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Synthesis, characterization and electrochemical studies of the heterometallic diclusters [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(diphosphine)] (diphosphine = dppm, dppip, dppe, dppp)

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Abstract

Treatment of [$(ClAu)_2$(diphosphine)] {diphosphine = bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)isopropane (dppip), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp)} with two equivalents of the anion $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^-$ in the presence of $TlBF_4$ gives the new heterometallic diclusters [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(diphosphine)] that have been isolated and characterized. Their ^{31}P-NMR spectra show different patterns as a function of the diphosphine ligand. The electrochemical behavior of these compounds has been investigated and compared with that of the mono- $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$ and tricluster [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_3$(triphos)] derivatives. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Heterometallic; Clusters; Diphosphine

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1. Introduction

Over the last few years, there have been several reports [1] dealing with mixed-metal cluster compounds in which gold diphosphine fragments [Au_2(diphosphine)]$^{2+}$ link two independent cluster units. In order to gain insight into this type of derivatives, in this paper we describe the synthesis of several homo polycluster compounds of the general formula [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(diphosphine)].

Given that all these species contain identical metal clusters, it seemed interesting to undertake the synthesis of compounds with two or more different metal fragments because of their interest in ^{31}P-NMR and electrochemical studies. For this, the previous formation of the compounds [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}(diphosphineAuCl)] and [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_x$(triphos)$(AuCl)_{3-x}$] was thought to be a good starting point due to the known lability of the chloride that could be substituted for metal anions. Two routes for such type of derivatives were considered: (i) the reaction of the phosphido bridged anion $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^-$, that has already been used as a building block in the synthesis of $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}MPPh_3)]$ [2] (M = Au, Ag, Cu) and [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_3$(triphos)] [3], with the gold compounds [$(ClAu)_n$(polyphosphine)] in the appropriate molar ratio and (ii) the treatment of the symmetric complexes [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_n$(polyphosphine)] with [$(ClAu)_n$(polyphosphine)] to promote metal ligand redistribution reactions which are not usual in the chemistry of gold.

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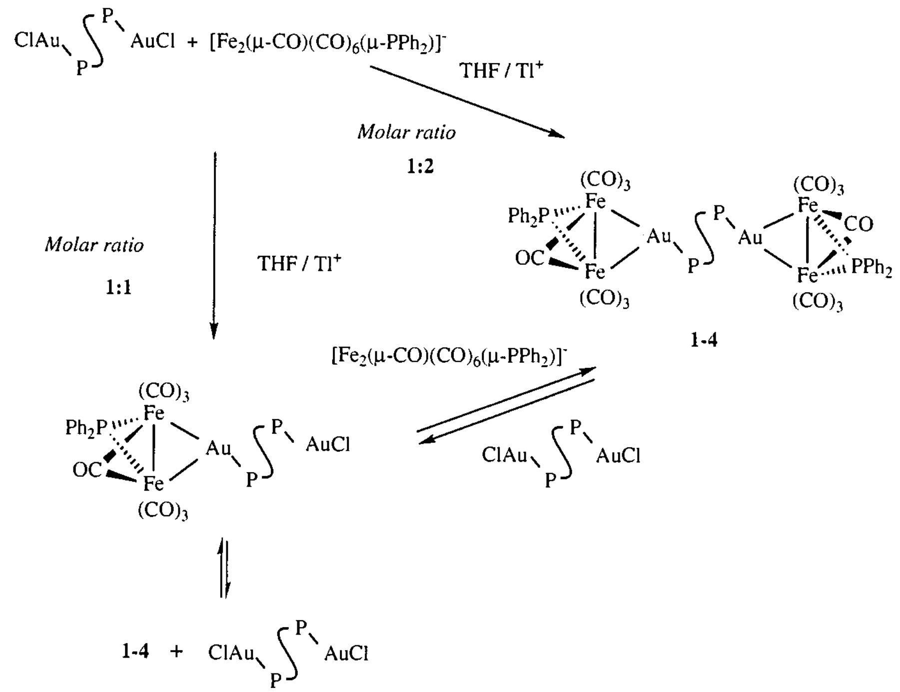
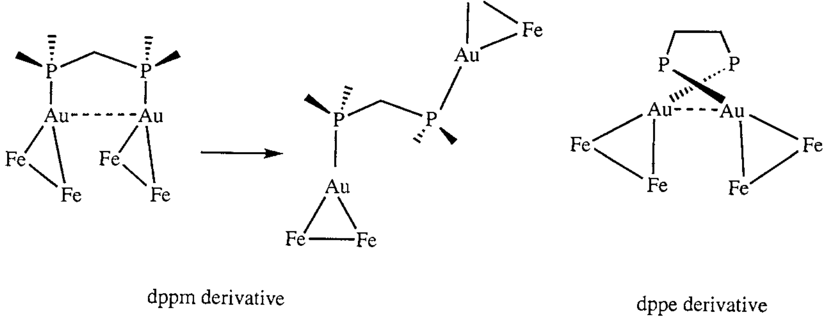


Scheme 1. Reaction of two equivalents of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ with $[(ClAu)_2(diphosphine)]$ in the presence of $TlBF_4$ giving the neutral metal compounds **1**–**4**.



