suitable for elemental analysis and X-ray structural investigations were grown from layered solutions of toluene and n-hexane. The yield was 240 mg (95%). IR ($\nu(CO)$, cm^{-1}) 1708 (KBr), 1714 (tol); ^{1}H NMR (THF-d_8, 23 °C) δ –22.67 (15 H, s), –44.92 (10 H, s), (tol-d_8, 23 °C) δ –24.03 (15 H), –46.12 (10 H). Anal. Calcd for $C_{22}H_{25}Co_2IrO_2$ (631.53): C, 41.84, H, 3.99. Co, 18.66, Ir, 30.44. Found: C, 41.93, H, 4.09, Co. 18.99, Ir, 30.30; mol wt, 648 (vapor osmometry in benzene solution), 632 (field-desorption mass spectrometry; reference isotope ^{193}Ir).

(2) Reaction of 3 with Ethylene. A NMR tube containing a frozen solution a ca. 2 mg of 3 dissolved in benzene-d_6 was filled

with ethylene (1 atm) and sealed with a torch. The benzene ice was melted immediately prior to recording the spectrum (5 min). The initial spectrum showed that 90% of 3 had reacted with ethylene to form 1 equiv each of 2 and 4. After 15 min two new species were observed and identified as the mononuclear degradation products $(\eta^5\text{-}C_5Me_5)Ir(CO)(\pi\text{-}C_2H_4)$ and $(\eta^5\text{-}C_5H_5)Co(CO)(C_2H_4)$.[11a] Preparatively, $(\eta^5\text{-}C_5Me_5)Ir(CO)(\pi\text{-}C_2H_4)$ may be isolated by chromatography on silica gel followed by sublimation at 40 °C. Thus 100 mg of 3 was dissolved in 30 mL of toluene and the mixture stirred under an ethylene atmosphere at 50 °C for 36 h. The solvent was removed under vacuum, and rapid chromatography under nitrogen on silica gel with n-hexane yielded a very pale yellow residue. Vacuum sublimation (5 mbar) at 50 °C onto a cold finger (–20 °C) gave waxy crystals of pure $(\eta^5\text{-}C_5Me_5)Ir(CO)(\pi\text{-}C_2H_4)$: IR ($\nu(CO)$, cm^{-1}) 1942, 1950 (KBr); ^{1}H NMR δ 1.748 (15 H, s), 2.272 (2 H, d of t, J_1 = 8 Hz, $J_2 = J_3$ = 2 Hz), 1.314 (2 H, d of t, J_1 = 8 Hz, $J_2 = J_3$ = 2 Hz); gated-decoupled ^{13}C NMR (C_6D_6) C_5Me_5 δ 9.705 (q, $^1J_{CH}$ = 127 Hz), C_5Me_5 95.142 (s), CO 172.45 (s), C_2H_4 18.289 (d of d, $^1J_{CH}$ = 153.3, 159.2 Hz); EI MS m/e 384 (M$^+$, ^{193}Ir), 356 (M – 28)$^+$, 328 (M – 56)$^+$.

(3) Reaction of 3 with Carbon Monoxide. In an inert-atmosphere box, a 50-mL round-bottom flask fitted with a Teflon stopcock was charged with 100 mg of 3, 30 mL of diethyl ether, and a stir bar. The flask was then sealed and removed from the box with complete exclusion of oxygen. The ether solution of 3 was exposed to carbon monoxide for ca. 1 min. Removal of the solvent yielded the trinuclear complex $(\eta^5\text{-}C_5Me_5)Ir[(\eta^5\text{-}C_5H_5)\text{-}Co]_2(CO)_3$ (4) as a microcrystalline product: yield >96 mg (>92%); IR ($\nu(CO)$, cm^{-1}) 1931, 1785 (KBr), 1945, 1780 (tol), ^{1}H NMR (C_6D_6) δ 1.814 (15 H, s), 4.816 (10 H, s); ^{13}C{^{1}H} NMR C_5Me_5 δ 8.82, C_5Me_5 99.07, C_5H_5 88.46; FD MS, $C_{23}H_{25}Co_2IrO_3$ (660, ^{193}Ir). Anal. Calcd for $C_{23}H_{25}Co_2IrO_3$ (659.34): C, 41.90; H, 3.70. Found: C, 41.70; H, 4.00.

(4) Reaction of 3 with Diazomethane. In an inert-atmosphere box, a 50-mL round-bottom flask fitted with a Teflon stopcock was charged with 100 mg of 3 and 30 mL of diethyl ether. The flask was sealed and removed from the box. The ether solution was then frozen in a liquid-nitrogen cooling bath and the stopcock removed under a strong stream of purified nitrogen. A 10 mL sample of a ~1 M solution of diazomethane in ether was pipetted onto the frozen ether solution of 3. After the mixed ether solution cooled for a few minutes, the round-bottom flask was placed under a slight vacuum to remove small traces of oxygen. The flask was then sealed (stopcock closed) and allowed to slowly warm to room temperature. The solvent and excess diazomethane were then removed under a water aspirator vacuum and finally an oil pump vacuum. The microcrystalline residue may be recrystallized from layered ether/n-hexane solutions: yield of 5, 91 mg (90%); IR ($\nu(CO)$, cm^{-1}) 1790, 1760 (KBr), 1810, 1770 (THF), 1801, 1769 (tol); ^{1}H NMR (C_6D_6) δ 1.739 (15 H, s), 4.645 (5 H, s), 4.598 (5 H, s), 6.908 (1 H, d, J = 1.1 Hz), 7.420 (1 H, d, J = 1.1 Hz); FD MS, $C_{23}H_{27}Co_2IrO_2$ (646, ^{193}Ir). Anal. Calcd for $C_{23}H_{27}Co_2IrO_2$ (645.34): C, 42.81; H, 4.19. Found: C, 42.79; H, 4.22.

(5) Reaction of 3 with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$. Approximately 2 mg of 3 and sublimed $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ were put into an NMR tube into which benzene-d_6 was then vapor-transfered from a benzophenone ketyl solution. The tube was sealed under vacuum with a torch. An initial NMR spectrum indicated only starting materials were present and no reaction had taken place. Heating the tube at 60° for 36 h caused a brown to deep red-violet color change to occur. A final NMR spectrum indicated that ~50 % of 3 had reacted cleanly with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ to form $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ (1). This reaction was repeated using thf-d_8 as the solvent; the results were identical except that heating for only 6 hr was required to cause most of the trinuclear starting material to react.

(6) X-ray Structure of the Cluster Compound 3. Collection of X-ray Data. A crystal measuring approximately 0.3 × 0.3 × 0.5 mm was selected. Rotation and Weissenberg photographs (Cu Kα radiation) showed the crystal to be monoclinic

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(10) Jonas, K.; Deffense, E.; Habermann, J. *Angew. Chem.* **1983**, *95*, 729.

