repulsions, and this complex readily rearranges under vacuum to the π-complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$.[16] The latter complex also contains a labile σ-bonded ligand that is substituted by dinitrogen.[7a] A parallel sequence of reactions (Scheme I) for the bulkier triphenylphosphine system could explain the formation of compound 1.

The recent discovery that two molybdenum(0) centers are required to reduce one dinitrogen ligand to ammonia[1c,17] makes the protonation reactions of binuclear dinitrogen complexes of which 1 is a rare example[18,19] of special interest. We are currently trying to make soluble binuclear dinitrogen complexes starting from 1 in order to investigate their reactions with strong acids.

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Note Added in Proof. We recently discovered that complex 1, when still damp with toluene after being filtered from its mother liquor, is soluble enough in tetrahydrofuran to obtain its ^{31}P NMR spectrum at 81 MHz: δ 62.4 (A), 48.0 (B) (AB pattern, J_{AB} = 28 Hz). This spectrum is consistent with the *rac* structure proposed for 1.

Registry No. 1, 89773-11-5; 4a, 89746-31-6; 4b, 89746-32-7.

Supplementary Material Available: Tables of calculated hydrogen atom positions (Table IV), bond lengths and bond angles in the phenyl rings (Table V), inter- and intraligand contacts within van der Waals' distances (Table VI), and final thermal parameters (Table VII) and a listing of structure factor amplitudes (Table VIII) (45 pages). Ordering information is given on any current masthead page.

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Study of the Reactivity of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)]^-$ toward the $CH_3OC(O)C{\equiv}CC(O)OCH_3$ and $CF_3C{\equiv}CCF_3$ Alkynes. Crystal Structure of the Products Resulting from Two Different Modes of Combination of the Alkynes with the Bridging Ligands $[Fe_2(CO)_6(\mu\text{-}C(C(O)OCH_3)C(C(O)OCH_3)C(O)C(C_6H_5)C(C_6H_5)H)]^-$ and $[Fe_2(CO)_6(\mu\text{-}C(C_6H_5)C(C_6H_5)C(CF_3)C(CF_3)H)]^-$

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$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)]^-$ was reacted with $RC{\equiv}CR$ alkynes ($R = CH_3OC(O), CF_3$) affording $[Fe_2(CO)_6(\mu\text{-}C(R)C(R)C(O)C(C_6H_5)C(C_6H_5)H)]^-$ ($R = CH_3OC(O)$ (3), CF_3 (5)) and $[Fe_2(CO)_6(\mu\text{-}C(C_6H_5)C(C_6H_5)C(R)C(R)H)]^-$ ($R = CF_3$ (4)). The structure of 3 and 4 has been determined by single-crystal X-ray crystallography. Complex 3 crystallizes in the space group $P2_1/n$ with $Z = 4$ and lattice constants a = 17.244 (6) Å, b = 23.419 (7) Å, c = 12.218 (5) Å, and β = 94.31 (4)°. This product results from the double insertion of carbon monoxide and alkyne into the Fe–C bond of the ethenyl ligand. Furthermore, the oxygen of the acyl group is bonded to a Fe atom. Complex 4 crystallizes in the space group $P\bar{1}$ with $Z = 2$ and lattice constants a = 15.397 (5) Å, b = 14.495 (4) Å, c = 11.258 (4) Å, α = 107.35 (3)°, β = 96.92 (2)°, and γ = 110.85 (3)°. This product results from the insertion of the alkyne into the carbon–hydrogen bond of the ethenyl ligand. Furthermore, the $C(CF_3)C(CF_3)H$ fragment of the organic part of the molecule is μ-η^1 bonded to the two iron atoms. A possible mechanism for the two types of insertion observed is proposed.

Introduction

The study of the reactivity of organic molecules linked to dinuclear metal centers is presently an extensive field of interest.[3,4] In a recent publication[5] we have shown that the anion $[HFe_3(CO)_{11}]^-$ reacts with diphenylacetylene at 60 °C giving two products: one in which the trinuclear iron

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unit is preserved ($[HFe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5))]^-$, **1**) and the other which is dinuclear ($[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)]^-$, **2**). The latter, according to the presence of the bridging 1,2-diphenylethenyl ligand, seems to be a good candidate for the study of its reactivity toward unsaturated organic molecules. This is why we have checked as an initial approach its reactivity toward the activated alkynes $CH_3OC(O)C{\equiv}CC(O)OCH_3$ and $CF_3{\equiv}CCF_3$. Unexpectedly, two types of products have been isolated depending on the nature of the alkyne. The first product is the result of the double insertion of the alkyne and carbon monoxide into the iron–carbon bond of **2**. The second, only obtained with hexafluorobutyne, appears as the result of the insertion of the alkyne into the CH bond of the 1,2-diphenylethenyl bridge and of the loss of one molecule of carbon monoxide. Furthermore, the $C(CF_3)\text{-}C(CF_3)H$ end of the organic ligand shows an unusual mode of bonding ($\mu\text{-}\eta^1$). This paper relates to the synthesis and structure of these two types of complexes.

Experimental Section

All reactions were performed under nitrogen atmosphere. ^1H NMR spectra were recorded on a Perkin-Elmer R12 or on a Bruker WH90 spectrometer and ^{13}C NMR spectra on a Bruker WM 250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer in dichloromethane solutions in the $\nu(CO)$ stretching region. $HFe_3(CO)_{11}P(C_6H_5)_4$ was prepared by published procedures.[6] Elemental analyses were performed by the Service Central de Microanalyse du CNRS and by Miss Magna in our laboratory.

Preparation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H))][P(C_6H_5)_4]$, 2. $[HFe_3(CO)_{11}][P(C_6H_5)_4]$ (1 g) and diphenylacetylene (0.2 g) were dissolved in acetone and refluxed overnight. At the end of the reaction, the acetone solution was evaporated to dryness and the residue was dissolved in a 1:1 mixture of dichloromethane/diethyl ether. The solution was cooled to −20 °C, giving 0.430 g of $[HFe_3(CO)_9(C_6H_5CCC_6H_5)][P(C_6H_5)_4]$, **1**.[5] To the supernatant was added an equal amount of diethyl ether, and the solution was cooled to −20 °C, giving 0.320 g of red crystals of **2** (32%): mp 108 °C dec; IR $\nu(CO)$ 2024 (s), 1976 (vs), 1930 (s), 1742 cm^{-1} (m); ^1H NMR ($(CD_3)_2CO$) 8–7.60 (phenyl resonances), 3.48 ppm (CH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) except C_6H_5 resonances 219.4 (CO), 167.1 ($Fe\mathit{C}(C_6H_5)$), 75.6 ppm ($\mathit{C}(H)(C_6H_5)$). Anal. Calcd for $C_{45}H_{21}Fe_2O_7P$: C, 64.63; H, 3.62. Found: C, 64.75; H, 3.70.

