Reactions of Bimetallic Complexes. 4.[1] Ligand Transfer Reactions between Different Metallic Sites. Synthesis, Characterization, and Reactivity of Acetylenic Cluster and Dimeric Complexes of Cobalt and Iron. Crystal Structures of [(η5-C5H5)Fe(CO){μ-SMeCH=C(CF3)}]2 and [(CO)3Co(μ-CF3C2CF3)Co(CO)2{(SMe)Fe(η5-C5H5)(CO)2}]

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Photolysis of the acyl–iron complex [Cp(CO)FeC(O)C(CF3)C(R)SMe] (1, R = H, CF3; Cp = η5-C5H5) gave [Cp(CO)Fe{μ-C(CF3)=C(R)(SMe)}2Fe(CO)Cp] (2) in almost quantitative yield. X-ray analysis of 2 (R = H) reveals that the dimeric structure is based on a tub-shaped Fe2S2C4 ring. The complex crystallizes in the space group *Pbca*, with a = 15.068 (4) Å, b = 18.649 (3) Å, c = 16.092 (3) Å, and Z = 8. R = 0.029 for refinement of 289 parameters with 3975 unique observations. Thermal reaction of 2 with Co2(CO)8 in toluene afforded the new tetracobalt cluster [Cp2Co4(CO)4(μ-CO)(μ-CF3C2CF3)] (3) and the dinuclear derivative [(C6H5Me)Co(μ-CF3C2CF3)Co(CO)3] (4); formation of these compounds implies that an exchange of ligands (hexafluorobut-2-yne, cyclopentadienyl, or carbonyl) took place. In 3 the alkyne is incorporated into a *closo*-Co4C2 cluster framework. Exchange of ligands is also observed when the dinuclear complexes [(CO)3Co(μ-CF3C2CF3)Co(CO)3] and [Cp(CO)Fe(μ-SMe)2Fe(CO)Cp] react in refluxing toluene to give the new isomers *cis*- and *trans*-[Cp(CO)2FeC(CF3)=C(CF3)Me] in addition to 3 and 4. At lower temperatures (50–90 °C) the same reactants produced a new trinuclear derivative, [(CO)3Co(μ-CF3C2CF3)Co(CO)2{(SMe)Fe(CO)2Cp}] (8), shown by X-ray analysis to be derived by substitution of [CpFe(CO)2(SMe)] for an axial CO ligand of [(CO)3Co(μ-CF3C2CF3)Co(CO)3]. 8 crystallizes in the space group *Cc*, with a = 13.978 (2) Å, b = 13.948 (3) Å, c = 23.221 (4) Å, β = 97.74 (1)°, and Z = 8. R = 0.045 for refinement of 336 parameters with 1663 observations.

Introduction

Thiolato ligands have proven to be of great value for the synthesis of metal carbonyl cluster compounds. Thiolato bridging ligands are particularly valuable because they contain a lone pair of electrons that can be used for donation to other unsaturated metal centers to form higher nuclearity and/or mixed-metal cluster compounds whose chemistry is of current interest.[3] Therefore, we examined the possibility of using such bridging thiolato complexes as synthetic tools. We have previously shown that neutral monomeric alkenyl iron complexes [(η5-C5H5)(CO)FeC-(O)C(CF3)=C(R)SMe] (R = H, 1a; R CF3, 1b) photochemically decarbonylate to form dimeric derivatives 2 containing two bridging thioalkenyl ligands.[4] We now describe the crystal structure of [(η5-C5H5)Fe(CO){μ-SMeCH=C(CF3)}]2 (2a). As an extension of this work we report here the new acetylenic cluster and dimeric complexes obtained by reacting (i) 2b with Co2(CO)8 and (ii) dimeric acetylenic cobalt derivatives with dinuclear (thiolato)iron compounds. We demonstrate that the new alkyne complexes studied here result from migration of ligands from one metal center to another, which provides a new route to clusters. Previously, ligand exchange re-

actions have been used to prepare dinuclear[5] and mononuclear[6] complexes. A preliminary communication of a part of this work has already appeared.[7]

Results and Discussion

Synthesis of Dimeric Iron Compounds 2 and X-ray Diffraction Study of [(η5-C5H5)(CO)Fe(μ-SMeCH=C-(CF3)]2 (2a). As described before,[4] the dimeric complexes 2 are obtained in good yields by photolysis of the acyl derivatives [Cp(CO)FeC(O)C(CF3)=C(R)SMe][8] (1) in tetrahydrofuran, according to eq 1. Complexes 2 were

1a, R = H
b, R = CF3

2a, R = H
b, R = CF3
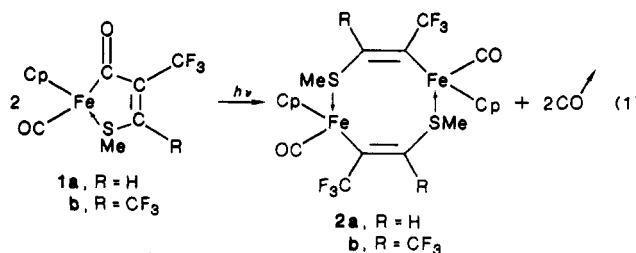
(1) Part 3: Gomes de Lima, M. B.; Guerchais, J. E.; Mercier, R.; Pétillon, F. Y. *Organometallics* **1986**, *5*, 1952.

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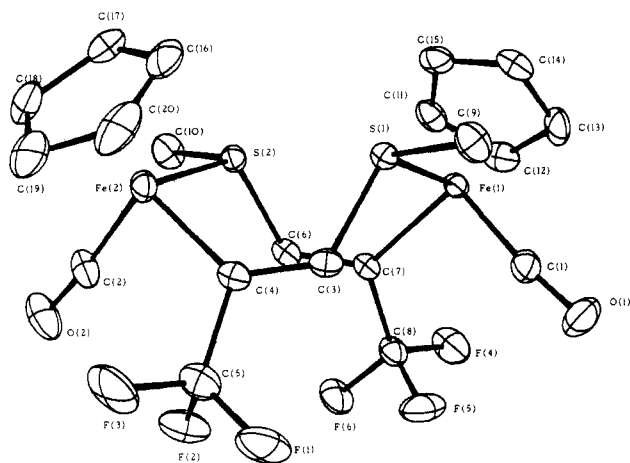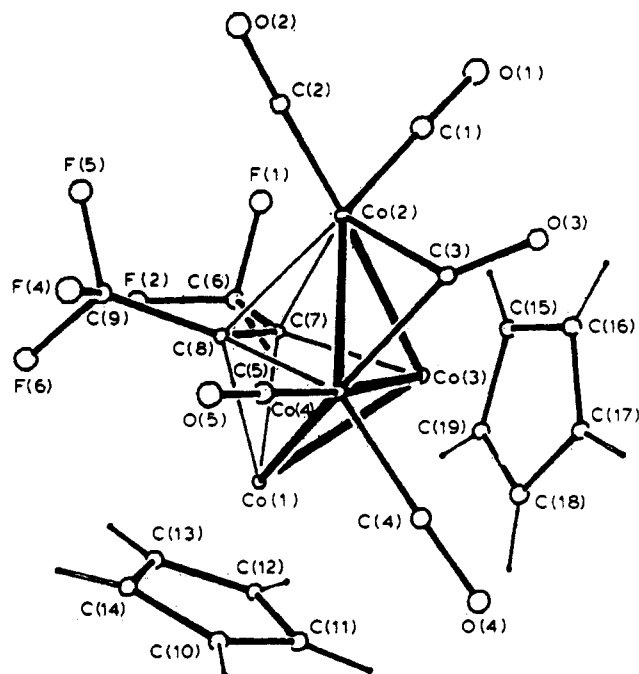
Figure 1. A view of the [(η^5-C$_5$H$_5$)Fe(CO){μ-S(Me)CH=C(CF$_3$)}]$_2$ molecule. Hydrogen atoms are omitted for clarity, and 50% probability ellipsoids are displayed.

originally formulated, from spectroscopic studies, as monomers.[4] We have now carried out an X-ray analysis of **2** (R = H) and found that it is in fact a dimeric derivative. The crystals are built of the well-separated dimeric molecules shown in Figure 1. Each iron atom attains an 18-electron configuration and displays pseudooctahedral coordination: SMe, CO, and η^1-alkenyl groups are arranged facially about each iron atom and the remaining octahedral sites are occupied by a cyclopentadienyl ring. S(Me)-CH=C(CF$_3$) units bridge the iron atoms, which are thereby incorporated into a tub-shaped Fe$_2$S$_2$C$_4$ ring. The molecule displays close to C$_2$ noncrystallographic point symmetry. Bond lengths (Table I) agree well with corresponding values in related dinuclear iron complexes.[9] They are consistent with the molecular formula **2**.

The eight-membered Fe$_2$S$_2$C$_4$ metallacycle shows signs of ring strain: endocyclic angles at the ring carbon atoms, particularly those at C(4) and C(7), are greater than the expected value of 120° and the Fe—C=C—S torsion angles differ slightly but significantly from zero (see Table I). There are also rather close transannular contacts: the most notable of these is that between S(1) and S(2) of 3.223 (2) Å, some 0.5 Å shorter than the van der Waals diameter of sulfur (3.7 Å); the C(3)···C(7) and C(4)···C(6) distances (3.123 (6) and 3.129 (6) Å, respectively) also appear short compared with 3.4 Å, the van der Waals diameter of a trigonal carbon atom. The S-methyl ring substituents are equatorial, the S–C(methyl) bonds being approximately normal to the molecular diad axis.
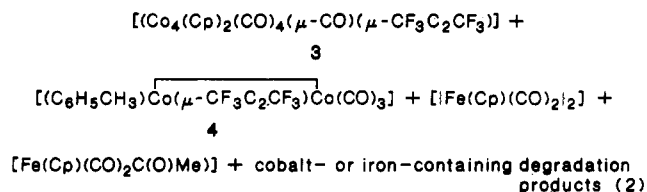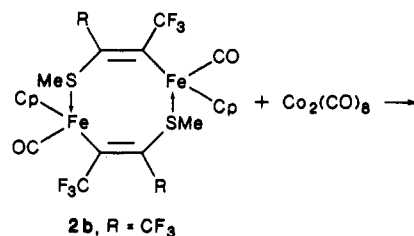
The two complexes **2a** and **2b** have similar IR and NMR spectra,[4] implying that they are isostructural.

