Formation of [FeM(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CR=CR'H)] (M = Fe or Ru) Complexes from the Reaction of [MH(η-C_5H_5)(CO)$_2$] with [$Fe_2(CO)_9$] and Acetylenes. *X*-Ray Structure of [FeRu(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CPhH)]†

Ramon Yáñez, Josep Ros,* and Isabel Moldes
Departament de Química A-10, Universitat Autónoma de Barcelona, Bellaterra, 08193 Barcelona, Spain
René Mathieu*
Laboratoire de Chimie de Coordination de C.N.R.S., Unité 8421 liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31077 Toulouse, France
Xavier Solans and Mercé Font-Bardía
Departament de Cristal. lografía i Mineralogía, Universitat de Barcelona, c/Martí i Franqués s/n, 08028-Barcelona, Spain

The complexes [MH(η-C_5H_5)(CO)$_2$] (M = Fe or Ru) react with an equimolar [$Fe_2(CO)_9$]–acetylene mixture in tetrahydrofuran affording [FeM(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CR=CR'H)] [M = Fe, R = R' = Ph, (**1**), or H, (**2**); R = Ph, R' = H (**3**); R = H, R' = Bu^t, (**4**); M = Ru, R = R' = Ph (**5**); R = SiMe$_3$, R' = H (**6**)]. The structure of (**5**) was established by single-crystal *X*-ray crystallography. It crystallizes in the space group $P2_1/n$ with $Z = 4$ and $a = 14.863(4)$, $b = 14.542(4)$, $c = 10.186(3)$ Å, and $\beta = 97.09(3)$°. The structure was solved by direct methods and refined by least squares to a final *R* of 0.067. It consists of Ru(C_5H_5)(CO) and Fe(CO)$_3$ fragments linked by CO and 1,2-diphenylethenyl bridges and a metal–metal bond. A possible mechanism for the formation of the complexes is proposed on the basis of the activation of the acetylenes by [$Fe_2(CO)_9$] and subsequent insertion into the M–H (M = Fe or Ru) bond.

Unsaturated organic molecules insert into metal–hydrogen bonds producing key intermediates in several homogeneous catalytic processes.[1] Acetylenes are very reactive toward the M–H bond leading to alkenyl ligands the chemistry of which is being extensively studied by our group.[2] In many complexes alkenyl ligands act as very strong bridges, supporting the molecular structure.[3] Some times the μ,η^2-alkenyl ligand undergoes transformation to alkylidene,[4] alkylidyne,[5] or allyl[6] bridging ligands which are models for C–C bond formation in heterogeneous catalytic systems.

We studied the reactivity of [$Fe_2(CO)_6$(μ-CO)(μ-CR=CR'H)]$^-$ complexes with electrophilic reagents[7] and acetylenes[8] and showed numerous C–C bond-formation reactions. We developed also a new method of synthesis of anionic vinyl-bridged di-iron complexes based on alkyne activation by [$Fe_2(CO)_9$] in tetrahydrofuran (thf) and subsequent reaction with [FeH(CO)$_4$]$^-$.[9] An extension of this reaction with other hydrides was then undertaken. We now describe the formation of vinyl-bridged, metal–metal bonded dinuclear complexes [FeM(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CR=CR'H)] from [MH(η-C_5H_5)(CO)$_2$] (M = Fe or Ru), [$Fe_2(CO)_9$], and acetylenes in thf solution. The complexes were formulated on the basis of i.r. and n.m.r. spectroscopy, elemental analyses, and an *X*-ray diffraction study of [FeRu(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CPhH)]. Previously, Nesmeyanov *et al.*[10] synthesized some complexes of the same type from the reaction of σ-vinyl derivatives with [$Fe_2(CO)_9$].