(11) (a) Theopold, K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464. (b) Schore, N. E.; Ilends, C. S.; Bergman, R. G. *Ibid.* **1977**, *99*, 1781. (c) Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87.

and provided rough lattice constants. Exact cell constants and the orientation matrix for data collection were determined from the setting angles of 25 machine-centered reflections. Data were collected with graphite-monochromated Mo Kα radiation on automatic SYNTEX R3 diffractometer (30 mA, 45 kV). The measured 4608 intensity data (θ-2θ; 3.0° $\leq 2\theta \leq$ 60°) were corrected for absorption (five reflections, ψ scan), and Lorentz and polarization corrections were applied. Crystal data are shown in Table III.

Solution and Refinement of the Structure. A total of 4608 independent reflections ($I > 2.5\sigma(I)$) were used in the refinement procedure. The positions of the atoms were taken from Patterson and Fourier maps. Final refinement using least squares and a cascade matrix converged with anisotropic temperature factors for all atoms with the following R values: $R = 0.047$, $R_w = 0.028$. All computing was performed with the SHELXTL system[12] and a DATA GENERAL NOVA 3 computer, scattering factors have been taken from ref 13.

The anisotropic temperature factor exponent in Table I takes the form $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + ... + 2hkb^{*2} U_{12})$. The R value is defined as follows: $R_{aniso} = (\sum||F_o| - |F_c||)/\sum|F_o|$.

Results and Discussion

Our curiosity about the possible existence of a complex that formally contained a "(η^5-C$_5$H$_5$)Co" unit added somehow to the dinuclear core of the dinuclear species (η^5-C$_5$Me$_5$)Ir(μ-CO)$_2$Co(η^5-C$_5$H$_5$) (1) was first awakened by an experiment in which half-equivalent amounts of the Jonas[10] bis(ethylene) complex (η^5-C$_5$H$_5$)Co(π-C$_2$H$_4$)$_2$ (2) were added successively to the dicarbonyl complex (η^5-C$_5$Me$_5$)Ir(CO)$_2$. After the first addition the expected ν(CO) bands (bridging CO) for 1 were observed in the IR spectra around 1730 cm^{-1} along with unreacted (η^5-C$_5$Me$_5$)Ir(CO)$_2$. Immediately (<1 min) after the second addition of the bis(ethylene) complex 2 no bridging carbonyls corresponding to 1 were observed. A new carbonyl band at ca. 1710 cm^{-1} was observed that slowly disappeared as the CO stretch for 1 reappeared. Further additions of the bis-(ethylene) complex caused similar changes in the IR spectra to occur until a considerable excess of the bis-(ethylene) complex had been added. Immediately after each addition the carbonyl band corresponding to the dinuclear complex 1 was replaced by a band at slightly lower frequency which, upon standing, was again replaced by the band for the dinuclear complex. Attempts at scaling up this reaction and isolating the new "CpCo" addition product were made difficult by two factors. First, the addition product was found to be extremely sensitive to oxygen and could not be worked up cleanly using standard Schlenk techniques. Secondly, all attempts at chromatographic purification of the addition product caused only immediate decomposition to the dinuclear precursor 1. These problems were finally overcome by conducting all reactions as quickly as possible in an inert-atmosphere box where the oxygen content was kept well below 4 ppm. Thus, mixing approximately 1 equiv of the bis(ethylene)cobalt complex 2 with the dinuclear cobalt/iridium species 1 caused an immediate color change from red-violet to burnt orange of the diethyl ether/n-hexane solution. Quick removal of the ethylene liberated by 2 (the addition product reacts slowly with ethylene (vide infra) along with the solvent under vacuum caused the precipitation of the desired product 3 (Scheme I) as a microcrystalline residue. This residue, after being washed with n-hexane, was found in most cases to be analytically pure. Single crystals

(12) Sheldrick, G. M. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Revision 3.0, Göttingen, 1981.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV, pp 55, 99, 145.

Scheme I
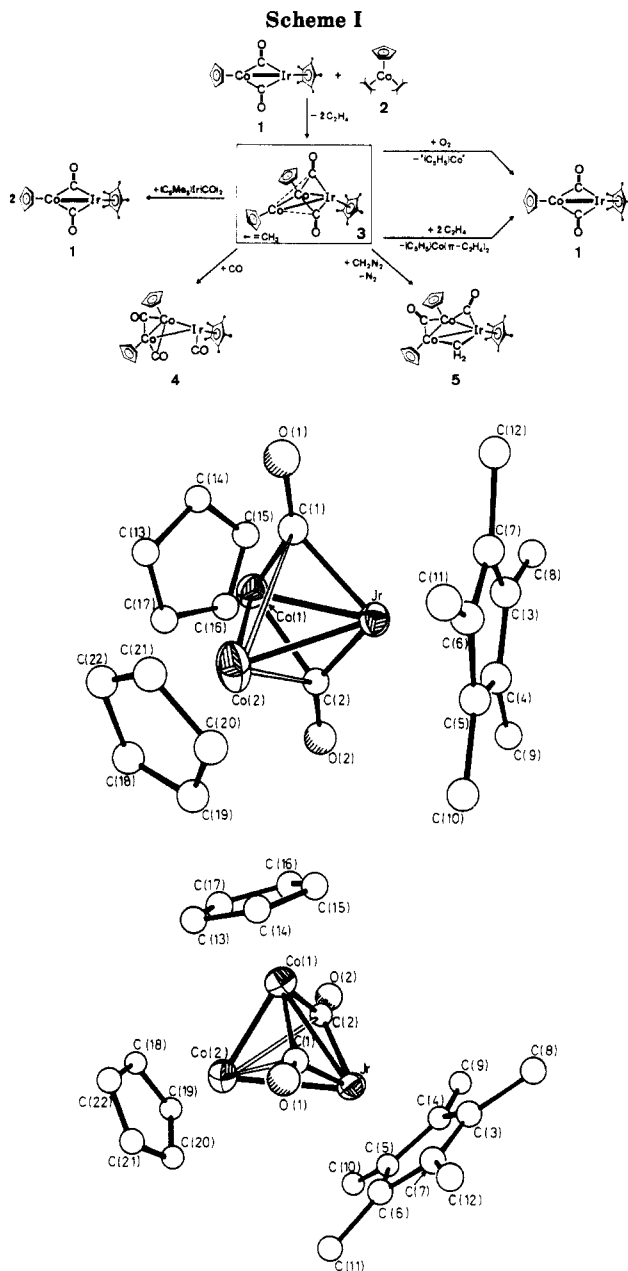
Figure 1. Two views of the molecular structure of the trinuclear paramagnetic cluster compound 3 in the crystal. Thermal ellipsoids of the metals are drawn to 50% probability. Hydrogen atoms are omitted for clarity.

suitable for X-ray diffraction were easily grown from layered solutions of toluene and n-hexane.

Crystal and Molecular Structure of the Trinuclear Cluster Compound 3. In order to accurately determine the molecular structure of 3 and, in particular, to find out the coordination mode of the two carbonyl ligands, a single-crystal X-ray diffraction study was carried out. The compound crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$) from layered n-hexane/toluene solutions at room temperature (Table III). Atomic positional and thermal parameters are listed in Table I; some important bond lengths and angles are given in Table II.

