Reactions of Di- and Polynuclear Complexes. 7.[1] Reaction of $[(CO)_3\overline{Co(\mu\text{-}RC_2R')Co}(CO)_3]$ (R = R′ = CF_3, CO_2Me; R = CF_3, C_6H_5 and R′ = H) with $[\{FeCp(CO)_2\}_2]$. Synthesis, Characterization, and Reactivity of Di- and Tetranuclear Mixed-Metal Complexes. Alkyne Coordination and Scission by a Tetrametallic Framework. Crystal Structures of $[Co_3FeCp(\mu_4\text{-}\eta^2\text{-}C{=}CHCF_3)(\eta^6\text{-}C_7H_8)(\mu\text{-}CO)_2(CO)_4]$ and $[Co_3FeCp_2(\mu_4\text{-}\eta^2\text{-}C{\equiv}CCF_3)(\mu\text{-}CO)(CO)_5]$

René Rumin, Françoise Robin, and François Y. Pétillon*

URA CNRS No. 322, Chimie, Electrochimie et Photochimie Moléculaires, Faculté des Sciences, Université de Bretagne Occidentale, 29287 Brest-Cedex, France

Kenneth W. Muir* and Iain Stevenson

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Great Britain

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The dinuclear complexes $[(CO)_3\overline{Co(\mu\text{-}R\text{-}C{\equiv}C\text{-}R')Co}(CO)_3]$ (R = R′ = CF_3, CO_2 Me) react with $[\{CpFe(CO)_2\}_2]$ in refluxing octane to afford tetranuclear mixed-metal complexes $[Co_2Fe_2Cp_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}RC_2R')]$ (R = R′ = CF_3, **1**; R = R′ = CO_2Me, **6**), $[CoFe_3Cp_3(CO)_2(\mu_3\text{-}CO)_2(\mu_4\text{-}RC_2R')]$ (R = R′ = CF_3, **2**) in good yields, together with the di- and tetranuclear species $[(CO)_3\overline{Co(\mu\text{-}C_4R_4)Fe}Cp]$ (R = R′ = CO_2Me, **7**), $[Co_4(CO)_{10}(\mu_4\text{-}RC_2R')]$ (R = R′ = CO_2Me, **5**), and $[Co_4Cp_2(CO)_6(\mu_4\text{-}RC_2R')]$ (R = R′ = CF_3, **4**). Reactions between $[(CO)_3\overline{Co(\mu\text{-}H{-}C{\equiv}C{-}R)Co}(CO)_3]$ (R = CF_3, Ph) and $[\{CpFe(CO)_2\}_2]$ in refluxing octane give the tetrametallic cluster compounds $[Co_3FeCp(CO)_7(\mu\text{-}CO)_2(\mu_4\text{-}C_2HR)]$ (R = CF_3, **9**; R = Ph, **12**) in good yields, together with small amounts of tetra- and dinuclear derivatives $[Co_3FeCp_2(CO)_7(\mu\text{-}C_2R)]$ (R = CF_3, **8**; R = Ph, **13**), $[Co_2Fe_2Cp_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}HC_2R)]$ (R = CF_3, **10**), and $[Co_2(CO)_6(\mu\text{-}RC_2CH{=}CHR)]$ (R = Ph, **11**). Heating **9**, in refluxing toluene yields the toluene-substituted cluster $[Co_3FeCp(CO)_4(\mu\text{-}CO)_2(C_6H_5Me)\{\mu_4\text{-}C_2H(CF_3)\}]$ (**17**). The molecular structures of compound **17** and **8** have been established by single-crystal X-ray diffraction studies. **17** crystallizes in the monoclinic space group $P2_1/n$ with a = 8.569 (2), b = 26.650 (6), c = 9.380 (10) Å, β = 90.41 (7)°; R = 0.040 for 1781 observed reflections. Cluster **17** is characterized by a "butterfly" arrangement of the $FeCo_3$ core. All four metal atoms interact with a μ_4-vinylidene ligand. **8** crystallizes in the triclinic space groups $P\bar{1}$ with a = 8.379 (1), b = 9.594 (2), c = 14.913 (2) Å, α = 89.06 (2), β = 75.18 (1), γ = 70.75 (2)°; R = 0.034 for 2240 observed reflections. The tetranuclear complex **8** has an Fe-spiked–Co_3-triangular metal atom frame. Thermolyses of **1** and **6** in refluxing toluene in presence of Me_3NO provide in good yield the dialkylidyne clusters $[Co_2Fe_2Cp_2(CO)_5(\mu_3\text{-}CR)_2]$ (R = CF_3 **3**; R = CO_2Me, **14**) which result from C≡C bond cleavage. The molecular structure of **3** has been previously established by a single-crystal X-ray diffraction study. Treatments of the dialkylidyne cluster **3** with phosphite and nitrosyl hexafluorophosphate give, respectively, the monosubstituted complex $[Co_2Fe_2Cp_2(CO)_4\{P(OMe)_3\}(\mu\text{-}C{-}CF_3)_2]$ (**15**) and the nitrosyl derivative $[Co_2Fe_2Cp_2(\mu\text{-}CO)_2(NO)_2(\mu\text{-}C{-}CF_3)_2]$ (**16**). Carbonylation of the μ_4-vinylidene product **9** affords the μ-carbyne complex $[Co_3(CO)_9(\mu_3\text{-}CCH_2CF_3)]$ (**18**). The mass, infrared, and ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra of the new compounds are reported and discussed.

Introduction

Alkyne complexes containing two or more transition metals are of much current interest[2] because they exhibit a wide variety of novel coordination modes which serve as models for the chemisorption of unsaturated hydrocarbons on metallic surfaces.[3] Several strategies for the systematic synthesis of mixed-metal complexes containing coordinated alkynes have been developed. We recently described in an initial report[4] a facile one-step preparation of tetranuclear mixed-metal clusters containing a μ-η^2-alkyne from two dissimilar dinuclear complexes. Such *closo* "M_4C_2" complexes are usually prepared (i) by reactions of *closo* tetrahedral clusters with alkynes,[5] (ii) by metal fragment condensation induced by alkynes,[6] (iii) by ligand exchange between metals[7] or by metal exchange on clusters,[8] and (iv) by cluster expansion from μ_3-η^2-alkyne or μ_2-vinylidene

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Table I. NMR Data for the Complexes (δ)[a]

1	4.75 (s, 10 H, C_5H_5)	−41.88 (s)	260.8 (s br, $\gtrdot CO$), 198.0 (s br, CO), 131.7 (m, $=C{-}CF_3$), 126.2 (q, $J_{C\text{-}F}$ = 274; CF_3), 92.5 (s, C_5H_5)
2	5.07 (s, 5 H, C_5H_5), 4.51 (s, 10 H, C_5H_5)	−39.41 (s)	292.1 (s, $\gtrdot C{=}O$), 152.5 (m, $C{=}C{=}CF_3$), 129.2 (q, $J_{C\text{-}F}$ = 275, CF_3), 92.2 (s, $2C_5H_5$), 87.4 (s, C_5H_5)
3	4.75 (s, 10 H, C_5H_5)	−47.61 (s)	344.2 (q, $^2J_{C\text{-}F}$ = 19, $\gtrdot C{-}CF_3$), 205.5 (s vbr, CO), 133.9 (q, $J_{C\text{-}F}$ = 274, CF_3), 88.2 (s, C_5H_5)
6	4.72 (s, 10 H, C_5H_5), 3.78 (s, 6 H, Me)		262.9 (s br, $\gtrdot C{=}O$), 199.1 (s br, CO), 172.7 (s, COMe), 136.8 (s, $C{=}C$), 92.2 (s, $J_{^{54}Fe\text{-}C}$ = 45, C_5H_5), 53.2 (s, CO_2Me)
7	4.88 (s, 5 H, C_5H_5), 3.85 (s, 6 H, Me), 3.82 (s, 6 H, Me)		195.65 (s br, CO), 174.9 (s, CO_2Me), 167.8 (s, CO_2Me), 155.9 (s br, (Co)$C{=}C$), 99.5 (s, $C{=}C$), 81.3 (s, C_5H_5), 52.8 (s, CO_2Me), 52.5 (CO_2Me)
8	4.98 (s, 5 H, C_5H_5), 4.65 (s, 5 H, C_5H_5)	−53.7 (s)	252.0 (s, $=C(Co)_2Fe$), 212.75 (s, CO), 209.2 (s br, $CO(Co)$), 197.5 (s vbr, $CO(Co)$), 129.7 (q, $J_{C\text{-}F}$ = 27, CF_3), 126.3 (m, $C{=}C$), 86.7 (s, C_5H_5), 81.5 (s, C_5H_5)
9	5.57 (q, 1 H, $J_{H\text{-}F}$ = 7, CH), 5.32 (s, 5 H, C_5H_5)	−58.35 (d, J = 7)	293.2 (s br, $\gtrdot C{=}C$), 213.0 (s vbr, CO), 206.0 (s br, CO), 126.5 (q, $J_{C\text{-}F}$ = 275, CF_3), 94.5 (s, C_5H_5), 70.5 (q, $C{=}C(CF_3H)$)
10	8.03, (s, 1 H, CH), 4.64 (s, 10 H, C_5H_5)	−46.4 (s)	262.9 (s br, $\gtrdot C{=}O$), 199.2 (s br, CO), 140.0 (m, $(CF_3)C{=}C$), 127.4 (s, $HC{=}C$), 125.1 (q, $J_{C\text{-}F}$ = 270, CF_3), 92.2 (s, C_5H_5)
11	7.6–7.0 (m, 10 H, Ph), 7.45 (1 H), and 7.05 (1 H) (AB system, $J_{A\text{-}B}$ = 15, $H{-}C{=}C{-}H$)		199.2[c] (s br, CO), 138.4 (t, $^2J_{C\text{-}H}$ = 7.5, C_{quat} ($Ph{-}CH{=}CH$)), 136.75 (m, C_{quat}, ($Ph{-}C{\equiv}C$)), 136.0 (dt, $J_{C\text{-}H}$ = 153 ($^3J_{C\text{-}H}$ = 4.5), $Ph{-}CH{=}C$), 130.3–126.6 (m, Ph), 125.8 (d, $J_{C\text{-}H}$ = 156, $Ph{-}CH{=}CH{-}$), 92.45 (m, $C{\equiv}C{-}Ph$), 90.0 (m, $C{\equiv}C{-}Ph$)
12	7.36 (m, 5 H, Ph), 7.04 (s, 1 H, CH), 5.20 (s, 5 H, C_5H_5)		297.4 (s br, $\gtrdot C{=}CPh(H)$), 213.0 (s vbr, CO), 206.6 (s br, CO), 146.6–126.6 (Ph), 94.15 (s, C_5H_5), 84.5 (s, $C{=}CPh(H)$)
13	7.6 (m, 5 H, Ph), 4.66 (s, 5 H, C_5H_5), 4.35 (s, 5 H, C_5H_5)		255.1 (s, $C{=}CFe(Co)_2$), 214.8 (s, CO), 197.5 (s vbr, CO) 191.2 (s, CO), 145.1–127.4 (Ph), 138.9 (s, $C{=}CPH$), 86.2 (s, C_5H_5), 82.0 (s, C_5H_5)
14	4.55 (s, 10 H, C_5H_5), 4.05 (s, 6 H, CH_3)		346 (s, $C{=}CO_2Me$), 207.1 (s br, CO), 180.5 (s, CO_2Me), 88.65 (s, C_5H_5), 52.5 (s, CH_3)
15	4.65 (s, 10 H, C_5H_5), 3.75 (d, 9 H, $J_{P\text{-}H}$ = 11, Me)	−46.7 (s), −45.7 (s)	
16	4.73 (s, 10 H, C_5H_5)	−45.9 (s)	
17	6.31 (m, 5 H, C_6H_5Me), 4.85 (s, 5 H, C_5H_5), 4.53 (q, 1 H, $J_{F\text{-}H}$ = 7.5, $C{=}CH(CF_3)$), 2.30 (s, C_6H_5Me)	−55.65 (d, $J_{F\text{-}H}$ = 7.5)	285.85 (s, $C{=}C(CF_3)H$), 248.65 (s, CO), 246.7 (s, CO), 212.2 (s, CO), 199.0 (s, CO), 126.1 (q, CF_3), 110.2–93.8 (C_6H_5Me), 92.8 (s, C_5H_5), 64.3 (s, $C{=}C(CF_3)H$), 20.95 (s, C_6H_5Me)
18	4.39 (q, 2 H, $J_{F\text{-}H}$ = 9.8, CH_2)	−65.82 (t, $J_{F\text{-}H}$ = 9.8)	273.5 (s br, $\gtrdot C{-}CH_2$), 199.2 (s, CO), 123.5 (q, $J_{C\text{-}F}$ = 279, CF_3), 56.85[c] (tq, $^2J_{C\text{-}F}$ = 27.5, $J_{C\text{-}H}$ = 130, $CH_2{-}CF_3$)

