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Reactions of Alkynes with $HFeCo_3(CO)_{12}$. Crystal Structrure of $FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$

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The reactions of $HFeCo_3(CO)_{12}$ with alkynes follow different pathways depending on the solvent characteristics. In apolar water-free solvents the major products are the novel tetranuclear derivatives $FeCo_3(CO)_9[RC_2(H)R](RC_2R)$, in which a hydrogen shift is occurred from the Co_3 face of the hydrido complex to an acetylenic moiety. The structure of the complex with R = Ph has been determined by X-ray methods. The compound crystallizes in the space group $P\bar{1}$ with Z = 2 in a unit cell of dimensions a =13.259(7), b = 12.994(8), c = 11.681(8) Å, α = 114.26(4), β = 110.66(3), γ = 71.32(4)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares to R = 4.4% for 1789 observed reflections. The complex is characterized by a tetranuclear cluster of three Co and one Fe atoms, in a butterfly arrangement, coordinated by nine carbonyls (seven terminal and two asymmetrically bridging the two Fe–Co sides). The two starting C_2Ph_2 molecules are bound to the cluster in a different way: the former interacts with all the metals in a μ_4–η^2 fashion being σ-bonded to the Co and Fe atoms on the hinge and π-bonded to the Co atoms on the wings; the latter, on which the hydridic hydrogen of the starting complex is shifted, interacts only with two Co atoms on one side of the cluster through one σ and one π bond respctively.

Introduction

Recently, among several studies dealing with transition metal clusters, noticeable attention has been devoted to mixed metal compounds [1]. They are expected to play an important role in stoichiometric and catalytic reactions as results of cooperation between adjacent dissimilar metals. Whereas the reactivity of homometallic clusters toward unsaturated hydrocarbons has been widely investigated [2], few reports concerning the reactivity of heterometallic compounds have appeared.

As a part of our studies of acetylenic iron–cobalt mixed metal complexes [3, 4], we describe herein the reactivity of $HFeCo_3(CO)_{12}$ toward alkynes in apolar water-free solvents. By comparison with our previous results a complete reaction scheme can be drawn and related to the nature of the solvent. The spectroscopic and X-ray characterization of the novel $FeCo_3(CO)_9[PhC_2(H)Ph]$ (PhC_2Ph) is reported; a compound with the same molecular formula has been already mentioned, but not characterized [1].

Experimental

Reactants and Physical Measurements

$HFeCo_3(CO)_{12}$ was prepared by the published procedure [5]. 3-Hexyne and diphenylacetylene were purchased from Farchan Division and used without further purification. Light petroleum (b.p. 40–70 °C) was repeatedly dehydrated on molecular sieves. Microanalyses were obtained by Pascher Microanalytisches Laboratorium, Bonn, West Germany. Infrared spectra were recorded on a Perkin-Elmer 580 B spectrophotometer, using 0.5 mm NaCl cells; mass spectra on a Hitachi Perkin-Elmer AMU-6 spectrometer. A Jeol-60-HL spectrophoto-

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meter was used to obtain ^{1}H NMR spectra. chemical shifts are reported as downfield positive with respect to $SiMe_4$.

Reaction of $HFeCo_3(CO)_{12}$ with 3-Hexyne

In a typical run 2.0 g (3.5 mmol) of $HFeCo_3(CO)_{12}$ and 2.0 ml (17.6 mmol) of 3-hexyne were refluxed in light petroleum for 3 h, under a N_2 atmosphere. After filtration the solvent (containing a trace of $Fe(CO)_5$) was removed *in vacuo* and the residue, dissolved in chloroform, was chromatographed on a silica-gel column. The elution was carried with n-hexane and repeated with mixtures increasingly enriched in benzene. The following stable derivatives were eluted: $Co_2(CO)_6(C_2Et_2)$ (≅30%), $FeCo_2(CO)_9(C_2Et_2)$ (≅15%) and $Co_4(CO)_{10}(C_2Et_2)$ (trace) (all readily identified); $FeCo_3(CO)_9(EtC_2(H)Et)(EtC_2Et)$ (I_A. ≅ 35%), black brown powder, Mr = 650, mass spectrum m/e 650 (M^+), followed by loss of nine carbonyl groups and concomitant loss of H_2. *Anal.* Calcd. for $C_{21}H_{21}Co_3FeO_9$: C, 38.77; H, 3.23; Co, 27.23; Fe, 8.62. Found: C, 38.96; H, 3.05; Co, 26.85; Fe, 8.92.

