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Cationic bis-diphosphaferrocene copper and gold complexes†

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The octa(ethyl)diphosphaferrocene **1** reacts with half an equivalent of $[Cu(MeCN)_4][PF_6]$ to afford the corresponding $[Cu(\mathbf{1})_2][PF_6]$ complex **2** in which **1** behaves as a chelate ligand. An X-ray crystal structural analysis reveals that the overall arrangement of the four phosphorus atoms around the Cu cation is distorted tetrahedral. The same strategy was applied to the synthesis of gold(I) complexes. Ligands **1** and the octa-(*n*-propyl)diphosphaferrocene **4** react with two equivalents of $[AuCl(SMe_2)]$ to yield the expected bimetallic complexes $[Au_2Cl_2(\mathbf{1})]$ **3** and $[Au_2Cl_2(\mathbf{4})]$ **5** respectively. In these two complexes, each phospholide unit is coordinated to an AuCl fragment. Surprisingly, crystallization of **5** affords the bis-chelate $[Au(\mathbf{4})_2][FeCl_4]$ derivative. A mechanism involving oxidation of the diphosphaferrocene ligand followed by nucleophilic attack of one chloride anion has been tentatively proposed. Complexes $[Au(\mathbf{1})_2][GaCl_4]$ **7** and $[Au(\mathbf{4})_2][GaCl_4]$ **8** can be conventionally prepared by the direct reaction of the two ligands with $[AuCl(SMe_2)]$ in the presence of $GaCl_3$ as chloride abstractor. A DFT study, coupled with a Charge Decomposition Analysis (CDA), performed on the $[Cu(dpf)_2]$ and $[Cu(dpe)_2]$ model complexes (dpf = $C_8H_8P_2Fe$, dpe = $H_2PCH_2CH_2PH_2$) indicates that σ-donation dominates in the two complexes. In homoleptic $[M(dpf)_2]$ and $[M(dpe)_2]$ complexes (M = Ni, Pd), dpf and dpe exhibit a stronger π-accepting capacity. A comparison between theoretical structures of the bis-carbonyl complexes $[NiL(CO)_2]$ (L = dpf or dpe or $Me_2PCH_2CH_2PMe_2$) indicates that dpf and dpe display a similar π-accepting capacity.

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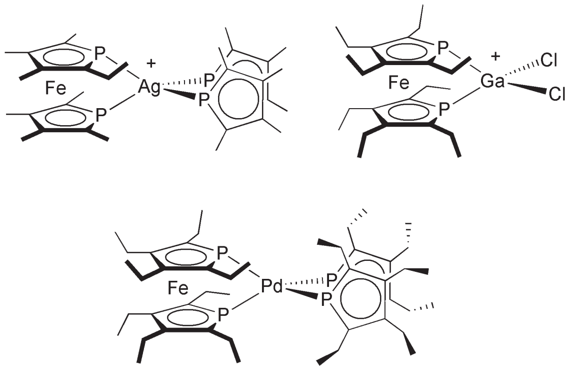
With regard to classical tertiary phosphines, low-coordinated phosphorus compounds possess a highly spherical lone pair at P.[1] This structural feature, which results from the weaker ability of phosphorus to give multiple bonding, renders these ligands very attractive for the elaboration of complexes displaying hemilabile properties. This particular feature has already been exploited with molecules such as phosphinines to build copper-based helices[2,3] and with diphosphaferrocenes[4] to synthesize unusual chelate species in which binding of the metal occurs through a side-on coordination mode. Initially, the first bis-diphosphaferrocene chelate complex $[(C_{16}H_{24}P_2Fe)_2Ag)][BF_4$, Scheme 1] was synthesized by Cowley *et al.* who attempted the oxidation of octamethyldiphosphaferrocene with $AgBF_4$.[5] Recently, we extended their syntheses to Pd(0)[6] and Ga(III)[7] derivatives using octa(ethyl)diphosphaferrocene as ligand. These palladium complexes were found to be particularly active in two catalytic processes, the Suzuki[6a] and the Miyaura cross coupling[6b] reactions that allow the creation of C_{sp2}–C_{sp2} and C_{sp2}–B bonds, respectively.



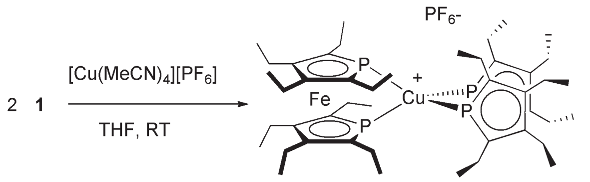
Scheme 1 Diphosphaferrocene d^{10} metal complexes.

In the course of our studies aimed at exploring the synthesis and the reactivity of other diphosphaferrocene based chelate complexes, we recently turned our attention on the preparation of cationic copper and gold (I) complexes. Herein, we report on these results.

Results and discussion

Syntheses and structures of complexes

Our first experiments were carried out with the octa(ethyl)diphosphaferrocene ligand which is easily available *via* a zirconocene-mediated route **1**.[6a] Attention was initially focused on the synthesis of copper(I) complexes. Among various possible routes, we found that the reaction of the complex $[Cu(MeCN)_4][PF_6]$ with **1** furnished the most straightforward access to the bis chelate complex **2** [eqn (1)]. The displacement of acetonitrile ligands readily takes place in dichloromethane as solvent at room temperature yielding **2** as a very stable pink powder.



