Figure 1. ORTEP representation of the structure of the Re$_2$(NCBH$_3$)$_4$-(dppm)$_2$(H$_2$O)$_2$ molecule with phenyl rings and hydrogen atoms omitted. The thermal ellipsoids are drawn at the 50% probability level. The halves of the molecule (labeled and unlabeled) are related by a C_2 axis that is perpendicular to the Re–Re bond.

$E_{1/2}$(ox) value of +0.29 V for the analogous chloride complex Re$_2$Cl$_4$(dppm)$_2$.[18]

The structural identity of Re$_2$(NCBH$_3$)$_4$(dppm)$_2$(H$_2$O)$_2$ has been confirmed by a single-crystal X-ray structure analysis with data collected at +20 °C. The ORTEP representation of the structure is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I–III. The dirhenium unit possesses a crystallographically imposed 2-fold axis of symmetry that bisects the Re–Re bond and relates the two rhenium units.

Discussion

The conversion of Re$_2$Cl$_4$(dppm)$_2$ to Re$_2$(NCBH$_3$)$_4$(dppm)$_2$-(H$_2$O)$_2$ represents the first example of the displacement of all four chloride ligands by another monoanionic ligand and attests to the stability of the [Re(μ-dppm)$_2$Re] unit. A comparison of the electrochemical properties of Re$_2$Cl$_4$(dppm)$_2$[18] and Re$_2$-(NCBH$_3$)$_4$(dppm)$_2$(H$_2$O)$_2$ shows that the value of $E_{1/2}$(ox) for the Re$_2^{5+}$/Re$_2^{4+}$ couple is shifted anodically by ca. 0.7 V in the cyanotrihydroborato complex, perhaps reflecting an increase in positive charge at the dirhenium core that leads to a relative stabilization of the HOMO δ^* orbital. This core charge difference may in turn explain the greater tendency of Re$_2$(NCBH$_3$)$_4$(dppm)$_2$ to be solvated by a hard σ-donor such as water. In the case of Re$_2$Cl$_4$(dppm)$_2$ and other such halide derivatives, 1:1 and 1:2 adducts are formed with CO,[6,19,20] isocyanides,[21,22] and phosphine[4] donors, but the resulting complexes are structurally quite different from the parent unsolvated species and from Re$_2$(NCBH$_3$)$_4$-(dppm)$_2$(H$_2$O)$_2$. Studies of the reactivity of Re$_2$(NCBH$_3$)$_4$-(dppm)$_2$(H$_2$O)$_2$ toward CO, nitriles, and isocyanides showed either no reaction or the formation of intractible mixtures.

The structure of Re$_2$(NCBH$_3$)$_4$(dppm)$_2$(H$_2$O)$_2$ is shown in Figure 1, and the important structure parameters are given in Table III. The structural characterization of Re$_2$(NCBH$_3$)$_4$-(dppm)$_2$(H$_2$O)$_2$ is the first for a hydrate of dirhenium(II). The structure resembles those of Re$_2$Cl$_4$(dppm)$_2$[23] and Re$_2$Cl$_4$(dppa)$_2$ (dppa = Ph$_2$PNHPPh$_2$)[18] in its essential details, namely, the presence of two bridging dppm ligands and a very short Re–Re bond distance (2.2874 (5) Å). The latter is a little longer than those of the two chloride complexes, which are 2.234 (3) and