Reaction of $HFeCo_3(CO)_{12}$ with Diphenylacetylene

In a typical run 2.0 g (3.5 mmol) of $HFeCo_3(CO)_{12}$ and 3.13 g (17.6 mmol) of diphenylacetylene were refluxed in light petroleum for 3 h under a N_2 atmosphere. With similar procedure the following stable complexes have been isolated: $Co_2(CO)_6(C_2Ph_2)$ (≅45%), $FeCo_2(CO)_9(C_2Ph_2)$ (≅10%) and $Co_4(CO)_{10}(C_2Ph_2)$ (trace) (all readily identified); $FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$ (I_B, ≅10%) black crystals, Mr = 842, mass spectrum m/e 842 [M^+] followed by the loss of nine carbonyl groups.

Anal. Calcd. for $C_{37}H_{21}Co_3FeO_9$: C, 52.73; H, 2.49; Co, 21.02; Fe, 6.65. Found: C, 53.04; H, 2.30; Co, 21.36; Fe, 6.48.

Thermal Stability of $FeCo_3(CO)_9[EtC_2(H)Et](EtC_2Et)$

0.2 g of I_A were refluxed in n-hexane for 5 hours under N_2 atmosphere. T.l.c. and I R monitoring showed that slow decomposition takes place giving rise to $FeCo_2(CO)_9(C_2Et_2)$ and $Co_2(CO)_6(C_2Et_2)$ as the major products.

Crystallographic Data Collection of $FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$ (I_B)

Black, air stable crystals of I_B were obtained by cooling at 0 °C a solution of I_B in a n-heptane–chloroform 3:1 mixture under N_2 atmosphere.

A small crystal of dimensions 0.08 X 0.16 X 0.20 mm was selected and used in the structure determination. Rotation and Weissenberg photographs indicated triclinic symmetry; preliminary unit cell parameters were determined from the same photographs. Refined cell parameters were derived from a least-squares fit to the setting angles of 27 reflections (with 2θ in the range 19–25°), accurately measured on an on-line single-crystal automated Siemens AED diffractometer using the niobium-filtered MoKα radiation ($\bar{\lambda}$ = 0.71069 Å). Crystal data are as follows: $C_{37}H_{21}Co_3FeO_9$, M = 842.21, triclinic, a = 13.259(7), b = 12.994(8), c = 11.681(8) Å, α = 114.26(4), β = 110.66(3), γ = 71.32(4)°, V = 1680(2) Å^3, Z = 2, D_{calcd} = 1.665 g/cm^3, $F(000)$ = 844, μ(MoKα) = 19.31 cm^{-1}, space group $P\bar{1}$ (from structural analysis).

A complete set of intensity data was collected within the angular range $3 \leqslant \theta \leqslant 23°$. The $\theta-2\theta$ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. The pulse-height discriminator was set to accept 90% of the MoKα peak. No decay was noted in the intensity of a reflection measured at intervals of 20 sequential reflections. For intensities and background the five-point technique [6] was used. A total of 4235 independent reflections were measured of which 1789 were employed in the analysis having $I \geqslant 2\sigma(I)$ [$\sigma^2(I)$ = total counts + (0.05 X intensity)^2]; the remaining 2446 were considered unobserved. The structure amplitudes were obtained after the usual Lorentz and polarization corrections, while the absorption effects were disregarded in view of the very low value of μr (0.12). Data were placed on an approximate absolute scale by means of a Wilson plot which also provided the average overall temperature factor.