2 (1)

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† Electronic supplementary information (ESI) available: Cartesian coordinates and optimized geometries for copper, nickel and palladium complexes. See http://www.rsc.org/suppdata/nj/b3/b301408h/

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The formulation of **2** could be unambiguously confirmed from the the ^{13}C NMR spectrum that exhibits a characteristic AXX′X″X‴ spin pattern for the Cα (C2 and C5) carbon atoms of the ligand. Another significant piece of data is given by the ^{31}P NMR spectrum. Indeed, as previously observed for Ga(III) and Pd(0) chelate complexes, a strong upfield shift results from the side-on coordination of diphosphaferrocene.[6a,7] Thus whereas the ^{31}P NMR signal of **1** appears at −66.0 ppm (CDCl$_3$, 298 K), that of complex **2** is at −163.7 ppm (CDCl$_3$, 298 K).

Definitive proof of the structure of complex **2** was given by an X-ray crystal structure analysis.‡ An ORTEP view of one molecule of **2** is presented in Fig. 1 (experimental details are given in Table 1) and relevant bond lengths and angles are listed in Table 2. As can be seen, the overall arrangement of the four phosphorus atoms around the Cu cation is distorted tetrahedral, the bite angle of the ligand (102.95(2) and 103.87(2)°) being slightly smaller than the other P–Cu–P angles (between 108.49(2)° – 119.38(2)°). Furthermore the two ligands are located in two nearly perpendicular planes (angle between the two planes P3–Cu1–P4 and P1–Cu1–P2 = 86.1°).

All P–Cu bond distances (between 2.3114(6) and 2.3263(6) Å) are lengthened compared to classical phosphine–Cu bond distances but a direct comparison is not appropriate because of the difference in hydridization. Previous studies have shown that P–Cu bond lengths in phosphinine complexes can vary from 2.22 Å to 2.33 Å.[3,8] However in **2**, the lengthening of the P–metal bonds probably results from the side-on coordination mode which reduces the overlap between the ligand and metal orbitals.

A similar observation was made in the case of palladium(II) complexes. Apart from this, metric parameters of the ligand are close to those recorded for the free ligand **1**.[6a] Thus the P–Cα bond lengths (1.780(2) Å in **2** *vs.* 1.782(1) Å in **1**), the Cα–Cβ (1.421(3) Å in **2** *vs.* 1.430(2) Å in **1**) and the Cβ–Cβ′ (1.444(3) Å in **2** *vs.* 1.432(2) Å in **1**) bond lengths are identical. Only the Fe–centroid bond distance is lengthened (1.682 Å in **2** *vs.* 1.662(2) Å in **1**) and the P atoms slightly deviate from the mean plane of the rings ($\theta = 4.3°$). Theoretical claculations carried out on a cationic Ga(III) derivative have already demonstrated that this distortion reflects the participation of the P–Fe bond in the bonding.[7]

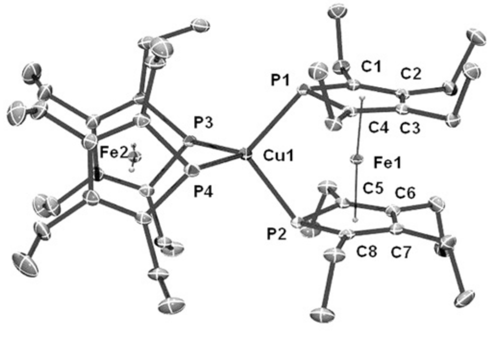

Fig. 1 The molecular structure of one molecule of **2**.

Table 1 Crystal data and details of the structure determination of complexes **2** and **6**

	2	6
Empirical formula	$C_{48}H_{80}CuFe_2$-$F_6P_5{\cdot}(CHCl_3)_2$	$C_{64}H_{112}AuCl_4$-Fe_3P_4
FW	1339.95	1511.73
T/K	150.0(1)	150.0(1)
λ/Å	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	16.9930(5)	18.610(1)
b/Å	19.0930(5)	19.960(1)
c/Å	18.8270(6)	19.351(1)
β/deg	102.773(14)	95.044(1)
U/Å^3	5957.2(3)	7160.2(6)
Z	4	4
μ/cm^{-1}	1.290	2.912
Reflections measured	41 822	29 169
Ind. reflections	17 371	16 267
Reflections used	13 227	10 579
R_{int}		
$R_1[I > 2\sigma(I)]$	0.0421	0.0366
$wR_2[I > 2\sigma(I)]$	0.1110	0.0818

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

The synthesis of gold(I) complexes turned out to be much more subtle. We first decided to explore the preparation of gold-chloride complexes of **1**. Reaction of two equivalents of [Au(SMe$_2$)Cl] with ligand **1** cleanly yielded a complex that appears as a singlet at δ(CH$_2$Cl$_2$) = 5.90 ppm in ^{31}P NMR spectroscopy. This chemical shift being not strongly upfield shielded, we logically assumed that complex **3** could be the dimetallic Au–Cl derivative, each ligand acting as a two-electron donor [eqn. (2)].

All NMR data support the formulation proposed for **3**. A significant piece of data is given by the ^{13}C NMR spectrum which indicates the absence of a second-order spin system as in complex **2**. The formulation of **3** was also confirmed by elemental data. In such gold-based bimetallic edifices, an interesting problem concerns the presence of an Au–Au interaction. Indeed, as previously showed by Laguna in bis(diphenylphosphino)ferrocene gold complexes, the presence of a short contact between the two [Au–Cl] forces the complex to adopt an eclipsed conformation in the solid state.[9] In order to verify whether such interaction could also occur, we attempted to crystallize the complex. Unfortunately, despite numerous attempts in different mixture of solvents, no single crystals suitable for an X-ray crystal structure analysis could be grown. During our attempts we found that **3** slowly decomposed upon standing in solvents for long periods.