Results and Discussion

The reaction of [MH(η-C_5H_5)(CO)$_2$] (M = Fe or Ru) dissolved in hexane with a thf solution containing a 1:1 mixture of RC≡CR' and [$Fe_2(CO)_9$] at room temperature produces crystalline complexes [FeM(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CR=CR'H)] [M = Fe, R = R' = Ph, (**1**), or H, (**2**); R = Ph, R' = H, (**3**); R = H, R' = Bu^t, (**4**); M = Ru, R = R' = Ph, (**5**); R = SiMe$_3$, R' = H, (**6**)]. The products are very soluble in dichloromethane and non-polar solvents but insoluble in alcohols allowing slow crystallizations for dichloromethane–alcohol mixtures. Elemental analyses, spectroscopic data, and an *X*-ray diffraction study confirmed the dinuclear metal–metal bonded structure with CO and alkenyl bridges. The i.r. spectra in the ν(CO) region show similar patterns for all complexes with strong terminal CO absorptions and a band at *ca.* 1 815 cm^{-1} corresponding to a bridging CO. The ^{1}H n.m.r. spectra exhibit one signal for the C_5H_5 group and signals of the vinylic protons. The chemical shifts of the alkenylic protons in the complexes are significantly different from those in other alkenyl-bridged di-iron complexes.[11,12] Therefore the inductive effect of the C_5H_5 ligand seems to induce an upfield shift of the =CHR and a downfield shift of the CH= hydrogens. A similar effect has been observed in σ-CH=CHR complexes of ruthenium(II), when a donor ligand is co-ordinated to the metal[13] and when R is an electron-withdrawing group.[14] In these complexes the displacement of charge in the alkenyl ligand produces a significant shift of the signals of protons in the ^{1}H n.m.r. spectra. The spectra of complexes (**3**), (**4**), and (**6**) reveal two types of terminal alkenyl ligands: those with geminal hydrogens in (**3**) and (**6**), and a *trans* disposition of hydrogens for (**4**). The ligand geometry can be deduced from the coupling constans: *J*(H–H)

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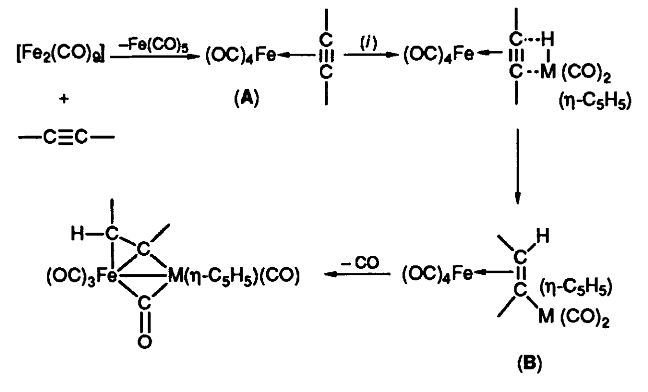
† μ-Carbonyl-tetracarbonyl-1κC,2$\kappa^3 C$-[1(η^5)-cyclopentadienyl][μ-1,2-diphenyl-1$\kappa C'$:2(η^2)-ethenyl]ironruthenium (*Fe–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) $[MH(\eta\text{-}C_5H_5)(CO)_2]$ (M = Fe or Ru)

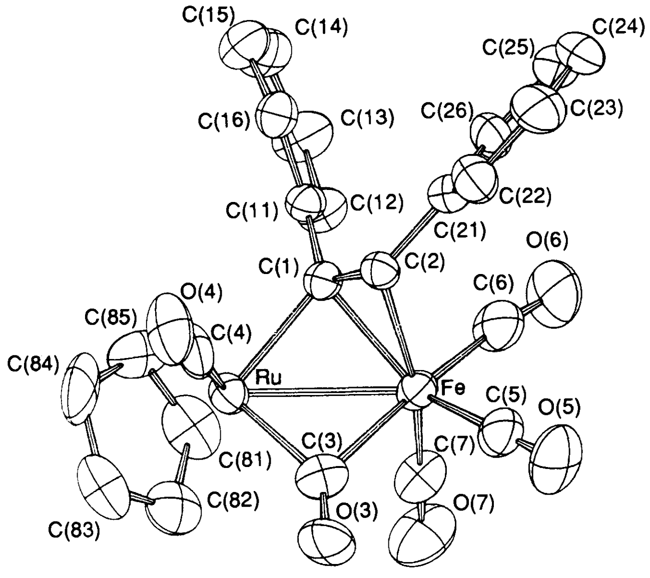


Figure. Structure of $[FeRu(\eta\text{-}C_5H_5)(CO)_4(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ (**5**) showing the atomic numbering scheme

(geminal) = 1.8 Hz for complex (**6**) and J(H-H) (*trans*) = 12 Hz for complex (**4**). For complex (**3**) the coupling was too small to be resolved. From these results it appears that the geometry of the alkenyl bridging ligand in the complexes is not dependent on the bulk of the substituents. Possibly, π interactions of $SiMe_3$ and Ph groups with the π system of the organic ligand may induce the formation of alkenyl bridges with geminal hydrogens.

