iron(II) triad yield relatively stable adducts whereas the reactions of these systems with dihalogen or pseudodihalogen radicals X_2^- such as Br_2^- and $(SCN)_2^-$, which have reduction potentials near that for OH, occur rapidly and without apparent intermediates to yield the corresponding complex for the metal in the next higher valent state (eq 19).[2,11,12,56] Furthermore, the M(II)/M(III)

$$[M(bpy)_3]^{2+} + X_2^- \rightarrow [M(bpy)_3]^{3+} + 2X^- \qquad (19)$$

couples are well noted for their very large self-electron exchange rate constants (in the range 10^8–10^{10} M^{-1} s^{-1}).[56,57] The implication is that there is a significant barrier to the transformation of neutral OH(aq) to the negatively charged OH^-(aq), i.e. to the occurrence of electron transfer.

In this context, it is germane to consider the process in eq 20 in order to consider in more detail the thermodynamic features associated with the reactions of OH and the complexes cited in

$$OH(aq) + \tfrac{1}{2}H_2(g) \rightarrow OH^-(aq) + H^+(aq) \qquad (20)$$

Table I. The $\Delta S°$ value for eq 20 is estimated to be ca. −110 J/(K mol) (based upon reported thermodynamic information along with the estimate made by Berdinkov and Bazhin of −84 J/(K mol) for the entropy of hydration of OH(g) to OH(aq)).[58–60] Electron-transfer processes involving the positively charged bipyridyl complexes as in eq 4 are anticipated to exhibit negative values of $\Delta S°$ (ca. −15 to −50 J/(K mol)) whereas for $[IrCl_6]^{3-}$, $[Fe(CN)_6]^{4-}$, and $[Fe(bpy)(CN)_4]^{2-}$, where electron transfer is realized, the entropic values are positive (ca. 15 to 150 J/(K mol)): in all instances, the corresponding enthalpies are exothermic (ca. −60 to −110 kJ/mol) with no discernible reactivity trend. While overall entropies and enthalpies represented but one contribution to activation processes for electron transfer, the negative $\Delta S°$ values for the tris(bipyridyl) complexes are one indication of a barrier to net charge exchange, and mechanistically one perceives substantial solvent reorganization around positively charged ions prior to the transformation of the neutral OH group to the hydroxide anion. In this regard, one can view the OH–bipyridine adducts as potential precursors to electron transfer even though more facile channels involving ligand modification–degradation predominate in the actual disappearance of the adducts. The occurrence of the adducts for the iron(II) bipyridyl complexes may in the first instance be favored by the presence of d–π^* back-bonding (this is also expected of the hexacyano systems) and by the conversion of the hydrophobic bipyridyl ligand to a less hydrophobic hydroxyl containing entity.[61] The potential loss of the hydrophilic OH group may consequently act as one of the impediments toward subsequent electron transfer. A further clue to a barrier may be indicated by the presence of charge-transfer bands for the OH adducts of the iron triad–bipyridyl complexes in the 700–850-nm region with molar extinction coefficients in the range (0.5–2.1) × 10^3 M^{-1} cm^{-1} (Figure 1 and ref 10). On the presumption that these bands are of an intervalent character (M(II) → OH), their optical features would imply a considerable barrier to the corresponding thermal electron transfer: notably, these bands are absent for the OH-addition products for $[Co(bpy)_3]^{3+}$ (where the corresponding cobalt(IV) is unknown) and for uncoordinated bipyridine.

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Notes

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Preparation and Crystal Structure of $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$

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As a part of our continuing studies on complexes containing metal–metal bonds, we have recently shown that the $[HFe(CO)_4]^-$ anion is a very useful reagent for the synthesis of complexes containing Fe–M (M = Zn, Cd, Hg),[1] Fe–Sb,[2] and Fe–Sn[3] bonds. We are now investigating the potential use of the related metal carbonylate $[Fe_2(CO)_8]^{2-}$ in similar preparative processes, since this dianion could give rise to polymetallic chains longer than the three-membered ones reported so far. Although the initial expectations have not been fully confirmed, we obtained the anionic triangular cluster $[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]^-$ (**1**), the first triangular cluster with an Fe_2Au skeleton. The preparation and structure of **1** are reported in this paper.