Ligand Transfer Reactions. 1. Reaction of 2b with Dicobalt Octacarbonyl. The reaction of an excess of Co$_2$(CO)$_8$ with **2b** in refluxing toluene produced a ~35% yield of the unexpected tetranuclear alkyne cluster [Co$_4$-(Cp)$_2$(CO)$_4$(μ-CO)(μ-CF$_3$C$_2$CF$_3$)] (**3**) which was separated from the new dimeric complex [(C$_6$H$_5$CH$_3$)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (**4**) and small amounts of other products by column chromatography (eq 2). Some [{Fe-

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Figure 2. A view of the structure of **3**.

(Cp)(CO)$_2$}$_2$] and traces of [Fe(Cp)(CO)$_2$C(O)Me] were always obtained as well.

2b, R = CF$_3$

[(Co$_4$(Cp)$_2$(CO)$_4$(μ-CO)(μ-CF$_3$C$_2$CF$_3$)] +

3

[(C$_6$H$_5$CH$_3$)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] + [{Fe(Cp)(CO)$_2$}$_2$] +

4

[Fe(Cp)(CO)$_2$C(O)Me)] + cobalt- or iron-containing degradation products (2)

The effects of varying the reaction conditions were studied. At a reaction temperature of 75–105 °C overnight the proportions of [{Fe(Cp)(CO)$_2$}$_2$] and [Fe(Cp)(CO)$_2$C-(O)Me] produced were increased, and dimeric [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$][10] was formed instead of the cluster **3** and the dimeric complex **4**. Reactions with equimolar quantities of **2b** and Co$_2$(CO)$_8$ resulted in poor yields of the cluster product. Reactions conducted in *n*-octane at 125 °C resulted in appreciable yields of the cluster **3** (38%), but the dinuclear compound **4** was not formed. It should be noted that cluster **3** is also obtained in high yield (65–70%) by heating [(CO)$_3$Co(CF$_3$C$_2$C-F$_3$)Co(CO)$_3$] with [CpCo(CO)$_2$].

The tetrametallic alkyne cluster **3** is a violet solid, soluble in hydrocarbon solvents, and is not particularly air-sensitive. This compound was characterized by IR, NMR, and mass spectra (Table III) and elemental analysis; a preliminary account of its crystal structure has been already given[7] (Figure 2). In the mass spectrum, successive loss of CO from the parent ion, [Co$_4$(Cp)(CO)$_5$(C$_4$F$_6$)]$^+$, is

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Table I. Selected Interatomic Distances (Å) and Angles (deg) in [(η^5-C$_5$H$_5$)Fe(CO){μ-S(Me)CH=C(CF$_3$)}]$_2$

Bond Lengths

Fe(1)–S(1)	2.256 (2)	Fe(2)–S(2)	2.254 (2)
Fe(1)–C(1)	1.726 (7)	Fe(2)–C(2)	1.735 (6)
Fe(1)–C(7)	2.000 (5)	Fe(2)–C(4)	1.977 (5)
Fe(1)–C(11)	2.107 (6)	Fe(2)–C(16)	2.104 (7)
Fe(1)–C(12)	2.074 (6)	Fe(2)–C(17)	2.103 (6)
Fe(1)–C(13)	2.078 (6)	Fe(2)–C(18)	2.083 (6)
Fe(1)–C(14)	2.092 (6)	Fe(2)–C(19)	2.072 (6)
Fe(1)–C(15)	2.117 (6)	Fe(2)–C(20)	2.086 (7)
S(1)–C(3)	1.775 (5)	S(2)–C(6)	1.768 (5)
S(1)–C(9)	1.806 (5)	S(2)–C(10)	1.805 (6)
F(1)–C(5)	1.338 (7)	F(4)–C(8)	1.331 (6)
F(2)–C(5)	1.332 (7)	F(5)–C(8)	1.342 (7)
F(3)–C(5)	1.330 (7)	F(6)–C(8)	1.339 (6)
O(1)–C(1)	1.159 (6)	O(2)–C(2)	1.141 (6)
C(3)–C(4)	1.318 (7)	C(6)–C(7)	1.326 (7)
C(4)–C(5)	1.507 (7)	C(7)–C(8)	1.486 (7)
C(11)–C(12)	1.372 (8)	C(16)–C(17)	1.397 (9)
C(11)–C(15)	1.367 (8)	C(16)–C(20)	1.395 (10)
C(12)–C(13)	1.422 (9)	C(17)–C(18)	1.399 (9)
C(13)–C(14)	1.393 (9)	C(18)–C(19)	1.390 (9)
C(14)–C(15)	1.369 (8)	C(19)–C(20)	1.387 (10)

Transannular Contact Distances

Fe(1)···S(2)	3.552 (1)	Fe(2)···S(1)	3.554 (1)
C(3)···C(6)	3.301 (6)	C(4)···C(7)	3.462 (6)
C(3)···C(7)	3.123 (6)	C(4)···C(6)	3.129 (6)
S(1)···S(2)	3.223 (2)	Fe(1)···Fe(2)	4.929 (1)

Interbond Angles

S(1)–Fe(1)–C(1)	93.9 (2)	S(2)–Fe(2)–C(2)	93.5 (2)
S(1)–Fe(1)–C(7)	92.0 (2)	S(2)–Fe(2)–C(4)	92.5 (2)
C(1)–Fe(1)–C(7)	96.2 (3)	C(2)–Fe(2)–C(4)	95.7 (3)
S(1)–Fe(1)–Cp1[a]	121.3	S(2)–Fe(2)–Cp2	123.0
C(1)–Fe(1)–Cp1	124.3	C(2)–Fe(2)–Cp2	123.2
C(7)–Fe(1)–Cp1	121.3	C(4)–Fe(2)–Cp2	121.1
Fe(1)–S(1)–C(3)	109.0 (2)	Fe(2)–S(2)–C(6)	108.5 (2)
Fe(1)–S(1)–C(9)	108.1 (2)	Fe(2)–S(2)–C(10)	106.8 (2)
C(3)–S(1)–C(9)	99.3 (3)	C(6)–S(2)–C(10)	99.2 (3)
Fe(1)–C(1)–O(1)	173.1 (6)	Fe(2)–C(2)–O(2)	175.1 (6)
S(1)–C(3)–C(4)	123.0 (4)	S(2)–C(6)–C(7)	123.4 (4)
Fe(2)–C(4)–C(3)	129.9 (4)	Fe(1)–C(7)–C(6)	128.6 (4)
Fe(2)–C(4)–C(5)	118.1 (4)	Fe(1)–C(7)–C(8)	117.9 (4)
C(3)–C(4)–C(5)	112.0 (5)	C(6)–C(7)–C(8)	113.5 (5)
F(1)–C(5)–F(2)	103.9 (6)	F(4)–C(8)–F(5)	105.9 (5)
F(1)–C(5)–F(3)	105.4 (6)	F(4)–C(8)–F(6)	103.8 (5)
F(1)–C(5)–C(4)	116.2 (6)	F(4)–C(8)–C(7)	113.7 (5)
F(2)–C(5)–F(3)	105.5 (6)	F(5)–C(8)–F(6)	103.4 (5)
F(2)–C(5)–C(4)	112.5 (5)	F(5)–C(8)–C(7)	112.4 (5)
F(3)–C(5)–C(4)	112.5 (6)	F(6)–C(8)–C(7)	116.5 (5)
C(12)–C(11)–C(15)	109.3 (6)	C(17)–C(16)–C(20)	107.6 (7)
C(11)–C(12)–C(13)	106.9 (6)	C(16)–C(17)–C(18)	108.2 (7)
C(12)–C(13)–C(14)	106.7 (5)	C(17)–C(18)–C(19)	107.4 (7)
C(13)–C(14)–C(15)	108.3 (6)	C(18)–C(19)–C(20)	108.7 (7)
C(11)–C(15)–C(14)	108.7 (6)	C(16)–C(20)–C(19)	108.1 (7)

Torsion Angles

C(7)–Fe(1)–S(1)–C(3)	35.0 (3)	C(4)–Fe(2)–S(2)–C(6)	36.2 (3)
Fe(1)–S(1)–C(3)–C(4)	-104.7 (5)	Fe(2)–S(2)–C(6)–C(7)	-104.2 (5)
S(1)–C(3)–C(4)–Fe(2)	-4.8 (3)	S(2)–C(6)–C(7)–Fe(1)	-6.6 (3)
C(3)–C(4)–Fe(2)–S(2)	53.0 (5)	C(6)–C(7)–Fe(1)–S(1)	54.8 (5)

[a] Cp1 and Cp2 are the centroids of rings C(11)–C(15) and C(16)–C(20), respectively.