Preparation of $[Fe_2(CO)_6(\mu\text{-}C(C(O)OCH_3)C(C(O)OCH_3)\text{-}C(O)C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$, 3. To **2** (0.5 g) in dichloromethane was added dimethyl acetylenedicarboxylate (75 μL, 1 equiv), and the solution was stirred for 1 h at room temperature. The solution was evaporated to dryness, and the residue was dissolved in a small amount of dichloromethane, and methanol was added. Cooling at −20 °C gave 0.350 g of **3** (59.7%) as brown crystals: mp 110 °C dec; IR $\nu(CO)$ 2042 (s), 1975 (vs), 1955 (sh), 190 cm^{-1} (m); ^1H NMR ($(CD_3)_2CO$) 8–7 ($P(C_6H_5)_4 + C_6H_5$), 6.28 (CH), 3.72 (OCH_3), 3.25 ppm (OCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 223.2, 210.6, 180.4, 168.4, 153.3, 144.1, 140.4, 136.3, 136, 134.8, 134.6, 131.0, 130.8, 129.3, 129, 128.6, 128.2, 127.8, 127.3, 127.2, 126.8, 126.3, 124, 118.5, 117.1, 70.7, 51.5, 50.9 ppm. Anal. Calcd for $C_{51}H_{37}Fe_2O_{11}P$: C, 63.22; H, 3.82. Found: C, 63.04; H, 4.12.

Preparation of $[Fe_2(CO)_6(\mu\text{-}C(C_6H_5)C(C_6H_5)C(CF_3)C\text{-}(CF_3)H)][P(C_6H_5)_4]$, 4, and $[Fe_2(CO)_6(\mu\text{-}C(CF_3)C(CF_3)C(O)\text{-}C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$, 5. From a vacuum line a stoichiometric amount of hexafluorobutyne was added to 0.5 g of **2** in dichloromethane in a vessel fitted with a Teflon stopcock. The solution was stirred for 15 h at room temperature. At the end of the reaction the solution was treated in the same manner as for **3**. Cooling at −20 °C gave 0.18 g of **4** (37.5%) as yellow crystals: mp 85 °C dec; IR $\nu(CO)$ 2038 (s), 1990 (vs), 1960 (s), 1945 (sh), 1930 cm^{-1} (sh); ^1H NMR ((CD_2Cl_2) 8–7 (C_6H_5)) 1.93 (qt, C(H)CF, J_{FH} = 13.5 Hz); ^{19}F NMR (($(CD_3)_2CO$)(ref $CFCl_3$) −64 (br), −66.7 ppm, (qt, J_{FF} = 9.7 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 216, 211.8, 175.2, 152.5, 139.6, 136, 134.8, 134.6, 131, 130.8, 129.1, 126.7, 125.8, 123.9, 118.4, 117, 111.4, 60 ppm (qt, J_{CF} = 27 Hz), 29.9 (qt, J_{CF} = 27.7 Hz). Anal. Calcd for $C_{48}H_{31}F_6Fe_2O_6P$: C, 60.00; H, 3.23. Found: C, 60.06; H, 3.16. Concentration of the mother solution and cooling at −20 °C gave brown crystals of **5**: 0.15 g (25%); mp 108 °C dec; IR $\nu(CO)$ 2045 (s), 1980 (vs), 1960 (sh), 1908 cm^{-1} (m); ^1H NMR (CD_2Cl_2) 8–7 (C_6H_5), 6.64 ppm (CH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 221.1, 217.6, 213.1, 210.3, 201.3, 142.1 (qt, J_{CF} = 37 Hz) 139.8, 136.3, 135, 134.7, 131, 130.8, 129, 128.2, 127.8, 127.2, 126.8, 126, 124, 118.4, 117.2, 69.8 ppm (qt, J_{CF} = 37 Hz). Anal. Calcd for $C_{49}H_{31}F_6Fe_2O_7P$: C, 59.51; H, 3.13. Found: C, 59.80; H, 3.12.

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Studies of 3 and 4

	3	4
formula	$C_{21}H_{17}O_4Fe_2\cdot(C_6H_5)_4P\cdot{}^1/_2H_2CCl_2$	$C_{24}H_{11}F_6O_6\text{-}Fe_2\cdot P(C_6H_5)_4$
system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	17.244 (6)	15.397 (5)
b, Å	23.419 (7)	14.495 (4)
c, Å	12.218 (5)	11.258 (4)
α, deg		107.35 (3)
β, deg	94.31 (4)	96.92 (2)°
γ, deg		110.85 (3)
V Å^3	4920 (5)	2168 (2)
D(calcd), g·cm^{-3}	1.12	1.21
Z	4	2
F(000)	1708	808
λ (Mo Kα), Å	0.710 69	0.710 69
μ (Mo Kα), cm^{-1}	7.30	7.75
intensity measurement:		
technique	ω scan	
scan width, deg	from −1 to +1	
scan speed, deg·s^{-1}	0.03	
scan range, deg	$2 < \theta < 25$	
measd intensities	3293	3572
obsd intensities ($I > 2.5\sigma(I)$)	3196	3475
R	0.080	0.075
R_w	0.090	0.077

Crystallographic Studies. Complex $3\cdot0.5CH_2Cl_2$. A small crystal grown from a dichloromethane/methanol solution was selected for intensity measurements on a Philips PW-1100 four-circle diffractometer. The unit cell was measured by automatic centering of 25 independent reflections and refining the orientation matrix by least squares. Intensities were collected with Mo Kα radiation monochromatized by reflection from a graphite crystal. Lorentz polarization but not absorption corrections were made. Full details on data collection and reduction are given in Table I. The structure was solved by direct methods with the MULTAN system of computer programs.[7] An E map computed from the set with the highest combined figure of merit revealed peaks for 52 non-hydrogen atoms that were refined isotropically by full-matrix least-squares method with the SHELX 76 computer program.[8] A difference synthesis revealed the position of three peaks, which were identified as 0.5 molecule of dichloromethane from a Fourier synthesis. New isotropic and anisotropic refinements lead to the final value of R = 0.080 for all observed reflections. The function minimized was $w\|F_o - |F_c|\|^2$, where $w = (\sigma^2(F_o) + 0.00067|F_o|^2)^{-1}$. Final atomic coordinates and temperature coefficients are given in Table II.