Experimental Section

All solvents were dried by standard methods, and all manipulations were performed in Schlenk-type flasks under nitrogen. Elemental analyses of C, H, and N were carried out at the Institut de Bio-Organica de Barcelona. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker WP 80SY spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. The compounds $(Et_4N)_2[Fe_2(CO)_8]$[4] and $[ClAuPPh_3]$[5] were prepared as described previously.

Synthesis of $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$ (1). To a slurry of 0.44 g of $(Et_4N)_2[Fe_2(CO)_8]$ (0.74 mmol) in 80 mL of THF was added 0.36 g of $[ClAuPPh_3]$ (0.74 mmol) at room temperature. The solution became deep orange within about 1 min, and all the carbonylmetalate dissolved. After being stirred for an additional 1 h, the mixture was filtered and hexane was added dropwise to the filtrate until orange microcrystals precipitated. This product was recrystallized from acetone–hexane to give 0.57 g of $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$ (0.61 mmol, 83% yield). IR (THF, cm^{-1}): ν_{CO} stretch 2000 m, 1950 s, 1915 s, 1750 br. IR (KBr

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Table I. Crystallographic Data for $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$

chem formula	$C_{34}H_{35}AuFe_2NO_8P$	space group	$P2_1/c$ (No. 14)
a, Å	10.079 (2)	*T*, °C	20
b, Å	19.622 (4)	λ(Mo Kα), Å	0.71069
c, Å	18.743 (4)	ρ_{calcd}, g cm^{-3}	1.70
β, deg	102.82 (2)	μ, cm^{-1}	49
V, Å^3	3614 (2)	transm coeff	0.76–0.83
Z	4	*R*	0.052
fw	925.3	R_w	0.040

Table II. Atomic Coordinates (×10^5 for Au and Fe; ×10^4 for Other Atoms) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound **1**

	x	*y*	*z*	*U*(eq)[a]
Au	14927 (3)	11730 (2)	24915 (2)	50 (1)
Fe(1)	6865 (11)	14985 (7)	11062 (6)	49 (1)
Fe(2)	−11270 (10)	14890 (7)	19037 (6)	46 (1)
P	2883 (2)	746 (1)	3510 (1)	43 (1)
C(11)	4507 (7)	1185 (4)	3792 (4)	42 (3)
C(12)	5168 (8)	1272 (5)	4514 (4)	54 (3)
C(13)	6419 (9)	1591 (5)	4691 (5)	67 (4)
C(14)	7024 (9)	1819 (6)	4153 (6)	75 (5)
C(15)	6369 (9)	1750 (5)	3430 (6)	70 (4)
C(16)	5093 (8)	1437 (5)	3239 (5)	59 (4)
C(21)	2157 (7)	734 (5)	4325 (4)	46 (3)
C(22)	2320 (8)	180 (5)	4798 (4)	58 (4)
C(23)	1757 (9)	198 (6)	5407 (5)	66 (4)
C(24)	1083 (9)	770 (7)	5555 (5)	70 (4)
C(25)	916 (9)	1319 (6)	5092 (5)	73 (4)
C(26)	1457 (8)	1302 (5)	4481 (5)	59 (4)
C(31)	3341 (8)	−138 (5)	3389 (4)	46 (3)
C(32)	4623 (9)	−399 (5)	3677 (4)	63 (4)
C(33)	4911 (13)	−1078 (6)	3573 (5)	81 (5)
C(34)	3931 (15)	−1491 (6)	3178 (7)	94 (6)
C(35)	2681 (14)	−1245 (7)	2885 (8)	106 (7)
C(36)	2375 (10)	−567 (6)	2983 (6)	77 (5)
C(1)	2010 (9)	2113 (6)	1416 (5)	61 (4)
O(1)	2857 (8)	2509 (5)	1587 (4)	108 (4)
C(2)	1767 (11)	782 (6)	1077 (5)	71 (4)
O(2)	2477 (10)	341 (5)	988 (5)	136 (5)
C(3)	187 (8)	1644 (6)	156 (5)	69 (4)
O(3)	−98 (7)	1735 (5)	−458 (3)	117 (4)
C(4)	−623 (9)	2218 (6)	1284 (5)	64 (4)
O(4)	−872 (8)	2788 (4)	1123 (4)	99 (4)
C(5)	−826 (9)	841 (6)	1123 (5)	59 (4)
O(5)	−1283 (8)	346 (4)	843 (4)	93 (4)
C(6)	−2885 (9)	1594 (6)	1515 (5)	62 (4)
O(6)	−4034 (6)	1665 (5)	1287 (4)	107 (4)
C(7)	−1191 (8)	770 (6)	2501 (5)	58 (4)
O(7)	−1314 (7)	333 (4)	2882 (4)	87 (3)
C(8)	−742 (8)	2090 (5)	2653 (5)	50 (3)
O(8)	−571 (7)	2469 (4)	3127 (4)	81 (3)
N	6023 (7)	8843 (4)	1222 (4)	57 (3)
C(41)	7015 (12)	8547 (7)	1870 (6)	104 (6)
C(42)	8469 (12)	8787 (8)	1999 (8)	154 (8)
C(43)	5931 (10)	9609 (5)	1302 (6)	76 (5)
C(44)	5522 (11)	9876 (6)	1975 (6)	100 (6)
C(45)	4646 (11)	8530 (6)	1215 (7)	93 (5)
C(46)	3522 (11)	8722 (8)	606 (8)	145 (8)
C(47)	6467 (10)	8692 (6)	521 (5)	76 (5)
C(48)	6587 (11)	7957 (7)	349 (7)	115 (7)

