Figure 2. Visible and near-infrared spectra of 1,1-dicyano-2,2-diferrocenylethylene (VIII): neutral, -·-; monocation, - - -; and dication, —.

rocenium systems but are shifted considerably due to the highly electron-withdrawing substituents. Unsubstituted ferrocene has an absorption in the visible region at 440 nm (ϵ 91), and it has been noted that this absorption exhibits a bathochromic shift when electron-withdrawing substituents are placed on the ring.[30] It is important to note, however, that there are no absorptions in the near-infrared region for any of the spectra. This is particularly important in the case of the mixed-valence monocation since the lack of any bands in the near-infrared spectrum of the monocation of VIII indicates that no intervalence charge transfer is occurring in this compound. This is not unexpected upon consideration of the recently completed X-ray structural investigation of VIII.[24] If the monocation

structure is similar to that of the neutral compound, then the observed iron–iron distance of 6.091 Å would be too large to permit direct metal–metal interaction. Electron transfer, if it were to take place, would then have to involve a ligand propagated exchange. No low-energy transitions are known for biferrocene type molecules bridged by saturated groups. In fact, diferrocenylacetylene is the only reported case[34] of intervalence charge transfer propagated through the bridging unit which in that case is a conjugated π system. Examination of the structure of VIII also eliminates this method of electron transfer. The cyclopentadienyl rings are tilted over 20° out of the plane of the bridging unit, and this results in an unconjugated system incapable of electron transfer through the π system. Thus since both known intervalence charge-transfer mechanisms are eliminated, the lack of evidence for this behavior is not unexpected.

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Metal Atom Reactions of Cobalt with Cyclopentadiene and Alkynes: Synthesis of Structurally Novel Organometallic Complexes

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The reactions of cobalt atoms and cyclopentadiene with various alkynes such as hexafluorobutyne, trifluoropropyne, and diphenylacetylene have been found to yield a variety of new organometallic compounds including both mono- and multimetal complexes. In general the products obtained fall into four categories: (1) complexes containing ligands resulting from dimerization or trimerization of the alkyne usually accompanied by hydrogen addition, i.e., $(\eta$-$C_5H_5)Co[C_4H_2(CF_3)_4]$, $(\eta$-$C_5H_5)_2Co_2[C_5H_2F(CF_3)_3]$, $(\eta$-$C_5H_5)_2Co_2[C_6H_5(CF_3)_3]$, $[\eta$-$C_5(CH_3)_5]Co[C_4H_2(CF_3)_4]$, $(\eta$-$C_5H_5)_2Co_2[C_2H_2(CF_3)]_2$, and $(\eta$-$C_5H_5)Co[C_4(C_6H_5)_4]$; (2) multimetal clusters containing cyclopentadienylcobalt units and alkynes, i.e., $(\eta$-$C_5H_5)_3Co_3[C_2(CF_3)_2]$, $(\eta$-$C_5H_5)_3Co_3[C_2(CF_3)_2](\mu_3$-CO), and $[\eta$-$C_5(CH_3)_5]_2Co_2[C_2(CF_3)_2]_2$; (3) complexes containing ligands resulting from cycloadditions of cyclopentadiene and alkynes, i.e., $(\eta$-$C_5H_5)Co[C_7H_6(CF_3)_2]$ and $(\eta$-$C_5H_5)Co[C_9H_6(CF_3)_4]$; (4) complexes containing ligands resulting from simple additions of cyclopentadiene and alkynes, i.e., $(\eta$-$C_5H_5)_2Co_2$-$[C_7H_8(CF_3)_2]$, $(\eta$-$C_5H_5)_2Co_2[C_9H_4(CF_3)_4]$, $(\eta$-$C_3H_5)_2Co_2[C_9H_6(CF_3)_4]$, and $(\eta$-$C_5H_5)Co[C_9H_6(C_6H_5)_4]$. The nature of these products implies the formation of certain reactive cyclopentadienylcobalt intermediates in these metal atom reactions, and an appropriate reaction scheme is discussed.

Introduction

In recent years the reactions of metal atoms with various olefins have been an area of intense investigation and have yielded a number of new and unusual organometallic complexes.[1] It is therefore somewhat surprising that the corresponding reactions of metal atoms with alkynes have met with much less success. In fact until the recent work of Klabunde,[2]

previous studies have shown that these reactions usually result in only the trimerization of the alkyne with little evidence for the formation of organometallic products.[3] Previously, we reported[4,5] that the reaction of cyclopentadiene and cobalt atoms with the various boranes and alkynes results in the

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Table I. NMR Spectra of New Complexes

complex[a]	^{1}H NMR, δ[b]	^{19}F NMR, ϕ[c]
I	5.11 (C_5H_5, s); −0.30 (=CHCF$_3$, q, 10.5 Hz)	53.17 (=CHCF$_3$, m); 54.05 (=CCF$_3$, m)
II	4.96 (C_5H_5, s); 3.28 (=CH, −CH, s); 0.94 (CH$_2$, m)	57.09 (=CCF$_3$, s)
III	4.79 (C_5H_5, s); 4.23 (=CH, m); 2.22 (−CH, m); 1.02 (CH$_2$, m)	52.86 (−CCF$_3$, m); 56.20 (=CCF$_3$, m)
IV[d]	4.96 and 4.46 (C_5H_5, s); 4.49 (=CH, s); 4.39 (=CH, s); 3.04 (=CH, s); 1.43 (CH$_2$, m); −0.49 (=CHCF$_3$, q, 13.5 Hz)	48.05 (=CCF$_3$, q); 54.36 (=CHCF$_3$, m); 60.85 and 62.70 (=CCF$_3$, q)
V[d]	5.00 and 4.64 (C_5H_5, s); 3.35 (=CH, m); 2.10 and 1.93 (CoCH$_2$, m); 1.78 (CH, m); 1.62 (CH$_2$, m); −0.48 (=CHCF$_3$, q, 13.4 Hz)	47.55 (=CCF$_3$, q); 53.22 (=CHCF$_3$, m)
VI[d]	5.01 and 4.73 (C_5H_5, s); 6.41 (=CH, m); 0.72 (CH$_2$, m)	49.58, 49.99, 50.55, and 56.91 (=CCF$_3$, m)
VII[d]	5.06 and 4.82 (C_5H_5, s); 3.60 (=CH, d of d, J_{HF} = 14.8 Hz, J_{HH} = 1.4 Hz); 2.82 (−CHCF$_3$, d of q, J_{HF} = 7.0 Hz, J_{HH} = 1.4 Hz)	17.84 (=CF, d, 14.8 Hz); 50.21 (Co–CCF$_3$, q); 52.48 (=CCF$_3$, m); 67.59 (−CHCF$_3$, m)
VIII	4.45 (C_5H_5, s); at −80 °C 4.48 and 4.44 (C_5H_5, s)	47.61 (≡CCF$_3$, s)
IX	4.65 (C_5H_5, s)	51.71 (≡CCF$_3$, s)
X	4.98 and 4.88 (C_5H_5, s)	51.29 and 63.57 (=CCF$_3$, q); 52.67 and 56.09 (=CCF$_3$, m)
XI	2.14 (CH$_3$, s); −0.25 (=CHCF$_3$, q, 11.3 Hz)	51.63 (=CCF$_3$, m) 52.45 (=CHCF$_3$, m)
XII	1.61 (CH$_3$, s)	51.63 and 55.54 (=CCF$_3$, m)
XIII[d]	4.96 (=CH, s); 4.77 and 4.74 (C_5H_5, s); 3.98 (CH$_2$, CHCF$_3$, m); 2.02 (Co–CH=, s)	59.09 (CF$_3$C=, q); 60.27 (CH–C(CF$_3$)=, s); 64.49 (CF$_3$CH, d of q)
XIV[d]	4.97 (C_5H_5, s); 3.23 (cis =CH$_2$, d, 3.0 Hz); 0.42 (trans =CH$_2$, m)	53.98 (=CCF$_3$, s)
XV[d]	7.02 (C_6H_5, m); 5.53 and 5.36 (=CH, m); 4.56 (C_5H_5, s); 3.88 and 3.61 (−CH, m); 2.48 and 2.08 (CH$_2$, m)	
XVI	6.88 (C_6H_5, m); 5.72 and 5.51 (=CH, m); 3.28 (−CH, m); 2.81 (CH$_2$, m)	

^{a} For structures, see text. ^{b} In CS$_2$/C$_6$D$_6$ solution relative to Me$_4$Si = 0.00 ppm; J_{HF} in parentheses unless otherwise noted. ^{c} In CS$_2$/C$_6$D$_6$/ C$_6$H$_5$CF$_3$ solution; relative to CFCl$_3$, ϕ 0.00 ppm; ϕ(CFCl$_3$) = ϕ(C$_6$H$_5$CF$_3$) + 63.75 ppm. NMR abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet. ^{d} Measured at 360 MHz.

formation of a number of new cobaltaborane and carborane clusters. We have now extended these studies and found that similar reactions involving the cocondensation of cyclopentadiene and cobalt atoms with various alkynes leads to the production of a number of new organometallic compounds, including several multimetal complexes. Furthermore, an examination of the types of products obtained in these reactions implies the initial formation of certain reactive intermediates in the metal atom reactions. Full details of this work are reported in this paper.

