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Journal of Organometallic Chemistry 598 (2000) 215–221

Synthesis, characterization and solution studies on heteronuclear iron–copper clusters containing diphosphine ligands: crystal structure of the dicluster [{Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)Cu}$_2$(dppp)]

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Received 12 July 1999; received in revised form 7 November 1999

Abstract

Treatment of dichloromethane solutions of the di-iron compound [NEt_4][$Fe_2(CO)_6$(μ-CO)(μ-PPh_2)] with one equivalent of [$Cu(NCCH_3)_4$]BF_4 at low temperatures, followed by the addition of half of an equivalent of diphosphine ligand (diphosphine = bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)isopropane (dppip), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane), produces high yields of the mixed-metal dicluster compounds [{Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)Cu}$_2$(diphosphine)]. The molecular structure of the dppp derivative has been determined by X-ray crystallography. For a 1:1:1 molar ratio of the reagents, complex mixtures have been obtained and studied by variable-temperature ^{31}P-NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Heterometallic; Clusters; Diphosphine; Copper; Gold

1. Introduction

The use of the reagents $(ClAu)_2$(diphosphine) has received some attention in the synthesis of compounds where diphosphine ligands are connecting two identical metal clusters together. We have reported recently the preparation of a series of gold–iron diclusters [{Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)Au}$_2$(diphosphine)] [2] and some other related species can be found in the literature [3].

However, the number of analogous diclusters containing copper–transition metal bonds is scarce and to the best of our knowledge only two examples have been described so far: [{Ru_4(μ_3-H)$_3(CO)_{12}$Cu}$_2$($Ph_2PCH_2CH_2PPh_2$)] [4] and [PPh_4] [{$Fe_2(CO)_8$Cu}$_2$($Cy_2PCH_2CH_2PCy_2$)] [5]. This could be because of either the unavailability of copper precursors of the $(ClCu)_2$(diphosphine) type, or the greater instability of the species formed in comparison with the gold derivatives.

To extend our studies of diclusters containing Group 11 metals, in this paper we describe first the synthesis and characterization of the copper–iron species [{Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)Cu}$_2$(diphosphine)]. Secondly, we report reactions performed in order to synthesize asymmetric dicluster species, because we failed to isolate them in our studies with gold derivatives; instead equilibrium mixtures were obtained [2]. Similar results with gold diclusters have been reported very recently by Housecroft et al. [3k].

2. Results and discussion

The related gold compounds [{Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)Au}$_2$(diphosphine)] reported recently by us [2] were synthesized by treating the [Fe_2(μ-CO)$(CO)_6$(μ-PPh_2)]$^-$ anion with the gold diphosphine complexes $(ClAu)_2$(diphosphine) in the presence of a halide abstractor. However, the non-existence of the analogous

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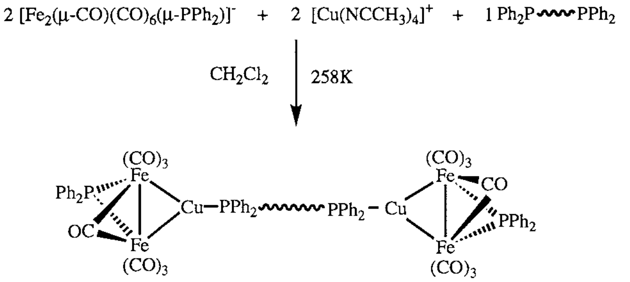
PII: S0022-328X(99)00707-X

copper precursors precluded the use of the mentioned strategy, and the synthetic route described by Salter [1] was used as an alternative.

Treatment of a CH_2Cl_2 solution of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ with an equimolar amount of $[Cu(CNCH_3)_4]BF_4$ at low temperatures followed by subsequent addition of the appropriate quantity of diphosphine ligand gave the neutral compounds $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(\text{diphosphine})]$ (diphosphine = dppm (**1**), dppip (**2**), dppe (**3**), dppp (**4**) or dppb (**5**)) as shown in Eq. (1).



