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$[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{PbPh_3\}]$: A Metal Cluster Containing an Open Fe−Fe−Pb Array

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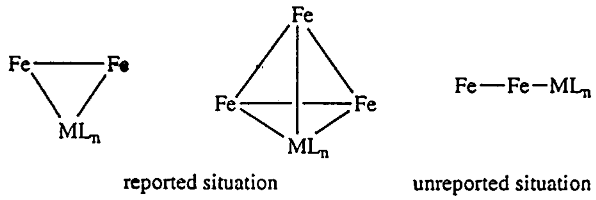
The reaction of $[PPh_4]_2[Fe_3(CO)_{11}]$ with $ClPbPh_3$ in tetrahydrofuran in the presence of $TlBF_4$ yields the new cluster $[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{PbPh_3\}]$, which exhibits an open Fe−Fe−Pb arrangement for the first time.

Introduction

The reaction of iron carbonyl anions containing at least two metal−metal-bonded iron atoms with cationic ML_n^+ fragments invariably leads to species in which the metal fragment appears to bridge edges or faces of the resulting polyhedra (Chart 1). Iron compounds of this type include those containing Au,[1] Ag,[2] Cu,[3] Hg,[4] In,[5] Tl,[6] Bi,[7] Sn,[8] and Pb[9−13] atoms. Remarkably, despite numerous efforts,[14] no report of metal clusters displaying open Fe−Fe−M arrays has been published to date. In this paper we describe the synthesis and structural characterization of $[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{PbPh_3\}]$ (**1**), which exhibits a Fe_3Pb spiked triangular metal skeleton and provides the first example of a compound showing an almost linear Fe−Fe−Pb array, and the analogous tin complex, $[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{SnPh_3\}]$ (**2**). It is worth noting that closely analogous compounds of Ru and Os have been reported in the past. These include $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1:\eta^2\text{-PhC=C(H)Ph}\}(SnPh_3)(CO)_7]$, for which two isomers have been crystallographically characterized,[15] and two similar osmium/tin compounds, $[Os_3(\mu\text{-}H)_2(CO)_{10}(SnMe_3)_2]$[16] and $[Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)]$.[17]

Chart 1



Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of prepurified nitrogen with standard Schlenk techniques. Solvents were distilled appropriately before use. Elemental analyses of C and H were carried out at the Institut de Bio-Orgànica de Barcelona. Infrared spectra were recorded in thf solutions on an FT-IR 520 Nicolet

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(6) See for example: (a) Cassidy, J. M.; Whitmire, K. H. *Inorg. Chem.* **1989**, *28*, 1432. (b) Whitmire, K. H.; Cassidy, J. M.; Rheingold, A. L.; Ryan, R. R. *Inorg. Chem.* **1988**, *27*, 1347.

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Table 1. Crystallographic Data for Complex 1

$[C_{24}H_{20}P][C_{29}H_{15}Fe_3O_{11}Pb]$
fw = 1253.57
cryst system: triclinic
space group: $P\bar{1}$
$a = 11.676(3)$ Å
$b = 11.974(4)$ Å
$c = 18.071(5)$ Å
$\alpha = 82.10(2)°$
$\beta = 87.52(2)°$
$\gamma = 88.44(2)°$
$V = 2500(1)$ Å^3
$Z = 2$
$D_{calcd} = 1.666$ g cm^{-3}
$F(000) = 1232$
μ(Mo Kα) = 43.02 cm^{-1}
max, min transm factors = 1.00−0.7101
no. of variables = 624
GOF^a = 1.05
$R(F_o)^b = 0.0371$
$R(F_o)^c = 0.0503$

^{a} GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

spectrophotometer. Electrospray and FAB mass spectra were recorded using a Fisons VG Quattro double quadrupole mass spectrometer in the negative ion mode. $[PPh_4]_2[Fe_3(CO)_{11}]$ was prepared according to the published method.[18] $ClPbPPh_3$ (Johnson Mathey) and $ClSnPPh_3$ (Strem) were used as received. The detailed methodology employed for cyclic voltammetry studies has been outlined elsewere.[19]