2.2417 (5) Å, respectively.[18,23] The average Re–P distance of 2.465 [14] Å compares to distances of 2.43 [2] and 2.45 [3] Å in Re$_2$Cl$_4$(dppm)$_2$[23] and Re$_2$Cl$_4$(dppa)$_2$.[18] The Re–O(H$_2$O) distance of 2.411 (4) Å is within the range observed for bis(hydrates) of quadruply bonded dirhenium(III) complexes; examples are 2.66 (3), 2.50 (2), and 2.28 (1) Å for Cs$_2$[Re$_2$Cl$_8$(H$_2$O)$_2$],[24] Re$_2$(O$_2$-CCH$_3$)$_2$Cl$_4$(H$_2$O)$_2$,[25] and Na$_2$[Re$_2$(SO$_4$)$_4$(H$_2$O)$_2$]·6H$_2$O,[26] respectively. The Re–Re–O angle of 175.9 (1) Å approaches linearity. The Re–N distances (2.052 [7] Å average) are much shorter (by ca. 0.25 Å) than the long *axial* Re–N bonds in *cis*-Re$_2$(O$_2$CCH$_3$)$_2$(NCBH$_3$)$_2$(dppm)$_2$[5] but are comparable to the Re–N distances in nitrile complexes of the type [Re$_2$Cl$_3$-(dppm)$_2$(NCR)$_2$]PF$_6$[2,4,5] and the Re–N distance involving the [BH$_3$CN]$^-$ ligand in Re(CO)$_3$(bpy)(NCBH$_3$).[27]

As with other dirhenium(II) compounds, in which there is no electronic barrier to rotation about the Re–Re bond,[28,29] the complex Re$_2$(NCBH$_3$)$_4$(dppm)$_2$(H$_2$O)$_2$ assumes a rotational geometry intermediate between those of a fully eclipsed conformation and a fully staggered conformation. This is most readily demonstrated by the torsional angles N(1)–Re–Re'–N(1)', N(2)–Re–Re'–N(2)', and P(1)–Re–Re'–P(2)', which are 25.3 (2), 17.6 (2), and 15.4 (1)°, respectively.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1) and listings of positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) (12 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Crystal Structure of [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC=CPhH)(μ-AuPPh$_3$)]: First Example of a Highly Asymmetric Triangular Fe$_2$Au System

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We have recently described the synthesis and structure of several metal clusters containing the triangular Fe$_2$M metal core (M = Cu, Ag, Au) as well as similar complexes in which the iron–iron bond is bridged by a phosphido ligand.[1,2] Both types of compounds

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display a practically symmetric triangular skeleton. This metal arrangement is also found in all the cases in which one gold atom is simultaneously bonded to two iron atoms.[3] Consequently, we thus decided to attempt the synthesis of analogous Fe_2Au clusters containing asymmetric iron–gold distances. This type of derivatives would enable us to compare such clusters with those described above in terms of structural features and/or chemical behavior. The asymmetric anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}RC= CRH)]^-$ was chosen as a building block to form such derivatives due to its proven nucleophilic character. Furthermore, taking into account the isolobal relationship $AuPPh_3^+/H^+$, some aspects of the mechanism involved in the reaction between $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}RC=CRH)]^-$ and H^+ to give the ferrole complex $[Fe_2(CO)_6(PhC\equiv CPh)]$ could be clarified.[4]

Experimental Section

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Elemental analyses of C and H were carried out at the Institut de Bio-Organica de Barcelona. Infrared spectra were recorded in CH_2Cl_2 or toluene solutions on a Perkin-Elmer 1330 spectrophotometer. The ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker WP 80SY spectrometer using TMS and $P(OMe)_3$ as references. Mössbauer spectra were recorded by using a 20 mCi of ^{57}Co source in a Rh matrix, and the calibration was with iron foil. Compounds $(PPh_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}RH=CRH)]$ (R = H, Ph)[5] and $ClAuPPh_3$[6] were prepared by procedures described previously. Complexes (Cl-Au)$_2$(PP) (PP = dppm, dppe, dppp) were synthesized and isolated as solids from ClAu(tht)[7] solutions by adding the appropriate amount of the corresponding diphosphine.