Structure Determination and Refinement

Initial coordinates of the Co and Fe atoms were determined by direct methods; all other non-hydrogen atoms were located from two successive Fourier syntheses. Refinement was carried out by least-squares full-matrix cycles using the SHELX-76 system [7] of computer programs: first isotropic and then anisotropic thermal parameters for the Fe and Co atoms only (because of the low number of observed reflections with respect to the variable parameters). At this stage (the R value was 5.1%) a ΔF synthesis revealed all the hydrogen atoms which were introduced in the calculations with isotropic thermal parameters and refined in a cycle; the improvement of the R index was to 4.4% (only observed reflections). The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F_o|$. Throughout the analysis the analytical scattering factors for neutral atoms were used, and both the real and imaginary components of anomalous dispersion were applied to the Fe and Co atoms [8]. The final positional parameters and the isotropic thermal parameters for the non-hydrogen atoms and for the hydrogen atoms are given in Tables I and II respectively. The anisotropic thermal parameters for the

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^4$) with E.s.d.'s in Parentheses for the Non-hydrogen Atoms.

	x/a	*y/b*	*z/c*	*U*
Co1	6858(2)	2685(2)	3682(2)	–
Co2	8609(2)	2680(2)	3570(2)	–
Co3	7784(2)	3528(2)	1820(2)	–
Fe	6957(2)	4521(2)	3670(2)	–
O1	4893(10)	2045(11)	3471(12)	717(37)
O2	6161(9)	4603(10)	5778(11)	573(32)
O3	10017(11)	4239(12)	5550(13)	815(41)
O4	360(11)	694(12)	2943(13)	813(42)
O5	7056(11)	3642(12)	–784(14)	846(43)
O6	7767(10)	5948(10)	2851(11)	627(35)
O7	5041(10)	6279(11)	3103(12)	700(37)
O8	7828(11)	6312(11)	6007(13)	817(40)
O9	10062(11)	3113(11)	1890(12)	729(38)
C1	5683(14)	2312(14)	3548(16)	561(49)
C2	6492(12)	4126(13)	4841(15)	386(41)
C3	9471(15)	3617(15)	4775(18)	586(50)
C4	9684(15)	1464(16)	3177(18)	586(51)
C5	7296(15)	3605(16)	273(20)	653(56)
C6	7627(13)	5060(15)	2723(16)	495(46)
C7	5768(14)	5558(14)	3351(16)	504(46)
C8	7512(14)	5571(15)	5045(18)	573(49)
C9	9149(15)	3247(15)	1885(17)	546(48)
C10	7436(11)	2167(11)	1990(13)	233(34)
C11	6519(12)	3098(12)	2050(14)	347(38)
C12	7461(12)	983(12)	1009(14)	306(37)
C13	6781(13)	316(13)	769(15)	578(41)
C14	6727(15)	–743(16)	–158(18)	566(51)
C15	7468(15)	–1175(17)	–915(18)	554(51)
C16	8179(16)	–551(17)	–700(19)	624(54)
C17	8204(13)	541(14)	241(15)	440(42)
C18	5435(11)	3078(11)	1101(13)	279(35)
C19	5301(14)	2519(14)	–218(16)	476(35)
C20	4239(16)	2506(16)	–1097(20)	631(53)
C21	3344(15)	3024(15)	–636(17)	547(48)
C22	3437(14)	3601(14)	656(17)	467(45)
C23	4475(12)	3616(13)	1511(15)	370(39)
C24	8320(11)	2150(12)	4769(13)	314(36)
C25	7801(11)	1188(12)	4171(15)	284(37)
C26	8883(11)	2487(12)	6142(13)	314(36)
C27	9692(13)	1645(15)	6627(16)	499(44)
C28	10298(15)	1903(17)	7892(18)	610(53)
C29	10166(17)	2985(17)	8719(21)	678(55)
C30	9383(17)	3837(19)	8309(21)	718(60)
C31	8792(15)	3580(16)	7009(18)	555(50)
C32	7434(11)	691(12)	4831(13)	290(36)
C33	7412(14)	–471(15)	4265(19)	538(49)
C34	7064(17)	–971(20)	4871(22)	795(63)
C35	6683(17)	–377(19)	5940(22)	771(63)
C36	6712(16)	764(18)	6467(21)	669(59)
C37	7063(14)	1315(16)	5934(17)	522(47)

Co and Fe atoms only are given in Table III. A list of observed and calculated structure factors is available from the authors on request.