The overall structure of 3 may be described as a triangular arrangement of the three metal atoms Ir, Co(1), and Co(2) with each corner asymmetrically capped by either a C$_5$H$_5$ or C$_5$Me$_5$ ring (Figure 1). Two carbonyl ligands occupy primarily edge-bridging positions along one Ir–Co bond of the metal triangle while bending slightly toward the unique CpCo(2) unit. As such, a clear analogy exists

Table I.   Atomic Positional Parameters and Thermal Parameters of the Trinuclear Cluster Molecule 3^a

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	0.025753 (2)	0.23188 (2)	0.08425 (1)	0.0302 (1)	0.0253 (1)	0.0281 (1)	-0.0012 (1)	0.0009 (1)	-0.0024 (1)
Co(1)	0.44300 (6)	0.39181 (7)	0.12348 (3)	0.0305 (3)	0.0388 (4)	0.0366 (4)	-0.0028 (3)	-0.0003 (3)	-0.0050 (3)
Co(2)	0.25548 (7)	0.37667 (8)	0.17910 (3)	0.0453 (4)	0.0559 (5)	0.0354 (4)	-0.0155 (3)	0.0097 (3)	-0.0108 (4)
C(1)	0.4068 (5)	0.2004 (6)	0.1440 (3)	0.050 (3)	0.046 (3)	0.050 (3)	0.006 (3)	-0.010 (3)	-0.005 (3)
O(1)	0.4607 (4)	0.1053 (4)	0.1728 (2)	0.078 (3)	0.058 (3)	0.099 (4)	0.035 (3)	-0.044 (3)	0.000 (2)
C(2)	0.2877 (5)	0.4368 (5)	0.0745 (2)	0.039 (3)	0.033 (2)	0.043 (3)	-0.000 (2)	-0.004 (2)	-0.004 (2)
O(2)	0.2443 (4)	0.5383 (4)	0.0469 (2)	0.064 (3)	0.029 (2)	0.074 (3)	0.012 (2)	-0.013 (2)	-0.000 (2)
C(3)	0.2231 (5)	0.0924 (5)	-0.0012 (7)	0.051 (3)	0.042 (2)	0.037 (3)	-0.010 (2)	0.011 (2)	-0.015 (3)
C(4)	0.1226 (5)	0.1937 (5)	-0.0014 (2)	0.056 (4)	0.038 (3)	0.042 (3)	-0.008 (2)	-0.006 (3)	-0.009 (3)
C(5)	0.0545 (5)	0.1710 (6)	0.0527 (3)	0.041 (3)	0.038 (3)	0.062 (4)	-0.018 (3)	-0.004 (3)	-0.007 (2)
C(6)	0.1155 (5)	0.0567 (5)	0.0868 (2)	0.054 (3)	0.043 (3)	0.039 (3)	-0.007 (2)	0.010 (2)	-0.019 (3)
C(7)	0.2206 (5)	0.0066 (5)	0.0527 (3)	0.055 (4)	0.027 (3)	0.054 (3)	-0.004 (2)	-0.003 (3)	-0.006 (2)
C(8)	0.3122 (7)	0.0712 (8)	-0.0519 (3)	0.090 (5)	0.086 (5)	0.065 (5)	-0.030 (4)	0.036 (4)	-0.031 (4)
C(9)	0.0899 (7)	0.3039 (7)	-0.0499 (3)	0.108 (6)	0.065 (4)	0.048 (4)	0.014 (3)	-0.304 (4)	-0.019 (4)
C(10)	-0.0666 (5)	0.2506 (7)	0.0678 (3)	0.037 (3)	0.089 (5)	0.099 (5)	-0.034 (4)	-0.003 (3)	0.002 (4)
C(11)	0.0737 (7)	-0.0080 (7)	0.1451 (3)	0.102 (6)	0.074 (5)	0.059 (4)	-0.002 (4)	0.025 (4)	-0.045 (4)
C(12)	0.3088 (7)	-0.1181 (6)	0.0707 (4)	0.086 (5)	0.134 (3)	0.119 (6)	-0.006 (4)	-0.025 (5)	0.011 (3)
C(13)	0.5841 (6)	0.4745 (7)	0.1863 (3)	0.057 (4)	0.126 (7)	0.057 (4)	-0.022 (4)	-0.010 (3)	-0.046 (4)
C(14)	0.6432 (5)	0.3779 (8)	0.1487 (3)	0.033 (3)	0.090 (3)	0.076 (5)	0.015 (5)	-0.013 (4)	-0.009 (3)
C(15)	0.6248 (5)	0.4285 (7)	0.0885 (3)	0.034 (3)	0.085 (5)	0.075 (4)	-0.005 (4)	0.009 (3)	-0.014 (3)
C(16)	0.5540 (6)	0.5544 (7)	0.0885 (4)	0.044 (4)	0.067 (5)	0.115 (6)	0.029 (4)	-0.006 (4)	-0.023 (3)
C(17)	0.5297 (6)	0.5842 (7)	0.1490 (4)	0.057 (4)	0.060 (4)	0.140 (7)	-0.038 (5)	0.003 (4)	-0.027 (4)
C(18)	0.2010 (11)	0.5556 (9)	0.2349 (4)	0.289 (14)	0.098 (7)	0.157 (9)	0.083 (6)	0.164 (9)	-0.087 (8)
C(19)	0.0850 (8)	0.3587 (11)	0.2319 (4)	0.067 (5)	0.128 (8)	0.067 (5)	-0.049 (5)	0.026 (4)	-0.027 (5)
C(20)	0.0928 (11)	0.4949 (13)	0.2116 (4)	0.140 (9)	0.122 (8)	0.072 (6)	-0.006 (6)	0.036 (6)	0.067 (7)
C(21)	0.1929 (11)	0.3353 (10)	0.2704 (3)	0.123 (8)	0.124 (7)	0.045 (7)	0.002 (4)	-0.043 (5)	0.024 (6)
C(22)	0.2659 (10)	0.4530 (17)	0.2728 (5)	0.087 (7)	0.254 (16)	0.077 (7)	-0.107 (8)	0.036 (6)	-0.077 (9)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(8a)	0.3934 (7)	-0.0453 (7)	-0.0302 (3)	H(12b)	0.4000 (7)	0.4000 (7)	0.0686 (4)
H(8b)	0.3189 (7)	0.1655 (6)	-0.0684 (3)	H(12c)	0.2841 (7)	-0.1988 (6)	0.0453 (4)
H(8c)	0.2921 (7)	0.005 (6)	-0.0849 (3)	H(13)	0.5813 (6)	0.4673 (8)	0.2302 (3)
H(9a)	0.0105 (7)	0.3169 (7)	-0.0301 (3)	H(14)	0.6881 (5)	0.2923 (8)	0.1618 (3)
H(9b)	0.0721 (7)	0.2510 (6)	-0.0874 (3)	H(15)	0.6562 (5)	0.3838 (7)	0.0528 (3)
H(9c)	0.1255 (7)	0.3951 (6)	-0.0593 (3)	H(16)	0.5266 (6)	0.6106 (7)	0.0529 (4)
H(10a)	-0.0697 (5)	0.3505 (7)	0.0585 (3)	H(17)	0.4836 (6)	0.6655 (7)	0.1627 (4)
H(10b)	-0.0777 (5)	0.2367 (7)	0.1108 (3)	H(18)	0.2297 (10)	0.6511 (9)	0.2280 (4)
H(10c)	-0.1350 (5)	0.2025 (7)	0.0436 (3)	H(19)	0.0165 (8)	0.2920 (11)	0.2210 (4)
H(11a)	0.1466 (7)	-0.032 (7)	0.1723 (3)	H(20)	0.0290 (11)	0.5409 (13)	0.1839 (4)
H(11b)	0.0242 (7)	-0.0902 (7)	0.1315 (3)	H(21)	0.2130 (11)	0.2483 (10)	0.2924 (3)
H(11c)	0.0196 (7)	0.0554 (7)	0.1666 (3)	H(22)	0.3482 (10)	0.4646 (17)	0.2961 (5)
H(12a)	0.2915 (10)	-0.1379 (6)	0.1126 (4)				