Preparation of $[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{EPh_3\}]$ (E = Pb (1), Sn (2)). To a suspension of $[PPh_4]_2[Fe_3(CO)_{11}]$ (0.49 g, 0.42 mmol, in 20 mL of thf) at −10 °C was added 0.20 g, 0.42 mmol, of $ClPbPh_3$ and 0.12 g, 0.42 mmol, of $TlBF_4$. The solution became deep green in a few minutes. After being stirred for an additional 1 h, the mixture was filtered and 10 mL of diethyl ether was added. After cooling overnight to ensure the total precipitation of the salts, the mixture was filtered off and the solvents were removed in vacuo. The green residue was extracted with 10 mL of CH_2Cl_2, and 5 mL of hexane was added. When the mixture stood at −30 °C for at least 12 h, green crystals were formed. Yield: 0.33 g, 62% based on the starting $[PPh_4]_2[Fe_3(CO)_{11}]$. Anal. Calcd for $C_{53}H_{35}Fe_3O_{11}PPb$: C, 50.77; H, 2.79. Found: C, 50.11; H, 2.89. IR (in thf): ν(CO) 2057 (m), 2011 (s), 1983 (vs), 1823 (w), 1792 (w). FABS (M^-) *m/e* Calcd for $C_{29}H_{15}Fe_3O_{11}Pb$, 915; found, 915.7. ESMS (M^-): *m/e* Found, 914.5.

A similar procedure was used to prepare the tin derivative **2**, although a longer reaction time (2 h) was needed. Anal. Calcd for $C_{53}H_{35}Fe_3O_{11}PSn$: C, 54.63; H, 3.01. Found: C, 54.68; H, 3.11. IR (in thf): ν(CO) 2056 (m), 2010 (s), 1980 (vs), 1823 (w), 1792 (w). ESMS (M^-): *m/e* Calcd for $C_{29}H_{15}Fe_3O_{11}Sn$, 827; found, 826.1.

X-ray Data Collection, Structure Determination, and Refinement for $[PPh_4][Fe_3(CO)_9(\mu\text{-}CO)_2\{PbPh_3\}]$ (1). A crystal of dimensions 0.15 × 0.22 × 0.30 mm was used for data collection on an Enraf Nonius CAD4 diffractometer at room temperature using the $\theta-2\theta$ scan technique. Crystallographic data are summarized in Table 1. A total of 12060 unique reflections were measured with θ in the range 3−28°; 7924 of them, having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined first by full-matrix least-squares procedures with isotropic thermal parameters and then by blocked full-matrix least-squares procedures with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions and refined by "riding" on the corresponding carbon atoms, isotropically. All calculations were carried out on the Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[20] An X-ray analysis has been carried out also for **2**.[21]

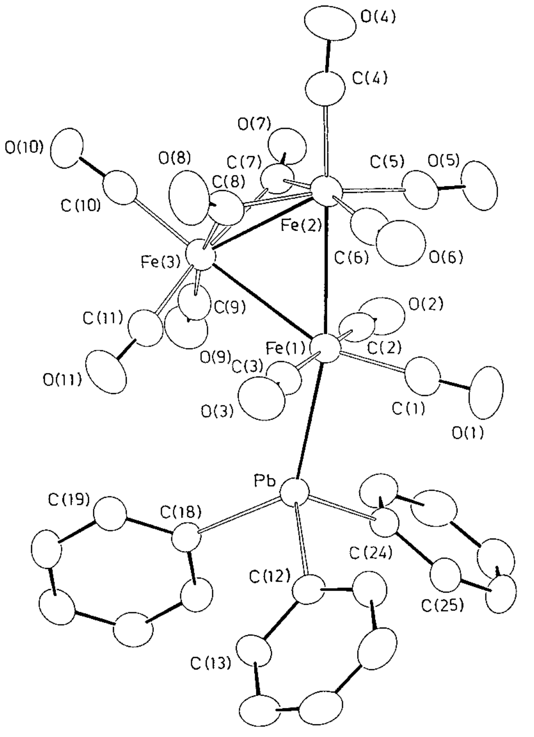

Figure 1. ORTEP view of the structure of the anionic cluster of **1** with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

Results and Discussion

$[PPh_4]_2[Fe_3(CO)_{11}]$ reacted in a few minutes with 1 mol equiv of $ClPbPh_3$ and $TlBF_4$, in tetrahydrofuran at −10 °C. After being up, green crystals of $[PPh_4][Fe_3(CO)_{11}\{PbPh_3\}]$ (**1**) were obtained from CH_2Cl_2/hexane. A single-crystal X-ray study of compound **1** was carried out, and its structure is shown in Figure 1 together with the atom-numbering scheme. Selected bond distances and angles are listed in Table 2. The most striking feature in this structure is the presence of a terminal $PbPh_3$ group attached to one iron atom of the Fe_3 triangle. If the $PbPh_3$ group is treated as a $[PbPh_3]^-$ ligand, the structure of **1** is essentially identical to one of the structurally characterized isomers of $[Fe_3(CO)_{11}(PPh_3)]$.[22] The value of the Pb−Fe(1)−Fe(2) angle is 164.3(1)°, and the Pb atom deviates 0.3130(6) on the same plane. The geometry about the lead atom is a distorted tetrahedron, according to the Fe−Pb−C and C−Pb−C angles (see Table 2). The Fe−Pb bond length, 2.651(1) Å, is comparable to the shortest ones found in $[NEt_4]_2[Pb\{Fe(CO)_4\}_4]$[9] and in $[Fe_2(CO)_8(PbEt_2)_2]$[10] but somewhat longer than those reported for the spiro cluster $[Pb\{Fe_2(CO)_8\}_2]$[12] and for $[NEt_4]_2[Pb\{Fe(CO)_4\}_3]$[13]. Another remarkable feature of **1** is the presence of two carbonyl groups bridging the Fe(2)−Fe-

