Polyhedron Vol. 2, No. 2, pp. 77–81, 1983
Printed in Great Britain.

0277–5387/83/020077–05$03.00/0
Pergamon Press Ltd.

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF HETEROBIMETALLIC (α-ALKYNYL)IRON–COBALT HEXACARBONYL COMPLEXES, $[\mu\text{-}(1\text{-}\sigma, 2\text{–}3, \eta^2\text{-}R_2C\text{–}C{\equiv}CR')]\,[(CO)_3Fe\text{–}Co(CO)_3]$ AND $[\mu\text{-}(1\text{-}\sigma, 2\text{–}3, \eta^2\text{-}H_2C\text{–}C{\equiv}CCH_2OH)]\,[(CO)_3Fe\text{–}Co(CO)_2(PPh_3)]$

SILVIO AIME and DOMENICO OSELLA*
Istituto di Chimica Generale ed Inorganica Dell'Università Corso Massimo d'Azeglio 48, 10125 Torino, Italy

LUCIANO MILONE
Istituto di Chimica Generale ed Inorganica dell'Università Viale Taramelli 12, 27100 Pavia, Italy

and

ANTONIO TIRIPICCHIO
Istituto di Chimica Generale ed Inorganica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via Massimo d'Azeglio 85, 43100 Parma, Italy

(*Received* 20 *June* 1982)

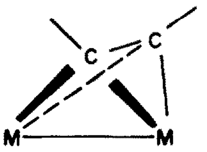
Abstract—The title compounds have been prepared from reactions of $Co_2(CO)_6(\mu\text{-}HOR_2CC_2R')$ or $Co_2(CO)_6(\mu\text{-}HOR_2CC_2CR_2OH)$ complexes with $Fe(CO)_5$ in acetone. In the latter set of reactions the homobimetallic butatriene compounds, $Fe_2(CO)_6\text{-}(\mu\text{-}R_2C{=}C{=}C{=}CR_2)$, are also obtained. The striking feature of these reactions is the ability of $Fe(CO)_5$ to dehydroxylate the organic moiety and to replace a $Co(CO)_3$ unit forming mixed iron-cobalt derivatives. A direct interaction between the iron and the carbon atom, originally bearing the lost -OH group, is evident from the bulk of the spectroscopic data; thus the organic chain acts as an overall 5 electron donor, according to the E.A.N. formalism. The heterobimetallic compounds have been characterized by elemental analysis, mass spectrometry, IR spectroscopy and NMR studies. For the phosphine derivative $FeCo(CO)_5(PPh_3)(H_2CC_2CH_2OH)$ a crudely refined X-ray analysis has been performed.

INTRODUCTION

Mixed metal compounds containing metal–metal bonds are receiving increasing attention since it has been suggested that the presence of different metallic centres on the same molecule can be important in the activation of organic substrates in stoichiometric and catalytic reactions.[1] Furthermore, they might represent a source for the preparation of highly dispersed metals on inorganic supports.[2] The development of new syntheses designed to produce stable heterometallic compounds is therefore worthwhile.

Actually, in the case of the synthesis of heterobimetallic complexes, all the possible combinations of metallic fragments bearing carbonyl and/or cyclopentadienyl ligands have been explored. Consequentely, a plethora of 34 electron heterobimetallic compounds has been obtained, mainly by Vahrenkamp[3] in the case of neutral complexes and by Ruff[4] in the case of ionic ones. Considering only first row Group VIII metals the following heterobimetallic complexes have been characterized: $FeCo(CO)_6(\eta\text{-}C_5H_5)$,[5] $FeNi(CO)_3(\eta\text{-}C_5H_5)_2$,[6] $CoNi(CO)_5(\eta\text{-}C_5H_5)$[5] and $[FeCo(CO)_8^-]$.[4]

