Inorg. Chem. **1982**, *21*, 501-505 **501**

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Reactions of 3-Hexyne with Cobalt and Iron Carbonyls. Crystal Structure and Fluxionality of $FeCo_2(CO)_9C_2Et_2$

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Oxygen incorporation α to the triple bond occurs by reacting a mixture of $Co_2(CO)_8$ and $Fe(CO)_5$ or $HFeCo_3(CO)_{12}$ with 3-hexyne: $Co_2(CO)_6EtC_2CHOHCH_3$ and $Co_2(CO)_6EtC_2COCH_3$ are obtained. Other products of the reactions are the two novel mixed-metal derivatives $FeCo_2(CO)_9C_2Et_2$ and $FeCo(CO)_6EtC_2CHCH_3$; the latter is obtained also by dehydroxylation of $Co_2(CO)_6EtC_2CHOHCH_3$ with $Fe(CO)_5$. The structure of $FeCo_2(CO)_9C_2Et_2$ has been determined by X-ray methods. It crystallizes in the triclinic space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 9.558$ (8) Å, $b = 10.449$ (9) Å, $c = 9.343$ (8) Å, $\alpha = 96.94$ (7)°, $\beta = 90.95$ (9)°, and $\gamma = 86.54$ (8)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares methods to $R = 4.1\%$ for 2306 observed reflections. The complex consists of an isosceles triangle of two Co atoms and one Fe atom (Fe–Co = 2.479 and 2.489 Å, Co–Co = 2.576 Å) bound to nine terminal carbonyls (three per each metal) and to one diethylacetylene ligand. The alkyne, σ bonded to the Co atoms and π bonded to the Fe atom, is disposed nearly parallel to the Co–Co side of the cluster. The fluxionality of $FeCo_2(CO)_9C_2Et_2$ has been investigated and compared with that of $FeCo_2(CO)_9S$.

Introduction

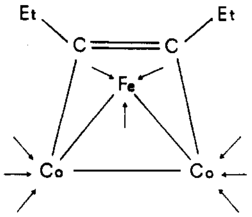
The interest in mixed-metal clusters is rapidly growing.[1] They are expected to be important in stoichiometric and catalytic reactions giving selective activation of different substrates at different metals; also they can allow more definitive mechanistic studies because of their low symmetry.

Whereas the chemistry of acetylenic homometal clusters has been thoroughly investigated,[2] few reports deal with acetylenic heterometal clusters. Considering the case of mixed-iron and -cobalt species, the attempt of producing mixed clusters by pyrolysis of $Co_2(CO)_6C_2Ph_2$ and $Fe(CO)_5$ failed.[3] $[FeCo_3(CO)_{10}C_2Ph_2]^-$, $FeCO_2(CO)_8C_2Ph_2$, and $HFeCo_3(CO)_9[C_2Ph_2]_2$ have been reported but not fully characterized from various reactions of C_2Ph_2 with $HFeCo_3(CO)_{12}$.[1,4] We have approached the study of acetylenic iron and cobalt mixed-metal clusters by reacting with 3-hexyne either a mixture of $Co_2(CO)_8$ and $Fe(CO)_5$ or $HFeCo_3(CO)_{12}$. Two novel mixed-metal acetylenic derivatives, a trinuclear and a binuclear species, have been obtained. Also two cobalt acetylenic derivatives in which oxygen incorporation occurs α to the triple bond have been isolated. The synthesis and characterization of these clusters is described herein, as well as the crystal and molecular structure and the fluxionality of the trinuclear mixed-metal derivative. A preliminary account on the homonuclear complexes only has already appeared.[5]

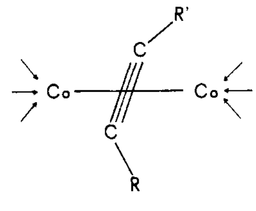
Experimental Section

Reactants and Physical Measurements. $Co_2(CO)_8$ and $Fe(CO)_5$ were obtained from Fluorochem Ltd. and used with further purification. $HFeCo_3(CO)_{12}$ was prepared by published procedure.[6] 3-Hexyne and 4-octyne were purchased from Farchan Division. ^{13}CO (94.3%) was obtained from Monsanto Research Corp. Microanalysis were by Pascher Microanalytisches Laboratorium, Bonn, Germany. Infrared spectra were recorded on a Beckman IR 12 spectrometer with grating optics, and mass spectra were recorded on a Hitachi Perkin-Elmer AMU-6 spectrometer at 70 eV. A JEOL-C60-HL and a JEOL-PS-100-FT NMR spectrometer were used to obtain ^1H and ^{13}C NMR spectra, respectively. Chemical shifts are reported as downfield positive with respect to $SiMe_4$. The temperature was monitored by a JEOL-JNM-DBT-P-5-H-100E temperature-control unit. $Cr(acac)_3$ (10^{-3} M) was added as a shiftless relaxation agent for the ^{13}C NMR measurements.