[a] Chemical shifts (δ) in ppm measured in $CDCl_3$ at room temperature; J in hertz. [b] Hydrogen^{-1} decoupled unless otherwise stated by c.

trinuclear complexes.[8,9] We have now extended our investigation of the interaction of pairs of dinuclear complexes by studying the reactions of $[\{CpFe(CO)_2\}_2]$ with dinuclear cobalt complexes $[(CO)_3Co(\mu\text{-}R{-}C{\equiv}C{-}R')Co(CO)_3]$ as a route to higher mixed-metal species. The cobalt complexes used contained a variety of coordinated alkynes: R = R′ = CF_3, CO_2Me, Ph, Me, $SiMe_3$, CH_2OH; R = CF_3, Ph, and R′ = H. We have found that these reactions lead to different cluster products depending on the nature of R and R′. With disubstituted electron-withdrawing alkynes (R = R′ = CF_3, CO_2Me), tetranuclear butterfly clusters are mainly obtained, whereas with monosubstituted alkynes $H{-}C{\equiv}C{-}R$ (R = CF_3, Ph) the products are mainly μ_4-vinylidene compounds $[Co_3FeCp(CO)_6L_x(\mu_4\text{-}\eta^2\text{-}C{=}CHR)]$ [L = CO (x = 3), C_6H_5Me (x = 1)] together with tetranuclear complexes showing a "spiked-triangular" metal atom frame. Although vinylidenes are well-known as terminal and doubly bridging ligands in organometallic chemistry,[10] the number of μ_4-bound C=CRR′ groups which have been characterized by X-ray analysis remains small.[8,10,11] It is noteworthy that, in the case where R = R′ = CF_3 or CO_2Me, the butterfly clusters are accompanied by a tetranuclear product $[Co_2Fe_2Cp_2(CO)_5(\mu\text{-}CR)_2]$ in which two C–R fragments cap in a μ_3-manner two of the faces of the tetrahedron of metal atoms. It is clear that the C–R fragments arise from a scission of the coordinated alkyne in the butterfly complex $[Co_2Fe_2Cp_2(CO)_6(\mu_4\text{-}\eta^2\text{-}RC_2R')]$. The resulting bis-carbyne complex could be considered as an intermediate in the formation of products formally derived from alkyne cleavage and metathesis.[2,3]

The reactivities of some of the new tetrametallic clusters have been investigated and are reported here. A preliminary account of some aspects of this work has already appeared.[4]

Results and Discussion

Reactions of $[\{CpFe(CO)_2\}_2]$ with $[(CO)_3Co(\mu\text{-}R{-}C{\equiv}C{-}R')Co(CO)_3]$ (R = R′ = CF_3, CO_2Me). The reaction of $[\{CpFe(CO)_2\}_2]$ with $[(CO)_3Co(\mu\text{-}CF_3{-}C{\equiv}C{-}CF_3)Co(CO)_3]$ in octane under reflux gave a mixture of compounds 1–4 (see Scheme Ia) which were separated by column chromatography.

The major product of the reaction is the mixed-metal complex 1 which was formulated as $[Co_2Fe_2Cp_2(\mu_3\text{-}CO)_2(CO)_4(\mu_4\text{-}CF_3C_2CF_3)]$ on the basis of mass, infrared, and NMR data (Table I and Experimental Section). Several attempts to solve the structure by X-ray diffraction failed; however, the Patterson function is consistent with the presence of at least one triangle of metal atoms with M–M distances of ca. 2.5 Å. The infrared spectrum of 1 in solution contains two peaks at 1752 and 1733 cm^{-1} which are attributable to two triply bridging CO.[1,12] In the mass

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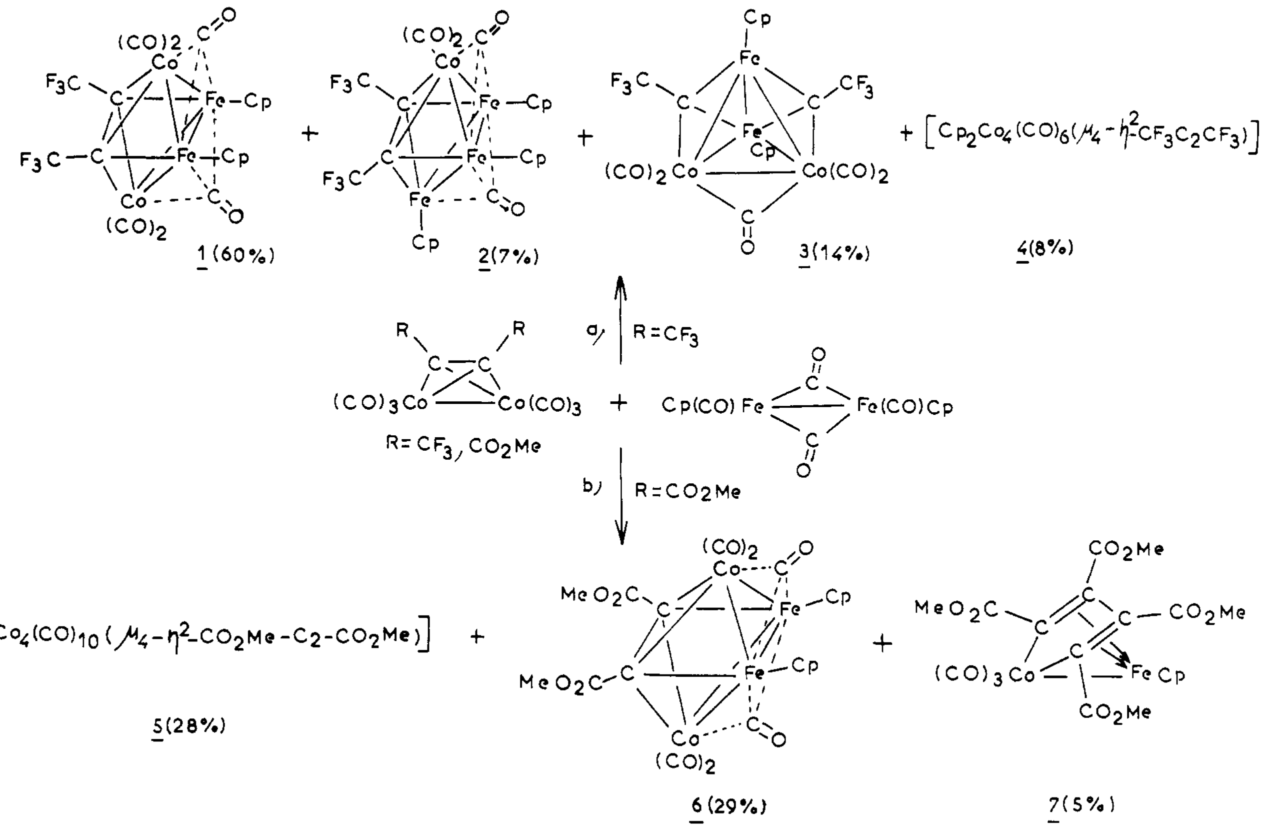
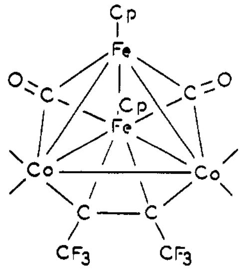
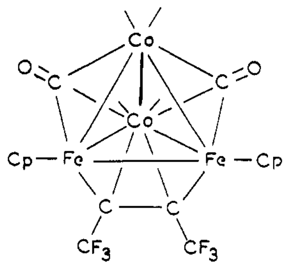
Scheme I



spectrum successive losses of CO from the parent ion $[Co_2Fe_2Cp_2(CO)_6(C_4F_6)]^+$ are observed; in addition, fragments arising from MF_2 (M = Fe, Co) loss are also obtained. The calculated isotopic distribution of the parent ion is in excellent agreement with that observed experimentally. Interaction of the alkyne ligand with only one or two of the metal atoms in a tetrametallic cluster is not expected from normal electron-counting procedures and we therefore do not consider such geometries plausible for 1. There are then two structures for 1 which appear worthy of consideration: a tetrahedral structure (A) where the alkyne interacts with three metals and a structure (B) in which the alkyne interacts with all four metal atoms. Tetrahedral geometry (A_1) is inconsistent with the ^1H NMR spectrum of 1 which indicates equivalent Cp groups. The absence in the low-temperature (−40 °C) NMR spectra of two sets of peaks attributable to two nonequivalent $Co(CO)_2$ groups rules out the alternative (A_2) geometry.


(A1)


(A2)

Now, when the alkyne interacts with all four metal atoms, three bonding modes are known.[13] Two of them occur in square-planar clusters which are characterized by the absence of triangular metallic cores believed to be present in 1. Finally, the infrared and ^1H, ^{19}F, and ^{13}C NMR data for 1 are fully consistent with a "butterfly" structure, a *closo* octahedron. ^1H and ^{13}C NMR spectroscopy indicates the presence of equivalent cyclopentadienyl groups which implies that the iron atoms are either both on wingtips or, alternatively, both in hinge positions. We suggest that the alkyne is parallel to the iron–iron hinge bond of the "butterfly" because of the better π-back-bonding capacity of FeCp compared to $Co(CO)_2$; indeed, such hinge atoms are particularly involved in back-bonding in the "butterfly" structure.[14] Throughout the temperature range −40 to +30 °C the ^{13}C NMR spectra of 1 reveal a two-line pattern in the carbonyl region. The resonance at 260.8 ppm is ascribed to μ_3-CO[1,12] the four CO atoms of the two $Co(CO)_2$ groups give rise to only one unresolved resonance at 198.0 ppm. However terminal-to-bridging and bridging-to-terminal rearrangement of the carbonyls bound to cobalt is not rapid on the NMR time scale up to at least 25 °C, since no averaged ^{13}C signal for these carbonyls in $[Co_2Fe_2Cp_2(CO)_6(CF_3C_2CF_3)]$ is observed.

As a byproduct of the reaction in Scheme Ia, the new complex 2 was obtained in yields of up to 7%. The structure of 2 can be confidently assigned on the basis of spectral relationships to 1. 2 is derived from 1 by replacement of $Co(CO)_2$ by an isoelectronic FeCp fragment. Complex 2 shows a mass pattern similar to that of 1. The ^1H NMR spectrum of 2 consists of two singlets at 5.07 and 4.51 ppm in a $^1/_2$ intensity ratio, in agreement with two different binding modes of the FeCp fragments. The ^{19}F NMR spectrum exhibits only one peak which suggests strongly that the cobalt atom occupies a wingtip position.

In addition to 1 and 2 two other complexes, 3 and 4, are formed in the reaction of Scheme Ia. Compound 3, which is derived from 1, will be described below. 4, which was

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obtained as a byproduct of a ligand exchange process, has been described earlier;[7] it is related in structure to **1** and **2**.

When $[\{CpFe(CO)_2\}_2]$ was treated with equimolecular amounts of $[(CO)_3\overline{Co(\mu\text{-}CO_2MeC_2CO_2Me)Co}(CO)_3]$ in octane under reflux, three complexes, **5**–**7** were formed (Scheme Ib) and were separated by column chromatography.

One of the major products of the reaction is the tetranuclear mixed-metal complex **6**, which was formulated as $[Co_2Fe_2Cp_2(\mu_3\text{-}CO)_2(CO)_4(\mu_4\text{-}CO_2MeC_2CO_2Me)]$ on the basis of spectral relationships to **1**. The similarities noted in the carbonyl region in the infrared as well as in the ^{13}C NMR spectra of **1** and **6**, coupled with the observation that each of these two isomers is dark-brown suggest that **6** has a cluster framework similar to that of **1**, with the iron atoms in hinge positions.

The product **5**, which was formed in 28% yield, was identified as $[Co_4(CO)_{10}(CO_2MeC_2CO_2Me)]$, a complex which has been previously characterized.[15] Two main hypotheses could be formulated for the formation of **5**, namely, the presence in solution of tetrametallic species formed upon pyrolysis of the bimetallic cobalt compound, or metal fragments recombination.[2]

Complex **7** was obtained as a byproduct in the reaction of Scheme Ib and was identified by its mass, infrared, and NMR spectra. In the mass spectra peaks higher than m/z 548 were not observed, and the stepwise loss of three carbonyls occurs: the complex is then formulated as $[CoFe(Cp)(CO)_3(CO_2MeC_2CO_2Me)_2]$. The observation of a broad resonance at 195.65 ppm in the ^{13}C NMR spectrum is indicative of carbonyls which are bonded to cobalt; moreover, the broad lowfield peak noted at 155.9 ppm must be related to two quaternary carbonyl atoms which are σ-bonded to cobalt. Therefore, on the basis of these spectral data, we suggest for the complex **7**, a cobaltacyclopentadiene structure in which the FeCp unit satisfies its electronic requirement by coordination with the $\{C(CO_2Me){=}C(CO_2Me)\}_2$ ligand via two π-Fe–C bonds. To our knowledge, heterodinuclear complex **7** is new, but there have been earlier reports of corresponding homodinuclear compounds such as $[Co_2Cp_2(C_4H_4)]$ and $[Fe_2\{C(CO_2Me){=}CHC(t\text{-}Bu){=}C(OMe)\}(CO)_6]$,[16] and also $[Co_2(C_8H_{12})_2(CO)_5]$[17] which is believed to be an intermediate in the $Co_2(CO)_8$-catalyzed cyclotrimerization of cyclooctyne.