Experimental Section

Materials. Cobalt metal was purchased from the Alfa Division of Ventron Products as either the powder (50 mesh, 99.8%) or pieces (99.5% pure) and used as received. Hexafluoro-2-butyne was obtained from PCR, Inc., and diphenylacetylene from Eastman Organic Chemical, and they were used without further purification. Penta-methylcyclopentadiene was prepared by literature methods[6] while 3,3,3-trifluoropropyne was either obtained from PCR, Inc., or prepared by literature methods.[7] Solvents were all reagent grade dried over molecular sieves (4A).

Physical Measurements and Chromatography. Proton NMR spectra at 100 MHz and fluorine-19 spectra at 94 MHz (Table I) were obtained on a JEOL PS-100 pulse Fourier transform spectrometer. All spectra were obtained by using Fourier-transform techniques. The 360-MHz proton spectra were obtained on a Bruker WH-360 Fourier-transform spectrometer located in the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. All NMR spectra (100 and 360 MHz, ^{1}H and ^{19}F) were obtained in CS$_2$/C$_6$D$_6$ solutions with trifluorotoluene added as internal reference in ^{19}F spectra. High-resolution mass spectra (Table II) were obtained on a Perkin-Elmer Hitachi RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. All reported exact masses are the result of a peak averaging of at least ten separate scans with each scan within a deviation of 15 ppm. Infrared spectra (Table III) were recorded on a Perkin-Elmer 521 infrared spectrometer in chloroform solution or potassium bromide pellets. Elemental analyses were performed by Galbraith Labs, Inc. All melting points were uncorrected. Thin-layer chromatography was conducted on 0.5 mm (20 cm × 20

cm) silica gel F-254 plates (Merck). Reversed-phase thin-layer chromatography (RP-TLC)[8] was conducted on 0.5-mm cellulose plates (20 cm × 20 cm, Analtech MN300F) impregnated with Nujol by development in a 10% w/w Nujol–benzene solution followed by air-drying. Compounds separated by RP-TLC were then freed of Nujol by washing with hexane on a short silica gel column. Column chromatography was conducted by employing silica gel, 0.05–0.2 mm (70–270 mesh) ASTM (MN-Kieselgel). Product yields are estimated on the basis of the approximate amount of vaporized cobalt which reaches the reaction zone. Thus, starting with 600 mg, about half of this is vaporized and only an estimated half of this 300 mg of vaporized metal reaches the reaction zone. This results in 150 mg (2.6 mmol) available for reaction upon which the estimated yields are based. These yields represent the average amount of product formed over several reactions.

Reactor. The reactor utilized in these experiments is based upon the general designs of Skell,[9] Timms,[10] and Klabunde.[11]

The reaction vessel consists of a 3-L flask (Kontes, K-612000) and ⊤ 24/40 four-necked top (Kontes, 613200). This reactor flask is mounted vertically and connected to a high-vacuum line by one of the ⊤ 24/40 necks. The center neck is used to accommodate the substrate sprayer which is connected to the substrate inlet system. This glass sprayer is designed to evenly input the substrate vapor to the reaction zone and carefully directed so that the vapor does not enter the area of the hot crucible. Two identical water-cooled copper electrodes are placed in the remaining two side ⊤ 24/40 necks of the reactor top. The metal evaporation source, an integral tungsten–alumina crucible (Sylvania Emissive Products, CS-100B), is connected to the electrode by means of split copper bolts and secured in place. Power to the electrodes is supplied by two transformers connected in series with a range of 0–10 V and up to 100 A.

General Reaction Procedure. Approximately 0.6 g of cobalt is placed in the evaporation source (crucible) already attached to the electrodes. The metal may be either powdered or small pieces although recent evidence indicates that powdered metal should be avoided due to oxide contamination. Cobalt vapor which is generated by electrical heating (~6.2 V, 58 A) is then condensed over a 1–2-h period with the

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Table II. High-Resolution Mass Spectra of New Complexes

complex	M^+ calcd	M^+ found	major peaks, m/e
I, $C_{13}H_7F_{12}Co$	449.9688	449.9667 (6.99%)	142.9633 $[(C_5H_5CoF)^+ (30.94\%)]$, 123.9718 $[(C_5H_5Co)^+ (100\%)]$, 97.9567 $[(C_3H_5Co)^+ (7.70\%)]$, 58.9354 $[(Co)^+ (13.80\%)]$
II, $C_{14}H_{11}F_6Co$	352.0097	352.0122 (29.16%)	333.0019 $[(C_{14}H_{11}F_5Co)^+ (9.23\%)]$, 209.0380 $[(C_9H_6F_5)^+ (16.55\%)]$, 189.0288 $[(C_9H_5F_4)^+ (57.31\%)]$ 162.0090 $[(C_7H_3F_4)^+ (20.59\%)]$, 123.9718 $[(C_5H_5Co)^+ (100\%)]$, 58.9350 $[(Co)^+ (16.20\%)]$
III, $C_{18}H_{11}F_{12}Co$	514.0001	514.0012 (17.27%)	371.0290 $[(C_{13}H_6F_{11})^+ (12.01\%)]$, 204.9683 $[(C_7H_5F_3Co)^+ (30.15\%)]$, 142.9722 $[(C_5H_5FCO)^+ (20.23\%)]$, 123.9721 $[(C_5H_5Co)^+ (100\%)]$, 58.9356 $[(Co)^+ (5.43\%)]$
IV, $C_{23}H_{16}F_{12}Co_2$	637.9274	637.9727 (6.88%)	514.0021 $[(C_{18}H_{11}F_{12}Co)^+ (13.82\%)]$, 495.0002 $[(C_{18}H_{11}F_{11}Co)^+ (63.35\%)]$, 351.0184 $[(C_{13}H_5F_{10})^+ (14.26\%)]$, 189.0124 $[(C_{10}H_{10}Co)^+ (73.66\%)]$, 142.9716 $[(C_5H_5FCo)^+ (73.71\%)]$, 123.9732 $[(C_5H_5Co)^+ (100\%)]$, 58.9353 $[(Co)^+ (17.34\%)]$
V, $C_{19}H_{18}F_6Co_2$	477.9976	477.9954 (3.80%)	475.9827 $[(C_{19}H_{16}F_6Co_2)^+ (22.64\%)]$, 353.9796 $[(C_{14}H_{13}F_6Co)^+ (22.18\%)]$, 335.0316 $[(C_{14}H_{13}F_5Co)^+ (32.85\%)]$, 315.0213 $[(C_{14}H_{12}F_4Co)^+ (30.37\%)]$, 191.0482 $[(C_9H_7F_4)^+ (66.06\%)]$, 189.0117 $[(C_{10}H_{10}Co)^+ (100\%)]$, 123.9707 $[(C_5H_5Co)^+ (94.09\%)]$, 58.9354 $[(Co)^+ (30.69\%)]$
VI, $C_{23}H_{14}F_{12}Co_2$	635.9568	635.9564 (32.54%)	492.9897 $[(C_{18}H_9F_{11}Co)^+ (83.33\%)]$, 472.9810 $[(C_{18}H_8F_{10}Co)^+ (19.11\%)]$, 300.0191 $[(C_{12}H_4F_8)^+ (42.85\%)]$, 189.0114 $[(C_{10}H_{10}Co)^+ (100\%)]$, 123.9710 $[(C_5H_5Co)^+ (93.16\%)]$, 66.0478 $[(C_5H_6)^+ (72.13\%)]$
VII, $C_{18}H_{12}F_{10}Co_2$	535.9446	535.9450 (60.65%)	392.9761 $[(C_{13}H_7F_9Co)^+ (30.07\%)]$, 248.9950 $[(C_5F_6Co)^+ (18.59\%)]$, 189.0103 $[(C_{10}H_{10}Co)^+ (85.69\%)]$, 143.9720 $[(C_5H_5FCo)^+ (100\%)]$, 123.9708 $[(C_5H_5Co)^+ (87.63\%)]$, 58.9357 $[(Co)^+ (33.30\%)]$
VIII, $C_{19}H_{15}F_6Co_3$	533.9074	533.9056 (63.67%)	313.0020 $[(C_{14}H_{10}F_4Co)^+ (9.79\%)]$, 294.0036 $[(C_{14}H_{10}F_3Co)^+ (12.04\%)]$, 189.0106 $[(C_{10}H_{10}Co)^+ (100\%)]$, 123.9717 $[(C_5H_5Co)^+ (31.29\%)]$ 58.9355 $[(Co)^+ (9.36\%)]$
IX, $C_{20}H_{15}F_6OCo_3$	561.9023	561.9021 (25.62%)	533.9053 $[(C_{19}H_{15}F_6Co_3)^+ (28.00\%)]$, 313.0024 $[(C_{14}H_{10}F_4Co)^+ (8.57\%)]$, 294.0039 $[(C_{14}H_{10}F_3Co)^+ (10.43\%)]$, 189.0115 $[(C_{10}H_{10}Co)^+ (100\%)]$ 123.9723 $[(C_5H_5Co)^+ (28.54\%)]$, 58.9359 $[(Co)^+ (7.38\%)]$
X, $C_{18}H_{10}F_{12}OCo_2$	587.9204	587.9185 (22.85%)	189.0117 $[(C_{10}H_{10}Co)^+ (100\%)]$, 123.9701 $[(C_5H_5Co)^+ (56.70\%)]$, 58.9358 $[(Co)^+ (12.01\%)]$
XI, $C_{18}H_{17}F_{12}Co$	520.0470	520.0401 (7.85%)	213.0454 $[(C_{10}H_{15}CoF)^+ (46.70\%)]$, 194.0494 $[(C_{10}H_{15}Co)^+ (100\%)]$, 193.0405 $[(C_{10}H_{14}Co)^+ (27.08\%)]$, 192.0356 $[(C_{10}H_{13}Co)^+ (41.79\%)]$, 133.1053 $[(C_{10}H_{13})^+ (45.70\%)]$
XII, $C_{28}H_{30}F_{12}Co_2$	712.0820	a	586.0965 $[(C_{23}H_{23}F_{12}Co)^+ (10.51\%)]$, 213.0498 $[(C_{10}H_{15}CoF)^+ (66.91\%)]$, 194.0505 $[(C_{10}H_{15}Co)^+ (100\%)]$, 133.1014 $[(C_{10}H_{13})^+ (34.79\%)]$, 58.9360 $[(Co)^+ (8.43\%)]$
XIII, $C_{19}H_{15}F_9Co_2$	531.9694	531.9697 (11.59%)	388.9976 $[(C_{14}H_{10}F_8Co)^+ (10.48\%)]$, 195.0142 $[(C_8H_4F_5)^+ (11.40\%)]$, 189.0111 $[(C_{10}H_{10}Co)^+ (100\%)]$, 123.9703 $[(C_5H_5Co)^+ (53.73\%)]$, 58.9352 $[(Co)^+ (13.47\%)]$
XIV, $C_{16}H_{14}F_6Co_2$	437.9651	437.9660 (5.93%)	435.9525 $[(C_{16}H_{12}F_6Co_2)^+ (22.24\%)]$, 294.9962 $[(C_{11}H_9F_5Co)^+ (10.18\%)]$, 189.0109 $[(C_{10}H_{10}Co)^+ (71.57\%)]$, 123.9705 $[(C_5H_5Co)^+ (100\%)]$, 58.9356 $[(Co)^+ (20.33\%)]$
XV, $C_{38}H_{31}Co$	546.1758	546.1753 (24.79%)	481.1353 $[(C_{33}H_{26}Co)^+ (23.91\%)]$, 479.1222 $[(C_{33}H_{24}Co)^+ (100\%)]$, 422.2023 $[(C_{23}H_{26})^+ (17.48\%)]$, 123.9724 $[(C_5H_5Co)^+ (5.73\%)]$, 58.9350 $[(Co)^+ (4.77\%)]$
XVI, $C_{33}H_{26}$	422.2066	422.2050 (100%)	420.1937 $[(C_{33}H_{24})^+ (76.58\%)]$, 331.1488 $[(C_{26}H_{19})^+ (15.09\%)]$, 243.1200 $[(C_{19}H_{15})^+ (10.43\%)]$