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Table II. Final Least-Squares Coordinates with Estimated Standard Deviation for $[Fe_2(CO)_6(\mu\text{-}C(C(O)OCH_3)C(C(O)OCH_3)C(O)C(C_6H_5)C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Fe(1)	3035 (1)	1868 (1)	2489 (2)	O(32)	1352 (7)	125 (5)	3363 (11)
Fe(2)	1725 (1)	1546 (1)	1491 (2)	O(33)	1707 (7)	123 (5)	1646 (10)
O(1)	2534 (6)	1658 (5)	3848 (9)	C(34)	1337 (14)	−456 (8)	1486 (19)
C(2)	2109 (9)	1228 (8)	3745 (13)	O(51)	3314 (7)	764 (5)	480 (12)
C(3)	2093 (8)	911 (7)	2705 (13)	O(52)	3341 (7)	271 (5)	2039 (10)
C(4)	2659 (9)	1114 (7)	1956 (13)	C(53)	3772 (11)	−217 (9)	1471 (16)
C(5)	3092 (9)	719 (7)	1370 (15)	C	5497 (25)	3112 (19)	2331 (38)
C(11)	3993 (13)	1694 (9)	3107 (18)	Cl	708 (8)	2429 (6)	6838 (12)
O(11)	4599 (9)	1546 (8)	3452 (14)	Cl′	−14 (6)	1843 (4)	8401 (9)
C(12)	2970 (13)	2581 (9)	2837 (20)	P	2510 (3)	3749 (2)	7202 (4)
O(12)	2900 (10)	3069 (8)	3086 (15)	C(101)	3097 (6)	4366 (4)	6933 (9)
C(13)	3404 (11)	2010 (8)	1267 (16)	C(102)	2808 (6)	4808 (4)	6252 (9)
O(13)	3665 (8)	2122 (6)	423 (13)	C(103)	3272 (6)	5282 (4)	6074 (9)
C(14)	1946 (10)	1679 (7)	184 (17)	C(104)	4025 (6)	5314 (4)	6576 (9)
O(14)	2077 (8)	1756 (6)	−772 (12)	C(105)	4313 (6)	4873 (4)	7257 (9)
C(15)	828 (12)	1240 (8)	1053 (15)	C(106)	3849 (6)	4399 (4)	7435 (9)
O(15)	250 (8)	1004 (7)	712 (12)	C(111)	1667 (6)	3731 (5)	6274 (9)
C(16)	1378 (10)	2208 (8)	1971 (15)	C(112)	1672 (6)	3422 (5)	5299 (9)
O(16)	1094 (9)	2629 (6)	2194 (10)	C(113)	999 (6)	3387 (5)	4593 (9)
C(21)	1710 (10)	1033 (7)	4736 (14)	C(114)	321 (6)	3663 (5)	4862 (9)
C(211)	832 (5)	1146 (5)	4678 (9)	C(115)	316 (6)	3972 (5)	5837 (9)
C(212)	346 (5)	772 (5)	5196 (9)	C(116)	989 (6)	4006 (5)	6543 (9)
C(213)	−428 (5)	919 (5)	5305 (9)	C(121)	2184 (7)	3782 (5)	8558 (7)
C(214)	−717 (5)	1440 (5)	4896 (9)	C(122)	1644 (7)	3382 (5)	8868 (7)
C(215)	−232 (5)	1813 (5)	4378 (9)	C(123)	1404 (7)	3386 (5)	9933 (7)
C(216)	543 (5)	1666 (5)	4269 (9)	C(124)	1703 (7)	3792 (5)	10687 (7)
C(22)	2064 (10)	838 (7)	5637 (17)	C(125)	2242 (7)	4193 (5)	10376 (7)
C(221)	2940 (6)	722 (5)	5842 (11)	C(126)	2483 (7)	4189 (5)	9312 (7)
C(222)	3444 (6)	641 (5)	5015 (11)	C(131)	3087 (6)	3125 (4)	7013 (9)
C(223)	4224 (6)	508 (5)	5287 (11)	C(132)	3575 (6)	3118 (4)	6152 (9)
C(224)	4498 (6)	456 (5)	6386 (11)	C(133)	3995 (6)	2627 (4)	5939 (9)
C(225)	3994 (6)	537 (5)	7213 (11)	C(134)	3928 (6)	2142 (4)	6587 (9)
C(226)	3215 (6)	670 (5)	6941 (11)	C(135)	3440 (6)	2148 (4)	7448 (9)
C(31)	1666 (10)	356 (8)	2621 (17)	C(136)	3020 (6)	2639 (4)	7661 (9)

Table III. Final Least-Squares Coordinates with Estimated Standard Deviation for $[Fe_2(CO)_6(\mu\text{-}C(C_6H_5)C(C_6H_5)C(CF_3)C(CF_3)H)][P(C_6H_5)_4]$