The main feature of the reactions of Scheme I is the facile one-step production of mixed-tetranuclear "butterfly" complexes as the major product. These *closo*-octahedra could be formed by the classical insertion of the alkyne into a metal–metal bond of a tetrametallic species which formed in solution upon pyrolysis of the dimeric carbonyl complexes. Alternatively, the mechanism may involve condensation of metal fragments: all evidence for metal fragments in solution is obtained by formation compounds **2** and **7**. However, a mechanism which implies a direct insertion of a CpFe–FeCp unit into a Co–Co bond of the $Co(\mu\text{-}RC_2R)Co$ framework is very tempting. In this case the byproduct **2** could be explained as resulting from **1** by replacement of the $Co(CO)_2$ unit by an isoelectronic FeCp fragment. These "butterfly" clusters distinguish themselves from previous examples[5-9] by their triply bridging carbonyl groups. It is noteworthy that neither chromatographic work-up nor VT NMR investigations and CO stretching patterns lead to the observation of isomeric forms for complexes **1**, **2**, and **6**. This is surprising in view of the framework isomerism observed very recently by Vahrenkamp and co-workers in ruthenium–transition metal *closo*-octahedra.[9]

Table II. Selected Distances and Angles in $[Co_3FeCp(\mu_4\text{-}\eta^2\text{-}C{=}CHCF_3)(\eta^6\text{-}C_7H_8)(\mu\text{-}CO)_2(CO)_4]$ (17)

	Distances, Å		
Co(1)–Co(2)	2.567 (2)	Co(1)–Co(3)	2.558 (2)
Co(1)–C(8)	1.986 (10)	Co(1)–C(9)	2.039 (9)
Co(2)–Co(3)	2.460 (2)	Co(2)–Fe	2.486 (2)
Co(2)–C(1)	1.754 (12)	Co(2)–C(2)	1.756 (11)
Co(2)–C(3)	1.917 (9)	Co(2)–C(9)	1.930 (10)
Co(3)–Fe	2.488 (2)	Co(3)–C(4)	1.924 (9)
Co(3)–C(5)	1.732 (11)	Co(3)–C(6)	1.760 (12)
Co(3)–C(9)	1.922 (8)	Fe–C(3)	1.877 (10)
Fe–C(4)	1.874 (10)	Fe–C(9)	1.951 (8)
C(7)–C(8)	1.446 (13)	C(8)–C(9)	1.447 (11)
Fe–C(A)	2.08 (1)–2.12 (1)	Co–C(B)	2.10 (1)–2.15 (1)
	Angles, deg		
Co(2)–Co(1)–Co(3)	57.4 (1)	Co(2)–Co(1)–C(8)	85.1 (3)
Co(2)–Co(1)–C(9)	47.9 (3)	Co(3)–Co(1)–C(8)	80.9 (3)
Co(3)–Co(1)–C(9)	47.8 (3)	C(8)–Co(1)–C(9)	42.1 (4)
Co(1)–Co(2)–Co(3)	61.1 (1)	Co(1)–Co(2)–Fe	100.7 (1)
Co(1)–Co(2)–C(9)	51.6 (3)	Co(3)–Co(2)–Fe	60.4 (1)
Co(3)–Co(2)–C(9)	50.2 (3)	Fe–Co(2)–C(9)	50.5 (3)
Co(1)–Co(3)–Co(2)	61.5 (1)	Co(1)–Co(3)–Fe	100.9 (1)
Co(1)–Co(3)–C(9)	51.8 (3)	Co(2)–Co(3)–Fe	60.3 (1)
Co(2)–Co(3)–C(9)	50.5 (3)	Fe–Co(3)–C(9)	50.6 (3)
Co(2)–Fe–Co(3)	59.3 (1)	Co(2)–Fe–C(9)	49.8 (3)
Co(3)–Fe–C(9)	49.5 (3)	Co(1)–C(8)–C(7)	120.2 (8)
Co(1)–C(8)–C(9)	79.4 (6)	C(7)–C(8)–C(9)	122.8 (8)
Co(1)–C(9)–Co(2)	80.5 (4)	Co(1)–C(9)–Co(3)	80.4 (3)
Co(1)–C(9)–Fe	154.2 (5)	Co(1)–C(9)–C(8)	67.0
Co(2)–C(9)–Co(3)	70.4 (4)	Co(2)–C(9)–Fe	79.6 (3)
Co(2)–C(9)–C(8)	133.5 (7)	Co(3)–C(9)–Fe	79.9 (3)
Co(3)–C(9)–C(8)	123.9 (6)	Fe–C(9)–C(8)	138.6 (7)

Reactions of $[\{CpFe(CO)_2\}_2]$ with $[(CO)_3\overline{Co(\mu\text{-}H{-}C{\equiv}C{-}R)Co}(CO)_3]$ (R = CF_3, Ph). When an octane solution of $[\{CpFe(CO)_2\}_2]$ and $[(CO)_3\overline{Co(\mu\text{-}H{-}C{\equiv}C{-}R)Co}(CO)_3]$ (R = CF_3, Ph) in mole ratio 1:2 was heated under reflux, no *closo* "$Co_2Fe_2C_2$" complex was formed when R = Ph, and only small amounts of the *closo* complex **10** were obtained when R = CF_3. Instead, compounds **9** (R = CF_3) and **12** (R = Ph) were isolated as the major products, together with **8** (R = CF_3) and **11** and **13** (R = Ph) (see Scheme II).

The related complexes **9** and **12** have been characterized by their infrared, NMR, and mass spectra which are consistent with the formulation given. A crystal structure of **17**, which results from heating **9** in toluene, confirms the proposed structures of **9**, **12**, and **17**.

Single crystals of **17** were obtained from a 2/1 mixture of hexanedichloromethane. The structure (see Figure 1 and Table II) is based on an $FeCo_3$ butterfly skeleton with the Fe atom at one of the wingtips. Two carbonyl ligands bridge the Fe–Co edges. The Co(1)–Co(2)–Co(3)–Fe torsion angle is 123.8 (1)°. The Fe, Co(2), and Co(3) atoms form a roughly equilateral triangle with bond lengths Co(2)–Co(3), 2.461 (2); Co(2)–Fe, 2.486 (2); and Co(3)–Fe, 2.488 (2) Å. Co(1), however forms slightly longer bonds with Co(2) and Co(3) [Co(1)–Co(2), 2.567 (2) Å; Co(1)–Co(3), 2.558 (2) Å]. C(9) is positioned centrally above the butterfly, nearly equidistant [1.92 (1)–1.95 (1) Å] from Fe, Co(2), and Co(3) and slightly further [2.04 (1) Å] from Co(1); it forms part of a vinylidene fragment that originated from the alkyne through a 1,2-hydrogen shift, so that C(8) now carries both H and CF_3 substituents. H[C(8)] was located in the diffraction analysis. C(8) and C(9) bond to the metal atoms in a $\mu_4\text{-}\eta^2$ arrangement. If the vinyl-

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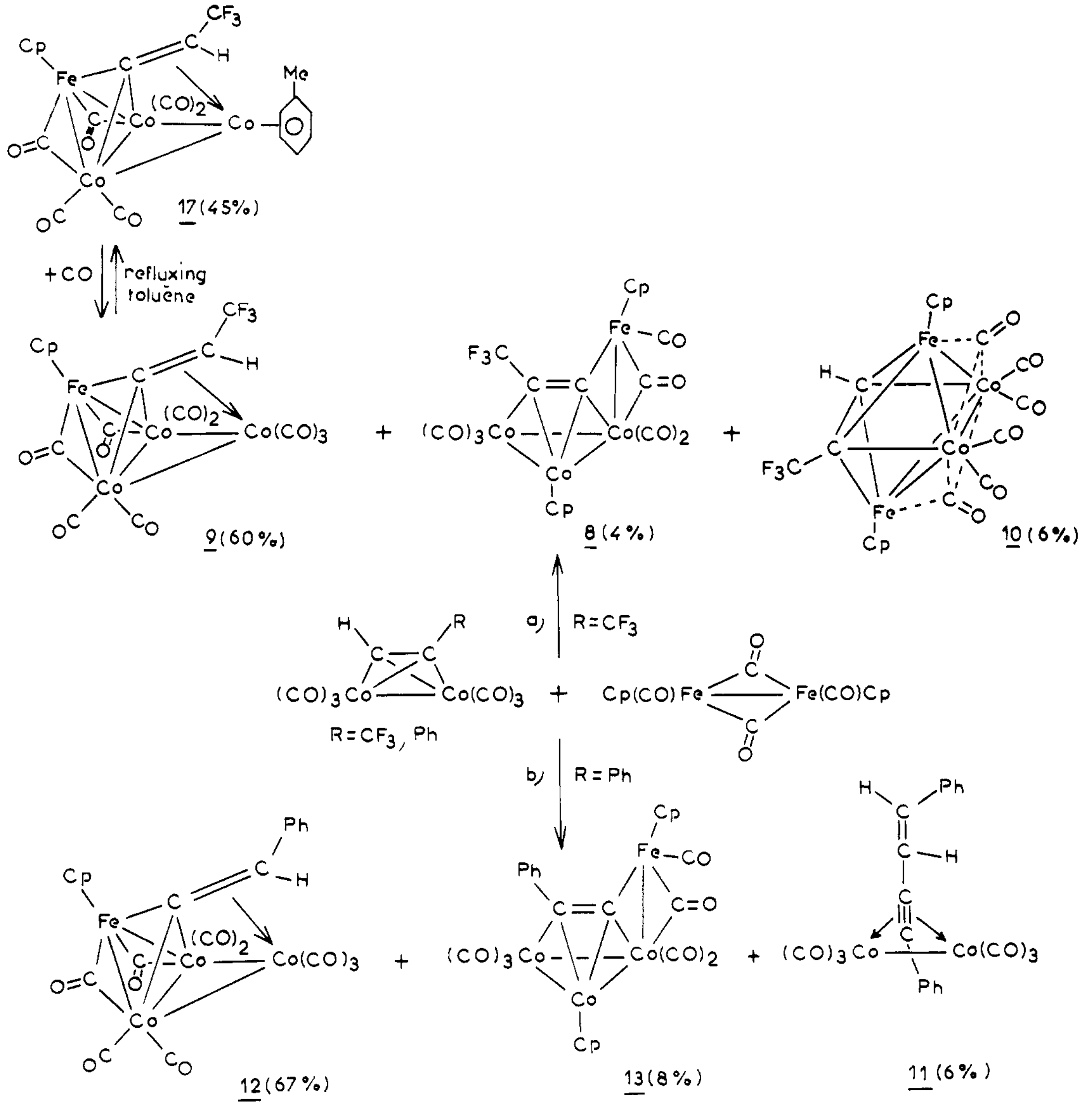
[15] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

[16] Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239.

[17] Bennett, M. A.; Donaldson, P. B. *Inorg. Chem.* **1978**, *17*, 1995.

Scheme II



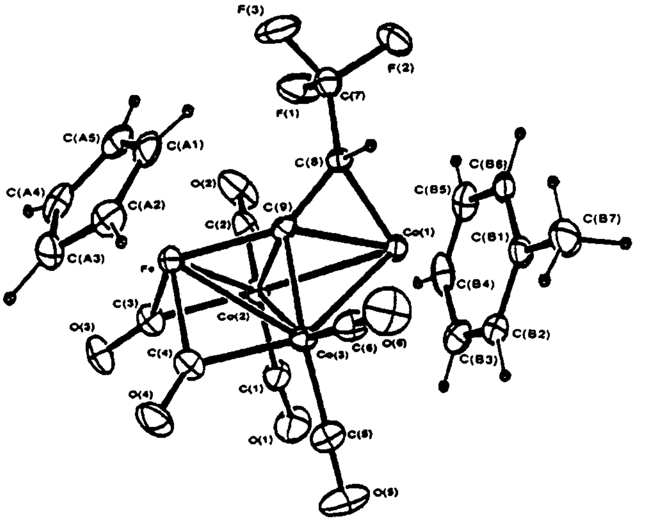


Figure 1. A perspective view of a molecule of [$Co_3FeCp(\mu_4$-η^2-C=$CHCF_3)(\eta^6$-$C_7H_8)(\mu$-$CO)_2(CO)_4$] (17) showing the atom numbering. Here and in Figure 2 20% ellipsoids are shown for non-hydrogen atoms and hydrogen atoms are represented by spheres of arbitrary size.

idene fragment is considered to be a 4-electron donor to the cluster, then all four metal atoms fulfil the 18-electron rule, and the cluster electron count is 62. As expected for a 62-electron butterfly structure, there are five metal–metal bonds. Butterfly clusters with carbon atoms bonding in a μ_4-η^2 manner have been known for some time. The first complex with this arrangement to be isolated was the [$Fe_4(CO)_{13}H]^-$ anion which contains an Fe_4 butterfly with a carbonyl group bonding in μ_4-η^2-manner.[18] Early examples of μ_4-η^2 vinylidene bonding to an Ru_4 and an Ru_3Ni butterfly were provided by Carty,[11c] Sappa[19] and coworkers. A cluster, [$Co_3FeCp(CO)_9(\mu_4$-η^2-C_2H_2)], very similar to 17, 9, and 12 was prepared by Stone et al.,[20] although by different synthetic route. Stone's structure differs from 17 in that the vinylidene originates from ethyne and thus has two hydrogen substituents; furthermore three carbonyl ligands replace the η^6-toluene ligand of 17. Corresponding bond lengths and angles are very similar for both structures and this lends credence to the assertion that replacement of three carbonyls in 9 to give 17 does not involve any fundamental change in cluster geometry. Stone's structure has a crystallographic mirror plane passing through the wingtip metal atoms. Although the inner skeleton of 17 approximate to *m* point symmetry the mirror plane being

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(18) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

(19) Carty, A. J.; Taylor, N. J.; Sappa, E.; Tiripicchio, A. *Inorg. Chem.* **1983**, *22*, 1871.

