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Synthesis and crystal structures of heterobimetallic 2-(diphenylphosphino)-pyridine complexes containing an Fe→M (M = Cu^I, Ag^I or Hg^{II}) donor–acceptor bond and a mononuclear iron(II) complex bearing a pair of planar strained four-membered chelate rings

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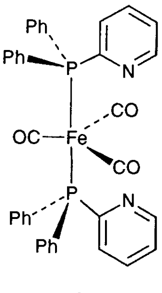
Four heterobimetallic Fe–M (M = Cu^I, Ag^I or Hg^{II}) complexes and a mononuclear iron(II) complex containing a pair of strained planar four-membered chelate rings have been synthesized *via* the reaction of a neutral organometallic *trans*-$Fe(CO)_3(dppy)_2$ L [dppy = 2-(diphenylphosphino)pyridine] with the corresponding metal perchlorates. Their structures have been determined by single-crystal X-ray analysis. In $[CuL(Me_2CO)]ClO_4\cdot1.75Me_2CO$ **1**, $[CuL(H_2O)]ClO_4\cdot CH_2Cl_2$ **2**, $[AgL(dppy)]ClO_4\cdot0.5MeOH$ **3**, $[HgL(H_2O)(OClO_3)]ClO_4\cdot2.5H_2O\cdot0.5MeOH$ **4** and *cis*-$[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2\cdot CH_2Cl_2$ **5**, the Fe–M (M = Cu, Cu, Ag or Hg) distances are 2.501(2), 2.512(2), 2.760(1) and 2.545(1) Å, respectively, unequivocally indicating the existence of a dative Fe→M bond. To our knowledge, **3** is the first binuclear iron(0)–silver(I) donor–acceptor complex to be fully characterized by single-crystal X-ray analysis, and **5** provides the first example of a first-row transition-metal complex which incorporates two planar four-membered chelate rings involving P and N donor atoms.

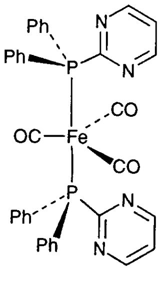
Two different transition metals brought into close proximity in a bimetallic complex have been subjected to extensive study in the past decade because they may display unique chemical properties compared to those of the individual fragments.[1–4] Particular interest has been focused on the synthesis of compounds containing an electron-deficient and an electron-rich transition metal, which exert a synergistic interaction on each other when used as catalysts in some catalytic reactions.[5]

The organometallic compound *trans*-$[Fe(CO)_3(dppy)_2]$ L [dppy = 2-(diphenylphosphino)pyridine] has a basic iron(0) centre and two pendant pyridyl nitrogen atoms. Being structurally analogous to terpyridine, it is an excellent precursor for the preparation of homo- or hetero-bimetallic complexes containing a dative metal–metal bond. Recently, a series of compounds of this type has been prepared and shown to exhibit catalytic activities for carbonylation of ethanol to form ethyl propionate,[6] and hydrogenation of carbon dioxide to methyl formate in methanol.[7] Although the crystal structures of a few of them have been determined, they are mainly confined to mercury(II) halide complexes. The reactivity and co-ordination behaviour of L toward other metals, especially the transition elements, as well as the relationship between the catalytic activity of its binuclear complexes and their structures are still unclear. Recently, a new neutral organometallic complex *trans*-$[Fe(CO)_3(dppym)_2]$ [dppym = 2-(diphenylphosphino)pyrimidine] (L′) has been synthesized and used in our laboratory to prepare various bimetallic complexes containing a dative metal–metal bond: $[HgL'X_2]$ (X = Cl, Br, I or SCN),[8] $[CdL'X_2]$ (X = Cl, Br, I or SCN) and $[CdL'(H_2O)(MeCN)][ClO_4]_2$.[9] The results show that L′ acts as a mono-, bi- or tridentate ligand toward HgX_2 depending on the nature of the ancillary halide/pseudohalide ligand attached to Hg^{II} and invariably as a tridentate ligand toward Cd^{II}.

In the present paper we report the interaction of L with some metal perchlorates, namely $[Cu(MeCN)_4]ClO_4$, $Cu(ClO_4)_2\cdot6H_2O$, $AgClO_4$, $Hg_2(ClO_4)_2\cdot8H_2O$ and $Fe(ClO_4)_3\cdot6H_2O$ in order to study its reactivity and co-ordination behaviour toward various transition metals, as well as the influence of the positive charge on the dative metal–metal bond.



L



L′

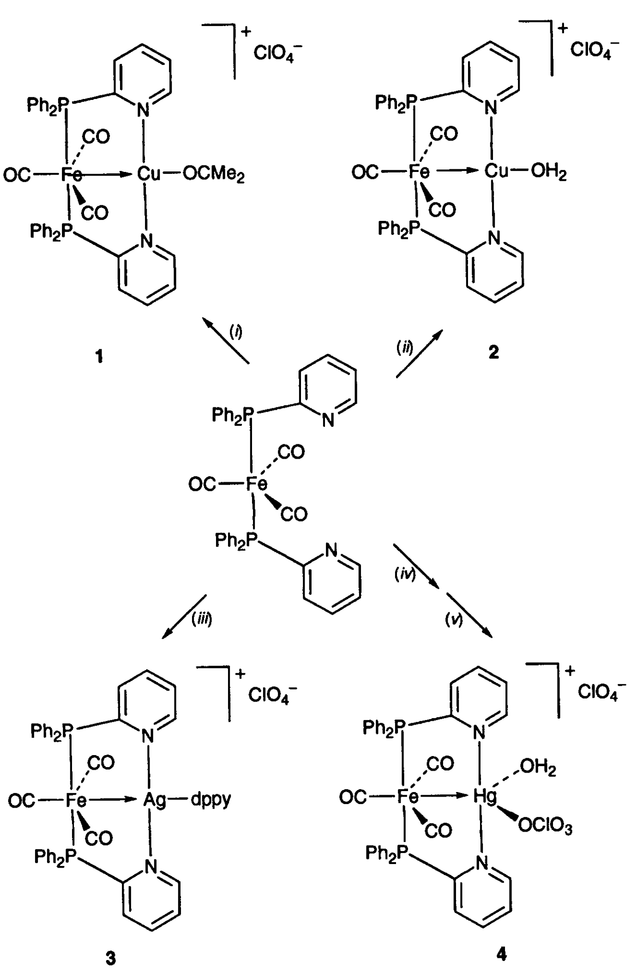
Experimental

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. The compound *trans*-$[Fe(CO)_3(dppy)_2]$ was synthesized by a literature method,[6] iron(III) perchlorate was prepared by the reaction of $FeCl_3$ with $HClO_4$ (70%) and dried at 120 °C for 72 h and $[Cu(MeCN)_4]ClO_4$ was by the reduction of $Cu(ClO_4)_2\cdot6H_2O$ with copper powder in acetonitrile and used as freshly prepared. The solvents and other chemicals were used without further purification. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer, solid-state ^{31}P NMR spectra on a Bruker ASX-300 solid-state FT-NMR spectrometer using 85% H_3PO_4 as the reference.

CAUTION: metal perchlorates are potentially explosive in reactions with organic compounds. Only small amounts should be prepared and handled with great care.

