Anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ as Building Blocks for the Synthesis of Mixed-metal Clusters. Crystal Structure of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Cu(PPh_3)\}]$ *

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Treatment of the salt $[NEt_4]_2[Fe_2(CO)_8]$ with a tetrahydrofuran solution of the complex $[CuI(PPh_3)]$ gives an anionic orange-red cluster $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Cu(PPh_3)\}]$ **1** which is air- and thermally unstable. When $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ and $[MX(PPh_3)]$ (M = Cu, Ag or Au) are allowed to react in the presence of $TlBF_4$, the new neutral clusters $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}M(PPh_3)\}]$ (M = Cu, **2**; Ag, **3**; or Au, **4**) are obtained in *ca.* 80% yield. These relatively air-stable clusters have been characterized by IR and ^{31}P NMR spectroscopy and the structure of **2** has been established by single-crystal X-ray diffraction studies: triclinic, space group $P\bar{1}$, with a = 11.081(3), b = 12.190(3), c = 15.808(4) Å, α = 76.41(2), β = 87.03(2), γ = 80.48(2)°, Z = 2 and R = 0.05. The basic skeleton consists of the first example of a Fe_2Cu triangle. In this, the iron–iron bond is bridged by a phosphido and a carbonyl group.

We have recently described the synthesis and X-ray crystal structure determination of the compound $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Au(PPh_3)\}]$.[1] In order to extend this class of derivatives to copper and silver, in this paper we report the synthesis of the complex $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Cu(PPh_3)\}]$ and the related new derivatives $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}M(PPh_3)\}]$ (M = Cu, Ag or Au).

Results and Discussion

Reaction of $[NEt_4]_2[Fe_2(CO)_8]$ with $[CuI(PPh_3)]$ in tetrahydrofuran (thf) leads to the trinuclear cluster $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Cu(PPh_3)\}]$ **1** along with NEt_4I. This compound can be manipulated in the air only for a few minutes. The analogous silver derivative could not be neither isolated nor characterized because it decomposed in solution even at −40 °C. The formation of compound **1** can be monitored by IR spectroscopy which shows a ν(CO) pattern almost superimposable on that reported for $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Au(PPh_3)\}]$[1] (Table 1). The remarkable instability of **1** as well as the analogous silver derivative prompted us to synthesise metal cluster compounds containing a μ-diphenylphosphido group bridging the iron–iron bond because this ligand appears to inhibit cluster fragmentation.[2] Thus, the reaction of the salt $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ with the cationic $[M(PPh_3)]^+$ (M = Cu, Ag or Au) species affords the neutral air-stable complexes $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}M(PPh_3)\}]$ (M = Cu, **2**; Ag, **3**; or Au, **4**) (Table 1). The ^{31}P NMR spectra of **2**–**4** in thf at −50 °C showed two resonances assigned to the phosphorus atoms of the $\mu\text{-}PPh_2$ and the $M\text{-}PPh_3$ groups respectively, coupled to each other. For complex **3** these signals are split into two doublets due to coupling with ^{107}Ag and ^{109}Ag. The ^{57}Fe Mössbauer spectrum of **4** shows the expected quadrupole doublet (0.996 mm s^{-1}), and the isomer shift (0.32 mm s^{-1}, relative to iron foil) corresponds approximately to a 1− charge, as found for the closely related compounds $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}HgMo(CO)_3(\eta\text{-}C_5H_5)\}]$[3] and $[N(PPh_3)_2]_2[(OC)_4FeHgFe(CO)_4]$.[4]

The molecular structure of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Cu(PPh_3)\}]$ **2** is shown in Fig. 1, while selected bond and angle parameters are listed in Table 2. The basic skeleton consists of a Fe_2Cu triangle. In this, the iron–iron bond appears to be almost symmetrically bridged by a carbonyl ligand and a phosphido group. Both iron atoms attain an 18-electron configuration with the PPh_2 group functioning as a three-electron donor. The co-ordination about each Fe is approximately octahedral and the iron–copper bond lengths, 2.481(1) and 2.509(1) Å, are shorter than those found in the iron–copper clusters $[Fe_3Cu(\mu\text{-}CMe)(CO)_{10}(PPh_3)]$ [2.564(1) and 2.494(1) Å][5] and $[Fe_4Cu(CO)_{13}(PPh_3)]^-$ [2.562(5), 2.526(5) and 2.579(5) Å].[6] The iron–iron distance, 2.627(1) Å, is in good agreement with that found between the bridged iron atoms in $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ [2.623(2) Å].[7]

Experimental

All manipulations were performed under an atmosphere of prepurified N_2 with standard Schlenk techniques and all solvents were distilled from appropriate drying agents. Elemental analyses of C, H and N were carried out at the Institut de Bio-Orgànica de Barcelona. Infrared spectra were recorded in thf solutions on a Perkin-Elmer 1330 spectrophotometer, $^{31}P\text{-}\{^1H\}$ NMR spectra on a Bruker WP 80SY spectrometer. The compounds $[NEt_4]_2[Fe_2(CO)_8]$,[8] $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$,[3] $[AuCl(PPh_3)]$,[9] $[CuI(PPh_3)]$[10] and $[AgI(PPh_3)]$[11] were prepared as described previously.