(20) Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357.

defined by atoms Co(1), C(9), and Fe, the molecule as a whole is unsymmetrical because of the nature of the substitution at C(8). Unlike Stone's compound, the cyclopentadienyl ring in **17** is not symmetrically oriented with respect to the approximate mirror plane. **9** is reversibly obtained from heating (45 °C, hexane) **17** under CO atmosphere (3 atm). Another very recent example of μ_4-η^2 vinylidene bonding to an Co_2RhFe butterfly was provided by Vahrenkamp et al.[8]

The mass, infrared, and NMR spectra of compounds **9** and **12** (Table I and Experimental section) show that they are isostructural with the toluene analogue **17** and only the spectra of **17** will be discussed. **17** exhibits a parent ion at m/z 652 in the mass spectrum and fragment ions corresponding to the successive loss of six CO molecules. In the solution-state infrared spectrum there are five bands in the CO stretching region, and those at 1842 and 1818 cm^{-1} may be assigned to the bridging carbonyls. In agreement with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum shows a resonance at 285.8 ppm assigned to the contact μ_4-$C{=}CH(CF_3)$ carbon, and peaks at δ 248.6 and 246.7 ppm which are attributable to bridging carbonyls. At higher field, the spectrum contains two signals at δ 212.2 and 199 ppm attributed to two nonequivalent $Co(CO)_2$ groups. The ^{19}F NMR spectrum exhibits a doublet and the F-H coupling (7.5 Hz) confirms that the CF_3 and H substituents are geminal.

Most of the μ_4-η^2-vinylidene tetranuclear complexes already known are formed by expansion of trinuclear μ_3-η^2-vinylidene clusters.[8,11b,19] In the formation of **9** and **12**, it is clear that a complex scrambling of the ligands occurs, but it is difficult to formulate a reaction pathway to these clusters. However, a possible mechanism involving as intermediate a trinuclear μ_3-η^2-vinylidene cluster, as shown by others,[8,11b,19] seems unlikely here. Although Vahrenkamp et al.[8] have shown, for example, that such trinuclear intermediates are formed and isolated in the reaction of $[(CO)_3\overline{Co(\mu\text{-}H{-}C{\equiv}C{-}R)Co}(CO)_3]$ (R = Me, Ph, t-Bu) with $Fe_3(CO)_{12}$ under forcing conditions (refluxing toluene)[21] similar to those used here, we have been unable to detect any trace of such trinuclear μ^3-η^2-vinylidene clusters in our reactions. This suggests that the pathway to the formation of **9** and **12** is different from that involved the reactions described by Vahrenkamp et al.[8]

The complexes **8** and **13** were obtained as byproducts in the reactions a and b of Scheme II, respectively. A crystal structure of **8** established the formulation of these compounds and will be described before their spectroscopic characteristics.

Table III. Selected Distances and Angles in $[Co_3FeCp_2(\mu_4\text{-}\eta^2\text{-}C{\equiv}CCF_3)(\mu\text{-}CO)(CO)_5]$ (8)

	Distances, Å		
Co(1)–Co(2)	2.622 (2)	Co(1)–Co(3)	2.418 (1)
Co(1)–C(1)	1.773 (8)	Co(1)–C(2)	1.783 (8)
Co(1)–C(3)	1.803 (7)	Co(1)–C(8)	2.361 (5)
Co(1)–C(9)	1.946 (6)	Co(2)–Co(3)	2.516 (2)
Co(2)–Fe	2.543 (2)	Co(2)–C(4)	1.767 (7)
Co(2)–C(5)	1.759 (7)	Co(2)–C(7)	1.982 (7)
Co(2)–C(8)	1.920 (6)	Co(2)–C(9)	2.932 (5)
Co(3)–C(8)	2.007 (5)	Co(3)–C(9)	1.948 (5)
Fe–C(6)	1.745 (6)	Fe–C(7)	1.871 (7)
Fe–C(8)	1.923 (6)	C(8)–C(9)	1.332 (8)
C(9)–C(10)	1.478 (9)		
Fe–C(B)	2.10 (1)–2.12 (1)	Co(3)–C(A)	2.04 (1)–2.06 (1)
	Angles, deg		
Co(2)–Co(1)–Co(3)	59.7 (1)	Co(2)–Co(1)–C(9)	78.3 (2)
Co(3)–Co(1)–C(9)	51.6 (2)	Co(1)–Co(2)–Co(3)	56.1 (1)
Co(1)–Co(2)–Fe	104.7 (1)	Co(1)–Co(2)–C(8)	60.3 (2)
Co(3)–Co(2)–Fe	91.7 (1)	Co(3)–Co(2)–C(8)	51.7 (2)
Fe–Co(2)–C(8)	48.6 (2)	Co(1)–Co(3)–Co(2)	64.2 (1)
Co(1)–Co(3)–C(8)	63.7 (2)	Co(1)–Co(3)–C(9)	51.6 (2)
Co(2)–Co(3)–C(9)	48.6 (2)	Co(2)–Co(3)–C(9)	81.0 (2)
C(8)–Co(3)–C(9)	39.3 (3)	Co(2)–Fe–C(8)	48.5 (2)
Co(2)–C(8)–Co(3)	79.7 (2)	Co(2)–C(8)–Fe	82.9 (3)
Co(2)–C(8)–C(9)	127.9 (5)	Co(3)–C(8)–Fe	135.1 (3)
Co(3)–C(8)–C(9)	67.9 (3)	Fe–C(8)–C(9)	148.0 (5)
Co(1)–C(9)–Co(3)	76.8 (2)	Co(1)–C(9)–C(8)	90.2 (4)
Co(1)–C(9)–C(10)	135.4 (5)	Co(3)–C(9)–C(8)	72.8 (4)
Co(3)–C(9)–C(10)	129.9 (4)	C(8)–C(9)–C(10)	128.7 (6)

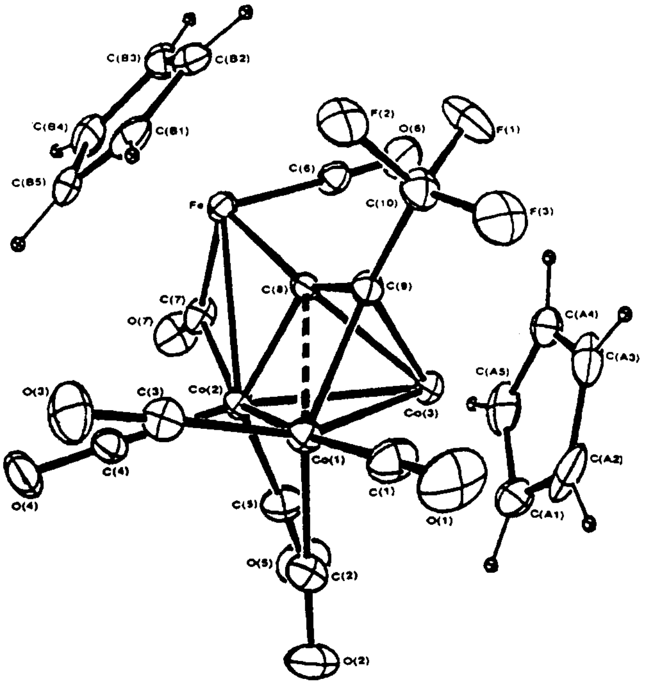

Figure 2. A perspective view of the molecular structure of $[Co_3FeCp_2(\mu_4\text{-}\eta^2\text{-}C{\equiv}CCF_3)(\mu\text{-}CO)(CO)_5]$ (**8**) showing the atom numbering. The weak Co(1)–C(8) interaction is indicated by a broken line.

Selected structural parameters for compound **8** are listed in Table III, and the molecular structure is shown in Figure 2. **8** contains an alkynyl group [C(8)–C(9)–CF_3], plainly derived by abstraction of the hydrogen atom from $HC{\equiv}CCF_3$ in the starting complex, and four metal atoms. The length of the C(8)–C(9) bond, 1.33 (1) Å, suggests that it retains some multiple character. The three Co atoms define a roughly equilateral triangle and the Fe atom is directly bonded only to Co(2). Such cluster compounds with spiked triangular configurations were rare until very recently,[11d,22,23] but their interactions with alkynyl groups are similar to those of trimetallic triangular complexes as can be seen from recent reviews.[2,11d] Alkynyl bonding to metals, whether μ_3-η^2 in triangular compounds, or μ_4-η^2 in spiked triangular compounds, is conventionally described as perpendicular (A) or parallel (B) to one of the metal–metal bonds. In A the C(1)–C(2) and M(1)–M(3) vectors are normal to each other, whereas in B they are inclined at 120°. A more obvious difference is in the number of M–C bonds: five in A but only four in B. Typical examples of the A(⊥) and B(∥) bonding modes are provided by $[Ru_3Pt(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)\}(CO)_9(COD)]$[11d] and

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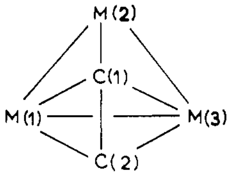
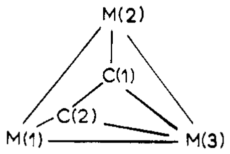
[21] Albiez, T.; Bernhardt, W.; von Schnering, C.; Roland, E.; Bantel, H.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 141.

[22] (a) Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9. (b) Nanni-Marchino, M. L.; Sappa, E.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1541.

[23] (a) Roland, E.; Bernhardt, W.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 2566. (b) Bernhardt, W.; Vahrenkamp, H. *J. Organomet. Chem.* **1988**, *355*, 427.



(A) : μ_3-η^2-⊥



(B) : μ_3-η^2-||

[$Fe_3Cp_2(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}$],[24] respectively. A wider survey[11d] suggests that these compounds display a range of geometries, and therefore bonding arrangements intermediate between A and B. **8** is unusual in that it lies almost exactly half-way along the deformation pathway between A and B: the angle between the Co(1)–Co(3) and C(8)–C(9) bonds is 104°, 14° greater than in the perpendicular model and 16° less than in the parallel model. The presence of a bond between Co(1) and C(8) must therefore be considered. Four of the C(8)–Co and C(9)–Co distances [Co(1)–C(9), Co(2)–C(8), Co(3)–C(8), and Co(3)–C(9)] lie in the range 1.92–2.01 Å and are consistent with Co–C covalent bonding. The Co(1)–C(8) distance of 2.361 (5) Å is considerably longer than these four Co–C distances. Indeed, by using Pauling's formula relating bond length to bond order,[25] the Co(1)–C(8) bond has an order of ca. 0.2 if the length of Co(1)–C(9) is taken as defining that of a single Co–C bond. Evidently there is a bonding interaction, albeit a weak one, between Co(1) and C(8). The Co(2)–C(9) distance of 2.932 (5) Å is too long for any suggestion of even weak bonding between these atoms to be plausible. Chemically equivalent bond lengths in **8** in general agree to within experimental error and values are close (within 0.03 Å) to those in the compilation of Orpen et al.[26] There is, however, a marked asymmetry in the μ_2-CO bridging of the Fe–Co(2) bond: the Fe–C(7) bond length [1.87 (1) Å] is 0.11 Å shorter than the Co(2)–C(7) bond length [1.98 (1) Å] and is also 0.06 Å shorter than the average Fe–C distance in (μ_2-CO)Fe systems.[26] This probably reflects the greater π-acidity of the terminal ligands on the metal atoms [2CO on Co(2) but Cp(CO) on Fe] than any intrinsic difference between Fe and Co.