^{a} U_{11} of the H-atoms: 0.143 (6). - Standard deviations (in parentheses) correspond to the least significant digit(s).

Table II. Selected Structural Parameters of the
Trinuclear Cluster Molecule 3

(A) Bond Distances (Å)[a]

Co(1)-Co(2)	2.359 (1)	C(1)-O(1)	1.203 (7)
Co(1)-Ir	2.527 (1)	C(2)-O(2)	1.195 (6)
Co(2)-Ir	2.473 (1)	Co(1)-C(13···17)	2.069-2.102[b]
Co(1)-C(1)	1.896 (5)	Co(2)-C(18···22)	2.157-2.175[c]
Co(1)-C(2)	1.901 (5)	Ir-C(3···7)	2.205-2.280[d]
Co(2)-C(1)	2.435 (6)	Ir-Cp[e]	1.889 (5)
Co(2)-C(2)	2.393 (5)	Co(1)-Cp[e]	1.715 (6)
Ir-C(1)	1.959 (5)	Co(2)-Cp[e]	1.839 (8)
Ir-C(2)	1.963 (5)		

(B) Bond Angles (deg)

Co(1)-Co(2)-Ir	63.0 (0)	Co(2)-C(1)-Ir	67.5 (2)
Co(1)-Ir-Co(2)	56.3 (0)	Co(2)-C(2)-Ir	68.4 (1)
Co(2)-Co(1)-Ir	60.7 (0)	Co(1)-C(1)-O(1)	137.4 (4)
Co(1)-C(1)-Ir	81.9 (2)	Co(2)-C(1)-O(1)	128.5 (4)
Co(1)-C(2)-Ir	81.7 (2)	Ir-C(1)-O(1)	140.0 (4)
Co(1)-C(1)-Co(2)	64.6 (2)	Co(1)-C(2)-O(2)	136.5 (4)
Co(1)-C(2)-Co(2)	65.5 (1)	Co(2)-C(2)-O(2)	126.3 (4)
		Ir-C(2)-O(2)	141.2 (4)

(C) Interplanar Angles (deg)

Plane A: Co(1), Co(2), Ir
Plane B: Co(1), C(1), Ir
Plane C: Co(1), C(2), Ir
Plane D: C(3), C(4), C(5), C(6), C(7)
Plane E: C(13), C(14), C(15), C(16), C(17)
Plane F: C(18), C(19), C(20), C(21), C(22)

	B	C	D	E	F
A	85.6	96.0	90.3	90.5	88.2
B		169.8			
D				27.6	106.2
E					78.6

[a] The carbon-carbon distances within the five-membered hydrocarbon ring ligands amount to 1.39-1.44 Å and the C-CH$_2$ distances of the C$_5$Me$_5$ ligand to 1.499-1.511 Å. [b] Standard deviation ±0.005-0.007. [c] Standard deviation ±0.005-0.011. [d] Standard deviation ±0.005. [e] Distances between the metal atoms and the centers of the corresponding ring ligands.

on Ir and Co(1), respectively, as has previously been discussed by Hoffmann et al.[14]

The distances separating Co(2) from Ir and Co(1) in the dinuclear fragment are, in contrast surprisingly short: Ir-Co(2) = 2.473 Å; Co(1)-Co(2) = 2.359 Å. These distances may be taken as a crude indication that strong interactions take place between the cobalt atom of the highly unsaturated "CpCo(2)" fragment and the metal atoms of the electron-rich, "ethylene-like" heterodinuclear fragment 1.[15] A more quantitative view of these interactions may be obtained through a comparison with the structurally and electronically similar cluster complex (η^5-C$_5$Me$_5$)IrFe$_2$(CO)$_9$,[16] the structure of which is schematically represented by 6. The carbonyl-bridged Ir-M bonds in 3 and 6, 2.53 (M = Co) and 2.61 Å (M = Fe), respectively, are quite similar while the unbridged Ir-Co(2) and Co(1)-Co(2) distances in 3 are significantly shorter than the corresponding Ir-Fe(CO)$_4$ (2.70 Å) and (CO)$_4$-Fe-Fe(CO)$_3$ (2.68 Å) distances in 6. Some of these dif-

6

ferences are accounted for by the fact that the Fe(CO)$_4$ fragment (isolobal with CH$_2$)[17] formally provides 16 electrons to the iron coordination sphere while the CpCo fragment (isolobal with CH$^+$)[17,18] provides only 14 electrons around the cobalt. The "CpCo" fragment is thereby much

between the solid-state structure of 3 and the two synthetic precursors from which it was synthesized; that is, the solid-state structure may be broken up into the original heterodinuclear fragment and a "CpCo" fragment formally derived from the original bis(ethylene) complex 2 (Scheme I). It is important to note, however, that we do not imply here that the unique "CpCo(2)" fragment is specifically derived from the bis(ethylene) precursor (vide infra) but, for the purposes of analyzing the solid-state structure of 3 and some of its chemical properties, it will be expedient to formally break the structure up into these two fragments.

The 2.527 (1) Å distance between the iridium atom and Co(1) is consistent with a formal single metal-metal bond in the presence of bridging carbonyls. For comparison, the related cluster complex (η^5-C$_5$Me$_5$)Ir(μ-CO)$_3$[Co(η^5-C$_5$H$_5$)]$_2$[9a] may be cited which has all three bridging carbonyls above a similar triangular arrangement of the metal atoms. The average Ir-Co bond distance in this complex is 2.538 Å (2.574, 2.530 Å) and may be taken as representative of an iridium-cobalt single bond in a similar bonding environment. These distances are significantly larger than the equilibrium separation observed in the dinuclear precursor 1.[9b] Thus the interaction of the unique CpCo(2) fragment with the original heterodinuclear complex 1 causes a lengthening of the Ir-Co(1) separation. Also characteristic of this interaction is a bending back of the symmetrically π-bonded C$_5$Me$_5$ and C$_5$H$_5$ ring ligands
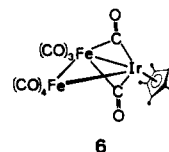
(14) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* 1980, 63, 29.