[a] *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths and Angles for the $[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]^-$ Anion with Estimated Standard Deviations in Parentheses

	Bond Distances (Å)		
Au–Fe(1)	2.622 (1)	Au–Fe(2)	2.698 (1)
Fe(1)–Fe(2)	2.605 (2)	Au–P	2.264 (2)
Fe(1)–C(1)	1.796 (10)	Fe(1)–C(2)	1.786 (12)
Fe(1)–C(3)	1.764 (9)	Fe(1)–C(4)	2.011 (11)
Fe(1)–C(5)	2.002 (10)	Fe(2)–C(4)	1.979 (11)
Fe(2)–C(5)	2.010 (11)	Fe(2)–C(6)	1.772 (9)
Fe(2)–C(7)	1.811 (11)	Fe(2)–C(8)	1.809 (9)
	Bond Angles (deg)		
Fe(1)–Au–Fe(2)	58.6 (1)	Fe(1)–Au–P	157.4 (1)
Au–Fe(1)–Fe(2)	62.2 (1)	Fe(2)–Au–P	142.8 (1)
Au–Fe(2)–Fe(1)	59.2 (1)	Fe(2)–Fe(1)–C(1)	112.6 (3)
Au–Fe(1)–C(1)	78.4 (3)	Fe(2)–Fe(1)–C(2)	121.5 (4)
Au–Fe(1)–C(2)	77.4 (3)	Fe(2)–Fe(1)–C(3)	120.1 (3)
Au–Fe(1)–C(3)	174.9 (4)	Fe(2)–Fe(1)–C(4)	48.7 (3)
Au–Fe(1)–C(4)	94.4 (3)	Fe(2)–Fe(1)–C(5)	49.7 (3)
Au–Fe(1)–C(5)	84.1 (2)	Fe(1)–Fe(2)–C(4)	49.8 (3)
Au–Fe(2)–C(4)	92.9 (3)	Fe(1)–Fe(2)–C(5)	49.4 (3)
Au–Fe(2)–C(5)	82.0 (2)	Fe(1)–Fe(2)–C(6)	121.9 (3)
Au–Fe(2)–C(6)	173.4 (4)	Fe(1)–Fe(2)–C(7)	119.0 (3)
Au–Fe(2)–C(7)	74.6 (3)	Fe(1)–Fe(2)–C(8)	112.6 (3)
Au–Fe(2)–C(8)	79.1 (3)	Fe(1)–C(4)–Fe(2)	81.5 (4)
Fe(1)–C(5)–Fe(2)	81.0 (4)		

pellet, cm^{-1}): 2025 w, 1955 s, 1900 br, 1760 s, 1750 s. $\delta(^{31}P) = 51.0$ ppm, relative to H_3PO_4 (35 °C, THF). Anal. Calcd for $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$: C, 44.14; H, 3.78; N, 1.51. Found: C, 44.18; H, 3.61; N, 1.46.

Determination of the Crystal Structure of $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$ (1). Dark red, irregular tablets were obtained by diffusion of hexane into an acetone solution of **1**. A crystal ca. 0.35 × 0.15 × 0.15 mm was sealed in a glass capillary. Intensity measurements were performed on a Stoe-Siemens four-circle diffractometer in profile-fitting mode[6] using monochromated Mo Kα radiation. Of 7624 reflections to $2\theta_{max} = 50°$, 6317 were unique ($R_{int} = 0.021$) and 4299 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its author, Prof. G. M. Sheldrick). An absorption correction based on ψ-scans were applied, with transmission factors of 0.76–0.83. Cell constants were refined from 2θ values of 54 reflections in the range 20–22°.