1-5

(1)

Elemental analysis, IR and NMR (^{31}P, ^1H, ^{13}C) spectral data of all compounds are reported in Section 5. The molecular structure of **4** has been established by X-ray crystallography. Infrared spectra in the carbonyl stretching region show similar patterns for all compounds and are similar to those for the related compound $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CuPPh_3)]$ [7].

In the ^{31}P-NMR spectra a pair of doublets is observed for **4** and **5**, corresponding to two different phosphorus environments (PCu, PFe$_2$). For compound **2**, one doublet is observed for PFe$_2$ and the signal attributable to the phosphorus attached to the copper atom appears as a broad singlet due to the quadrupolar moment of ^{65}Cu and ^{63}Cu nuclei even at 220 K.

In the case of **1** and **3**, and similarly to that reported for the gold derivatives [2], second-order patterns are observed for the PFe$_2$ while PCu gives broad resonances that made the calculation of the coupling constants by simulation of the spectra impossible.

In order to synthesize the derivative that incorporates three Fe_2Cu cluster units analogously to the reported cluster $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_3(\text{triphos})]$ [6], the reaction with the triphosphine triphos was carried out, but unfortunately only phosphine copper derivatives were obtained and were not studied further.

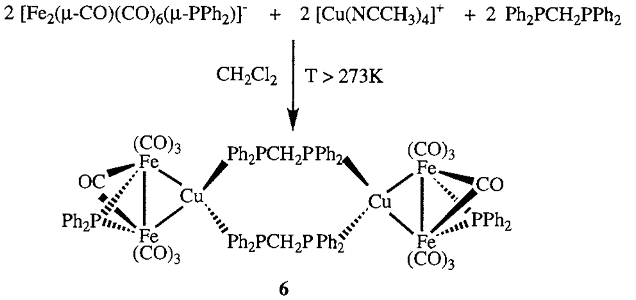
2.1. Solution studies

With the aim of investigating the possibility of the formation of Fe_2Cu(diphosphine) species that could be used in subsequent reactions to link clusters of different Group 11 metals, we studied the reactions between the relatively unstable copper–iron precursor $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu(CNCH_3)]$ (prepared in situ by addition of $[Cu(CNCH_3)_4]BF_4$ to a CH_2Cl_2 solution of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ [1]) and the diphosphine ligands in a 1:1 molar ratio. The reaction conditions were the same as described previously. Variable-temperature ^{31}P-NMR spectroscopy was used to identify the different species formed in solution. These studies confirmed that the composition of the resulting mixtures was dependent on the diphosphine nature.

For dppm a temperature-dependent behavior was detected. At 220 K, two signals are observed both in the PFe$_2$ and PCu regions of the spectrum. The resonance at 125.3 ppm (PFe$_2$) corresponds to the iron anion $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^-$ while the peak at -12.7 ppm (PCu) is assignable to the reported compound $[Cu_2(\mu\text{-}dppm)_2(NCCH_3)_2]^{2+}$ [9]. The two signals centered at 117.4 ppm (PFe$_2$) and -15.4 ppm (PCu) appear as a triplet and doublet, respectively (J(P–P) = 5 Hz) and correspond to a new compound (**6**). The integration of the upfield resonance is approximately twice that of the downfield signal. When raising the temperature, the spectra exhibit the same set of signals but a progressive intensity increase of the compound **6** with respect to the others is observed.

At temperatures above 273 K, only two broad resonances, whose chemical shifts correspond to that of the new compound (**6**), were obtained. Moreover, the process is reversible since at each temperature the mixture exhibits a particular spectrum.

On the basis of NMR data and the solution IR ν(CO) spectrum, we propose tentatively the formation of the new hexanuclear compound $[Cu_2\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}dppm)_2]$ (**6**) (Eq. (2)). However, attempts to isolate this new complex in pure form were unsuccessful (see Section 5), precluding its complete characterization.



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(2)

The upfield shifting of the phosphorus atoms of dppm by comparison with that of $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(\text{dppm})]$ (**1**) is in agreement with the increase in the coordination number of the copper atoms from three in **1** to four in **6** [8].