More significant results were obtained when **1** was replaced by the octa(n-propyl)diphosphaferrocene ligand **4**. Synthesis of complex **5** was carried out under the same experimental conditions that used for the preparation of **3** [eqn. (2)]. The

Table 2 Selected bond distances (Å) and angles (°) for [(FeC$_{24}$H$_{40}$P$_2$)$_2$Cu][PF$_6$] **2**

P1–C1	1.780(2)	P1–C1–C2	111.8(2)
C1–C2	1.421(3)	C1–C2–C3	112.6(2)
C2–C3	1.444(3)	C2–C3–C4	112.6(2)
C3–C4	1.419(3)	C3–C4–P1	111.7(2)
C4–P1	1.782(2)	C4–P1–C1	90.8(1)
P1–Cu1	2.3114(6)	P1–Cu1–P2	103.87(2)
P2–Cu1	2.3263(6)	P2–C5–C6	112.2(2)
P2–C5	1.782(2)	C5–C6–C7	112.3(2)
C5–C6	1.422(3)	C6–C7–C8	112.7(2)
C6–C7	1.442(3)	C7–C8–P2	112.0(2)
C7–C8	1.423(3)	C8–P2–C5	90.5(1)
C8–P2	1.782(2)	P3–Cu1–P4	102.95(2)
P4–Cu1	2.3194(6)	P1–Cu1–P3	110.83(2)
P3–Cu1	2.3137(6)	P1–Cu1–P4	108.49(2)

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† CCDC reference numbers 203940 and 203941. See http://www.rsc.org/suppdata/nj/b3/b301408h/ for crystallographic data in .cif or other electronic format.

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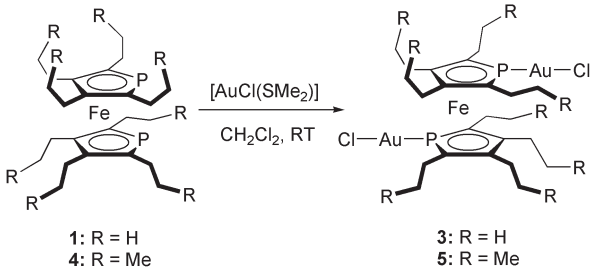
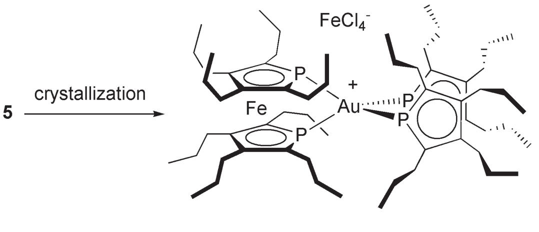
formulation of **5** was established on the basis of NMR data by comparison with those of **3** and elemental analysis.



(2)

Our crystallization attempts were more successful and single crystals could be obtained by diffusing hexane into a dichloromethane solution of the complex at room temparature. Though **5** proved to be much more stable than **3** upon standing in solution, partial decomposition could not be avoided and a gold mirror slowly deposited on the inner side of the flask during crystallization.

Surprisingly, the structure of this new complex **6** does not correspond to what expected [eqn. (3)]. An ORTEP view of one molecule of **6** is presented in Fig. 2 and the most significant bond lengths and bond angles are listed in Table 3 (experimental details are given in Table 1).



6

(3)

As can be seen **6** is not a bimetallic species but a chelate complex featuring two diphosphaferrocene ligands which bind the Au$^+$ cation through their phosphorus atom lone pair. The counter anion is $[FeCl_4]^-$ showing that a concommitant decomposition of the ligand occurred. In good agreement with a chelate structure, the ^{31}P NMR (δ(CH$_2$Cl$_2$) $= -178.6$ ppm) chemical shift (recorded on microcrystals) is shielded to highfield and different from that of **5**.

Like in **2**, complex **6** adopts a distorted tetraedral geometry, the bite angle of the ligand being smaller than the P–Au–P angles. Interestingly, the two ligands do not adopt an eclipsed conformation and there is a small dihedral angle (P–Ct–Ct–P) between the two P atoms of each ligand ($\theta = 13°$), which probably tends to reduce the overlap between the ligands and the Au center. Accordingly, P–Au bond distances (from 2.464(1) to 2.4794(9) Å) are long. Comparatively, in phosphinine Au(I) complexes, P–Au bond lengths (from 2.21 to 2.31 Å) are relatively similar to those recorded in classical tertiary phosphine complexes.[10] Like in **2**, metric parameters within the ligands are not significantly modified and compare with those of the free ligand **1**.