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Fe(1)	7984 (1)	3186 (1)	5315 (2)	O(63)	8817 (8)	5252 (7)	5111 (11)
Fe(2)	6220 (1)	2448 (1)	4015 (2)	C(71)	6044 (8)	1651 (11)	2394 (14)
C(2)	6226 (7)	1273 (7)	4733 (11)	O(71)	5911 (6)	1174 (8)	1301 (10)
C(3)	7151 (7)	1869 (8)	5696 (12)	C(72)	5018 (8)	2194 (8)	4091 (12)
C(4)	7198 (7)	2869 (7)	6632 (12)	O(72)	4255 (6)	2061 (7)	4145 (9)
C(5)	6793 (7)	3326 (7)	5875 (11)	C(73)	6359 (9)	3504 (8)	3492 (15)
C(21)	6039 (9)	220 (9)	3682 (14)	O(73)	6396 (8)	4144 (8)	3083 (12)
F(22)	6696 (5)	232 (4)	2988 (7)	P	8625 (2)	−1305 (2)	1298 (3)
F(23)	5184 (5)	−201 (5)	2837 (7)	C(101)	9143 (4)	−2006 (4)	221 (7)
C(24)	6004 (5)	−528 (4)	4196 (7)	C(102)	9759 (4)	−2387 (4)	716 (7)
C(31)	7630 (10)	1290 (10)	6248 (14)	C(103)	10179 (4)	−2930 (4)	−95 (7)
F(32)	7918 (5)	706 (5)	5336 (7)	C(104)	9982 (4)	−3092 (4)	−1401 (7)
F(33)	8414 (5)	1910 (5)	7214 (7)	C(105)	9366 (4)	−2711 (4)	−1897 (7)
F(34)	7048 (6)	611 (6)	6685 (8)	C(106)	8946 (4)	−2168 (4)	−1085 (7)
C(41)	7509 (6)	3268 (7)	8061 (8)	C(111)	7870 (4)	−2175 (5)	1961 (7)
C(42)	8256 (6)	4264 (7)	8749 (8)	C(112)	7408 (4)	−1788 (5)	2850 (7)
C(43)	8525 (6)	4641 (7)	10091 (8)	C(113)	6810 (4)	−2462 (5)	3357 (7)
C(44)	8045 (6)	4020 (7)	10743 (8)	C(114)	6674 (4)	−3522 (5)	2974 (7)
C(45)	7298 (6)	3024 (7)	10055 (8)	C(115)	7137 (4)	−3909 (5)	2084 (7)
C(46)	7029 (6)	2648 (7)	8714 (8)	C(116)	7735 (4)	−3235 (5)	1578 (7)
C(51)	6578 (6)	4261 (5)	6577 (8)	C(121)	7892 (4)	−881 (5)	458 (6)
C(52)	6027 (6)	4154 (5)	7465 (8)	C(122)	6902 (4)	−1485 (5)	30 (6)
C(53)	5746 (6)	4957 (5)	8049 (8)	C(123)	6320 (4)	−1158 (5)	−638 (6)
C(54)	6015 (6)	5867 (5)	7744 (8)	C(124)	6729 (4)	−226 (5)	−878 (6)
C(55)	6566 (6)	5975 (5)	6856 (8)	C(125)	7720 (4)	378 (5)	−449 (6)
C(56)	6847 (6)	5171 (5)	6272 (8)	C(131)	9552 (4)	−152 (4)	2555 (6)
C(61)	8048 (7)	2497 (10)	3792 (15)	C(132)	10522 (4)	46 (4)	2697 (6)
O(61)	8192 (6)	2119 (7)	2789 (10)	C(133)	11219 (4)	948 (4)	3684 (6)
C(62)	9122 (9)	3471 (10)	6248 (13)	C(134)	10947 (4)	1653 (4)	4530 (6)
O(62)	9881 (6)	3691 (8)	6839 (10)	C(135)	9978 (4)	1456 (4)	4388 (6)
C(63)	8465 (9)	4449 (8)	5190 (15)	C(136)	9280 (4)	553 (4)	3400 (6)

Complex 4. A small crystal of the complex 4 was mounted on a Philips PW-1100 four-circle diffractometer. The procedure used for crystal structure determination and refinement was the same as for complex 3. A summary of the main crystallographie data is given in Table I. The final R factor was equal to 0.075 for all observed reflections. The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.000\,46|F_o|^2)^{-1}$. Final atomic coordinates and temperature coefficients are given in Table III.

Table IV. Selected Interatomic Distances (Å) and Bond Angles (deg) with Esd's for [$Fe_2(CO)_6(\mu$-$C(C(O)OCH_3)C(C(O)OCH_3)C(O)C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$, 3

Bond Distances					
Fe(1)-Fe(2)	2.596 (3)	C(2)-C(3)	1.47 (2)	C(16)-O(16)	1.14 (2)
Fe(1)-O(1)	1.99 (1)	C(2)-C(21)	1.51 (2)	C(21)-C(211)	1.53 (2)
Fe(1)-C(4)	1.97 (1)	C(3)-C(4)	1.47 (2)	C(21)-C(22)	1.30 (2)
Fe(1)-C(11)	1.81 (2)	C(3)-C(31)	1.49 (2)	C(31)-O(31)	1.22 (2)
Fe(1)-C(12)	1.73 (2)	C(4)-C(5)	1.42 (2)	C(31)-O(33)	1.32 (2)
Fe(1)-C(13)	1.70 (2)	C(5)-O(51)	1.18 (2)	O(33)-C(34)	1.50 (2)
Fe(2)-C(3)	2.16 (2)	C(5)-O(52)	1.38 (2)	O(52)-C(53)	1.55 (2)
Fe(2)-C(4)	1.95 (2)	C(11)-O(11)	1.15 (3)	P-C(101)	1.81 (1)
Fe(2)-C(14)	1.70 (2)	C(12)-O(12)	1.19 (3)	P-C(111)	1.78 (1)
Fe(2)-C(15)	1.75 (2)	C(13)-O(13)	1.18 (2)	P-C(121)	1.79 (1)
Fe(2)-C(16)	1.78 (2)	C(14)-O(14)	1.22 (3)	P-C(131)	1.79 (1)
O(1)-C(2)	1.25 (2)	C(15)-O(15)	1.19 (2)		
Bond Angles					
O(1)-Fe(1)-Fe(2)	84.5 (3)	C(5)-C(4)-C(3)	120 (1)	C(211)-C(21)-C(22)	126 (2)
C(4)-Fe(1)-Fe(2)	48.1 (5)	Fe(1)-C(4)-C(5)	125 (1)	O(32)-C(31)-C(3)	125 (2)
C(4)-Fe(2)-Fe(1)	49.0 (5)	C(4)-C(5)-O(51)	129 (2)	O(33)-C(31)-C(3)	111 (2)
O(1)-Fe(1)-C(4)	84.4 (6)	C(4)-C(5)-O(52)	111 (1)	O(33)-C(31)-O(32)	123 (2)
O(1)-Fe(1)-C(13)	175.0 (7)	O(51)-C(5)-O(52)	120 (1)	C(34)-O(33)-C(31)	116 (1)
Fe(1)-O(1)-C(2)	114 (1)	Fe(1)-C(11)-O(11)	175 (2)	C(53)-O(52)-C(5)	116 (1)
O(1)-C(2)-C(3)	118 (1)	Fe(1)-C(12)-O(12)	178 (2)	C(101)-P-C(111)	110.2 (5)
C(2)-C(3)-C(4)	114 (1)	Fe(1)-C(13)-O(13)	178 (2)	C(101)-P-C(121)	110.6 (5)
C(3)-C(4)-Fe(1)	108 (1)	Fe(2)-C(14)-O(14)	177 (1)	C(101)-P-C(131)	107.7 (5)
O(1)-C(2)-C(21)	118 (1)	Fe(2)-C(15)-O(15)	175 (2)	C(111)-P-C(121)	107.0 (5)
C(3)-C(2)-C(21)	124 (1)	Fe(2)-C(16)-O(16)	173 (2)	C(111)-P-C(131)	109.5 (6)
C(2)-C(3)-C(31)	118 (1)	C(22)-C(21)-C(2)	125 (1)	C(121)-P-C(131)	111.8 (6)
C(4)-C(3)-C(31)	126 (1)	C(211)-C(21)-C(2)	115 (1)		