In conclusion, the NMR studies described here suggest that a temperature-dependent equilibrium is established (Eq. (3)) and it can be shifted to the left by lowering the temperature. This equilibrium confirms the special ability of this kind of complex to undergo dissociation processes in solution, probably as a result of the known capacity of copper to adopt three and four co-ordination. Alternatively, compound **6** can be obtained in solution by reaction of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ with previously prepared $[Cu_2(\mu\text{-}dppm)(NCCH_3)_2][BF_4]$ [9] in a 1:1 molar ratio at room temperature [10].

$$\begin{aligned} &2[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^- \\ &\quad + [Cu_2(\mu\text{-}dppm)_2(CNCH_3)_2]^{2+} \\ &\rightleftharpoons [Cu_2\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}dppm)_2]\ (\mathbf{6}) \\ &\quad + 2CH_3CN \qquad (3) \end{aligned}$$

Experiments with both dppe and dppp gave rise to completely different results. A mixture of the corresponding dicluster compound $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(diphosphine)]$ (diphosphine = dppe (**3**), dppp (**4**)), the bischelated $[Cu(diphosphine)_2]^+$ (diphosphine = dppe, dppp) and free iron anion $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^-$ has been seen to coexist in CH_2Cl_2 solution. Assigning the resonances that belong to compounds **3** and **4** and the iron anion was straightforward. The broad peaks at 7.3 for dppe and −8.3 for dppp have been assigned to the corresponding bischelated complexes $[Cu_2(diphosphine)_2]^{2+}$ by comparison with data published very recently [11].

The reaction with dppb yielded two main products containing Fe_2Cu linkages. A down-field pair of doublets corresponding to two different phosphido groups accounted for the existence of these two products. One of them corresponds to the dicluster compound **5**, and the second centered at 119.6 ppm $^4J(P\text{–}P) = 14.4$ Hz, could be assigned to the asymmetric species $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}(dppb)Cu(dppb)_n]^+$ as in the PCu zone a very broad resonance was observed. No assignments could be made, although the broad signal is indicative of coordination of the dppb to copper (no free dppb was detected).

When the diphosphine was dppip, ^{31}P-NMR spectra showed no sharp peaks although integration indicated the presence of diphosphine–copper species in solution.

2.2. Metal exchange reactions

It has been described [1] that treatment of clusters containing Group 11 metals with the complex $[ClAu(SC_4H_8)]$ can promote the replacement by gold of one or more of the lighter coinage metals in the initial cluster. Since we have prepared diclusters containing two copper atoms, this kind of reaction could be potentially a very useful synthetic route to new compounds containing one gold and one copper atom.

The reaction of a precooled (240 K) CH_2Cl_2 solution of the most stable copper clusters $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(diphosphine)]$ (diphosphine = dppp, dppb) with a $[ClAu(SC_4H_8)]$ solution in the same solvent in a 1:1 molar ratio was investigated by ^{31}P-NMR but unfortunately, only the corresponding di-gold compounds $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_2(diphosphine)]$ (diphosphine = dppp, dppb) as main products together with decomposition species were detected.

The addition of $TlBF_4$ as a halide abstractor did not change the composition of the final mixtures.

3. Electrochemical studies

The electrochemical properties of $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(diphosphine)]$ (diphosphine = dppm (**1**), dppip (**2**), dppe (**3**), dppp (**4**) or dppb (**5**)) were studied in dichloromethane. All of them exhibit an oxidation wave around 0.75 V and a reduction process at about −1.45 V. Both processes are irreversible independent of the scan rate. Data for both oxidation and reduction processes of the compounds are summarized in Table 1. Cyclic voltammograms of compound **5** are shown in Fig. 1 as representative of all compounds.

Controlled potential coulometry at 0.8 V, using a platinum gauze electrode at room temperature in dichloromethane with $[n\text{-}NBu_4][BF_4]$ as the supporting electrolyte, indicated that two electrons are transferred. The lifetime of oxidized compounds is extremely short and an immediate breakdown of Fe–Cu bonds after the oxidation process releases the di-iron radical together with copper-containing decomposition products.