Preparation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}RC=CRH)(\mu\text{-}AuPPh_3)]$ (1, R = Ph; 2, R = H). Details of the synthesis of **1** apply also to **2**. Solid ClAuPPh$_3$ (0.330 g, 0.67 mmol) and TlBF$_4$ (0.195 g, 0.67 mmol) were added to a solution of $(PPh_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC=CPhH)]$ (0.555 mg, 0.67 mmol) in CH_2Cl_2 (100 mL) at –40 °C. The solution was allowed to warm to room temperature and was stirred for 3 h, filtered, and evaporated to dryness in vacuo. The residual solid was extracted three times with hexane (3 × 50 mL) to give a deep green solution. After filtration through Celite, the solution was concentrated until microcrystals were deposited. Yield: 0.450 g (70%). Spectroscopic data for **1** are as follows. IR (CH_2Cl_2; cm^{-1}): ν_{CO} stretch 2040 m, 2010 vs, 1970 vs, br, 1770 m. $\delta(^{31}P)$ in CH_2Cl_2 (ppm): –88.5. $\delta(^1H)$ in $CDCl_3$ (ppm): 7.4 (m, C_6H_5), 4.5 (s, HC$_\beta$). Anal. Calcd: C, 49.50; H, 2.77. Found: C, 48.57; H, 2.58. Spectroscopic data for **2** are as follows. IR (CH_2Cl_2; cm^{-1}) ν_{CO} stretch 2040 m, 2010 vs, 1970 vs, br, 1780 m. $\delta(^{31}P)$ in CH_2Cl_2 (ppm): –89.2. $\delta(^1H)$ in $CDCl_3$ (ppm): 7.5 (m, C_6H_5), 3.13 (d, $^3J = 8$ Hz, HC$_\beta$), 3.26 (d, $^3J = 13$ Hz, HC$_\beta$), 8.05 (dd, $^3J = 8$ Hz, $^3J = 13$ Hz, HC$_\alpha$). Anal. Calcd: C, 40.83; H, 2.27. Found: C, 39.61; H, 2.70.

Preparation of $[\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC=CPhH)(\mu\text{-}Au)\}_2(PP)]$ (3, PP = dppm; 4, PP = dppe; 5, PP = dppp). A general synthesis for all three compounds is described. A solution of $(PPh_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC=CPhH)]$ (0.415 mg, 0.5 mmol) in CH_2Cl_2 (100 mL) at room temperature was treated with the stoichiometric amount of solid (ClAu)$_2$(PP) and TlBF$_4$. After 1 h of stirring, the mixture was filtered through Celite, and the resulting green solution was evaporated to dryness. The residue was extracted with toluene (3 × 20 mL) and concentrated to 10 mL. After addition of 15 mL of hexane, green crystals were obtained in ca. 40–60% yield. Spectroscopic data for **3** are as follows: IR (toluene, cm^{-1}): ν_{CO} stretch 2040 m, 2010 vs, 1965 vs br, 1785 m. $\delta(^{31}P)$ in CH_2Cl_2: –99.1 ppm. $\delta(^1H)$ in $CDCl_3$: 7.4 ppm (m, C_6H_5), 4.48 ppm (s, HC$_\beta$). Anal. Calcd: C, 45.91; H, 2.51. Found: C. 45.21; H, 2.47. Spectroscopic data for **4** are as follows. IR (toluene; cm^{-1}): ν_{CO} stretch 2040 m, 2010 vs, 1965 vs br, 1782 m. $\delta(^{31}P)$: –89.33 ppm. $\delta(^1H)$: 7.4 ppm (m), 4.52 ppm (s). Anal. Calcd: C, 46.22; H, 2.61. Found:

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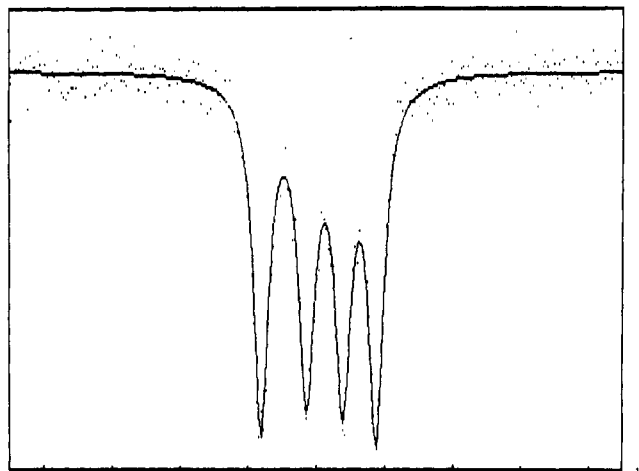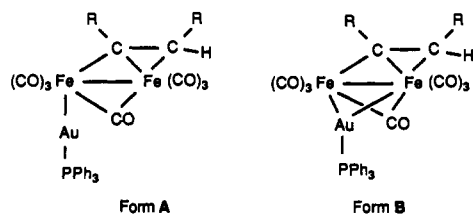(7) Usón, R.; Laguna, A. *Organomet. Synth.* **1986**, *3*, 324.

Table I. Crystallographic Data for $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC=CPhH)(\mu\text{-}AuPPh_3)]$ (1)

chem formula	$C_{39}H_{26}AuFe_2O_7P$	space group	$P2_1/n$
a, Å	18.334 (8)	T, °C	20
b, Å	15.374 (5)	λ(Mo Kα), Å	0.7107
c, Å	13.430 (4)	ρ_{calcd}, g cm^{-3}	1.699
β, deg	102.27 (2)	μ, cm^{-1}	48.122
V, Å^3	3699 (2)	R	0.071
Z	4	R_w	0.075
fw	946.26		

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound 1[a]