Reaction of $Co_2(CO)_8$ and $Fe(CO)_5$ with 3-Hexyne (Reaction A). In a typical run 2.0 g (5.8 mmol) of $Co_2(CO)_8$, 2.5 mL (18.1 mmol) of $Fe(CO)_5$, and 2 mL (17.6 mmol) of 3-hexyne were refluxed in acetone for 5 h, under a N_2 atmosphere. After filtration the excess of $Fe(CO)_5$ and the solvent were removed in vacuo, and the residue, dissolved in chloroform, was chromatographed on silica gel column. The elution was carried, with a mixture of petroleum ether (bp 40–70 °C) and chloroform (2:1), and repeated with mixtures increasingly enriched in chloroform. The following derivatives have been eluted: $FeCo_2(CO)_9C_2Et_2$ (I (trace), black-brown powder, $M_r = 508$, mass spectrum m/e 480 (highest peak) followed by loss of eight carbonyl groups. Anal. Calcd for $C_{15}H_{10}Co_2FeO_9$: C, 35.47; H, 1.98; Co, 23.20; Fe, 10.99. Found: C, 35.71; H, 1.66; Co, 23.51; Fe, 11.22); $Co_2(CO)_6C_2Et_2$ (IIa, 70%), $Co_4(CO)_{10}C_2Et_2$ (IIIa, 5%), and $Fe_3(CO)_{12}$ (trace) (all readily identified); $Co_2(CO)_6EtC_2CHOHCH_3$ (IVa (7%), red-brown oil, $M_r = 384$, mass spectrum m/e 384 (M^+) followed by loss of six carbonyl groups); $Co_2(CO)_6EtC_2COCH_3$ (V (2%), red-brown oil, $M_r = 382$, mass spectrum m/e 382 (M^+) followed by loss of six carbonyl groups + intense peaks expected for fragmentation of the ketone ligand); $FeCo(CO)_6EtC_2CHCH_3$ (VI (trace), orange



(I)



(IIa): R = R' = Et; (IVa): R = Et, R' = CHOHMe;
(V): R = Et, R' = COMe; (IIb): R = R' = n-Pr;
(IVb): R = n-Pr, R' = CHOHEt.

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[2] E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).

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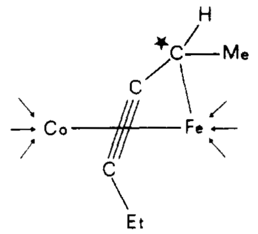
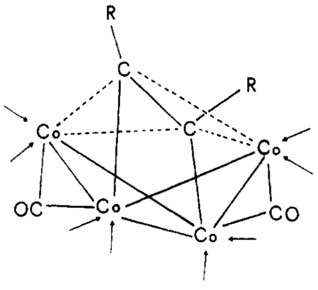


(VI)



(IIIa): R = Et; (IIIb): R = n-Pr.

oil, M_r = 364, mass spectrum *m/e* 364 (M^+) followed by loss of six carbonyl groups. Anal. Calcd for $C_{12}H_9CoFeO_6$: C, 39,60; H, 2.49; Co, 16.19; Fe, 15.34. Found: C, 40.12; H, 2.18; Co, 16.33; Fe, 15.81).

Reaction of $HFeCo_3(CO)_{12}$ with 3-Hexyne (Reaction B). In a typical run 2.0 g (3.5 mmol) of $HFeCo_3(CO)_{12}$ and 2 mL (17.6 mmol) of 3-hexyne were refluxed in acetone for 20 h, under a N_2 atmosphere. With the above procedure I (50%), IIa (15%), IIIa (trace), IVa (7%), and V (2%) were isolated.

Reaction A with 4-Octyne. From the reaction of 0.5 g (1.4 mmol) of $Co_2(CO)_8$, 0.5 mL (3.6 mmol) of $Fe(CO)_5$ and 0.5 mL (3.4 mmol) of 4-octyne, the following derivatives were isolated: $Co_2(CO)_6C_2$-*n*-Pr_2 (IIb, 70%), $Co_4(CO)_{10}C_2$-*n*-Pr_2 (IIIb, 5%), and $Co_2(CO)_6$-*n*-$PrC_2CHOHEt$ (IVb, 7%). IVb: M_r = 412; mass spectrum *m/e* 412 (M^+), followed by loss of six carbonyl groups; IR (CCl_4) ν(OH) 3625 m, ν(CO) 2093 m, 2053 vs, 2032 vs, 2021 s, 2008 m (sh) cm^{-1}; ^1H NMR (CCl_4) δ(CH) 4.58 (t), δ(OH) 2.68 (s), δ(*n*-Pr) 2.74 (t), 1.69 (m), 1.04 (t), δ(Et) 1.69 (m), 1.09 (t).

Reactions A and B in Dehydrated Petroleum Ether. Reactions A and B were carried out in petroleum ether (bp 40–70 °C), repeatedly dehydrated on molecular sieves. In both cases the analysis of the reaction products did not show a trace of either IV or V. In addition to the other products obtained from reaction B in acetone, in this case products of metal nuclearity higher than three have been isolated but not yet characterized.