As pointed out above, the reduction process occurred in the region around −1.4 V (Table 1). The relative peak height of the wave is double that observed in the oxidation step. Exhaustive controlled-potential electrolysis at −1.80 V consumed twice as many electrons as in the oxidation step, corresponding to a transfer of four electrons. The peak at −0.13 V (observed in both the oxidation and reduction voltammograms) (Fig. 1) was attributed to the interconversion between the anion $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-$ and the radical $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^{\bullet}$ compared with the voltammogram of an authentic sample.

Table 1
Cyclic voltammetry data for the oxidation and reduction step of compounds **1**–**5** in diclorométhane 0.1 M $[n\text{-}Bu_4N][BF_4]$ at 0.1 V s^{-1}

Compound	*E* (V)	*E* (V)
	Oxidation	Reduction
1	0.71	−1.44
2	0.74	−1.43
3	0.74	−1.43
4	0.77	−1.46
5	0.77	−1.56

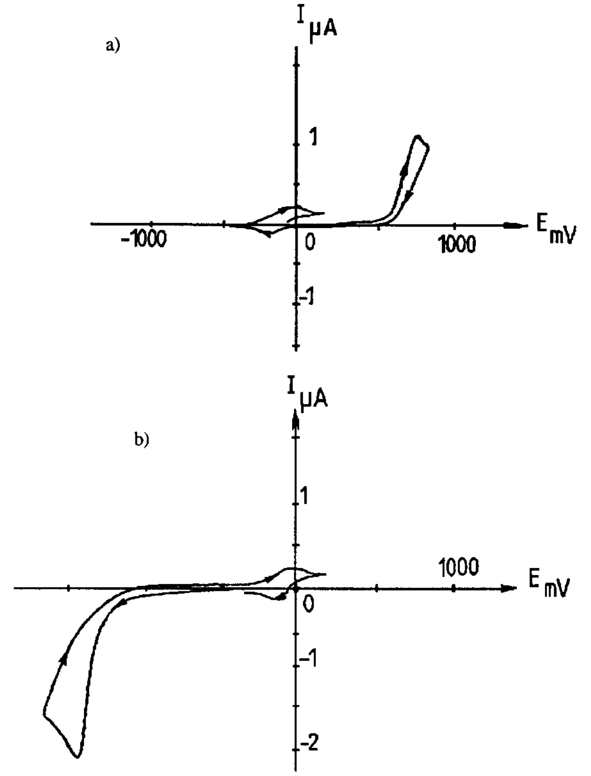


Fig. 1. Cyclic voltammograms of compound **5** at 0.1 V s^{-1}. (a) Oxidation. (b) Reduction.

Bearing that in mind, the proposed mechanisms for both oxidation and reduction are depicted in Scheme 1.

It can be concluded that, as in the gold complexes after either oxidation or reduction processes, cleavage of Fe–Cu bonds occurs, giving two fragments: (i) a fragment with Fe–Fe bonds and (ii) some kind of phosphine–copper derivative. The fact that both oxidation and reduction peak potentials are nearly the same, independent of the phosphine ligand, clearly indicates that the electrons involved in these processes belong to the metallic cores and that there is no electronic communication through the linking phosphine ligands.