TABLE II. Fractional Atomic Coordinates ($\times 10^3$) and Isotropic Thermal Parameters ($\times 10^3$) with E.s.d.'s in Parentheses for the Hydrogen Atoms.

	x/a	*y/b*	*z/c*	*U*
H13	620(10)	640(10)	136(12)	43(38)
H14	621(12)	–119(12)	–27(13)	99(46)
H15	742(11)	–198(12)	–173(14)	107(46)
H16	877(12)	–92(12)	–129(14)	104(47)
H17	877(10)	102(11)	37(12)	80(39)
H19	589(11)	235(11)	–52(12)	64(42)
H20	417(12)	209(12)	–218(15)	73(47)
H21	261(11)	306(11)	–120(13)	60(43)
H22	271(10)	403(11)	100(12)	85(41)
H23	454(9)	406(10)	254(12)	58(37)
H25	793(13)	57(13)	318(16)	109(54)
H27	980(10)	74(11)	600(13)	79(41)
H28	1091(12)	123(12)	825(14)	131(46)
H29	1070(12)	315(12)	976(15)	111(49)
H30	924(12)	456(14)	887(15)	144(51)
H31	824(11)	431(12)	662(13)	67(45)
H33	768(11)	–98(12)	340(14)	56(44)
H34	710(12)	–191(14)	446(15)	107(54)
H35	640(13)	–77(13)	640(15)	158(55)
H36	643(12)	126(13)	735(16)	106(49)
H37	705(10)	222(12)	638(13)	85(43)

All the calculations were performed on the CYBER-76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

Characterisation of the Products

The MS spectra of I_A and I_B show stepwise loss of nine carbonyl groups, the peaks corresponding to $[M - 8CO]^+$ and $[M - 9CO]^+$ fragments appear very low in intensity. This behaviour is sometimes diagnostic for the presence of bridging COs (Table IV).

The IR spectra are similar to those of the $Co_4(CO)_{10}(C_2R_2)$ 'butterfly' compounds [9, 10], but two absorptions in the bridging carbonyl region are present, suggesting different environments of the bridging COs. Both the ^{1}H-NMR spectra indicate that, upon complexation, the two acetylenic moieties are no longer equivalent. Furthermore a new peak of relative intensity 1 appears as a triplet at $\delta = 4.15$ for I_A and as singlet at $\delta = 4.75$ for I_B. By assuming that the former acetylenic moiety is coordinated in a μ_4–η^2 fashion to a 'butterfly' cluster, the E.A.N. formalism requires that the latter acts as a 3 e^- donor. Then the spectroscopic data

TABLE III. Anisotropic Thermal Parameters ($\times 10^4$) for the Fe and Co Atoms. They are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	295(13)	321(13)	273(13)	118(10)	53(10)	-33(10)
Co2	297(13)	375(13)	348(14)	174(11)	38(10)	-47(10)
Co3	390(13)	398(13)	372(14)	206(11)	91(11)	-67(11)
Fe	355(14)	260(13)	347(14)	101(11)	40(11)	-40(11)

TABLE IV. Spectroscopic Data.