Table II. Fractional Atomic Coordinates and Isotropic Displacement Parameters (Å^2) for [(η^5-C$_5$H$_5$)Fe(CO){μ-S(Me)CH=C(CF$_3$)}]$_2$

	x/a	y/b	z/c	U^a
Fe(1)	0.08826 (4)	0.17961 (3)	0.06824 (4)	0.038
Fe(2)	0.1331 (5)	0.01253 (4)	0.30182 (4)	0.048
S(1)	0.03781 (7)	0.16232 (6)	0.19871 (7)	0.039
S(2)	0.13304 (8)	0.01089 (6)	0.16176 (8)	0.044
F(1)	0.2568 (2)	0.2072 (2)	0.3680 (2)	0.101
F(2)	0.3214 (2)	0.1159 (2)	0.3208 (2)	0.093
F(3)	0.2455 (3)	0.1077 (3)	0.4314 (2)	0.123
F(4)	0.2910 (2)	0.1959 (2)	-0.0030 (2)	0.100
F(5)	0.2970 (2)	0.2308 (2)	0.1231 (3)	0.096
F(6)	0.3632 (2)	0.1369 (2)	0.0854 (2)	0.083
O(1)	0.1379 (3)	0.3266 (2)	0.0978 (3)	0.096
O(2)	0.3097 (3)	-0.0449 (3)	0.3140 (3)	0.102
C(1)	0.1229 (4)	0.2662 (3)	0.0876 (4)	0.059
C(2)	0.2413 (4)	-0.0192 (4)	0.3087 (4)	0.065
C(3)	0.1277 (3)	0.1708 (3)	0.2693 (3)	0.043
C(4)	0.1655 (3)	0.1153 (3)	0.3056 (3)	0.042
C(5)	0.2455 (4)	0.1367 (4)	0.3559 (4)	0.069
C(6)	0.2187 (3)	0.0678 (3)	0.1259 (3)	0.044
C(7)	0.2042 (3)	0.1325 (3)	0.0945 (3)	0.038
C(8)	0.2869 (3)	0.1725 (3)	0.0751 (4)	0.057
C(9)	-0.0256 (4)	0.2403 (3)	0.2286 (4)	0.063
C(10)	0.1787 (4)	-0.0744 (3)	0.1306 (4)	0.073
C(11)	0.0677 (4)	0.1018 (3)	-0.0248 (4)	0.066
C(12)	0.0888 (4)	0.1668 (4)	-0.0598 (3)	0.071
C(13)	0.0208 (5)	0.2157 (3)	-0.0364 (4)	0.075
C(14)	-0.0379 (4)	0.1780 (4)	0.0141 (3)	0.066
C(15)	-0.0087 (4)	0.1087 (3)	0.0202 (3)	0.067
C(16)	-0.0042 (4)	0.0157 (4)	0.3240 (5)	0.090
C(17)	0.0208 (4)	-0.0542 (4)	0.3034 (4)	0.084
C(18)	0.0830 (5)	-0.0776 (3)	0.3620 (5)	0.087
C(19)	0.0952 (5)	-0.0223 (5)	0.4188 (4)	0.096
C(20)	0.0421 (6)	0.0351 (4)	0.3957 (5)	0.100

[a] U is the mean latent root of the anisotropic vibration tensor.

donor, functions as an olefin coordinating group by forming σ-bonds with two cobalt atoms, Co(3) and Co(4), and a "bent" four-center μ-type bond with the two other cobalt atoms. The coordination of the alkyne results in the lengthening of the C–C bond and the bending of the C–CF$_3$ bonds away from the metal core; these values (1.442 (2) Å and 125.8° (average), respectively) are undoubtedly in agreement with an olefinic character of the coordinated hexafluorobut-2-yne. From another point of view, the complex can be seen as a dicarbatetracobalt cluster with a nearly octahedral arrangement that is fully consistent with Wade's[11] skeletal electron-counting rules, which predict a *closo*-M$_4$C$_2$ structure. The hinge bond is longer (2.471 (4) Å) than the bridged wing bonds (ca. 2.40 Å). The dihedral angle between the wings of the butterfly is slightly opened (ca. 117°) with respect to the angle between octahedral faces (109°). Although the Co–Co distances are close, the cobalt–cobalt bond of the wing subtending the bridging carbonyl is shorter than the other three (2.387 (4) Å vs 2.402 Å (average)). The Co–C and C–O distances of the terminal carbonyl ligands fall within the usual ranges. However, the Co(2)–C(1) and Co(2)–C(2) bonds are significantly shorter than the Co(4)–C(4) and Co(4)–C(5) bonds (1.71 Å (average) vs 1.75 Å (average)), reflecting the increased cobalt – π^* carbonyl back-donation when the metal is π-bonded to the alkyne. Other clusters with analogous Co$_4$C$_2$ skeletons have already been structurally characterized,[12] but 3 is the first with cyclopentadienyl ligands to be observed.

observed. In addition, fragments arising from Co–Co scission are also obtained. The calculated isotopic distribution of the parent ion is in excellent agreement with that observed experimentally. Infrared spectra display four absorptions between 2060 and 1970 cm^{-1} and one absorption at 1840 cm^{-1} which are assigned to terminal carbonyl stretches and to a bridging carbonyl, respectively. Such a pattern of ν(CO) absorptions is consistent with that predicted for a molecule of C$_1$ symmetry.

Single crystals of 3 are obtained from a 2/1 mixture of hexane–dichloromethane. X-ray diffraction analysis[7] confirms the proposed elemental composition (Figure 2). The cobalt atoms can be described as having a butterfly configuration in which the alkyne, a formal six-electron

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Table III. A Spectroscopic Data (Room Temperature)

compd	IR, cm^{-1}		^{1}H NMR^c δ	^{19}F NMR^c δ	^{13}C NMR^c δ
	ν(CO)	ν(C≡C)			
3	2052 (s), 2024 (s), 1995 (s), 1975 (s), 1840 (s)^a		5.33 (s, 5 H), 4.79 (s, 5 H)	45.57 (s)	145.1 (m, =CCF$_3$), 126.36 (q, $J_{\text{C-F}}$ = 275 Hz, CF$_3$), 126.0 (q, $J_{\text{C-F}}$ = 275 Hz, CF$_3$), 86.46 (s, C$_5$H$_5$), 83.32 (s, C$_5$H$_5$)^e
4	2077 (s), 2026 (s), 2012 (s)	1600^b	6.10 (s, 5 H), 2.38 (s, 3 H)	52.07 (s)	126.8 (q, $J_{\text{C-F}}$ = 269 Hz, CF$_3$), 108.8 (s, CCF$_3$), 92.8–93.8–95.0 (C$_6$H$_5$), 20.7 (s, CH$_3$)
5^d	2035 (s), 1995 (s), 1885 (sh)^a		3.80–3.50 (m)	48.66 (q, $J_{\text{F-F}}$ = 3.5 Hz)	
6	2040 (s), 1994 (s)^b		4.98 (s, 5 H), 2.13 (q, 3 H, $J_{\text{F-H}}$ = 3.7 Hz)	60.17 (q, $J_{\text{F-F}}$ = 1.7 Hz), 48.0 (m, $J_{\text{F-F}}$ = 3.7 Hz)	213.4 (s, CO), 142.8 (qq, $^2J_{\text{C-F}}$ = 29.5 Hz, $^3J_{\text{C-F}}$ = 5.5 Hz, =CCF$_3$), 128.8 (q, $J_{\text{C-F}}$ = 278 Hz, CF$_3$), 124.9 (q, $J_{\text{C-F}}$ = 274 Hz, CF$_3$), 86.1 (s, C$_5$H$_5$), 19.1 (m, $J_{\text{C-F}}$ = 2.8 Hz, CH$_3$)
7	2040 (s), 1994 (s)^b		5.02 (s, 5 H), 2.25 (m, 3 H)	58.82 (q, $J_{\text{F-F}}$ = 16.8 Hz), 48.74 (qq, $J_{\text{F-F}}$ = 16.8 Hz, $J_{\text{F-H}}$ = 2.3 Hz)	213.0 (s, CO), 133.5 (qq, $^2J_{\text{C-F}}$ = 34 Hz, $^3J_{\text{C-F}}$ = 4.6 Hz, =CCF$_3$), 126.6 (q, $J_{\text{C-F}}$ = 275 Hz, CF$_3$), 120.6 (q, $J_{\text{C-F}}$ = 279 Hz, CF$_3$), 86.2 (s, C$_5$H$_5$), 25.6 (q, $J_{\text{C-F}}$ = 3.7 Hz, CH$_3$)
8	2090 (s), 2048 (vs), 2034 (s), 2000 (m, br)	1590 (m)^a	5.22 (s, 5 H), 1.90 (s, 3 H)	51.20 (s)	211.85 s, CO|Fe|), 202.55 (s, br, CO|Co|), 196.80 (s, br, CO|Co|), 127.80 (q, $J_{\text{C-F}}$ = 269 Hz, CF$_3$), 86.50 (s, C$_5$H$_5$), 71.0 (q, $^2J_{\text{C-F}}$ = 47 Hz, =CCF$_3$), 26.48 (s, CH$_3$)

^{a} CH$_2$Cl$_2$. ^{b} Hexane. ^{c} CDCl$_3$. ^{d} ^{31}P NMR (H$_3$PO$_4$): δ 159 ($\Delta\nu$ = 300 Hz). ^{e} ^{13}C NMR: (i) at room temperature, δ(CO), unresolved peaks; (ii) in CD$_2$Cl$_2$ at -40 °C, δ(CO) 222.4, 207.4, 197.8, 188.1, 185.2.

The ^{1}H NMR spectrum of **3** shows two singlets due to nonequivalent cyclopentadienyl groups; no temperature dependence is observed. Throughout the temperature range, -80 to +20 °C, the ^{13}C NMR spectra reveal a five-line pattern in the carbonyl region, and there are two Cp lines; carbonyl scrambling between cobalt atoms is not rapid on the NMR time scale up to at least 20 °C. The fact that the two-line Cp ^{13}C spectrum persists, with sharp lines, at 20 °C rules out occurrence of any rearrangement of the central "Co$_4$Cp$_2$" unit in the temperature range -80 to +20 °C. The ^{19}F NMR spectra for **3** show two A$_3$X$_3$ CF$_3$ resonances at low temperatures. When the temperature is increased collapse and coalescence of the CF$_3$ signals occur (Figure 3). At >278 K sharpening of the signals continues. This phenomenon, which is concentration independent and reversible with temperature, could be interpreted as either (i) being a consequence of a rapid intramolecular exchange of two CF$_3$ groups at higher temperature or (ii) due to a rapid rotation about the axis which is perpendidular to the C(7)–C(8) bond. The approximate activation parameter for these processes, obtained in the usual way,[13] was calculated from the Eyring relation at the coalescence temperature (278 K) and was $\Delta G^*_0 \approx 13.5$ kcal mol^{-1}. The NMR results confirm the lack of any symmetry in the arrangement of the ligands around the "Co$_4$C$_2$" core, as was observed by X-ray analysis.