Results and Discussion

The [$Fe_2(CO)_6(\mu$-$CO)(\mu$-$C(C_6H_5)C(C_6H_5)H)]^-$ anion reacts readily with the two alkynes at room temperature.

With dimethyl acetylenedicarboxylate, only one product 3 has been isolated, and infrared analysis in the ν(CO) stretching region of the mother solution after crystallization confirms that 3 is the sole product formed during the reaction. This product shows four infrared-active bands in the ν(CO) stretching region, and proton NMR gives evidence of the insertion of the alkyne by the appearance of two singlets characteristic of the OCH_3 groups. Furthermore, the CH resonance of the vinyl group moves from 3.48 ppm for 2 to 6.28 ppm, giving strong evidence of the change of bonding mode of this group. This is corroborated by the ^{13}C NMR spectrum in which the resonance for $CH(C_6H_5)$ detected at 75.6 ppm (J_{CH} = 150 Hz) for 2 has disappeared for 3 and is certainly obscured by the carbon phenyl resonances. The appearance of a new resonance non-hydrogen coupled at 70.7 ppm suggests an olefinic carbon bonded to a metal center.[9] The precise nature of 3 has been determined by X-ray analysis and shown to be the result of the double insertion of carbon monoxide and dimethyl acetylenedicarboxylate into the iron-carbon bond of the vinyl group (see below).

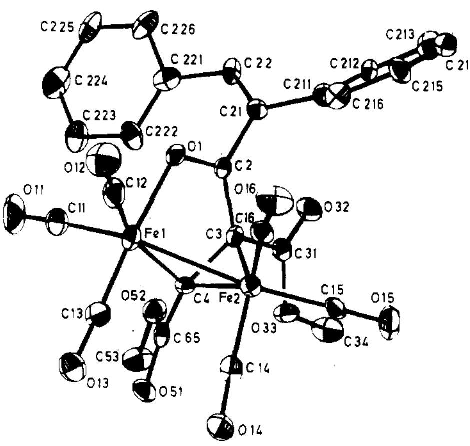

Figure 1. Molecular diagram and atom labeling scheme for 3.

In the case of hexafluorobutyne, two complexes have been isolated. For the first complex isolated, 4, the infrared spectrum in the ν(CO) stretching region is quite different from 3, showing five infrared-active bands. Proton NMR results corroborate the different nature of 4 as, except for the phenyl resonances, a quarted signal observed at 1.93 ppm (J = 13.5 Hz), suggesting a $C(CF_3)H$ group. ^{13}C NMR confirms the presence of this group by the appearance of a doublet of quartets centered at 29.9 ppm (J_{CF} = 27.7 Hz, J_{CH} = 135 Hz). This indicates an insertion of the alkyne into the CH bond of the vinyl group of 2, but the position of the ^{13}C resonance of the $C(CF_3)H$ group seems quite high for a π-bonded vinyl group.[10] For this reason, we undertook the X-ray structure determination which showed that 4 resulted from the insertion of hexafluorobutyne into the CH bond of the vinyl group of 2 and from the loss of 1 mol of carbon monoxide. Furthermore the CCF_3CF_3H group is μ-η^1 bonded to the two iron atoms (see below).

The second complex isolated, 5, shows a very similar infrared spectrum to 3 in the ν(CO) stretching region. The proton NMR spectrum gives evidence of a proton vinyl resonance at 6.64 ppm, and in the ^{13}C NMR spectrum quartets centered at 142.1 and 69.8 ppm (J_{CF} = 37 Hz) for the $C(CF_3)$ carbons strongly suggest a structure similar to 3 in which the hexafluorobutyne and a molecule of carbon monoxide would be inserted into the iron-carbon bond of the vinyl group of 2. The chemical analysis is in agreement with this formulation.

The exact structure of 3 and 4 has been established by X-ray analysis.

X-ray Molecular Structure of 3. The structure consists of discrete ions and solvate molecules linked by van der Waals and ionic forces. A view of the $Fe_2(CO)_6(\mu$-$C(C(O)OCH_3)C(C(O)OCH_3)C(O)C(C_6H_5)C(C_6H_5)H)$ anion with the numbering of atoms is shown in Figure 1. Bond distances and angles of interest are given in Table IV.

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Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) with Esd's for $[Fe_2(CO)_6(\mu\text{-}C(C_6H_5)C(C_6H_5)C(CF_3)C(CF_3)H)][P(C_6H_5)_4]$, 4

Bond Angles

Fe(1)-Fe(2)	2.589 (2)	C(2)-C(3)	1.46 (1)	C(31)-F(34)	1.33 (2)
Fe(1)-C(3)	2.09 (1)	C(2)-C(21)	1.53 (1)	C(61)-O(61)	1.18 (2)
Fe(1)-C(4)	2.08 (1)	C(3)-C(4)	1.49 (1)	C(62)-O(62)	1.15 (2)
Fe(1)-C(5)	2.07 (1)	C(3)-C(31)	1.51 (2)	C(63)-O(63)	1.13 (2)
Fe(2)-C(3)	2.09 (1)	C(4)-C(5)	1.43 (2)	C(71)-O(71)	1.17 (2)
Fe(2)-C(5)	1.99 (1)	C(4)-C(41)	1.49 (1)	C(72)-O(72)	1.13 (2)
Fe(1)-C(61)	1.74 (1)	C(5)-C(51)	1.52 (1)	C(73)-O(73)	1.14 (2)
Fe(1)-C(62)	1.77 (1)	C(21)-F(22)	1.35 (2)	P-C(101)	1.793 (8)
Fe(1)-C(63)	1.77 (1)	C(21)-F(23)	1.34 (1)	P-C(111)	1.795 (8)
Fe(2)-C(71)	1.77 (1)	C(21)-F(24)	1.36 (2)	P-C(121)	1.768 (9)
Fe(2)-C(72)	1.77 (1)	C(31)-F(32)	1.35 (2)	P-C(131)	1.799 (5)
Fe(2)-C(73)	1.74 (1)	C(31)-F(33)	1.33 (1)		