So far, however, there have been few reports which have dealt with their reactivity toward unsaturated hydrocarbons. In principle an acetylenic moiety should be able to replace two CO groups in each of these complexes leading to the tetrahedral M_2C_2 structural framework, schematically represented below, already found in the corresponding homobimetallic compounds: $Fe_2(CO)_6(\mu\text{-}C_2Bu^t_2)$ (which formally has an Fe–Fe double bond)[7], $Co_2(CO)_6(\mu\text{-}C_2R_2)$[8] and $Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_2R_2)$.[9]



The heterobimetallic acetylenic complex $[(CO_3Co\text{–}Ni(\eta\text{-}C_5H_5)](\mu\text{-}C_2R_2)$ has been recently isolated from both the reaction of $Ni(\eta\text{-}C_5H_5)_2(\mu\text{-}C_2R_2)$ with $Co_2(CO)_8$ and the reaction of $Co_2(CO)_6(\mu\text{-}C_2R_2)$ with $[Ni(CO)(\eta\text{-}C_5H_5)]_2$.[10,11] Its solid state structure confirmed the expected pseudo-tetrahedral M_2C_2 framework.[10] On the contrary in 1963 Bassett,[12] in an attempt to prepare an acetylenic iron-nickel complex, observed only disproportionation:

$$2\ FeNi(CO)_3(\eta\text{-}C_5H_5)_2 + RC{\equiv}CR \rightarrow [Fe(CO)_2(\eta\text{-}C_5H_5)]_2\ Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_2R_2).$$

A quite different synthetic route was employed by Yasufuku *et al.*[13] who carried out the reaction of an ethynyltriphenylphosphonium salt with $(\eta\text{-}C_5H_5)_2Ni$ and $Fe_2(CO)_9$ obtaining the complex $[(CO)_3Fe\text{–}Ni(\eta\text{-}C_5H_5)](\mu\text{-}Ph_3PC_2H)$, formulated as an internal salt, in which the functionalized alkyne formally acts as a 5e-donor.

During our previous studies of the reactions of alkynes

---

*Author to whom correspondence should be addressed.

with cobalt and iron carbonyls,[14] we found that the homobimetallic complex, $Co_2(CO)_6(EtC_2CHOHMe)$ (**Ia**) (formed *in situ* by oxygen incorporation from water present in the solvent) reacted further with excess $Fe(CO)_5$ to give the heterobimetallic compound $FeCo(CO)_6(MeHCC_2Et)$ (**IIa**). This reaction offers further evidence of the dehydroxylation ability of iron carbonyls toward unsaturated alcohols. With the aim of testing the validity of this method in synthesizing novel mixed iron-cobalt derivatives, we have carried out the reactions of $Fe(CO)_5$ with $Co_2(CO)_6(\mu\text{-acetylene})$ complexes, bearing one or two hydroxyl group α to the triple bond. In this way several $FeCo(CO)_6(\mu\text{-alkynyl})$ complexes have been obtained and spectroscopic analysis has unambiguously established their structure.

EXPERIMENTAL

Reactants and physical measurements

All reactions were carried out under nitrogen. $Co_2(CO)_8$ and $Fe(CO)_5$ were purchased from Fluorochem Ltd., 2-butyn-1-ol, 2-butyn-1, 4-diol and 2, 5-dimethyl-3-hexyn-2, 5-diol were from Farchan Division. $Co_2(CO)_6(MeC_2CH_2OH)$ (**Ib**), $Co_2(CO)_6(HOCH_2C_2CH_2OH)$ (**Ic**) and $Co_2(CO)_6(HOMe_2CC_2CMe_2OH)$ (**Id**) complexes were synthesized using $Co_2(CO)_8$ and the corresponding alkyne according to previously reported procedures.[16] The purity of these compounds was checked by IR and MS spectroscopy, ^{13}CO (94.3%) was obtained from Monsanto Res. Corp. The heterobimetallic complexes were analyzed by use of a F & M 185 C, H, N analyzer and a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 580 B instrument using 0.5 mm NaCl cells. The mass spectra were measured on a Hitachi Perkin-Elmer RMU-6H spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol C60-HL and a Jeol-PS-100-FT instruments respectively. Chemical shifts were reported downfield positive with respect to $SiMe_4$. $Cr(acac)_3 (\simeq 10^{-3}\,M)$ was added as a shiftless relaxation agent for the ^{13}C NMR measurements. The temperature was monitored by a Jeol-JNM-BT-P-5-H-100E temperature control unit. The physical properties, analytical data, IR spectra for the complexes are listed in Table 1; ^1H and ^{13}C NMR data in Table 2.