(15) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* 1979, 18, 654. Bottomley, F. *Ibid.* 1983, 22, 2656.

(16) Guggolz, E.; Ziegler, M. L.; Kalcher, W.; Plank, J.; Riedel, D.; Herrmann, W. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1981, 36B, 0153. The analogous RhOs$_2$-containing complex has also recently been reported: Hsu, L.-J.; Hsu, W.-L.; Jan, D.-Y.; Marshall, A. G.; Shore, S. G. *Organometallics* 1984, 3, 591. The RhFe$_2$ and CoFe$_2$ complexes have also been reported: Knight, J.; Mays, M. J. *J. Chem. Soc. A* 1970, 654. Howell, J. A. S.; Matheson, T. W.; Mays, M. J. *J. Organomet. Chem.* 1975, 88, 363.

(17) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 711. (b) Hofmann, P.; Padmanabhan, M. *Organometallics* 1983, 2, 1273. (c) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* 1976, 15, 1148.

(18) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* 1976, 15, 1148.

Table IV. Structural Comparison of Trinuclear Cluster Compounds[a]

compound	θ_{av}	ξ_1	ξ_2	Φ_{av}	ref
$(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co_2(\eta^5\text{-}C_5H_5)_2$ (3)	84.9	164.1	164.9	174.4	this work
$(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2$	(65)	(150)	(150)	(158)	15, 24
$[(\eta^5\text{-}C_5H_5)_2Rh_3(CO)_4]^-$	77.5	159.4	159.4	170	22
	(74)	(157)	(157)	(176)	15, 24
$[(\eta^5\text{-}C_5Me_5)Rh]_2Pt[P(C_6H_5)_3](CO)_3$	79.8	155.0	149.2	176	23

[a] Angles given in deg; numbers in parentheses correspond to angles calculated by Hoffmann et al. which minimize the energies of orbital interactions.
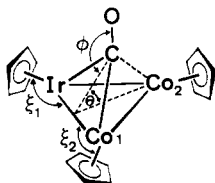
Figure 2. Structural parameters ξ_1, ξ_2, θ, and Φ of the trinuclear paramagnetic complex **3** (for comparison of data see Table IV).

more electron deficient than the Fe(CO)$_4$ fragment and is expected to interact more strongly with the corresponding dinuclear fragment. The Co(1)–Co(2) separation in **3** is actually quite similar to the metal–metal separation found in a series of related trinuclear cluster compounds containing first-row metals. For example, metal-to-metal bond lengths of 2.389 Å in $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$,[19] 2.358 Å (average) in $(\eta^5\text{-}C_5H_5)_3CoNi_2(CO)_2$,[20] and 2.365 Å in $(\eta^5\text{-}C_5H_5)_3Co_3(O)(CO)$ have been reported.[20] In all of these cases the bridging carbonyl or oxo groups are symmetrically located over the triangle of metal atoms and may be described as fully face (or triply) bridging ligands. The carbonyl ligands in **3**, while primarily edge bridging between iridium and Co(1), also show a very slight tilting toward the CpCo(2) fragment (θ_{av} = 84.9°, see Figure 2).[21] Similar tilting of bridging carbonyl groups is also observed in two related cluster complexes. Bergman et al.[22] have reported the synthesis and structural characterization of $[(\eta^5\text{-}C_5H_5)_2Rh_3(CO)_4]^-$ where the tilting angle is 77.5°. More recently, Green et al.[23] have published the structure of an intriguing trinuclear cluster that is formally composed of the carbene-like Pt(PR$_3$)(CO) (R = C$_6$H$_5$) fragment added to the unsaturated complex $(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)_2Rh(\eta^5\text{-}C_5Me_5)$ with the latter framework being analogous to the dinuclear fragment $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ in **3**. The tilting angle for this complex is observed to be 79.8°. A slight bending of the carbonyl oxygen atoms and cyclopentadienyl rings of the dinuclear fragment away from the "incoming" electron-deficient fragment is also characteristic of this type of interaction. Such carbonyl tilting toward the formally electron-deficient fragment in each of these examples may be interpreted as a

structural adjustment within the cluster to more fully satisfy the electronic requirements of one of its constituent parts.

An eloquent theoretical analysis of these adjustments has been presented by Hoffmann and his co-workers.[15] In their EHMO-type calculations the bonding in the anion $[(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_4]^-$ and the hypothetical neutral complex $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_2$[24] was considered in terms of three geometrical parameters θ, ϕ, and ξ (see Figure 2 and Table IV). Table IV summarizes the results obtained by Hoffmann for the last-named sepecies and the corresponding experimental data reported by Bergman and Stone. Comparison of these parameters for **3** and the other cluster molecules indicates the interaction between the bridging carbonyl groups and Co(2) in **3** is relatively small in the solid-state structure.

This hypothesis is supported by the rather long distances observed between Co(2) and the two carbonyl carbon atoms, cf. Co(2)–C(1) = 2.435 (6) Å; Co(2)–C(2) = 2.393 (5) Å. For comparison, the sum of the covalent radii for cobalt (1.16 Å) and carbon (0.77 Å) amounts to 1.86 Å.[25]

In summary, the solid-state structure is characterized by the dinuclear framework of the (isolabal) molecule $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ to which the (unstable) fragment $(\eta^5\text{-}C_5H_5)Co$ is coordinated. Evidence for strong metal–metal interactions is seen in the very short unbridged Ir–Co and Co–Co bonds. Weak interactions between the primarily edge-bridging carbonyl groups and the unique $(\eta^5\text{-}C_5H_5)Co$ fragment is supported by the observation of a very slight tilting and leaning back of the carbonyl ligands toward the unique $(\eta^5\text{-}C_5H_5)Co$ moiety.

^{1}H NMR Studies: Magnetic Properties and Structure in Solution. Due to the extreme oxygen sensitivity of **3** in solution, samples for NMR analysis were best prepared by vacuum transfering scrupulously dried and oxygen-free solvent into a tube preloaded with solid sample which was then sealed. At room temperature (23 °C), solutions of **3** in toluene-d_8 or benzene-d_6 exhibit two fairly sharp singlets at −24.57 and −46.52 ppm! Thus, compound **3** is paramagnetic in solution. The relative intensities of the two signals are exactly 3:2, respectively, thus establishing that the furthest upfield signal (−46.52 ppm) arises from the protons of *both* cyclopentadienyl rings and the singlet at −24.57 ppm from the methyl protons of the π-C$_5$Me$_5$ ligand. It is important to note that in contrast to the solid-state structure the two CpCo fragments of **3** are *equivalent* on the NMR time scale in solution. Within a spectral window of ±100 ppm around SiMe$_4$ no other signals were observed. To more fully characterize the paramagnetism exhibited by **3**, the temperature depen-

(19) Hock, A. A.; Mills, O. S. *Proc. Int. Conf. Coord. Chem., 6th* 1961, 640.

(20) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* 1969, *91*, 3763.

