Synthesis and Characterization of New Heterobimetallic Iron–Cobalt Complexes with Ethenyl Bridges $CR^2{=}CHR^1$ [R^1 = H or C(O)OMe, R^2 = C(O)OMe or C(O)OEt]. *X*-Ray Structure of [$FeCo(CO)_6$\{μ-MeOC(O)C=C(H)C(O)OMe\}]†

Isabel Moldes and Josep Ros *
Departament de Química, Div. Inorgànica, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain
René Mathieu
Laboratoire de Chimie de Coordination du C.N.R.S., Unité No 8241 liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31400 Toulouse, France
Xavier Solans and Mercé Font-Bardía
Department de Cristal. lografia i Mineralogia, Universitat de Barcelona, Gran Via 585, 08007 Barcelona, Spain

The reaction of [$Fe(\eta^3$-$R^1HC{=}CR^2CO)(CO)_3]^-$ (**1**) with [$Co_2(CO)_8$] yields two types of new heterobimetallic Fe–Co complexes. When R^1 = H and R^2 = C(O)OMe or C(O)OEt, the products are the μ-ethenyl complexes [$FeCo(CO)_7(\mu$-$R^2C{=}CH_2)$] (**2**), while when $R^1 = R^2$ = C(O)OMe the complex [$FeCo(CO)_6$\{μ-MeOC(O)C=C(H)C(O)OMe\}] (**3**) is formed. In this complex one ester group of the μ-ethenyl ligand is co-ordinated *via* oxygen to iron. This feature has been confirmed by a single-crystal *X*-ray diffraction study. The reaction of (**2**) and (**3**) with one equivalent of PMe_2Ph yields the complexes (**4**) and (**5**), respectively, in which one molecule of CO has been substituted by the phosphine. The site of substitution is different in (**4**) and (**5**); thus in complexes (**4**) the phosphine ligand is bonded to iron but in (**5**) it is bonded to cobalt.

The chemistry of dinuclear complexes containing organic bridges has been an increasing field of interest in the last few years.[1] Recently in our laboratories we have developed the chemistry of μ-ethenyl dinuclear carbonyl iron complexes.[2] One objective of our studies was the synthesis of heteronuclear cluster complexes by cluster-expansion reactions, coupling dinuclear iron complexes with other metal complexes. As a result of these reactions we have shown that the anion [$Fe_2(CO)_6(\mu$-$CO)(\mu$-$CHCH_2)]^-$ reacts with [$Co_2(CO)_8$] to give the dinuclear mixed complex [$FeCo(CO)_7(\mu$-$CHCH_2)$]. This complex showed great facility of rearrangement, producing trinuclear complexes with Fe_2Co and $FeCo_2$ cores.[3]

Literature reports of dinuclear mixed Fe–Co complexes containing organic bridges are limited to complexes with low possibilities to build new mixed-metal clusters.[4] In order to obtain new ethenyl-bridged dinuclear Fe–Co complexes we have checked the reactivity of mononuclear anionic complexes [$Fe(\eta^3$-$R^1HC{=}CR^2CO)(CO)_3]^-$ [(**1a**), R^1 = H, R^2 = C(O)OMe; (**1b**), R^1 = H, R^2 = C(O)OEt; (**1c**), $R^1 = R^2$ = C(O)OMe] toward [$Co_2(CO)_8$]. In this reaction, [$Co_2(CO)_8$] acts as an oxidizing agent by elimination of [$Co(CO)_4]^-$. The complexes of type (**1**) are obtained by reaction of [$FeH(CO)_4]^-$ with activated alkynes.[5] The results of these reactions and the reactivity of the products with PMe_2Ph are presented in this paper.

Experimental

All reactions were performed under a nitrogen atmosphere. Hydrogen-1 n.m.r. spectra were recorded on a Bruker WP80 spectrometer in $CDCl_3$ solutions and ^{31}P n.m.r. spectra on a Bruker WP90 spectrometer in $CDCl_3$ referenced to aqueous 85% H_3PO_4. Infrared spectra were recorded in the ν(CO) stretching region on a Beckman IR 20A spectrometer in cyclohexane solution. Mass spectra were measured on a Hewlett-Packard 2985 GC/MS spectrometer.

The complexes [PPh_4][$Fe(\eta^3$-$R^1HC{=}CR^2CO)(CO)_3$] (**1a**)—(**1c**) were prepared by a published procedure.[5] Elemental analysis (C and H) was performed on a Perkin-Elmer 240-B analyzer.