Preparation of $FeCo(CO)_6(H_2CC_2CH_3)$ (**IIb**)

In a typical run 1.0 g (2.7 mmol) of $Co_2(CO)_6(HOH_2CC_2CH_3)$ (**Ib**) and 2.0 ml (14.4 mmol) of $Fe(CO)_5$ were refluxed in 200 cm³ of acetone for 10 hr. After cooling and filtration the excess of $Fe(CO)_5$ and the solvent were removed *in vacuo* and the residue dissolved in dichloromethane and chromatographed on tlc preparative plates (Kieselgel P. F. Merck, eluant light petroleum and 10% diethyl ether). Besides unreacted **Ia** ($\simeq$ 20%) and a small amount of $Fe_3(CO)_{12}$, $FeCo(CO)_6(H_2CC_2CH_3)$ (**IIb**), ($\simeq$ 40%) was eluted. Mass spectrum *m/e* 336 [M^+], followed by loss of six carbonyl groups.

Preparation of $FeCo(CO)_6(H_2CC_2CH_2OH)$ (**IIc**)

Ic and $Fe(CO)_5$ in the above ratio were refluxed in acetone for 10 hr. The same separation procedure afforded unreacted **Ic** ($\simeq$ 25%), small amount of $Fe_3(CO)_{12}$, $Fe_2(CO)_6(H_2CC_2CH_2)$ (**IIIc**) ($\simeq$ 5%) and $FeCo(CO)_6(H_2CC_2CH_2OH)$ (**IIc**), ($\simeq$ 25%). Mass spectrum *m/e* 352 [M^+] followed by loss of six carbonyl groups and concomitant loss of H_2O.

Preparation of $FeCo(CO)_6(HMeCC_2CMe_2OH)$ (**IId**)

Id and $Fe(CO)_5$ reacted in the same conditions to afford unreacted **Id** ($\simeq$ 15%), small amount of $Fe_3(CO)_{12}$, $Fe_2(CO)_6(Me_2CC_2CMe_2)$ (**IIId**) ($\simeq$ 35%) and $FeCo(CO)_6(Me_2CC_2CMe_2OH)$ (**IId**) ($\simeq$ 25%). Mass spectrum *m/e* 408 [M^+] followed by loss of six carbonyl groups and concomitant loss of H_2O.

Isotopic enrichment of **IIc** *and* **IId**

0.2 g of complex (**IIc** or **IId**) were dissolved in 100 cm³ of cyclohexane and stirred for 4 days at +40°C in the presence of < 1 Atmosphere of ^{13}CO. Further purification on a SiO_2 column using light petroleum with 20% $CHCl_3$ as eluant was carried out before running the spectra.

Preparation of $FeCo(CO)_5(PPh_3)(H_2CC_2CH_2OH)$ (**IVc**)

1.0 g (2.8 mmol) of **IIc** was dissolved in 100 cm³ of acetone and added with 0.73 g (2.8 mmol) of PPh_3. The mixture was refluxed for 20 hr. After cooling and filtration, the solvent was removed under vacuum and the residue dissolved in CH_2Cl_2 and chromatographed on tlc (eluant light petroleum and 20% $CHCl_3$). Unreacted **IIc** ($\simeq$ 25%) and $FeCo(CO)_5(PPh_3)(H_2CC_2CH_2OH)$ (**IVc**) ($\simeq$ 40%) have been eluted.