In the mass spectra of complexes **8** and **13** the highest signals are observed at *m/z* 652 and 660, respectively, corresponding to [$Co_3Fe(Cp)_2(CO)_7(C_2R)$] (R = CF_3, Ph) with an isotopic pattern of Co_3Fe; then release of seven CO groups is observed and finally decomposition involving release of FeF_2. Similar ^{1}H NMR patterns are observed for **8** and **13**; they both show two singlet resonances, in a 1/1 intensity ratio owing to two inequivalent cyclopentadienyl groups. The solution-state infrared spectra of both complexes are comparable in the carbonyl stretching region; they display a band at ca. 1840 cm^{-1} attributed to a bridging carbonyl. The ^{13}C NMR spectra of **8** and **13** show downfield comparable four-line patterns. Two broad resonances at ca. δ 205 and 195 ppm are assigned to the carbonyls in the two $Co(CO)_x$ (x = 2, 3) groups. The signal at ca. 214 ppm is attributed to the two carbonyls bound to iron; the observation at ambient temperature of only one such resonance suggests rapid terminal-to-bridging and bridging-to-terminal rearrangement of these two carbonyls. The signals at ca. δ 253 and 126.3 (**8**) [138.9 (**13**)] ppm can be assigned, respectively, to the Cα and Cβ carbons of the alkynyl ligands. The chemical shifts of these alkynyl Cα and Cβ carbons are close to the average of the values for such systems recently compiled by Carty et al.[27]

The reaction pathway leading to the out-of-plane clusters **8** and **13** would seem to involve a 62-electron butterfly species which by flattening metal–metal bond cleavage, and rearrangement would give spiked triangular 64-electron clusters (on the basis that the alkynyl ligand was contributing 5 electrons to the cluster framework). The production of small amounts of the butterfly "$Co_2Fe_2C_2$" cluster in reaction of Scheme IIa would agree with such a mechanism. However, a more realistic hypothesis for the formation of complexes **8** and **13** could be the "condensation" of fragments as evidenced by the presence of CpCo entities in these molecules.

A second byproduct **10** was obtained in the reaction of Scheme IIa. The spectroscopic properties of **10** correspond to those found for **1**, **2**, and **6**; on this basis we propose for **10** a *closo* octahedral structure. In the ^{1}H and ^{13}C NMR spectra, only one resonance (Table I) corresponding to the cyclopentadienyl groups is observed, this implies that the CpFe groups are both at the wingtips. At ambient temperature, the ^{13}C NMR low-field pattern shows two signals at δ 262.8 and 199.2 ppm, this latter resonance is assigned to the carbonyls in the two $Co(CO)_2$ groups, the former is due to the μ_3-CO. The signal at δ 199.2 ppm is very broad, indicating carbonyl scrambling in the two equivalent $Co(CO)_2$ entities.

In the reaction of Scheme IIb, a dinuclear compound **11** was formed in low yield. This molecule exhibits a parent ion at *m/z* 490 in the mass spectrum and fragment ions corresponding to the loss of six CO molecules. The pattern of ν(CO) bands in the infrared spectrum corresponds closely to that of [$(CO)_3Co(\mu\text{-Ph—C}{\equiv}\text{C—H})Co(CO)_3$], which suggests that **11** is isostructural with this starting derivative and this is confirmed by the ^{13}C NMR analysis. An examination of the low-field region reveals only one broadened resonance at δ 199.2 ppm corresponding to carbonyls, and indicating complete carbonyl scrambling. Two signals at δ 138.4 and 136.75 ppm are assigned to two quaternary carbon atoms, and the ^{1}H-coupled spectra reveal a triplet about the former resonance. Two acetylenic resonances and two olefinic resonances at respectively δ 90.0, 92.45, and 125.8, 136.0 ppm are observed. All this suggests the presence in **11** of a Ph—CH=CH—C≡C—Ph ligand, π bonded to two cobalt atoms as shown in Scheme II. ^{1}H NMR confirms the *trans*-HC=CH entity (AB system: J_{H-H} = 15 Hz). **11** may result from a dimerization of the alkyne activated by the metals and subsequent hydrogen shifting to give the new ligand Ph—CH=CH—C≡C—Ph which bonds to both cobalt atoms.

Attempted Reactions of [$\{CpFe(CO)_2\}_2$] with [$(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3$] (R = R′ = Ph, Me, $SiMe_3$, CH_2OH). Although the reaction of the dimeric iron complex [$\{CpFe(CO)_2\}_2$] with [$(CO)_3Co(\mu\text{-R—C}{\equiv}\text{C—R}')Co(CO)_3$] (R = R′ = CF_3, CO_2Me; R = H, R′ = CF_3, Ph) proceeded cleanly to give the series of *closo* octahedral, and μ_4-vinylidene complexes, other dinuclear cobalt alkyne (R = R′ = Ph, Me, $SiMe_3$, CH_2OH) complexes did not exhibit similar reactivity. Complex mixtures of products (low yields) resulted from the reactions of [$\{CpFe(CO)_2\}_2$] with [$(CO)_3Co(\mu\text{-Me—C}{\equiv}\text{C—Me})Co(CO)_3$] along with hexamethylbenzene (27% yield), but no evidence for mixed

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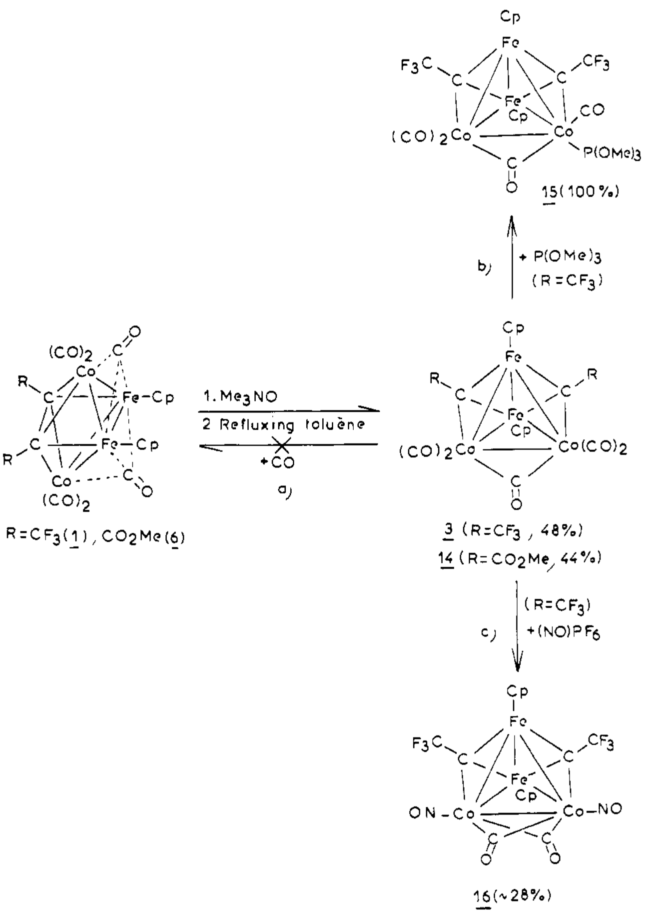
Scheme III



tetranuclear clusters was obtained. No reaction was observed when [{CpFe(CO)$_2$}$_2$] was heated in the presence of [(CO)$_3$Co(μ-R—C≡C—R')Co(CO)$_3$] (R = R' = Ph, SiMe$_3$, CH$_2$OH) in refluxing octane.

Therefore, we conclude that the desired reactions are observed only when alkynes with electron withdrawing or hydrogen substituents are used.

Alkyne Scission Reactions on Fe$_2$Co$_2$ Clusters. When a refluxing toluene solution of 1 and 6 was treated with Me$_3$NO, new clusters 3 and 14 can be isolated in good yields (see Scheme IIIa), and analytical and spectroscopic data fit the formulation [Co$_2$Fe$_2$Cp$_2$(CO)$_5$(μ-CR)$_2$] (R = CF$_3$ and CO$_2$Me). When the reaction (R = CF$_3$, 1) was undertaken in refluxing benzene instead of toluene, the tetrahedral cluster 3 was again formed, together with the dimeric compound [CpFe(μ-CO)$_2$(μ-CF$_3$C$_2$CF$_3$)FeCp].[1] The structure of 3 obtained from a single crystal X-ray study was reported in our preliminary communication.[4]

Compound 3 has an Co$_2$Fe$_2$ core which is essentially tetrahedral, with both CoFe$_2$ faces capped by a triply bridging C(CF$_3$) ligand. These μ_3-carbyne fragments result from the scission of the initial alkyne. Spectroscopic data for 3 and 14 are very similar. The close similarities of the carbonyl regions of the infrared spectra for 3 and 6 indicate strongly that 14 adopts a structure analogous to that of 3; both spectra display a band at ca. 1850 cm^{-1} due to the bridging carbonyl. Both complexes 3 and 14 exhibit in their mass spectra parent ions at m/z 662 and 642, respectively, and fragment ions corresponding to the loss of 5 CO molecules. The ^{13}C{^{1}H} NMR spectra are especially informative in the low-field region, showing one resonance for the μ_3-CR group at δ ca. 345 ppm and only one peak for the carbonyls bonded to cobalt atoms, indicating complete carbonyl scrambling at ambient temperature. The ^{13}C{^{1}H} and ^{1}H NMR spectra of 3 and 14 show that these molecules retain in solution the effective mirror plane they are known to possess in the solid state;[4] only one signal attributable to the two cyclopentadienyl groups is seen in the appropriate region in both spectra. This is confirmed by the ^{19}F NMR spectra of 3 which shows also only one resonance which is assigned to two equivalent CF$_3$ groups.

The structure of the complexes 3 and 14 is closely related to that found for the tetrahedral dialkylidyne cluster [Os$_3$WCpH(CO)$_9$(μ_3-C-Tol)$_2$][28] and for the monoalkylidyne derivative [Os$_3$WCp(CO)$_{11}$(μ_3-C-C$_6$H$_4$Me)].[29]

Cleavage of C≡C bonds involving trinuclear complexes is not unusual and leads to numerous types of products.[30] Examples involving tetranuclear species are scarce. However, in two recent reports Shapley, Churchill, and co-workers[31] described an alkyne scission implying tetranuclear species; these authors observed that the carbon–carbon cleavage happens on heating tetrahedral mixed-metal clusters, such as [Os$_3$WCpH(CO)$_{10}$(RC$_2$R')] complexes. The alkyne cleavage described here is so far the first example which implies *closo* octahedral mixed-metal clusters. The observation that pyrolysis of 1 and 6 in toluene gives only 3 and 14 suggests strongly that the alkyne scission process occurs without extensive fragmentation of the metal framework. The mechanism of the transformation of 1 and 6 into 3 and 14, respectively, can be explained in terms of weakening of the triple bond of the alkyne coordinated to iron and cobalt atoms in the complexes 1 and 6; this can be brought about both by the removal of electron density from C–C bonding orbitals and by population of antibonding C–C orbitals through retrodative bonding. The presence of electron-attracting CF$_3$ and CO$_2$Me substituents in the alkyne facilitates retrodative bonding and may also directly weaken the coordinated C≡C bond. Now, the carbonyl ligand is implicated in reducing the barrier of the C—C bond-breaking process. Indeed, initial decarbonylation results in the formation of "M$_4$(CO)$_5$" groups which are more efficient charge transfer (M → π*) systems[31b] than "M$_4$(CO)$_6$" groups. The alkyne scission observed here contrasts sharply with the behavior of [Co$_4$Cp$_2$(CO)$_5$(μ_4-CF$_3$C$_2$CF$_3$)][7] which is isoelectronic with [Co$_2$Fe$_2$Cp$_2$(CO)$_6$(μ_4-RC$_2$R)] (1 and 6). Subjecting the tetracobalt complex to extended thermal treatment resulted only in decomposition and alkyne cleavage was not detected. This is consistent with the proposal that the C≡C bond breaking process in octahedral cluster complexes involves the presence of strongly π-acidic substituents at the hinge metal atoms. This is the case with the FeCp groups in 1 and 6 which have better π-back-bonding capacity than the Co(CO)$_2$ groups in [Co$_4$Cp$_2$(CO)$_5$-(CF$_3$C$_2$CF$_3$)]. The transformation of 1 and 6 into, respectively, 3 and 14 implies the formation of a cobalt–

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cobalt bond, in order to get two μ_3-CR ligands from a μ_4-C_2R_2 ligand.

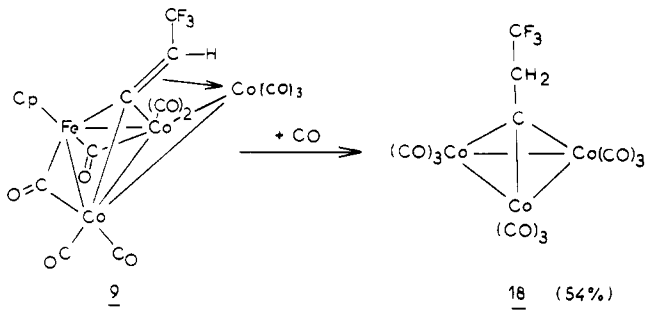
In fine, no coupling of the carbyne fragments was observed when complexes **3** and **14** reacted with carbon monoxide (1 atm, 1 h); the alkyne scission reaction is therefore irreversible.