Preparations

$[CuL(Me_2CO)]ClO_4\cdot1.75Me_2CO$ 1. Compound L (0.33 g, 0.5 mmol) and $[Cu(MeCN)_4]ClO_4$ (0.16 g, 0.5 mmol) were



Scheme 1 Synthesis of complexes **1**–**4**. (*i*) $[Cu(MeCN)_4]ClO_4$, CH_2Cl_2–Me_2CO, 25 °C, 1 h; (*ii*) $Cu(ClO_4)_2{\cdot}6H_2O$, CH_2Cl_2–MeOH, 25 °C, 1 h; (*iii*) $AgClO_4$, CH_2Cl_2–MeOH, 25 °C, 1 h; (*iv*) $Hg_2(ClO_4)_2{\cdot}8H_2O$, CH_2Cl_2–thf, 25 °C, 2 h; (*v*) dmf–MeOH, 15 °C, 1 d

dissolved in CH_2Cl_2–Me_2CO (*ca.* 5 : 5 cm^3) and stirred for 1 h at ambient temperature. Golden-yellow prismatic crystals of complex **1** were obtained after the reaction mixture was allowed to stand at −30 °C for 1 d (0.30 g, 62%).

$[CuL(H_2O)]ClO_4{\cdot}CH_2Cl_2$ 2. To a mixture of compound L (0.33 g, 0.5 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.19 g, 0.5 mmol) was added MeOH (*ca.* 3 cm^3) with stirring until the $Cu(ClO_4)_2{\cdot}6H_2O$ was completely dissolved, and then CH_2Cl_2 (*ca.* 10 cm^3) was added and stirred for 1 h at room temperature. Storing the solution at −15 °C in a refrigerator for 1 d afforded orange prismatic crystals of complex **2** (0.18 g, 40%).

$[AgL(dppy)]ClO_4{\cdot}0.5MeOH$ 3. Compound L (0.33 g 0.5 mmol) and $AgClO_4$ (0.11 g, 0.5 mmol) were dissolved in CH_2Cl_2–MeOH (1 : 1 v/v, 10 cm^3) and stirred for 1 h in the dark at room temperature. Then the mixture was filtered to remove the silver precipitate formed. Keeping the filtrate at 15 °C for 1 d yielded yellow granular crystals of complex **3** (0.18 g, 33%).

$[HgL(H_2O)(OClO_3)]ClO_4{\cdot}2.5H_2O{\cdot}0.5MeOH$ 4. Compound L (0.33 g, 0.5 mmol) and $Hg_2(ClO_4)_2{\cdot}8H_2O$ (0.34 g, 0.5 mmol) were dissolved in CH_2Cl_2–thf (tetrahydrofuran) (1 : 1 v/v, *ca.* 10 cm^3). The mixture was stirred for 2 h in the dark at ambient temperature. The greenish yellow precipitate produced was washed using CH_2Cl_2, dried in the air and collected (0.53 g). The IR spectrum exhibits three intense carbonyl stretching frequencies at 1889, 1989 and 2057 cm^{-1}. This product was dissolved in dimethylformamide (dmf) (*ca.* 5 cm^3) and the solution filtered to remove the dark solid formed; then MeOH (*ca.* 5 cm^3) was added. Yellow block-like crystals of complex **4** were obtained after the solution was kept at 15 °C for 1 d (0.21 g, 38%).

$[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2{\cdot}CH_2Cl_2$ 5. Compound L (0.33 g, 0.5 mmol) was dissolved in CH_2Cl_2 (*ca.* 10 cm^3). To this solution was added $Fe(ClO_4)_3{\cdot}6H_2O$ (0.23 g, *ca.* 0.5 mmol) in acetone (*ca.* 3 cm^3) and stirred for 1 h. Pale yellow crystals of complex **5** were deposited upon cooling at −15 °C (0.25 g, 54%).

Crystallography

The X-ray data collection and structure refinement is summarized in Table 9. Selected crystals were enclosed in Lindemann glass capillaries. The intensities of complex **1** were collected at 290 K in the ω-scan mode[10] on a Rigaku AFC7 diffractometer, using Mo-Kα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 25 selected strong reflections. Crystal stability was monitored by recording three check reflections at intervals of 120 data measurements, and no significant variation was detected. An empirical absorption correction based on ψ scans was applied to the raw intensities in data processing.[11]

The intensity data for complexes **2**–**5** were collected at 290 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo-Kα radiation (λ = 0.71073 Å, 50 kV and 90 mA) ($2\theta_{max}$ = 55°, 36 5° oscillation frames in the range 0–180°, exposure 12 min per frame for **2**–**4**, 10 min per frame for **5**).[12] A self-consistent semiempirical absorption correction based on symmetry-equivalent reflections was applied using the REQAB program.[13]

The structures of all five complexes were solved by direct methods. All non-hydrogen atoms other than the disordered oxygen atoms of the perchlorate group (with distance restraints of Cl–O 1.42 ± 0.02 and O ··· O 2.43 ± 0.02 Å), the solvated MeOH molecule of **3**, and the H_2O molecules of **4**, were refined anisotropically by full-matrix least squares on *F*. The hydrogen atoms of the ligands were placed in their calculated positions with C–H 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were included in the structure-factor calculations, but their positions were not refined. All calculations were carried out on a PC 486 using the SHELXTL PLUS program package.[14] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[15] Selected bond lengths and angles are listed in Tables 2–5 and 8.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/162.

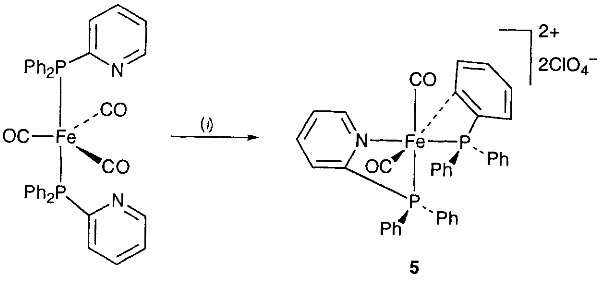
Results and Discussion

Synthesis of the complexes

The complexes **1**–**4** were prepared as shown in Scheme 1, and **5** as in Scheme 2; **1**, **2** and **5** are air sensitive. Reaction of L with $[Cu(MeCN)_4]ClO_4$ in a mixed CH_2Cl_2–Me_2CO solvent led to the formation of the expected bimetallic iron–copper(I) complex **1**. However, the corresponding reaction with $Cu(ClO_4)_2{\cdot}6H_2O$ in CH_2Cl_2–MeOH failed to afford the corresponding iron–copper(II) complex. A reduction-oxidation process occurred in this reaction: first Cu^{II} was reduced by L to Cu^{I}, which then combined with another L to yield complex **2** which is isostructural with **1**. Reaction of L with anhydrous

Table 1 Infrared carbonyl absorption spectra for complexes 1–5

Compound	$\tilde{\nu}$(CO)/cm^{-1}
1 $[(OC)_3Fe(\mu\text{-dppy})_2Cu(Me_2CO)]ClO_4\cdot 1.75Me_2CO$	2033, 2044, 2094
2 $[(OC)_3Fe(\mu\text{-dppy})_2Cu(H_2O)]ClO_4\cdot CH_2Cl_2$	1890, 1918, 1994
3 $[(OC)_3Fe(\mu\text{-dppy})_2Ag(dppy)]ClO_4\cdot 0.5MeOH$	1892, 1924, 1989
4 $[(OC)_3Fe(\mu\text{-dppy})_2Hg(H_2O)(OClO_3)]ClO_4\cdot 2.5H_2O\cdot 0.5MeOH$	1890, 1985, 2053
5 $[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2\cdot CH_2Cl_2$	2038, 2094