Bond Distances

Fe(2)-Fe(1)-C(3)	70.7 (3)	C(31)-C(3)-C(2)	120.1 (9)	F(32)-C(31)-F(34)	106.0 (10)
Fe(2)-Fe(1)-C(4)	76.6 (3)	C(31)-C(3)-C(4)	115.6 (11)	F(33)-C(31)-F(34)	105.9 (13)
Fe(2)-Fe(1)-C(5)	49.0 (3)	C(41)-C(4)-C(3)	127.7 (12)	O(61)-C(61)-Fe(1)	172.5 (9)
Fe(1)-Fe(2)-C(2)	76.7 (3)	C(41)-C(4)-C(5)	126.6 (10)	O(62)-C(62)-Fe(1)	177.1 (14)
Fe(1)-Fe(2)-C(5)	51.6 (3)	C(51)-C(5)-C(4)	118.0 (10)	O(63)-C(63)-Fe(1)	176.3 (14)
C(3)-Fe(1)-C(4)	41.9 (4)	F(22)-C(21)-F(23)	106.6 (11)	O(71)-C(71)-Fe(2)	175.5 (16)
C(3)-Fe(1)-C(5)	68.1 (5)	C(22)-C(21)-F(24)	104.7 (11)	O(72)-C(72)-Fe(2)	178.0 (11)
C(4)-Fe(1)-C(5)	40.5 (5)	F(23)-C(21)-F(24)	104.4 (8)	O(73)-C(73)-Fe(2)	175.3 (10)
C(2)-Fe(2)-C(5)	79.9 (4)	F(22)-C(21)-C(2)	116.6 (9)	C(101)-P-C(111)	109.7 (3)
C(3)-C(2)-Fe(2)	99.1 (7)	F(23)-C(21)-C(2)	112.7 (12)	C(101)-P-C(111)	110.3 (4)
C(4)-C(3)-C(2)	111.8 (10)	F(24)-C(21)-C(2)	110.8 (12)	C(101)-P-C(131)	110.5 (3)
C(5)-C(4)-C(3)	105.5 (10)	F(32)-C(31)-C(3)	110.4 (13)	C(111)-P-C(121)	107.3 (3)
Fe(2)-C(5)-C(4)	116.2 (7)	F(33)-C(31)-C(3)	115.2 (10)	C(111)-P-C(131)	110.8 (3)
C(21)-C(2)-C(3)	119.7 (11)	F(34)-C(31)-C(3)	113.2 (12)	C(121)-P-C(131)	108.2 (3)
C(21)-C(2)-Fe(2)	121.6 (8)	F(32)-C(31)-F(33)	105.4 (11)		

Figure 1 shows that 3 is the result of the double insertion of the carbon monoxide and alkyne into the iron–carbon σ bond of the starting complex 2. Furthermore, the organic group is σ bonded to Fe(1) by the C(4) carbon, π bonded by the C(3)–C(4) bond to Fe(2), and bonded by the oxygen O(1) of the carbonyl group to Fe(2). It may be described as a substituted divinyl ketone radical. The Fe(1)Fe(2)-O(1)C(2)C(3)C(4) five-membered ring has an envelope form with Fe(1) tilting up out −0.335 Å from the plane defined by O(1),C(2),C(3),C(4) with Fe(1) out of this same plane by 1.890 (3) Å. The C(3)–C(4) bond length (1.42 (2) Å) is longer than in the $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2CH_3OCOC{=}CHCOOCH_3]^+$ cation (1.340 (6) Å) where the vinyl group is not π bonded.[4b] This is normally expected for π-bonded vinyl groups.[10-13] The 1,2-diphenylvinyl group shows distances usually expected for a nonbonded vinyl group. The C(2)–O(1) distance (1.25 (2) Å) also is in a normal range for an O-bonded CO group.[4b,14,15]

Considering the $Fe_2(CO)_6$ unit, the Fe(1)–Fe(2) bond length of 2.596 (3) Å is close to the Fe–Fe distances found for most structures containing the $Fe_2(CO)_6$ group.[19] Taking into account this metal–metal bond the coordination sphere of each iron is a distorted octahedron. The Fe(1) iron atom is bonded to three carbonyl groups and one oxygen, O(1), of the C(2)O(1) ketonic group. This O(1) atom is nearly trans to the C(13)O(13) carbonyl group (O(1)Fe(1)C(13) = 175.0 (7)°) which certainly explains why the Fe(1)–C(13) bond length is the shortest iron–carbon distance in the Fe(1)(CO)$_3$ unit. The C(4) atom is nearly equidistant from the Fe(1) and Fe(2) atoms. The Fe(2) atom is bonded to three carbonyl groups and to the C(3) and C(4) carbon atoms of the organic ligand. The bonding of the organic ligand gives a more distorted geometry around the Fe(2) than around the Fe(1) atom, and there is no clear difference between the Fe(2)(CO) groups.

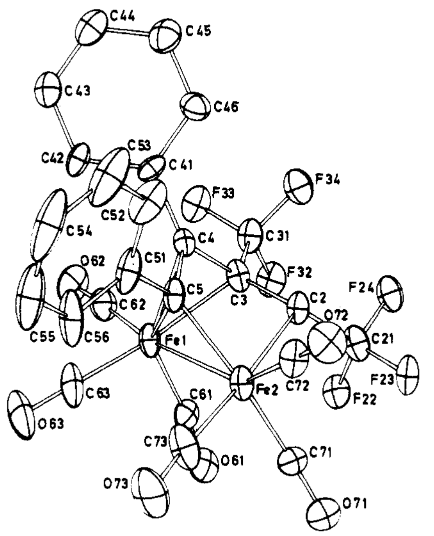

Figure 2. Molecular diagram and atom labeling scheme for 4.