Scheme 2. Possible conformations of the dppm five-membered and dppe six-membered rings.

2. Results and discussion

The reaction of two equivalents of $[NEt_4][Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]$ with $[(ClAu)_2(diphosphine)]$ in the presence of $TlBF_4$ gave neutral metal compounds of the type $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_2(diphosphine)]$ {diphosphine = dppm (**1**), dppip (**2**), dppe (**3**), dppp (**4**)}, in which the diphosphine acts as a bridge between two independent cluster units (Scheme 1). The temperature of the reaction depended on the diphosphine. Whereas for dppm and dppip derivatives low temperatures were required to avoid decomposition of the formed products, high yields of dppe and dppp complexes were obtained at room temperature (r.t.).

Compounds **1**–**4** were characterized by elemental analysis as well as IR, ^1H-, ^{31}P- and ^{13}C-NMR. The $\nu(CO)$ IR pattern for **1**–**4** is very close, in agreement with previous data on the related compound $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$ [2]. The low temperature ^{31}P-NMR spectra in $CDCl_3$ solutions varied according to the diphosphine derivative. For dppip (**2**) and dppp (**4**) typical AX spectra consisting in one doublet for each type of phosphorus atoms were obtained. However, compounds **1** and **3** displayed two sets of symmetrically equivalent but magnetically inequivalent phosphorus nuclei that gave rise to two identical AA′XX′ patterns. The P–P coupling constants and chemical shift values were calculated by spectra simulation. Curiously, the coupling constant $^3J(PP)$ for the dppe derivative was greater (63 Hz) than the $^2J(PP)$ for the dppm derivative (17 Hz), in spite of the lower number of bonds between the phosphorus atoms. This fact could be interpreted considering the existence or not of aurophilic interaction. The small coupling constant in compound **1** is consistent with values found in related compounds where dppm links two independent

Table 1
^{31}P-NMR data for compounds [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}(diphosphineAuCl)]

Phosphine	PFe_2AuP–PAuCl	PFe_2AuP–PAuCl	PFe_2AuP–PAuCl
dppm	45.5 (dd, $^2J(PP) = 56$, $^3J(PP) = 24$)	19.4 (d, $^2J(PP) = 56$)	131.5 (d, $^3J(PP) = 24$)
dppip	76.8 (dd, $^2J(PP) = 37$, $^3J(PP) = 23$)	49.1 (d, $^2J(PP) = 37$)	133.2 (d, $^3J(PP) = 23$)
dppe	49.9 (dd, $^3J(PP) = 63$, $^3J(PP) = 25$)	31.8 (d, $^3J(PP) = 63$)	129.7 (d, $^3J(PP) = 25$)
dppp	46.8 (d, $^3J(PP) = 24$)	26.4 s	129.8 (d, $^3J(PP) = 24$)

THF solutions were used and $P(OMe)_3$ was the external reference.

metallic units [4] whereas larger constants are found when M–M interaction exists ([4]a, [5]). On the other hand, only two exemples of ^3J(PP) are reported in the literature for dppe since in most of the compounds either dppe bridges identical metallic units or acts as a chelating ligand [6]. The mentioned examples have been recently described for the compounds [$Mn_3(CO)_{12}(\mu_3\text{-}H)(\mu\text{-}dppe)AuCl$]$^-$ ([1]g) ($^3J(PP) = 63$ Hz) ([$Fe_6AuC(CO)_{16}(\mu\text{-}dppe)AuCl$] ([1]i) ($^3J(PP) = 64$ Hz), but the existence or not of interaction between the gold atoms could not be determined due to the absence of crystal structures. In spite of this, the relatively large J(PP) in **3** could be indicative of the existence of aurophilic interaction between the gold atoms of the two cluster units. As a consequence, ^3J(PP) can be expressed as ^{3+3}J(PP).