The experimental results allow us to postulate the mechanism presented in the Scheme. The $[Fe_2(CO)_9]$–acetylene mixture in thf induces the formation of the $[Fe(CO)_4(\eta^2\text{-}RC{\equiv}CR)]$ intermediate (**A**). This type of complex has been isolated by Carty *et al.*[15] and recently by Takats and co-workers[16] and there is spectroscopic evidence of an increase in the olefinic character of the η^2-alkyne.[17] After co-ordination the η^2-alkyne is activated and inserts into the M–H bond giving rise to intermediate (**B**) in which the vinyl ligand is σ bonded to a $M(\eta\text{-}C_5H_5)(CO)_2$ fragment and π bonded to a $Fe(CO)_4$ group. Complexes of the type (**B**) have been synthesized by Nesmeyanov *et al.*[10] in a general study of the reactivity of σ-alkenyl derivatives of Fe, W, and Re which were transformed into μ,η^2-alkenyl metal–metal bonded compounds similar to those described in this work. The stereochemistry of the insertion of alkynes into the M–H bond is certainly affected by the bulk and donor–acceptor character of the substituents. From our results it seems that, probably, some π interactions between the substituents and the alkenyl group predominate over steric effects. The loss of one molecule of CO transforms (**B**) into products containing a metal–metal bond, with migration of a terminal to a bridging carbonyl in the way described by Nesmeyanov *et al.*[10]

Table 1. Selected bond distances (Å) and angles (°) for $[FeRu(\eta\text{-}C_5H_5)(CO)_4(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ (**5**)

Fe–Ru	2.648(1)	C(1)–Ru	2.082(9)
C(3)–Ru	1.98(1)	C(4)–Ru	1.89(1)
C(81)–Ru	2.25(1)	C(82)–Ru	2.28(1)
C(83)–Ru	2.331(9)	C(84)–Ru	2.34(1)
C(85)–Ru	2.23(1)	C(1)–Fe	2.036(9)
C(2)–Fe	2.164(8)	C(3)–Fe	2.09(1)
C(5)–Fe	1.79(1)	C(6)–Fe	1.80(1)
C(7)–Fe	1.75(1)	C(2)–C(1)	1.40(1)
O(3)–C(3)	1.15(1)	O(4)–C(4)	1.09(1)
O(5)–C(5)	1.13(1)	O(6)–C(6)	1.13(1)
O(7)–C(7)	1.17(1)		
C(3)–Ru–C(1)	92.3(4)	C(4)–Ru–C(1)	85.9(4)
C(4)–Ru–C(3)	86.3(5)	C(2)–Fe–C(1)	38.9(3)
C(3)–Fe–C(1)	90.6(4)	C(3)–Fe–C(2)	91.2(4)
C(5)–Fe–C(1)	130.2(4)	C(5)–Fe–C(2)	91.7(4)
C(5)–Fe–C(3)	83.7(4)	C(6)–Fe–C(1)	93.0(4)
C(6)–Fe–C(2)	94.9(5)	C(6)–Fe–C(5)	97.9(5)
C(2)–C(1)–Fe	75.5(5)	C(11)–C(1)–C(2)	122.7(8)
C(1)–C(2)–Fe	65.6(5)	C(21)–C(2)–Fe	122.0(6)
C(21)–C(2)–C(1)	127.2(8)	Fe–C(3)–Ru	81.1(4)
O(3)–C(3)–Ru	141.9(9)	O(3)–C(3)–Fe	136.9(9)
O(4)–C(4)–Ru	175.6(9)	O(5)–C(5)–Fe	178.9(10)
O(6)–C(6)–Fe	173.2(10)	O(7)–C(7)–Fe	179.1(11)
C(12)–C(11)–C(1)	123.4(8)	C(7)–Fe–C(1)	126.0(4)
C(7)–Fe–C(2)	164.9(4)	C(7)–Fe–C(3)	87.8(5)
C(7)–Fe–C(5)	103.2(5)	C(7)–Fe–C(6)	85.8(5)
Fe–C(1)–Ru	80.0(3)	C(2)–C(1)–Ru	115.5(6)