Crystallographic data collection of **IVc**

Red-orange crystals of **IVc** were grown by slow cooling of a saturated solution of **IVc** in *n*-heptane, chloroform 2 : 1 mixture under N_2 atmosphere. A very thin crystal was used for the X-ray analysis. Crystal data are as follows: $C_{27}H_{20}FeCoO_6P$, $M = 586.21$, $a = 10.505(8)$, $b = 12.787(12)$, $c = 10.477(9)$ Å, $\alpha = 111.13(6)$, $\beta = 105.25(6)$, $\gamma = 84.60(7)°$, $U = 1266$ Å³, $Z = 2$, $D_c = 1.54$ g/cm³, space group $P\bar{1}$.

The intensities of 1949 reflections with θ in the range 3–22° were measured on a Siemens AED diffractometer (using the Nb-filtered Mo-$K\,\alpha$ radiation), but only 519, having $I \geq 2\,\sigma(I)$ were considered observed and used in the analysis. The structure was solved by Patterson and Fourier methods, but the limited number of the observed reflections and the poor quality of them prevented a satisfactory refinement of the structure.

RESULTS AND DISCUSSION

Although all the reactions were performed in identical conditions, higher yields of the heterobimetallic complexes (**II**) were obtained from the alkyneol reactants (**Ia**, **Ib**) than from the alkynediols (**Ic**, **Id**). This is due to successive dehydroxylation and ligand transfer to Fe, which lead to the well known butatriene derivatives (**IIIc**, **IIId**) as shown in the following scheme:

$$\begin{array}{ll}
\mathrm{Co_2(CO)_6(HOR_2C{-}C{\equiv}C{-}R')} & [\mathbf{Ia, Ib}] \\
+\mathrm{Fe(CO)_5}\ \Big\downarrow\ -\mathrm{OH} & \\
\mathrm{FeCo(CO)_6(R_2C{-}C{\equiv}C{-}R')} & [\mathbf{IIa, IIb}]
\end{array}$$

$$\begin{array}{ll}
\mathrm{Co_2(CO)_6(HOR_2C{-}C{\equiv}C{-}CR_2OH)} & [\mathbf{Ic, Id}] \\
+\mathrm{Fe(CO)_5}\ \Big\downarrow\ -\mathrm{OH} & \\
\mathrm{FeCo(CO)_6(R_2C{-}C{\equiv}C{-}CR_2OH)} & [\mathbf{IIc, IId}] \\
+\mathrm{Fe(CO)_5}\ \Big\downarrow\ -\mathrm{OH} & \\
\mathrm{Fe_2(CO)_6(R_2C{=}C{=}C{=}CR_2)} & [\mathbf{IIIc, IIId}]
\end{array}$$

The heterobimetallic compounds are quite stable in the solid state under N_2 atmosphere, but they smoothly decompose in solution. They all have similar IR spectra (see Table 1), the slight shifts observed for the CO stretching frequencies can be related to the different electronic properties of the sustituents (H, Me, Et, OH). In the complexes **IIc** and **IId** the presence of the –OH group is confirmed by weak absorptions near 3600 cm⁻¹, which can be observed in concentrated CCl_4 solution.

Also their MS characteristics are very similar and strongly resemble those of the $Co_2(CO)_6(\mu\text{-alkyne})$