It is interesting to speculate on the reasons for the different behavior towards aurophilic attraction between **1** and **3**. Although in the structure of the gold derivative [$(ClAu)_2$(dppm)] [7], the distance Au–Au is found at 3.345 Å, corresponding to a bonding interaction, the establishment of Au–Au attraction in **1** would involve the formation of a sterically very constrained five-membered ring, due to the bulkiness of the substituents in both arms of the diphosphine (Scheme 2). In consequence, it seems more reasonable to expect a conformation in which the two limbs of [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(dppm)] point away from each other in order to minimize the sterical demands. On the other hand, the six-membered ring formed by the more flexible dppe derivative is much less congested, as can be observed in Scheme 2, and could allow a certain degree of aurophilic interaction.

For compound **2**, similar behavior of the dppm complex could reasonably be expected. However, it was impossible to determine the coupling constant value due to the lack of second order spectrum.

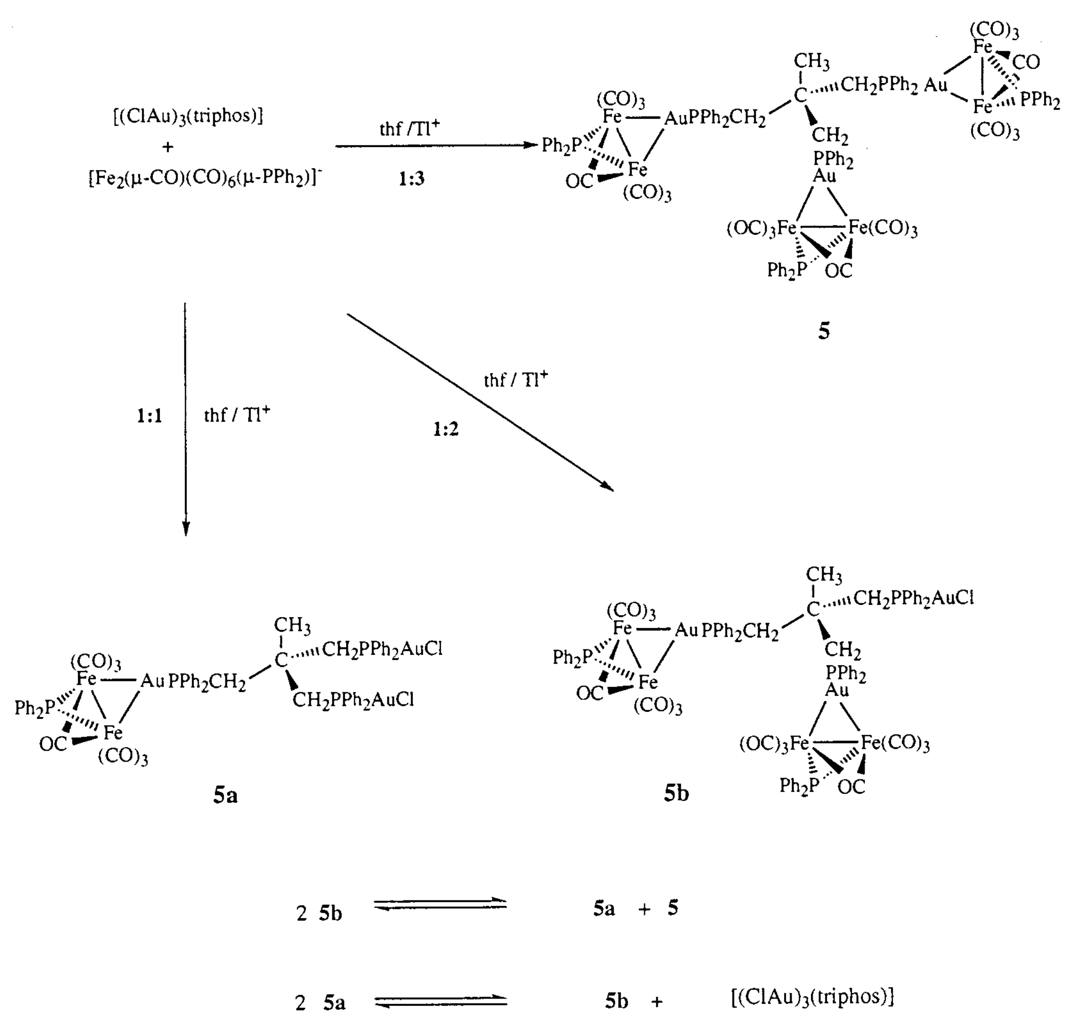
Unfortunately, the existence or not of aurophilic attraction in **1**–**4** could not be confirmed structurally, since all attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful.