(21) Detailed analysis of the thermal ellipsoids for the CpCo(2) group and the two bridging carbonyls indicates a correlated disorder may exist between these two groups. The ellipsoid calculated for Co(2) as well as the CpCo(2) unit as a whole shows a slight distortion perpendicular to the average plane through the metal atoms. The carbon and oxygen atoms of the two carbonyl groups also show pronounced distortions in the direction of Co(2). These distortions may indicate that in the crystal the CpCo(2) unit occupies a position slightly above or below the average metal atom plane alternately bringing it close to one carbonyl group. However, these systematic deformations are within three standard deviations of the calculated mean spherical radius for each atom, thus making unequivocal statements about such disorders and/or interactions impossible in this case.

(22) Jones, W. D.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1978, *100*, 6770.

(23) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1982, 1309.

(24) A preliminary description of the pentamethylcyclopentadienyl analogue has appeared recently: Green, M.; Hankey, D. R.; Howard, J. A. K.; Louca, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1983, 757; (b) Compounds similar to the cluster species 4 have been synthesized previously: Bailey, W. I., jr.; Cotton, F. A.; Jamerson, J. D.; Kolthammer, B. W. S. *Inorg. Chem.* 1982, *21*, 3131. Lawson, R. J; Shapley, J. R. *Inorg. Chem.* 1978, *17*, 772.

(25) Taken from: Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972; p 82.
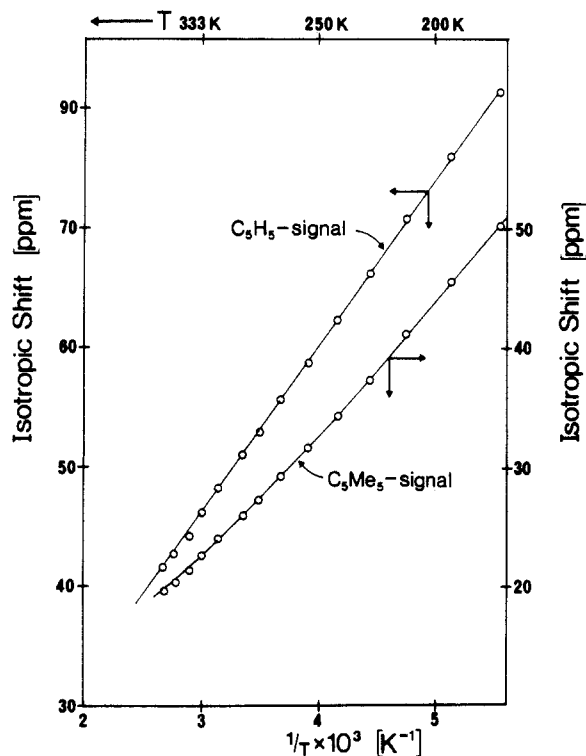
Figure 3. Temperature dependence of the paramagnetic shift (C_5H_5 and C_5Me_5 proton resonances) of the trinuclear paramagnetic compound 3.

Scheme II

● = CO

dence of its ^{1}H NMR spectrum was investigated in detail. The results of these studies are presented graphically in Figure 3. Both signals exhibit a dramatic temperature dependency over the range studied (–93 to +100 °C) while the integral ratio of 3:2 between them remained constant. The signal assigned to the protons of the two cyclopentadienyl rings exhibits an excellent linear dependence of its chemical shift with inverse temperature over the entire temperature range. Extrapolation to infinite temperature ($1/T = 0$) does, however, yield a significant paramagnetically derived intercept. The temperature dependence of the C_5Me_5 protons is slightly more complex. At low temperature (<–20 °C), good linear dependence on $1/T$ is observed while above this point a slight curviture in the plot appears. The linear dependence of the C_5H_5 proton signal with $1/T$ is good evidence that the Curie law is obeyed by 3.

Measurement of the bulk susceptibility of 3 in toluene solution (Evans method[26]) on two independently prepared samples over a temperature range of –30 to +60 °C yields a value for the effective magnetic moment μ_{eff} of 3.36 ± 0.4 μ_B. Although this value is somewhat higher than expected from the spin-only approximation assuming a triplet ground state ($S = 1$; $\mu_{eff} = 2(S(S + 1))^{1/2} = 2.83$), such deviations are quite common among complexes containing 5d metals.[27] Nevertheless, the fair agreement of μ_{eff} with the spin-only approximation and the Curie behavior of the C_5H_5 proton resonance strongly indicate that 3 exists in a single triplet ground state with two unpaired
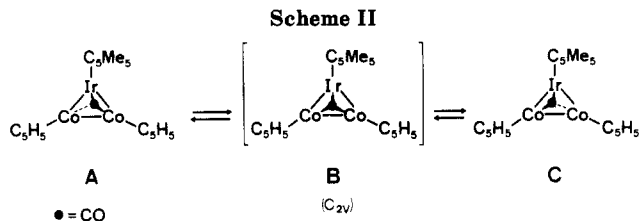
electrons. The solid-state structure and NMR integration data also independently support this hypothesis. In the solid state, 3 exists as discrete trinuclear clusters formally having a total of 46 valence electrons. The relative integrals of the C_5Me_5 and the C_5H_5 signals indicates the molecular constitution of $(C_5Me_5)Ir + 2(C_5H_5)Co$ fragments remains the same in solution.[28]

Two structural possibilities exist for 3 that are consistent with the NMR equivalency of the two cyclopentadienyl rings. First, a dynamic interconversion between two limiting structures similar to what is observed in the solid state would render the two (η^5-C_5H_5)Co fragments equivalent (on the NMR time scale). This type of fluxional behavior is represented by the direct A ⇌ C interconversion shown in Scheme II. Secondly, 3 may undergo a single rearrangement to the more symmetric isomer B (Scheme II) when dissolved in solution. As drawn, B exhibits fully face-bridging carbonyl groups. However, semitriply bridging carbonyl ligands more associated with the two (η^5-C_5H_5)Co fragments are also consistent with the available experimental data. Structure B is in fact the presumed transition state on the potential energy surface for the interconversion of A and C. With the data at hand we are unable to rule out either of these two possibilities. It is however possible to state that since no evidence of coalescence broadening is observed in the Cp proton signal exhibited by 3 even at –93 °C, such an interconversion, A ⇌ C, must be extremely facile and have relatively low-energy barriers. It is informative now to return to the theoretical analysis Hoffmann et al.[14] where the analogous hypothetical cluster compound (η^5-C_5H_5)$_3$Rh$_3$(CO)$_2$ was studied. These results may be summarized as follows: starting from a limiting structure with edge-bridging carbonyl groups perpendicular to the metal atom plane, the authors studied what became of the various valence orbitals as the carbonyl groups were bent over toward the unique CpRh unit until limiting threefold symmetry was attained by the cluster. In the noninteracting edge-bridging structure, a diamagnetic ground state is predicted with the HOMO being an in-plane MO of b_2 symmetry primarily composed of rhodium 4d orbital character. As carbonyl interaction with the unique CpRh fragment is "turned on", this b_2 orbital is stabilized by increased interaction with an orbital of the unique CpRh fragment, also with b_2 symmetry. A low-lying LUMO derived from the unique CpRh fragment is also stabilized by the progression of the carbonyls toward triply bridging positions. As the limiting C_{3v} structure is reached, both the previous HOMO b_2 and LUMO b_1 orbitals join slightly destabilized filled orbitals to form two new sets of degenerate MO's having e symmetry. The upper one of these becomes the new HOMO of the C_{3v} cluster in what is predicted to be an open-shell complex. However, the authors point out that any reduction of the effective symmetry from D_{3h} would lift the degeneracy of these two pairs of e orbitals,

(26) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791. Ostfeld, D.; Cohen, I. A. *J. Chem. Educ.* **1972**, *49*, 829.