atom	x	y	z	U_{eq}, Å^2
Au(1)	0.2269 (0)	0.0747 (0)	0.0105 (0)	532 (6)
Fe(1)	0.2035 (1)	0.0867 (1)	0.2064 (1)	414 (7)
Fe(2)	0.2925 (1)	0.1932 (1)	0.1400 (1)	468 (7)
P(1)	0.2033 (2)	−0.0032 (2)	−0.1371 (2)	517 (13)
O(1)	0.3567 (5)	0.1011 (7)	0.3299 (8)	749 (39)
O(2)	0.2632 (6)	−0.0833 (7)	0.1680 (9)	873 (48)
O(3)	0.0495 (5)	0.0371 (7)	0.1067 (8)	766 (41)
O(4)	0.1914 (7)	0.0311 (9)	0.4094 (8)	1003 (55)
O(5)	0.4312 (6)	0.1175 (9)	0.1061 (10)	1097 (60)
O(6)	0.2657 (7)	0.2793 (9)	−0.0625 (9)	1060 (58)
O(7)	0.3655 (6)	0.3406 (8)	0.2572 (10)	991 (55)
C(1)	0.3104 (6)	0.1231 (8)	0.2590 (10)	495 (44)
C(2)	0.2404 (8)	−0.0159 (9)	0.1767 (10)	593 (51)
C(3)	0.1081 (7)	0.0603 (8)	0.1404 (10)	533 (45)
C(4)	0.1951 (9)	0.0555 (9)	0.3319 (12)	670 (58)
C(5)	0.3771 (8)	0.1448 (10)	0.1178 (11)	670 (56)
C(6)	0.2702 (8)	0.2443 (10)	0.0151 (13)	703 (61)
C(7)	0.3365 (7)	0.2840 (10)	0.2106 (12)	614 (53)
C(8)	0.1925 (5)	0.2204 (7)	0.1695 (9)	407 (37)
C(9)	0.1847 (6)	0.2178 (8)	0.2718 (8)	456 (40)
C(10)	0.1196 (6)	0.2379 (7)	0.3121 (8)	436 (40)
C(11)	0.1321 (7)	0.2703 (9)	0.4135 (9)	593 (50)
C(12)	0.0730 (11)	0.2935 (12)	0.4569 (12)	842 (73)
C(13)	0.0018 (10)	0.2845 (12)	0.4031 (15)	848 (74)
C(14)	−0.0122 (7)	0.2519 (10)	0.3056 (13)	683 (57)
C(15)	0.0458 (7)	0.2284 (10)	0.2609 (9)	552 (46)
C(20)	0.1339 (6)	0.2651 (7)	0.0908 (9)	423 (45)
C(21)	0.1167 (7)	0.3516 (8)	0.1117 (9)	517 (44)
C(22)	0.0646 (7)	0.3976 (9)	0.0428 (12)	627 (51)
C(23)	0.0268 (7)	0.3594 (9)	−0.0442 (11)	653 (52)
C(24)	0.0428 (7)	0.2749 (10)	−0.0666 (10)	626 (51)
C(25)	0.0968 (6)	0.2278 (8)	0.0009 (8)	480 (40)
C(30)	0.2821 (8)	−0.0034 (9)	−0.2009 (11)	629 (55)
C(31)	0.3518 (9)	0.0104 (11)	−0.1414 (13)	776 (65)
C(32)	0.4120 (9)	0.0094 (13)	−0.1901 (18)	1046 (90)
C(33)	0.4017 (12)	−0.0043 (13)	−0.2928 (19)	1082 (99)
C(34)	0.3345 (12)	−0.0182 (12)	−0.3470 (15)	983 (89)
C(35)	0.2718 (8)	−0.0169 (10)	−0.3057 (12)	731 (62)
C(40)	0.1237 (7)	0.0341 (10)	−0.2321 (10)	568 (50)
C(41)	0.0731 (9)	−0.0236 (13)	−0.2859 (13)	872 (71)
C(42)	0.0128 (12)	0.0090 (20)	−0.3592 (16)	1149 (105)
C(43)	0.0081 (15)	0.0981 (26)	−0.3739 (16)	1382 (145)
C(44)	0.0553 (16)	0.1535 (16)	−0.3173 (16)	1305 (121)
C(45)	0.1168 (9)	0.1250 (12)	−0.2457 (12)	829 (72)
C(50)	0.1867 (7)	−0.1187 (8)	−0.1145 (9)	542 (45)
C(51)	0.1400 (8)	−0.1386 (10)	−0.0501 (11)	695 (58)
C(52)	0.1305 (9)	−0.2265 (15)	−0.0266 (13)	905 (79)
C(53)	0.1613 (10)	−0.2877 (13)	−0.0693 (13)	860 (73)
C(54)	0.2069 (10)	−0.2720 (10)	−0.1328 (13)	824 (69)
C(55)	0.2212 (8)	−0.1853 (10)	−0.1586 (11)	652 (54)

[a] Thermal parameter as $U_{eq} = (1/3)\sum[U_{ij}a_i^*\cdot a^*a_i\cdot a_j \cos(a_i,a_j)] \times 10^4$.

C. 45.61; H, 2.52. Spectroscopic data for **5** are as follows. IR (toluene, cm^{-1}): ν_{CO} stretch 2040 m, 2010 vs, 1967 vs, br, 1785 m. $\delta(^{31}P)$: –93.70 ppm. $\delta(^1H) = 7.4$ ppm (m), 4.45 ppm (s). Anal. Calcd: C, 46.53; H, 2.70. Found: C, 46.33; H, 2.68.

X-ray Crystal Structure of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC=CPhH)(\mu\text{-}AuPPh_3)]$ (1). The title compound crystallizes as dark, very well formed prisms by diffusion of hexane into a toluene solution of **1**. A crystal ca. 0.5 × 0.4 × 0.4 mm was selected for data collection. Intensity measurements were performed on a Philips PW 1100 four-circle diffractometer using monochromated Mo Kα radiation. Two reference reflections checked every 90 reflections showed no variation in intensity. Intensity

Figure 1. ^{57}Fe Mössbauer spectrum of [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC=CPhH)(μ-AuPPh$_3$)] (1).