In order to explore the possibility of obtaining species containing AuCl fragments that allow the synthesis of compounds where di or triphosphines act as a bridge among different cluster units, the reaction between the dimetallic anion [$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)$]$^-$ and [$(ClAu)_2$(diphosphine)] in the presence of $TlBF_4$ in a 1:1:1 molar ratio was studied The reaction conditions were the same as those described above. After 30 min no further changes were detected by ^{31}P-NMR and a mixture of symmetric products [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(diphosphine)], asymmetric products [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}(diphosphineAuCl)] and gold derivative [$(ClAu)_2$(diphosphine)] were obtained (Scheme 1). Subsequent addition of one further equivalent of the metallic anion and $TlBF_4$ resulted in the formation of **1**–**4** as the only products. Interestingly, the addition of gold derivatives to solutions of pure compounds **1**–**4** led to the formation of the mixture mentioned above.

Although the asymmetric products [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}(diphosphineAuCl)] could not be isolated, ^{31}P-NMR data are shown in Table 1. The relative large values of the J(PP) coupling constants for dppm, dppe and dppip derivatives show the possibility of aurophilic interaction. Remarkably, a $^2J(PP) = 56$ Hz was found for the asymmetric derivative of dppm, whereas this value was 17 Hz for the symmetric compound **1**. This difference could be interpreted in terms of the existence of aurophilic attraction in the less sterically-demanding asymmetric compound, where ^{2+3}J(PP) could be considered instead of ^2J(PP).

For the dppe derivatives, no variation of the value of the coupling constant was observed which is consistent with that both symmetric and asymmetric products have Au–Au interaction.

The reaction between the anion [$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)$]$^-$ and the triphosphine derivative [$(ClAu)_3$(triphos)] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) led to similar results. For a $3Fe_2$:$1Au_3$ molar ratio, the only compound isolated was [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_3$(triphos)] (**5**) [3]. However, for smaller Fe_2:Au_3 ratios, a mixture of compounds containing one, two or three Fe_2 fragments was obtained. Again, addition of [$(ClAu)_3$(triphos)] to a solution of [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_3$(triphos)] led to the formation of, first [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au$}$_2$(triphosAuCl)] (**5a**) and then [{$Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)$Au}(triphos)$(AuCl)_2$] (**5b**), if an excess of gold compound [$(ClAu)_3$(triphos)] was used (Scheme 3).



Scheme 3. Reaction of $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)]^-$ with $[(ClAu)_3(triphos)]$, leading to the formation of (**5**), (**5a**) and (**5b**), depending on the concentration of gold compound used.

The ligand redistribution processes observed here are rather unusual in the chemistry of gold, and only a few examples have been reported to date [8]. In this case, their occurrence precluded the isolation of chemically pure asymmetric complexes and consequently the synthesis of compounds in which the polyphosphines act as a bridge between different cluster units was impossible.

2.1. Electrochemical studies

The electrochemical properties of $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$ (**6**), $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_2(diphosphine)]$ {diphosphine = dppm (**1**), dppip (**2**), dppe (**3**), dppp (**4**)} and $[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_3(triphos)]$ (**5**) were studied in dichloromethane. All of them exhibit an oxidation wave at about 0.75 V and a reduction process at about − 1.4 V. The reversibility of the first process (oxidation step) depends on the scan rate. Compounds **3**–**6** (Fig. 1) show a quasi-reversible process at scan rates > 3 Vs^{-1}, whereas for **1** and **2** 600 Vs^{-1} are required in order to observe the return peak. Data for oxidation of the compounds are summarized in Table 2. Cyclic voltammograms of compound **6** are displayed in Fig. 1 as representative of all compounds.

Controlled potential coulometry at 0.8 V, using a platinum gauze electrode at r.t. in dichloromethane with $[n\text{-}NBu_4][BF_4]$ as the supporting electrolyte, indicated that the number of transferred electrons depends on the number of Fe_2Au units present in the compound (one electron per Fe_2Au unit). During this time the violet solution changes to green and its frozen-glass EPR spectra shows the resonance attributable to the radical $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^{\bullet}$ by comparison with literature data [9]. So, we conclude that lifetime of oxidized compounds is extremely short and an immediate breakdown of Fe–Au bonds after oxidation process gives the diiron radical together with gold containing decomposition products.