Table 1. Analysis and IR spectra of the heterobimetallic complexes

Compd.	Physical state	Elemental analysis Found (calc.)% C	H	Fe	Co	IR,[a] ν(CO), cm^{-1}
$\mathrm{FeCo(CO)_6(MeHCC_2Et)}$ **IIa***	orange oil					2083m, 2039vs, 2022s, 2013cm, 1991w, 1982m,
$\mathrm{FeCo(CO)_6(H_2CC_2Me)}$ **IIb**	orange oil	34.69 (35.71)	1.30 (1.49)	16.41 (16.67)	17.83 (17.56)	2084m, 2041vs, 2022s, 2014m, 1993w, 1981m.
$\mathrm{FeCo(CO)_6(H_2CC_2CH_2OH)}$ **IIc**	orange powder	33.60 (34.13	1.22 (1.43)	16.03 (15.87)	16.97 (16.75)	3628w,[b] 2087m, 2044vs, 2026s, 2019m, 1995w, 1989m.
$\mathrm{FeCo(CO)_6(Me_2CC_2CMe_2OH)}$ **IId**	red powder	40.78 (41.21)	3.55 (3.21)	13.95 (13.69)	15.03 (14.44)	3609w,[b] 2080m, 2036vs, 2020s, 2012m, 1985w, 1976m.
$\mathrm{FeCo(CO)_5(PPh_3)(H_2CC_2CH_2OH)}$ **IVc**	red-orange crystals	54.60 (55.29)	3.80 (3.41)	10.02 (9.56)	10.43 (10.07)	2055vs, 2009s, 1993vs, 1973m.

[a]*n*-hexane, [b]γ(OH) measured in concentrated $\mathrm{CCl_4}$ solution, *two enantiomers ref. 14.

Table 2. ^{1}H and ^{13}C NMR data and tentative assignments of the heterobimetallic complexes

Compd.	^{1}H NMR,[a,b] δ/ppm	^{13}C NMR,[a] δ/ppm
$\mathrm{FeCo(CO)_6(MeHCC_2Et)}$ **IIa***	$\mathrm{C_2H_5}$: 2.83(m, 4), 1.69(t, 6); CH: 5.04(q, 1), 4.78(q, 1); $\mathrm{CH_3}$: 1.27(d, 3), 1.20(d, 3).	FeCO: 210.3; CoCO: 203.1; $\mathrm{C_2}$: 123.7, 118.4, 97.5, 94.8; CH: 89.3, 87.0; $\mathrm{C_2H_5}$: 29.3, 27.2, 16.3, 15.9; $\mathrm{CH_3}$: 25.2, 19.4.
$\mathrm{FeCo(CO)_6(H_2CC_2CH_3)}$ **IIb**	$\mathrm{CH_2}$: 3.98 and 3.92 (each s, 1); $\mathrm{CH_3}$: 2.69(s, 3)	FeCO: 209.0; CoCO: 202.2; $\mathrm{C_2}$: 121.0, 87.4; $\mathrm{CH_2}$: 66.1; $\mathrm{CH_3}$: 18.5.
$\mathrm{FeCo(CO)_6(H_2CC_2CH_2OH)}$ **IIc**	FeCH_2: 4.86 and 4.80 (each s, 1); OHCH_2: 4.10(s, 2), OH: 2.10(s, br, 1)[c]	FeCo: 209.5; CoCO: 201.0; $\mathrm{C_2}$: 122.4, 92.1; FeCH_2: 69.2(J_{CH} = 161 Hz); OHCH_2: 62.8 (J_{CH} = 142 Hz).
$\mathrm{FeCo(CO)_6(Me_2CC_2CMe_2OH)}$ **IId**	OHCH_3: 1.95 and 1.92 (each *s*, 3); FeCH_3: 1.69 and 1.65 (each s,3); OH: 1.72(s, br,1)[c]	FeCO: 209.9; CoCO: 201.4; $\mathrm{C_4}$: 117.6, I 13.2, 101.2, 73.7; FeCH_3: 32.7; OHCH_3: 26.9.
$\mathrm{FeCo(CO)_5(PPh_3)(H_2CC_2CH_2OH)}$ IVc	Ph: 7.27(m, 15); OHCH_2: 4.11 (s, 2); FeCH_2: 3.94 and 3.91 (each s, 1); OH: 1.48(s, br, 1)	FeCO: 211.5; CoCO: 207.6, 205.5; Ph: 135.1, 133.2, 130.4, 128.7; $\mathrm{C_2}$: 122.0, 90.4; FeCH_2: 67.2(J_{CH} = 166 Hz); OHCH_2: 61.6(J_{CH} = 148 Hz).