a Parent peak not observed.

substrate vapor on the walls of the reactor which are maintained at −196 °C. A large excess of the desired substrates, typically 10 mL of each ligand, is used. In those reactions involving low-volatile substrates, a large excess of the ligand (approximately 3 g) is placed in the bottom of the reaction vessel before assembly. After metal deposition is complete, the matrix is allowed to warm gradually to room temperature, followed by removal of the volatiles in vacuo. At this point the reactor is vented with an inert gas such as N_2 to avoid reaction of any residual pyrophoric metal with the atmosphere. The reactor is carefully opened and the residue remaining in the reactor extracted and filtered. This extract is then separated and purified by normal techniques such as column chromatography, thin-layer chromatography, and sublimation. All compounds were air stable.

Cobalt Atoms + Cyclopentadiene + Hexafluoro-2-butyne. Cobalt vapor was condensed with 10 mL (~120 mmol) of cyclopentadiene and 10 mL (~50 mmol) of hexafluoro-2-butyne at −196 °C. After metal deposition was complete, the mixture was allowed to gradually warm to room temperature, and all the volatile materials were removed in vacuo. The remaining residue was extracted with methylene chloride, and the products were separated by preparation thin-layer chromatography (TLC).

Initial separation of the large number of products obtained was by TLC using an 80/20 CCl_4/benzene developing mixture. This yielded four bands (R_f 0.87, 0.70, 0.58, and 0.14) which were then rechromatographed in different solvent systems to yield the final products as described below.

The first band (R_f 0.87) was dark orange and when rechromatographed in 90/10 hexane/benzene resulted in four pure products: I, $(\eta\text{-}C_5H_5)Co(C_8F_{12}H_2)$ (R_f 0.70, yellow-orange, mp 128.5–130 °C, yield 148.0 mg (12.6%). Anal. Calcd: C, 34.67; H, 1.56; F, 50.67. Found: C, 34.33; H, 2.03; F, 51.23); II, $(\eta\text{-}C_5H_5)Co(C_9H_6F_6)$ (R_f 0.75, yellow, mp 185–186 °C, yield 35.4 mg (4.0%)); III, (η-

$C_5H_5)Co(C_{13}H_6F_{12})$ (R_f 0.82, yellow, mp 76–78 °C, yield 8.0 mg (0.8%)); and VIII, $(\eta\text{-}C_5H_5)_3Co_3(C_4F_6)$ (R_f 0.60, red, mp 164–165 °C, yield 20.4 mg (4.5%)).

The 80/20 CCl_4/benzene mixture also yielded a green band (R_f 0.70) which was rechromatographed in 50/50 CCl_4/pentane to yield two green bands only the most mobile of which (R_f 0.33) was present in sufficient quantity to collect. This green band appeared pure by TLC (using a variety of solvent systems) although spectroscopic evidence indicated at least two compounds were present. After conventional TLC methods were exhausted, reversed-phase TLC (80/20 methanol/water) was employed to isolate V, $(\eta\text{-}C_5H_5)_2Co_2\text{-}(C_9H_8F_6)$ (R_f 0.56, green, mp 134–136 °C, yield 22 mg (3.6%). Anal. Calcd: C, 47.69; H, 3.76; F, 23.84. Found: C, 47.73; H, 4.09; F, 23.78), and VII, $(\eta\text{-}C_5H_5)_2Co_2(C_8H_2F_{10})$ (R_f 0.72, green, mp 226 °C, yield 19.2 mg (2.8%). Anal. Calcd: C, 40.30; H, 2.24; F, 35.45. Found: C, 41.18; H, 2.52; F, 34.87).

The next band of the initial separation (R_f 0.58) was green-brown and found to consist of three complexes by redevelopment in 60/40 hexane/benzene. The most mobile band was not produced in sufficient quantity to isolate, but VI, $(\eta\text{-}C_5H_5)_2Co_2(C_{13}H_4F_{12})$ (R_f 0.52, brown, mp 143 °C, yield 15.2 mg (1.9%)), and IV, $(\eta\text{-}C_5H_5)_2Co_2(C_{13}H_6F_{12})$ (R_f 0.44, green, mp >360 °C, yield 24.4 mg (3.0%). Anal. Calcd: C, 43.26; H, 2.57; F, 35.74. Found: C, 43.67; H, 2.51; F, 34.91.), were collected.

The fourth band of the initial separation (R_f 0.14) yielded several new bands upon redevelopment in 50/50 methylene chloride/benzene. The first two of these bands (R_f 0.91 and 0.88) were not collected due to their small yields, but pure IX was isolated, $(\eta\text{-}C_5H_5)_3Co_3\text{-}(C_4F_6)(CO)$ (R_f 0.60, brown, mp 181 °C dec, yield 8.0 mg (1.7%)). The final band using this developing mixture was rechromatographed in an 80/20 chloroform/benzene mixture to yield two minor bands not collected and a brown band, X, $(\eta\text{-}C_5H_5)_2Co_2(C_8F_{12}O)$ (R_f 0.45,

Table III. Infrared Spectra (cm^{-1})

I^a 2970 w, 1424 m, 1374 m, 1312 w, 1260 vs, 1241 m, 1199
           s, 1170 vs, 1148 s, 1130 s, 1107 m, 1030 w, 881 w, 850
           w, 830 w

II^b 2977 w, 1420 m, 1325 s, 1280 w, 1123 w, 1090 vs, 979 m,
           913 s, 647 m

III^c 2935 m, 2863 w, 1450 m, 1360 s, 1279 m, 1100 s, 978 m,
           880 w, 855 w, 642 m

IV^c 1668 w, 1431 w, 1342 m, 1330 m, 1289 s, 1272 sh, w,
           1240 m, 1168 s, 1157 s, 1119 vs, 1088 s, 1057 w, 1032
           w, 1014 w, 1000 w, 922 w, 830 m, 762 w, 651 m, 622 w

V^c 2950 w, 2920 m, 1429 m, 1392 w, 1323 s, 1232 m, 1217
           w, sh, 1152 vs, 1110 vs, 1090 vs, 1010 w, 993 w, 952 w,
           819 s, 789 m, 648 m, 620 w

VI^c 2924 m, 2859 w, 1460 w, 1367 w, 1323 w, 1288 m, 1254
           s, 1198 s, 1183 s, 1139 m, 1092 s, 1013 m, 860 m, 792
           s, 743 w, 648 m

VII^c 2965 w, 2863 w, 1415 m, 1372 m, 1353 m, 1288 w, 1257
           s, 1239 s, 1221 m, 1150 s, 1138 vs, 1115 vs, 1010 m,
           941 m, 831 m, 818 m, 747 w, 728 w, 707 w, 639 m,
           562 w

VIII^b 2912 m, 2860 w, 1720 m, 1278 m, br, 1089 s, 997 w, 962
           s, 520 w

IX^c 2930 m, 2860 w, 1739 w, 1698 s, 1413 m, 1300 m, 1271
           m, 1230 m, 1189 vs, 1128 s, 1097 s, 1008 w, 847 w, 829
           m, 811 m, 722 w, 698 m, 632 w