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* μ-Carbonyl-1:2κ²*C*-hexacarbonyl-1κ³*C*, 2κ³*C*-μ-diphenylphosphido-1:2κ²*P*-triphenylphosphine-3κ*P*-*triangulo*-copperdiiron (2*Cu–Fe*)(*Fe–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical[a] data and physical parameters of complexes

Compound	Analysis (%) C	H	N	$\nu(CO)^b$/cm^{-1}	$\delta[P(\mu\text{-}PPh_2)]^c$ (ppm)	$\delta[P(MPPh_3)]$ (ppm)	^3J(P–P)/ Hz
1	50.30	4.40	1.75	2005m, 1950vs, 1900s, 1740w	—	−141.3	—
	(52.25)	(3.20)	(1.80)				
2	54.40	3.60		2030m, 2000vs, 1965s, 1930s, 1785m	−17.7	−139.8	14
	(54.25)	(3.05)					
3[d]	51.75	2.85		2030m, 2000vs, 1965s, 1940s, 1780m	1.3	−127.2	11.5
	(51.50)	(2.90)					
4	46.55	2.55		2030m, 2010vs, 1970s, 1950(sh), 1940(sh), 1780m	−10.4	−88.2	24.5
	(46.65)	(2.65)					

[a] Required values are given in parentheses. [b] In thf solution. [c] Relative to $P(OMe)_3$. [d] Other NMR parameters: $^1J(^{109}Ag\text{–}P)$ = 496, $^1J(^{107}Ag\text{–}P)$ = 430, $^2J(^{109}Ag\text{–}P)$ = 15 and $^2J(^{107}Ag\text{–}P)$ = 13 Hz.

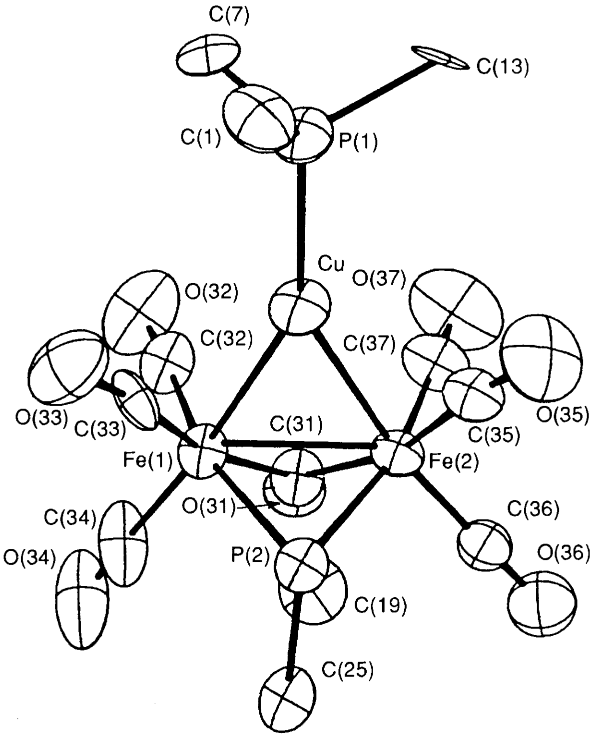

Fig. 1 Molecular structure of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Cu(PPh_3)\}]$ **2** including the atom-numbering scheme. Phenyl groups have been omitted for clarity.