Structure of Complex (**5**).—The molecular structure of complex (**5**) consists of discrete $[FeRu(\eta\text{-}C_5H_5)(CO)_4(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ units linked by van der Waals forces. A view of the molecule with the atomic numbering scheme is shown in the Figure. Relevant bond distances and angles are given in Table 1, atomic co-ordinates with standard deviations in Table 2. The structure contains $Ru(\eta\text{-}C_5H_5)(CO)$ and $Fe(CO)_3$ units bridged by CO and diphenylethenyl, with a metal–metal bond. The Ru–Fe distance of 2.648(1) Å is longer than Fe–Fe bonds in related di-iron complexes[7,18] but is in the range of Ru–Fe single bonds.[19] The C_5H_5 ligand is symmetrically bonded to Ru with a $Ru\text{–}C(C_5H_5)$ distance averaging 2.3 Å and is nearly *trans* to the Ru–C(1) bond. The diphenylethenyl ligand is σ bonded to Ru [Ru–C(1) 2.082(9) Å] and π bonded to Fe [Fe–C(1) 2.036(9) and Fe–C(2) 2.164(8) Å]. The Ru–C(3) bond length [1.983(10) Å] involving the bridging CO ligand is shorter than the Fe–C(3) distance of 2.089(11) Å. This shortening appears to be induced by the donor ability of the C_5H_5 ligand co-ordinated to ruthenium. On the other hand the Fe–CO(terminal) bonds average 1.77 Å, less than the Ru–C(4) bond length of 1.890(11) Å. Some interesting features of the molecule are that C(1) is equidistant from the metals suggesting a carbenic character, and the cisoid disposition of phenyl groups on the alkenyl bridge (dihedral angle 16°).

Experimental

All reactions were performed under a nitrogen atmosphere using Schlenk techniques. Hydrogen-1 n.m.r. spectra were recorded on a Bruker AM 400 spectrometer in $CDCl_3$ solutions, i.r. spectra in the ν(CO) region on a Perkin-Elmer IR

Table 2. Fractional atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for [FeRu(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CPhH)] (**5**)

Atom	*X/a*	*Y/b*	*Z/c*
Ru	21 911(5)	21 670(5)	21 993(7)
Fe	15 291(8)	14 335(9)	−976(13)
C(1)	2 769(6)	2 004(6)	453(8)
C(2)	2 957(6)	1 094(6)	118(9)
C(3)	1 437(7)	1 048(7)	1 857(11)
O(3)	1 072(5)	485(5)	2 392(8)
C(4)	3 114(8)	1 370(8)	2 969(10)
O(4)	3 641(6)	930(6)	3 489(8)
C(5)	1 218(7)	265(9)	−449(10)
O(5)	1 013(6)	−469(5)	−690(9)
C(6)	1 492(7)	1 831(9)	−1 775(11)
O(6)	1 379(7)	2 062(7)	−2 838(9)
C(7)	484(7)	1 985(6)	−101(11)
O(7)	−218(6)	2 348(6)	−89(12)
C(81)	1 741(11)	2 803(9)	4 025(13)
C(82)	1 081(9)	3 005(8)	2 997(12)
C(83)	1 452(9)	3 584(7)	2 055(12)
C(84)	2 318(8)	3 769(7)	2 412(16)
C(85)	2 545(10)	3 274(11)	3 684(15)
C(11)	3 208(6)	2 800(6)	−91(9)
C(12)	2 718(7)	3 549(6)	−729(10)
C(13)	3 155(7)	4 291(8)	−1 192(12)
C(14)	4 106(8)	4 326(7)	−1 005(12)
C(15)	4 595(7)	3 627(7)	−361(11)
C(16)	4 133(7)	2 858(6)	88(10)
C(21)	3 420(6)	775(6)	−1 025(9)
C(22)	3 491(7)	1 285(7)	−2 161(9)
C(23)	3 934(7)	921(9)	−3 172(11)
C(24)	4 314(7)	44(9)	−3 069(12)
C(25)	4 249(7)	−427(8)	−1 958(13)
C(26)	3 804(7)	−96(8)	−946(11)

1710FT spectrometer in hexane solution. Elemental analyses (C and H) were performed on a Perkin-Elmer 240-B analyzer. The complexes [$Fe_2(CO)_9$],[20] [PPh_4][FeH(CO)$_4$],[21] [FeH(C_5H_5)(CO)$_2$],[22] and [RuH(C_5H_5)(CO)$_2$][23] were prepared by literature methods. Acetylenes were used as supplied. Tetrahydrofuran was used after distillation over sodium using benzophenone as indicator.

Preparation of Complexes [FeM(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CR=CR′H)], [M = Fe, R = R′ = Ph, (**1**); R = Ph, R′ = H, (**3**); R = H, R′ = Bu^t, (**4**); M = Ru, R = R′ = Ph (**5**); R = SiMe$_3$, R′ = H, (**6**)].—A solution of [MH(η-C_5H_5)(CO)$_2$] (M = Fe or Ru) (9 mmol dm^{-3}) in hexane was added to a mixture of stoicheiometric amounts (10 mmol dm^{-3}) of [$Fe_2(CO)_9$] and an acetylene in thf (20 cm^3) and stirred for 45 min at room temperature. The resulting solution was evaporated to dryness and the residue chromatographed on a silica column eluted with hexane–dichloromethane (5:1). Crystallization from a dichloromethane–methanol mixture at −20 °C gave green crystals of complexes (**1**), (**3**), and (**4**) and brown crystals of (**5**) and (**6**) in *ca.* 25% yield.