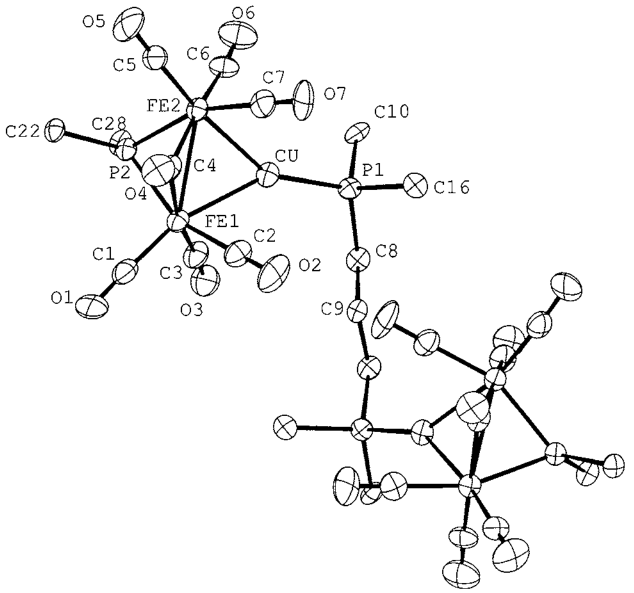
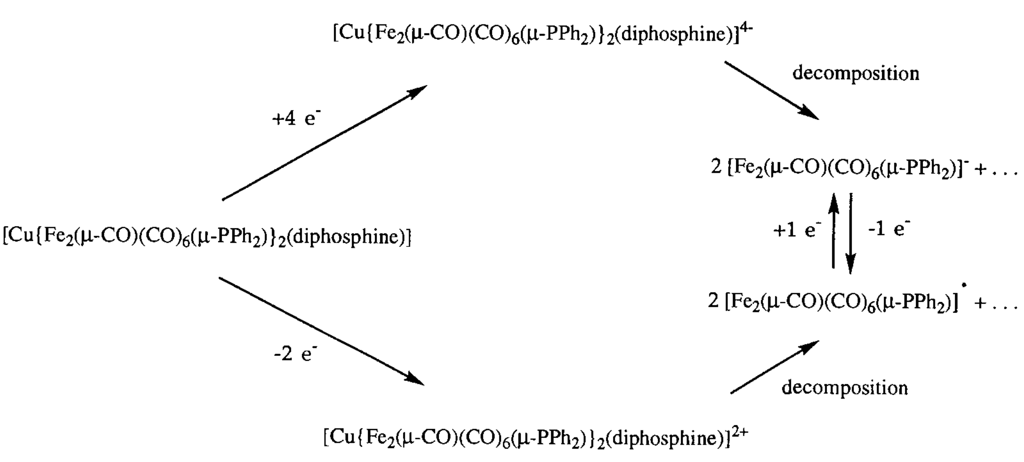


Fig. 2. ORTEP view of the structure of the complex **4** together with the atom numbering scheme. The carbon atoms (excepting those attached to the P atoms) of the phenyl rings of dppp have been omitted for clarity.

Moreover the total irreversibility of the redox processes reflects the greater instability of the Fe_2Cu core compared with the Fe_2Au, which has also been observed in chemical reactions.

4. Crystal structure of [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu$}$_2$(dppp)] (4)

The structure of the compound **4** is depicted in Fig. 2, together with the atomic numbering system. The main bond distances and angles are given in Table 2. The structure of the cluster consists of two triangular $CuFe_2$ subunits linked by the bidentate diphosphine ligand $Ph_2P(CH_2)_3PPh_2$. The molecule is chiral (C_2) due to the existence of a unique twofold axis passing



Scheme 1.

Table 2
Selected bond distances (Å) and angles (°) for **4**·3toluene

Bond distances			
Fe(1)–Fe(2)	2.613(2)	Fe(1)–C(4)	1.959(8)
Cu–Fe(1)	2.490(2)	Fe(2)–C(4)	1.979(8)
Cu–Fe(2)	2.485(2)	P(1)–C(8)	1.850(7)
Cu–P(1)	2.198(2)	P(1)–C(10)	1.824(7)
Fe(1)–P(2)	2.226(2)	P(1)–C(16)	1.812(7)
Fe(2)–P(2)	2.228(2)	C(8)–C(9)	1.511(8)
Bond angles			
Fe(1)–Cu–Fe(2)	63.35(4)	C(4)–Fe(1)–Fe(2)	48.8(2)
Cu–Fe(1)–Fe(2)	58.23(4)	Fe(1)–Cu–P(1)	146.20(7)
Cu–Fe(2)–Fe(1)	58.42(4)	Cu–P(1)–C(8)	116.6(2)
Fe(1)–P(2)–Fe(2)	71.84(7)	Cu–P(1)–C(10)	109.1(2)
P(2)–Fe(1)–Fe(2)	54.11(6)	P(1)–C(8)–C(9)	111.5(5)
Fe(1)–C(4)–Fe(2)	83.1(3)		