The major product (55% yield) obtained in reaction 2 is the dinuclear compound [(C$_6$H$_5$Me)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (**4**). To our knowledge this π-arene complex is new. Other routes to **4** are given in the Experimental Section. **4** was characterized by analysis and spectroscopic data (Table III). In the mass spectrum successive loss of CO from the parent ion, [Co$_2$(C$_4$F$_6$)(C$_6$H$_5$Me)(CO)$_3$]$^+$, is accompanied by a parallel sequential loss from [Co$_2$-(C$_4$F$_6$)(C$_6$H$_5$Me)(CO)$_3$]$^+$, but there was no evidence of fragments arising from Co–toluene scission. Infrared spectra display three ν(CO) bands as expected for a C_s geometry; the ^{19}F NMR is also consistent with this structure. One outstanding feature of the η^6-toluene complexes is the facile substitution of η^6-toluene for other ligands, this being attributed to the weakness of the

transition-metal–arene bond,[14] this seems to be inconsistent with the mass spectrum that suggests a strong cobalt–toluene interaction. In order to solve this contradiction, we allowed complex **4** to react with a large excess of trimethyl phosphite. Substitution of the η^6-toluene ligand by three molecules of phosphite takes place, giving compound [{P(OMe)$_3$}$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (**5**) in high yield (ca. 95%). **5** is formulated on the basis of its mass and NMR spectra. Since this compound results from **4** by reaction with trimethyl phosphite, the substitution pattern could be two equatorial and one axial phosphite groups on only one cobalt atom. Indeed such a geometry would fit the ^{19}F NMR data better than a mixed structure which is suggested by Cullen et al.[15] for the phenylalkyne analogue [{P(OMe)$_3$}$_2$(CO)Co(μ-PhC$_2$Ph)Co(CO)$_2${P-(OMe)$_3$}]. An electrochemical analysis confirms that **5** has redox potentials different[16] from those of the diaxial, equatorial configuration recently attributed to [{P-(OMe)$_3$}$_2$(CO)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_2${P(OMe)$_3$}] by Robinson and Simpson.[17]

2. Reaction of Dinuclear Complex [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] with the Dimeric Iron Compound [Cp(CO)Fe(μ-SMe)$_2$Fe(CO)Cp]. Reaction of [(CO)$_3$-Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] with the iron thiolate dimer [Cp(CO)Fe(μ-SMe)$_2$Fe(CO)Cp] in refluxing toluene resulted in transfer of hexafluorobut-2-yne, carbonyl, and cyclopentadienyl ligands (eq 3). The complexes obtained in reaction 2 are again formed here, but they are accompanied by two isomeric derivatives, **6** and **7**, which are the major products.

Compounds **6** and **7** are new and are formulated as shown on the basis of spectroscopic studies and elemental analyses. The mass spectra of the two complexes are similar and show, in addition to the parent ions, [Fe-

(13) Martin, M. L.; Martin, G. J. *Manuel de Résonance Magnétique Nucléaire*; Azoulay: Paris, 1971; p 141.
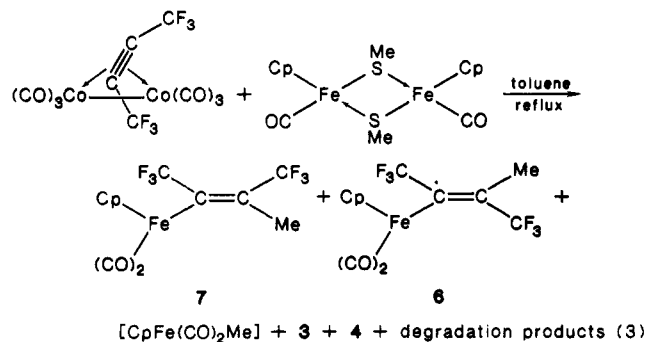
(14) (a) Radonovich, L. J.; Koch, F. J.; Albright, T. *Inorg. Chem.* **1980**, *19*, 3373. (b) Brezincski, M. M.; Klabunde, K. J.; Janiskowski, S. K.; Radonovich, L. J. *Inorg. Chem.* **1985**, *24*, 3305.

(15) Chia, L. S.; Cullen, W. R.; Frenklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521.

(16) Talarmin, J., personal communication.

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$[CpFe(CO)_2Me] + 3 + 4 + \text{degradation products}$ (3)

$(C_5H_5)(CO)_2\{C_2(CF_3)_2Me\}]^+$, fragments arising from successive loss of carbonyl groups. Their ^1H NMR spectra exhibit two types of signals: a singlet, ca. 5.0 ppm, corresponding to the cyclopentadienyl groups, and a multiplet, ca. 2.2 ppm, corresponding to the methyl groups. The ^{13}C NMR spectra show a similar pattern to the ^1H NMR spectra. Both the ^{19}F NMR spectra of 6 and 7 exhibit one quartet and a multiplet. A strong F–F coupling (16.8 Hz) suggests that CF_3 groups have a cis configuration in 7 whereas a trans configuration ($J \approx 1.7$ Hz) is found for 6. Such vinyliron complexes are already well-known.[18] These alkenyl complexes are usually obtained by insertion of an alkyne into a metal–X bond (X = H,[18] R,[18] or SR^4) or by reaction of nucleophiles with cationic π-alkyne compounds.[19] Complex 7 undergoes cis–trans isomerization on photolysis (100% yield).
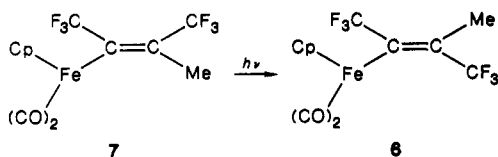
The effects of varying the conditions of the reaction 3 were studied. On lowering the temperature (50–90 °C) and on bubbling nitrogen through the solution, complexes 6 and 7 and cluster 3 were not formed but, instead, a new iron–cobalt derivative 8 (eq 4) is obtained in good yield (~65%). The new complex 8 was characterized by
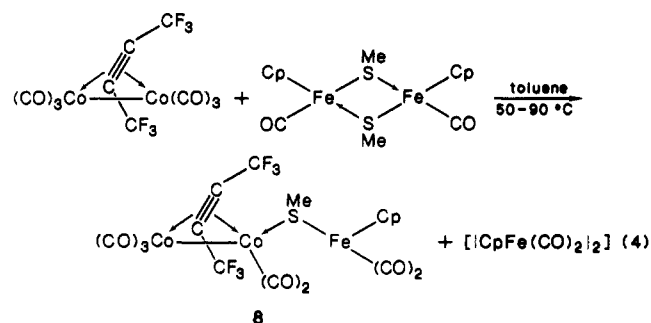
spectral data, and its structure has been established by X-ray diffraction. This heterotrinuclear compound has retained the $Co_2(CF_3C_2CF_3)$ structure of the cobalt reactant, but a carbonyl group has been substituted by a (thiolato)iron ligand. It should be noted that when $[(PhMe)Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ was used as reactant instead of $[(CO)_3Co(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$, no reaction

(18) Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 4, p 331.
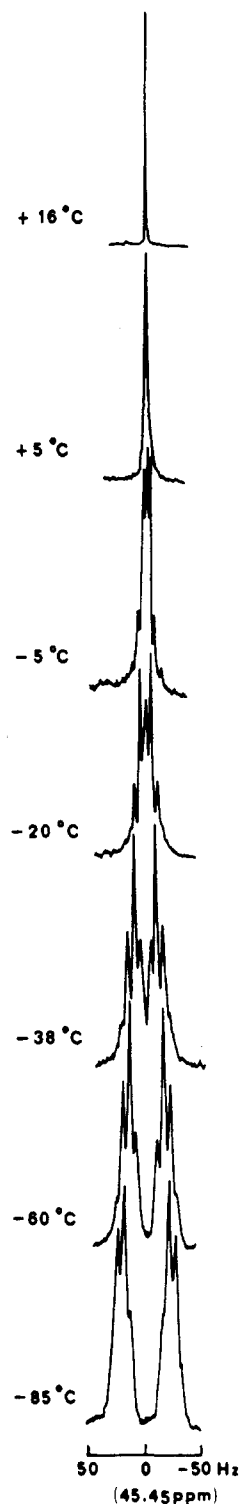(19) Reger, D. L.; McElligott, J. *J. Am. Chem. Soc.* 1980, *102*, 5923.

Figure 3. Variable ^{19}F NMR spectra of 3 at low temperatures.

was observed. The substitution of three good acceptor carbonyl groups by a donor η^6-toluene ligand in 4 makes the remaining CO less labile than those of the hexacarbonyl parent. The room-temperature ^{13}C NMR spectrum (Table III) of 8 shows at low field a well-resolved peak due to carbonyl groups located on iron and two unresolved singlets attributed to carbonyl groups bonded to cobalt. No coalescence phenomenon was observed in solution throughout the temperature range –80 °C to +60 °C, showing that the carbonyl groups do not exchange on the NMR time scale, up to +60 °C.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in [(OC)₃Co(μ-CF₃C₂CF₃)Co(CO)₂{(SMe)Fe(CO)₂Cp}] (8)