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(21) Crystals of **2** resulted in being isostructural with those of **1**. Crystal data for **2**: $[C_{24}H_{20}P][C_{29}H_{15}Fe_3O_{11}Sn]$, $M = 1165.06$, triclinic, space group $P\bar{1}$, $a = 11.615(4)$ Å, $b = 11.944(3)$ Å, $c = 17.933(6)$ Å, $\alpha = 82.05(2)°$, $\beta = 87.62(2)°$, $\gamma = 88.51(2)°$, $V = 2461(1)$Å^3, $Z = 2$, $D_c = 1.572$ g cm^{-3}, $F(000) = 1168$, μ(Mo Kα) = 14.61 cm^{-1}. Because of the poor quality of the crystals, accurate results of the structure determination were not obtained. The only important structural feature to mention is the Fe(1)−Sn bond distance: 2.586(3) Å.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

Fe(1)–Fe(2)	2.684(1)	Fe(3)–C(11)	1.784(7)
Fe(1)–Fe(3)	2.700(1)	Pb–C(12)	2.248(6)
Fe(2)–Fe(3)	2.577(1)	Pb–C(18)	2.258(5)
Pb–Fe(1)	2.651(1)	Pb–C(24)	2.257(5)
Fe(1)–C(1)	1.773(7)	Fe(1)–C(2)	1.783(7)
Fe(1)–C(3)	1.798(7)	Fe(2)–C(4)	1.783(7)
Fe(2)–C(5)	1.813(8)	Fe(2)–C(6)	1.815(8)
Fe(2)–C(7)	2.024(6)	Fe(2)–C(8)	1.920(8)
Fe(3)–C(7)	2.013(6)	Fe(3)–C(8)	1.990(7)
Fe(3)–C(9)	1.797(6)	Fe(3)–C(10)	1.801(7)
Fe(3)–C(11)	1.784(7)		
Fe(2)–Fe(1)–Fe(3)	57.2(1)	Fe(2)–C(6)–O(6)	174.7(7)
Fe(1)–Fe(2)–Fe(3)	61.7(1)	Fe(2)–C(7)–O(7)	140.5(5)
Fe(1)–Fe(3)–Fe(2)	61.1(1)	Fe(2)–C(8)–O(8)	142.2(6)
Pb–Fe(1)–Fe(2)	164.3(1)	Fe(3)–C(7)–O(7)	140.1(5)
Pb–Fe(1)–Fe(3)	108.5(1)	Fe(3)–C(8)–O(8)	135.4(6)
Fe(1)–C(1)–O(1)	178.4(7)	Fe(3)–C(9)–O(9)	174.7(6)
Fe(1)–C(2)–O(2)	175.7(6)	Fe(3)–C(10)–O(10)	176.9(6)
Fe(1)–C(3)–O(3)	176.0(6)	Fe(3)–C(11)–O(11)	175.7(6)
Fe(2)–C(4)–O(4)	174.6(7)	Fe(2)–C(7)–Fe(3)	79.4(2)
Fe(2)–C(5)–O(5)	177.0(7)	Fe(2)–C(8)–Fe(3)	82.4(3)
Fe(1)–Pb–C(24)	109.3(1)	Fe(1)–Pb–C(18)	128.9(1)
Fe(1)–Pb–C(12)	113.4(1)	C(18)–Pb–C(24)	98.0(2)
C(12)–Pb–C(24)	104.0(2)	C(12)–Pb–C(18)	100.0(2)

(3) edge, in clear contrast with the geometries adopted by the $[Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}ML_n\}]^-$ (M = Au, Hg) species, which exhibit only one carbonyl group bridging the Fe–Fe edge subtended by the ML_n fragment.[1c,19] All these structural differences prompted us to carry out a theoretical analysis based on extended Hückel molecular orbital calculations[23] and using standard atomic parameters from the literature.[24] The only simplification adopted in the model molecules used for the calculations is the substitution of the phenyl groups by hydrogen atoms.