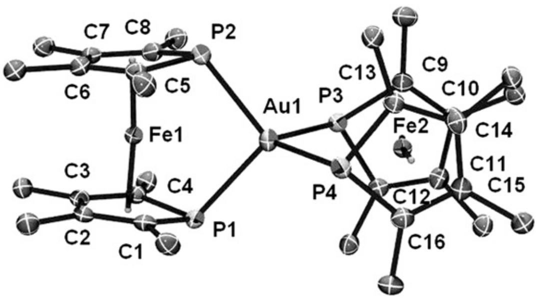


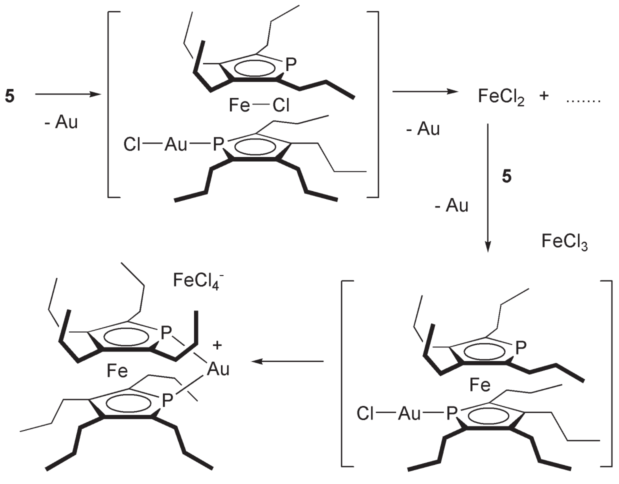
Fig. 2 The molecular structure of one molecule of **6**. The ethyl groups of *n*-propyl substituents have been omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for $[(FeC_{32}H_{56}P_2)_2Au][FeCl_4]$ **6**

Au1–P1	2.464(1)	P1–Au1–P2	101.03(3)
Au1–P2	2.466(1)	P3–Au1–P4	100.87(3)
Au1–P3	2.4794(8)	P1–Au1–P3	114.08(3)
Au1–P4	2.4699(8)	P1–Au1–P4	112.94(3)
P1–C1	1.784(3)	P2–Au1–P3	116.41(3)
C1–C2	1.413(4)	P2–Au1–P4	112.09(3)
C2–C3	1.437(4)	P1–C1–C2	111.7(2)
C3–C4	1.421(4)	C1–C2–C3	113.1(3)
C4–P1	1.781(3)	C2–C3–C4	112.0(3)
P2–C5	1.789(3)	C3–C4–P1	112.0(2)
C5–C6	1.429(4)	C4–P1–C1	90.2(2)
C6–C7	1.441(4)	P2–C5–C6	111.7(2)
C7–C8	1.415(4)	C5–C6–C7	112.2(3)
C8–P2	1.781(3)	C6–C7–C8	112.7(3)
Fe1–Ct1	1.699	C7–C8–P2	112.3(2)
Fe2–Ct2	1.696		

The formation of cationic diphosphaferrocene complexes by oxidation of the ligand is not an unprecedented phenomenon and a similar observation has already been made during the study of palladium(II) complexes. In line with electrochemical experiments, it is now well established that phosphaferrocenium ions are decomposed by nucleophilic attack of halide anions at the iron atom to yield the $[FeCl_2(solv)_4]^+[FeCl_4]^-$ complex.[11] Thus, the formation of **6** is probably initiated by the decomposition of the complex to form metallic gold and a Fe(III) derivative. In a second step, this complex evolves to yield Au(0), FeCl$_2$ and decomposition products resulting from the release of the ligands. Then formation of FeCl$_2$, which behaves as a reducing agent, probably initiates the decomposition of a second molecule of **5** (Scheme 2) to yield FeCl$_3$ and a mononuclear gold complex that can react with FeCl$_3$ (Lewis acid) to produce a cationic chelate species. A similar mechanism has already been proposed to explain the formation of diphosphaferrocene-based chelate cationic Pd(II) complexes.[6c] In order to test the validuty of this mechanism, complex **5** was treated with a catalytic amount (5% per mol of **5**) of FeCl$_2$ in dichloromethane at room temperature. Under these conditions, complex **6** formed within a few minutes.

More conventionally, these cationic Au(I) chelates could also be prepared from the reaction of diphosphaferrocenes with one equivalent of gold in the presence of GaCl$_3$ as chloride abstractor. The reaction takes place in dichloromethane at room temperature yielding complex **7** and **8** as stable powders.



Scheme 2 Proposed mechanisme for the formation of complex **6**.

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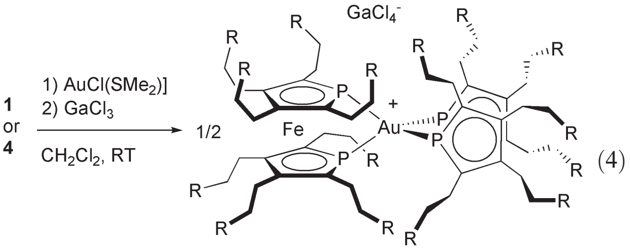
NMR data of the two complexes support the proposed formulation [eqn. (4)]. In ^{31}P NMR, they both appear as singlet at −179.20 and −178.60 ppm. In good agreement with the chelate structure, ^{13}C NMR spectra show the classical AXX′X″X‴ spin system pattern for the Cα carbon atoms.



7: R = H
8: R = Me

Theoretical study

A theoretical study using DFT was undertaken to gain further insight on the bonding of diphosphaferrocene in these tetrahedral d^{10} metal complexes. An optimization was carried out on the [Cu(dpf)$_2$] (C$_8$H$_8$P$_2$Fe = dpf) complex incorporating two parent diphosphaferrocene (dpf) as ligands (Scheme 3). Different combination of functionals (BP86, B3PW91 and B3LYP) and basis sets were studied. The most satisfying compromise in terms of accuracy *versus* computer time was obtained by the combination of the B3LYP functional with relativistic effective core potentials (ECP) of Hay and Wadt for Fe and Cu, and 6-31G(d) all-electron basis sets for C, P and H.[12] Note that all-electron basis sets such as DZVP and DZVPII were also tested but did not yield significant improvements in terms of metric parameters.