Scheme 2 Synthesis of complex **5**. (*i*) $Fe(ClO_4)_3\cdot 6H_2O$, CH_2Cl_2–Me_2CO, 25 °C, 1 h

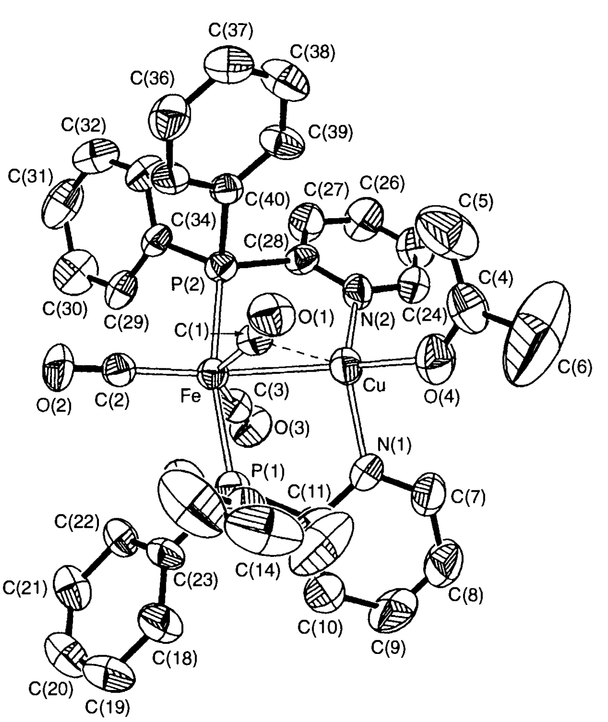


Fig. 1 Molecular structure and atom numbering of the $[CuL(Me_2CO)]^+$ cation in complex **1**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 35% probability level

$AgClO_4$ in a mixed solvent of CH_2Cl_2 and MeOH led to the formation of **3** with some Ag^I reduced to Ag^0. Surprisingly, treatment of an equimolar quantity of L with anhydrous $AgClO_4$ and dppy under the same conditions failed to give complex **3**, and the starting materials remained intact as shown by IR analysis. This result suggests that the formation of **3** may be initially dependent on the oxidation-reduction potential of L used as a reductant and silver species used as an oxidant. Blagg *et al.*[16a] have studied the reaction of *fac*- or *mer*-$[M(CO)_3(dppm\text{-}P,P')(dppm\text{-}P)]$ (M = Cr, Mo or W; dppm = $Ph_2PCH_2PPh_2$) with silver(I) compounds. Treatment with $AgNO_3$ at 20 °C in CH_2Cl_2 gave metallic silver and Group 6 metal species, but the same reaction using 0.25 mol equivalent of $[Ag_4Cl_4(PPh_3)_4]$ gave no oxidation products.[16] A similar phenomena was also observed in the reaction of $[Fe_2(CO)_6\{C(NHR)CH(Ph)\}PPh_2]$ with silver(I) salts: instead of leading to isolable adducts, a two-electron oxidation occurred with deposition of a silver mirror.[17] Reaction of equimolar L and $Hg_2(ClO_4)_2\cdot xH_2O$ in CH_2Cl_2–thf afforded a greenish yellow precipitate which was believed to contain an Fe–Hg–Hg unit according to IR spectroscopic analysis. However, attempts to recrystallize this product from dmf–MeOH failed to give crystals of the desired mercury(I) complex, but instead caused disproportionation of the Hg–Hg unit to yield crystalline complex **4**. Reaction of L with $Fe(ClO_4)_3\cdot xH_2O$ in CH_2Cl_2–Me_2CO did not afford the desired iron(0)–iron(III) binuclear complex. On the other hand, an unexpected and very unusual mononuclear organometallic complex $[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2\cdot CH_2Cl_2$ **5** which contains a pair of strained *planar* four-membered chelate rings was obtained.

Spectroscopic characterization

The carbonyl stretching frequencies of complexes **1**–**5** are listed in Table 1. The IR spectra of the bimetallic complexes **1**–**4** are typical and exhibit three ν(CO) vibrations which shift to higher frequencies as compared with ν(CO) for L,[6] indicating a change of local symmetry from D_{3h} to C_s at the iron atom due to donor–acceptor bonding. It is worthy of note that ν(CO) for **3** are lower than those for **1**, **2** and **4**. The ^{31}P NMR spectrum of complex **3** gives two single peaks at δ 4.16 and 107.65, which indicate that two kinds of phosphorus atoms are present. In comparison with ^{31}P NMR results for complexes $[(OC)_3Fe(\mu\text{-dppy})_2MX_n]$,[6] the former may be assigned to the silver-bonded phosphorus atom and the latter to the iron-bonded one.

Crystal structures of bimetallic complexes 1–4

As illustrated in Figs. 1–4, in all four complexes the 18-electron neutral organometallic L acts as a tridentate ligand and the iron(0) atom as a Lewis base toward another metal atom M (Cu, Ag or Hg). Two metal centres are linked by a pair of dppy bridges and a metal–metal bond to form a heterobinuclear core, and the resulting five-membered metallacyclic rings are severely twisted out of plane, as shown by the selected torsion angles listed in Table 6.

Complex **1** comprises organometallic cations $[(OC)_3Fe(\mu\text{-dppy})_2Cu(Me_2CO)]^+$ (Fig. 1), anions ClO_4^- and molecules of Me_2CO packed together in the crystal lattice. The Fe–Cu distance of 2.501(2) Å falls within the range 2.394–2.580 Å reported for polynuclear complexes containing an Fe–Cu bond.[18] It is shorter than the sum (2.54 Å)[19] of the atomic radii of iron and copper and the Fe–Cu distance [2.540(2) Å][18] found in the neutral binuclear complex $[(Ph_3P)Cu(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$, in which the iron and copper centres are joined by a dppm bridge. This bonding distance is comparable to the values found in the trinuclear complex $[\{Cu(PPh_3)_2\}_2Fe(CO)_4]$, which contains a nearly linear Cu–Fe–Cu chain [2.499(4) and 2.522(4) Å].[20] The Fe atom is surrounded by the Cu atom, two phosphorus atoms from the dppy ligands [Fe–P 2.209(3) and 2.212(3) Å], and three carbonyl groups in a distorted-octahedral environment similar to that found in $[(OC)_3Fe(dppy)_2Hg(SCN)_2]$ [Fe–P 2.259(2), 2.265(2) Å][6] and $[(OC)_3Fe(dppy)_2HgI_2]$ [Fe–P 2.254(1), 2.251(1) Å].[7] The Fe–P distances are somewhat longer than those found in L [2.202(1), 2.206(1) Å],[7] which is consistent with electron donation from Fe^0 to Cu^I,