X^b 1510 m, 1471 m, 1417 m, 1100 w, 1223 s, 1182 s, 1039
           m, 1026 m, 920 s, 868 m, 840 w, 800 s, 778 s, 700 m,
           650 w

XI^c 1472 w, 1370 m, 1327 w, 1269 vs, 1232 s, 1191 vs, 1163
           vs, 1146 vs, 1107 s, 1090 s, 1019 w, 823 w, 654 m, 618 m

XII^c 2955 m, 2920 w, 2865 w, 1475 w, 1444 w, 1374 m, 1352
           m, 1280 m, 1267 s, 1221 vs, 1191 vs, 1150 vs, 1101 s,
           1082 s, 1017 m, 1004 m, 820 w, 797 w, 652 m, 631 m

XIII^b 1508 m, 1479 w, 1420 m, 1375 m, 1322 m, 1271 m, 1220
           s, 1188 s, 1107 m, 1038 s, 920 s, 870 m, 843 m, 789 s,
           618 m

XIV^b 1475 w, 1423 m, 1375 w, 1341 m, 1276 m, 1221 s, 1190
           s, 1104 w, 1027 m, 931 m, 844 w, 622 w

XV^b 3100 w, 2998 w, sh, 2941 m, 2908 m, 2856 w, 1599 s,
           1572 w, sh, 1492 s, 1440 m, 1409 w, 1400 w, 1350 w,
           br, 1310 w, 1107 m, 1070 m, 1011 w, 995 m, 898 w,
           831 w, 796 m, 689 s

XVI^b 3010 m, 2920 m, 1590 s, 1565 m, 1475 m, 1438 m, 982
           w, 800 m, 677 s

^{a} Solution (CCl$_4$ vs. CCl$_4$). ^{b} Solution (CHCl$_3$ vs. CHCl$_3$).
^{c} KBr pellet.

brown, mp 78 °C dec, yield 3.8 mg (0.5%)).

Additionally, the origin of the initial purification was extracted with ethyl acetate. However, no organometallics were isolated from this fraction. Finally, trace amounts of hexakis(trifluoromethyl)-benzene were also identified in this reaction.

Cobalt Atoms + Pentamethylcyclopentadiene + Hexafluoro-2-butyne. Approximately 0.6 g of cobalt was cocondensed with 10 mL of each ligand at −196 °C (~100 mmol of pentamethylcyclopentadiene, ~50 mmol of hexafluorobutyne). The matrix was allowed to warm to room temperature after metal deposition was complete. Extraction of the nonvolatile residue with methylene chloride gave the crude product mixture which was purified by TLC.

Initial separation of the crude product by TLC using a 70/30 hexane/methylene chloride developing mixture yielded several bands of various colors, but only the most mobile band (R_f 0.90) was collected in sufficient yields to completely purify. This band was then further purified by 80/20 hexane/methylene chloride TLC to yield two orange bands, compound XI, (η-C$_5$(CH$_3$)$_5$)Co(C$_8$H$_2$F$_{12}$) (R_f 0.65, orange, mp 186 °C, yield 224.6 mg (17.0%)). Anal. Calcd: C, 41.54; H, 3.27; F, 43.85. Found: C, 41.80; H, 3.45; F, 43.61), and compound XII, (η-C$_5$(CH$_3$)$_5$)$_2$Co$_2$(C$_8$F$_{12}$) (R_f 0.76, orange, mp 272–273 °C, yield 109.6 mg (13.2%)). Anal. Calcd: C, 47.19; H, 4.21; F, 32.02. Found: C, 47.43; H, 4.21; F, 32.27).

Cobalt Atoms + Cyclopentadiene + 3,3,3-Trifluoropropyne. The same general procedure detailed above was employed to cocondense cobalt atoms, cyclopentadiene (~120 mmol) and trifluoropropyne (~50 mmol) at −196 °C. In separate reactions the matrix was either warmed directly to room temperature or kept at an intermediate temperature (−78 or −95 °C) for 0.5–1 h and then allowed to warm

to room temperature. Comparison of the various reaction conditions did not reveal any major differences in product formation although some minor differences in product distribution were apparent. In all cases the reactions were worked up as previously through extraction of the nonvolatile residue with methylene chloride followed by product separation by TLC.

Due to the unsymmetrical nature of the alkyne, this reaction would be expected to produce a large number of products. In fact, 30 distinct compounds are observable by various TLC methods, all but two of which were not isolable in sufficient quantities to characterize (>3 mg).

Separation of the crude reaction mixture was achieved by TLC (CCl$_4$ or 70/30 hexane/methylene chloride). A brown band of this separation (R_f 0.55) was found to contain the major product of this reaction. RP-TLC (98/2 methanol/water developing system) was used to purify this band and yielded complex XIII, (η-C$_5$H$_5$)$_2$Co$_2$-(C$_9$H$_5$F$_9$) (R_f 0.84, brown, mp 206–208 °C, yield 29.8 mg (4.3%)). A second band (R_f 0.70) of the initial separation was rechromatographed in a 65/35 hexane/methylene chloride TLC developing system which yielded XIV, (η-C$_5$H$_5$)$_2$Co$_2$(C$_6$H$_4$F$_6$) (R_f 0.61, red-brown, mp 159–160 °C, yield 5.2 mg (0.9%)).

Cobalt Atoms + Cyclopentadiene + Diphenylacetylene. The cobalt and cyclopentadiene were cocondensed as previously and then this matrix was allowed to melt into an excess of diphenylacetylene (3 g, ~20 mmol) in the bottom of the reaction vessel. The reaction mixture was stirred during warmup and also for an additional 0.5 h, and then the reaction was worked up by using previously described procedures.

Column chromatography (methylene chloride/silica gel) was employed to remove the nonmobile portion of the crude reaction mixture which did not contain any organometallics. Next sublimation of the mobile fraction removed excess diphenylacetylene and also the small amount of hexaphenylbenzene produced in this reaction (identified by high-resolution mass spectrometry). Further purification was achieved by TLC (80/20 hexane/methylene chloride) which yielded three bands. The most mobile band (R_f 0.38, yellow) was identified as the known cyclobutadiene complex (η-C$_5$H$_5$)Co(C$_4$Ph$_4$) by its mass spectrum (M$^+$ calcd 480.1288, found 480.1267) and mp 258–260 °C (lit.[12] 262 °C) and collected in 6.1% yield (74.8 mg). Also isolated were XV, (η-C$_5$H$_5$)Co(C$_{33}$H$_{26}$) (R_f 0.30, orange, mp 204 °C, yield 90.2 mg (6.5%)), and XVI, C$_{33}$H$_{26}$ (R_f 0.34, white, mp 170–178 °C, yield 5.2 mg).

Results

The reactions of cobalt atoms with cyclopentadiene (C$_5$H$_6$ or C$_5$(CH$_3$)$_5$H) and several alkynes such as hexafluoro-2-butyne, 3,3,3-trifluoropropyne, and diphenylacetylene were explored. In general, compounds derived from these alkyne reactions were characterized by NMR, IR, high-resolution exact mass determinations (on both the parent and fragmentation ions), and, where sufficient quantities of material produced, elemental analysis. All compounds exhibited characteristic mass spectral fragmentation (Table II) consistent with those formulations given below, such as initial loss of C$_5$R$_5$Co or C$_5$R$_5$CoF (R = H or CH$_3$). Additionally, monometal complexes are indicated by the appearance of a C$_5$R$_5$Co peak while multimetal systems characteristically show a C$_{10}$R$_{10}$Co peak as well.

The following comments pertain to the structural assignment of each compound isolated.

Complexes Derived from the Reaction of Cobalt Atoms, Cyclopentadiene, and Hexafluoro-2-butyne. (η-C$_5$H$_5$)Co-(C$_8$H$_2$F$_{12}$) (I). The product formed in the greatest amounts was assigned the butadiene structure (I) on the basis of the spectroscopic data. Thus the ^{1}H NMR spectrum shows, in addition to the cyclopentadienyl resonance at 5.11 ppm, a quartet of intensity 2 at −0.30 ppm (J = 10.5 Hz) which can be assigned to the protons on the butadiene fragment which are coupled to geminal trifluoromethyl groups. The unusual high-field shift of these protons is characteristic of the anti-protons of coordinated butadiene complexes and has previously

(12) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).

I
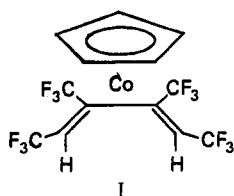
been suggested[13] to indicate a partial σ character for the bonds between cobalt and the terminal carbons of the butadiene. As expected the ^{19}F NMR spectrum shows two separate resonances of equal intensity, each with complicated fine structure. Finally, that both double bonds are indeed coordinated is supported by the infrared spectrum which shows no absorption in the free $\nu_{C=C}$ region.

(η-C$_5$H$_5$)Co(C$_9$H$_6$F$_6$) (II). A second yellow monometal complex obtained in this reaction exhibited spectroscopic data consistent with a cyclopentadienyl cobalt bound to a norbornadienyl unit formed by the cycloaddition of a hexafluorobutyne and a cyclopentadiene (II). The ^{19}F NMR

II
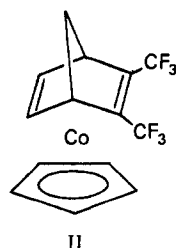
spectrum shows a sharp signal consistent with a trifluoromethyl group on an sp^2 carbon and in agreement with the proposed structure. However, the ^1H NMR spectra consist of only three separate resonances instead of the expected four. This is attributed to an accidental overlap of the bridgehead and olefinic protons which gives a single resonance of intensity 4 at 3.28 ppm. Such an accidental equivalency had previously been observed[14] in the ^1H NMR spectrum of the structurally similar norbornadiene complex, (C$_7$H$_8$)Fe(CO)$_3$. The absence of free $\nu_{C=C}$ bands in the infrared again supports both double bonds being coordinated.