Reaction of $Fe(CO)_5$ with $Co_2(CO)_6EtCHOHCH_3$. $Fe(CO)_5$ (1 mL, 7.2 mmol) was added to 0.5 g (1.3 mmol) of IVa and refluxed in acetone for 5 h, under a N_2 atmosphere. After filtration the excess of $Fe(CO)_5$ and the solvent were removed in vacuo, and the residue, dissolved in dichloromethane, was chromatographed on a silica gel column with use of a petroleum ether/chloroform mixture (4:1) as eluant. VI (50%), unreacted IVa (30%), and $Fe_3(CO)_{12}$ (trace) have been separated.

Thermal Stability of $FeCo_2(CO)_9C_2Et_2$. I (0.1 g) was refluxed in pentane for 6 h under a N_2 atmosphere. The IR monitoring showed that the ν(CO) of I are gradually disappearing, while those of IIa are appearing.

Isotopic Enrichment of I. I (0.1 g) was dissolved in cyclohexane and stirred for 7 days in a sealed ampule in the presence of <1 atm of ^{13}CO. Before use the sample was purified on a silica gel column.

Crystallographic Data Collection of I. Black, air-stable crsytals of I have been obtained by cooling at −10 °C a solution of I in a heptane/chloroform 2:1 mixture under a N_2 atmosphere.

Rotation and Weissenberg photographs indicated triclinic symmetry; preliminary unit cell dimensions were determined from the same photographs. A flatted crystal of dimensions 0.14 × 0.30 × 0.40 mm was mounted and aligned on an on-line single-crystal automated Siemens AED diffractometer using niobium-filtered Mo Kα radiation (λ = 0.710688 Å) at a takeoff angle of 4°. The settings of 16 reflections with θ in the range 11.05–15.40° were determined and used to calculate the refined cell constants. Crystal data are as follows: $C_{15}H_{10}Co_2FeO_9$, M_r 507.95, triclinic, a = 9.558 (8) Å, b = 10.449 (9) Å, c = 9.343 (8) Å, α = 96.94 (7)°, β = 90.05 (9)°, γ = 86.54 (8)°, V = 925 (1) Å^3, Z = 2, ρ_{calcd} = 1.82 g/cm^3, μ(Mo Kα) = 25.89 cm^{-1}, space group $P\bar{1}$ (from structure determination). A complete set of intensity data was collected within the angular range 3° < θ < 24°. The θ–2θ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. The scan range was ±0.5° from the peak center. The pulse-height discriminator was set to accept 90% of the Mo Kα peak. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. For intensities and background the five-point technique[7] was used. A total of 2762 independent reflections were measured of which 2306 were employed in the analysis having $I > 2\sigma(I)$ [$\sigma^2(I)$ = total counts + $(0.05I)^2$]; the remaining 456 were considered unobserved. The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by Wilson's method. No correction for absorption was applied because of the low value of μr.

Table I. Fractional Atomic Coordinates (×10^4) for Complex I with Esd's in Parentheses

atoms	*x/a*	*y/b*	*z/c*
Fe	821 (1)	1927 (1)	2762 (1)
Co(1)	2777 (1)	2188 (1)	1102 (1)
Co(2)	3243 (1)	1370 (1)	3562 (1)
O(1)	−1465 (7)	3152 (8)	1236 (8)
O(2)	−774 (7)	1689 (7)	5361 (7)
O(3)	516 (7)	−716 (6)	1434 (7)
O(4)	1194 (7)	3263 (7)	−1213 (7)
O(5)	5409 (7)	3418 (7)	826 (8)
O(6)	3293 (8)	−355 (6)	−615 (6)
O(7)	6054 (7)	2321 (7)	3936 (8)
O(8)	3993 (8)	−1318 (6)	2370 (8)
O(9)	2597 (8)	709 (7)	6437 (7)
C(1)	−568 (8)	2643 (9)	1839 (9)
C(2)	−153 (9)	1777 (8)	4341 (9)
C(3)	639 (8)	337 (9)	1947 (8)
C(4)	1816 (9)	2835 (8)	−315 (9)
C(5)	4398 (9)	2911 (8)	939 (8)
C(6)	3114 (9)	611 (8)	84 (8)
C(7)	4949 (9)	1955 (7)	3772 (8)
C(8)	3663 (9)	−265 (8)	2779 (8)
C(9)	2856 (9)	973 (8)	5322 (9)
C(10)	1959 (7)	3501 (6)	2594 (7)
C(11)	2204 (7)	3052 (6)	3899 (7)
C(12)	2020 (9)	3831 (9)	5374 (8)
C(13)	3341 (13)	4282 (14)	6056 (13)
C(14)	1467 (9)	4841 (7)	2335 (10)
C(15)	2596 (13)	5760 (10)	2248 (17)
H(121)	1360 (75)	3332 (69)	5838 (77)
H(122)	1437 (79)	4524 (74)	5289 (77)
H(131)	3311 (97)	4813 (93)	6883 (105)
H(132)	3597 (96)	4912 (87)	5477 (98)
H(133)	3966 (103)	3825 (93)	6098 (107)
H(141)	852 (76)	4752 (69)	1378 (83)
H(142)	1032 (79)	5086 (73)	3133 (85)
H(151)	2235 (93)	6658 (96)	2106 (95)
H(152)	3146 (108)	5366 (95)	1526 (105)
H(153)	3409 (108)	5618 (94)	2853 (105)