Preparation of Complexes (**2a**), (**2b**), *and* (**3**).—To complex (**1a**), (**1b**), or (**1c**) (1 g) dissolved in dichloromethane (10 cm^3) was added a stoicheiometric amount of [$Co_2(CO)_8$] and the solution was stirred for 30 min at room temperature. The solution was evaporated to dryness and the residue extracted with hexane; the solvent was eliminated by evaporation. The residue was dissolved in a minimum amount of dichloromethane and methanol was added (3 cm^3). Cooling at −20 °C gave crystals of (**2a**), (**2b**), or (**3**) in *ca.* 40% yield. [$FeCo(CO)_7(\mu$-$MeO_2CC{=}CH_2)$] (**2a**). I.r.: ν(CO) at 2 112m, 2 057s, 2 028s, 1 986m, and 1 700m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 3.64 (s, 1 H), 3.70 (s, 1 H), and 3.82 (s, 3 H) (Found C, 33.6; H, 1.35. Calc. for $C_{11}H_5CoFeO_9$: C, 33.35; H, 1.25%). [$FeCo(CO)_7(\mu$-$EtO_2CC{=}CH_2)$], (**2b**). I.r.: ν(CO) at 2 115m, 2 058s, 2 031s, 1 995m, and 1 700m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 1.23 (t, *J* 7.4 Hz, 3 H), 3.32 (d, *J* 1.2 Hz, 1 H), 3.69 (d, *J* 1.2 Hz, 1 H), and 4.24 (q, *J* 7.4 Hz, 2 H) (Found: C, 35.15; H, 1.80. Calc. for $C_{12}H_7CoFeO_9$: C, 35.15; H, 1.70%). [$FeCo(CO)_6$\{μ-MeOC(O)C=C(H)C(O)OMe\}] (**3**). I.r.: ν(CO) at 2 084m, 2 041s, 2 012m, 1 705m, and 1 570m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 3.61 (s, 3 H), 3.86 (s, 3 H), and 4.41 (s, 1 H) (Found: C, 34.25; H, 1.75. Calc. for $C_{12}H_7CoFeO_{10}$: C, 33.8; H, 1.65%).

Preparation of Complexes (**4a**), (**4b**), *and* (**5**).—Complex (**2a**), (**2b**), or (**3**) (0.25 g) was dissolved in dichloromethane (5 cm^3) and a stoicheiometric amount of PMe_2Ph was added. The solution was stirred for 30 min at room temperature. Concentration of dichloromethane and addition of methanol (3 cm^3) and cooling to −20 °C gave crystals of (**4a**), (**4b**), or (**5**) respectively. The reactions are all nearly quantitative. [FeCo-

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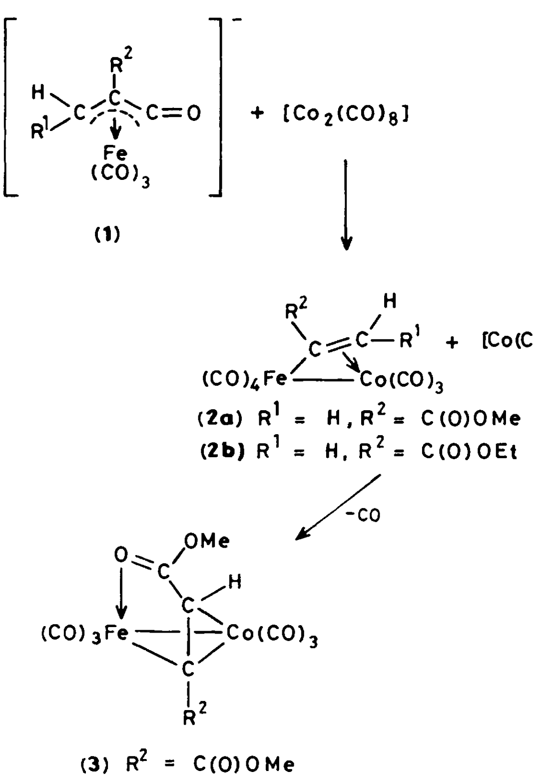
† 1,1,1,2,2,2-Hexacarbonyl-μ-[1,2-di(methoxycarbonyl)ethen-1-yl-C^1(Fe,Co)C^2(Co)O^2(Fe)]-cobaltiron(*Co–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme.