Reactivity of the Dialkylidyne Complex 3 toward Phosphite and Nitrosyl Hexafluorophosphate. Reaction at ambient temperature of 1 equiv of $P(OMe)_3$ with a $CDCl_3$ solution of $[Co_2Fe_2Cp_2(CO)_4(\mu\text{-}CO)(\mu\text{-}C{-}CF_3)_2]$ (**3**) led to the ready replacement of one CO molecule to give the mono (phosphite) complex **15** in quantitative yield (see Scheme IIIb). Compound **15** is formulated as $[Co_2Fe_2Cp_2(CO)_4\{P(OMe)_3\}(\mu\text{-}C{-}CF_3)_2]$ on the basis of spectroscopic studies and elemental analysis. The mass spectrum of this product shows the parent ion $M^{\bullet+}$ and the successive loss of four carbonyls; fragments arising from MF_2 (M = Fe, Co) scission are also obtained. In the infrared spectrum, **15** shows two strong terminal carbonyl stretching bands at 2038 and 1994 cm^{-1}; the band noted at 1830 cm^{-1} is assignable to a bridging CO group. In the proton NMR spectra two signals are observed in a 10:9 ratio in the area of cyclopentadienyl and methyl resonances; the methyl resonance is coupled to phosphorus. The inequivalence of the two CF_3 groups accords with the observation at room temperature of two signals in the ^{19}F NMR spectrum.

Similarly, the reaction at ambient temperature of 2 equiv of $(NO)PF_6$ with a dichloromethane solution of **3** gave rise to the nitrosyl complex **16** (see Scheme IIIc). **16** has been characterized by its infrared, NMR, and mass spectra and by elemental analysis, all of which are consistent with the formulation given. The mass spectrum of **16** shows the parent ion, fragment ions corresponding to loss of the two carbonyl ligands, and a mass peak attributable to the corresponding $Co_2Fe_2Cp_2(CF_3)_2(NO)_2^+$ ion. In the infrared spectra no bands assignable to terminal carbonyl groups are observed but two absorptions at 1872 and 1843 cm^{-1} are consistent with the presence of terminal nitrosyl groups. Each of the ^1H and ^{19}F NMR spectra displays only one signal attributable, respectively, to the cyclopentadienyl and to the CF_3 ligands, thus showing that the molecule is symmetrical. The mixed cluster $[Co_2Fe_2Cp_2(CO)_2(NO)_2(C{-}CF_3)_2]$ (**16**) is formally an electron-rich 60-electron species if the C–CF_3 ligands are regarded as a three-electron donors. According to the EAN formalism, the structure expected for a 60-electron tetrametallic cluster is a tetrahedron.[6b] Hence, it appears that the tetrahedron structure of **3** is retained in **16** [after replacement of four terminal CO ligands by two terminal NO groups and a bridging carbonyl].

Reactivity of the μ_4-Vinylidene Cluster 9 toward Carbonylation. We have also tested the reactivity of the cluster $[Co_3FeCp(CO)_9\{\mu_4\text{-}C_2H(CF_3)\}]$ (**9**) toward carbonylation. In the presence of a large excess of carbon monoxide (5 atm), the reaction (boiling hexane) gave complex **18** in good yield (see Scheme IV). We suggest for **18** the formulation $[Co_3(CO)_9(\mu_3\text{-}C\text{-}CH_2\text{-}CF_3)]$ on the basis of spectroscopic studies and elemental analysis. The mass spectrum established that **18** was a trinuclear metal cluster. It exhibits a parent ion at m/z 524, and fragment ions corresponding to the loss of nine CO molecules; in addition a fragment arising from $C_2H_2F_2$ loss is also obtained. The infrared spectrum in the carbonyl region shows four peaks between 2108 and 2020 cm^{-1}, excluding those attributable to bridging carbonyl groups. In the proton NMR spectrum one quartet is observed; the coupling constant (J = 9.8 Hz) is in agreement with that expected for $^3J_{H\text{-}F}$. The ^{19}F NMR spectrum shows a triplet (J = 9.8 Hz) which is consistent with the presence of CH_2–CF_3 group in the cluster. The low-field pattern in the $^{13}C\{^1H\}$ NMR spectrum shows at ambient temperature a signal at δ 273.5 ppm which may be assigned to μ_3-C, and a peak at δ 199.2 ppm attributable to terminal carbonyl ligands bonded to cobalt atoms. The presence of only one signal due to carbonyls indicates that at room temperature site exchange of carbonyl ligands of the three $Co(CO)_3$ groups occurs. The high-field ^{13}C NMR pattern shows a triplet ($J_{C\text{-}H}$ = 130 Hz) which may be assigned to an CH_2 group. Hence, compound **18** has a triangular Co_3 core which is capped by a triply bridging C–CH_2–CF_3 ligand. The overall geometry of the $[Co_3(CO)_9(C{-}CH_2{-}CF_3)]$ unit closely resembles that of the cluster $[Co_3(CO)_9(\mu_3\text{-}C{-}CH_3)]$.[32] The carbonylation of **9** to give **18** involves partial fragmentation of the metal framework and hydrogenation of the Cβ atom of the $-C{=}CH(CF_3)$ ligand; the hydrogen source is very likely moisture from the solvent.

Scheme IV



Experimental Section

The reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques and solvents deoxygenated and dried by standard methods. Infrared spectra were obtained with a Pye-Unicam SP 2000 spectrophotometer in hexane or dichloromethane solutions in the ν(CO) and ν(NO) region. The mass spectra were measured on a VARIAN MAT 311 in the "Mesures Physiques" laboratory, University of Rennes, or on a GC/MS Hewlett Packard 5995C in the Chemistry Department, University of Brest. NMR spectra (^1H, ^{13}C, ^{19}F), in $CDCl_3$ solution, were recorded on a JEOL FX 100 or a Bruker AC 300 and were referenced to Me_4Si or $CFCl_3$. Chemical analyses were performed either by the "Centre de Microanalyses du CNRS de Lyon" or by the "Océanographie Chimique" laboratory at the University of Brest.

The complexes $[(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3]$ were prepared by literature methods.[15] All other reagents were commercial grade and were used as obtained.

Reaction of $[(CO)_3Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ with $[\{FeCp(CO_2)\}_2]$. In a typical procedure ca. 1 g of $[(CO)_3Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ (2.2×10^{-3} mol) was dissolved in n-octane (60 cm^3) and octane solution containing $[\{FeCp(CO)_2\}_2]$ (0.8 g, 2.2×10^{-3} mol) was added under nitrogen. The reaction mixture was refluxed for 7 h. After evaporation of the solvent in vacuo, the residue was extracted with CH_2Cl_2. Chromatography of the dichloromethane solution on a silica gel column eluting with hexane/CH_2Cl_2 (9:1) afforded a violet band, from which **3** (0.2 g, 14%) was isolated. Further elution yielded the dark-violet complex **4** (8%). Elution with hexane/CH_2Cl_2 (6:4) gave a dark-brown fraction which yielded complex **1** (0.92 g, 60%). Finally elution with hexane/CH_2Cl_2 (3:7) afforded a black fraction of **2** (0.1 g, 7%). A single crystal suitable for an X-ray analysis[4] was grown from an hexane/dichloromethane solution of **3** at −30 °C.

1: IR ν(CO) 2047 m, 2028 vs, 1999 s, 1997 s, 1752 s, 1733 s cm^{-1} (hexane); mass spectrum, m/z 690 $[M]^+$, other peaks, $M^+ - [x$-

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[32] Sutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261.

(CO)] (x = 1–6), M^+ – [x(CO) + FeF_2] (x = 4–6), M^+ – [6(CO), FeF_2 + CoF_2]. Anal. Calcd for $C_{20}H_{10}Co_2F_6Fe_2O_6$: C, 34.8; H, 1.5; Co, 17.1; Fe, 16.2. Found: C, 35.1; H, 1.6; Co, 17.2; Fe, 16.1.

2: IR ν(CO) 2034 vs, 1987 s, 1732 m, 1680 m cm^{-1} (CH_2Cl_2); mass spectrum, m/z 696 $[M]^+$, other peaks, M^+ – [x(CO) (x = 1–4), M^+ – [x(CO) + y(FeF_2)] (x = 3, 4; y = 1–3). Anal. Calcd for $C_{23}H_{15}CoF_6Fe_3O_4$: C, 39.7; H, 2.2; Co, 8.4; Fe, 24.1. Found: C, 39.6; H, 2.2; Co, 8.4; Fe, 23.8.

3: IR ν(CO) 2050 s, 2028 vs, 2000 s, 1990 sh, 1851 m cm^{-1} (hexane); mass spectrum, m/z 662 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–5), M^+ – [x(CO) + y(FeF_2)] (x = 4, 5; y = 1, 2], M^+ – [5(CO) + 2(FeF_2) + CoF_2]. Anal. Calcd for $C_{19}H_{10}Co_2F_6Fe_2O_5$: C, 34.5; H, 1.5; Co, 17.8; Fe, 16.9. Found: C, 34.6; H, 1.5; Co, 17.8; Fe, 16.8.

Reaction of $[(CO)_3Co(\mu\text{-}CO_2MeC_2CO_2Me)Co(CO)_3]$ with $[\{FeCp(CO)_2\}_2]$. The reaction of $[(CO)_3Co(\mu\text{-}CO_2MeC_2CO_2Me)Co(CO)_3]$ (1.3 g, 3 × 10^{-3} mol) with $[\{FeCp(CO)_2\}_2]$ (1.1 g, 3 × 10^{-3} mol) was carried out in a similar manner to that described above. Evaporation of the solvent and separation by column chromatography gave by elution with hexane/CH_2Cl_2 (6:4) $[\{FeCp(CO)_2\}_2]$ (0.7 g) and dark-blue **5** as a product (0.28 g, 28%), by elution with CH_2Cl_2 afforded dark-brown product **6** (0.65 g, 29%), and finally by elution with CH_2Cl_2/THF (10:1) yielded black complex **7** (0.08 g, 5%).

6: IR ν(CO) 2045 w, 2026 s, 1992 sbr, 1750 m, 1725 m, 1704 s cm^{-1} (CH_2Cl_2); mass spectrum, m/z 670 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–8). Anal. Calcd for $C_{22}H_{16}Co_2Fe_2O_{10}$: C, 39.4; H, 2.4; Co, 17.6; Fe, 16.7. Found: C, 39.2; H, 2.4; Co, 17.8; Fe, 16.7.

7: IR ν(CO) 2087 s, 2042 s br, 1725 s br, 1706 s br cm^{-1} (CH_2Cl_2); mass spectrum, m/z 548 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 2, 3). Anal. Calcd for $C_{20}H_{17}CoFeO_{11}$: C, 43.8; Co, 10.7; Fe, 10.2. Found: C, 43.8; Co, 10.6; Fe, 10.4.

Reaction of $[(CO)_3Co(\mu\text{-}CF_3C_2H)Co(CO)_3]$ with $[\{FeCp(CO)_2\}_2]$. An octane solution of $[(CO)_3Co(\mu\text{-}CF_3C_2H)Co(CO)_3]$ (1 g, 2.6 × 10^{-3} mol) was added under nitrogen to an octane solution of $[\{FeCp(CO)_2\}_2]$ (0.45 g, 1.3 × 10^{-3} mol). The reaction mixture was refluxed for 1 h. The mixture was evaporated to dryness under high vacuum. Chromatography of the residue on a silica gel column eluting with hexane/CH_2Cl_2 (9.5:0.5) afforded a red band which yielded complex **8** (0.05 g, 4%). Further elution with hexane/CH_2Cl_2 (8:2) gave the most abundant dark brown fraction from which **9** was collected and purified by crystallization from hexane/CH_2Cl_2 (2:10) solution at –30 °C (0.77 g, 60%). Elution with hexane/CH_2Cl_2 (6:4) gave a black fraction of **10** (0.1 g, 6%). A single crystal suitable for an X-ray analysis was obtained from an hexane/dichloromethane solution at **8**, at –30 °C.

8: IR ν(CO) 2063 s, 2040 w, 2025 s, 2011 m, 1992 s, 1838 s cm^{-1} (hexane); mass spectrum, m/z 652 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–7), M^+ – [7(CO) + FeF_2]. Anal. Calcd for $C_{20}H_{10}Co_3F_3FeO_7$: C, 36.8; H, 1.5; F, 8.7. Found: C, 37.0; H, 1.5; F, 8.3.

9: IR ν(CO) 2092 s, 2050 vs, 2030 vw, 2019 w, 2004 w, 1860 s, 1834 s cm^{-1} (hexane); mass spectrum, m/z 664 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–9), M^+ – [9(CO) + FeF_2], M^+ – [9(CO) + $CoFeF_2$], M^+ – [9(CO) + $CoFeF_3$]. Anal. Calcd for $C_{17}H_6Co_3F_3FeO_9$; C, 31.7; H, 1.0; Co, 27.5; F, 8.8; Fe, 8.7. Found: C, 31.6; H, 1,2; Co, 27.7; F, 8.7; Fe, 8.6.