Table 2 Principal bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **2**

Fe(1)–Cu	2.481(1)	C(35)–Fe(2)	1.815(7)
Fe(2)–Cu	2.509(1)	C(36)–Fe(2)	1.773(7)
P(1)–Cu	2.218(2)	C(37)–Fe(2)	1.792(8)
Fe(2)–Fe(1)	2.627(1)	C(31)–O(31)	1.183(8)
P(2)–Fe(1)	2.233(2)	C(32)–O(32)	1.170(8)
C(31)–Fe(1)	1.979(6)	C(33)–O(33)	1.200(8)
C(32)–Fe(1)	1.766(6)	C(34)–O(34)	1.116(12)
C(33)–Fe(1)	1.749(6)	C(35)–O(35)	1.141(9)
C(34)–Fe(1)	1.799(9)	C(36)–O(36)	1.147(8)
P(2)–Fe(2)	2.222(2)	C(37)–O(37)	1.145(11)
C(31)–Fe(2)	1.966(7)		
Fe(2)–Cu–Fe(1)	63.5(1)	C(31)–Fe(1)–P(2)	80.8(2)
P(1)–Cu–Fe(1)	148.5(1)	Fe(1)–Fe(2)–Cu	57.7(1)
P(1)–Cu–Fe(2)	147.9(1)	P(2)–Fe(2)–Cu	87.3(1)
Fe(2)–Fe(1)–Cu	58.7(1)	P(2)–Fe(2)–Fe(1)	54.1(1)
P(2)–Fe(1)–Cu	87.8(1)	C(31)–Fe(2)–Cu	94.8(2)
P(2)–Fe(1)–Fe(2)	53.7(1)	C(31)–Fe(2)–Fe(1)	48.5(2)
C(31)–Fe(1)–Cu	95.4(2)	Fe(2)–P(2)–Fe(1)	72.3(1)
C(31)–Fe(1)–Fe(2)	48.0(2)	Fe(2)–C(31)–Fe(1)	83.5(3)

Preparation of $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)_2\{\mu\text{-}Cu(PPh_3)\}]$ **1**.—To a suspension of $[NEt_4]_2[Fe_2(CO)_8]$ (0.44 g, 0.74 mmol) in thf (80 cm^3) was added $[CuI(PPh_3)]$ (0.33 g, 0.74 mmol) at −40 °C. The resulting solution became deep orange and all the carbonylmetalate dissolved. The solution was allowed to reach −20 °C after which the salts were filtered off and the solvent reduced to 10 cm^3. Cold diethyl ether (10 cm^3) was then added to the filtrate and red microcrystals formed upon cooling the solution to −35 °C for at least 12 h. After filtration, the microcrystals were washed with a small amount of diethyl ether and dried under vacuum. Yield: 0.40 g, 70%.

Preparation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}M(PPh_3)\}]$ (M = Cu, **2**: Ag, **3** *or* Au **4**).—Details of the synthesis of compound **2** apply also to **3** and **4**. The compounds $[CuI(PPh_3)]$ (0.31 g, 0.69 mmol), $TlBF_4$ (0.20 g, 0.69 mmol), and $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ (0.43 g, 0.69 mmol) were stirred in thf (80 cm^3) for 30 min at −20 °C. The orange solution obtained, after filtration, was taken to dryness. Then the solid was extracted in toluene (40 cm^3), filtered through Celite, and taken once more to dryness. The dark red residue was dissolved in diethyl ether at room temperature and, after cooling, red microcrystals of compound **2** were formed; yield 0.45 g, 80%. Similar yields resulted for **3** and **4**.

Crystallography.—Crystal data. $C_{37}H_{25}CuFe_2P_2O_7{\cdot}0.5C_4H_{10}O$, M = 855.23, triclinic, space group $P\bar{1}$, a = 11.081(3), b = 12.190(3), c = 15.808(4) Å, α = 76.41(2), β = 87.03(2), γ = 80.48(2)°, U = 2047(2) Å^3, D_c = 1.387 g cm^{-3}, Z = 2, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 13.76 cm^{-1}, room temperature.