Solution and Refinement of the Structure. Initial positional parameters of the three metal atoms were determined from a Patterson map. A Fourier map calculated with phases of the three metal atoms revealed the positions of all other nonhydrogen atoms. Refinement was carried out by full-matrix least-squares[8] methods isotropically to R = 8.1% and anisotropically to R = 4.5%. At this stage a ΔF synthesis revealed all hydrogen atoms, which were refined with isotropic thermal parameters; the improvement of the R index was to 4.1%. In the last stage of the refinement no parameter shifted by more than 0.5 times its estimated standard deviation. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$; unit weights were chosen

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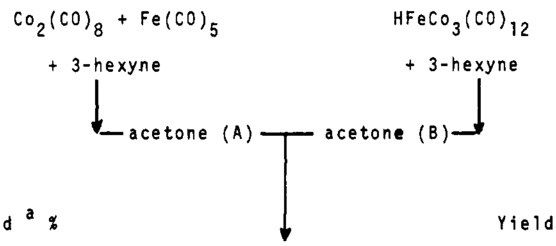
(7) W. Hoppe, *Acta Crystallogr., Sect. A.*, **A25**, 67 (1969).

(8) Computer programs were those of the SHELX-76 system (G. M. Sheldrick, University of Cambridge, England).

Scheme I



Yield[a] %		Yield[b] %
trace	$FeCo_2(CO)_9C_2Et_2$ (I)	50
70	$Co_2(CO)_6C_2Et_2$ (IIa)	15
5	$Co_4(CO)_{10}C_2Et_2$ (IIIa)	trace
trace	$Fe_3(CO)_{12}$	=
7	$Co_2(CO)_6EtC_2CHOHMe$ (IVa)	7
2	$Co_2(CO)_6EtC_2COMe$ (V)	2
trace	$FeCo(CO)_6EtC_2CHMe$ (VI)[c]	=

[a] Calculated on the basis of $Co_2(CO)_8$. [b] Calculated on the basis of $HFeCo_3(CO)_{12}$. [c] Two enantiomers.

at each stage of the refinement after the variation of $|\Delta F|$ with respect to $|F_o|$ was analyzed. The atomic scattering factors (corrected for the anomalous dispersion of Co and Fe) were taken from ref 9. The final positional parameters are given in Table I. Atomic thermal parameters and a list of the observed and calculated structure factors are available as supplementary material or from the authors on request. All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Elettronico Interuniversitario della Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

Synthesis. The products separated from reaction A are also isolated from reaction B, except for $Fe_3(CO)_{12}$ and $FeCo(CO)_6EtC_2CHCH_3$. However the yields are quite different: the cobalt only containing derivatives are 85% in the first case, whereas the mixed iron and cobalt derivatives are over 50% in the latter. The cobalt carbonyl is more reactive than the iron one toward the alkyne, yielding $Co_2(CO)_6C_2Et_2$ and $Co_4(CO)_{10}C_2Et_2$ (total 75% yield): these are known to be the products of the reaction of the cobalt carbonyl alone with an alkyne.[10] The total yield of IIa and IIIa drops to about 15% if the starting material is $HFeCo_3(CO)_{12}$ (see Scheme I).

The presence of iron determines in both reactions the formation of $Co_2(CO)_6EtC_2CHOHCH_3$ and of $Co_2(CO)_6EtC_2COCH_3$: they are not obtained by refluxing the alkyne and the cobalt carbonyl alone in acetone. However the actual mechanism is presently unclear. IVa and V are not observed by reacting $Co_2(CO)_6C_2Et_2$ with $Fe(CO)_5$.

We were able to observe in the dried reaction mixture IR bands typical of IVa and V which alllow us to discard that the oxygen insertion is the result of the interaction between products in the reaction mixture and OH groups in the silica column used for separation. The importance of the water content of the solvent on the yields of IVa and V has been investigated: the best are achieved with use of acetone (0.2%). They are slightly lower in methanol (0.05%). In dehydrated petroleum ether neither IVa nor V is formed. Trace quantities of $FeCo(CO)_6EtC_2CHCH_3$ are obtained from reaction A only. The mechanism of its formation has been understood by refluxing in acetone $Fe(CO)_5$ with $Co_2(CO)_6EtC_2CHOHCH_3$: the yield of VI is increased to 50%. This represents a novel dehydroxylation by iron carbonyl: the validity of this method in obtaining mixed-metal acetylenic derivatives will be explored. Finally the formation of $FeCo_2(CO)_9C_2Et_2$ is accounted for by the coordination of the alkyne on one of the $FeCo_2$ triangular faces of $[FeCo_3(CO)_{12}]^-$, $[FeCo_3(CO)_{10}C_2Et_2]^-$ being the likely intermediate. $[FeCo_3(CO)_{12}]^-$ is produced directly in reaction A and by the solvent deprotonation of the parent hydrido in reaction B.[11]