The structure was solved by the heavy-atom method and subjected to full-matrix anisotropic least-squares refinement on *F*. H atoms were included at calculated positions with isotropic temperature factors 1.2 times those of the attached C carbons and were refined by using a riding model. The final *R* value was 0.052, with $R_w = 0.040$ (weighting scheme $w^{-1} = \sigma^2(F) + 0.000175F^2$; 424 parameters; $S = 1.4$; maximum Δ/σ in final cycle 0.002; maximum $\Delta\rho = 1.1$ e Å^{-3} near Au).

For a summary of crystal data, see Table I. Final atomic coordinates are presented in Table II, with selected bond lengths and angles in Table III.

Results

When $[ClAuPPh_3]$ is allowed to react with solid $(Et_4N)_2[Fe_2(CO)_8]$ in THF in a 2:1 molar ratio, the solution becomes deep orange and the carbonylmetalate is quickly dissolved. After a short time, orange-brown microcrystalline crystals can be isolated by addition of hexane. The same product is also obtained from a 1:1 molar ratio, although in this case no excess of the starting gold compound remains in solution (monitored by ^{31}P NMR), indicating that the stoichiometry of the reaction is 1:1. Solutions of the compound show a complex spectrum in the CO stretching region consistent with a product containing both terminal and bridging carbonyl groups. It is notable that this IR spectrum is similar to that reported for the $[HFe_2(CO)_8]^-$ anion.[7] The ^{31}P NMR spectrum has a single peak at room temperature, and elemental analyses suggested the formula $(NEt_4)[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]$. In order to confirm the structure of this complex, an X-ray crystal structure determination was carried out.

Discussion

A view of the anion with the atomic numbering is shown in Figure 1. The structure of **1** can be regarded as derived from that of $[HFe_2(CO)_8]^-$ by replacing the hydride by the gold atom of the $AuPPh_3$ moiety to give a triangular Fe_2Au unit. This substitution supports once more the analogy between H and $AuPPh_3$.[8] The Fe–Au bond distances are 2.622 (1) (Fe(1)–Au) and 2.698 (1) Å (Fe(2)–Au). Although no simple Fe_2Au triangular cluster was previously known, in several large clusters there is a gold atom bridging an Fe–Fe bond,[9] and the Au–Fe bond

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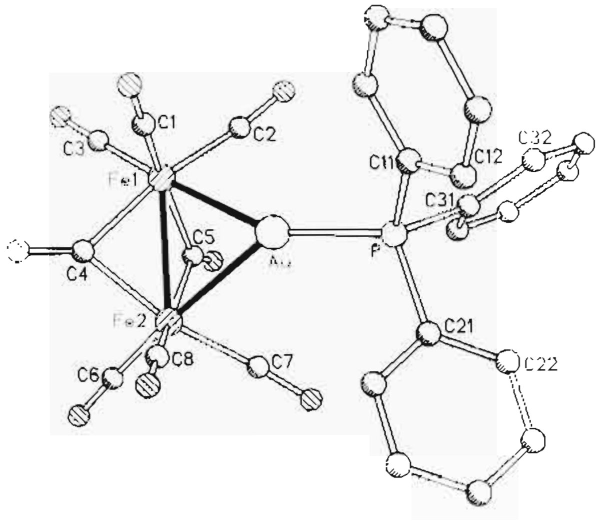

Figure 1. Molecular structure and atom-numbering scheme of the $[Fe_2(CO)_8(\mu\text{-}AuPPh_3)]^-$ anion.

distances are in the range 2.659–2.717 Å (the average of nine experimental distances is 2.68 (2) Å). Two carbonyl ligands also bridge the two iron atoms, the Fe–Fe distance of 2.605 (2) Å being midway between that found in the $[HFe_2(CO)_8]^-$ (2.521 (1) Å)[7] and its parent $[Fe_2(CO)_8]^{2-}$ (2.787 (2) Å).[10] It should be noted that the coordination about Fe is not strictly octahedral, since the terminal carbonyl groups are not collinear with the bridging atoms; e.g., C(1)–Fe(1)–C(5) = 160.1 (4)°. The bridging CO groups are situated closer to the Fe–Fe bond than they would be if the angles were 180°. A similar feature was observed in the species $[HFe_2(CO)_8]^{-7}$ and $[Fe_2(CO)_9]$.[11]

Acknowledgment. Financial support of this work was generously provided by CICYT (Spain) (Project PB84-0920) and by the Fonds der Chemischen Industrie (Frankfurt, West Germany). X-ray intensity measurements were carried out at the Institut fur Anorganische Chemie, University of Göttingen, West Germany.