The most relevant bond distances and angles are presented in Table 4. The small discrepancy between theoretical and experimental parameters probably results from the difference of substitution scheme between the two ligands. Thus, whereas bond lengths and bond angles within the ligand of the optimized structure are quite close to the experimentals values, P–Cu bond distances are lengthened (2.403 Å in the theoretical structure *vs.* 2.3114(6) and 2.3263(6) Å in **2**). Interestingly the out-of plane distorsion of the phosphorus atom is also reproduced ($\theta = 4.8°$ in *vs.* $\theta = 4.3°$ in **2**).

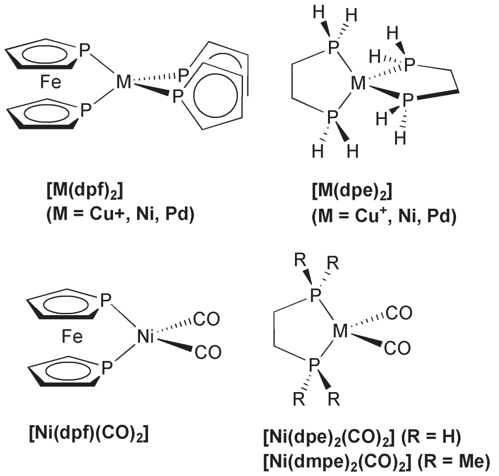
Inspection of the molecular orbitals reveal that nine orbitals mainly account for the bonding of the dpf ligands to the Cu atom: H-4 (H meaning HOMO), H-5 and H-6 (degenerate), H–16 and H–17 (degenerate), H-19 and H-20 (degenerate), H-21 and H-22. Four of these orbitals are shown in Fig. 3.

Table 4 Theoretical bond lengths (Å), bond angles (°) in [Cu(dpf)$_2$]$^+$

P–Cα	1.794	Cα–P–Cα′	89.1
Cα–Cβ	1.412	P–Cα–Cβ	112.6
Cβ–Cβ′	1.429	Cα–Cβ–Cβ′	112.6
P–Cu	2.403	P–Cu–P	105.0 (bite angle)
Cu–Fe	2.903	P–Cu–P	111.8

The highest orbital (H-4) results from the combination of two non-bonding orbitals at iron (d$_{z^2}$ and d$_{x^2-y^2}$) and the 3p$_x$ at phosphorus with the d$_{y^2-z^2}$ and 4p$_x$ at copper. The H-5 and H-6 orbitals involve the combination of the H-2 and the LUMO of the dpf ligand (calculated separately in the geometry of the complex) with the 3d$_{xz}$ orbital at Cu. Interestingly, these orbitals are antibonding between the 3d$_{xz}$ at iron and the 3d$_{xz}$ at Cu but bonding occurs through a π overlap with the 3p$_x$ orbital at phosphorus. The in-phase combination of the two 3d$_{xz}$ orbitals at iron and copper occurs in the H-17 orbital. Note that this orbital also involves a significant contribution of the 3p$_z$ orbital at phosphorus (LUMO of dpf). As previoulsy noted in a theoretical investigation of the GaCl$_2$ complex, this orbital probably accounts for the out-of plane deviation of the phosphorus atom from the mean plane of the rings since the contribution of the 3d$_{xz}$ orbital at iron decreases the overlap between Fe and P.[7] On the other hand, the H-20 and H-21 feature a small participation of the 3d$_{xz}$ orbital at iron but an important contribution of the σ$_\text{p}$ orbitals of the phospholide ligands (mainly 3p$_x$ and 3s at P). The other contributions to the bonding are given by the H-21 and H-22 which involve the combination of the σ$_\text{p}$ orbital of the phospholide ligands with the 3d$_{y^2-z^2}$ and 4p$_x$ orbitals (H-21) and the empty 4s orbitals (H-22) at copper. These two orbitals only feature a weak contribution of the iron atom.

As often encountered in ferrocennyl-based bimetallic complexes, dative bonding can occur between non-bonding orbitals at iron and metals.[13] Such bonding does not occur here since no empty d orbitals are available at the metal (d^{10} electronic configuration). However, as shown by the shape of the H-4 orbital contact can exist between Fe and Cu atoms but the very weak amplitude of the Wiberg bond index (P(Fe–Cu) = 0.04)) suggests that it is probably negligible. Contrary to the GaCl$_2$ complex, no significant electronic transfer occurs between the dpf ligands and the copper atom. Indeed, the Natural Bond Orbital (NBO) population analysis reveals that the charge distribution within the ligand is not dramatically modified by coordination. Thus, the positive charge at phosphorus (+0.578 in the complex *vs.* +0.648 in free dpf) and the negative charge at the two carbon atoms are decreased (−0.584 *vs.* −0.629 in free dpf). These data are summarized in Table 5.



Scheme 3 Theoretical structures studied.

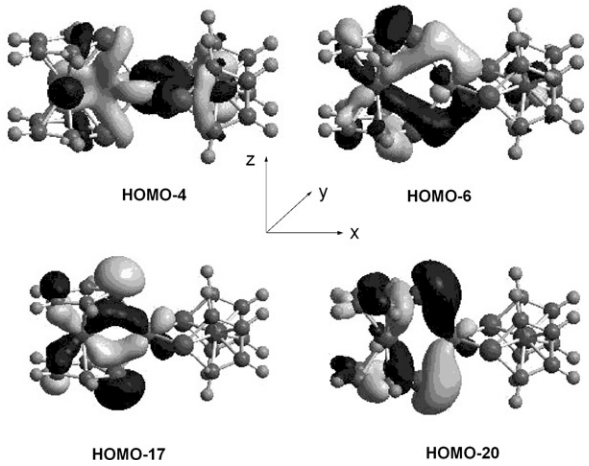


Fig. 3 Selected orbitals describing the bonding in [Cu(dpf)2]$^+$.