$(CO)_6(PMe_2Ph)(\mu\text{-}MeO_2CC{=}CH_2)]$ (**4a**). I.r.: ν(CO) at 2 045m, 2 004s, 1 984s, and 1 670m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.86 (d, *J* 7.4 Hz, 3 H), 2.03 (d, *J* 7.4 Hz, 3 H), 3.18 (s, 1 H), 3.60 (s, 1 H), 3.61 (s, 3 H), and 7.47 (s, 5 H). ^{31}P-{^{1}H} N.m.r. ($CDCl_3$): δ 26.17 (s) (Found: C, 42.95; H, 3.20. Calc. for $C_{18}H_{16}CoFeO_8P$: C, 42.7; H, 3.15%). $[FeCo(CO)_6(PMe_2Ph)(\mu\text{-}EtO_2CC{=}CH_2)]$, (**4b**). I.r.: ν(CO) at 2 050m, 2 010s, 1 990s, and 1 675m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.19 (t, *J* 8 Hz, 3 H), 1.79 (d, *J* 4 Hz, 3 H), 1.95 (d, *J* 4 Hz, 3 H), 3.10 (s, 1 H), 3.55 (s, 1 H), 3.99 (q, *J* 8 Hz, 2 H), and 7.28 (s, 5 H) (Found: C, 43.6; H, 3.45. Calc. for $C_{19}H_{18}CoFeO_8P$: 43.85; H, 3.45%). $[FeCo(CO)_5(PMe_2Ph)(\mu\text{-}MeO_2CC{=}CHCO_2Me)]$ (**5**). I.r.: ν(CO) at 2 052s, 1 998s, 1 975w, 1 940m, 1 680m, and 1 555m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.31 (s, 3 H), 1.54 (s, 3 H), 3.26 (s, 3 H), 3.53 (s, 1 H), 3.71 (s, 3 H), and 7.34 (s, 5 H). ^{31}P-{^{1}H} N.m.r. ($CDCl_3$): δ 27.81 (s, br) (Found: C, 42.6; H, 3.60. Calc. for $C_{19}H_{19}CoFeO_9P$: C, 42.55; H, 3.35%).

Crystal Data for (**3**).—$C_{12}H_7CoFeO_{10}$, $M = 425.0$, monoclinic, $a = 9.716(2)$, $b = 24.076(4)$, $c = 6.712(2)$ Å, $\beta = 96.71(2)°$, $U = 1\,559(1)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/a$, $Z = 4$, $D_c = 1.810$ g cm^{-3}. $F(000) = 844$. Dark violet needles; dimensions of a poor quality crystal, 0.4 × 0.4 × 0.1 mm; $\mu(\text{Mo-}K_\alpha) = 21.11$ cm^{-1}.

Data Collection and Processing.—Phillips PW-1100 diffractometer, ω-scan technique with scan width 1°, scan speed 0.03° s^{-1}, graphite-monochromated Mo-K_α radiation; 1 682 independent reflections measured ($\theta \leqslant 24°$), 896 unique with $I \geqslant 2.5\sigma(I)$. Significant intensity decay was not observed. Lorentz-polarization, but no absorption corrections were made.

Structure Analysis and Refinement.—Patterson synthesis (Fe and Co) followed by DIRDIF system of computer programs (remaining non-hydrogen atoms). Full-matrix least-squares refinement (isotropic and anisotropic). The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.014|F_o|^2]^{-1}$. Final R and R' values 0.055 and 0.059. Computer programs used are given in refs. 6 and 7.