Bearing all that in mind, the proposed mechanism (electrochemical and chemical values of *n* depending on the nature of the ligand L) is as follows:

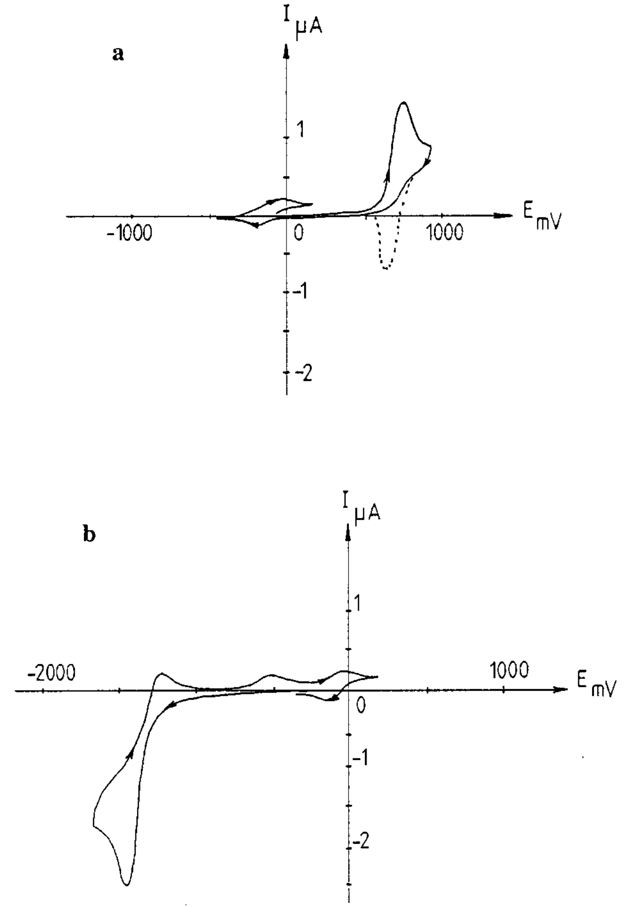


Fig. 1. Cyclic voltammograms of compound **6** at 0.1 V s^{-1}. (a) Oxidation. Dashed line shows the quasi-reversible oxidation wave at 3 V s^{-1}. (b) Reduction.

$$[\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]$$

$$\underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} [\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]^{n+}$$

$$[\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]^{n+}$$

$$\rightarrow n[Fe_2(CO)_7(\mu\text{-PPh}_2)] + (Au)_nL^{n+}$$

where L = PPh$_3$, $n = 1$; L = dppm, dppip, dppe, dppp, $n = 2$; L = triphos, $n = 3$.

Table 2
Cyclic voltammetry data for the oxidation step of compounds **1**–**6** in dicloromethane 0.1 M [n-Bu$_4$N][BF$_4$]

Compound	E^0 (V)	ΔE_p (mV)	$i_{p,c}/i_{p,a}$	n
1	0.74	140[a]	0.30[a]	2
2	0.76	160[a]	0.30[a]	2
3	0.75	60[b]	0.45[b]	2
4	0.75	60[b]	0.43[b]	2
5	0.75	60[b]	0.60[b]	3
6	0.71	60[b]	0.70[b]	1

[a] 600 V s^{-1}. [b] 3 V s^{-1}.

As pointed out above, a reduction process occurred in the region around −1.4 V (Table 3). The relative peak height of the wave is double compared to that observed at the oxidation step, with the high values of ΔE_p consistent with a slow heterogeneous electron transfer. Exhaustive controlled-potential electrolysis at −1.80 V consumed twice the amount of electrons than in the oxidation step, corresponding to a transfer of two electrons per Fe$_2$Au unit. In the reverse scan, the voltammograms showed two additional peaks that suggest that chemical reactions occur after reduction. The peak at −0.13 V (Fig. 1) was attributed to the oxidation of $[Fe_2(CO)_7(\mu\text{-PPh}_2)]^-$ to the radical $[Fe_2(CO)_7(\mu\text{-PPh}_2)]^{\bullet}$ when compared with the voltammogram of an authentic sample. The other peak at about −0.50 V corresponds to an irreversible oxidation probably related to the oxidation of gold–phosphine fragments. In view of these findings, the following mechanism is proposed:

$$[\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]$$

$$\underset{-2ne^-}{\overset{+2ne^-}{\rightleftharpoons}} [\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]^{2n-}$$

$$[\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_nL]^{2n-}$$

$$\rightarrow n[Fe_2(CO)_7(\mu\text{-PPh}_2)]^- + (Au)_nL^{n-}$$

where L = PPh$_3$, $n = 1$; L = dppm, dppip, dppe, dppp, $n = 2$; L = triphos, $n = 3$.

As a conclusion from these studies, it can be seen that in both the oxidation and reduction processes cleavage of Fe–Au bonds occurs, giving two fragments: (i) a fragment with Fe–Fe bonds and (ii) some kind of phosphine–gold derivative. The fact that both oxidation and reduction peak potentials are nearly the same, independently 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.