Compound	IR[a], ν(CO), cm^{-1}	^{1}H NMR[b,c], δ/ppm
$FeCo_3(CO)_9[EtC_2(H)Et](EtC_2Et)$ (I_A)	2066m, 2029vs, 2025vs, 2014s, 1985m, 1865m, 1856m	CH: 4.15(t,1)[d]; CH_2: 2.60(m,4) and 1.97(q,4); CH_3: 1.25(t,6) and 1.14(t,6)
$FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$ (I_B)	2070m, 2036vs, 2032vs, 2028s, 1991m, 1867m, 1852m	Ph: 7.12 and 6.90 (m,20); CH: 4.75(s,1)

[a] n-Hexane. [b] $CDCl_3$. [c] Multiplicity and integrated intensities in parenthesis. [d] $J_{H-H} \cong 6$ Hz.

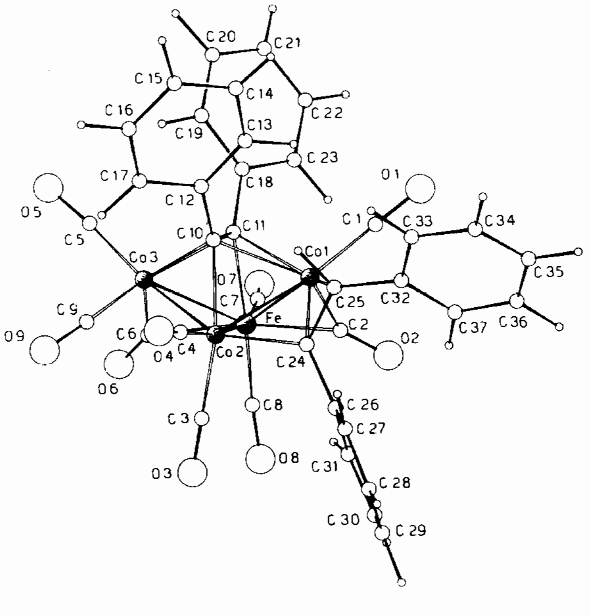

Fig. 1. View of the molecular shape of the complex $FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$ with the atomic numbering scheme.

can be interpreted in terms of a hydrogen shift from the Co_3 face to an alkyne, giving rise to a σ–π alkenyl system. The chemical shift values of the signals of intensity *1* in ^{1}H NMR spectra are consistent with those found for the bridging vinyl complexes $HOs_3(CO)_{10}(HC:CHR)$ [11] and $H_3Os_4(CO)_{11}(HC:CHR)$ [12]. In order to define the overall structural feature of these molecules, X-ray analysis was undertaken for compound I_B, which only gave crystals suitable for such determination.

Crystal Structure of I_B

The structure consists of discrete complexes $FeCo_3(CO)_9[PhC_2(H)Ph](PhC_2Ph)$, separated by normal van der Waals distances. A view of the complex, with the system for labelling the atoms, is shown in Fig. 1. Bond distances and angles are contained in Table V. The complex is characterized by a tetranuclear cluster of three Co and one Fe atoms coordinated by nine carbonyls and two differently bonded unsaturated organic moieties. The cluster presents a butterfly arrangement of the metal atoms with the heteroatom occupying a corner of the hinge side, which is longer [Fe–Co(2) = 2.670(4) Å] than the other sides [Fe–Co(1) = 2.437(4), Fe–Co(3) = 2.452(3), Co(1)–Co(2) = 2.369(4) and Co(2)–Co(3) = 2.468(4) Å]. The non-bonding Co(1)–Co(3) distance is 3.485(4) Å; the dihedral angle between the two triangular Co(1)–Co(2)Fe andCo(3)–Co(2)–Fe wings is 118°. Of the nine carbonyls, seven (one on Co(1), two on the other metals) are terminal, the angles Co–C–O and Fe–C–O being in the range 174–179°, and two bridge unsymmetrically the two Fe–Co(1) and Fe–Co(3) adjacent sides [Fe–C(2) = 1.972(10) and Co(1)–C(2) = 1.837(10), Fe–C(6) = 2.057(11) and Co(3)–C(6) = 1.812(12) Å].