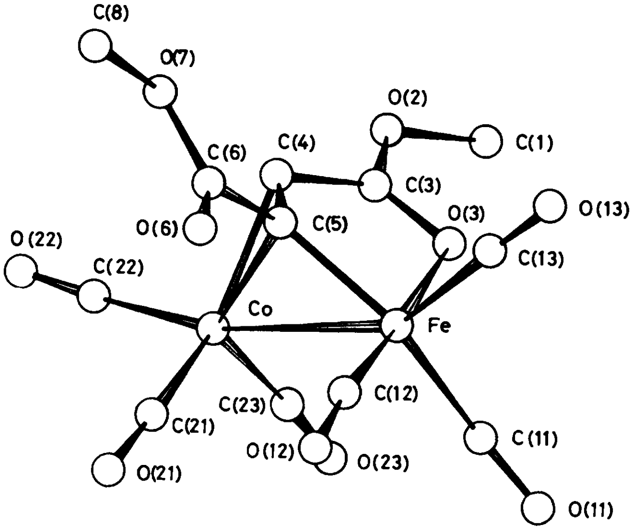


Figure 1. Structure of complex (**3**) showing the atomic numbering scheme

Results and Discussion

The reaction of (**1a**) or (**1b**) with $[Co_2(CO)_8]$ at room temperature in CH_2Cl_2 yields black crystalline complexes, $[FeCo(CO)_7(\mu\text{-}R^2C{=}CH_2)]$ (**2a**) or (**2b**), in *ca.* 40% yield in both cases. These complexes are very soluble in non-polar solvents and quite stable in the solid state but decompose slowly in solution at room temperature even under a nitrogen atmosphere.

The i.r. spectra in the ν(CO) region of complexes (**2a**) and (**2b**) in cyclohexane solution show only terminal CO with the same pattern as that reported for the complex $[FeCo(CO)_7(\mu\text{-}CH{=}CH_2)]$.[3] The ^{1}H n.m.r. spectra in $CDCl_3$ at 20 °C display two signals [δ 3.64 and 3.70 for (**2a**) and 3.32 and 3.69 for (**2b**)] corresponding to geminal hydrogens of the vinyl bridge and signals assigned to methyl or ethyl ester groups. The mass spectrum of (**2b**) shows the parent ion at $m/z = 410$ and the successive loss of seven molecules of CO. The highest ion detected corresponds to the $[M^+ - CO]$ fragment ($m/z = 368$) and the loss of six carbonyls.

When (**1c**) is reacted with $[Co_2(CO)_8]$ at room temperature in CH_2Cl_2, the red crystalline complex $[FeCo(CO)_6\{MeOC(O)C{=}C(H)C(O)OMe\}]$ (**3**) is obtained in *ca.* 35% yield. This complex is stable in the solid state and in solution at room temperature under a nitrogen atmosphere. The elemental analyses and spectroscopic data of (**3**) suggest the presence of six CO groups. Although the parent ion is not observed, the $[M^+ - CO]$ fragment ($m/z = 398$), the loss of five molecules of CO, and the $[FeCo]^+$ fragment are detected. The i.r. pattern in the ν(CO) region in cyclohexane solution is different to those of (**2a**) and (**2b**). Furthermore, two absorptions corresponding to ν(C=O) of the ester groups are observed (1 705 and 1 570 cm^{-1}). The low absorption suggests that one ester group is co-ordinated to one metal *via* an oxygen atom.[8] The ^{1}H n.m.r. spectrum of (**3**) at room temperature exhibits two singlets at δ 3.61 and 3.86 corresponding to methyl ester groups and one singlet at δ 4.41 assigned to the vinyl proton.

The spectroscopic properties of the complexes (**2a**), (**2b**), and (**3**) support the structures presented in the Scheme. The

Table 1. Atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for (**3**)