Finally, the mode of bonding of the organic ligand allows each iron atom to be surrounded by 18 valence electrons, taking into account the metal–metal bond.

X-ray Molecular Structure of 4. The structure consists of discrete ions separated by larger distances than the sum of van der Waals radii. A view of the $C_{24}H_{11}F_6O_6Fe_2$ anion with numbering of atoms is shown in Figure 2. Bond distances and angles of interest are gathered in Table V.

The structure of 4 shows that this product is formally the result of the insertion of hexafluorobutyne into the CH bond of the vinyl group of 2 with the loss of 1 mol of carbon monoxide. A further point of interest is that the C(CF$_3$)C(CF$_3$)H unit is not π bonded to one iron atom. A

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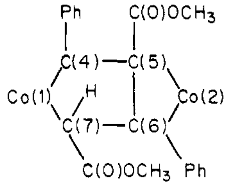
Table VI. Comparative Bond Distances (Å) and Bond Angles (deg) for 5 and $C_5H_5Co(C(C_6H_5)C(C(O)OCH_3)C(C_6H_5)C(C(O)OCH_3)H)Co(\mu\text{-}CO)(CO)_2$[17]



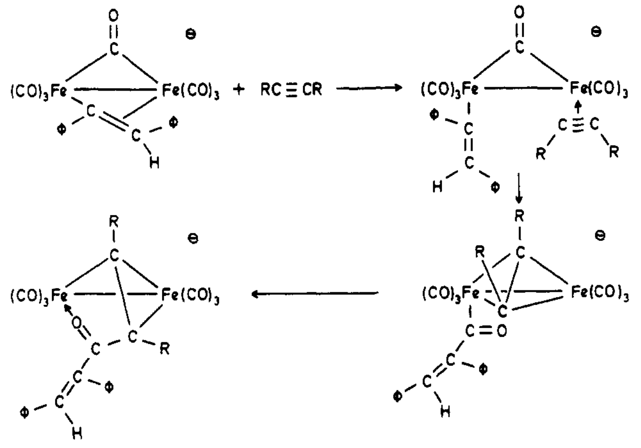
Bond Distances

Fe(2)-C(5)	1.99 (1)	Co(1)-C(4)	1.963 (5)
C(4)-C(5)	1.43 (2)	C(4)-C(5)	1.414 (5)
C(3)-C(5)	1.49 (1)	C(5)-C(6)	1.422 (7)
C(2)-C(3)	1.46 (1)	C(6)-C(7)	1.514 (6)
Fe(2)-C(2)	2.09 (1)	Co(1)-C(7)	2.026 (4)

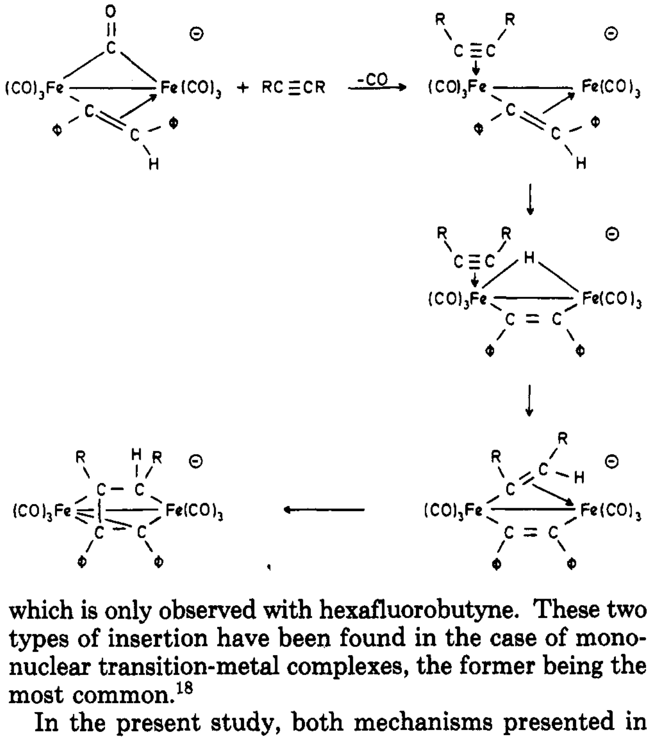
Bond Angles

C(2)-Fe(2)-C(5)	79.9 (4)	C(4)-Co(1)-C(7)	84.1 (2)
Fe(2)-C(5)-C(4)	116.2 (7)	Co(1)-C(4)-C(5)	113.0 (4)
C(5)-C(4)-C(3)	105.5 (10)	C(4)-C(5)-C(6)	113.6 (4)
C(4)-C(3)-C(2)	111.8 (10)		
Fe(2)-C(2)-C(3)	99.1 (7)	Co(1)-C(7)-C(6)	104.0 (3)

Scheme I



Scheme II



similar situation has previously been encountered for this vinyl group in the case of the $HOs_3(CO)_{10}(CF_3CCHCF_3)$ compound.[16] The whole organic part of the molecule is σ bonded by the C(2) and C(5) carbon atoms to Fe(2) and bonded by C(3), C(4), and C(5) to Fe(1). The hydrogen atom bonded to C(2) occupies an exo position. This five-membered ring has an envelope form with the C(2) atom tilting up out −0.82 (2) Å of the plane containing Fe(2), C(3), C(4), and C(5). Fe(1) is out of the same plane by 1.740 (4) Å. Examination of the carbon–carbon distances shows extensive electron delocalization as the longer distance is C(3)–C(4) and not C(2)-C(3) as expected. This situation has to be contrasted with that found for the $Co(C(C_6H_5)C(C(O)(OCH_3))C(C_6H_5)CH(C(O)OCH_3)$ ring in the isoelectronic $(C_5H_5)Co_2(CO)_3C(C_6H_5)C(C(O)OCH_3)C(C_6H_5)CH(C(O)OCH_3)$ molecule.[17]

For comparison, we have gathered in Table VI comparable bond distances and bond angles for the two complexes. In the cobalt complex, the organic ligand appears to be σ bonded by C(4) and C(7) to Co(1) and Co(2) is π bonded to an allylic portion C(4), C(5), and C(6). Furthermore, in the iron complex the five-membered ring is more constrained. The precise reason for this difference is difficult to ascertain and is presumably the consequence of the presence of the two electronegative CF_3 groups on C(2) and C(3).