Characterization of the Products. The identification of the cobalt complexes was readily achieved on the basis of the instrumental evidence. The data obtained for IIa and IIIa are fully consistent with those reported in the literature.[10] The IR spectrum of IVa and V in the CO stretching region compares well with that of IIa but for the shift to higher wave numbers of the resonances due to the insertion of oxygen in the ligand. The resonances of OH and of the ketonic CO are observed in the IR spectrum as well as in the ^1H and ^{13}C NMR spectra. The other features of the NMR spectra are in complete accord with those reported for the $Co_2(CO)_6$(alkyne) derivatives.[10,12] The NMR data show that the oxygen insertion occurs α to the triple bond. This has also been observed for $Co_2(CO)_6$-*n*-$PrC_2CHOHEt$ (IVb) isolated from the reaction of $Fe(CO)_5$, $Co_2(CO)_8$, and 4-octyne.

In the mass spectrum of the trinuclear mixed-metal derivative peaks higher than 480 were not observed and the stepwise loss of eight carbonyls is observed: the compound is then formulated as $FeCo_2(CO)_8C_6H_{10}$. In the carbonyl region infrared spectrum no bands assignable to bridging carbonyls are observed. The ^1H and ^{13}C NMR spectra show that the organic fragment has maintained its identity. According to the carbonyl region ^{13}C NMR spectrum the cobalt-bound carbonyls are twice as abundant as the iron-bound carbonyls.

It is not possible to suggest a structure in accord with the formulation as a $(CO)_8$ species and the other spectroscopic data. From the X-ray analysis, I turned out to be a $(CO)_9$ species, a formulation which easily allows the interpretation of the IR and NMR data.[13] The impossibility to observve the molecular ion might be due to the rearrangement in the mass spectrometer of I to a $(CO)_8$ species, because of either thermal effects or the interaction of the electron beam with the sample. The second is more likely since the monitoring by IR of the refluxinng of I in pentane does not give any evidence of its rearrangement by loss of one CO: it just slowly decomposes.

The NMR spectra of VI show that CH_3CH_2 and CH_3CH are at the ends of the hydrocarbon chain, which is completed by two carbon atoms not bearing hydrogen. Two almost equal resonances are observed in the CO region ^{13}C NMR spectrum and are assigned to the set of the iron-bound CO's and to that of the cobalt-bound CO's. Too many resonances for just one species are observed.

On this basis we suggest a structure in which the $FeCo(CO)_6$ unit satisfies its electronic requirement by coordination with the ligand via one σ and two π bonds. The suggestion of the σ bond between the iron atom and the dehydroxylated carbon atom is in accord with the mechanism of formation of VI. Furthermore this bonding scheme requires the chirality of the σ-bond carbon atom as shown by the doubling of the NMR peaks. All spectroscopic data for compounds I, IVa, V, and VI are summarized in Table II.

Crystal Structure of I. I crystallizes as discrete molecules with a configuration depicted in Figure 1. Bond distances

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(9) "International Tables for X-Ray Crsytallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(10) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 323 (1975).

(11) W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).

(12) S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Inorg. Chim. Acta*, **22**, 135 (1977).

(13) On the basis of the close similarity of the mass spectra features and of the IR data of I and of $FeCo_2(CO)_8C_2Ph_2$[4,14] the latter should be reformulated as a $(CO)_9$ species.

(14) IR for $FeCo_2(CO)_9C_2Ph_2$ (hexane): ν(CO) 2095 m, 2057 s, 2040 s, 2023 m, 2000 m cm^{-1}. C. G. Cooke and M. J. Mays, personal communication.

Table II. Spectroscopic Data

compd	IR[a] ν(CO), cm^{-1}	^{1}H NMR[b,c] δ	^{13}C NMR[b] δ
$FeCo_2(CO)_9C_2(C_2H_5)_2$	2095 m, 2053 vs, 2038 vs, 2017 m, 1988 m	C_2H_5 2.57 (q), 1.13 (t)	FeCO and CoCO 204.1; C 137.9; C_2H_5 21.7, 15.2
$FeCo(CO)_6C_2H_5C_2CHCH_3$[d]	2083 m, 2039 vs, 2022 s, 2013 m, 1991 w, 1982 m	C_2H_5 2.83 (m), 1.69 (t); CH 5.04 (q), 4.78 (q); CH_3 1.27 (d), 1.20 (d)	FeCo 210.3; CoCO 203.1; C_2 123.7, 118.4, 97.5, 94.8; CH 89.3, 87.0; C_2H_5 29.3, 27.2, 16.3, 15.9; CH_3 25.2 19.4
$Co_2(CO)_6C_2H_5C_2CHOHCH_3$	3623 w,[e] 2093 m, 2053 vs, 2030 vs, 2021 s, 2010 m (sh)	CH 5.02 (q); OH 2.72 (s); C_2H_5 2.83 (q), 1.25 (t); CH_3 1.46 (d)	CoCO 200.4; CH_2*C*: 102.2; CHOH CHOH*C* 100.7; CH 68.1; C_2H_5 26.1, 15.0; CH_3 24.4
$Co_2(CO)_6C_2H_5C_2COCH_3$	2100 m, 2063 vs, 2038 vs, 2034 s (sh), 2020 m (sh), 1665 ms	C_2H_5 2.91 (q), 1.32 (t); CH_3 2.41 (s)	CO 200.6; CoCO 198.9; CH_2*C* 102.6; CO*C* 87.2; C_2H_5 26.3, 15.0; CH_3 30.0

[a] CCl_4. [b] $CDCl_3$. [c] Multiplicity in parentheses. [d] Two enantiomers; IR (hexane). [e] ν(OH).