Atom	x	y	z	Atom	x	y	z
Co	3 615(2)	1 082(1)	1 222(4)	C(11)	−65(23)	1 327(7)	1 555(26)
Fe	1 588(2)	1 410(1)	3 130(4)	C(12)	1 766(17)	2 103(9)	2 421(28)
C(1)	1 712(18)	−488(7)	4 616(35)	O(11)	−1 153(15)	1 284(7)	621(23)
O(2)	2 898(10)	−117(5)	4 588(18)	O(12)	1 756(13)	2 572(6)	1 823(20)
C(3)	2 701(19)	419(6)	4 208(25)	C(13)	1 011(18)	1 595(7)	5 490(34)
O(3)	1 491(12)	592(4)	3 926(16)	O(13)	621(15)	1 702(6)	−3 065(23)
C(4)	3 860(17)	758(7)	4 110(25)	C(21)	3 780(21)	1 741(11)	42(31)
C(5)	3 534(16)	1 336(7)	4 062(25)	O(21)	3 931(16)	2 129(7)	−795(23)
C(6)	4 593(19)	1 753(7)	4 821(24)	C(22)	5 170(23)	792(7)	508(30)
O(6)	4 418(12)	2 248(5)	4 591(16)	O(22)	6 129(16)	568(6)	95(26)
O(7)	702(12)	3 461(4)	5 827(18)	C(23)	2 297(19)	674(8)	−210(31)
C(8)	6 740(17)	1 919(7)	6 717(26)	O(23)	1 477(16)	425(6)	−1 226(24)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Fe–Co	2.593(3)	O(2)–C(1)	1.458(19)	O(3)–Fe	2.044(10)	O(11)–C(11)	1.169(21)
C(4)–Co	2.077(17)	C(3)–O(2)	1.325(15)	C(4)–Fe	2.724(16)	O(12)–C(12)	1.200(21)
C(5)–Co	2.012(17)	O(3)–C(3)	1.241(17)	C(5)–Fe	1.929(16)	O(13)–C(13)	1.112(19)
C(21)–Co	1.788(26)	C(4)–C(3)	1.400(22)	C(11)–Fe	1.827(21)	O(21)–C(21)	1.110(22)
C(22)–Co	1.781(21)	C(5)–C(4)	1.425(22)	C(12)–Fe	1.749(23)	O(22)–C(22)	1.139(20)
C(23)–Co	1.801(21)	C(6)–C(5)	1.485(23)	C(13)–Fe	1.797(22)	O(23)–C(23)	1.154(19)
C(3)–Fe	2.684(15)	O(6)–C(6)	1.212(18)				
C(4)–Co–Fe	70.4(4)	C(23)–Co–Fe	84.0(6)	C(4)–Fe–C(3)	30.0(5)	C(6)–C(5)–Fe	131.5(13)
C(5)–Co–Fe	47.5(4)	C(23)–Co–C(4)	106.8(8)	C(3)–C(4)–Fe	73.4(9)	C(6)–C(5)–C(4)	120.6(15)
C(5)–Co–C(4)	40.8(6)	C(23)–Co–C(5)	124.6(8)	C(5)–C(4)–Co	67.2(10)	O(6)–C(6)–C(5)	122.7(16)
C(21)–Co–Fe	93.5(6)	C(23)–Co–C(21)	110.1(9)	C(5)–C(4)–Fe	42.4(8)	O(11)–C(11)–Fe	176.8(17)
C(21)–Co–C(4)	137.7(8)	C(23)–Co–C(22)	102.4(8)	C(5)–C(4)–C(3)	113.1(14)	O(12)–C(12)–Fe	173.3(16)
C(21)–Co–C(5)	99.6(8)	C(3)–Fe–Co	63.8(4)	Fe–C(5)–Co	82.3(6)	O(13)–C(13)–Fe	178.1(18)
C(22)–Co–Fe	165.8(7)	O(3)–Fe–Co	84.1(3)	C(4)–C(5)–Co	72.1(10)	O(21)–C(21)–Co	174.7(19)
C(22)–Co–C(4)	95.5(8)	O(3)–Fe–C(3)	26.2(4)	C(4)–C(5)–Fe	107.7(11)	O(22)–C(22)–Co	174.7(18)
C(22)–Co–C(5)	120.2(8)	C(4)–Fe–Co	45.9(3)	C(6)–C(5)–Co	115.3(11)	O(23)–C(23)–Co	176.1(17)
C(22)–Co–C(21)	96.1(9)						

structure of (**3**) was confirmed by *X*-ray diffraction studies. In the first step of the Scheme the dicobalt octacarbonyl acts as an oxidizing agent, forming the dinuclear ethenyl-bridged complexes (**2**), isolated for R^2 = C(O)OMe or C(O)OEt and R^1 = H. In the case where R^1 = R^2 = C(O)OMe, the ester group is in a suitable situation to substitute one CO group on iron leading quickly to (**3**). Efforts made to isolate complexes of type (**2**) where R^1 = R^2 = C(O)OMe or C(O)OEt were unsuccessful, showing that co-ordination of oxygen is rapid. In all these reactions the acyl ligand is decarbonylated. The same phenomenon has been observed during the protonation of complexes of type (**1**).[5]

X-*Ray Crystal Structure of* [FeCo(CO)$_6${μ-MeOC(O)C=C(H)C(O)OMe}] (**3**).—The structural data from the *X*-ray diffraction study of (**3**) are summarized in Tables 1 and 2. A view of the molecule is shown in Figure 1. The structure consists of an FeCo(CO)$_6$ unit in which one MeOC(O)C=C(H)C(O)OMe ligand bridges a single Co–Fe bond [2.593(3) Å].[9] The organic bridge is σ-bonded to iron [1.929(16) Å] and asymmetrically π-bonded to cobalt [2.012(17) and 2.077(17) Å]. The methyl carboxylate groups are in a *trans* configuration due to the co-ordination of O(3) to iron [2.044(10) Å]. The ligand forms a nearly planar metallacycle with the Fe atom. The donor behaviour of O(3) appears to induce the shortening of the Fe–C(12) bond [1.749(23) Å] and lengthening of the C(12)–O(12) bond [1.200(21) Å]. The CO *trans* to C(5)–Fe has the longer Fe–CO distance [1.827(21) Å] which demonstrates the *trans* effect of the σ-bonded ethenyl ligand. The co-ordination geometry about Fe, including the Fe–Co bond, can be described as a distorted octahedron. On the other hand, considering the π-bond of the organic bridge as a unidentate interaction, the Co atom has distorted trigonal-bipyramidal geometry. The CO ligands are disposed, almost symmetrically, around the metal–metal bond showing a 'sawhorse' configuration.