Bond Lengths

	molecule A	molecule B^a			molecule A	molecule B^a	
Co(1)–Co(2)	2.468 (4)	2.468 (6)		Fe–C(6)	1.67 (3)		
Co(1)–C(1)	1.72 (3)	1.73 (3)		Fe–C(7)	1.74 (3)	1.84 (3)	1.74 (3)
Co(1)–C(2)	1.78 (3)	1.81 (3)		Fe–C(12)	2.08 (3)	1.92 (3)	2.23 (3)
Co(1)–C(3)	1.73 (4)	1.79 (3)		Fe–C(13)	2.15 (3)	1.90 (4)	2.39 (3)
Co(1)–C(9)	1.92 (2)	1.96 (2)		Fe–C(14)	2.11 (3)	2.11 (3)	2.15 (3)
Co(1)–C(10)	1.89 (2)	1.94 (2)		Fe–C(15)	2.07 (3)	2.33 (3)	1.92 (3)
Co(2)–S	2.270 (7)	2.30 (1)	2.34 (1)	Fe–C(16)	2.12 (3)	2.24 (3)	2.02 (3)
Co(2)–C(4)	1.77 (3)	1.80 (3)		S–C(17)	1.79 (3)		
Co(2)–C(5)	1.74 (3)	1.77 (3)		C(8)–C(9)	1.43 (3)	1.43 (4)	
Co(2)–C(9)	1.90 (3)	1.94 (2)		C(9)–C(10)	1.32 (3)	1.36 (3)	
Co(2)–C(10)	1.89 (2)	1.91 (2)		C(10)–C(11)	1.48 (4)	1.38 (4)	
Fe–S	2.274 (8)	2.32 (1)	2.20 (2)				

	mean	range		mean	range
C–F	1.35 (1)	1.32 (3)–1.42 (3)	C–C(Cp)	1.39 (2)	1.27 (4)–1.47 (4)
C–O	1.17 (1)	1.12 (4)–1.23 (4)			

Bond Angles

	molecule A	molecule B^a			molecule A	molecule B^a	
Co(2)–Co(1)–C(1)	99.4 (9)	98.4 (9)		C(4)–Co(2)–C(5)	105.3 (11)	105.5 (13)	
Co(2)–Co(1)–C(2)	150.2 (9)	148.9 (9)		C(4)–Co(2)–C(9)	102.1 (10)	108.0 (11)	
Co(2)–Co(1)–C(3)	97.3 (10)	97.4 (8)		C(4)–Co(2)–C(10)	139.9 (10)	145.0 (11)	
Co(2)–Co(1)–C(9)	49.5 (6)	50.3 (6)		C(5)–Co(2)–C(9)	145.2 (10)	141.0 (11)	
Co(2)–Co(1)–C(10)	49.3 (6)	49.7 (6)		C(5)–Co(2)–C(10)	106.0 (10)	100.2 (10)	
C(1)–Co(1)–C(2)	98.6 (12)	99.4 (12)		C(9)–Co(2)–C(10)	40.6 (9)	41.2 (9)	
C(1)–Co(1)–C(3)	103.7 (13)	106.5 (12)		S–Fe–C(6)	90.9 (8)		
C(1)–Co(1)–C(9)	102.9 (10)	99.7 (11)		S–Fe–C(7)	89.7 (9)	83 (1)	90 (1)
C(1)–Co(1)–C(10)	140.7 (10)	138.2 (11)		C(6)–Fe–C(7)	93.9 (12)		
C(2)–Co(1)–C(3)	101.2 (13)	101.7 (12)		Co(2)–S–Fe	117.5 (3)	116 (1)	116 (1)
C(2)–Co(1)–C(9)	103.2 (11)	101.4 (10)		Co(2)–S–C(17)	108.2 (8)		
C(2)–Co(1)–C(10)	103.2 (11)	101.4 (10)		Fe–S–C(17)	104.8 (9)		
C(3)–Co(1)–C(9)	140.4 (12)	141.4 (10)		Co(1)–C(9)–Co(2)	80.5 (8)	78.7 (8)	
C(3)–Co(1)–C(10)	103.5 (12)	104.2 (10)		Co(1)–C(9)–C(8)	133.4 (15)	131.5 (16)	
C(9)–Co(1)–C(10)	40.4 (9)	40.7 (8)		Co(1)–C(9)–C(10)	68.6 (12)	69.1 (12)	
Co(1)–Co(2)–S	147.0 (3)	143 (1)	145 (1)	Co(2)–C(9)–C(8)	139.7 (16)	141.2 (16)	
Co(1)–Co(2)–C(4)	98.9 (8)	99.3 (10)		Co(2)–C(9)–C(10)	69.2 (12)	68.5 (12)	
Co(1)–Co(2)–C(5)	104.2 (8)	104.3 (9)		C(8)–C(9)–C(10)	135.9 (19)	138.3 (19)	
Co(1)–Co(2)–C(9)	50.1 (6)	51.0 (6)		Co(1)–C(10)–Co(2)	81.5 (8)	79.6 (8)	
Co(1)–Co(2)–C(10)	49.2 (6)	50.7 (6)		Co(1)–C(10)–C(9)	71.0 (12)	70.2 (12)	
S–Co(2)–C(4)	98.9 (8)	87 (1)	109 (1)	Co(1)–C(10)–C(11)	132.1 (15)	134.5 (17)	
S–Co(2)–C(5)	97.5 (8)	109 (1)	89 (1)	Co(2)–C(10)–C(9)	70.2 (12)	70.3 (12)	
S–Co(2)–C(9)	99.0 (6)	92 (1)	99 (1)	Co(2)–C(10)–C(11)	137.0 (16)	139.5 (17)	
S–Co(2)–C(10)	101.1 (7)	107 (1)	95 (1)	C(9)–C(10)–C(11)	138.2 (19)	133.9 (20)	

	range		range		range		range
M–C–O^b	162 (2)–179 (2)	C–C–F	113 (2)–119 (2)	F–C–F	100 (2)–106 (2)	C–C–C(Cp)	104 (2)–114 (2)

^a Fe and S of molecule B are disordered over two alternative sites. Distances and angles involving these atoms are subject to systematic error. ^b M = Co or Fe.

The structure of 8 has been confirmed by X-ray analysis (see Tables IV and V) of a crystal grown from CH_2Cl_2/hexane. The asymmetric unit of the crystal structure contains two independent molecules, A and B. The structure of molecule A is shown in Figure 4. Disorder complicates the description of B. Our discussion will, therefore, focus on molecule A.

A is derived structurally from [(CO)₃Co(μ-CF₃C₂CF₃)Co(CO)₃] by substitution of an axial CO, roughly trans to the Co–Co bond, by a [CpFe(CO)₂(SMe)] moiety attached to Co(2) through sulfur. Electronic factors are thought to favor replacement of axial rather than equatorial CO in [(OC)₃Co(μ-CF₃C₂CF₃)Co(CO)₃], especially when the entering ligand is a weaker π-acid than CO.[17] Displacement of CO at a transition metal by the sulfur atom of a transition-metal thiolate has been observed previously.[20] The sawhorse [(CO)₂Co(μ-CF₃C₂CF₃)Co(CO)₃] portion of A is structurally similar to the corresponding portion of [(CO)₃Co(μ-CF₃C₂CF₃)Co(CO)₃][21] and is evidently not sensitive to the replacement of CO by sulfur. The iron atom in 8 has an 18-electron configuration, and the expected pseudooctahedral coordination also found in 2a. Bond lengths and angles in A are fully in accord with the proposed formulation.
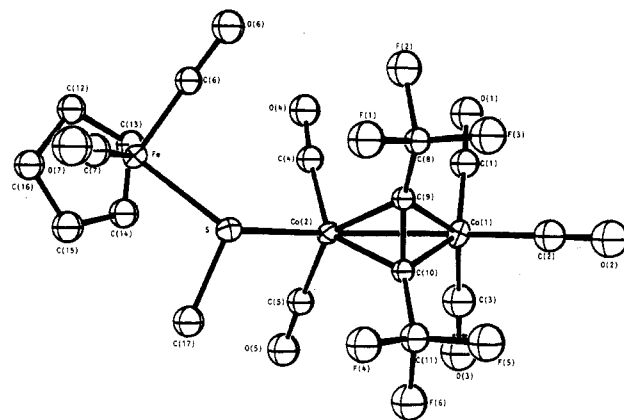
Disorder in B mainly involves the region corresponding to the roughly planar C(17)–S–Fe–C(6)–O(6) segment of A. The disorder (Figure 5) roughly maps the carbonyl and methyl carbon atoms on to one another and also involves two slightly different positions for the Fe and S atoms. The results of the analysis are, however, fully consistent with A and B being chemically identical.

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(21) Baert, F.; Guelzin, A.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Sci.* **1984**, *B40*, 590 and ref therein.

Table V. Fractional Atomic Coordinates and Isotropic Displacement Parameters (Å²) for

[(CO)₂Co(μ-CF₃C₂CF₃)Co(CO)₂{(SMe)Fe(CO)₂Cp}] (8)