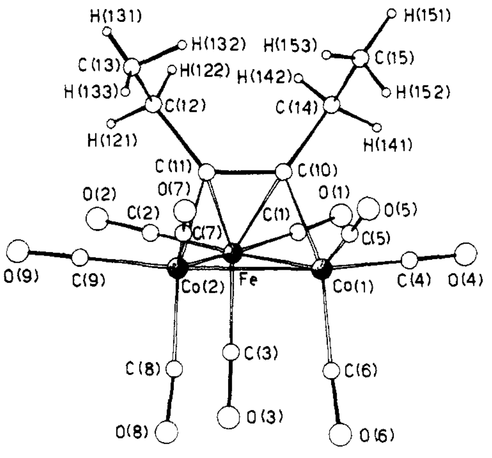

Figure 1. View of the molecular shape of the complex $FeCo_2(CO)_9C_2Et_2$ with the atomic numbering scheme.

and angles in I are given in Table III. The molecule consists of a triangular heterometallic cluster of two Co and one Fe atoms. Nine carbonyls, three on each metal, are terminally bound to the metal atoms (the angles Co–C–O and Fe–C–O are in the range 174.8–179.5°). The diethylacetylene ligand interacts with all the three metal atoms: it is, in a symmetric way, σ bonded to the two Co atoms [Co(1)–C(10) = 1.961 (6) Å and Co(2)–C(11) = 1.957(6) Å] and π bonded to the Fe atom through the C(10)–C(11) triple bond [Fe–C(10) = 2.047 (6) Å, and Fe–C(11) = 2.035 (7) Å], which is disposed nearly parallel to the Co–Co side of the cluster. The three metal atoms form an isoceles triangle in which the Co–Co side [2.576 (1) Å] is longer than the other two Co–Fe sides [2.479 (1) and 2.489 (1) Å]. With neglect of the ethyl substituents, the complex has a close C_s-*m* symmetry, as an approximate mirror plane passes through the Fe atom and the midpoint of the Co–Co bond.

Only two other hydrocarbon $FeCo_2$ clusters have been so far reported, $(Cp)FeCo_2(CO)_6C_2R$[15] and $HFeCo_2(CO)_9Cr$[16]; together with I they constitute a set of derivatives in which the organic moiety acts as a five-, four-, or three-electron donor. Such a set is observed for trinuclear iron clusters but not for cobalt derivatives; it is also the first example in the chemistry of heterometallic clusters.

The structure of I is the first determined by X-ray methods for $FeCo_2$ clusters substituted by a hydrocarbon. In $FeCo_2(CO)_9S$,[17] where the sulfur atom symmetrically bridges the three metal atoms, the three metal–metal bonds are nearly equal, the average metal–metal bond length being 2.554 Å. In I the different bonds can be due to the different bonding of the alkyne to the metals.

The C(10)C(11)Co(1)Co(2) group is perfectly planar, and C(12), C(14), and Fe atoms are displaced from this plane of –0.26, –0.28, and 1.78 Å, respectively. Also the C(10)C(11)C(12)C(14) moiety is strictly planar; the plane passing through them is inclined at ca. 70° to the cluster triangle, thus placing the olefinic fragment parallel to the Co–Co side of the triangle, in an ideal orientation to coordinate to the Fe atom. From the C(10)–C(11) length of 1.37 (1) Å it is clear that the acetylenic bond has been reduced beyond olefinic bond order in accord with its activity as a four-electron donor to the trimetallic unit.

The bonding ($2\sigma + \pi$) mode between an acetylene and a triangle of metals [often indicated as $\mu_3(\eta^2\text{-}\|)$ type[18]] as that found in I, is already established for several homometallic complexes, whose structural parameters have been recently summarized and compared.[19]

Only a few examples of this bonding are known for heterometallic clusters. The isostructural $(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$ and $(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ complexes[19] show symmetric structures comparable with that of I. This can be expected when it is considering that these complexes can be obtained by I replacing two $Co(CO)_3$ units with two isoelectronic Ni(Cp) units. Recently, Schilling and Hoffman[20] have suggested that the orientation of the acetylene ligand can be related to the nature of the frontier orbitals in the $Me_3(CO)_9$ unit. Then, in $Fe_3(CO)_9C_2R_2$ the alkyne is perpendicular to a metal–metal bond, but in the $[Fe_3(CO)_9C_2R_2]^{2-}$ system the alkyne is expected to be oriented in a parallel fashion to a metal–metal bond. The latter complex is isoelectronic with the above class of heterometallic clusters. This change in the acetylene orientation may also be explained in Wade's approach.[21] $Fe_3(CO)_9C_2R_2$ has six skeleton electron pairs, and therefore its structure is a closo trigonal bipyramid $[\mu_3(\eta^2\text{-}\perp)]$; on the contrary complex I has seven skeleton electron pairs and its structure is expected to be a nido octahedron $[\mu_3(\eta^2\text{-}\|)]$.