(η-C$_5$H$_5$)Co(C$_{13}$H$_6$F$_{12}$) (III). A third monometal complex involves a cyclopentadienyl cobalt bound to a ligand formed from the double cycloaddition of two hexafluorobutynes to one cyclopentadiene and was assigned a structure similar to II on the basis of spectroscopic data. Unlike II though, the ^1H NMR of III does contain the expected four resonances with

III
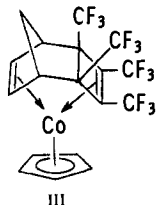
peaks of equal intensity at 4.43 and 2.22 ppm due to the olefinic and bridgehead protons, respectively, as well as peaks attributable to the cyclopentadienyl and methine protons. The ^{19}F NMR spectrum shows two resonances of equal intensity in the same general shift region as II, each with complicated fine structure. This indicates that both hexafluorobutyne units are adjacent as shown; if nonadjacent, then two singlets would be observed. Again the absence of a free $\nu_{C=C}$ band in the

(13) G. Vitulli, L. Porri, and A. L. Segre, *J. Chem. Soc. A*, 3246 (1971).
(14) (a) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 989 (1960); (b) M. Tsutsui, M. Levy, A. Nakamura, M. Ichikawa, and K. Muri, "Introduction to Metal π-Complex Chemistry", Plenum Press, New York, 1970, p 64.

infrared spectrum supports that both double bonds are coordinated.

(η-C$_5$H$_5$)$_2$Co(C$_{13}$H$_6$F$_{12}$) (IV). This compound consists of a central ligand which is formed by the addition reaction of a hexafluorobutyne molecule and cyclopentadiene. The spectroscopic data indicate that this ligand is bound to one metal in a butadiene fashion similar to I and to a second metal in an η^2 fashion. Thus the ^1H NMR spectrum shows two inequivalent cyclopentadienyls as singlets of intensity 5 at 4.96 and 4.46 ppm as well as resonances attributable to the substituted cyclopentadiene ring shown in the proposed structure (IV). The ^1H NMR also exhibits a quartet of intensity 1 at

IV
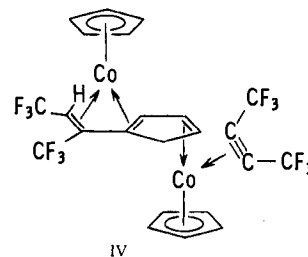
−0.49 ppm (J = 13.5 Hz) which is characteristic of the fluorine-coupled antiproton of a coordinated butadiene as observed previously in I. The ^{19}F NMR is also in agreement with the proposed structure as it shows the characteristic quartet and multiplet for the fluorines of a coordinated bis-(trifluoromethyl)vinyl group. The ^{19}F NMR also shows two other resonances of equal intensity which are assigned to a hexafluorobutyne which is η^2 bound to the second metal. Since the trifluoromethyls are inequivalent, they are coupled and appear as quartets. The chemical shifts of these quartets reflect the reduction of the acetylenic bond order upon coordination and are observed at relatively high field. Additionally, the infrared spectrum shows an adsorption attributable to a coordinated carbon–carbon triple bond (1668 cm^{-1}) as well as bands indicating trifluoromethyl and cyclopentadienyl groups.

(η-C$_5$H$_5$)$_2$Co$_2$(C$_9$H$_8$F$_6$) (V). The structure of this compound was deduced from both ^1H and ^{19}F NMR data and consists of a flyover-bridged two-metal system formed from the addition of a hexafluorobutyne to an opened cyclopentadiene.


V
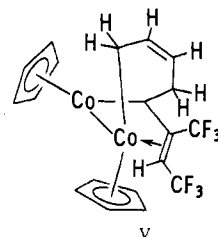
The NMR exhibits resonances due to inequivalent cyclopentadienyl groups as singlets of intensity 5 (5.0 and 4.64 ppm). Additionally complex resonances at 3.35 (=CH), 2.10 and 1.93 (Co–CH$_2$), 1.78 (CH), and 1.62 ppm (CH$_2$) can be attributed to the protons on the bridging unit. Finally the ^1H NMR also shows the characteristic quartet at high field (−0.48 ppm, J = 13.4 Hz) due to the fluorine-coupled proton of the bis(trifluoromethyl)vinyl group. The inequivalent trifluoromethyls of this group are again observed in the ^{19}F NMR spectrum as a quartet and multiplet of equal intensity with chemical shifts similar to those observed for this group in IV.

(η-C$_5$H$_5$)$_2$Co$_2$(C$_{13}$H$_4$F$_{12}$) (VI). This compound is related to IV and also contains a central ligand formed by the addition reaction of hexafluorobutyne to cyclopentadiene, but in this case a second alkyne has added to yield a closed ring. The ^1H NMR of VI exhibits resonances attributable to the two inequivalent cyclopentadienyl groups (5.01 and 4.73 ppm) and
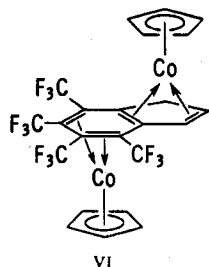
VI

also the complex resonances of the protons on the substituted cyclopentadiene (6.41 ppm, =CH, and 0.72 ppm, CH$_2$). The ^{19}F NMR spectrum shows four complex resonances of equal intensity due to the coupling of the four inequivalent trifluoromethyl groups. All of the double bonds in the proposed structure are shown to be coordinated, as would be expected by the lack of any absorptions in the free $\nu_{C=C}$ region of the infrared spectrum.

(η-C$_5$H$_5$)$_2$Co$_2$(C$_8$H$_2$F$_{10}$) (VII). Elemental and mass spectral analysis of this compound indicated that it contained ten fluorines and thus must contain fluorine groups other than just trifluoromethyls. The structure shown (VII) is based on the
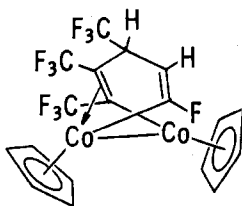

VII

established composition and supported by both ^{1}H and ^{19}F NMR data. The structure consists of a two-metal system bridged by a flyover unit formed by the addition of two hexafluorobutynes, protonation of one of these, elimination of F$_2$, and finally rearrangement. The ^{1}H NMR exhibits inequivalent cyclopentadienyl resonances and two other resonances. The first of these is observed at 3.60 ppm as a doublet of doublets and can be assigned to the vinyl proton coupled to the vicinal fluorine (J = 14.8 Hz) and also coupled to the –CHCF$_3$ proton (J = 1.4 Hz). The second proton is observed at 2.82 ppm as a doublet of quartets coupled not only to the vinyl proton but also to the geminal trifluoromethyl group (J = 7.0 Hz). The ^{19}F NMR spectrum supports this structural assignment further and consists of four resonances indicative of this formulation. A doublet at relatively low field of intensity 1 is assignable to the lone fluorine coupled to the adjacent proton (J = 14.8 Hz). The shift of this fluorine (17.84 ppm) is anomalously low perhaps due to its proximity to the metal. A quartet of intensity 3 is attributed to the terminal vinyl trifluoromethyl group coupled to the other vinyl trifluoromethyl. This vinyl trifluoromethyl and the remaining trifluoromethyl group are then observed as multiplets due to both fluorine–fluorine and proton–fluorine coupling.

(η-C$_5$H$_5$)$_3$Co$_3$(C$_4$F$_6$) (VIII). Analogous compounds of this general type have been previously reported and recognized to be electron deficient; that is, they do not have enough electrons to account for the bonding in terms of two-center, two-electron bonds. The application of simple cluster electron counting rules[15] predicts a gross structure for VIII on the basis of a trigonal-bipyramidal geometry such as the one shown diagrammatically.

This geometry has been previously proposed[16] for the (η-C$_5$H$_5$)$_3$M$_3$(C$_6$H$_5$C)$_2$ (M = Rh, Ir) and confirmed by an X-ray
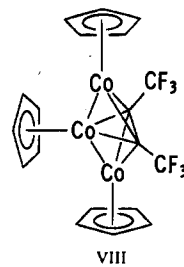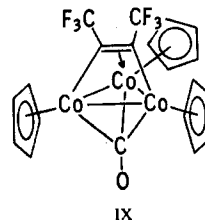

VIII

investigation for the compound (C$_6$H$_5$C)$_2$Fe$_3$(CO)$_9$.[17]

The ^{19}F NMR of VIII which consists of only one sharp singlet is in agreement with the proposed structure, but the similarly simple ^{1}H NMR spectrum (also only one singlet) seems at first to contradict this structure since at least two resonances would be expected due to inequivalent cyclopentadienyls. However, similar simple ^{1}H NMR spectra have been observed[16] for the related rhodium and iridium complexes. This behavior has been shown to arise from the fluxionality of these molecules at room temperature, and indeed, a variable-temperature ^{1}H NMR study of VIII resolved the cyclopentadienyl resonances into two distinct peaks (1:2 ratio) at approximately –78 °C.