through the middle carbon of the diphosphine C(9), but the racemate crystallizes because the unit crystal cell is centrosymmetric. The two subunits are equivalent and lie far apart in order to minimize sterical interaction. The structural features of one $Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu$ fragment are essentially the same as those reported for $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(CuPPh_3)]$ [7]. Bond distances and angles of dppp ligand are comparable with species where this ligand is linking bulky metallic fragments such $[\{Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)\}_2(\mu\text{-}dppp)]$ [12], $[\{Mo(CO)_5\}_2(\mu\text{-}dppp)]$ [13] and $[Au_2\{(PPh_2C_2B_9H_{10}\}_2(\mu\text{-}dppp)]$ [14].

5. Experimental

All manipulations were performed under an atmosphere of pre-purified N_2 with use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Infrared spectra were recorded in toluene solutions on an FT IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$-NMR (δ (85% H_3PO_4) = 0.0 ppm), ^1H-NMR, and ^{13}C-NMR (δ (TMS) = 0.0 ppm) spectra were obtained on a Bruker DXR 250 spectrometer. The compounds $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ [15] and $[Cu(CH_3CN)_4]BF_4$ [16] were prepared as described previously. The diphosphines dppm, dppip, dppe, dppp and dppb were synthesized using literature methods.

Electrochemical measurements were carried out with an Electrokemat potentiostat [17] using the interrupt method to minimize the uncompensated resistance (IR) drop. Electrochemical experiments were performed at room temperature in an airtight three-electrode cell connected to a vacuum argon–N_2 line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the nonaqueous solutions by a bridge compartment. The counter electrode was a spiral of ca. 1 cm^2 apparent surface area, made of Pt wire 8 cm long and 0.5 mm in diameter. The working electrode was Pt (1 mm) for cyclic voltammetry and Pt (100 μm) for ultramicroelectrode voltammetry. For electrolysis experiments, a Pt gauze or foil was used. The supporting electrolyte ($[n\text{-}Bu_4N][BF_4]$) was used as received (Fluka electrochemical grade). All solutions measured were $0.5–1.0 \times 10^{-3}$ M in the organometallic complex and 0.1 M in supporting electrolyte. Under the same conditions ferrocene was oxidized at $E° = 0.42$ V versus SCE.

5.1. Synthesis of $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(dppm)]$ (**1**)

Details of the synthesis of **1** also apply to **2**–**5**. Solid $[Cu(CH_3CN)_4]BF_4$ (0.125 g, 0.40 mmol) was added to a precooled (258 K) solution of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ (0.25 g, 0.40 mmol) in 50 ml of CH_2Cl_2. The color of the solution darkened immediately. At this point, solid dppm (0.077 g, 0.20 mmol) was added. After 1 h of stirring, the deep-red mixture was taken to dryness. The remaining solid was extracted with 10 ml of cold toluene and the solution was filtered via cannula to eliminate $[NEt_4][BF_4]$. The solvent was removed in vacuo and the residue was dissolved in 10 ml of CH_2Cl_2. Subsequent addition of 50 ml of *n*-pentane and cooling overnight (233 K) afforded deep-red microcrystals of **1**. The compound was recrystallized in toluene–*n*-pentane. Yield: 0.18 g (60%). IR (toluene, cm^{-1}) ν(CO) 2041 (m), 2008 (vs), 1974 (s), 1933 (m), 1789 (m); $^{31}P\{^1H\}$-NMR (240 K, CH_2Cl_2): δ 121.2 (m, $Fe_2\mathit{P}Ph_2$), −12.4 (s, br, $Cu\mathit{P}Ph_2$).^1H-NMR (298 K, C_6D_6): δ 7.42–6.77 (m, Ph), 3.60 (t, $PC\mathit{H}_2P$, ^2J(H–P) = 5.7). ^{13}C-NMR (298 K, C_6D_6): δ 139.0–128.8 (m, Ph), 24.1 (s, br). Anal. Calc. for $C_{63}H_{42}Cu_2Fe_4O_{14}P_4$: C, 50.53; H, 2.83. Found: C, 50.15; H, 2.68%.