(27) With the presence of iridium in 3 where the 5d orbitals are involved in valence bonding within the cluster, spin–orbit coupling interactions for the unpaired electrons are probably significant and cannot be neglected as the spin-only approximation does. These second-order interactions may also be the sources of the nonzero intercepts observed for the C_5Me_5 signal in Figure 3. See: Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, PA, 1977; Chapter 6.

(28) Obviously other multiples of the unit [CpMe$_5$Ir(CpCo)$_2$] are consistent with the NMR data, but it is difficult to construct reasonable chemical structures that could reversibly rearrange to the observed monomeric unit in the solid state and also account for the magnetic susceptibility data.
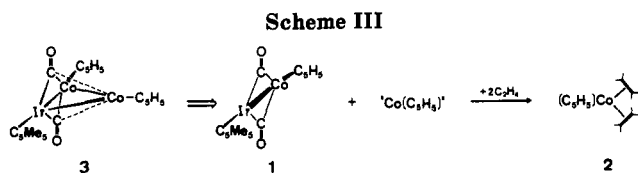
Scheme III

thus avoiding the open-shell structure. In the case at hand, the maximum symmetry attainable by 3, occurring when the carbonyl groups are placed symmetrically between the two CpCo fragments, is C_{2v} (structure b, Scheme II). The $(\eta^5\text{-}C_5Me_5)Ir$ fragment has now assumed the role of the unique CpRh fragment in Hoffmann's analysis. Therefore, if structure B is a true representation of the structure of 3 in solution, then its observed paramagnetism is at variance with analysis of Hoffmann et al. Furthermore, we may also say that for the interconversion A $\rightleftharpoons$ C to occur through an intermediate or transition state resembling B requires that A, B, and C all have triplet ground states; otherwise such interconversions would be formally spin forbidden.

In an attempt to answer the questions raised above concerning the solution vs. solid-state structure of 3, we have also measured the magnetic susceptibility of 3 in the solid state (Faraday method). The room-temperature magnetic moment for 3 in the solid state (corrected for diamagnetic ligand contributions) is 4.06 μ_B. Thus 3 is indeed paramagnetic in the solid state and a rapid equilibrium between A, B, and C is not in any way ruled out with the data in hand.

When comparing the theoretical predictions of Hoffmann et al. with the observed properties of 3, it is important to bear in mind the differences between the two cases, namely, substituting all the rhodium atoms for iridium and cobalt and one of the Cp rings for C_5Me_5. These changes could easily shift the energies of the various orbitals to such a degree that comparisons between the two systems are no longer appropriate. It is, however, interesting to note that, given the rather severe symmetry restrictions imposed upon 3 and the manyfold ways in which it might distort slightly to remove possible orbital degeneracies, it nevertheless remains a ground-state triplet molecule.

Reactivity of the Trinuclear Paramagnetic Complex 3. We have begun to investigate the reactivity of the trinuclear complex 3 with a variety of organic and inorganic substrates. The extreme oxygen sensitivity has already been noted. Solutions of 3 react instantaneously with air to give the dinuclear precursor molecule $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ (1) in good yield (Scheme I). In the solid state 3 shows varying sensitivity to oxygen. Microcrystalline samples of 3 are stable for several hours in air while grinding 3 in air with KBr for IR samples causes extensive decomposition.

Surprisingly, solutions of 3 react smoothly with ethylene, yielding the two synthetic precursors 1 and 2 (Scheme I). Thus 3 is formally in equilibrium with the heterodinuclear complex 1 and the mononuclear bis(ethylene) complex 2 (Scheme III). Removal or addition of ethylene determines which set of products will be formed. Over longer periods of time, however, we have observed that the heterodinuclear species is thermodynamically unstable in the presence of ethylene (with or without the bis(ethylene)cobalt adduct as a catalyst). The final products (after several days) for the reaction of 3 or the heterodinuclear species 1 with ethylene are the mononuclear complexes $(\eta^5\text{-}C_5Me_5)Ir(CO)(\pi\text{-}C_2H_4)$ and $(\eta^5\text{-}C_5H_5)Co(CO)(\pi\text{-}C_2H_4)$.[11a]

The 46-electron cluster compound 3 readily reacts with two-electron donor ligands without fragmentation of the

triangular Co_2Ir core. Carbon monoxide reacts instantly with 3 in diethyl ether solution to yield the formally saturated 48-electron cluster complex $(\eta^5\text{-}C_5Me_5)Ir[(\eta^5\text{-}C_5H_5)Co]_2(CO)_3$ (4). Interestingly, the IR spectrum of 4 indicates the presence of both terminal (1925 cm^{-1}) and bridging (1775 cm^{-1}) carbonyl groups. The NMR spectrum of 4 shows only a single sharp C_5H_5 signal (δ 4.816 (10 H)) and a C_5Me_5 signal (δ 1.814 (15 H)). The equivalency of the two CoCp fragments on the NMR time scale together with the IR data (indicating both terminal and bridging CO groups), and mass spectral data (M$^+$· 660, ^{193}Ir) support the structure shown for 4 in Scheme I.

It is noteworthy that as an additional molecule of carbon monoxide is incorporated into 3, a rearrangement of the two existing CO groups takes place (with respect to the solid-state structure) such that 4 represents the formal addition of a $(\eta^5\text{-}C_5Me_5)Ir(CO)$ fragment (isolobal with CH_2)[17a,b] to the known dinuclear cobalt complex $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$.[11] In the subsequent paper of this series we report the synthesis and structure of another isomer of 4 where all three carbonyl groups occupy *edge-bridging positions on one side* of the trimetallic[9b] plane. Similar structural isomerism is observed for trinuclear cobalt analogues[29] as well as for a trinuclear rhodium cluster compound having η^5-indenyl ligands.[30] We are currently investigating the structural details of 4 along with its thermodynamic and kinetic stability with respect to its isomeric partner.

The unsaturated cluster 3 also readily catalyzes the decomposition of diazomethane producing the new trinuclear complex 6 (M$^+$· 646, ^{193}Ir) containing only bridging carbonyl groups (ν(CO) 1810 and 1770 cm^{-1} (KBr)). The ^{1}H NMR spectrum show two C_5H_5 signals (δ 4.64 and 4.60), one C_5Me_5 signal (δ 1.74), and two coupled doublets that integrate as one proton each and are assigned to the diastereotopic protons of a bridging methylene moiety. On the basis of the above spectroscopic data we propose the structure shown for 5 in Scheme I. This molecule thus is similar to the known and structurally characterized analogue (CO in place of CH_2) where all three bridging CO groups are above the plane of the metal atom core.[9b] Other structures having the bridging groups both above and below the metal atom plane possess inherent steric and electronic problems with respect the placement of the cyclopentadienyl rings.