(η-C$_5$H$_5$)$_3$Co$_3$(C$_4$F$_6$)(CO) (IX). Compounds analogous to IX, such as (η-C$_5$H$_5$)$_3$Rh$_3$(C$_4$F$_6$)(CO)[18] and (η-C$_5$H$_5$)$_3$Rh$_3$-(C$_6$H$_5$C)$_2$(CO), have previously been synthesized and demonstrated to adopt a structure similar to the one shown for IX.

IX

This structure is also in agreement with the cluster electron counting rules[15] which predict an overall geometry for VIII on the basis of a square-based pyramid.

The composition of VIII was established by the mass spectrum which exhibits a parent peak at m/e 561.9021 with an initial loss of the carbonyl readily observable as a peak at m/e 533.9053. The infrared spectrum of IX also shows the presence of CO with an absorption due to a triply bridging carbonyl at 1698 cm^{-1}. Additionally, the ^{19}F NMR spectrum exhibits a single resonance due to the equivalent trifluoromethyl groups. Like VIII, two resonances would be expected in the ^{1}H NMR for the structure shown, but only one sharp singlet is observed at room temperature. Complexes of this type have also been suggested to be fluxional,[16] and this is supported by the broadening of the ^{1}H NMR signal for IX as the temperature is lowered.

Finally, it should be noted that the source of the carbonyl is unknown although it may be due to oxide contamination of the cobalt metal. Previous incorporation of CO has been noted[4] in metal atom reactions involving the formation of metalloboranes in the absence of carbon monoxide as a ligand.

Trace Products. This reaction also resulted in a number of other products which were not possible to isolate and characterize due to their low yields (less than 0.5%). One of these products was, however, partially characterized by spectroscopic means although a definite structural representation could not be deduced from the data. Its high-resolution mass spectrum exhibited a parent ion at m/e 587.9185 which could correspond to (η-C$_5$H$_5$)$_2$Co$_2$(C$_8$F$_{12}$O) (X). The

(15) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972).
(16) S. A. Gardner, M. D. Rausch, and P. S. Andrews, *Inorg. Chem.*, **12**, 2396 (1973).

(17) J. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Am. Chem. Soc.*, **88**, 292 (1966).
(18) R. S. Dickson and H. P. Kirsch, *Aust. J. Chem.*, **25**, 2535 (1972).

X
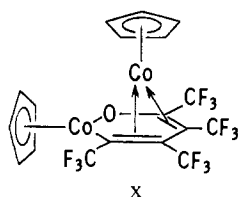
NMR spectra were supportive of this formulation with the ^{1}H NMR showing only two resonances due to the equivalent cyclopentadienyls and the ^{19}F NMR exhibiting four resonances of equal intensities. Two of these ^{19}F resonances were observed as quartets and the other two as complex multiplets. The structure shown could be proposed to account for these spectroscopic data, but enough doubt is present to prevent a definite structural assignment.
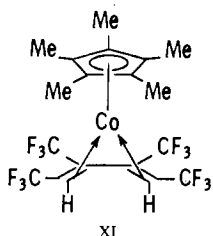
Complexes Derived from the Reaction of Cobalt Atoms, Pentamethylcyclopentadiene, and Hexafluoro-2-butyne. (η-C$_5$Me$_5$)Co(C$_8$H$_2$F$_{12}$) (XI). The product formed in the greatest amounts in this reaction was assigned a butadiene structure similar to I on the basis of spectroscopic and analytical data. The ^{1}H NMR spectrum of XI exhibits a singlet of intensity

XI

15 at 2.19 ppm due to the cyclopentadienyl methyl groups as well as a characteristic upfield quartet at −0.25 ppm (J = 11.3 Hz) assignable to the butadiene protons. As expected the ^{19}F NMR spectrum of XI is similar to that of compound I and shows two complex resonances of equal intensity at similar chemical shifts.

(η-C$_5$Me$_5$)$_2$Co$_2$(C$_8$F$_{12}$) (XII). A dinuclear compound was also obtained in this reaction and assigned its composition only on the basis of elemental analysis due to the lack of an observed parent peak in the mass spectrum of XII. Its ^{1}H NMR is quite simple exhibiting only a single sharp resonance at 1.61 ppm which is assignable to the methyl groups of the cyclopentadienyl ligands. In contrast, the ^{19}F NMR spectrum of XII exhibits two complex resonances of equal intensity. The structure assigned on the basis of these spectroscopic data is the metallocyclopentadiene (XII).


XII
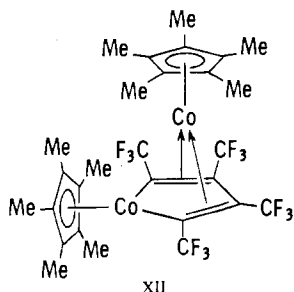
Although XII was previously unknown, compounds of this general type have been synthesized by other methods.[16] The known metallocyclopentadienes contain unsubstituted cyclopentadiene and exhibit at least two resonances in their ^{1}H NMR spectra due to the inequivalency of the cyclopentadienyl groups. Further investigations have shown that these complexes exhibit fluxional behavior and heating causes collapse of the two resonances to one peak. The metallocyclopentadiene structure is assigned to XII even though two methyl resonances are not observed for the inequivalent pentamethylcyclo-

pentadienyls. The methyl protons are presumably less sensitive to the slight inequivalency of the cyclopentadienyls, and therefore only one resonance is observed in the ^{1}H NMR spectrum.

Additionally, this structure is consistent with cluster electron counting rules. Thus compound XII contains 16 skeletal electrons or eight pairs and is therefore an $n + 2$ or nido case since there are six cage atoms. The structure can then be considered as a pentagonal bipyramid with one vertex removed.

Complexes Derived from the Reaction of Cobalt Atoms, Cyclopentadiene, and 3,3,3-Trifluoropropyne. (η-C$_5$H$_5$)$_2$Co$_2$-(C$_9$H$_5$F$_9$) (XIII). The main product obtained in this reaction was determined to consist of a two-metal system bridged by a flyover unit formed from the condensation of three trifluoropropynes. The NMR data for XIII are complex, but either of the structures shown (XIIIa,b) is in agreement with

XIIIa   XIIIb
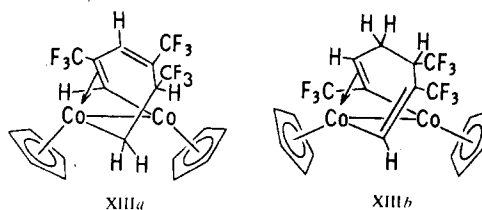
the spectroscopic results. Thus the ^{1}H NMR spectrum consists of two inequivalent cyclopentadienyls (4.77 and 4.74 ppm) and three additional resonances. A singlet of intensity 1 is observed at 4.96 ppm due to the central vinyl proton in both cases, while a similar singlet of intensity 1 is attributable to the vinyl proton on the carbon bound to the metal and is appropriately shifted upfield (2.02 ppm). The lack of coupling in the central vinyl proton in structure XIIIb can be explained upon close examination. Vicinal coupling in this type of system would be expected to be approximately 2–3 Hz; however, it has been shown that several factors such as the presence of electron-withdrawing substituents (trifluoromethyls) or actual geometry (dihedral angle of coupled protons) result in decreased coupling,[19] in some cases less than 1 Hz. Thus, the coupling of the vicinal protons in XIIIb could easily be less than the spectrum line width and therefore not observed. In both structural cases, a complex multiplet of intensity 3 centered at 3.98 ppm can be assigned to overlapping resonances of the remaining protons. These protons would be coupled to each other, and the single proton geminal to the trifluoromethyl group would be coupled to it, thus yielding the complex multiplet observed.

Further support of both these proposed structures is seen in the ^{19}F NMR data. The spectrum exhibits a singlet, quartet, and doublet of quartets, all of equal intensity. In the case of XIIIa, the singlet can be assigned to the trifluoromethyl group of the vinyl group directly bound to a cobalt. The other vinyl trifluoromethyl group is coupled to the remaining sp^3 trifluoromethyl and is therefore observed as a quartet. The final resonance, the doublet of quartets, is then attributable to the sp^3 trifluoromethyl which is coupled not only to the vinyl trifluoromethyl but also to the geminal proton. The quartet and doublet of quartets are similarly assigned in XIIIb but in this case the singlet observed in the ^{19}F NMR spectrum is due to the trifluoromethyl on the carbon directly bound to a cobalt. This would account for the slight upfield shift (to 60.27 ppm) of this singlet as compared to the other vinyl trifluoromethyl (59.09 ppm).

On consideration of the chemical shifts of the sp^3 protons as well as the most desirable structure for the olefin–metal interaction, XIIIb would then appear to be the most likely

(19) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, p 135.

structure for $(\eta\text{-}C_5H_5)_2Co_2(C_9H_5F_9)$.