	x/a	y/b	z/c	U^c
Co(1A)ᵃ	0.00000	0.18396 (20)	0.25000	0.054
Co(2A)	0.0180 (3)	0.0758 (2)	0.3349 (2)	0.044
Co(1B)	0.1854 (3)	-0.5501 (2)	0.4986 (2)	0.052
Co(2B)	0.1029 (3)	-0.5729 (2)	0.5851 (2)	0.061
Fe(A)	0.1432 (3)	-0.1064 (2)	0.4472 (2)	0.053
Fe(B1)ᵇ	-0.0668 (6)	-0.5951 (4)	0.7059 (4)	0.034
Fe(B2)ᵇ	-0.0512 (7)	-0.6547 (5)	0.7008 (4)	0.062
S(A)	0.0330 (5)	-0.0775 (4)	0.3677 (3)	0.053
S(B1)ᵇ	-0.0267 (8)	-0.6480 (7)	0.6173 (4)	0.023
S(B2)ᵇ	-0.0468 (10)	-0.5754 (12)	0.6193 (5)	0.064
F(1A)	0.1236 (11)	-0.0910 (10)	0.2414 (6)	0.092 (4)
F(2A)	0.2158 (11)	0.0283 (10)	0.2518 (6)	0.091 (4)
F(3A)	0.1163 (11)	0.0114 (10)	0.1740 (6)	0.092 (5)
F(4A)	-0.1250 (10)	-0.0923 (10)	0.2391 (6)	0.084 (4)
F(5A)	-0.1385 (12)	0.0094 (10)	0.1704 (7)	0.095 (4)
F(6A)	-0.2104 (11)	0.0328 (10)	0.2421 (6)	0.097 (5)
F(1B)	0.0489 (11)	-0.7754 (10)	0.4829 (6)	0.093 (5)
F(2B)	0.0046 (10)	-0.6746 (9)	0.4151 (6)	0.084 (4)
F(3B)	-0.0812 (10)	-0.6956 (10)	0.4825 (6)	0.085 (4)
F(4B)	0.0171 (10)	-0.3523 (10)	0.5094 (6)	0.093 (5)
F(5B)	-0.0994 (12)	-0.4518 (11)	0.5049 (7)	0.105 (5)
F(6B)	-0.0239 (11)	-0.4314 (10)	0.4320 (7)	0.094 (5)
O(1A)	0.1732 (14)	0.3012 (13)	0.2816 (8)	0.100 (6)
O(2A)	-0.0261 (14)	0.2068 (13)	0.1240 (9)	0.108 (6)
O(3A)	-0.1701 (16)	0.2884 (15)	0.2796 (9)	0.126 (7)
O(4A)	0.1988 (13)	0.1616 (11)	0.3942 (7)	0.088 (5)
O(5A)	-0.1404 (14)	0.1308 (12)	0.3988 (7)	0.096 (6)
O(6A)	0.2957 (12)	-0.0567 (11)	0.3812 (7)	0.082 (5)
O(7A)	0.1476 (14)	-0.3007 (14)	0.4094 (8)	0.103 (6)
O(1B)	0.3090 (14)	-0.7207 (13)	0.5102 (8)	0.100 (6)
O(2B)	0.1717 (12)	-0.5239 (12)	0.3720 (8)	0.088 (5)
O(3B)	0.2954 (15)	-0.3778 (15)	0.5409 (8)	0.116 (7)
O(4B)	0.2293 (15)	-0.7223 (14)	0.6426 (9)	0.114 (7)
O(5B)	0.1454 (14)	-0.3992 (14)	0.6507 (9)	0.111 (6)
O(7B)	-0.2484 (13)	-0.6999 (12)	0.6697 (7)	0.085 (5)
C(1A)	0.0998 (18)	0.2556 (17)	0.2684 (11)	0.075 (7)
C(2A)	-0.0146 (19)	0.2014 (18)	0.1735 (12)	0.082 (8)
C(3A)	-0.0943 (22)	0.2521 (21)	0.2693 (12)	0.101 (10)
C(4A)	0.1258 (17)	0.1242 (16)	0.3730 (10)	0.064 (7)
C(5A)	-0.0731 (17)	0.1110 (16)	0.3743 (10)	0.063 (7)
C(6A)	0.2335 (17)	-0.0750 (15)	0.4104 (10)	0.055 (6)
C(7A)	0.1466 (18)	-0.2263 (19)	0.4273 (11)	0.076 (8)
C(8A)	0.1211 (15)	0.0047 (15)	0.2308 (9)	0.050 (6)
C(9A)	0.0524 (14)	0.0569 (13)	0.2592 (8)	0.042 (5)
C(10A)	-0.0421 (14)	0.0564 (14)	0.2578 (8)	0.040 (5)
C(11A)	-0.1265 (17)	0.0026 (17)	0.2284 (10)	0.063 (6)
C(12A)	0.2232 (18)	-0.0807 (16)	0.5281 (10)	0.069 (7)
C(13A)	0.1723 (18)	0.0084 (17)	0.5090 (10)	0.071 (7)
C(14A)	0.0745 (18)	-0.0167 (18)	0.5022 (11)	0.076 (7)
C(15A)	0.0606 (19)	-0.1098 (19)	0.5147 (11)	0.081 (8)
C(16A)	0.1489 (19)	-0.1488 (16)	0.5354 (11)	0.071 (7)
C(17A)	-0.0801 (17)	-0.1136 (16)	0.3887 (10)	0.073 (7)
C(1B)	0.2599 (18)	-0.6493 (18)	0.5069 (10)	0.074 (7)
C(2B)	0.1774 (19)	-0.5345 (19)	0.4208 (12)	0.081 (8)
C(3B)	0.2580 (18)	-0.4496 (18)	0.5249 (10)	0.074 (7)
C(4B)	0.1764 (21)	-0.6675 (20)	0.6201 (12)	0.090 (8)
C(5B)	0.1332 (19)	-0.4694 (19)	0.6277 (12)	0.082 (8)
C(7B)	-0.1757 (19)	-0.6682 (16)	0.6841 (10)	0.071 (7)
C(8B)	0.0094 (17)	-0.6856 (17)	0.4722 (10)	0.062 (6)
C(9B)	0.0615 (14)	-0.6111 (14)	0.5055 (8)	0.041 (5)
C(10B)	0.0558 (13)	-0.5148 (13)	0.5121 (8)	0.037 (5)
C(11B)	-0.0095 (19)	-0.4461 (18)	0.4897 (11)	0.075 (7)
C(12B)	0.0438 (17)	-0.5569 (17)	0.7589 (10)	0.068 (7)
C(13B)	-0.0385 (22)	-0.5516 (22)	0.7837 (13)	0.102 (9)
C(14B)	-0.0688 (20)	-0.6463 (20)	0.7910 (11)	0.090 (8)
C(15B)	0.0066 (19)	-0.7031 (19)	0.7749 (11)	0.087 (8)
C(16B)	0.0751 (17)	-0.6413 (17)	0.7538 (10)	0.068 (7)
X(1B)ᵇ	-0.1191 (20)	-0.4473 (18)	0.6583 (11)	0.180
X(2B)ᵇ	-0.0081 (16)	-0.7919 (20)	0.6321 (10)	0.175

ᵃA and B refer to the two crystallographically independent molecules. The same atom numbering scheme is used for each molecule. ᵇDisordered sites. ᶜFor Co, Fe, S, and X atoms U is the mean latent root of the anisotropic vibration tensor. Otherwise it defines the isotropic temperature factor $\exp(-8\pi^2 U(\sin^2 \theta)/\lambda^2)$.

Figure 4. A view of the structure of [(CO)₃Co(μ-CF₃C₂CF₃)-Co(CO)₂{(SMe)Fe(CO)₂Cp}] (8). Molecule A is shown with 20% probability ellipsoids, and hydrogen atoms are omitted.
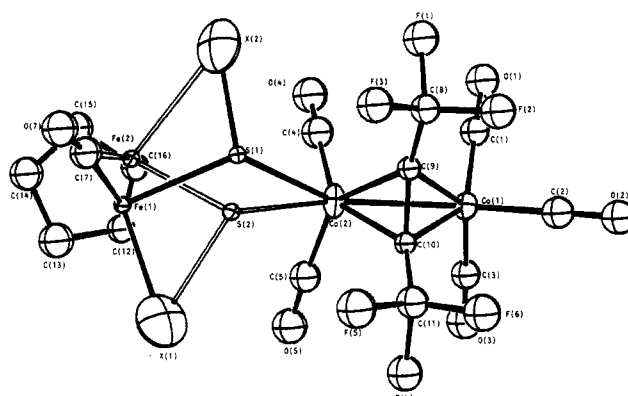
Figure 5. A view of molecule B. Sites X(1B) and X(2B) involve overlap of the S-methyl carbon atom of one orientation with a CO group attached to Fe(B) of the alternative orientation. The 20% probability ellipsoids are shown except for the iron and sulfur atoms which are shown as spheres of arbitrary size.

3. Discussion. The initial aim of this work was to prepare new heterometallic clusters, in which interest is rapidly growing, by adding dinuclear (thiolato)iron compounds to derivatives containing cobalt–cobalt bonds. This resulted in fact in formation of homometallic cluster and dinuclear complexes by transfer of coordinated ligands to another metal (eq 2–4). The formation of cluster 3 and of the dinuclear derivative 4 in reaction 2 is the first example for the transfer of a σ-coordinated CF₃C₂CF₃ ligand to another metal.

In reaction 3 cluster 3 results from the transfer of only one ligand, cyclopentadienyl, from iron to cobalt, whereas in reaction 2 two ligands are transferred. It is tempting to rationalize the formation of cluster 3 in reaction 2 in terms of a ligand transfer occurring in several steps. The first steps involve the formation of Co₄(CO)₁₂ from heating Co₂(CO)₈ and then the formation of an iron–cobalt complex in which two cyclopentadienyl–alkyne–iron ligands act as bridges between the cobalt atoms. It should be stressed that no spectroscopic evidence has been obtained for the existence of a heteronuclear intermediate in that reaction. The next stage consists of the expulsion of carbonyl–iron and thiolate groups yielding cluster 3. Such a mechanism, based upon a cobalt–thiolato–iron intermediate, is supported by the fact that the cobalt–thiolato–iron derivative 8 reacted with an excess of Co₂(CO)₈ to give cluster 3 in appreciable yield (37%). The high stability of the starting alkyne complex 2b in refluxing

toluene or *n*-octane excludes a pathway involving the thermal reaction of the disrupted $CF_3C_2CF_3$ with Co_2-$(CO)_8$.[22]

In reaction 3 cluster **3** is accompanied by two isomeric iron complexes which result from the transfer of the $(CF_3)_2C_2$ ligand from the cobalt to the iron atoms. In the cobalt reactant the hexafluorobut-2-yne is π-bonded to the two cobalt atoms and is somewhat more labile that in **2b**. It might, therefore, react more readily with the (thiolato)iron derivative to yield **6** or **7**. In such reactions, the insertion of the alkyne into the Fe–S(Me) bond would be expected; in fact the sulfur atom is expelled and no sulfur complex was obtained.

Despite the exchange processes observed in reactions 2–4, we have not been able so far to obtain heterometallic complexes bearing both the cyclopentadienyl and the alkyne ligands on the metal atoms. The transfer reactions described here would provide an alternative route for cluster syntheses. We have now extended this method to other similar systems; this will be published in a separate paper.