10: IR ν(CO) 2044 w, 2026 s, 1992 s, 1760 s, 1742 m cm^{-1} (hexane); mass spectrum, m/z 622 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–6), M^+ – [x(CO) + FeF_2] (x = 4–6), M^+ – [5(CO) + $CoFeF_2$]. Anal. Calcd for $C_{19}H_{11}Co_2F_3Fe_2O_6$: C, 36.7; H, 1.8; Co, 19.0; Fe, 18.0. Found: C, 36.3; H, 1.9; Co, 19.6; Fe, 18.1.

Reaction of $[(CO)_3Co(\mu\text{-}C_6H_5C_2H)Co(CO)_3]$ with $[\{FeCp(CO)_2\}_2]$. The reaction of $[(CO)_3Co(\mu\text{-}C_6H_5C_2H)Co(CO)_3]$ (2.2 g, 5.5 × 10^{-3} mol) and $[\{FeCp(CO)_2\}_2]$ (1 g, 2.25 × 10^{-3} mol) was carried out by following a procedure similar to that for $[(CO)_3Co(\mu\text{-}CF_3C_2H)Co(CO)_3]$. Evaporation of the solvent and separation by column chromatography gave red-violet **11** (0.16 g, 6%) (eluted with hexane/CH_2Cl_2 (9.5:0.5)). Elution with hexane/CH_2Cl_2 (8:2) served to remove a minor green band which was evaporated to yield a product which was not characterized. A third dark-red band was eluted with hexane/CH_2Cl_2 (7.5:2.5) which yielded complex **12** (1.62 g, 67%). Further elution have a second dark-red band affording **13** (0.18 g, 8%).

11: IR ν(CO) 2085 s, 2058 s, 2028 vs, 2012 w, 1983 w cm^{-1} (hexane); mass spectrum, m/z 490 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–6), M^+ – [6(CO) + Co].

12: IR ν(CO) 2081 s, 2043 s, 2032 s, 2002 mw, 1996 w, 1852 s, 1827 m cm^{-1} (hexane); mass spectrum, m/z = 652 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–8). Anal. Calcd for $C_{22}H_{11}Co_3FeO_9$: C, 40.5.; H, 1.7; Co, 27.1; Fe, 8.6. Found: C, 40.6; H, 1.8; Co, 27.4; Fe, 8.7.

13: IR ν(CO) 2048 s, 2010 s, 1997 s, 1970 s, 1848 s cm^{-1} (hexane); mass spectrum, m/z 660 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–6).

Reaction of $[(CO)_3Co(\mu\text{-}RC_2R)Co(CO)_3]$ (R = Ph, Me, $SiMe_3$, CH_2OH) with $[\{FeCp(CO)_2\}_2]$. No heterometallic cluster was obtained when the bis(dicarbonyl(η^5-cyclopentadienyl)iron(I)) complex was treated with $[(CO)_3Co(\mu\text{-}RC_2R)Co(CO)_3]$ (R = Ph, Me, $SiMe_3$, CH_2OH) in a similar procedure to that described above. Only $[Co_4(CO)_{10}(RC_2R)]$ (R = Ph, 60% yield) and hexamethylbenzene (R = Me, 27% yield) were formed and characterized in these reactions.

Decarbonylation Reaction of 1. On refluxing in toluene for 3 h a mixture of **1** (0.1 g, 0.15 × 10^{-3} mol) and sublimed Me_3NO (0.01 g, 0.15 × 10^{-3} mol), the bis-carbyne complex **3** was obtained in 48% yield and separated by column chromatography from the unreacted compound **1**.

On refluxing **1** with Me_3NO in benzene instead of toluene, **3** was formed in 40% yield together with $[CpFe(\mu\text{-}CO)_2(\mu\text{-}CF_3C_2CF_3)FeCp]$ (36% yield).

Decarbonylation Reaction of 6. The reaction was carried out in toluene by the procedure described for **1** with use of **6** (0.4 g, 0.6 × 10^{-3} mol). Evaporation of the solvent and separation by column chromatography on silica gel gave violet bis-carbyne complex **14** (eluted with CH_2Cl_2) (0.17 g, 44%) and unreacted compound **6** (eluted with ether/CH_2Cl_2, 1:99) (0.2 g).

14: IR ν(CO) 2044 s, 2018 s, 1994 s, 1856 w, 1676 m cm^{-1} (CH_2Cl_2); mass spectrum, m/z 642, other peaks, M^+ – [x(CO)] (x = 1–5).

Reaction of $[Co_2Fe_2Cp_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CCF_3)_2]$ (3) with Phosphite. Crystals of complex **3** (0.04 g, 6 × 10^{-5} mol) were transferred to an NMR tube and degassed; chloroform-*d* and trimethyl phosphite (6 × 10^{-5} mol) were added; the solution was then stirred. The disappearence of **3** and the formation of the monosubstituted complex **15** (100% yield) were monitored by ^1H, ^{19}F, and ^{31}P NMR. **15** was purified by recrystallization from hexane/CH_2Cl_2.

15: IR ν(CO) 2038 s, 1994 vs, 1830 m cm^{-1} (hexane); mass spectrum, m/z 758 $[M]^+$, other peaks, M^+ – $2CH_3$, M^+ – [x(CO)] (x = 3, 4), M^+ – [4(CO) + y(FeF_2)] (y = 1, 2), M^+ – [4(CO) + CoF_2 + FeF_2]. Anal. Calcd for $C_{21}H_{19}Co_2F_6Fe_2O_7P$: C, 33.3; H, 2.5. Found: C, 33.2; H, 2.6.

Reaction of $[Co_2Fe_2Cp_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CCF_3)_2]$ (3) with $NO(BF_4)$ or $NO(PF_6)$. A mixture of **3** (0.055 g, 8 × 10^{-5} mol) and $NO(BF_4)$ or $NO(PF_6)$ (2 equiv) was stirred at room temperature for 3 h to give the substituted derivative **16** in ca. 28% yield. Complex **16** was purified by chromatography. Elution with pentane afforded a violet band that gave unreacted **3**; elution with pentane/CH_2Cl_2 (9:1) removed the deep-green band, and evaporation gave product **16**.

16: IR ν(CO) 1872 m, 1843 m cm^{-1}, ν(NO) 1803 m cm^{-1} (hexane); mass spectrum, m/z 638 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1, 2), M^+ – [2CO + NO], M^+ – [2CO + y(NO) + z(FeF_2)] (y = 1, 2; z = 1, 2), M^+ – [2CO + 2NO + FeF_2 + CoF_2]. Anal. Calcd for $C_{16}H_{10}Co_2F_6Fe_2N_2O_4$: C, 30.2; H, 1.6; N, 4.4. Found: C, 30.3; H, 1.7; N, 4.3.

Reaction of $[Co_3FeCp(CO)_7(\mu\text{-}CO)_2(\mu\text{-}C_2HCF_3)]$ (9) with Toluene. On refluxing **9** (0.1 g, 0.15 × 10^{-3} mol) in toluene for 1 h, cluster **17** was obtained in 45% yield. **17** was purified by chromatography on a silica gel column; elution with hexane/CH_2Cl_2 (8:2) gave unreacted **9** (0.055 g). Further elution afforded a maroon fraction which yielded **17** (0.045 g, 45%).

17: IR ν(CO) 2030 s, 2002 s, 1980 s, 1842 s, 1818 w cm^{-1}; mass spectrum, m/z 652 $[M]^+$, other peaks, M^+ – [x(CO)] (x = 1–6).

Table IV. Fractional Coordinates and Displacement Parameters[a] (Å^2) for $[\mathrm{Co_3FeCp_2}(\mu_4\text{-}\eta^2\text{-C}{\equiv}\mathrm{CCF_3})(\mu\text{-CO})(\mathrm{CO})_5]$ (8)

	x/a	*y/b*	*z/c*	*U*
Co(1)	0.109 77 (11)	0.243 22 (8)	0.138 94 (5)	0.043
Co(2)	0.053 78 (10)	0.221 78 (7)	0.319 00 (5)	0.038
Co(3)	0.191 15 (11)	0.398 59 (7)	0.232 20 (5)	0.041
Fe	0.346 66 (11)	0.056 04 (8)	0.340 56 (5)	0.038
F(1)	0.633 2 (5)	0.200 9 (5)	0.135 2 (3)	0.093
F(2)	0.588 5 (5)	0.034 8 (4)	0.064 5 (2)	0.075
F(3)	0.530 0 (6)	0.252 0 (5)	0.017 9 (3)	0.099
O(1)	0.183 7 (9)	0.339 3 (6)	−0.048 5 (3)	0.118
O(2)	−0.240 6 (7)	0.447 9 (5)	0.206 0 (4)	0.086
O(3)	0.075 3 (7)	−0.043 9 (5)	0.098 1 (3)	0.094
O(4)	−0.139 2 (6)	0.018 1 (5)	0.320 6 (3)	0.086
O(5)	−0.223 7 (8)	0.476 3 (5)	0.426 7 (4)	0.102
O(6)	0.493 9 (7)	0.260 6 (5)	0.339 8 (3)	0.086
O(7)	0.063 4 (7)	0.158 5 (5)	0.509 6 (3)	0.076
C(1)	0.156 8 (10)	0.301 8 (7)	0.024 7 (5)	0.069
C(2)	−0.109 5 (10)	0.366 0 (7)	0.183 6 (5)	0.062
C(3)	0.092 6 (9)	0.066 4 (7)	0.113 5 (4)	0.056
C(4)	−0.062 3 (8)	0.097 4 (7)	0.320 9 (4)	0.052
C(5)	−0.113 7 (9)	0.379 6 (7)	0.380 9 (5)	0.066
C(6)	0.433 6 (8)	0.181 4 (6)	0.375 6 (4)	0.051
C(7)	0.134 3 (9)	0.146 0 (6)	0.429 9 (4)	0.052
C(8)	0.289 0 (7)	0.179 6 (5)	0.242 7 (4)	0.036
C(9)	0.340 2 (7)	0.216 6 (5)	0.156 3 (4)	0.040
C(10)	0.519 7 (9)	0.178 5 (7)	0.094 5 (4)	0.056
C(A1)	0.039 7 (11)	0.613 7 (7)	0.275 2 (9)	0.091
C(A2)	0.138 6 (18)	0.607 1 (8)	0.184 4 (7)	0.110
C(A3)	0.317 4 (13)	0.547 1 (8)	0.183 7 (6)	0.081
C(A4)	0.321 4 (10)	0.521 4 (6)	0.272 6 (7)	0.072
C(A5)	0.154 2 (14)	0.561 5 (7)	0.329 3 (5)	0.080
C(B1)	0.438 2 (11)	−0.133 0 (6)	0.246 0 (5)	0.065
C(B2)	0.577 3 (9)	−0.114 7 (6)	0.273 7 (5)	0.054
C(B3)	0.543 2 (9)	−0.124 0 (6)	0.371 1 (5)	0.058
C(B4)	0.382 3 (11)	−0.147 5 (6)	0.402 5 (5)	0.068
C(B5)	0.316 0 (10)	−0.151 1 (6)	0.325 5 (6)	0.070