Reactions with PMe$_2$Ph.—The presence of two different metal centres in the complexes (**2a**), (**2b**), and (**3**) prompted us to check their reactivity with PMe$_2$Ph. This ligand is easy to handle and has a low 'cone angle'.[10] Addition of one equivalent of PMe$_2$Ph to a CH$_2$Cl$_2$ solution of (**2a**), (**2b**), or (**3**) yields the complexes [FeCo(CO)$_6$(PMe$_2$Ph)(R^{2}C=CH$_2$)] [(**4a**), R^2 = C(O)OMe; (**4b**), R^2 = C(O)OEt] and [FeCo(CO)$_5$(PMe$_2$Ph){MeO(O)CC=C(H)C(O)OMe}] (**5**). In all complexes one molecule of CO is substituted by one of phosphine. The ^{1}H n.m.r. spectra of complexes (**4a**), (**4b**), and (**5**) show the presence of PMe$_2$Ph and protons of the ethenyl bridge. Otherwise, they are not significantly different from the unsubstituted complexes (**2a**), (**2b**), and (**3**). The more interesting aspect of the reactivity of mixed Fe–Co complexes toward phosphines is the site of substitution of CO. From the mass spectra of the substituted complexes it is possible to infer whether the phosphine is co-ordinated to iron or cobalt. The parent ion is not observed for (**4a**) and (**4b**) but more significant is the abundant presence of the [FePMe$_2$Ph]$^+$ fragment (m/z = 194) with relative intensity 60% and 100% respectively. The hypothetical fragment [CoPMe$_2$Ph]$^+$ is not observed for either complex.

On the other hand, the mass spectrum of complex (**5**) exhibits a parent ion (m/z = 536), the loss of six carbonyls, and the [CoPMe$_2$Ph]$^+$ fragment (m/z = 197, relative intensity 20%). In this case, the [FePMe$_2$Ph]$^+$ fragment is not observed. These

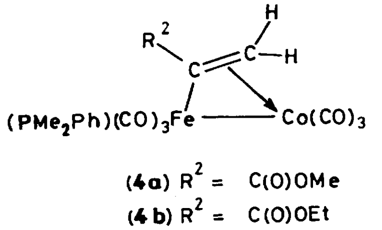


Figure 2. Proposed structure for complexes (**4a**) and (**4b**)

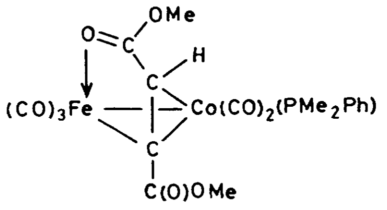


Figure 3. Proposed structure for complex (**5**)

observations suggest that the PMe_2Ph ligand is bonded to iron in (**4a**) and (**4b**) and to cobalt in (**5**). The ^{31}P n.m.r. spectra of complexes (**4a**) and (**5**) confirm this hypothesis, assuming that the broad signal for (**5**) is characteristic of phosphorus atoms attached to cobalt. The proposed structures shown in Figures 2 and 3 agree with spectroscopic data. We propose that the PMe_2Ph ligand is *trans* to the metal–metal bond, a situation generally observed in substitution reactions of dinuclear complexes with metal–metal bonds.[11] The selectivity in the metal for substitution reactions of a carbonyl group could be due to the presence of electron-withdrawing groups on the σ-bonded carbon of the ethenyl bridge. This effect favours the presence of the phosphine bonded to iron in (**4a**) and (**4b**). However, when one ester group is bonded to iron *via* an oxygen atom, the phosphine is co-ordinated to cobalt [complex (**5**)]. The increase of electron density on iron prevents the substitution of one CO by the more basic PMe_2Ph ligand.

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