Experimental Section

Preparations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and degassed before use. The complex $[Co_2(CO)_8]$ was used without further purification, and $[\{Cp(CO)Fe(SMe)\}_2]$ and $[(CO)_3Co(\mu$-$CF_3C_2CF_3)Co(CO)_3]$ were prepared according to literature methods.[4,10]

Measurements. Infrared spectra of hexane or dichloromethane solutions were obtained with a Pye-Unicam SP 2000 spectrophotometer. Mass spectra were recorded on a Varian Mat 311 in the "Mesures Physiques" laboratory, University of Rennes, and NMR spectra, in $CDCl_3$ or CD_2Cl_2 solution, were measured on a JEOL FX 100 spectrometer (^1H, ^{13}C, ^{19}F) and were referenced to Me_4Si or $CFCl_3$. Chemical analyses were performed by the "Centre de Microanalyses du CNRS de Lyon".

Crystal Structure of $[\{Cp(CO)Fe[\mu$-S(Me)CH=C(CF_3)]\}_2]$ (2a). The specimen was a red plate of dimensions $0.50 \times 0.18 \times 0.08$ mm. All measurements were made with Mo K α X-rays, $\lambda = 0.71069$ Å, on an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator.

Crystal data: $C_{20}H_{16}F_6Fe_2O_2S_2$, M_r 580.2, orthorhombic, space group *Pbca*, a = 15.068 (4) Å, b = 18.649 (3) Å, c = 16.092 (3) Å, $U = 4522$ Å^3, $Z = 8$, $D_{calcd} = 1.704$ g·cm^{-3}, F(000) = 2336, μ(Mo Kα) = 15.2 cm^{-1}, and $T = 295$ K.

Unit-cell dimensions and crystal orientation were determined by a least-squares fit to the setting angles of 25 reflections with $11 < \theta < 14°$. The space group was determined from the systematic absences.

The intensities of 5464 reflections with $2 \le \theta$(Mo Kα) $\le 25°$ and $-1 \le h \le 17$, $-1 \le k \le 19$, and $-1 \le l \le 22$ were measured from $\theta/2\theta$ scans of $0.55°$ in θ; background was estimated by extending the scan by 25% at each end. A fast initial scan was used to adjust the final scan speed so as to obtain $\sigma(I)/I \le 0.02$, subject to a maximum counting time of 120 s. Correction was made for Lorentz–polarization effects but not for crystal decomposition, absorption, or extinction. Merging 824 duplicate measurements ($R_{int} = 0.024$) gave 3975 independent structure amplitudes, of which 1868 with $l \ge 3\sigma(l)$ were used in subsequent calculations.

The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares minimization of $\sum w$ $(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2$ (F) + 0.0004F^2. All hydrogen atoms were observed in difference syntheses, but their position were deduced from geometrical consideration (C–H = 0.98 Å) and they were allowed to ride on the carbon atoms to which they are bonded, with U(H) = 1.2U(C). Anisotropic displacement parameters were used for all non-hydrogen atoms. Refinement of 289 structure parameters converged ($\Delta/\sigma < 0.08$) with $R = 0.029$,

$R_w = 0.033$, and $S = 1.41$. Final $|\Delta\rho|$ values did not exceed 0.40 e Å^{-3}. Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref 23. Calculations were performed with the GX program package[24] on a Gould 3227 computer. Final atomic coordinates are listed in Table II.

Crystal Structure of $[(CO)_3Co(\mu$-$CF_3C_2CF_3)Co(CO)_2$-$\{(SMe)Fe(CO)_2Cp\}]$ (8). Unless otherwise stated experimental and computational procedures were identical with those used for **2a**. The specimen dimensions were $0.24 \times 0.24 \times 0.16$ mm.

Crystal data: $C_{17}H_8Co_2F_6FeO_7S$, M_r 644, 0, monoclinic, space group *Cc*, a = 13.978 (2) Å, b = 13.948 (3) Å, c = 23.221 (4) Å, $\beta = 97.74$ (1)°, $U = 4486$ Å^3, $Z = 8$, $D_{calcd} = 1.907$ g·cm^{-3}, F(000) = 2528, μ(Mo Kα) = 22.7 cm^{-1}, $T = 295$ K.

The intensities of 3092 reflections were measured from $\theta/2\theta$ scans of $0.75°$ in θ. Reflections in the *hkl* and *hk̄l* octants with $2 \le \theta$(Mo Kα) $\le 22°$ were surveyed, as were those in the *hkl* and *hk̄l* octants with $2 \le \theta$(Mo Kα) $\le 9°$. After the intensities of 197 pairs of reflections equivalent under *m* point group symmetry were averaged ($R_{int} = 0.028$) and 1232 reflections with $I < 3\sigma(I)$ were rejected, 1663 intensities, including those of 83 0*kl*/0*k̄l* Friedel pairs, were obtained. These intensities were used in the subsequent calculations.

The systematic absences were compatible with the space groups *C2/c* and *Cc*, the latter requiring that the asymmetric unit contain two crystallographically independent molecules. However, direct methods and difference Fourier syntheses led to a successful structure analysis in space group *Cc*.

Full-matrix least-squares refinement of 336 parameters converged (maximum parameter shift/error ratio < 0.05) at $R = 0.045$ and $R_w = 0.052$ with $S = 1.96$ (see Table V). All Co, Fe, and S atoms and the atoms of the disordered X sites (see below) were allowed anisotropic displacement parameters whereas F, O, and C atoms were refined with isotropic displacement parameters. Allowance was made for the scattering of the cyclopentadienyl and C(17A)–methyl H atoms. The positions of the H atoms were initially deduced from those of the heavier atoms; in the final refinement H atoms rode on the C atoms attached to them with C–H = 0.96 Å and U(H) = 1.2U(C). In the final difference synthesis $|\Delta\rho|$ values were less than 0.5 e Å^{-3}. The chirality parameter $\eta = 0.92$ (15).[25]

Of the two crystallographically independent molecules A and B, A is ordered but B is partially disordered. The disorder most obviously affects Fe(B) and S(B), one of the two CO groups attached to Fe(B), and the methyl carbon atom attached to S(B) (see Figure 5). In the final structural model "atoms" X(1B) and X(2B) correspond to sites partially occupied both by CO and CH_3 groups; they were assigned oxygen scattering factors. The atom Fe(B) was distributed over two sites 0.87 (1) Å apart, and S(B) likewise was distributed over two sites 1.05 (2) Å apart; fixed occupancies of 0.5 were assigned to the disordered Fe(B) and S(B) sites. Distances and angles in molecule B (Table IV), though subject to some error arising from disorder, are consistent with the superposition of two molecules of type A, each with slightly different orientations of the $CpFe(CO)_2SMe$ group relative to the $Co_2(CO)_5(CF_3C_2CF_3)$ moiety.

Syntheses of Complexes $[\{Cp(CO)Fe[\mu$-S(Me)C(R)=C-(CF_3)]\}_2]$ (R = H, 2a: R = CF_3, 2b). Complexes **2a** and **2b** have been obtained according to a method described previously.[4] However, the yields could be increased up to 95% by direct immersion of the UV lamp in the tetrahydrofuran solution of complexes **1** and by bubbling nitrogen through the solution.

Syntheses of Complexes $[Co_4Cp_2(CO)_4(\mu$-$CO)(\mu$-$CF_3C_2CF_3)]$ (3) and $[(C_6H_5Me)Co(\mu$-$CF_3C_2CF_3)Co(CO)_3]$ (4). Method A. Reaction of $[Cp(CO)Fe(\mu$-S(Me)C(CF_3)=C(CF_3)Fe(CO)Cp]$ (2b) with $[Co_2(CO)_8]$. Complex **2b** (0.5 g, 0.7 mmol) was dissolved in toluene (30 cm^3), and the toluene solution containing $[Co_2(CO)_8]$ (1.9 g, 5.6 mmol) was added under nitrogen. The reaction mixture was refluxed for 6 h. The mixture was evaporated to dryness under high vacuum. Chromatography of the residue

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on a silica gel column eluting with hexane afforded a yellow band which yielded about 5% of [Cp(CO)$_2$Fe(CH$_3$)] which was identified by comparison of its spectroscopic properties with those of an authentic sample. Further elution with CH$_2$Cl$_2$/hexane (1:10) gave the most abundant dark brown fraction from which 4 was collected and purified by crystallization from hexane/CH$_2$Cl$_2$ solution at -40 °C (0.35 g, 55%). Elution with CH$_2$Cl$_2$/hexane (2:10) served to remove the violet band which was evaporated to yield product 3, purified by crystallization from hexane/CH$_2$Cl$_2$ solution (0.16 g, 34%). Finally elution with CH$_2$Cl$_2$ gave a red fraction of [{CpFe(CO)$_2$}$_2$] (0.01 g, 6%).

When the reaction was conducted in *n*-octane, at 125 °C, 3 was obtained in 38% yield. 3 is a deep violet solid which is soluble in common organic solvents. Anal. Calcd for C$_{19}$H$_{10}$Co$_4$F$_6$O$_5$: C, 34.1; H, 1.5. Found: C, 33.8; H, 1.5. The mass spectrum showed ions corresponding to [M]$^+$, m/e 668, [Co$_4$(C$_5$H$_5$)$_2$(CO)$_4$(C$_4$F$_6$)]$^+$, m/e 640, [Co$_4$(C$_5$H$_5$)$_2$(CO)$_3$(C$_4$F$_6$)]$^+$, m/e 612, [Co$_4$(C$_5$H$_5$)$_2$-(CO)$_2$(C$_4$F$_6$)]$^+$, m/e 584, [Co$_4$(C$_5$H$_5$)$_2$(CO)(C$_4$F$_6$)]$^+$, m/e 556, [Co$_4$(C$_5$H$_5$)$_2$(C$_4$F$_6$)]$^+$, m/e 528, [Co$_2$(C$_5$H$_5$)$_2$(C$_4$F$_2$)]$^+$, m/e 334, and [Co(C$_5$H$_5$)$_2$(C$_4$)]$^+$, m/e 237. UV spectrum (pentane): λ_{max} (nm) 540 (ϵ 2950), 320 (sh, ϵ 17400), 280 (sh, ϵ 19700). 4 (this complex could also be synthesized in quantitative yield by refluxing [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] in toluene under a nitrogen flow) is a dark brown solid that is soluble in common organic solvents. Anal. Calcd for C$_{14}$H$_8$Co$_2$F$_6$O$_3$: C, 36.9; H, 1.8. Found: C, 36.9; H, 1.8. The mass spectrum showed ions corresponding to [M]$^+$, m/e 456, [Co$_2$(CO)$_2$(C$_4$F$_6$)(C$_7$H$_8$)]$^+$, m/e 428, [Co$_2$-(CO)$_2$(C$_4$F$_5$)(C$_7$H$_8$)]$^+$, m/e 409, [Co$_2$(CO)(C$_4$F$_6$)(C$_7$H$_8$)]$^+$, m/e 400, [Co$_2$(CO)(C$_4$F$_5$)(C$_7$H$_8$)]$^+$, m/e 381, [Co$_2$(C$_4$F$_6$)(C$_7$H$_8$)]$^+$, m/e 372, [Co(C$_4$F$_6$)(C$_7$H$_8$)]$^+$, m/e 313, [Co(CO)$_3$(C$_7$H$_8$)]$^+$, m/e 294, and [Co(C$_4$F$_4$)(C$_7$H$_8$)]$^+$, m/e 275. UV spectrum (pentane): λ_{max} (nm) 402 (ϵ 2660), 325 (ϵ 9230), 264 (sh, ϵ 14400).