[a] The equivalent isotropic displacement parameter, *U*, is one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Fractional Coordinates and Displacement Parameters[a] (Å^2) for $[\mathrm{Co_3FeCp}(\mu_4\text{-}\eta^2\text{-C}{=}\mathrm{CHCF_3})(\eta^6\text{-}\mathrm{C_7H_8})(\mu\text{-CO})_2(\mathrm{CO})_4]$ (17)

	x/a	*y/b*	*z/c*	*U*
Co(1)	0.074 51 (14)	0.147 88 (5)	0.038 97 (11)	0.039
Co(2)	0.205 12 (14)	0.174 04 (5)	0.263 85 (11)	0.038
Co(3)	−0.002 76 (13)	0.110 39 (5)	0.268 38 (10)	0.040
Fe	0.258 23 (15)	0.090 53 (5)	0.366 90 (11)	0.040
F(1)	0.454 7 (7)	0.133 9 (3)	0.001 9 (6)	0.095
F(2)	0.358 1 (7)	0.092 4 (3)	−0.157 6 (5)	0.105
F(3)	0.466 9 (8)	0.055 7 (3)	0.002 3 (6)	0.100
O(1)	0.026 1 (1)	0.262 1 (3)	0.342 7 (8)	0.094
O(2)	0.480 1 (10)	0.225 5 (3)	0.165 6 (7)	0.100
O(3)	0.298 0 (8)	0.175 6 (3)	0.549 4 (6)	0.069
O(4)	−0.004 7 (8)	0.072 9 (3)	0.544 3 (6)	0.079
O(5)	−0.255 2 (9)	0.171 9 (3)	0.3676 (10)	0.115
O(6)	−0.156 1 (10)	0.021 3 (3)	0.162 4 (8)	0.104
C(1)	0.096 2 (13)	0.226 2 (4)	0.316 2 (10)	0.061
C(2)	0.371 5 (13)	0.205 1 (4)	0.203 6 (9)	0.054
C(3)	0.267 7 (11)	0.154 9 (4)	0.444 2 (9)	0.051
C(4)	0.059 7 (11)	0.085 8 (4)	0.444 6 (9)	0.053
C(5)	−0.153 9 (12)	0.147 0 (4)	0.329 0 (10)	0.061
C(6)	−0.098 9 (11)	0.056 3 (4)	0.208 6 (10)	0.056
C(7)	0.370 2 (12)	0.093 4 (5)	−0.023 5 (9)	0.056
C(8)	0.221 4 (10)	0.090 3 (4)	0.044 4 (8)	0.040
C(9)	0.197 3 (9)	0.108 3 (4)	0.181 5 (7)	0.037
C(A1)	0.378 1 (13)	0.025 5 (4)	0.301 7 (10)	0.062
C(A2)	0.295 5 (12)	0.015 7 (4)	0.419 2 (11)	0.068
C(A3)	0.357 4 (15)	0.046 9 (5)	0.521 1 (10)	0.076
C(A4)	0.473 4 (13)	0.076 4 (5)	0.462 0 (13)	0.076
C(A5)	0.484 9 (12)	0.062 7 (4)	0.324 5 (11)	0.062
C(B1)	−0.099 3 (11)	0.135 1 (4)	−0.116 2 (9)	0.054
C(B2)	−0.163 4 (11)	0.164 6 (5)	−0.014 7 (10)	0.064
C(B3)	−0.087 7 (16)	0.207 7 (5)	0.025 6 (11)	0.074
C(B4)	0.053 3 (17)	0.222 4 (5)	−0.028 5 (11)	0.076
C(B5)	0.119 3 (12)	0.194 4 (5)	−0.129 5 (11)	0.067
C(B6)	0.044 6 (12)	0.150 2 (4)	−0.173 6 (8)	0.055
C(B7)	−0.177 4 (12)	0.088 0 (6)	−0.161 3 (10)	0.092

[a] The equivalent isotropic displacement parameter, *U*, is one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Carbonylation Reaction of 17. Complex 17 (0.05 g, 8 × 10^{-5} mol) was heated in hexane at 45 °C for 15 h under 3 atm carbon monoxide. Compound 9 was formed in 91% yield and separated from the unreacted product by column chromatography.

Reaction of 9 with Carbon Monoxide. On heating 9 (0.2 g, 0.3 × 10^{-3} mol) in hexane for 30 h at 90 °C under 5 atm carbon monoxide, cluster 18 was obtained. 18 was purified by chromatography on a silica gel column. Elution with hexane/$\mathrm{CH_2Cl_2}$ (9:1) gave violet complex 18 (0.085 g, 54%); further elution with hexane/$\mathrm{CH_2Cl_2}$ (8:2) afforded the unreacted product (0.05 g).

18: IR ν(CO) 2108 w, 2060 vs, 2044 s, 2020 m cm^{-1} (hexane); mass spectrum, *m/z* 524 $[\mathrm{M}]^+$, other peaks, $\mathrm{M}^+ - [x(\mathrm{CO})]$ (x = 1–9), $\mathrm{M}^+ - [\mathrm{C_2H_2F_2}]$, $\mathrm{M}^+ - [9(\mathrm{CO}) + \mathrm{CoF_2}]$, $\mathrm{M}^+ - [9(\mathrm{CO}) + \mathrm{CoF_3}]$.

Crystal Structure of $[\mathrm{Co_3FeCp_2}(\mathrm{C}{\equiv}\mathrm{CCF_3})(\mathrm{CO})_7]$ (8). The specimen was a black plate of dimensions 0.20 × 0.50 × 0.06 mm. All measurements were made with Mo Kα X-rays, λ = 0.710 69 Å, on an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator.

Crystal Data: $\mathrm{C_{20}H_{10}Co_3F_3FeO_7}$: fw = 651.93; triclinic; space group, $P\bar{1}$; a = 8.379 (1), b = 9.594 (2), c = 14.913 (2) Å; α = 89.06 (2), β = 75.18 (1), γ = 70.75 (2)°; U = 1091.1 (3) Å^3; Z = 2; D_{calcd} = 1.984 g cm^{-3}; $F(000)$ = 640, μ(Mo Kα) = 29.6 cm^{-1}; and T = 297 K.

Unit-cell dimensions were obtained by a least-squares fit of the setting angles of 22 reflections with $12 < \theta(\mathrm{Mo\ K}\alpha) < 15°$.

The intensities of 5137 reflections with $2 \leqslant \theta(\mathrm{Mo\ K}\alpha) \leqslant 25°$ and $-9 \leqslant h \leqslant 2$, $-11 \leqslant k \leqslant 11$, and $-17 \leqslant l \leqslant 17$ were measured from $\omega/2\theta$ scans of 0.75° in ω. Correction for Lp and absorption effects (transmission factors on F 0.82–1.12 were obtained by an empirical method[33]) and averaging (R_{int} = 0.026) yielded 3823 unique intensities of which 2240 with $I \geqslant 2\sigma(I)$ were subsequently used.

The structure was successfully solved in the centrosymmetric space group $P\bar{1}$. The metal atom positions were obtained from the Patterson synthesis, and the remaining atoms were located from subsequent difference syntheses. Refinement was by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$ with use of the GX program system on a VAX 3600 computer.[34] Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 35. Hydrogen atoms were constrained to ride on the parent carbon atoms with C–H = 0.96 Å and $U(\mathrm{H}) \approx 1.2U(\mathrm{C})$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Refinement of 307 structure parameters converged ($\Delta/\sigma < 0.02$) with R = 0.034 and R_w = 0.033. Final $|\Delta\rho|$ values did not exceed 0.48 eÅ^{-3}. Final atomic coordinates are listed in Table IV.

Crystal Structure of $[\mathrm{Co_3FeCp}(\mathrm{C}{=}\mathrm{CHCF_3})(\mathrm{CO})_6(\mathrm{C_7H_8})]$ (17). Unless otherwise stated experimental and computational procedures were identical with those used for 8. The specimen was a black opaque needle of dimensions 0.40 × 0.11 × 0.05 mm.

Crystal Data: $\mathrm{C_{21}H_{14}Co_3F_3FeO_6}$; fw = 651.98; monoclinic; space group $P2_1/n$; a = 8.569 (2), b = 26.650 (6), c = 9.830 (10) Å; β = 90.41 (7)°; U = 2244.8 (24) Å^3; Z = 4; D_{calcd} = 1.929 g cm^{-3}; $F(000)$ = 1288; μ(Mo Kα) = 28.7 cm^{-1}; T = 295 K.

The intensities of 5605 reflections with $2 \leqslant \theta(\mathrm{Mo\ K}\alpha) \leqslant 25°$ and $0 \leqslant h \leqslant 10$, $-31 \leqslant k \leqslant 8$, and $-11 \leqslant l \leqslant 11$ were measured from $\omega/2\theta$ scans of 0.80° in ω. Averaging (R_{int} = 0.032) yielded 3932 independent structure amplitudes, of which 1781 with $I \geqslant 2\sigma(I)$ were used in subsequent calculations.

The metal atoms were located by direct methods and the other atoms from difference syntheses. Positional and vibrational parameters of H-atoms were deduced from those of adjacent carbon atoms assuming C–H = 0.96 Å and $U(\mathrm{H}) \approx U(\mathrm{C})$; however, H($\mathrm{C_8}$) was refined without constraints after being first located

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from a difference synthesis. The orientation of the methyl group was also established from a difference synthesis. Full-matrix least-squares refinement of 311 parameters converged ($\Delta/\sigma < 0.06$) at $R = 0.040$ and $R_w = 0.039$. In the final difference synthesis $|\Delta\rho|$ values were less than 0.60 eÅ^{-3}. Final atomic coordinates are listed in Table V.

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Supplementary Material Available: For 17 and 8 tables of hydrogen atom parameters and anisotropic vibrational parameters and complete geometry listings (10 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Halide-Promoted CO Labilization Applied to the Synthesis of Alkyne-Substituted Derivatives of $Ru_3(CO)_{12}$

Soa Rivomanana, Guy Lavigne,* Noël Lugan, and Jean-Jacques Bonnet

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France

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Among the three halide-promoted complexes $[PPN][Ru_3(Cl)(CO)_{11}]$ ([PPN][**1**]), $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ ([PPN][**2**]), and $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ ([PPN][**3**]) (the last complex is observed here for the first time), which are readily obtained by addition of [PPN][Cl] (PPN = bis(triphenylphophoranylidene)ammonium) to $Ru_3(CO)_{12}$, the complexes [PPN][**2**] and [PPN][**3**] react with alkynes ((**a**) acetylene, (**b**) phenylacetylene, (**c**) diphenylacetylene, (**d**) dimethylacetylene) to produce the activated species $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR')(CO)_9]$ ([PPN][**4**]; THF, 25 °C, 10 min, 100% spectroscopic yield), in which the halide behaves as a good leaving group whose displacement can be catalyzed by a protic solvent. The scope of this synthetic procedure is examined. The complex $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**4c**]) has been crystallized in 87% yield, and its X-ray structure is reported. Crystal data: triclinic, $P\bar{1}$ (No. 2), $a = 15.913$ (4) Å, $b = 16.307$ (4) Å, $c = 10.992$ (4) Å, $\alpha = 82.73$ (2)°, $\beta = 98.55$ (3)°, $\gamma = 103.21$ (4)°, $V = 2733$ Å^3, $Z = 2$, $\mu(\text{Mo K}\alpha) = 9.65$ cm^{-1}; Enraf-Nonius CAD4 diffractometer; final $R_w = 0.046$ and $R = 0.045$ (from 6490 observations and 340 variables). The structure consists of an open triruthenium cluster unit where the alkyne ligand is coordinated in a $\mu_3\text{-}\eta^2\text{-}\|$ fashion. The bridging halide spans the open edge of the metal triangle and is slightly shifted below this plane. The reactivity of [PPN][**4b–d**] has been investigated. Protonation of the anion $[\mathbf{4c}]^-$ at −78 °C gives the corresponding neutral hydrido complex $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$ (**5c**). The complex [PPN][**4d**] reacts with CO at 25 °C in dichloromethane/methanol solution to yield $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(\mu\text{-}CO)(CO)_9$ (**6d**) selectively. This complex can be isolated in pure form by extraction from a biphasic methanol/hexane mixture, a procedure avoiding chromatographic workup (yield, crystallized, 60%). Its X-ray structure is reported. Crystal data for **6d**: monoclinic, $P2_1/c$ (No. 14), $a = 14.716$ (1) Å, $b = 14.153$ (2) Å, $c = 18.226$ (2) Å, $\beta = 96.70$ (2)°, $V = 3770$ Å^3, $Z = 8$ (two independent cluster molecules in the asymmetric unit); final $R = 0.030$ and $R_w = 0.037$ (from 6362 observations and 523 variables). The alkyne is coordinated in a $\mu_3\text{-}\eta^2\text{-}\|$ mode, and there is one bridging carbonyl spanning the metal–metal edge parallel to the alkyne. Attempts to isolate the elusive nonacarbonyl derivative "$Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$" are described: the addition of methanol or ethanol to THF solutions of [PPN][**4b**] gives instantaneously the known acetylide species $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-}CC(C_6H_5))(CO)_9]$ ([PPN][**7b**]; yield, crystallized, 80%). In the case of internal alkynes such as diphenylacetylene, the reaction of [PPN][**4c**] with methanol requires more forcing conditions and results in a simple substitution of the halide by a hydrido ligand to give the complex $[PPN][Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**8c**]). In addition, attempts to release one carbonyl ligand from the decacarbonyl derivative **6c** by a controlled thermolysis result in an aggregation of the metal framework, leading to the formation of the known butterfly complex $Ru_4(\mu_4\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_{12}$ (**9c**) in 25% yield. The disubstituted-alkyne triruthenium derivative ("violet isomer") $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (**10c**) is obtained by treatment of [PPN][**4c**] with $[Ag][BF_4]$ in the presence of an excess of alkyne (yield 54%). The X-ray structure of this complex is reported. Crystal data for **10c**: monoclinic, $C2/c$ (No. 15), $a = 38.440$ (7) Å, $b = 8.544$ (2) Å, $c = 22.002$ (2) Å, $\beta = 114.67$ (1)°, $V = 6566$ Å^3, $Z = 8$; $R = 0.025$ and $R_w = 0.032$ (from 4843 observations and 423 variables). The differences between the catalytic halide-promoted incorporation of phosphines into $Ru_3(CO)_{12}$ and the stoichiometric reactions reported here are discussed.

Introduction

Though halides are currently used as additives in several homogeneous Ru-based catalytic processes of potential industrial relevance,[1] fundamental studies dealing with their interaction with ruthenium carbonyl complexes have been only recently developed.[2] The discovery that highly dissociated salts of halides or pseudohalides catalyze the substitution of CO by phosphines into $Ru_3(CO)_{12}$[3] has prompted us to develop mechanistic studies of this acti-

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