Chart I

Form A   Form B

measurement was performed up to $\theta = 25°$, with a $\omega/2\theta$ scan technique and a scan speed of 0.050 s^{-1}. A total of 6700 independent reflections were measured, with 4863 observed with an $I > 2\sigma(I)$ criterium, and were used for structure solution and refinement. Data were corrected for geometrical factors and absorption correction.[8] The structure was solved by Patterson and Fourier synthesis and refined by full-matrix least-squares methods with anisotropic thermal parameters. H atoms were positioned by geometrical calculation; only H(9) was found by a difference synthesis. H atoms were included in the structure factor calculations but their positional and isotropic parameters were not refined. An empirical weighting scheme was applied so as to give no trends in $\langle w\Delta^2F \rangle$ vs $\langle F_o \rangle$ and $\langle (\sin\theta)/\lambda \rangle$. Scattering factors were taken from ref 9. All calculations were performed on a VAX 6410 computer using the X-Ray 76 system[10] and several local programs. For a summary of crystal data, see Table I. Final atomic coordinates are presented in Table II.

Results

The reaction of (PPh$_4$)[Fe$_2$(CO)$_6$(μ-CO)(μ-RC=CRH)] (R = Ph, H) with a dichloromethane solution of ClAuPPh$_3$ and TlBF$_4$ gives neutral metal clusters of the type [Fe$_2$(CO)$_6$(μ-CO)(μ-RC=CRH)(μ-AuPPh$_3$)] (1, R = Ph; 2, R = H). These complexes were isolated, after concentration of the solution and addition of hexane, as green crystalline solids in good yields. Given their limited air stability, they can only be manipulated in air for a few minutes.

Formation of compounds 1 and 2 was monitored by IR spectroscopy from their CH$_2$Cl$_2$ solutions, which show a shift of the ν_{CO} bands to higher frequency with respect to the starting products. Their ^{31}P NMR spectra show only one signal due to the PPh$_3$ group attached to the gold atom, and their ^{1}H NMR spectra in CDCl$_3$ show, in addition to the phenyl resonances, the characteristic signals of the vinylic protons.

The ^{57}Fe Mössbauer spectrum of 1 (Figure 1) shows two split signals with IS of –0.08 and 0.01 mm s^{-1} and QS values of 0.52 and 1.65 mm s^{-1} respectively, in agreement with the presence of two different iron atoms.
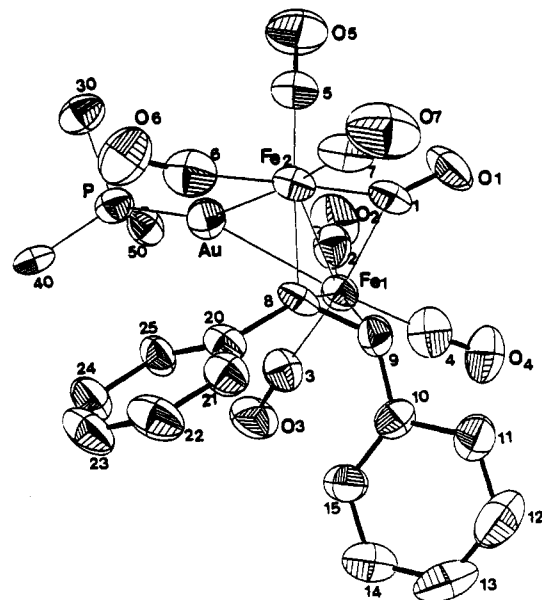
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Figure 2. ORTEP drawing of the molecular structure of 1, showing the atomic numbering scheme.