On the basis of its solid-state structure where the unique "CpCo" fragment interacts only weakly with the two bridging carbonyls and its reactivity with oxygen and ethylene where one CpCo fragment is lost quite easily, we felt that 3 might generally function as a "CpCo" transfer reagent. Our first attempt to investigate this hypothesis involved the simple transfer of CpCo from 3 to the mononuclear complex $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ whereby two molecules of the dinuclear complex 1 would be produced. Reaction of 3 with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ in benzene-d_6 solution proceeded sluggishly to the desired dinuclear product 1 (50% 3 consumed after 36 h at 60 °C). The same reaction repeated in THF-d_8 was observed to go to completion after only 6 h at 60 °C. Thus a significant solvent assistance effect is observed in the transfer of the "CpCo" fragment to the mononuclear dicarbonyliridium complex. Encouraged by the success of these initial reactions, we attempted to perform the same reaction using the analogous compound $(\eta^5\text{-}C_5H_5)Ir(CO)_2$. In a sealed NMR tube (THF-d_8) we have observed clear evidence that not only

(29) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227.

(30) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.

does the desired "CpCo" transfer occur producing the new dinuclear complex $(\eta^5\text{-}C_5H_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ in addition to 1 but also the homodinuclear iridium analogue of composition $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Ir(\eta^5\text{-}C_5H_5)$. Attempts to run this reaction on a preparative scale have, however, been thwarted by the extreme reactivity of compounds of type $(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)_2M'(\eta^5\text{-}C_5H_5)$ (M/M' = Co/Co, Co/Ir, Ir/Ir).[9b,31] Work in this and related areas is ongoing and will be reported in the near future.

Summary and Conclusions

A high-yield synthesis for the title complex $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2[Co(\eta^5\text{-}C_5H_5)]_2$ (3) is described and a detailed discussion of its properties in solution and in the solid state presented. The solid-state structure of 3 is derived from the unsaturated heterodinuclear precursor complex $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ (1), to which a $Co(\eta^5\text{-}C_5H_5)$ fragment has been added. This observation fits neatly into the growing number of examples illustrating the isolobal concepts developed by Hoffmann and co-workers.[17] The unique CoCp fragment interacts strongly with the metal atoms of the dinuclear fragment and weakly with the two edge-bridging carbonyl ligands in the solid state. In solution, a low-energy CO scrambling process equilibrates the two CoCp fragments. 3 is paramagnetic in solution and in the solid state.

Trinuclear 3 is extremely labile by virtue of its formal 46 valence electron count and the reactivity of one of the CoCp fragments. Loss of this fragment is easily initiated by briefly exposing the complex to oxygen, ethylene, or mononuclear cyclopentadienyl dicarbonyl complexes. In all such cases the heterodinuclear precursor complex 1 is also produced initially. 3 readily adds carbon monoxide and catalyzes the decomposition of diazoalkanes to give saturated 48 valence electron cluster complexes, the latter case having a new μ-methylene group on the trinuclear frame. Thus 3 would appear to be a valuable synthetic precursor for a number of studies. On the one hand, small organic fragments are quite easily incorporated into 3 without disruption of the cluster backbone. Under other circumstances 3 appears to cleanly transfer a CoCp fragment to a variety of interesting substrates. These and other studies of the reactivity of 3 and similar analogues are in progress and will be reported in the near future.

(31) Reaction of $CpIr(CO)_2$ with $CpCo(C_2H_4)_2$ has, under all conditions investigated thus far, yielded only a complex mixture of tri- and tetranuclear clusters.

Synthesis and Reactions of Thermally Stable Platinum(II) Carboxylic Acids (Hydroxycarbonyls) Containing Bis(tertiary phosphines)[†]

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Platinum(II) carboxylic acids (or hydroxycarbonyls) of general formula $Pt(CO_2H)(C_6H_9)(P\text{-}P)$ (C_6H_9 = 1-cyclohexenyl; P-P = $Ph_2PCH_2CH_2PPh_2$ (1), cis-$Ph_2PCH{=}CHPPh_2$ (2), $Ph_2PCH_2CH_2CH_2PPh_2$ (3), and $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (4)) have been prepared by the successive reaction of water and carbon monoxide with the cyclohexyne complexes $Pt(C_6H_8)(P\text{-}P)$. Complex 3 readily inserts a second molecule of CO into the platinum(II)–cyclohexenyl bond to give an acylplatinum(II) carboxylic acid, $Pt(CO_2H)\text{-}(COC_6H_9)(Ph_2PCH_2CH_2CH_2PPh_2)$ (5). The complexes, which have been characterized by elemental analysis, IR spectroscopy and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, are monomeric in dichloromethane but appear to be associated through hydrogen bonds in the solid state. Complexes 1–5 do not decarboxylate in the solid state up to ca. 80 °C and do not form carboxylate ions by loss of a proton. These properties probably arise from the presence of nondissociating, strongly electron-donating ligands in the coordination sphere. The platinum(II) carboxylic acids do readily undergo esterification with alcohols, and 3 reacts with dimethylamine or tert-butylamine to give carbamoyl complexes $Pt(CONR^1R^2)(C_6H_9)(Ph_2PCH_2CH_2CH_2PPh_2)$ (R^1 = R^2 = Me, 6; R^1 = t-Bu, R^2 = H, 7). These reactions, and the ready exchange of ^{13}CO with the Pt–CO_2H group, indicate that the carboxylic acids behave as $[Pt(C_6H_9)(CO)(P\text{-}P)]OH$, although the carbonyl cations could not be detected in solutions of the acids. Treatment of 5 with HBF_4 gives $[Pt(COC_6H_9)(CO)\text{-}(Ph_2PCH_2CH_2CH_2PPh_2)]BF_4$, as expected, whereas 3 undergoes competitive cleavage of the platinum(II)–cyclohexenyl bond and consequent β-elimination of CO_2 from the Pt–CO_2H group.

Introduction

Metallocarboxylic acids (hydroxycarbonyl metal complexes), L_nMCO_2H, have been proposed as key intermediates in several important reactions involving carbon monoxide. They include oxidation of CO (either free or coordinated) by metal ions,[1] the isotopic exchange of metal carbonyls with ^{18}O-labeled water (first observed by Muetterties),[2] the homogeneously catalyzed water gas shift

(1) (a) Harkness, A. C.; Halpern, J. *J. Am. Chem. Soc.* 1961, *83*, 1258. (b) Nakamura, S.; Halpern, J. *Ibid.* 1961, *83*, 4102. (c) Bercaw, J. E.; Goh, L. Y.; Halpern, J. *Ibid.* 1972, *94*, 6534.