[Fe_2(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CPhH)] (**1**). I.r.: ν(CO) at 2 042vs, 1 986vs, 1 965s, and 1 816 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 6.9—6.6 (m, 10 H), 4.75 (s, 5 H), and 2.6 (s, 1 H) (Found: C, 58.05; H, 3.25. Calc. for $C_{24}H_{16}Fe_2O_5$: C, 57.95; H, 3.20%).

[Fe_2(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CH$_2$)] (**3**). I.r.: ν(CO) at 2 050vs, 1 997vs, 1 991vs, 1 968s, and 1 816s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.7—7.2 (m, 5 H), 4.84 (s, 5 H), 2.07 (s, 1 H), and 1.15 (s, 1 H) (Found: C, 51.45; H, 2.85. Calc. for $C_{18}H_{12}Fe_2O_5$: C, 51.40; H, 2.85%).

[Fe_2(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CH=CBu^{t}H)] (**4**). I.r.: ν(CO) at 2 041vs, 1 988vs, 1 978vs, 1 967s, and 1 808 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 10.18 (d, *J* 12, 1 H), 5.02 (s, 5 H), 2.64 (d, *J* 12 Hz, 1 H), and 0.97 (s, 9 H) (Found: C, 49.50; H, 3.90. Calc. for $C_{17}H_{16}Fe_2O_5$: C, 49.55; H, 3.85%).

[FeRu(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CPh=CPhH)] (**5**). I.r.: ν(CO) at 2 035vs, 1 980vs, 1 960s, and 1 810s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 6.95 (m, 10 H), 5.16 (s, 5 H), and 2.98 (s, 1 H) (Found: C, 53.25; H, 2.95. Calc. for $C_{24}H_{16}FeO_5Ru$: C, 53.20; H, 2.90%).

[FeRu(η-C_5H_5)(CO)$_4$(μ-CO)(μ-CSiMe$_3$=CH$_2$)] (**6**). I.r.: ν(CO) at 2 035vs, 1 978vs, 1 955s, and 1 810s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): 5.40 (s, 5 H), 2.62 (d, *J* 1.8, 1 H), 1.83 (d, *J* 1.8 Hz, 1 H), and 0.33 (s, 9 H) (Found: C, 39.05; H, 3.45. Calc. for $C_{15}H_{16}FeO_5RuSi$: C, 39.15; H, 3.40%).

Preparation of Complex (**2**).—To a suspension of [$Fe_2(CO)_9$] (10 mmol dm^{-3}) in thf (20 cm^3) was added a solution of [FeH(η-C_5H_5)(CO)$_2$] (9 mmol dm^{-3}) in hexane. Acetylene gas was bubbled slowly into the solution at room temperature. After 1 h the solution was evaporated to dryness and the residue chromatographed on a silica column. Elution with hexane–dichloromethane (5:1) gave successively (**2**) and [Fe_2(η-C_5H_5)(CO)$_4$]. Crystallization from a dichloromethane–methanol mixture at −20 °C gave green crystals of (**2**) in *ca.* 10% yield. Spectroscopic data were consistent with those in the literature.[10]

Crystallography.—*Crystal data.* $C_{24}H_{16}FeO_5Ru$, (**5**), M = 541.31, monoclinic, space group $P2_1/n$, a = 14.863(4), b = 14.542(4), c = 10.186(3) Å, β = 97.09(3)°, U = 2 185(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.645 g cm^{-3}, $F(000)$ = 1 080.0, brown crystals, 0.1 × 0.1 × 0.2 mm, μ(Mo-K_α) = 13.9 cm^{-1}, 298 K.

Data collection and processing. Philips PW-1100 diffractometer, ω-scan technique with scan width 0.8°, scan speed 0.03° s^{-1}, graphite-monochromated Mo-K_α radiation; 3 327 independent reflections measured ($2 \leqslant \theta \leqslant 25°$), 2 803 of which [$I \geqslant 2.5\sigma(I)$] were assumed as observed. Significant intensity decay was not observed. Lorentz-polarization, but not absorption, corrections were made.

Structure analysis and refinement. Direct methods (MULTAN[24] system of programs). Full-matrix least-squares refinement, isotropic and anisotropic (SHELX 76).[25] The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, where $w = [\sigma^2(F_o) + 0.021|F_o|^2]^{-1}$. Final R and R' values 0.067 and 0.077.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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