[a]$\mathrm{CDCl_3}$ at +25°C, [b]multiplicity and integrated intensities in parenthesis, [c]these chemical shifts were temperature- and concentration-dependent, *two enantiomers ref. 14.

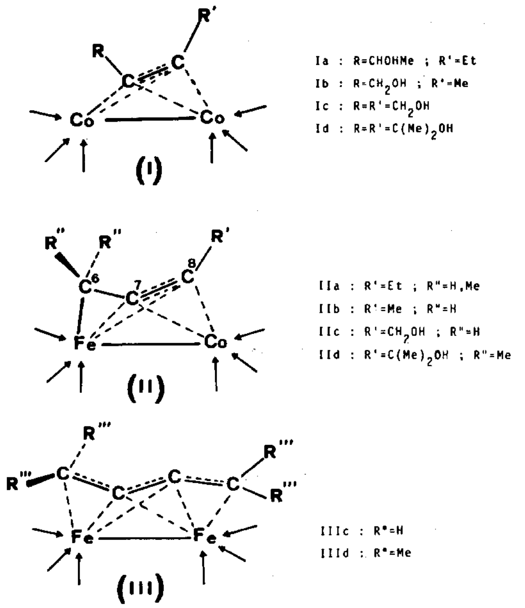


Fig. 1. Structures of the homometallic complexes (I) and (III) and proposed structure of the heterobimetallic complex (II).

compounds.[17] It is interesting to note the relatively high abundance of the fragment corresponding to the $[FeCoC_3H_3]^+$ ion. Analogous $[Co_2C_3H_n]^+$ fragments have not been observed in the MS spectra of the $Co_2(CO)_6(\mu\text{-}C_2R_2)$ complexes. This supports the view that the heterobimetallic moiety is bonded to three carbon atoms of the organic chain. The high stability of the Fe–Co bond is suggested from the presence of 50–80% $[FeCo]^+$ ions in all the spectra. For **IIc** and **IId** the presence of the -OH group is further corroborated by the observation of a fragment ion which constitutes loss of H_2O from $[M^+]$.

The assignment of the ^1H NMR signals of $FeCo(CO)_6(H_2CC_2CH_3)$ (**IIb**) is straightforward: the methylene group appears as two broad singlets of relative intensity 1 at δ 3.98 and 3.93 respectively, the methyl group as a singlet of intensity 3 at δ 2.69. This pattern remains unchanged as the temperature is increased up to +80°C; above this temperature decomposition of sample is observed. The room temperature ^1H NMR spectrum of $FeCo(CO)_6(MeCC_2CMe_2OH)$ (**IId**) shows four methyl resonances (see Table 2); as the temperature is increased the two lowfield signals broaden and merge into a new resonance at +45°C ($\Delta G^\ddagger = 74.4$ kJ/mol) and on this basis we assign the two lowfield peaks to the $-CMe_2OH$ group. This dynamic process has to be related to a partially hindered rotation around the $\equiv C\text{–}CMe_2OH$ bond. Similar arguments were used to assign the resonances in the other compounds prepared here. The ^{13}C NMR spectra of the title compounds are quite similar: of the two quaternary acetylenic carbon resonances one is found in the spectral region typical of the $Co_2(CO)_6(\mu\text{-alkyne})$ complexes[18] and one in a lower field region (117.6–123.7 ppm) of the spectrum, which is assigned to the acetylenic carbon bonded to the carbon σ interacting with the iron atom. This low field shift is indicative of a change from sp to sp^2 hybridisation and suggests a delocalized bonding framework for the $\mu_2-\eta^3$ system. In Fig. 1 are shown the structures of $Co_2(CO)_6(\mu\text{-alkyne})$[8] (**I**) and $Fe_2(CO)_6(\mu\text{-butatriene})$[19] (**III**) coplexes together with the proposed structure of the title compounds (**II**). Complexes **I**, **II** and **III** are isoelectronic: two, three and four carbon atoms are engaged in the bonding scheme with the bimetallic fragment and the organic chain acts as a four-, five- and six-electron donor.