5.2. $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(dppip)]$ (**2**)

Yield: 0.15 g (50%). IR (toluene, cm^{-1}) ν(CO) 2040 (m), 2007 (vs), 1971 (s), 1940 (m), 1784 (m); $^{31}P\{^1H\}$-NMR (240 K, CH_2Cl_2): δ 130.3(d, $Fe_2\mathit{P}Ph_2$, ^3J(PP) = 11), 25.5(br, $Cu\mathit{P}Ph_2$). ^1H-NMR (298 K, C_6D_6): δ 7.50–6.81 (m, Ph), 1.91 (t, $PC(C\mathit{H}_3)_2P$, ^3J(H–P) = 17.1). ^{13}C-NMR (298 K, C_6D_6): δ 138.9–127.4 (m, Ph), 29.9 (t, $PC(\mathit{C}H_3)_2P$, ^2J(C–P) = 10.2). Anal. Calc. for $C_{65}H_{46}Cu_2Fe_4O_{14}P_4$: C, 51.18; H, 3.04. Found: C, 52.05; H, 2.90%.

5.3. $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Cu\}_2(dppe)]$ (**3**)

Reaction time: 45 min. Yield: 0.19 g (62%). IR (toluene, cm^{-1}) ν(CO) 2040 (m), 2007 (vs), 1973 (s), 1935 (m) 1791 (m); $^{31}P\{^1H\}$-NMR (240 K, CH_2Cl_2): δ 119.8(m, Fe_2PPh_2), −3.9(br, $Cu\mathit{P}Ph_2$). ^1H-NMR (298 K, C_6D_6): δ 7.49–6.74 (m, Ph), 2.64 (br s, $PC\mathit{H}_2C\mathit{H}_2P$).

Table 3
Crystal data and data collection parameters for **4**·3toluene

Empirical formula	$C_{86}H_{70}Cu_2Fe_4O_{14}P_4$
M	1801.88
Temperature (K)	283(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	14.923(7)
b (Å)	10.566(7)
c (Å)	26.304(8)
β (°)	100.43(3)
V (Å^3)	4079(4)
Z	2
$D_{calc.}$ (g cm^{-3})	1.467
μ?Mo–K$_\alpha$? (cm^{-1})	138.5
F(000)	1840
h, k, l ranges	$-17 \leq h \leq 17$
	$0 \leq k \leq 12$
	$0 \leq l \leq 31$
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	7119/0/476
Goodness-of-fit on F^2	0.726
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0945$
R indices (all data)	$R_1 = 0.1329$, $wR_2 = 0.2390$
Extinction coefficient	0.0000(2)
Largest difference peak and hole (e Å^{-3})	0.634 and -0.282

^{13}C-NMR (298 K, C_6D_6): δ 138.6–126.7 (m, Ph), 22.7 (dd, PCH_2CH_2P, ^1J(C–P) = 29.1, ^2J(C–P) = 15.0). Anal. Calc. for $C_{64}H_{44}Cu_2Fe_4O_{14}P_4$: C, 50.86; H, 2.93. Found: C, 51.41; H, 2.78%.

5.4. *[{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Cu}$_2$(dppp)] · 3toluene* ***(4)***

Reaction time: 30 min. Yield: 0.20 g (62%). IR (toluene, cm^{-1}) ν(CO) 2040 (m), 2006 (vs), 1971 (s), 1940 (m), 1789 (m); ^{31}P{^{1}H}-NMR (298 K, CH_2Cl_2): δ 122.8(d, Fe$_2$*P*Ph$_2$, ^3J(PP) = 14), -5.7(d, Cu*P*Ph$_2$). ^{1}H-NMR (298 K, C_6D_6): δ 7.44–7.06 (m, Ph), 2.24 (m, 4H, PCH_2CH$_2$$CH_2$P), 1.52 (br, 2H, PCH$_2$$CH_2CH_2$P). ^{13}C-NMR (298 K, C_6D_6): δ 138.8–125.3 (m, Ph), 28.9 (dd, PCH_2CH$_2$$CH_2$P, ^1J(C–P) = 21.3, ^3J(C–P) = 17.0), 20.5 (t, PCH$_2$$CH_2CH_2$P, ^2J(C–P) = 7.0). Anal. Calc. for $C_{86}H_{70}Cu_2Fe_4O_{14}P_4$: C, 57.33; H, 3.92. Found: C, 57.25; H, 3.86%.