Fluxionality of $FeCo_2(CO)_9C_2Et_2$. According to the X-ray structure five resonances are expected in the carbonyl region ^{13}C NMR spectrum. Because of the poor solubility of the sample, we were unable to obtain spectra below –90 °C. At this temperature the spectrum shows a lump at ca. 213 ppm and three broad resonances at 206.9, 197.0, and 196.0 ppm, respectively (Figure 2). When the temperature is raised, the downfield peak sharpens (212.9 ppm) while the three upfield

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Table III. Bond Distances (Å) and Angles (Deg) (Not Involving Hydrogen Atoms) with Esd's

(i) In the Coordination Sphere of the Metals			
Fe–Co(1)	2.479 (1)	Co(1)–C(4)	1.787 (8)
Fe–Co(2)	2.489 (1)	Co(1)–C(5)	1.779 (9)
Co(1)–Co(2)	2.576 (1)	Co(1)–C(6)	1.811 (8)
Fe–C(1)	1.761 (8)	Co(1)–C(10)	1.961 (6)
Fe–C(2)	1.773 (8)	Co(2)–C(7)	1.778 (8)
Fe–C(3)	1.761 (9)	Co(2)–C(8)	1.797 (8)
Fe–C(10)	2.047 (6)	Co(2)–C(9)	1.788 (8)
Fe–C(11)	2.035 (7)	Co(2)–C(11)	1.957 (6)
Co(1)–Fe–Co(2)	62.5 (1)	Fe–Co(1)-C(10)	53.4 (2)
Fe–Co(1)–Co(2)	59.0 (1)	Co(2)–Co(1)–C(4)	158.6 (3)
Fe–Co(2)–Co(1)	58.6 (1)	Co(2)–Co(1)–C(5)	97.4 (2)
Co(1)–Fe–C(1)	99.4 (3)	Co(2)–Co(1)–C(6)	94.1 (2)
Co(1)–Fe–C(2)	162.3 (3)	Co(2)–Co(1)–C(10)	72.4 (2)
Co(1)–Fe–C(3)	91.0 (2)	C(4)–Co(1)–C(5)	100.1 (4)
Co(1)–Fe–C(10)	50.3 (2)	C(4)–Co(1)–C(6)	94.1 (4)
Co(1)–Fe–C(11)	72.9 (2)	C(4)–Co(1)–C(10)	93.3 (3)
Co(2)–Fe–C(1)	160.4 (3)	C(5)–Co(1)–C(6)	102.2 (4)
Co(2)–Fe–C(2)	100.9 (3)	C(5)–Co(1)–C(10)	96.6 (3)
Co(2)–Fe–C(3)	91.7 (3)	C(6)–Co(1)–C(10)	158.2 (3)
Co(2)–Fe–C(10)	73.2 (2)	Fe–Co(2)–C(7)	143.3 (2)
Co(2)–Fe–C(11)	50.0 (2)	Fe–Co(2)–C(8)	105.9 (3)
C(1)–Fe–C(2)	96.1 (4)	Fe–Co(2)–C(9)	99.3 (3)
C(1)–Fe–C(3)	96.2 (4)	Fe–Co(2)–C(11)	52.8 (2)
C(1)–Fe–C(10)	89.6 (3)	Co(1)–Co(2)–C(7)	95.4 (2)
C(1)–Fe–C(11)	120.1 (3)	Co(1)–Co(2)–C(8)	93.6 (2)
C(2)–Fe–C(3)	96.0 (4)	Co(1)–Co(2)–C(9)	157.7 (3)
C(2)–Fe–C(10)	121.6 (3)	Co(1)–Co(2)–C(11)	71.8 (2)
C(2)–Fe–C(11)	91.8 (3)	C(7)–Co(2)–C(8)	100.7 (4)
C(3)–Fe–C(10)	141.2 (3)	C(7)–Co(2)–C(9)	102.8 (4)
C(3)–Fe–C(11)	141.8 (3)	C(7)–Co(2)–C(11)	96.8 (3)
C(10)–Fe–C(11)	39.3 (3)	C(8)–Co(2)–C(9)	95.6 (4)
Fe–Co(1)–C(4)	99.8 (3)	C(8)–Co(2)–C(11)	158.2 (3)
Fe–Co(1)–C(5)	144.7 (2)	C(9)–Co(2)–C(11)	93.1 (3)
Fe–Co(1)–C(6)	105.1 (3)		
(ii) In the Carbonyl Groups			
O(1)–C(1)	1.16 (1)	O(6)–C(6)	1.14 (1)
O(2)–C(2)	1.14 (1)	O(7)–C(7)	1.15 (1)
O(3)–C(3)	1.16 (1)	O(8)–C(8)	1.15 (1)
O(4)–C(4)	1.15 (1)	O(9)–C(9)	1.14 (1)
O(5)–C(5)	1.14 (1)		
Fe–C(1)–O(1)	177.9 (8)	Co(1)–C(6)–O(6)	176.4 (7)
Fe–C(2)–O(2)	179.5 (8)	Co(2)–C(7)–O(7)	178.5 (7)
Fe–C(3)–O(3)	178.8 (7)	Co(2)–C(8)–O(8)	174.8 (7)
Co(1)–C(4)–O(4)	179.2 (8)	Co(2)–C(9)–O(9)	179.1 (8)
Co(1)–C(5)–O(5)	177.3 (8)		
(iii) In the Organic Ligand			
C(10)–C(11)	1.37 (1)	C(10)–C(14)	1.50 (1)
C(11)–C(12)	1.52 (1)	C(14)–C(15)	1.50 (1)
C(12)–C(13)	1.49 (1)		
Fe–C(10)–Co(1)	76.4 (2)	Fe–C(11)–C(10)	70.8 (4)
Fe–C(10)–C(11)	69.9 (4)	Fe–C(11)–C(12)	128.9 (5)
Fe–C(10)–C(14)	129.5 (5)	Co(2)–C(11)–C(10)	108.7 (5)
Co(1)–C(10)–C(11)	107.1 (5)	Co(2)–C(11)–C(12)	123.7 (5)
Co(1)–C(10)–C(14)	124.2 (5)	C(10)–C(11)–C(12)	126.2 (6)
C(11)–C(10)–C(14)	127.4 (6)	C(11)–C(12)–C(13)	114.9 (8)
Fe–C(11)–Co(2)	77.1 (2)	C(10)–C(14)–C(15)	115.5 (7)