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Table 5 NBO charges (e) in the $[Cu(dpf)]^+$ complex given by calculations. Numbers in parentheses refer to NBO charges in the free ligand calculated at the same level of theory in the geometry of the complex

Atoms	Charges
P	+0.578 (+0.648)
Cα	−0.584 (−0.619)
Cβ	−0.242 (−0.263)
Fe	0.093 (+0.101)
Cu	0.550
Σ(q) ligand	0.225

On the other hand the charge at iron is nearly comparable (+0.093 in the complex *vs.* +0.101 in free dpf). A charge of +0.550 at copper indicates that the electron deficiency of each ligand is not very important ($\Sigma q = +0.225$ per ligand).[14]

In order to gain further insight on the binding capacity of diphosphaferrocenes in these chelate species, a Charge Decomposition Analysis (CDA) was carried out. This method developed by Frenking and colleagues proved to be particularly efficient to estimate the ratio between donation and back donation for bonding following the classical Dewar–Chatt–Duncanson (DCD) model concept.[15] Details about the method, the terms used and their relevance are given in the Experimental. The results of this CDA analysis are presented in Table 6. A first important remark concerns the value of the residual term (Δ) which is very small and confirms that the bonding can be described in terms of the DCD model.[16] As can be seen in Table 6, the magnitude of the d/b ratio (12.73) clearly suggests that, in such chelate Cu complexes, diphosphaferrocenes essentially behave as σ-donors. This result is somewhat surprising if we take into account that phosphaferrocenes are known to possess a substantial π-accepting capacity. However it has already been demonstrated that homoleptic copper(I) complexes are not the best cases to estimate the π-accepting capacity of a 2e donor ligand. Thus, CDA analyses have shown that CO, in homoleptic cationic $[Cu(CO)_n]^+$ ($n = 1$ to 4) complexes, behaves as a poor π-acceptor ligand, the d/b ratio varying from 7.98 to 9.80.[17] The same behavior is observed for phosphine complexes. Thus, a CDA analysis carried out on the $[Cu(dpe)_2]^+$ complex (dpe = $H_2PCH_2CH_2PH_2$), calculated at the same level of theory, reveals that the dpe ligand also behaves as a relatively poor π-acceptor ($d/b = 7.45$). Therefore, in order to improve our analysis of the bonding in these d^{10} phosphaferrocene chelate complexes, we extended our study to the homoleptic Ni and Pd species.

Theoretical structures of the $[Ni(dpf)_2]$ and $[Pd(dpf)_2]$ complexes were calculated at the same level of theory as well as those of the corresponding diphosphine $[Ni(dpe)_2]$ and $[Pd(dpe)_2]$ complexes. Theoretical bond lengths and bond angles of these four structures are given in the Electronic Supplementary Information.† An examination of molecular orbitals of these two complexes reveal that the same MOs as in the $[Cu(dpf)_2]^+$ complex describe the bonding. The most interesting information is given by the CDA analysis which shows that dpf effectively behaves as a good π-acceptor ligand, the d/b ratio being close to that of the corresponding diphosphine (dpe) ligand (1.81 *vs.* 2.38 in the Ni complex and 2.18 *vs.* 1.78 in the Pd complex, see Table 6). However, it is somewhat unsafe to compare the d/b ratio between two ligands towards two different fragments. Therefore, in order to set a better comparison, the three model complexes $[Ni(dpf)(CO)_2]$, $[Ni(dpe)(CO)_2]$ and $[Ni(dmpe)(CO)_2]$ (dmpe = $Me_2PCH_2CH_2PMe$) were calculated (same level of theory) and a CDA analysis was performed (see Table 6). Whereas the more electron-rich dmpe ligand acts as the better σ-donor ligand, as expected, these data suggest that the π-accepting capacity of dpf compares with that of dpe. However, though these preliminary data are interesting, extension of this study to substituted derivatives is needed. Indeed, it is now well established that susbtituent effects play a decisive role in the coordinative behavior of diphosphaferrocenes. Thus, it was observed that these chelate complexes (M = Ni, Pd) only form when alkyl groups are present at the periphery of the ring.[6a]

Table 6 Results of the charge decomposition analysis for dpf, dpe and dmpe ligands in $[M(L)_2]$, (M = Cu^+, Ni, Pd) and $[Ni(L)(CO)_2]$ complexes. Donation and back donation values are expressed in e

Complexes	d[a]	b[b]	d/b	$b/d+b$[c]	r[d]	Δ[e]
$[Cu(dpf)_2]^+$	0.802	0.063	12.73	7.28	−0.397	−0.030
$[Cu(dpe)_2]$	0.827	0.111	7.45	11.84	−0.276	−0.011
$[Ni(dpf)_2]$	0.598	0.330	1.81	35.56	−0.390	−0.039
$[Ni(dpe)_2]$	0.934	0.393	2.38	29.62	−0.233	−0.022
$[Pd(dpf)_2]$	0.649	0.297	2.18	31.40	−0.461	−0.040
$[Pd(dpe)_2]$	0.737	0.415	1.78	36.02	−0.423	−0.005
$[Ni(dpf)(CO)_2]$	0.620	0.151	4.105	19.58	−0.369	−0.030
$[Ni(dpe)(CO)_2]$	0.780	0.199	3.92	20.33	−0.413	−0.005
$[Ni(dmpe)(CO)_2]$	0.878	0.180	4.88	17.01	−0.440	−0.021

[a] d = donation. [b] b = back donation. [c] The $b/d+b$ ratio is given in percent. [d] r = repulsion. [e] Δ = residual.