3. Experimental section

All manipulations were performed under an atmosphere of prepurified N$_2$ with use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. IR spectra were recorded in toluene solutions on an FT-IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$-NMR [δ (85% H$_3$PO$_4$) = 0.0 ppm], ^{1}H-NMR and ^{13}C-NMR [δ (TMS) = 0.0 ppm] were obtained on a Bruker DXR 250 spectrometer. The compounds $[NEt_4][Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)]$ [10], $[Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)(\mu\text{-AuPPh}_3)]$ [2], and $[\{Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-PPh}_2)Au\}_3(\text{triphos})]$ [3] were prepared as described previously. The complexes $[(ClAu)_2(\text{diphosphine})]$ and $[(ClAu)_3(\text{triphos})]$ were synthesized and isolated as a solids from a [AuCl(tht)] [11] solution by adding the appropriate amount of the corresponding phosphine.

Table 3
Cyclic voltammetry data for the reduction step of compounds **1**–**6** in dicloromethane 0.1 M [n-Bu$_4$N][BF$_4$] at 0.1 Vs^{-1}

Compound	E^0 (V)	ΔE_p (mV)	$i_{p,a}/i_{p,c}$	E^0 (V)	$E_{p,a}$ (V)[a]	n
1	−1.32	170	0.35	−0.13	−0.47	4
2	−1.40	170	0.25	−0.13	−0.62	4
3	−1.40	180	0.40	−0.13	−0.50	4
4	−1.45	200	0.45	−0.13	−0.54	4
5	−1.47	180	0.25	−0.13	−0.62	6
6	−1.37	210	0.40	−0.13	−0.50	2

[a] $E_{p,a}$ (irreversible oxidation).

Electrochemical measurements were carried out with an Electrokemat potentiostat [12] using the interrupt method to minimize the uncompensated resistance (IR) drop. Electrochemical experiments were performed at r.t. 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 non-aqueous 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 was [n-Bu$_4$N][BF$_4$] (Fluka electrochemical grade), used as received. All solutions measured were 0.5–1.0 × 10^{-3} M in the organometallic complex and 0.1 M in supporting electrolyte. Ferrocene (Fc) was used as an internal reference in these studies, with the redox couple, Fc|Fc$^+$, occurring at $E° = 0.42$ V versus SCE. E^0 values were determined as the average of cathodic and anodic peak potencials, i.e [$(E_{p,c} + E_{p,a})/2$].

3.1. Synthesis of [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(dppm)] (1)

Solid [(ClAu)$_2$dppm] (0.20 g, 0.24 mmol) and TlBF$_4$ (0.14 g, 0.48 mmol) were added to a pre-cooled (268 K) solution of [NEt$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.30 g, 0.48 mmol) in 40 ml of THF. The solution turned deep violet immediately. After 30 min of stirring the mixture was filtered and taken to dryness. The remaining solid was extracted with 10 ml of cold toluene. Subsequent addition of n-pentane and cooling overnight (233 K) afforded purple–red microcrystals of compound **1**. The compound was recrystallized in CH$_2$Cl$_2$/n-pentane. Yield: 0.25 g, 60%. IR (toluene, cm^{-1}) ν(CO): 2043 (m), 2013 (vs), 1976 (s, br), 1783 (m). ^{31}P{^{1}H}-NMR (240 K, CDCl$_3$): δ 130.1 (m, Fe$_2$$PPh_2$, AA′XX′ spin system, ^2J(PP) = 17, ^3J($_{Fe2}$PP$_{Au}$) = 25, ^5J($_{Fe2}$PP$_{Au}$) = 0.1, ^8J($_{Fe2}$PP$_{Fe2}$) = 0), 42.0 (m, AuPPh$_2$) (data from spectral simulation). ^{1}H-NMR (240 K, CDCl$_3$): δ 7.32–7.05 (m, Ph), 3.74 (t, PCH_2P, ^2J(H–P) = 7.7). ^{13}C-NMR (240 K, CDCl$_3$): δ 138.2–128.1 (m, Ph), 29.3 (t, PCH$_2$P, ^1J(C–P) = 12). Anal. Calc. for C$_{63}$H$_{42}$Au$_2$Fe$_4$O$_{14}$P$_4$: C 42.89, H 2.40. Found: C 42.99, H 2.60%.

3.2. [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(dppip)] (2)

A similar procedure (reaction temperature 258 K) was used to prepare compound **2**. Yield: 0.32 g, 75%. IR (toluene, cm^{-1}) ν(CO): 2042 (m), 2012 (vs), 1973 (s, br), 1778 (m). ^{31}P{^{1}H}-NMR (240 K, CDCl$_3$): δ 133.6 (d, Fe$_2$$PPh_2$, ^3J(PP) = 23), 78.2 (d, AuPPh$_2$). ^{1}H-NMR (240 K, CDCl$_3$): δ 7.46–7.09 (m, Ph), 1.68 (t, PC(CH_3)$_2$P, ^2J(H–P) = 17.3). ^{13}C-NMR (240 K, CDCl$_3$): δ 138.5–125.3 (m, Ph), 39.1 (t, PC(CH$_3$)$_2$P, ^2J(C–P) = 4), 30.6 (t, PC(CH$_3$)$_2$P, ^1J(C–P) = 7). Anal. Calc. for C$_{65}$H$_{46}$Au$_2$Fe$_4$O$_{14}$P$_4$: C 43.53, H 2.59. Found: C 43.99, H 2.69%.