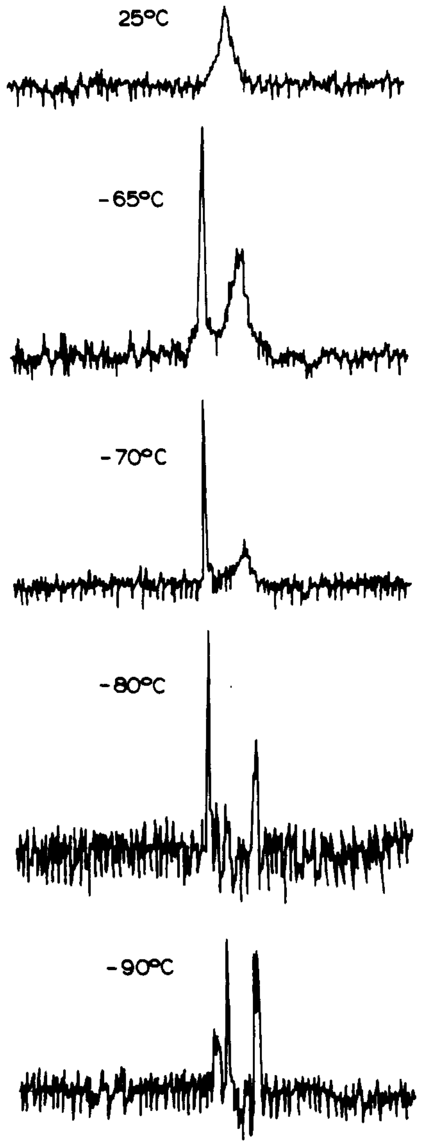

Figure 2. Variable-temperature ^{13}C NMR spectra of $FeCo_2(CO)_9C_2Et_2$ in the carbonyl region.

peaks coalesce and merge in a new peak centered at 199.5 ppm. At −65 °C the upfield peak is almost twice as abundant as the downfield one. A further increase in the temperature causes the broadening of both resonances which coalesce and merge into a new peak which at room temperature is centered at 204.1 ppm ($\nu_{1/2}$ = ca. 50 Hz[22]). These features are first consistent with the assignment, in the −90°C spectrum, of the low-field resonance to the iron-bound carbonyls and of the other resonances to the three nonequivalent sets of CO's on each cobalt atom. Second, three distinct CO exchange proceses occur: the low-energy one concerns the iron-bound carbonyls and is not completely frozen on the NMR time scale; in the intermediate-energy process the cobalt-bound carbonyls are exchanging; finally the internuclear CO's exchange among iron and cobalt atoms in the high-energy process. This behavior duplicates that observed for $FeCo_2(CO)_9S$,[23] but for the inversion of the energy barrier of the low and intermediate CO exchange processes. Similarly, the total CO scrambling is associated with the motion of the alkyne ligand on the metal triangle as already found for $Os_3(CO)_{10}$(alkyne).[24]

Registry No. I, 78109-40-7; IIa, 41626-27-1; IIb, 34766-99-9; IIIa, 78109-41-8; IIIb, 73210-65-8; IVa, 72427-41-9; IVb, 72427-40-8; V, 72427-42-0; VI, 78109-42-9; $Co_2(CO)_8$, 10210-68-1; $Fe(CO)_5$, 13463-40-6; $HFeCo_3(CO)_{12}$, 21750-96-9; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: A table of atomic thermal parameters and a listing of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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