Although the chemical and spectroscopic evidence strongly support the proposed structure (**II**), several attempts were made to confirm it by X-ray analyses. However all were unsuccessful. In order to overcome crystallization problems the $FeCo(CO)_5(PPh)(R_2CC_2CR')$ derivatives were synthesized. The best result was achieved for R=H, R'=CH_2OH (**IVc**), though also in this case the quality of the crystals was poor and the crystals were twinned. An accurate structure determination was thus impossible, but the most significant features of the molecular structure could be extracted. The proposed structure, shown in Fig. 2, is in agreement with that proposed on the basis of the spectroscopic data (**II**). The organic ligand is σ-bonded to the Fe atom through the terminal C(6) carbon and η^2-interacts with both the metal atoms (Fe–Co distance: 2.55 Å) *via* the C(7)–C(8) bond. The triphenylphosphine group has substituted one carbonyl in an apical position on the cobalt atom. Similar regiospecific substitution of the phosphine for CO group in $Co_2(CO)_5(PR_3)(\mu\text{-alkyne})$

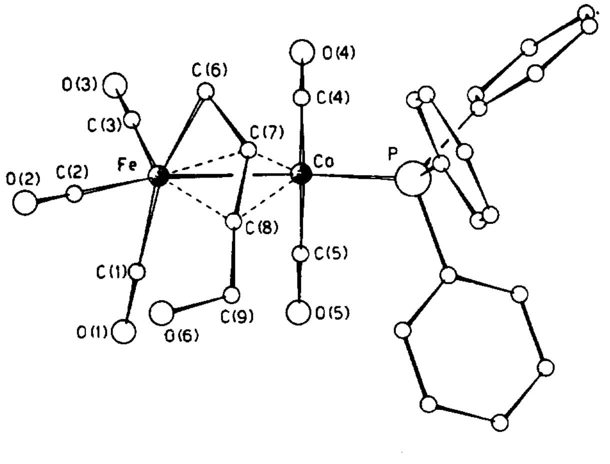


Fig. 2. Proposed molecular shape of the compound $FeCo(CO)_5(PPh_3)$ $(H_2CC_2CH_2OH)$ (**IVc**).

derivatives has been reported on the basis of IR[20] and ^{13}C NMR[18] data. The poor accuracy of the structural parameters hampers a detailed discussion of the molecular structure. The J_{CH} values in the ^{13}C NMR spectrum of $FeCo(CO)_6(H_2CC_2CH_2OH)$ (**IIc**) also supports this picture. In the proton-coupled spectrum two triplets are observed at δ 62.8 and 69.2. The first shows $J_{CH} =$ 142 Hz consistent with an sp^3 carbon bearing an electron withdrawing substituent (HO–*CH*$_2$), while the second shows $J_{CH} = 161$ Hz, suggesting a partial rehybridation towards an sp^2 character (Fe–*CH*$_2$). Similar features are observed for the corresponding monophosphine derivative (**IVc**) (see Table 2).

In conclusion, we feel that the structure of the title compounds (**II**) can be envisaged as the result of building up two halves obtained by dividing along the organic chain and the metal–metal bond the two homometallic compounds (**I**) and (**III**).

Dynamic behaviour

All the ^{13}C NMR spectra of the title complexes show two sets of CO absorptions at room temperature: the sharp Fe–*CO* resonances lie in the range 211.5–209.0 ppm, the very broad Co–*CO* resonances in the 207.6–201.0 ppm region. This assignment is consistent with previous observations of mixed iron-cobalt clusters, showing that the COs bonded to Fe resonate at lower field than the Co bonded ones.[21] In the VT ^{13}C NMR studies of ^{13}CO enriched samples of **IIc** and **IId**, lowering of temperature to -80°C results in a progressive sharpening of the Co–*CO* resonances. It then follows that the broadening observed in room temperature spectra is only due to the moderately rapid quadrupolar relaxation induced by the Co nuclei ($I = 7/2$). On the other hand, in the same temperature range the Fe–*CO* resonance splits into three peaks of relative intensity ratio 1 : 1 : 1, whose weighted average chemical shifts are in good accord with the room temperature value (**IIc**, -50°C, Fe*CO*: 212.4, 210.3, 205.6; **IId**, -60°C, Fe*CO*: 211.9, 209.4, 206.7).