$(\eta\text{-}C_5H_5)_2Co_2(C_6H_4F_6)$ **(XIV).** Another complex isolated from the trifluoropropyne reaction was determined to have a bridged dinuclear vinyl structure on the basis of spectroscopic data. This type of structure was recently established[20] by an X-ray diffraction study for the similar complex $[Rh_2(CH\!\!=\!\!CH_2)(CMe\!\!=\!\!CHMe)(\eta^5\text{-}C_9H_7)_2]$. The symmetrical nature of XIV results in simple ^1H and ^{19}F NMR spectra. The ^1H

XIV
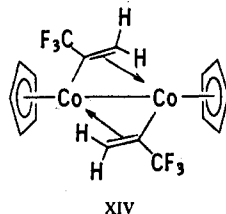
NMR exhibits a singlet due to the equivalent cyclopentadienyl groups and also a doublet ($J = 3.0$ Hz) attributable to the vinyl proton cis to the trifluoromethyl and geminally coupled to the trans vinyl proton. The resonance of this trans proton is observed as a poorly resolved doublet at 0.42 ppm apparently being shifted upfield due to its proximity to the metal. A single sharp peak is observed in the ^{19}F NMR spectrum of XIV indicating equivalent trifluoromethyl groups and the absence of any proton–fluorine coupling. Coupling of this type is not observed in the ^1H NMR spectrum either, although vinyl complexes with a proton cis to trifluoromethyl groups generally exhibit couplings on the order of 2 Hz. The absence of proton–fluorine coupling in a similar case, $Co_2(CO)_6(CF_3C_2H)$,[21] has been attributed to a reduction of the acetylenic triple bond order of (CF_3C_2H) to something less than two which would then not exhibit observable proton–fluorine coupling ($J_{CH-CCF_3} = 0$). Thus coordination of the vinyl group in XIV must reduce the double bond order to something less than two, and therefore no proton–fluorine coupling is observed. Both vinyl groups are, in fact, shown to be coordinated by the lack of any absorptions in the free $\nu_{C=C}$ region in the infrared spectrum of XIV.

Complexes Derived from the Reaction of Cobalt Atoms, Cyclopentadiene, and Diphenylacetylene. This reaction yielded three previously known compounds, two of which, the cyclobutadiene $(\eta\text{-}C_5H_5)Co(C_4Ph_4)$ (Ph = C_6H_5) and the alkyne trimer hexaphenylbenzene, were obtained in the analogous thermal reaction.[12] The third known compound isolated was 5,9-dihydro-1,2,3,4-tetraphenylindene, XVI, which had previously been found[22] in the reaction of (tetraphenylcyclobutadiene)palladium dichloride dimer with cyclopentadiene in the presence of triphenylphosphine but was not completely characterized. The remaining complex isolated in this reaction was the cyclopentadienyl cobalt complex of this dihydroindene which is related to compound VI in that they both involve addition of two alkynes to a cyclopentadiene to yield a closed ring.

$(\eta\text{-}C_5H_5)Co(C_{33}H_{26})$ **(XV).** The cyclopentadienyl cobalt complex of the dihydroindene was initially identified by its high-resolution mass spectrum. Structural assignment was

XV
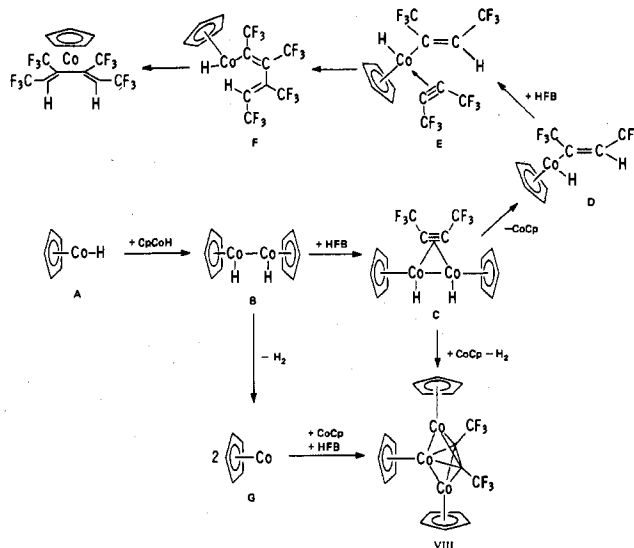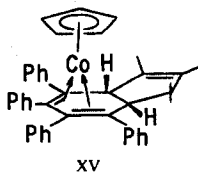
Figure 1. Possible reaction pathway for the formation of butadiene complexes and multimetal clusters in the reaction of cobalt atoms, cyclopentadiene, and hexafluorobutyne.

based on isolation of the organic ligand (XVI) as well as spectroscopic data on the cobalt complex. The ^1H NMR is complex but similar to the unsubstituted dihydroindene complex of iron, $C_9H_{10}Fe(CO)_3$.[23] Thus the complex multiplet centered at 7.02 ppm is easily assigned to the phenyl protons as is the singlet at 4.56 ppm assigned to the cyclopentadienyl group. The remaining resonances can be attributed to the olefinic (5.53 and 5.36 ppm), bridgehead (3.88 and 3.61 ppm), and methylene (2.48 and 2.08 ppm) protons on the basis of their chemical shifts. The infrared spectrum of XV exhibits several bands in the free $\nu_{C=C}$ region which can be attributed to both the uncoordinated double bond of the indene and also the phenyl groups.

Discussion

In general, the major products obtained from the metal atom reactions of the alkynes investigated fall into several categories: (1) complexes containing ligands resulting from alkyne dimerization or trimerization usually accompanied by hydrogen addition yielding butadienes or flyover-bridged systems, such as compounds I, VII, XI, XIII, and XIV; (2) multimetal clusters containing cyclopentadienyl cobalt units and alkynes such as compounds VIII, IX, and XII; (3) complexes containing ligands resulting from cycloaddition of cyclopentadiene and alkynes including compounds II and III; (4) complexes containing ligands resulting from simple additions of cyclopentadiene and alkynes such as compounds IV, V, VI, and XV. Examination of these products suggests the formation of certain reactive intermediates and allows the development of an appropriate reaction pathway. This is illustrated for the hexafluoro-2-butyne reaction in Figures 1 and 2 and discussed in detail below.

The basic intermediate can actually be envisioned as coming about by insertion of the metal into a C–H bond to yield $(\eta\text{-}C_5H_5)CoH$ which can rearrange to $(\eta^5\text{-}C_5H_5)CoH$ (A). The formation of this fragment is consistent with previously proposed mechanisms[1] for reactions of metal atoms with cyclopentadiene. This intermediate (A) can then dimerize to produce the metal–metal bound dihydride (B) which is coordinatively unsaturated (16 electrons for each cobalt) and would be expected to try to achieve saturation through coordination of another ligand.
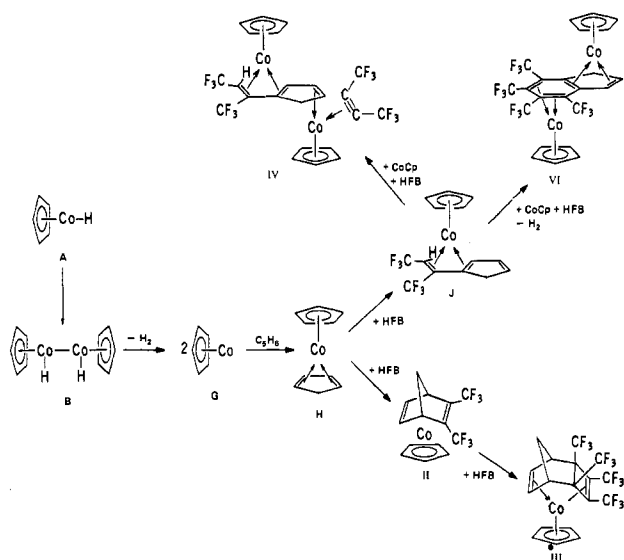
(20) P. Caddy, M. Green, L. E. Smart, and N. White, *J. Chem. Soc., Chem. Commun.*, 839 (1978).
(21) D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. A*, 1765 (1968).
(22) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

(23) G. Deganello, H. Maltz, and J. Kozarich, *J. Organomet. Chem.*, **60**, 323 (1973).

Figure 2. Possible reaction pathway for the formation of cycloaddition and simple addition complexes in the reaction of cobalt atoms, cyclopentadiene, and hexafluorobutyne.

This pathway (illustrated in Figure 1) is one of the several reaction pathways available for (B) and demonstrates the formation of alkyne-dimerized and cluster products discussed above. To form the butadiene complex, the dimer (B) could coordinate hexafluorobutyne (C) in a similar fashion to the well-known reactions for cobalt octacarbonyl and certain cyclopentadienyl cobalt compounds with alkynes.[24] Subsequent hydride transfer and loss of a cyclopentadienyl cobalt unit (D) generates another 16-electron intermediate which could bind an additional hexafluorobutyne (E). Migration of the vinyl group such as previously observed in reactions of hexafluorobutyne with iron and ruthenium complexes[25] would yield (F) which can then rearrange to I, the final product.

Alternatively, the dimer (B) could lose hydrogen to yield two cyclopentadienyl cobalt units (G). Cluster formation then can be achieved by trimerization of cyclopentadienyl cobalt units with coordination of hexafluorobutyne to yield VIII. This product could also be produced through intermediate (C) by addition of a cyclopentadienyl cobalt and loss of hydrogen.

The formation of several cycloaddition and simple addition complexes of hexafluorobutyne and cyclopentadienyl cobalt is illustrated in Figure 2. A cyclopentadienyl cobalt unit (G) could bind a cyclopentadiene to yield (H) which is the final product in the reaction of cobalt atoms with just cyclopentadiene.[10] In the presence of hexafluorobutyne, however, this compound can react further to yield the cycloaddition and double cycloaddition products II and III, perhaps through a $(\eta\text{-}C_5H_5)Co(\eta^2\text{-}C_5H_6)(\eta^2\text{-}C_4F_6)$ intermediate. Alternatively, the hexafluorobutyne could insert into the Co–C bond of an $(\eta\text{-}C_5H_5)CoH(\eta^5\text{-}C_5H_5)$ intermediate (not shown) followed by hydride transfer and rearrangement to intermediate (J). Formation of both IV and VI is then possible by addition of cyclopentadienyl cobalt and hexafluorobutyne, in one case (VI) to give the closed ring and in the other to yield the η^2-alkyne (IV).