TABLE V. Bond Distances (Å) andAngles (°) (not involving hydrogen atoms).

i) In the coordination sphere of the metals

Fe–Co(1)	2.437(4)	Co(1)–C(11)	2.051(11)
Fe–Co(2)	2.670(4)	Co(1)–C(24)	1.996(10)
Fe–Co(3)	2.452(3)	Co(1)–C(25)	2.127(11)
Co(1)–Co(2)	2.369(4)	Co(2)–C(3)	1.765(12)
Co(2)–Co(3)	2.468(4)	Co(2)–C(4)	1.778(12)
Fe–C(2)	1.972(10)	Co(2)–C(10)	1.974(10)
Fe–C(6)	2.057(11)	Co(2)–C(24)	1.981(11)
Fe–C(7)	1.754(11)	Co(3)–C(5)	1.725(12)
Fe–C(8)	1.730(11)	Co(3)–C(6)	1.812(12)
Fe–C(11)	2.092(10)	Co(3)–C(9)	1.708(11)
Co(1)–C(1)	1.713(12)	Co(3)–C(10)	2.063(10)
Co(1)–C(2)	1.837(10)	Co(3)–C(11)	2.059(11)
Co(1)–C(10)	2.143(10)		
Co(1)–Fe–Co(2)	55.0(1)	C(24)–Co(1)–C(25)	40.2(7)
Co(1)–Fe–Co(3)	90.9(1)	Fe–Co(2)–Co(1)	57.5(1)
Co(2)–Fe–Co(3)	57.4(1)	Fe–Co(2)–Co(3)	56.8(1)
Fe–Co(1)–Co(2)	67.5(1)	Fe–Co(3)–Co(2)	65.7(1)
C(10)–Co(1)–C(11)	39.3(6)	C(10)–Co(3)–C(11)	40.1(6)

ii) In the carbonyl groups

O(1)–C(1)	1.17(2)	O(6)–C(6)	1.17(3)
O(2)–C(2)	1.18(2)	O(7)–C(7)	1.16(2)
O(3)–C(3)	1.14(3)	O(8)–C(8)	1.18(2)
O(4)–C(4)	1.12(3)	O(9)–C(9)	1.16(2)
O(5)–C(5)	1.18(3)		
Co(1)–C(1)–O(1)	179(2)	Co(2)–C(6)–O(6)	147(1)
Co(1)–C(2)–O(2)	142(2)	Fe–C(6)–O(6)	135(1)
Co(1)–C(2)–Fe	79(1)	Co(3)–C(6)–Fe	78(1)
Fe–C(2)–O(2)	138(2)	Fe–C(7)–O(7)	174(2)
Co(2)–C(3)–O(3)	179(2)	Fe–C(8)–O(8)	176(2)
Co(2)–C(4)–O(4)	179(2)	Co(3)–C(9)–O(9)	175(2)
Co(3)–C(5)–O(5)	174(2)		

iii) In the organic ligand

C(10)–C(11)	1.41(2)	C(24)–C(25)	1.42(2)
C(10)–C(12)	1.49(2)	C(24)–C(26)	1.45(2)
C(11)–C(18)	1.47(2)	C(25)–C(32)	1.46(2)
Co(1)–C(10)–C(12)	122(2)	C(10)–C(11)–C(18)	125(1)
Co(2)–C(10)–C(12)	127(1)	Co(1)–C(11)–C(18)	122(1)
Co(3)–C(10)–C(12)	126(1)	Co(3)–C(11)–C(18)	122(1)
C(11)–C(10)–C(12)	126(1)	C(25)–C(24)–C(26)	121(1)
Co(1)–C(10)–C(11)	67(1)	Co(1)–C(24)–C(26)	136(1)
Co(2)–C(10)–C(11)	107(1)	Co(2)–C(24)–C(26)	121(1)
Co(3)–C(10)–C(11)	70(1)	Co(1)–C(24)–C(25)	75(1)
Fe–C(11)–C(10)	109(1)	Co(2)–C(24)–C(25)	116(1)
Co(1)–C(11)–C(10)	74(1)	Co(1)–C(25)–C(24)	65(1)
Co(3)–C(11)–C(10)	70(1)	Co(1)–C(25)–C(32)	122(1)
Fe–C(11)–C(18)	125(1)	C(24)–C(25)–C(32)	126(1)