A complete theoretical study aimed at understanding the influence of steric and electronic factors in diphosphaferrocene ligands and complexes is currently underway in our laboratories and will be reported in due course.

Experimental

General

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na–benzophenone and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Dry CD_2Cl_2 was distilled and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm) ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference and coupling constants are expressed in Hz. The following abbreviations are used: b; broad; s, singlet; d, doublet; t, triplet; m, multiplet; p, quintetet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. $[Cu(MeCN)_4][PF_6]$[18] and $[AuCl(SMe_2)]$[19] were according to published procedures.

Syntheses

$[Cu\{octa(ethyl)diphosphaferrocene)_2\}][PF_6]$ complex (2). The $[Cu(MeCN)_4][PF_6]$ complex (0.123 mg, 0.33 mmol) was added to a solution of diphosphaferrocene **1** (0.3 g, 0.61 mmol) in THF (15 mL) at room temperature. The resulting solution instantaneously turned red-violet and complex **2** precipitated. After ten minutes stirring, half of the solvent was evaporated and hexane was added (10 mL). After filtration, **2** was recovered as a brownish red solid. Yield: 309 mg (85%). Anal; calcd. for $C_{48}H_{80}CuF_6Fe_2P_5$: C, 52.35; H, 7.32. Found: C, 51.98; H, 7.48%. ^{31}P NMR ($CDCl_3$): $\delta - 163.70$. ^1H NMR ($CDCl_3$): δ 1.06 (br t, 24H, ^3J(H–H) = 7.00, 8 × Me), 1.23 (br t, 24H, ^3J(H–H) = 7.00, 8 × Me), 1.82 (m, 16H, 8 × CH_2), 2.27 (m, 8H, 4 × CH_2), 2.62 (m, 8H, 4 × CH_2). ^{13}C NMR ($CDCl_3$): δ 16.65 (s, Me), 20.60 (s, Me), 21.60 (s, 2 × CH_2), 105.00

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(m, AXX′X″X‴, ΣJ(C–P) = 32.60, C2 and C5), 105.95 (s, C3 and C4).

[Au$_2$Cl$_2${octa(ethyl)diphosphaferrocene}] complex (3). The [AuCl(SMe$_2$)] complex (114 mg, 0.39 mmol) was added to a solution of diphosphaferrocene **1** (90 mg, 0.19 mmol) in dichloromethane (6 mL). The resulting solution rapidly turned yellow. After ten minutes stirring, half of the solvent was evaporated and hexane was added. After filtration, complex **3a** was recovered as a yellow solid. Yield: 162 mg (91%). Anal; calcd. for $\mathrm{C_{24}H_{40}Au_2Cl_2FeP_2}$: C, 31.64; H, 4.42. Found: C, 31.80; H, 4.27%. ^{31}P NMR (CDCl$_3$): δ 0.75. ^{1}H NMR (CDCl$_3$): δ 1.18 (t, 24H, ^{3}J(H–H) = 7.30, Me), 2.09 (m, 4H, CH$_2$), 2.13 (m, 4H, CH$_2$), 2.43 (m, 4H, CH$_2$), 2.77 (m, 4H, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 16.65 (s, Me), 19.30 (d, ^{3}J(C–P) = 5.70, Me), 21.05 (d, ^{2}J(P–C) = 14.30, CH$_2$), 22.15 (d, ^{3}J(P–C) = 4.40, CH$_2$), 94.40 (d, ^{1}J(P–C) = 18.20, C2 and C5), 99.60 (d, ^{2}J(P–C) = 11.70, C3 and C4).

[Au$_2$Cl$_2${octa(*n*-propyl)diphosphaferrocene}] complex (5). The [AuCl(SMe$_2$)] complex (106 mg, 0.36 mmol) was added to a solution of diphosphaferrocene **4** (106 mg, 0.19 mmol) in dichloromethane (5 ml). The resulting solution rapidly turned brown. After ten minutes stirring, half of the solvent was evaporated and hexane was added. After filtration, complex **3b** was recovered as a brown solid. Yield: 171 mg (93%). Anal; calcd. for $\mathrm{C_{32}H_{56}Au_2Cl_2FeP_2}$: C, 37.55; H, 5.52. Found: C, 37.90; H, 5.94%). ^{31}P NMR (CDCl$_3$): δ −7.20. ^{1}H NMR (CDCl$_3$): δ 1.01 (t, 24H, ^{3}J(H–H) = 7.20, Me), 1.31 (m, 16H, CH$_2$), 2.15 (m, 8H, CH$_2$), 2.52 (m, 4H, CH$_2$), 2.69 (m, 4H, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 15.26 (s, Me), 16.21 (s, Me), 18.03 (d, ^{3}J(C–P) = 5.80, CH$_2$), 18.76 (s, Me), 22.56 (d, ^{2}J(P–C) = 15.10, CH$_2$), 25.15 (d, ^{3}J(P–C) = 3.95, CH$_2$), 99.51 (d, ^{1}J(P–C) = 17.70, C2 and C5), 103.52 (d, ^{2}J(P–C) = 9.90 Hz, C3 and C4).