We have analyzed the interaction between the fragments $[Fe_3(CO)_9(\mu\text{-}CO))(\mu_3\text{-}CO)]^{2-}$ and $[AuPPh_3]^+$ or $[PbPh_3]^+$, respectively, and the results can be summarized as follow:

(i) From the overlap population data the best orbital interactions occur when the gold fragment bridges an iron–iron edge. In the lead compound the best results are achieved when the lead fragment is bonded in a terminal manner.

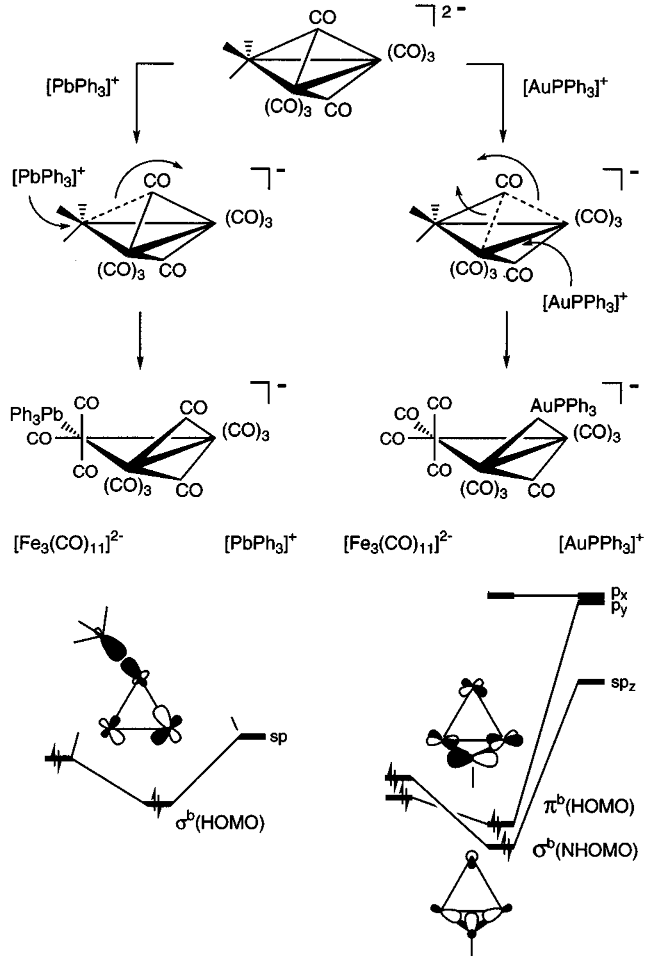
(ii) The interaction of the gold fragment with the iron dianion in a bridge form leads to a reduction of the overlap population between the carbon of the μ_3-CO ligand and the two iron atoms bonded to the $[AuPPh_3]^+$ fragment.

(iii) The interaction of the $[PbPh_3]^+$ as a terminal fragment gives a slight increase in the overlap population between the carbon of the μ_3-CO group and the two iron atoms bonded to the CO bridge ligand.

These results indicate the tendency of the μ_3-CO group to break two Fe–C bonds in the gold case, thus becoming a terminal carbonyl. In contrast, for lead, only one bond is broken resulting in a μ-CO ligand. In both cases a rearrangement of carbonyls is needed to give the most stable geometry of the final products.

The orbital diagram (Scheme 1) could explain the different electrochemical behavior observed for the two types of clusters. In 0.1 M $CH_2Cl_2{\cdot}Bu_4NPF_6$ medium the $[Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}ML_n\}]^-$ species exhibit a well-defined reversible wave around +0.3 V vs SCE. Controlled potential coulometry indicated that one electron is exchanged, and EPR spectra of the resulting solution can be observed.[19] In the same conditions compounds **1** and **2** show an irreversible one-electron oxidation process at 0.30 and 0.25 V vs SCE, respectively. The EPR spectra of the oxidized forms suggest the destruction of the cluster. It can be concluded that the loss of one electron from the HOMO (π bonding character) in the former compounds leaves untouched the σ^b molecular orbital (NHOMO), whereas, in the latter case, the electron is removed from the HOMO (σ bonding character) implying the facile breaking of the Fe–Pb or Fe–Sn bond.

Scheme 1



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Supporting Information Available: Tables of final values of atomic coordinates and *U* values for the non-hydrogen atoms, calculated coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, and complete bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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