3.3. Synthesis of [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(dppe)] (3)

Solid [(ClAu)$_2$dppe] (0.20 g, 0.24 mmol) and TlBF$_4$ (0.14 g, 0.48 mmol) were added to a solution of [NEt$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.30 g, 0.48 mmol) in 40 ml of THF at r.t. The solution turned deep violet immediately. After 30 min of stirring the mixture was filtered and taken to dryness. The remaining solid was extracted with 20 ml of toluene. Subsequent addition of n-pentane and cooling overnight (233 K) afforded purple–red microcystals of **3**. The compound was recrystallized in CH$_2$Cl$_2$/n-pentane. Yield: 0.30 g, 70%. IR (toluene, cm^{-1}) ν(CO): 2043 (m), 2012 (vs), 1974 (s, br), 1784 (m); ^{31}P{^{1}H}-NMR (240 K, CDCl$_3$): δ 129.8 (m, Fe$_2$$PPh_2$, AA′XX′ spin system, ^{3+3}J(PP) = 63, ^3J($_{Fe2}$PP$_{Au}$) = 25, ^6J($_{Fe2}$PP$_{Au}$) = 0.2, ^9J($_{Fe2}$PP$_{Fe2}$) = 0), 50.7 (m, AuPPh$_2$) (data from spectral simulation). ^{1}H-NMR (298 K, CDCl$_3$): δ 7.43–7.11 (m, Ph), 2.62 (br s, PCH_2CH_2P). ^{13}C-NMR (298 K, CDCl$_3$): δ 138.3–127.6 (m, Ph), 24.9 (m, PCH$_2$$CH_2$P). Anal. Calc. for C$_{64}H_{44}Au_2Fe_4O_{14}P_4$: C 43.23, H 2.49. Found: C 43.51, H 2.68%.

3.4. *[{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(dppp)]* (**4**)

A similar procedure was used to prepare compound **4**. Yield: 0.32 g, 75%. IR (toluene, cm^{-1}) ν(CO): 2042 (m), 2011 (vs), 1972 (s, br), 1781 (m). ^{31}P{^{1}H}-NMR (240 K, CDCl$_3$): δ 129.2 (d, Fe$_2$*P*Ph$_2$,^{3}*J*(PP) = 24), 47.1(d, Au*P*Ph$_2$). ^{1}H-NMR (298 K, CDCl$_3$): δ 7.59–7.23 (m, Ph), 2.69 (m, 4H, PC*H*$_2$CH$_2$C*H*$_2$P), 2.07 (m, 2H, PCH$_2$C*H*$_2$CH$_2$P). ^{13}C-NMR (298 K, CDCl$_3$): δ 132.9–127.9 (m, Ph), 40.0 (dd, P*C*H$_2$CH$_2$*C*H$_2$P, ^{1}*J*(C–P) = 29, ^{3}*J*(C–P) = 17), 20.8 (t, PCH$_2$*C*H$_2$CH$_2$P, ^{2}*J*(C–P) = 7). Anal. Calc. for C$_{65}$H$_{46}$Au$_2$Fe$_4$O$_{14}$P$_4$: C 43.53, H 2.59. Found: C 43.75, H 2.71%.

3.5. *Experimental conditions for the redistribution reactions between [Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)]$^-$ and[(ClAu)$_3$(triphos)]*

Solid [(ClAu)$_3$(triphos)] (0.16 g, 0.12 mmol) and TlBF$_4$ (0.035 g, 0.12 mmol) were added to a THF solution (40 ml) of [NEt$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.075 g, 0.12 mmol) at r.t. After 30 min of stirring a ^{31}P-NMR spectrum of the solution was carried out at 298 K and the data obtained were as follows: [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}(triphos)(AuCl)$_2$] (**5a**) (major product) δ 130.6 (d, Fe$_2$*P*Ph$_2$, ^{3}*J*(PP) = 24), 36.3 (d, Fe$_2$Au*P*Ph$_2$), 16.8 (s, ClAu*P*Ph$_2$), [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(triphosAuCl)] (**5b**) (minor product) δ 131.0 (d, Fe$_2$*P*Ph$_2$, ^{3}*J*(PP) = 24), 35.7 (d, Fe$_2$Au*P*Ph$_2$), 16.8 (s, ClAu*P*Ph$_2$), [(ClAu)$_3$(triphos)] (minor product) δ 16.9 (s). No further changes in the spectrum were observed on stirring longer.