At room temperature the carbonyls are locally exchanging at each "$M(CO)_3$" unit, but only the scrambling at $Fe(CO)_3$ can be frozen in the low temperature limiting spectrum. On the contrary the room temperature ^{13}C NMR spectrum of **IVc** shows three CO absorptions, one sharp at $\delta = 211.5$ and two very broad at $\delta = 207.6$ and 205.5 of relative intensity ratio 3 : 1 : 1. It follows that the presence of the bulky triphenylphosphine group quenches, even at room temperature, the localized exchanged process at the $Co(CO)_2$ unit. Owing to the broadening of these two resonances, no J_{CP} could be extracted.

Acknowledgements—This research was supported by the Italian C.N.R. (Progetto Finalizzato Chimica Fine e Secondaria, Contratto No. 8100727.95). We wish to thank Mr. M. Matis for recording the NMR spectra.

REFERENCES

[1] D. A. Roberts and G. L. Geoffroy, *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel), Chap. 40. Pergamon Press, Oxford (1982).
[2] M. Ichikawa, *J. Catal.* 1979, **56**, 127.
[3] T. Madach and H. Vahrenkamp, *Chem. Ber.* 1980, **113**, 2675.
[4] J. K. Ruff, *Inorg. Chem.* 1968, **7**, 1818.
[5] K. K. Joshi and P. L. Pauson, *Z. Naturforsch.* 1962, **17**, 565.
[6] J. F. Tilney-Bassett, *Proc. Chem. Soc. London* 1960, 419.
[7] F. A. Cotton, J. D. Jamerson and B. R. Stults, *J. Am. Chem. Soc.* 1976, **98**, 1774.
[8] W. G. Sly, *J. Am. Chem. Soc.* 1959, **81**, 18.
[9] Y. Wang and P. Coppens, *Inorg. Chem.* 1976, **15**, 1123.
[10] B. H. Freeland, J. E. Hux, N. C. Payne and K. G. Kyers, *Inorg. Chem.* 1980, **19**, 693.
[11] E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day and A. B. Anderson, *J. Am. Chem. Soc.* 1978, **100**, 2090.
[12] J. F. Tilney-Bassett, *J. Chem. Soc.* 1963, 4748.
[13] K. Tasufuku, K. Aoki and H. Yamazaki, *J. Organomet. Chem.* 1975, **84**, C28.
[14] S. Aime, L. Milone, D. Osella, A. Tiripicchio, A. M. Manotti-Lanfredi, *Inorg. Chem.* 1982, **21**, 501.
[15] R. Victor, *J. Organomet. Chem.* 1977, **127**, C25.
[16] R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.* 1975, 323.
[17] O. Gambino, G. A. Vaglio, R. P. Ferrari, M. Valle and G. Cetini, *Org. Mass Spectrom.* 1972, **6**, 723.
[18] S. Aime, L. Milone, R. Rossetti and P. L. Stanghellini, *Inorg. Chim. Acta*, 1977, **22**, 135.
[19a] D. Bright and O. S. Mills, *J. Chem. Soc. Dalton* 1972, 2465; [b] J. N. Gerlach, R. M. Wing and P. C. Ellgen, *Inorg. Chem.* 1976, **15**, 2959.
[20] G. Varadi, A. Vizi-Oroz, S. Vastag and G. Pàlyi, *J. Organomet. Chem.* 1976, **108**, 255.
[21] S. Aime and L. Milone, *Progress in NMR Spectroscopy*, 1977 **11**, 149.