Registry No. 1, 123752-66-9; $[ClAuPPh_3]$, 14243-64-2; $(Et_4N)_2[Fe_2(CO)_8]$, 26024-88-4; Fe, 7439-89-6; Au, 7440-57-5.

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) (4 pages); a listing of structure factors (Table S4) (21 pages). Ordering information is given on any current masthead page.

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Model Systems for Initial Stages in Oxidative-Addition Reactions. Theoretical Investigation of η^1 and η^2 Coordination of F_2 and H_2 to $PtCl_4^{2-}$ and $Cr(CO)_5$

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There is considerable interest in the bonding of dihalogens and H_2 to transition metals, because of its relevance to homogeneous catalysis and because X_2 complexes (X = H, halogen) may serve as models for intermediates formed during early stages of oxidative-addition reactions.[1-3] Van Koten et al.[1] reported the first example of a complex in which the highly reactive halogen I_2 is coordinated to a transition metal. They synthesized the square-pyramidal organoplatinum(II) compound $[Pt^{II}I\{C_6H_3(CH_2NMe_2)\text{-}o,o'\}(\eta^1\text{-}I_2)]$ (**1**), in which the iodine molecule interacts with the platinum d^8 center in the η^1-coordination mode.

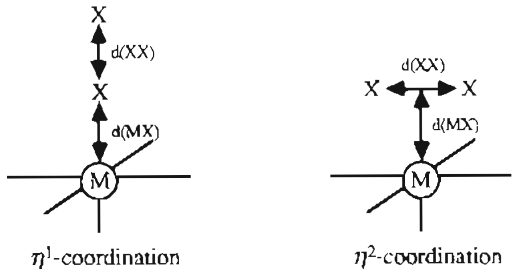
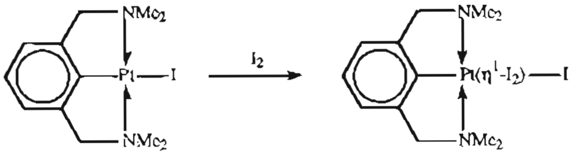
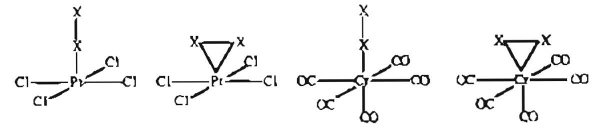


Figure 1. Geometry parameters $d(M-X)$ and $d(X-X)$. For all Pt complexes, first-order relativistic effects[21] are taken into account in determining the optimum geometry. However, the analysis of the bonding mechanism (see tables) is purely nonrelativistic.



2 **1**

In this work we present the first theoretical study of η^1 coordination of X_2 to a d^8 Pt center, using a density-functional MO-LCAO method commonly referred to as the Hartree–Fock–Slater (HFS) method.[4-8] The purpose of this study is to understand why I_2 coordinates in a monohapto fashion to $[Pt^{II}I\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**2**). We present results of HFS calculations on the model complex $PtCl_4^{2-}$ (D_{4h} symmetry) (**3**) and the monohapto (**4**) and dihapto (**5**) complexes of **3** with F_2. The nodal structure of the frontier orbitals ($3\sigma_u$ (σ^*) of F_2 and $2e_{1g}$ (Pt $5d_\pi$ –Cl $3p_\pi$) of $PtCl_4^{2-}$) is shown to play a key role in determining the preference for end-on coordination. As will be explained, it is important for the stability of a complex such as **1** that the platinum d^8 center is embedded in a rigid square-planar structure that (in good approximation) keeps its geometry fixed[1] as the iodine coordinates to it. In contrast to the η^1 coordination found in **1**, it is known that H_2 coordinates side-on to $Cr(CO)_5$. For a better understanding of the factors that influence the bonding in **1** and for comparison with the literature,[9-11] calculations are



X = F	4	5	9	10
X = H	6	7	11	12

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