Solid TlBF$_4$ (0.035 g, 0.12 mmol) and [NEt$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.075 g, 0.12 mmol) were added to the above reported solution. After 30 min of stirring a ^{31}P-NMR spectrum of the solution was carried out at 298 K and the data obtained were as follows: [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_2$(triphos)(AuCl)] (**5b**) (major product), [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}(triphos)(AuCl)$_2$] (**5a**) (minor product), [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)-Au}$_3$(triphos)] (**5**) (minor product) δ 131.1 (d, Fe$_2$*P*Ph$_2$, ^{3}*J*(PP) = 24), 35.5(d, Fe$_2$Au*P*Ph$_2$), [(ClAu)$_3$(triphos)] (minor product) δ 16.9 (s). No further changes in the spectrum were observed on stirring longer.

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References

[1] (a) R. Reina, O. Rossell, M. Seco, J. Ros, R. Yáñez, A. Perales, Inorg. Chem. 30 (1991) 3973. (b) S. Alvarez, O. Rossell, M. Seco, J. Valls, M.A. Pellinghelli, A. Tiripicchio, Organometallics 10 (1991) 2309. (c) M. Ferrer, R. Reina, O. Rossell, M. Seco, S. Alvarez, M.A. Pellinghelli, A. Tiripicchio, Organometallics 11 (1992) 3753. (d) A.J. Amoroso, A.J. Edwards, B.F.G. Johnson, et al., J. Organomet. Chem. 443 (1993) C11. (e) R. Reina, O. Rossell, M. Seco, M. Font-Bardia, X. Solans, Organometallics 13 (1994) 2127. (f) P.M.N. Low, Y.K. Yan, H.S.O. Chan, T.S. Andy Hor, J. Organomet. Chem. 454 (1993) 205. (g) O. Rossell, M. Seco, G. Segalés, J. Organomet. Chem. 503 (1995) 225. (h) P.M.N. Low, A.L. Tan, T.S.A. Hor, Y-S. Wen, L-K. Liu, Organometallics 15 (1996) 2595. (i) O. Rossell, M. Seco, G. Segalés, B.F.G. Johnson, P.J. Dyson, S.L. Ingham, Organometallics 15 (1996) 884.

[2] M. Ferrer, R. Reina, O. Rossell, M. Seco, X. Solans, J. Chem. Soc. Dalton Trans. (1991) 347.

[3] M. Ferrer, A. Julià, O. Rossell, M. Seco, M.A. Pellinghelli, A. Tiripicchio, Organometallics 16 (1997) 3715.

[4] (a) P. Braunstein, M. Knorr, M. Strampfer, et al., J. Chem. Soc. Dalton Trans. (1994) 1533. (b) P. Braunstein, M. Knorr, M. Strampfer, A. Tiripicchio, F. Ugozzoli, Organometallics 13 (1994) 3038.

[5] (a) P. Braunstein, M. Knorr, A. Tiripicchio, M. Tiripiccio-Camellini, Inorg. Chem. 31 (1992) 3685. (b) A. Pons, O. Rossell, M. Seco, A. Perales, Organometallics 14 (1995) 555.

[6] R.J. Puddephatt, Chem. Soc. Rev. 12 (1983) 99.

[7] H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama, G. Huttner, Chem. Ber. 110 (1977) 1748.

[8] (a) M. Bardají, N.G. Connelly, M.C. Gimeno, J. Jiménez, P.G. Jones, A. Laguna, M. Laguna, J. Chem. Soc. Dalton Trans. (1994) 1163. (b) E. Cerrada, M.C. Gimeno, J. Jiménez, A. Laguna, M. Laguna, Organometallics 13 (1994) 1470. (c) S.M. Draper, C.E. Housecroft, J.E. Rees, M.S. Shongwe, B.S. Haggerty, A.L. Rheingold, Organometallics 11 (1992) 2356.

[9] R.T. Baker, P.J. Krusic, J.C. Calabrese, D.C. Rose, Organometallics 5 (1986) 1506.

[10] R. Reina, O. Rossell, M. Seco, J. Organomet. Chem. 398 (1990) 285.

[11] R. Usón, A. Laguna, Organomet. Synth. 3 (1986) 324.

[12] P. Cassoux, R. Dartiguepeyron, C. David, D. de Montauzon, J.B. Tommasino, P.L. Fabre, Actual. Chim. 1 (1994) 49.