Method B. Reaction of [(CO$_3$)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] with [Cp(CO)Fe(μ-SMe)$_2$Fe(CO)Cp]. The dinuclear derivative [Co$_2$(CO)$_6$(C$_4$F$_6$)] (1.2 g, 3 mmol) and the dimeric complex [{Cp-(CO)Fe(μ-SMe)}$_2$] (2.7 g, 6 mmol) were heated in toluene at reflux for 4 h. The solvent was then evaporated to dryness, and the residue was redissolved in a minimum of dichloromethane and the solution chromatographed on silica gel. Hexane eluted a yellow band which, upon removal of solvent, gave 0.05 g (4%) of yellow [Cp(CO)$_2$Fe(CH$_3$)]. A second, orange band was eluted with 10% dichloromethane/hexane. Removal of the solvent under reduced pressure gave a yellow-brown oil of *trans*-[Cp(CO)$_2$FeC(CF$_3$)=C(CF$_3$)Me] (6) (0.43 g, 20%). Further elution with 10% dichloromethane/hexane gave successively a dark brown band yielding 4 (0.16 g, 6% relative to cobalt complex) and a yellow fraction from which 0.21 g (10%) of a yellow-gray solid, *cis*-[Cp(CO)$_2$FeC(CF$_3$)=C(CF$_3$)Me] (7), was isolated and purified by crystallization from pentane at -20 °C. Finally a mixture of 20% dichloromethane/hexane eluted a violet band which, upon removal of solvent, gave 0.22 g (11%) of 3.

Method C. Reaction of [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] with [CpCo(CO)$_2$]. On refluxing in toluene for 3 h a mixture of (CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$ (1.7 g, 3.9 mmol) and [CpCo-(CO)$_2$] (1.4 g, 7.7 mmol), cluster 3 and the dinuclear derivative 4 are obtained in 66% and 4.5% yields, respectively.

Method D. Reaction of [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_2$-{(SMe)Fe(CO)$_2$Cp}] (8) with [Co$_2$(CO)$_8$]. 8 (0.65 g, 1 mmol) was refluxed in toluene with an excess of [Co$_2$(CO)$_8$] (1.3 g, 4 mmol) for 3 h. The mixture was then evaporated to dryness, and the residue was chromatographed on silica gel. Three compounds, the cluster 3 (37%), the dinuclear derivative 4 (30%), and [{CpFe(CO)$_2$}$_2$] (16%), were isolated according to this method.

Syntheses of Complexes *trans*- and *cis*-[Cp(CO)$_2$FeC-(CF$_3$)=C(CF$_3$)Me] (6 and 7, respectively). These compounds have been prepared according to the method B described above in the previous section on synthetic work. 6 is soluble in common organic solvents. The mass spectrum showed ions corresponding to [M]$^+$, m/e 354, [Fe(C$_5$H$_5$)(CO)$_2$C$_4$F$_5$(Me)]$^+$, m/e 335, [Fe-(C$_5$H$_5$)(CO)C$_4$F$_6$(Me)]$^+$, m/e 326, [Fe(C$_5$H$_5$)C$_4$F$_6$(Me)]$^+$, m/e 298, [Fe(C$_5$H$_5$)$_2$]$^+$, m/e 186, and [Fe(C$_5$H$_5$)F]$^+$, m/e 140. UV spectrum (pentane): λ_{max} (nm) 498 (ϵ 130), 362 (ϵ 845), 285 (sh, ϵ 2550). 7 is soluble in common organic solvents; mp 112 °C. Anal. Calcd for C$_{12}$H$_8$F$_6$FeO$_2$: C, 40.7; H, 2.3; Fe, 15.7. Found: C, 40.2; H,

2.2; Fe, 15.5. The mass spectrum showed ions corresponding to [M]$^+$, m/e 354, [Fe(C$_5$H$_5$)(CO)C$_4$F$_6$(Me)]$^+$, m/e 326, [Fe-(C$_5$H$_5$)C$_4$F$_6$(Me)]$^+$, m/e 298, [Fe(C$_5$H$_5$)$_2$]$^+$, m/e 186, and [Fe-(C$_5$H$_5$)F]$^+$, m/e 140. UV spectrum (pentane): λ_{max} (nm) 500 (ϵ 160), 355 (ϵ 1100), 287 (sh, ϵ 2200).

Syntheses of Complex [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_2$-{(SMe)Fe(CO)$_2$Cp}] (8). [{Cp(CO)Fe(μ-SMe)}$_2$] (0.75 g, 2 mmol) was heated with a slight excess of [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co-(CO)$_3$] (1.0 g, 2.3 mmol) in toluene at 55 °C for 32 h under a nitrogen stream. The solvent was then evaporated, the residue redissolved in a minimum of dichloromethane, and the solution chromatographed on silica gel. Elution with hexane/CH$_2$Cl$_2$ (1:1) afforded a red band which yielded about 65% (relative to cobalt complex) (0.93 g) of 8, purified by crystallization from hexane/dichloromethane solution at -20 °C. Further elution with CH$_2$Cl$_2$ gave the red fraction from which 0.34 g of [{CpFe(CO)$_2$}$_2$] (51% relative to iron complex) was collected.

Such a reaction conducted at 90 °C for 6 h gave 8 and [{CpFe(CO)$_2$}$_2$] in similar yields. 8 is a deep red solid that is soluble in common organic solvents. Anal. Calcd for C$_{17}$H$_8$Co$_2$F$_6$FeO$_7$S: C, 31.7; H, 1.3; Co, 18.3; F, 17.7; Fe, 8.7; S, 4.9. Found: C, 31.7; H, 1.3; Co, 17.9; F, 17.7; Fe, 8.6; S, 4.0. The mass spectrum showed ions corresponding to [M]$^+$, m/e 644, [M - nCO]$^+$, n = 1, m/e 616, n = 2, m/e 588, n = 3, m/e 560, n = 4, m/e 532, n = 5, m/e 504, n = 6, m/e 476, n = 7, m/e 448, [Co$_2$(CO)$_5$(C$_4$F$_6$)]$^+$, m/e 420, [Co$_2$(CO)(C$_4$F$_6$)]$^+$, m/e 308, and [Co$_2$(C$_4$F$_6$)]$^+$, m/e 280. UV spectrum (pentane): λ_{max} (nm) 402 (ϵ 12200) 290 (sh, ϵ 11100).

Attempted Preparation of [(C$_6$H$_5$Me)Co(μ-CF$_3$C$_2$CF$_3$)Co-(CO)$_2${(SMe)Fe(CO)$_2$Cp}]. When a mixture of [(C$_6$H$_5$Me)Co-(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (1.5 mmol) and [{Cp(CO)Fe(SMe)}$_2$] (0.75 mmol) was heated in toluene or *n*-octane at 90 °C for 6 h, no reaction was observed.

Synthesis of [{P(OMe)$_3$}$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (5). Complex [(C$_6$H$_5$Me)Co(μ-CF$_3$C$_2$CF$_3$)Co(CO)$_3$] (4) (0.25 g, 0.5 mmol) was dissolved in hexane, and a toluene solution of a large excess of trimethyl phosphite (5 mmol) was added under nitrogen. The mixture was warmed for 1 h and then evaporated to dryness. Chromatography of the residue on a silica gel column eluting with CH$_2$Cl$_2$/hexane (2:10) afforded a brown band which yielded traces of the starting complex 4. Further elution with CH$_2$Cl$_2$ gave the most abundant orange fraction from which 5 was collected and purified by crystallization from a hexane–CH$_2$Cl$_2$ solution at -20 °C (0.38 g, 95%).

5 is an orange solid which is soluble in common organic solvents. Anal. Calcd for C$_{16}$H$_{27}$Co$_2$F$_6$O$_{12}$P$_3$: C, 26.1; H, 3.7; Co, 16.0; F, 15.4; P, 12.6. Found: C, 26.3; H, 3.6; Co, 15.4; F, 14.7; P, 12.5. The mass spectrum showed ions corresponding to [M]$^+$, m/e 736, [Co$_2$(CO)$_3$(C$_4$F$_5$){P(OMe)$_3$}$_3$]$^+$, m/e 717, [Co$_2$(CO)$_2$(C$_4$F$_6$){P-(OMe)$_3$}$_3$]$^+$, m/e 708, [Co$_2$(CO)(C$_4$F$_6$){P(OMe)$_3$}$_3$]$^+$, m/e 680, [Co$_2$(C$_4$F$_6$){P(OMe)$_3$}$_3$]$^+$, m/e 652, [Co$_2$(C$_4$F$_6$){P(OMe)$_3$}$_2$]$^+$, m/e 528, and [Co{P(OMe)$_3$}$_3$]$^+$, m/e 431.