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–Fe	2.501(2)	Cu–C(1)	2.276(11)
Cu–O(4)	2.117(8)	Cu–N(1)	2.049(8)
Cu–N(2)	2.061(10)	Fe–C(1)	1.815(11)
Fe–C(2)	1.778(10)	Fe–C(3)	1.782(11)
Fe–P(1)	2.209(3)	Fe–P(2)	2.212(3)
C(1)–O(1)	1.162(14)	C(2)–O(2)	1.151(12)
C(3)–O(3)	1.151(14)		
Fe–Cu–O(4)	139.8(3)	Fe–Cu–N(1)	97.8(2)
O(4)–Cu–N(1)	90.0(3)	Fe–Cu–N(2)	98.6(2)
C(1)–Cu–N(2)	113.6(4)	O(4)–Cu–N(2)	109.6(3)
N(1)–Cu–N(2)	123.6(4)	Cu–Fe–C(1)	61.2(3)
Cu–Fe–C(2)	165.5(3)	Cu–Fe–C(3)	80.0(3)
C(1)–Fe–C(2)	104.3(5)	C(1)–Fe–C(3)	141.2(4)
C(2)–Fe–C(3)	114.5(5)	P(1)–Fe–P(2)	165.7(1)
Cu–C(1)–Fe	74.4(4)	Fe–C(1)–O(1)	168.9(9)
Fe–C(2)–O(2)	179.3(11)	Fe–C(3)–O(3)	178.5(8)
Cu–O(4)–C(4)	136.6(9)	Cu–N(1)–C(11)	120.2(6)
Fe–P(1)–C(11)	111.7(4)	P(1)–C(11)–N(1)	113.5(7)
Fe–P(2)–C(28)	111.9(3)	Cu–N(2)–C(28)	119.2(7)
P(2)–C(28)–N(2)	114.7(9)	P(2)–C(28)–C(27)	123.3(7)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–Fe	2.512(2)	Cu–C(1)	2.320(6)
Cu–O(1w)	2.245(6)	Cu–N(1)	2.025(5)
Cu–N(2)	2.048(5)	Fe–C(1)	1.778(6)
Fe–C(2)	1.770(6)	Fe–C(3)	1.799(5)
Fe–P(1)	2.214(2)	Fe–P(2)	2.214(2)
C(1)–O(1)	1.178(8)	C(2)–O(2)	1.147(8)
C(3)–O(3)	1.139(7)		
Fe–Cu–O(1w)	140.5(2)	Fe–Cu–N(1)	98.5(2)
O(1w)–Cu–N(1)	96.0(2)	Fe–Cu–N(2)	99.0(1)
N(1)–Cu–N(2)	135.0(2)	Cu–Fe–C(1)	62.8(2)
Cu–Fe–C(2)	172.1(2)	Cu–Fe–C(3)	73.5(2)
C(1)–Fe–C(2)	109.4(3)	C(1)–Fe–C(3)	136.2(3)
C(2)–Fe–C(3)	114.4(3)	P(1)–Fe–P(2)	169.0(1)
Cu–C(1)–Fe	74.3(2)	Cu–C(1)–O(1)	114.9(5)
Fe–C(1)–O(1)	170.8(6)	Fe–C(2)–O(2)	178.0(5)
Fe–C(3)–O(3)	177.9(6)	Fe–P(1)–C(8)	112.8(2)
Cu–N(1)–C(8)	120.6(4)	P(1)–C(8)–N(1)	115.6(4)
Fe–P(2)–C(25)	113.4(2)	Cu–N(2)–C(25)	119.7(4)

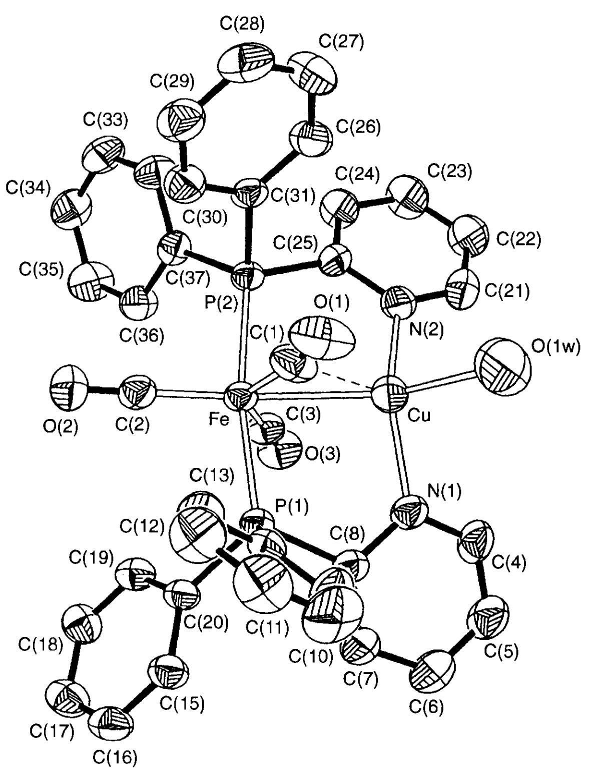


Fig. 2 Molecular structure and atom numbering of the $[CuL(H_2O)]^+$ cation in complex **2**. Details as in Fig. 1

consequently reducing the electron density on the iron centre and weakening the Fe–P bond. The P–Fe–P angle of 165.7(1)° is significantly smaller than that in L [177.08(3)°]. The co-ordination polyhedron around the Cu^I consists of the Fe atom, two pyridyl nitrogen atoms of the dppy ligands [Cu–N 2.049(8) and 2.061(10) Å], and the oxygen atom from an acetone ligand molecule [Cu–O 2.117(8) Å]. The angles of 90.0(3)–139.8(3)° around Cu^I indicate that its co-ordination environment is distorted tetrahedral.

An interesting feature of this compound is the semibridging interaction between the copper atom and one of the carbonyl ligands, C(1)O(1). The contact Cu(1)–C(1) 2.276(11) Å falls well within the copper–carbonyl group distance range of 2.25–2.46 Å which is considered as a semibridging interaction in mixed iron–copper carbonyl clusters.[20] It is comparable to the semibridging interaction distance of 2.267(8) Å found in the binuclear complex $[(OC)_2W(\mu\text{-dppm})_2(\mu\text{-Cl})Cu]$ [16a] and longer than that in $[(OC)_2(\eta\text{-}C_5H_5)W(\mu\text{-CO})(\mu\text{-MeCO}_2)_2Cu(mpy)]$ (mpy = 4-methylpyridine) [Cu–C 2.137(9) Å],[16b] in which the copper atom is in oxidation state +2. In addition, the Fe–C(1)–O(1) angle of 168.9(9)°, deviating significantly from linearity, is also consistent with the semibridging interaction between the Cu^I and carbonyl group C(1)O(1).

Complex **2** comprises organometallic cations $[(OC)_3Fe(\mu\text{-dppy})_2Cu(H_2O)]^+$ (Fig. 2), anions ClO_4^-, water and CH_2Cl_2 molecules packed together in the crystal lattice. As depicted in Fig. 2, the cation $[(OC)_3Fe(\mu\text{-dppy})_2Cu(H_2O)]^+$ of complex **2** is isostructural with that of **1**. The Fe–Cu distance of 2.512(2) Å is comparable to the corresponding value in **1**. A semibridging interaction also exists in **2** [Cu–C(1) 2.320(6) Å; Fe–C(1)–O(1) 170.8(6)°]; however, it is weaker than that in complex **1**. The Cu–O (acetone) distance of 2.117(8) Å in **1** is significantly shorter than the Cu–O (aqua) distance of 2.245(6) Å in complex **2**. This can be rationalized on the basis of π-back bonding from the copper atom to the carbonyl group of the co-ordinated acetone molecule in **1**, which reduces the electron density on the copper atom and enhances its Lewis-acid strength, thus making the Fe–Cu and semibridging bonding distances relatively shorter.