Considering now the $Fe_2(CO)_6$ unit, the Fe–Fe distance is 2.589 (2) Å within the range of distances found for other dinuclear $Fe_2(CO)_6$ units.[19] The FeCO units are normal, and the main features are that Fe(2)C(72) is nearly orthogonal to Fe(2)C(2) and Fe(2)C(5) and that Fe(1)C(62) is nearly orthogonal to Fe(1)C(4).

As a summary, both X-ray molecular structure determinations for 3 and 4 clearly show that two cases have been encountered in the reaction of 2 with dimethyl acetylenedicarboxylate and hexafluorobutyne. In the first case, double insertion of carbon monoxide and alkyne into the iron–carbon bond of the vinyl group of 2 occurs, which is observed with the two alkynes. In the second case, insertion formally occurs into the C–H bond of the vinyl group of 2 with loss of one molecule of carbon monoxide, which is only observed with hexafluorobutyne. These two types of insertion have been found in the case of mononuclear transition-metal complexes, the former being the most common.[18]

In the present study, both mechanisms presented in Schemes I and II are consistent with the results. In the first case, the insertion of alkyne would result from the creation of a vacant site by the opening of the vinyl bridge. The alkyne then induces CO insertion into the vinyl–iron bond by moving to a μ-η^2 mode of bonding, and in further stage, carbon–carbon coupling leads to the final product of type 3. In the second case, the creation of a vacant site would result from the loss of one molecule of carbon monoxide. Carbon–hydrogen bond breaking in the vinyl group would then create a propitious situation to lead to a complex of type 4 through intermediate III in Scheme II. Nevertheless, as the two alkynes have quite similar properties, it is not clear why a complex of type 4 is not formed with the dimethyl acetylenedicarboxylate. As the reaction with hexafluorobutyne was performed in partial vacuo (see Experimental Section), this was a possible reason for this difference of reactivity. We have conducted an experiment with dimethyl acetylenedicarboxylate in a

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sealed tube in vacuo, but still, only compound **3** has been detected in the reaction solution. Possibly the steric bulk of the $C(O)OCH_3$ group prevents the situation III in Scheme II. This is suggested by the structure of $[((\mu\text{-}SCH_3)Fe(COe)(P(CH_3)_3)_2)_2CH_3OC(O)C{=}CHC(O)OCH_3]^+$ in which the vinyl group is not π bonded but is bonded by a vinylic carbon for one iron atom and by an oxygen atom of the α-carbonyl ester group for the other. This strained situation could prevent further carbon–carbon coupling to lead to type **4** like products. Nevertheless, this difference of reaction pathways could be more subtle. To get a better insight of this problem, we are presently extending this study to other families of alkynes and binuclear iron systems bridged by other vinyl groups.

Acknowledgment. This work has been supported by the CNRS and by a grant of the University of Barcelona. J.R. thanks the Spanish Ministry of Education and Science for a fellowship.

Registry No. **2**, 89891-19-0; **3**, 89891-21-4; **4**, 89891-23-6; **5**, 89891-25-8; $[HFe_3(CO)_{11}][P(C_6H_5)_4]$, 40806-49-3; diphenylacetylene, 501-65-5; dimethyl acetylenedicarboxylate, 762-42-5; hexafluorobutyne, 692-50-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and structure factors (16 pages). Ordering information is given on any current masthead page.

Phosphido-Bridged Mixed-Metal (Ru/Co) Compounds via the Reaction of (arene)$RuCl_2(PPh_2X)$ (X = H, Cl) with $Co_2(CO)_8$: X-ray Structure of $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$

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A strategy for the synthesis of heterobi- and heterotrinuclear phosphido-bridged complexes via the reactions of the readily available η^6-arene compounds (*p*-cymene)$RuCl_2(PPh_2X)$ (X = H, Cl) with $Co_2(CO)_8$ is described. This route has afforded heterobinuclear $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**3**), (*p*-cymene)$(CO)Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**7**), small amounts of $Ru_2(\mu\text{-}PPh_2)_2(CO)_6$ (**4**), and the heterotrinuclear clusters $Ru_2Co(\mu\text{-}PPh_2)(CO)_{10}$ (**5**) and $RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ (**6**). These compounds have been characterized by microanalysis and mass, infrared, and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Single crystals of $RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ are monoclinic of space group $P2_1/n$ with a = 12.714 (2) Å, b = 15.600 (3) Å, c = 17.246 (3) Å, β = 108.33 (1)°, and Z = 4. The structure was solved and refined by using 3610 unique, observed reflections measured on a Syntex $P2_1$ diffractometer to R and R_w values of 0.034 and 0.039. In the triangular cluster the trans axial PPh_2 groups bridge the Ru–Co(1) and Co(1)–Co(2) edges with a semibridging CO group across the remaining Ru–Co bond.

Introduction

The chemistry of transition-metal cluster compounds has seen an explosive growth over the past decade, stimulated in part by the belief that such compounds may have potential applications as homogeneous catalysts or catalyst precursors. A specific class of cluster compounds, those which contain two or more different catalytic metals, is now receiving special attention because of the possibility of using these mixed-metal compounds for the preparation of supported polymetallic, heterogeneous catalysts or to promote unique patterns of substrate activation via cooperative interactions. Mixed ruthenium–cobalt systems are especially attractive for the following substantial reasons: (i) Cobalt carbonyls have found wide application as carbonylation catalysts, particularly for hydroformylation. (ii) Ruthenium compounds are among the most effective catalysts for hydrogenation. Moreover as one of the cheaper catalytically active platinum metals, efforts are being made to develop ruthenium catalysts to replace the more expensive rhodium systems. (iii) There is accumulating evidence that selectivity for ethanol synthesis via methanol homologation using cobalt catalysts is substantially improved by additions of ruthenium derivatives.[1,2] Recent work by Hidai and co-workers also suggests that mixed ruthenium–cobalt systems are very effective in homologation.[3]

In developing a strategy for the synthesis of robust Ru/Co complexes, we were faced with two problems. The first of these was to find an appropriate source of mononuclear ruthenium containing a phosphorus group to combine with the cobalt reagent of choice $Co_2(CO)_8$. Previous syntheses have generally employed metathetical reactions of $RuCl_3{\cdot}XH_2O$,[3,4] $[Ru(CO)_3Cl_2]_2$,[5] and Ru(H)-

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