5.5. *[{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Cu}$_2$(dppb)] · 1toluene* ***(5)***

Reaction time 30 min. Yield: 0.20 g (65%). IR (toluene, cm^{-1}) ν(CO) 2040 (m), 2006 (vs), 1972 (s), 1933 (m), 1790 (m); ^{31}P{^{1}H}-NMR (298 K, CH_2Cl_2): δ 120.3(d, Fe$_2$*P*Ph$_2$, ^3J(PP) = 14), -5.2(d, Cu*P*Ph$_2$). ^{1}H-NMR (298 K, C_6D_6): δ 7.55–6.83 (m, Ph), 2.02 (m, br, 4H, PCH_2CH$_2$CH$_2$$CH_2$P), 1.52 (br, 4H, PCH$_2$$CH_2$$CH_2CH_2$P). ^{13}C-NMR (298 K, C_6D_6): δ 139.3–125.8 (m, Ph), 27.3 (dd, PCH$_2$$CH_2$$CH_2CH_2$P, ^2J(C–P) = 16.5, ^3J(C–P) = 7.8), 26.9 (d, PCH_2CH$_2$CH$_2$$CH_2$P, ^1J(C–P) = 23.4). Anal. Calc. for $C_{73}H_{56}Cu_2Fe_4O_{14}P_4$: C, 53.74; H, 3.54. Found: C, 50.75; H, 2.91%.

5.6. *Synthesis of [Cu$_2${Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)}$_2$(μ-dppm)$_2$]* ***(6)***

Solid [Cu(CH_3CN)$_4$]BF$_4$ (0.125 g, 0.40 mmol) was added to a solution of [NEt$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.25 g, 0.40 mmol) in 50 ml of CH_2Cl_2. The color of the solution darkened immediately. At this point, dppm (0.150 g, 0.40 mmol) was added as a solid. After 30 min of stirring, the deep-red mixture was taken to dryness. The remaining solid was extracted with 15 ml of toluene and the solution was filtered via cannula to eliminate [NEt$_4$][BF$_4$]. The solvent was removed in vacuo giving an oil that was dissolved in CH_2Cl_2. The ^{31}P-NMR of the dichloromethane solution showed partial decomposition. IR (CH_2Cl_2, cm^{-1}) ν(CO) 2040 (m), 2007 (vs), 1973 (s), 1934 (m), 1919 (m, sh), 1789 (m); ^{31}P{^{1}H}-NMR (298 K, CH_2Cl_2): δ 117.3(t, Fe$_2$*P*Ph$_2$, ^3J(PP) = 5), -15.4(d, Cu*P*Ph$_2$).

5.7. *X-ray crystal structure determination of* ***4·****3toluene*

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf–Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo–K$_\alpha$ radiation, using $\omega/2\theta$ scan technique. 7172 reflections were measured in the range $2.08 \leq \theta \leq 24.98$. 3638 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

The structure was solved by direct methods, using the SHELXS computer program [18] and refined by the full-matrix least-squares method with the SHELX93 computer program [19], using 7119 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1135P)^2 + 15.902P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, f, f' and f'' were taken from International Tables of X-ray crystallography [20]. The extinction coefficient was 0.0000(2). The refinement of toluene ring (C40–C45) was the planarity and the bond length constrained. Six hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 18 hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R(on F) factor was 0.037, wR (on $|F|^2$) = 0.094 and goodness-of-fit = 0.552 for all observed reflections. The number of refined parameters and further details concerning the crystal structure of compound **4** are summarized in Table 3.

6. Supplementary materials

Details of the crystal structure (CIF files) of compound **4** are available from the Cambridge Crystallographic Data Centre; the CSD number is CCDC 128486.

Acknowledgements

Financial support for this work was generously given by DGICYT (Spain) through grant no. PB96-0174.

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