Complex **3** contains a packing of $[(OC)_3Fe(\mu\text{-dppy})_2Ag(dppy)]^+$ cations (Fig. 3), ClO_4^- anions and MeOH molecules. To our knowledge, this is the first binuclear iron(0)–silver(I) donor–acceptor complex to be structurally fully characterized by single-crystal X-ray analysis, although the structures of a few Fe–Ag clusters have been reported.[17,21] In the cation $[(OC)_3Fe(\mu\text{-dppy})_2Ag(dppy)]^+$ the Fe–Ag bond distance of 2.760(1) Å is significantly longer than the values found in the triangular two-co-ordinate silver cluster $[Fe_2Ag(CO)_6\{CHC(NHMe)Ph\}PPh_2]ClO_4$ [2.685(1) and 2.703(1) Å] [17] in which the interaction between Ag and Fe atoms is regarded as a two-electron, three-centre bond, the nonanuclear six-co-ordinate silver cluster $[Ag_6\{Fe(CO)_4\}_3\{(Ph_3P)_3\text{-}CH)\}]$ [2.664(1)–2.720(1) Å],[21] as well as the sum of the atomic radii of Fe and Ag atoms (2.70 Å),[19] and may be attributed to the rigidity imposed by the bite of the pair of bridging dppy ligands. The atoms Fe, Ag, C(1)–C(3) and P(3) are coplanar with a mean atomic deviation of 0.024(1) Å from the least-squares plane. The co-ordination environment of the Fe atom is best described as a distorted octahedron consisting of a silver atom, two phosphorus atoms from dppy [Fe–P 2.223(2), 2.224(2) Å] and three carbon atoms from the terminal carbonyl groups, which is similar to that in **1**, **2** and analogous Fe–Hg complexes.[6,7] The Fe–P distances are nearly the same as those in **1** and **2**. However, the P–Fe–P angle of 173.4(1)° is smaller than that in L [177.08(3)°] [7] but larger than those in **1**

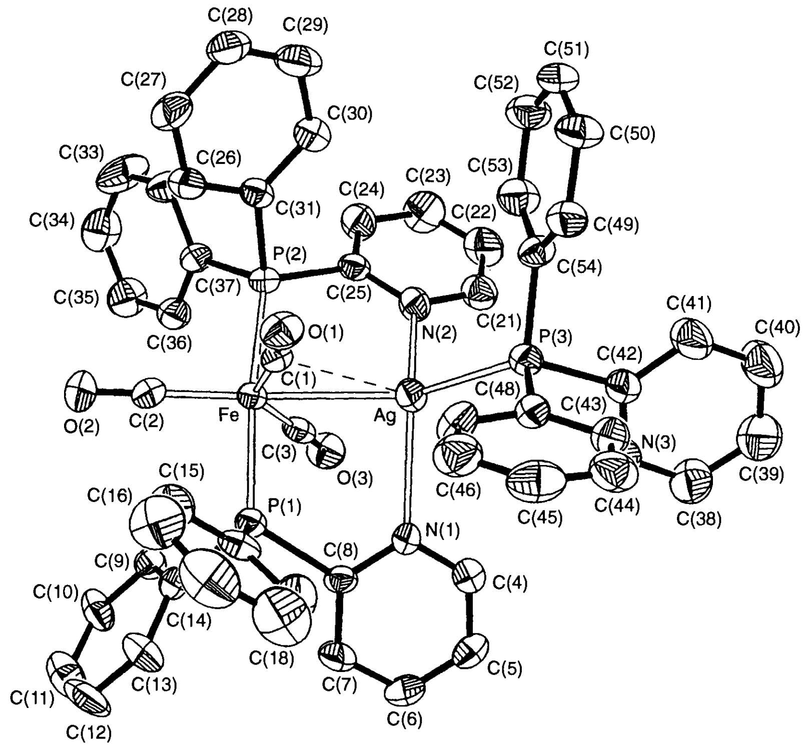


Fig. 3 Molecular structure and atom numbering of the $[AgL(dppy)]^+$ cation in complex **3**. Details as in Fig. 1

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Ag–Fe	2.760(1)	Ag–C(1)	2.562(6)
Ag–N(1)	2.456(5)	Ag–N(2)	2.478(6)
Ag–P(3)	2.449(2)	Fe–C(1)	1.804(7)
Fe–C(2)	1.782(7)	Fe–C(3)	1.791(7)
Fe–P(1)	2.223(2)	Fe–P(2)	2.224(2)
C(1)–O(1)	1.137(9)	C(2)–O(2)	1.153(9)
C(3)–O(3)	1.152(8)		
Fe–Ag–N(1)	85.9(1)	Fe–Ag–N(2)	84.9(1)
N(1)–Ag–N(2)	122.5(2)	Fe–Ag–P(3)	149.6(1)
N(1)–Ag–P(3)	110.4(1)	N(2)–Ag–P(3)	105.5(1)
Ag–Fe–C(1)	64.4(2)	Ag–Fe–C(2)	169.3(3)
Ag–Fe–C(3)	75.4(2)	C(1)–Fe–C(2)	105.1(3)
C(1)–Fe–C(3)	139.7(3)	C(2)–Fe–C(3)	115.3(3)
P(1)–Fe–P(2)	173.4(1)	Ag–C(1)–Fe	76.2(2)
Ag–C(1)–O(1)	113.4(4)	Fe–C(1)–O(1)	170.4(5)
Fe–C(2)–O(2)	178.9(6)	Fe–C(3)–O(3)	178.0(5)
Fe–P(1)–C(8)	114.1(2)	Ag–N(1)–C(8)	122.7(4)
P(1)–C(8)–N(1)	114.4(4)	Fe–P(2)–C(25)	114.3(2)
Ag–N(2)–C(25)	122.4(4)	P(2)–C(25)–N(2)	116.1(5)

and **2** [165.7(1) and 169.0(1)°]. The distorted-tetrahedral co-ordination geometry around Ag is obvious from the angles around Ag^I [84.9(2)–149.6(1)°]. It involves the Fe atom, two pyridyl nitrogen atoms of the bridging dppy ligands [Ag–N 2.456(5) and 2.478(6) Å] and a phosphorus atom from the terminal dppy ligand [Ag–P 2.449(2) Å]; the metal–ligand distances are comparable to the corresponding bond lengths in the binuclear complex $[Ag_2(\mu\text{-}Cl)_2(dppy)_2(\mu\text{-}dppy)]$ [Ag–N 2.451(9), Ag–P (terminal dppy) 2.432(3) and 2.436(4) Å].[22]

In view of the fact that the atomic radius of silver is 0.16 Å longer than that of copper,[19] the bond length and angles Ag–C(1) 2.562(6) Å, Ag–Fe–C(1) 64.4(2), Ag–Fe–C(3) 75.4(2), Fe–C(1)–O(1) 170.4(5)° indicate that the Ag atom possibly has a semibridging interaction with one of the carbonyl groups, as discussed in the case of complexes **1** and **2**.