Table III. Selected Bond Lengths and Angles for 1 with Estimated Standard Deviations in Parentheses

Bond Distances (Å)			
Au–Fe(1)	2.761 (2)	Au–Fe(2)	2.627 (2)
Au–P	2.278 (3)	Fe(1)–Fe(2)	2.600 (3)
Fe(1)–C(1)	2.015 (10)	Fe(1)–C(2)	1.795 (14)
Fe(1)–C(3)	1.831 (12)	Fe(1)–C(4)	1.789 (16)
Fe(1)–C(8)	2.114 (10)	Fe(1)–C(9)	2.253 (12)
Fe(2)–C(1)	1.896 (12)	Fe(2)–C(5)	1.801 (15)
Fe(2)–C(6)	1.818 (16)	Fe(2)–C(7)	1.780 (14)
Fe(2)–C(8)	2.001 (10)	C(1)–O(1)	1.183 (14)
C(2)–O(2)	1.132 (18)	C(3)–O(3)	1.131 (15)
C(4)–O(4)	1.121 (20)	C(5)–O(5)	1.117 (19)
C(6)–O(6)	1.160 (21)	C(7)–O(7)	1.135 (18)
C(8)–C(9)	1.412 (16)	C(8)–C(20)	1.503 (14)
C(9)–C(10)	1.445 (17)	C(9)–H(9)	1.027 (10)

Bond Angles (deg)			
Fe(2)–C(1)–Fe(1)	83.2 (4)	Fe(2)–C(8)–Fe(1)	78.3 (4)
Fe(2)–Au–Fe(1)	37.6 (1)	Fe(1)–C(8)–C(9)	76.5 (6)
Fe(1)–C(9)–C(8)	65.3 (6)	C(8)–Fe(1)–C(9)	37.5 (4)
Fe(2)–Au–P	156.4 (1)	Fe(1)–Au–P	145.6 (1)
C(20)–C(8)–C(9)	119.5 (9)	C(8)–C(9)–C(10)	128.3 (10)
Fe(2)–C(8)–C(9)	118.2 (7)	C(2)–Fe(1)–C(8)	145.5 (5)
Fe(1)–Fe(2)–C(1)	50.3 (3)	Fe(2)–Fe(1)–C(1)	46.4 (3)
C(8)–Fe(2)–Fe(1)	52.7 (3)	C(8)–Fe(1)–Fe(2)	48.9 (3)
C(8)–Fe(2)–C(5)	167.6 (6)	C(7)–Fe(2)–Au	171.0 (5)
C(6)–Fe(2)–C(1)	170.7 (6)	C(5)–Fe(2)–Fe(1)	114.9 (5)
C(1)–Fe(1)–C(3)	171.4 (5)	Au–Fe(1)–C(4)	160.2 (4)

Discussion

From the analysis of the spectroscopic data for complexes 1 and 2, it can not be determined whether the fragment AuPPh$_3$ attachment to the [Fe$_2$(CO)$_6$(μ-CO)(μ-RC=CRH)]$^-$ anion occurs via one iron atom affording a metal chain (Chart I, A form) or through both metal atoms giving an Fe$_2$Au triangular geometry (Chart I, B form).

The X-ray crystal structure determination of 1 revealed that the last form was the one adopted by the metal atoms, corroborating the tendency of the AuPPh$_3$ units to coordinate two or more metal centers.[11]

The molecular structure of [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC=CPhH)(μ-AuPPh$_3$)] (1) is shown in Figure 2. Selected bond parameters are listed in Table III. The basic skeleton consists of an Fe$_2$Au triangle where the Fe–Fe bond is bridged by a carbonyl ligand and a σ,π-diphenylethenyl group, both iron atoms