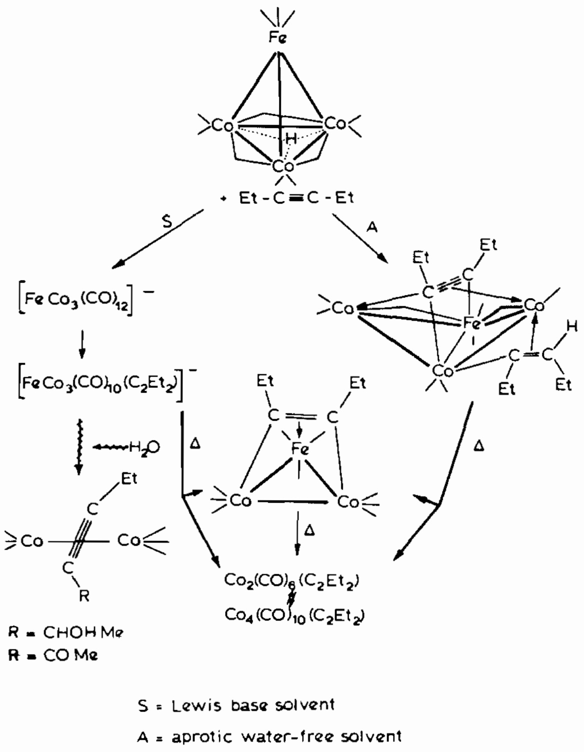

Fig. 2. Overall reaction scheme.

The two starting diphenylacetylene molecules are bound to the metal cluster in different ways. The former interacts with all the metal atoms in a μ_4–η^2 fashion: it is, in an unsymmetric way, σ-bonded to the Co(2) and Fe atoms on the hinge side [Co(2)–C(10) = 1.974(10) and Fe–C(11) = 2.092(10) Å] and π-bonded to the Co(1) and Co(3) atoms on the wingtips [Co(1)–C(10) = 2.143(10) and Co(1)–C(11) = 2.051(11), Co(3)–C(10) = 2.063(10) and Co(3)–C(11) = 2.059(11) Å], through the multiple bond [C(10)–C(11) = 1.41(2) Å] which is disposed nearly parallel to the hinge side of the cluster. Both C(12), C(10), C(11), C(18) and Co(2), C(10), C(11), Fe groups are nearly coplanar as indicated by the C(18)–C(11)–C(10)–C(12) and Co(2)–C(10)–C(11)–Fe torsion angles [3.6 and 4.8°] respectively.

The second molecule of diphenylacetylene, on which the hydridic hydrogen of the starting complex is shifted, acts as a *cis*-diphenyl-substituted vinyl ligand, interacting only with the Co(1) and Co(2) atoms of the shortest side of the cluster: it is σ-bonded to the Co(2) atom [Co(2)–C(24) = 1.981(11) Å] and π-bonded to the Co(1) atom [Co(1)–C(24) = 1.996(10) and Co(1)–C(25) = 2.127(11) Å] through the multiple bond [C(24)–C(25) = 1.42(2) Å]. The C(26), C(24), C(25) and C(32) atoms deviate significantly from the planarity as shown by the C(26)–C(24)–C(25)–C(32) torsion angle [22.0°].

The complex I_B is very similar to the homometallic $Co_4(CO)_{10}(C_2Et_2)$ [13], from which it can be formally derived by substituting one Co atom in the hinge side with the Fe atom, shifting both the bridging carbonyls to the Co–Fe edges and replacing a carbonyl attached to a Co atom on a wingtip with the π-vinyl interaction. Since this ligand acts as a three-electron donor, the two resulting butterfly complexes are isoelectronic. The comparison of the metal–metal bond distances in the two complexes shows that also the Co–Co bond of the hinge side in the homometallic complex is the longest one [2.552 Å] with respect to the other [ranging from 2.416 to 2.450 Å] which are very close to those in I_B, excepting the Co(1)–Co(2) bond, evidently shortened by the vinyl bonding.