It should be noted that while the schemes presented in Figures 1 and 2 allow for the formation of all the major products, there is no definite proof that this is indeed the actual mechanism, and several other reaction pathways may also be valid.

The reaction pathways illustrated in Figure 2 demonstrate that many of the products formed in the reaction of cobalt atoms, cyclopentadiene, and hexafluorobutyne result from reactions between the alkyne and cyclopentadiene. Elimination of these addition and insertion reactions could increase the specificity of the reaction and conceivably increase the yields of the resultant products. Therefore, pentamethylcyclopentadiene was employed in a similar reaction which was hoped to proceed only along those reaction pathways of the reaction scheme which did not contain alkyne–cyclopentadiene interactions (Figure 1) due to the increased steric hindrance of the methyl groups. The assumption was also made that the electron-releasing methyl groups would not greatly affect the reaction course. In fact, the number of products produced in the pentamethylcyclopentadiene reaction was much lower than found for the unsubstituted cyclopentadiene, and the products isolated appear to arise only from the reaction pathway illustrated in Figure 1. The product formed in the greatest amount was again assigned a butadiene structure, XI, analogous to compound I with, however, a higher yield than I (19% vs. 12.6%) in support of the proposed reaction. The formation of the cluster XII is also consistent with the assumption that this reaction does not involve intermediates containing alkyne–cyclopentadiene interactions. Somewhat surprisingly though, the formation of three metal clusters, an expected reaction pathway, was not observed for this pentamethylcyclopentadiene reaction. This may be due to the differences in steric and electronic effects between the substituted and unsubstituted cases.

The additional metal atom reactions involving cobalt atoms, cyclopentadiene, and alkynes can also be considered as following similar reaction pathways to those detailed in Figures 1 and 2. For example, the reaction of trifluoropropyne was naturally more complex than the hexafluorobutyne reaction due to the unsymmetrical nature of the alkyne leading to the formation of a great number of products, but the major products isolated could easily be formed from similar intermediates to those shown in Figure 1. That is, both the dinuclear vinyl compound XIV and the flyover-bridged XIII could arise from the trifluoropropyne intermediate analogous to (C) (in Figure 1) by the addition of one or two trifluoropropynes, respectively, followed by rearrangement. Similarly, the diphenylacetylene reaction could also proceed through intermediates analogous to those postulated for the hexafluorobutyne reaction. Thus the cyclobutadiene complex could be formed identically with the butadiene compex, I, but followed by loss of hydrogen from the butadiene unit and cyclization. The formation of a cyclobutadiene rather than a butadiene is not unexpected since this affords aromatic stability to the complex. Among the reactions studied, however, this is likely only in the case of diphenylacetylene since the conjugation of the phenyl substituents is necessary to stabilize these rings.[26] The other diphenylacetylene product, the tetraphenyldihydroindene complex XV, is similar to compound VI of the hexafluorobutyne reaction and is therefore postulated to arise from similar intermediates.

It is of interest to compare the types of products obtained by more conventional techniques. For example, the thermal reaction[27] $(\eta\text{-}C_5R_5)Co(CO)_2$ (R = H or CH_3) with hexafluorobutyne produces mainly the cyclopentadienone complex $(\eta\text{-}C_5R_5)Co(C_8F_{12}CO)$ and a small amount of the trimerized alkyne complex $(\eta\text{-}C_5R_5)Co(C_4F_6)_3$. The cyclopentadienone complex along with the cyclobutadiene, $(\eta\text{-}C_5H_5)Co(C_4Ph_4)$, and hexaphenylbenzene are the major products in both the

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(25) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 106 (1974).

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thermal[12] and photochemical[28] reactions of (η-C$_5$H$_5$)Co(CO)$_2$ with diphenylacetylene. When the photolysis is performed at low temperatures,[29] the dinuclear compound (η-C$_5$H$_5$)$_2$Co$_2$-(μ-CO)(C$_2$Ph$_2$) is also produced. The cyclobutadiene complex is also obtained in the thermal reaction of cyclopentadienyl-cobalt cyclooctadiene with diphenylacetylene.[30] Similar cyclopentadienylcobalt reactions with trifluoropropyne have not been reported, but thermal reaction[21] of this alkyne with cobalt octacarbonyl has been shown to yield the dinuclear complexes Co$_2$(CO)$_6$(CF$_3$C$_2$H) and Co$_2$(CO)$_4$(CF$_3$C$_2$H)$_3$ as well as a three-metal system, Co$_3$(CO)$_9$(CF$_3$CH$_2$C).

It is clear, then, that in general the products formed in the metal atom reactions of cobalt atoms, cyclopentadiene, and alkynes differ considerably from those produced in the analogous thermal and photochemical reactions. Evidently, the products found in each type of reaction are a function of the intermediate species produced in that reaction. For instance, in the photochemical reaction of (η-C$_5$H$_5$)Co(CO)$_2$ with diphenylacetylene, the primary intermediate has been postulated[31] to be the unsaturated monocarbonyl species (η-

C$_5$H$_5$)Co(CO) which can then coordinate two alkynes to yield the cyclopentadienone complex. Similar intermediates have also been suggested for the thermal reactions of (η-C$_5$H$_5$)-Co(CO)$_2$. It is apparent then that the presence of the carbonyl ligand has a large effect on both the intermediates and products formed in these thermal and photochemical reactions of cyclopentadienyl cobalt. In contrast, the analogous metal atom reactions which do not include the carbonyl ligands may proceed through a (η-C$_5$H$_5$)CoH reactive fragment as noted above. This different reactive species in conjunction with the unique synthetic conditions results in the production of a variety of compounds including both mono- and multimetal systems which are not found in the conventional reactions.

Registry No. I, 72893-59-5; II, 72893-58-4; III, 72882-26-9; IV, 72882-25-8; V, 72882-24-7; VI, 72882-23-6; VII, 72882-22-5; VIII, 72882-21-4; IX, 73048-39-2; X, 72882-20-3; XI, 72882-19-0; XII, 72882-18-9; XIIIb, 72882-17-8; XIV, 72882-16-7; XV, 72882-15-6; XVI, 72869-15-9; (η-C$_5$H$_5$)Co(C$_4$Ph$_4$), 1278-02-0; hexafluoro-2-butyne, 692-50-2; 3,3,3-trifluoropropyne, 661-54-1; diphenylacetylene, 501-65-5; cyclopentadiene, 542-92-7; pentamethylcyclopentadiene, 41539-64-4.

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Lewis Basicity, Reactivity, and Bond Order of Metal Acetyls. Boron and Aluminum Halide Adducts of (η^5-C$_5$H$_5$)Fe(CO)$_2$(C(=O)CH$_3$)

R. E. STIMSON and D. F. SHRIVER*

The formation and characterization of the compounds (η^5-C$_5$H$_5$)Fe(CO)$_2$(C(=O)CH$_3$)·MX$_3$ (M = B, X = F, Cl, Br; M = Al, X = Br, CH$_3$) was undertaken to provide a comparison of basicities and reactivities of the carbonyl moiety in ketones, a metal acetyl, and polynuclear metal carbonyls. A quantitative equilibrium study, using FT-IR methods and qualitative BF$_3$ dissociation pressure data, demonstrates the following order of basicity toward the reference acid BF$_3$: (CH$_3$)$_2$C=O < (η^5-C$_5$H$_5$)Fe(CO)$_2$(C(=O)CH$_3$) > (η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$. Upon interaction with a Lewis acid ν(CO) decreases for the basic CO in all three of the above-mentioned bases, with the order of decrease being (CH$_3$)$_2$C=O < (η^5-C$_5$H$_5$)-Fe(CO)$_2$(C(=O)CH$_3$) < (η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$. This trend is attributed to the tendency of adduct formation to induce delocalization of electrons from d orbitals on the metal to the >C=O moiety, and such an interpretation is borne out by vibrational spectroscopic data. For example, a ν(CO) vs. bond order correlation demonstrates that metal acetyl adducts are analogues of Fischer-type metal carbene complexes. Reactions other than basicity are compared for ketonic, metal acetyl, and metal-bridging carbonyls.

Introduction

Ketones are well-known as mild Lewis bases, and the resulting complexes with boron and aluminum halides have been studied with respect to their physical properties and reactivity.[1-5] More recently, CO-bridged polynuclear metal complexes have been found to display Lewis basicity through the oxygen of the bridging carbonyls (e.g., reaction 1).[6] In the

(1)
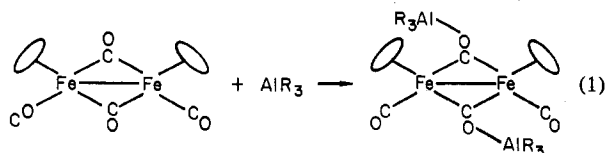
present work we have explored the Lewis basicity and reactivity of metal acyls, which at least in a structural sense, can be considered to be intermediate between ketones and CO-bridged polynuclear carbonyls. Lukehart and co-workers have studied extensively the chemistry of diacyl complexes,[7-9] but the basicity of neutral monoacyl metal complexes has received very little attention. Two noticeable exceptions are the observation of adduct formation between the NMR shift reagent Eu(fod)$_3$ with the acyl oxygen of (η^5-C$_5$H$_5$)Fe(CO)[P(η-C$_4$H$_9$)$_3$](C-(=O)CH$_3$)[10] and protonation of the acyl oxygen in (η^5-C$_5$H$_5$)Fe(CO)(L)(C(=O)CH$_3$).[11]

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