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attaining an 18-electron configuration. The Fe–Au distances are markedly asymmetric, the Fe(2)–Au length (2.627 (2) Å) being shorter than the Fe(1)–Au (2.761 (2) Å). In addition, the carbonyl bridging group is closer to Fe(2) (1.896 (12) Å) than to Fe(1) (2.015 (10) Å). The notable asymmetry of this system can be explained in terms of the 18-electron rule assuming that the negative charge in the precursor anion is basically localized on the Fe(2) atom. The organic bridge is σ-bonded to Fe(2) with a Fe(2)–C(8) distance of 2.001 (10) Å and is unsymmetrically π-bonded to Fe(1) (C(8)–Fe(1) = 2.114(10) Å and C(9)–Fe(1) = 2.253 (12) Å). These distances are in the expected range for this ligand with this mode of bonding. This compound is, to our knowledge, the first example of a Fe$_2$ system bridged by a ethenyl group along with two different bridging ligands. Complexes containing, besides the vinyl group, another bridging ligand such as Cl, PPh$_2$, CO, COEt, or SCH$_2$Ph are well-known.[12]

The isolation and structural characterization of **1** suggests the possibility that the formation of [Fe$_2$(CO)$_6$(PhC≡CPh)][4] from [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC≡CPhH)]$^-$ and H$^+$ could proceed through a mechanism in which the initial step would involve the protonation of an iron center of the anion to give the asymmetric hydride [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC≡CPhH)(μ-H)], which was not isolated or detected spectroscopically. This idea is supported by the fact that the related [Fe(μ-SMe)(CO)$_2$L]$_2$ (L = phosphine) complexes are easily protonated, giving rise to cationic complexes containing a symmetrically bridging hydride ligand.[13] However, more work in this field is required in order to confirm this point.

Having established the X-ray crystal structure of **1**, we attempted to form compounds containing two Fe$_2$Au units linked by a chelating ligand. We aimed to explore the possibility of promoting condensation reactions between the two cluster units. The reaction of the anionic ethenyl-bridged complex [Fe$_2$-(CO)$_6$(μ-CO)(μ-PhC≡CPhH)]$^-$ with (ClAu)$_2$(PP) (PP = dppm,

dppe, dppp) in dichloromethane solution at room temperature in the presence of TlBF$_4$ gave deep green solutions whose IR spectra show ν_{CO} patterns identical with that displayed by **1** and **2**. On the other hand, the ^{31}P NMR spectrum presents only one signal, which is consistent with a symmetric disposition of the PP ligand; the ^{1}H NMR spectra contain only the expected resonances due to the vinylic proton. These results, summarized in eq 1, confirm that, in our case, no condensation reaction occurs between the two cluster units and that according to the spectroscopic and analytical data the compounds [{Fe$_2$(CO)$_6$(μ-CO)(μ-PhC≡CPhH)(μ-Au)}$_2$(PP)] (**3**, PP = dppm; **4**, PP = dppe; **5**, PP = dppp) can be formulated as shown. In conclusion, the use of (μ-di-

2 (PPh$_4$) [Fe$_2$(CO)$_6$(μ-CO)(μ-PhC≡CPhH)] + (ClAu)$_2$(PP) + 2 TlBF$_4$
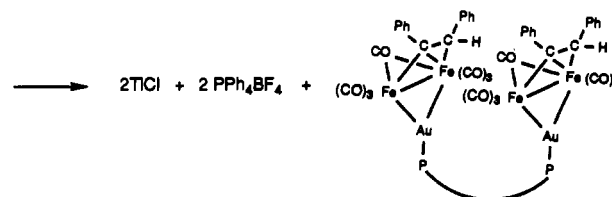
3: PP = dppm; 4: PP = dppe; 5: PP = dppp (1)

phosphine)digold complexes opens up new possibilities for the study of species containing two metal cluster fragments linked by a bridging ligand, as we have recently described for other iron–gold systems.[14]

Supplementary Material Available: Tables of all bond distances and angles (Table S1), hydrogen atom coordinates and isotropic displacement parameters (Table S2), and anisotropic thermal parameters (Table S3) (5 pages); a listing of structure factors (Table S4) (27 pages). Ordering information is given on any current masthead page.

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