Data collection. A non-stable prismatic crystal was selected and mounted on a Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo-Kα radiation. Crystals decrepitated after several hours, so it was necessary to use five different ones in the data-collection process (crystal size from 0.1 × 0.1 × 0.15 to 0.08 × 0.07 × 0.1 mm). The crystallinity degree of the crystals was lost after their decrepitation. Intensities were collected overlapping the *hkl* range for each crystal. Intensities with appreciable decay measured before the decrepitation process were not considered. Different sets were scaled according to intensity-control values; equivalent intensities were emerged. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 \leqslant \theta \leqslant 16°$) and refined by the least-squares method. Intensities were collected using the ω–2θ scan technique. 5429 Reflections were measured in the range $2 \leqslant \theta \leqslant 30°$ and 5323 were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three standard reflections were measured every 2 h as orientation and intensity control and significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Table 3 Final positional coordinates (× 10^5 for Cu and Fe, × 10^4 for other atoms) of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Cu(PPh_3)\}]$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	83 721(7)	8 772(6)	73 973(6)	C(25)	7 463(5)	4 043(5)	9 023(5)
Fe(1)	91 404(7)	15 929(7)	85 799(6)	C(26)	6 648(6)	4 136(6)	9 699(5)
Fe(2)	83 368(8)	29 947(7)	71 194(6)	C(27)	6 772(8)	4 898(8)	10 202(6)
P(1)	7 954(2)	−591(1)	6 923(1)	C(28)	7 681(8)	5 531(7)	10 074(6)
P(2)	7 461(1)	2 913(1)	8 424(1)	C(29)	8 491(7)	5 487(6)	9 360(5)
C(1)	6 606(6)	−1 106(6)	7 492(4)	C(30)	8 380(6)	4 738(6)	8 822(5)
C(2)	6 535(7)	−2 243(7)	7 784(6)	C(31)	9 812(5)	2 877(5)	7 795(5)
C(3)	5 491(8)	−2 619(9)	8 243(7)	O(31)	10 715(4)	3 291(4)	7 737(4)
C(4)	4 489(8)	−1 792(9)	8 340(7)	C(32)	10 520(5)	733(6)	8 375(5)
C(5)	4 559(6)	−661(8)	8 051(5)	O(32)	11 446(5)	147(5)	8 292(5)
C(6)	5 620(6)	−295(7)	7 603(5)	C(33)	8 362(5)	435(6)	8 975(4)
C(7)	9 156(6)	−1 812(5)	7 111(5)	O(33)	7 911(5)	−373(4)	9 361(4)
C(8)	9 926(7)	−2 025(6)	7 808(6)	C(34)	9 562(7)	1 918(6)	9 567(5)
C(9)	10 846(8)	−2 972(8)	7 980(6)	O(34)	9 854(7)	2 199(6)	10 136(4)
C(10)	11 044(7)	−3 733(6)	7 423(7)	C(35)	7 070(6)	2 587(5)	6 646(4)
C(11)	10 274(8)	−3 458(7)	6 707(7)	O(35)	6 254(4)	2 453(5)	6 292(4)
C(12)	9 377(7)	−2 539(7)	6 520(6)	C(36)	7 967(6)	4 504(6)	6 791(5)
C(13)	7 629(6)	−299(5)	5 760(4)	O(36)	7 694(6)	5 476(5)	6 574(4)
C(14)	6 696(8)	−726(8)	5 447(7)	C(37)	9 333(7)	2 785(7)	6 222(5)
C(15)	6 548(9)	−496(10)	4 532(7)	O(37)	9 990(6)	2 632(7)	5 663(5)
C(16)	7 301(10)	150(11)	3 995(7)	O(38)	6 514(11)	4 853(10)	3 786(6)
C(17)	8 211(9)	624(8)	4 361(12)	C(39)	6 232(40)	4 676(73)	4 185(39)
C(18)	8 313(9)	354(8)	5 259(9)	C(40)	5 624(24)	3 391(20)	3 375(20)
C(19)	5 911(5)	2 563(5)	8 630(4)	C(41)	6 883(29)	5 264(72)	4 439(27)
C(20)	5 619(5)	1 768(5)	9 336(5)	C(42)	6 989(32)	6 509(26)	4 231(21)
C(21)	4 419(6)	1 539(6)	9 480(6)	C(39′)	14 137(33)	6 484(24)	6 255(32)
C(22)	3 515(6)	2 129(6)	8 906(6)	C(40′)	13 686(25)	6 199(20)	5 854(20)
C(23)	3 790(6)	2 951(7)	8 194(5)	C(41′)	12 563(50)	3 977(38)	5 822(26)
C(24)	4 983(5)	3 187(6)	8 039(5)	C(42′)	13 061(60)	4 759(34)	5 647(35)

Structure solution and refinement. The structure was solved by Patterson synthesis, using the SHELX 86[12] and the DIRDIF 84[13] computer programs, and refined by full-matrix least squares, with the SHELX 76 computer program.[14] The function minimized was $w(F_o - F_c)^2$, where $w = \sigma^{-2}(F_o)$; f, f' and f'' were taken from ref. 15. A difference synthesis showed an ether molecule with two atomic sites for each carbon atom. Thereby, the disorder of these atoms was assumed, with an occupancy factor of 0.5, according to the height of the peaks. The positions of the 25 H atoms were obtained from a difference synthesis and refined with an overall isotropic thermal parameter. The final R factor was 0.05 (R' = 0.05) for all observed reflections. The number of refined parameters was 525. Maximum shift/e.s.d. = 0.1; Maximum and minimum peaks in final difference synthesis 0.4 and −0.4 e Å^{-3}, respectively. Atomic coordinates are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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