Complex **4** consists of a packing of cations $[(OC)_3Fe(\mu\text{-}dppy)_2Hg(H_2O)(OClO_3)]^+$ (Fig. 4), anions ClO_4^-, and MeOH and H_2O molecules in the crystal lattice. The octahedral co-ordination environment about the Fe atom is similar to that in **1**–**3**. The trigonal-bipyramidal co-ordination about Hg involves the tridentate organometallic ligand, an aqua ligand at 2.290(4) Å, and a weakly co-ordinated monodentate perchlorate anion at 2.657(5) Å.

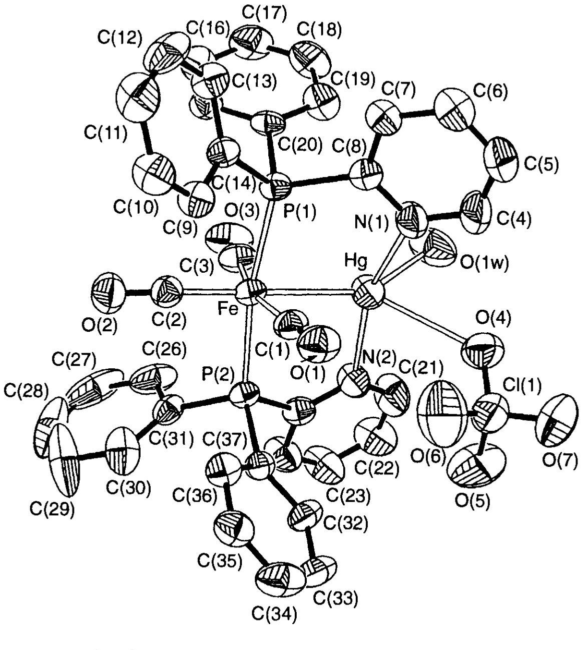


Fig. 4 Molecular structure and atom numbering of $[HgL(H_2O)(OClO_3)]^+$ cation in complex **4**. Details as in Fig. 1

Complexes containing an Fe–Hg bond have been extensively studied, and bond lengths for some examples are listed in Table 7. These compounds can be classified into three types: (*i*) in $[(OC)_3Fe(dppy)_2Hg(SCN)_2]$,[6] $[(OC)_3Fe(dppy)_2HgI_2]$[7] and $[(OC)_3Fe(dppym)_2HgX_2]$ (X = Cl, Br, I or SCN)[8] the Fe atom is in oxidation state zero and forms a donor bond to Hg; (*ii*) in $[Fe(CO)_4\{HgCl(py)\}_2]$[23] (py = pyridine), $[Fe(CO)_4(HgCl)(HgCl_2)]^-$,[24] $[Hg\{Fe(CO)_2(NO)(PEt_3)\}_2]$,[25] $[Fe(CO)_4(HgBr)_2]$[26] and $[Fe(CO)_4(HgSCN)_2]$[27] the Fe atom is in formal oxidation state −2; and (*iii*) in $[(Me_3P)(OC)_3(Ph_2MeSi)FeHgBr]$[28] and $[Hg\{Fe[Si(OMe)_3](CO)_3(dppm\text{-}P)\}_2]$[29] the Fe atom is in the oxidation state −1. The interaction between iron and mercury atoms in complexes (*ii*) and (*iii*) is best regarded as covalent rather than donor–acceptor bonding. In the pentanuclear cluster $[Hg\{Fe_2Co(\eta\text{-}C_5H_5)(\mu_3\text{-}COMe)(CO)_7\}_2]$[30] each iron moiety bears a formal −1 charge, and the mercury atom is squarely co-ordinated by four equivalent iron atoms (see Table

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

Hg–O(1w)	2.290(4)	Hg–O(4)	2.657(5)
Hg–Fe(1)	2.545(1)	Hg–N(1)	2.469(5)
Hg–N(2)	2.423(5)	Fe–C(1)	1.786(4)
Fe–C(2)	1.772(5)	Fe–C(3)	1.794(4)
Fe–P(1)	2.278(2)	Fe–P(2)	2.282(2)
C(1)–O(1)	1.148(5)	C(2)–O(2)	1.148(7)
C(3)–O(3)	1.139(5)		
O(1w)–Hg–O(4)	75.9(2)	O(1w)–Hg–Fe	144.3(1)
O(4)–Hg–Fe	139.8(1)	Hg–O(4)–Cl(1)	121.0(3)
Hg–Fe–C(1)	81.1(2)	Hg–Fe–C(2)	178.7(1)
Hg–Fe–C(3)	81.6(2)	C(1)–Fe–C(2)	100.1(2)
C(1)–Fe–C(3)	162.6(2)	C(2)–Fe–C(3)	97.2(2)
P(1)–Fe–P(2)	170.8(1)	Fe–C(1)–O(1)	177.3(5)
Fe–C(2)–O(2)	178.3(5)	Fe–C(3)–O(3)	178.7(5)
Fe–P(1)–C(8)	115.9(2)	Hg–N(1)–C(8)	113.9(3)
P(1)–C(8)–N(1)	116.9(4)	Fe–P(2)–C(25)	117.4(2)
Hg–N(2)–C(25)	115.7(3)	P(2)–C(25)–N(2)	118.0(4)

Table 8 Selected bond lengths (Å) and angles (°) for complex **5**

Fe–C(1)	1.788(3)	Fe–C(2)	1.837(2)
Fe–P(1)	2.253(1)	Fe–N(1)	2.015(2)
Fe–P(2)	2.345(1)	Fe–N(2)	2.004(3)
C(1)–O(1)	1.138(4)	C(2)–O(2)	1.128(3)
P(1)–C(7)	1.813(3)	N(1)–C(7)	1.365(4)
P(2)–C(24)	1.818(4)	N(2)–C(24)	1.361(3)
C(1)–Fe–C(2)	91.3(1)	C(1)–Fe–P(1)	97.6(1)
C(2)–Fe–P(1)	93.1(1)	C(1)–Fe–N(1)	168.7(1)
C(2)–Fe–N(1)	91.2(1)	P(1)–Fe–N(1)	71.3(1)
C(1)–Fe–P(2)	93.4(1)	C(2)–Fe–P(2)	165.3(1)
P(1)–Fe–P(2)	100.1(1)	N(1)–Fe–P(2)	86.9(1)
C(1)–Fe–N(2)	95.2(1)	C(2)–Fe–N(2)	96.0(1)
P(1)–Fe–N(2)	164.1(1)	N(1)–Fe–N(2)	95.5(1)
P(2)–Fe–N(2)	69.7(1)	Fe–C(1)–O(1)	176.6(3)
Fe–C(2)–O(2)	178.4(3)	Fe–P(1)–C(7)	82.2(1)
Fe–N(1)–C(7)	104.0(2)	P(1)–C(7)–N(1)	102.4(2)
Fe–P(2)–C(24)	80.7(1)	Fe–N(2)–C(24)	106.6(2)
P(2)–C(24)–N(2)	102.8(2)		

Table 6 Torsion angles (°) in five-membered metallacyclic rings for complexes **1**–**4**