Reactivity

The nature of the solvent employed in the reaction of $HFeCo_3(CO)_{12}$ with 3-hexyne plays an important role in the product distribution, as shown in the following scheme:

Using Lewis base solvents (S: acetone, methanol or T.H.F.) the hydrido compound is readily deprotonated to $[FeCo_3(CO)_{12}]^-$ anion*. The coordination of the alkyne to one of its $FeCo_2$ triangular faces

$HFeCo_3(CO)_{12}$ + 3-hexyne

acetone (S) yield %		*petroleum ether (A)* yield %
–	$FeCo_3(CO)_9[EtC_2(H)Et](EtC_2Et)$	35
50	$FeCo_2(CO)_9(EtC_2Et)$	15
15	$Co_2(CO)_6(EtC_2Et)$	30
trace	$Co_4(CO)_{10}(EtC_2Et)$	trace
7	$Co_2(CO)_6(EtC_2CHOHMe)$	
2	$Co_2(CO)_6(EtC_2COMe)$	–
trace	$Fe(CO)_5$	trace

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*Please for footnote see on facing page.

leads to the formation of the neutral compound $FeCo_2(CO)_9(EtC_2Et)$, $[FeCo_3(CO)_{12}(C_2Et_2)]^-$ being the likely intermediate [14]. In these reactions a noticeable result is the activation of the alkyne to give the homometallic derivatives $Co_2(CO)_6EtC_2$-CHOHMe and $Co_2(CO)_6EtC_2COMe$, in which oxygen incorporation has occurred α to the triple bond. Although the mechanism of their formation is still unclear, there is experimental evidence [3] which supports the view that the water present in the polar solvent is the source of the oxygen (Fig. 2).

On the other hand the use of apolar water-free solvent (*A*) does not afford any acetylenic complexes characterized by oxygen incorporation. Since in this case solvent deprotonation cannot occur, it is likely that a direct hydrogen shift from the cluster to an acetylenic moiety affords the main complex $FeCo_3(CO)_9[EtC_2(H)Et](EtC_2Et)$. The insertion of an alkyne into a metal–hydrogen bond is a well known process with mononuclear hydrido complex [15], but only few examples are reported for polynuclear derivatives [11, 12]. Both the heterometallic cluster $FeCo_3(CO)_9[EtC_2(H)Et](EtC_2Et)$ and $FeCo_2(CO)_9(EtC_2Et)$ decompose smoothly upon warming to the more stable $Co_2(CO)_6(EtC_2Et)$. The formation of $Co_4(CO)_{10}(EtC_2Et)$ species is clearly related to its interconversion with the binuclear complex, as has already been widely investigated [10]. The reaction of $HFeCo_3(CO)_{12}$ with diphenylacetylene, carried out in the same experimental conditions, gives similar heterometallic products, but in lower yields; a marked declusterification is occurring with this ligand as shown by the increased yield of $Co_2(CO)_6(PhC_2Ph)$.

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*In a separate experiment $HFeCo_3(CO)_{12}$ (100 mg) was dissolved in 50 ml of acetone at room temperature under N_2. IR monitoring revealed that the hydrido complex is quickly deprotonated, $[FeCo_3(CO)_{12}]^-$ being the sole species present in solution after 10′; ν(CO), cm^{-1}: 2062w, 2006vs, 1969m, 1932m, 1813m, When the acetone was removed under reduced pressure and the residue dissolved in warm hexane the hydrido complex was recovered in >85% yield, ν(CO), cm^{-1}; 2098w, 2058vs, 2050vs, 2027m, 1988m, 1886m. This behaviour suggests a facile acid–base reaction: $HFeCo_3(CO)_{12} + S \rightleftharpoons [FeCo_3(CO)_{12}]^- + HS^+$.

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