[Au{octa(ethyl)diphosphaferrocene}$_2$][GaCl$_4$] complex (7). The [AuCl(SMe$_2$)] complex (26.5 mg, 0.09 mmol) was added to a solution of diphosphaferrocene **1** (80 mg, 0.18 mmol) in dichloromethane (6 mL). After ten minutes stirring, in a glovebox, half an equivalent of gallium trichloride (16 mg, 0.09 mmol) was added and the solution was allowed to stir for ten minutes. The resulting solution rapidly turned green with red glints. Half of the solvent was evaporated and hexane was added. After filtration, complex **7** was recovered as a yellow solid (105 mg, 90%). Anal; calcd. for $\mathrm{C_{48}H_{80}AuCl_4Fe_2GaP_4}$: C, 44.31; H, 6.20. Found: C, 44.65; H, 6.13%. ^{31}P NMR (CD$_2$Cl$_2$): δ – 179.20. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.01 (br s, 24H, Me), 1.25 (br s, 24H, Me), 1.60 (m, 16H, CH$_2$), 2.26 (m, 8H, CH$_2$), 2.69 (m, 8H, CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ 16.05 (s, Me), 19.50 (s, Me), 20.55 (br s, CH$_2$), 21.40 (s, CH$_2$), 105.40 (m, AX′X″X‴, $\Sigma^{1}J$(P–C) = 38.30 Hz, C2 and C5), 106.55 (s, C3 and C4).

[Au{octa(*n*-propyl)diphosphaferrocene}$_2$][GaCl$_4$] complex (8). The [AuCl(SMe$_2$)] complex (26.5 mg, 0.09 mmol) was added to a solution of diphosphaferrocene **4** (100 mg, 0.18 mmol) in dichloromethane (6 mL). After ten minutes stirring, in the glovebox, half an equivalent of gallium trichloride (16 mg, 0.09 mmol) was added and the solution was allowed to stir for ten minutes. The resulting solution rapidly turned green with red glints. Half of the solvent was evaporated and hexane was added. After filtration, complex **8** was recovered as a yellow solid. Yield: 124 mg (91%). Anal; calcd. for $\mathrm{C_{64}H_{112}AuCl_4Fe_2GaP_4}$: C, 50.38; H, 7.40. Found: C, 50.62; H, 7.83%. ^{31}P NMR (CD$_2$Cl$_2$): δ – 178.60. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.95 (br s, 24H, Me), 1.03 (br s, 24H, Me), 1.26 (m, 16H, CH$_2$), 1.41 (m, 16H, CH$_2$), 1.77 (m, 16H, CH$_2$), 2.18 (m, 8H, CH$_2$), 2.76 (m, 8H, CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ 14.53 (s, Me), 15.42 (s, Me), 15.99 (s, CH$_2$), 18.51 (s, CH$_2$), 21.94 (br s, CH$_2$), 23.12 (s, CH$_2$), 103.08 (m, AX′X″X‴, $\Sigma^{1}J$(P–C) = 37.60 Hz, C2 and C5), 107.96 (s, C3 and C4).

Theoretical methods

Calculations were carried out using the GAUSSIAN 98[20] set of programs within the framework of DFT using the three-parameter fit of the exchange-correlation potential suggested by Becke (B3LYP).[21] The 6-31G(d) all-electron basis set was used for C, H and P atoms. A relativistic effective core potential (ECP) of Hay and Wadt with a (341/311/41) split-valence basis set was used for Fe, (311111/22111/411) for Cu, (341/311/41) for Ni and (341/32111/31) for Pd.[22] Vibrational frequencies of the stationary points were calculated at B3LYP with numerical second derivatives of the energy with respect to the coordinates. The structures calculated were located at minima on the potential-energy surface. The bonding situation of the experimental structure was analyzed using the natural bond orbital (NBO) method developed by Weinhold.[23] Inspection of the ligand L$_2$ (L$_2$ = dpf or dpe) M(L$_2$) fragments were performed using the charge-decomposition analysis (CDA) developped by Frenking.[15] In the CDA method the (canonical, natural, or Kohn–Sham) molecular orbitals of the complex are expressed in terms of MOs of the appropriately chosen fragments. In the cases studied, the Kohn–Sham orbitals of the calculations are formed in the CDA procedure as a linear combination of the MOs of the ligand and those of the remaining fragment [ML$_2$]$^+$ (for Cu) and [ML$_2$] (for Ni and Pd). The ligands and the [ML$_2$] fragments were computed in the geometry of the corresponding complexes. The orbital contributions are divided in four parts: (i) the mixing of the occupied MOs of the ligand and the unoccupied MOs of the metal fragment. This value (noted d) represents the donation ligand → [metal fragment]; (ii) the mixing of the unoccupied MOs of the ligand and the occupied MOs of the metal fragment. This value (noted b) accounts for the back donation [metal fragment] → ligand; (iii) the mixing of the occupied MOs of the ligand and the occupied MOs of the metal fragment. This term (noted $<r>$), which describes the repulsive polarization ligand ↔ [metal fragment], is negative because electronic charge is removed from the overlapping area of the occupied orbitals; (iv) the residual term (Δ) which results from the mixing of the unoccupied MOs of the two respective fragments. Usually this term is very close to zero for closed-shell interactions. This value constitutes an important probe to determine whether the bonding studied can be really classified as a donor–acceptor interaction following the Dewar–Chatt–Duncanson model. Important deviations from $\Delta = 0$ imply that the bond studied is more conventionally described as a normal covalent bond between two open shell fragments.[16] A more detailed presentation of the CDA method and the interpretation of the results can be found in the literature.[15c] CDA calculations were performed with the program CDA version 2.1.[15a]

X-Ray structural determination‡

Single crystals of compounds **2** and **6** suitable for X-ray crystallography were obtained by diffusing hexane into a dichloromethane solution of the compound in a tube. Crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[24] and SHELXL-97.[25] ORTEP drawings were made using ORTEP III for Windows.[26]

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