Complex				
1	Fe–Cu–N(1)–C(11)–P(1)		Fe–Cu–N(2)–C(28)–P(2)	
	Fe–Cu–N(1)–C(11)	−16.0	Fe–Cu–N(2)–C(28)	9.8
	Cu–N(1)–C(11)–P(1)	−8.1	Cu–N(2)–C(28)–P(2)	13.4
	N(1)–C(11)–P(1)–Fe	33.7	N(2)–C(28)–P(2)–Fe	−35.0
	C(11)–P(1)–Fe–Cu	−34.1	C(28)–P(2)–Fe–Cu	31.7
	P(1)–Fe–Cu–N(1)	26.1	P(2)–Fe–Cu–N(2)	−22.3
2	Fe–Cu–N(1)–C(8)–P(1)		Fe–Cu–N(2)–C(25)–P(2)	
	Fe–Cu–N(1)–C(8)	−14.9	Fe–Cu–N(2)–C(25)	8.0
	Cu–N(1)–C(8)–P(1)	−3.7	Cu–N(2)–C(25)–P(2)	10.1
	N(1)–C(8)–P(1)–Fe	24.5	N(2)–C(25)–P(2)–Fe	−27.1
	C(8)–P(1)–Fe–Cu	−26.2	C(28)–P(2)–Fe–Cu	24.7
	P(1)–Fe–Cu–N(1)	21.2	P(2)–Fe–Cu–N(2)	−17.4
3	Fe–Ag–N(1)–C(8)–P(1)		Fe–Ag–N(2)–C(25)–P(2)	
	Fe–Ag–N(1)–C(8)	−15.9	Fe–Ag–N(2)–C(25)	19.6
	Ag–N(1)–C(8)–P(1)	−8.4	Ag–N(2)–C(25)–P(2)	1.8
	N(1)–C(8)–P(1)–Fe	37.4	N(2)–C(25)–P(2)–Fe	−30.3
	C(8)–P(1)–Fe–Ag	−39.3	C(28)–P(2)–Fe–Ag	36.0
	P(1)–Fe–Ag–N(1)	25.9	P(2)–Fe–Ag–N(2)	−25.5
4	Fe–Hg–N(1)–C(8)–P(1)		Fe–Hg–N(2)–C(25)–P(2)	
	Fe–Hg–N(1)–C(8)	−32.1	Fe–Hg–N(2)–C(25)	−6.9
	Hg–N(1)–C(8)–P(1)	10.7	Hg–N(2)–C(25)–P(2)	−10.5
	N(1)–C(8)–P(1)–Fe	20.9	N(2)–C(25)–P(2)–Fe	27.5
	C(11)–P(1)–Fe–Hg	−36.1	C(28)–P(2)–Fe–Hg	−25.2
	P(1)–Fe–Hg–N(1)	30.5	P(2)–Fe–Hg–N(2)	15.6

Table 7 Iron–mercury bond distances in some related complexes

Complex		Fe–Hg/Å	Ref.
a	$[(OC)_3Fe(dppy)_2Hg(SCN)_2]$	2.648(1)	6
b	$[(OC)_3Fe(dppy)_2HgI_2]$	2.678(1)	7
c(1)	$[\{(OC)_3Fe(dppym)_2HgCl_2\}_2]\cdot 2CH_2Cl_2\cdot MeOH$	2.653(1), 2.617(1)	8
c(2)	$[(OC)_3Fe(dppym)_2HgBr_2]$	2.632(3)	8
c(3)	$[(OC)_3Fe(dppym)_2HgI_2]$	2.664(2)	8
c(4)	$[(OC)_3Fe(dppym)_2Hg(SCN)_2]$	2.648(1)	8
d	$[Fe(CO)_4\{HgCl(py)\}_2]$	2.553	23
e	$[Fe(CO)_4(HgCl)(HgCl_2)]^-$	2.516, 2.560	24
f	$[Hg\{Fe(CO)_2(NO)(PEt_3)\}_2]$	2.534	25
h	$[Fe(CO)_4(HgBr)_2]$	2.44, 2.59	26
i	$[Fe(CO)_4(HgSCN)_2]$	2.506	27
j	$[(Me_3P)(OC)_3(Ph_2MeSi)FeHgBr]$	2.515	28
k	$[Hg\{Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)\}_2]$	2.574, 2.576	29
l	$[Hg\{Fe_2Co(\eta\text{-}C_5H_5)(\mu_3\text{-}COMe)(CO)_7\}_2]$	2.727(1), 2.735(1) 2.729(1), 2.726(1)	30

Table 9 Crystallographic data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$[CuL(Me_2CO)]ClO_4\cdot1.75Me_2CO$	$[CuL(H_2O)]ClO_4\cdot CH_2Cl_2$	$[AgL(dppy)]ClO_4\cdot0.5MeOH$	$[HgL(H_2O)(OClO_3)]ClO_4\cdot2.5H_2O\cdot0.5MeOH$	$[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2\cdot CH_2Cl_2$
M	989.1	930.3	1153	1135.9	921.9
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Crystal size/mm	0.18 × 0.20 × 0.28	0.20 × 0.35 × 0.45	0.20 × 0.20 × 0.32	0.15 × 0.20 × 0.60	0.15 × 0.20 × 0.35
a/Å	26.600(5)	12.388(1)	14.701(1)	10.204(1)	10.615(1)
b/Å	14.815(3)	13.473(1)	13.349(1)	13.180(1)	14.207(1)
c/Å	26.075(5)	14.248(1)	27.780(1)	18.022(1)	15.045(1)
α/°		103.01(1)		83.08(1)	80.90(1)
β/°	108.75(5)	91.02(1)	100.03(1)	89.49(1)	72.19(1)
γ/°		110.39(1)		73.51(1)	69.42(1)
U/Å^3	9730(5)	2160(1)	5368(1)	2306(1)	2019(1)
Z	8	2	4	2	2
D_c/g cm^{-3}	1.350	1.431	1.427	1.636	1.516
$F(000)$	4080	944	2348	1114	940
μ/cm^{-1}	9.10	11.37	8.28	38.89	7.76
Transmission coefficients	0.87–0.96	*	*	*	*
$2\theta_{max}$/°	50	55.2	55.2	55.2	55.2
No. independent data	8570	7237	7348	7786	7332
No. data used [$F > 4\sigma(F)$], n	4048	3685	5484	5766	5635
No. variables, p	569	560	638	608	578
R	0.074	0.068	0.060	0.055	0.045
R'	0.088	0.074	0.062	0.075	0.056
S	1.98	1.08	1.15	2.28	1.33

$R = \Sigma\Delta/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma|F_o|^2]^{\frac{1}{2}}$ and $S = [w\Delta^2/(n - p)]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$, $\Delta = ||F_o| - |F_c||$; 10^5K = 30, 20, 60, 120 and 50 for complexes **1**, **2**, **3**, **4** and **5**, respectively. Extinction parameter χ = 0.000 01, 0.000 29, 0.000 09, 0.000 92 and 0.002 67 for **1**–**5** where $F_{corr} = F_c(1 + 0.002\,\chi F_c^2/\sin 2\theta)^{-\frac{1}{4}}$. * Absorption corrections applied by using REQAB.

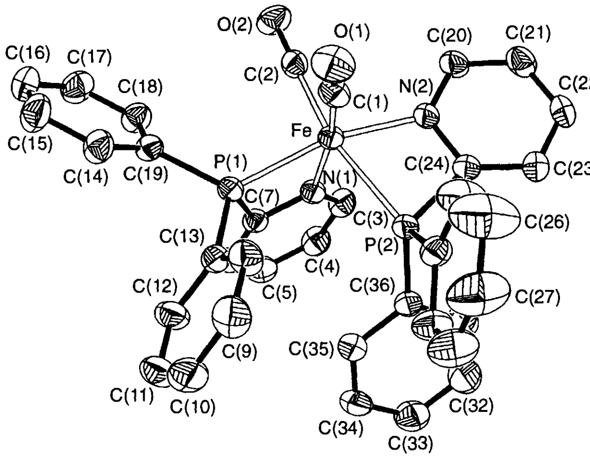


Fig. 5 Molecular structure and atom numbering of the *cis*-$[Fe(CO)_2(dppy\text{-}P,N)_2]^{2+}$ dication in complex **5**. Details as in Fig. 1

7). The Fe–Hg bonds could not be distinguished either as covalent or donor–acceptor in this case. However, the longer bonds in the cluster may be due to a strong *trans* influence of the Fe atoms on each other.

In the organometallic cation $[FeHg(CO)_3(\mu\text{-dppy})_2(H_2O)(OClO_3)]^+$ of complex **4** the Hg^{II} is co-ordinated by a water molecule and weakly by a perchlorate anion, and accordingly bears a formal +1 charge. In view of the donor–acceptor character of the Fe–Hg bond it is expected that the positive charge on the Hg^{II} favours the formation of a stronger Fe–Hg bond. This expectation is supported by the fact that the Fe–Hg distance [2.545(1) Å] in the cation is significantly shorter than those in the analogous neutral donor–acceptor complexes *a*–*c* and in the Fe–Hg cluster *l* (see Table 7). However, it is comparable to those in compounds *d*–*k* the Fe–Hg bonds of which are classified as covalent. The effect of a positive charge on the donor–acceptor metal–metal bond distance is also observed in $[Co(\eta\text{-}C_5H_5)(CO)_2(HgCl)]Cl$[31] as compared with $[Co(\eta\text{-}C_5H_5)(CO)_2(HgCl_2)]$.[32]

The ionic character of the Hg^{II} in complex **4** also has a great influence on the other co-ordination bonds and geometry of the complex: (*i*) the C–Fe–C angle adjacent to the Hg^{II} atom [162.6(2)°] is much larger than those in complexes *a* [146.6(3)] and *b* [149.6(1)°], which is consistent with the shorter Fe–Hg distance in **4** and consequently a stronger repulsive interaction between carbonyl groups and the Fe–Hg bond pair in **4**; (*ii*) the Hg–N distances in **4** [2.423(5) and 2.469(5) Å] are much shorter than those in *a* [2.595(6) and 2.867(6)] and *b* [2.658(2) and 2.731(2) Å], in agreement with the increased hardness of the Hg^{II} in **4** as compared with *a* and *b*. However, the interaction between the Hg^{II} and pyridyl groups in complexes *a* and *b* may be best regarded as secondary overlap between the 6p orbital of Hg^{II} and π orbitals of the pyridyl rings.[33]

Crystal structure of mononuclear complex $[Fe(CO)_2(dppy\text{-}P,N)_2][ClO_4]_2\cdot CH_2Cl_2$ 5

Compound **5** crystallizes with discrete $[Fe(CO)_2(dppy\text{-}P,N)_2]^{2+}$, ClO_4^-, and CH_2Cl_2 moieties packed in the crystal lattice. As displayed in Fig. 5, the mononuclear organometallic cation $[Fe(CO)_2(dppy\text{-}P,N)_2]^{2+}$ contains a pair of strained *planar* four-membered chelate rings. The iron(II) has a distorted octahedral co-ordination with the carbonyl groups occupying *cis* positions, and the two four-membered chelate rings are each planar (sum of interior angles = 359.8 and 359.9°) and nearly mutually orthogonal (dihedral angle 85.6°). The organometallic ligands are *cis* co-ordinated to the iron atom such that the P atom of one dppy ligand is *trans* to the N atom of the other, and *vice versa*. The Fe–C(2) [1.837(2) Å] and Fe–P(2) [2.345(1) Å] bonds are significantly longer than Fe–C(1) [1.788(3) Å] and Fe–P(1) [2.253(1) Å], respectively, indicating that a strong *trans* influence is operative between P(2) and C(2)–O(2), but not between P(1) and N(2). The Fe–N(1) [2.015(2) Å] and Fe–N(2) [2.004(3) Å] bond distances are nearly equal despite the fact that the C(1)–O(1) group is expected to exert some *trans* influence on the N(1) atom. The angular distortion in either metallacycle is similar to that in related complexes containing a *single* four-membered chelate ring, for example $[RuCl_2(CO)_2(dppy\text{-}P,N)]$[34] and $[PtCl(dppy\text{-}P,N)(dppy\text{-}P)][RhCl_2(CO)_2]$.[35] Apparently a co-ordination rearrangement about the newly formed iron(II) centre occurred in the course of oxidation of the iron(0) species to the +2 state by iron(III) perchlorate, such that the stronger π acceptors take up *cis* ligand sites. To our knowledge the present complex is the first example of that of a first-row transition metal which incorporates two *planar* four-membered chelate rings involving P and N donor atoms. When the reaction is carried out in the presence of other metal-containing species relief of the angular strain in the mononuclear species through ring opening may lead to the formation of a binuclear complex.[34]

Conclusion

Reaction of the neutral organometallic complex L with $[Cu(MeCN)_4]ClO_4$, $Cu(ClO_4)_2\cdot 6H_2O$, $AgClO_4$, $Hg_2(ClO_4)_2\cdot 8H_2O$ and $Fe(ClO_4)_3\cdot 6H_2O$, respectively, led to the formation of heterobimetallic complexes **1**–**4**, and a mononuclear organometallic iron(II) complex containing a pair of strained *planar* four-membered chelate rings, **5**. In **1**–**4** L acts as a neutral organometallic tridentate ligand, and in **1**–**3** a semibridging interaction exists between the Cu or Ag atom and one of the carbonyl groups, which may be important for the catalytic activity of this kind of compound in the carbonylation of ethanol forming ethyl propionate according to the proposed mechanism.[6] The dative Fe→Hg bond distance in the cation $[(OC)_3Fe(\mu\text{-dppy})_2Hg(H_2O)(OClO_3)]^+$ of complex **4** is comparable to the covalent Fe–Hg distance in related complexes.

Other interesting findings in the present study are concerned with the reactivity of L: (*i*) reaction with $Cu(ClO_4)_2\cdot 6H_2O$ failed to yield the expected Fe^0–Cu^{II} complex and an Fe^0–Cu^I complex **2** was obtained instead; (*ii*) complex **3** formed with an initial reduction of some Ag^I by L to metallic silver; (*iii*) reaction of L and $Fe(ClO_4)_3\cdot xH_2O$ afforded a very unusual iron(II) complex **5** *via* the oxidation of L by Fe^{III}. These results indicate that L is a strong reductant, so that it may be used to synthesize complexes that are otherwise difficult to prepare by the direct reaction of metal agents with dppy, such as **5**, which in turn may serve as a starting material for the generation of new complexes containing metal–metal bonds.

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