

Synthesis and structural characterization of hetero-binuclear complexes containing a $\text{Fe}^0 \rightarrow \text{M}^{n+}$ bond bridged by a non-rigid *P,N*-phosphine ligand

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Abstract

A new non-rigid phosphine ligand, *N*-(diphenylphosphinomethyl)morpholine (L), has been synthesized. Its reaction with $\text{K}[\text{HFe}(\text{CO})_4]$ results in the formation of the organometallic tridentate ligand *trans*- $[\text{Fe}(\text{CO})_3(\mu\text{-L})_2]$ which exhibits different coordinate modes in generating hetero-binuclear $\text{Fe}^0 \rightarrow \text{M}^{n+}$ complexes ($\text{M} = \text{Hg}(\text{II}), \text{Cd}(\text{II}), \text{Cu}(\text{I}), \text{Ag}(\text{I})$). In the copper(I) complex, both tertiary amino groups coordinate to the Cu atom at $\text{Cu-N1} = 2.059(4)$ and $\text{Cu-N2} = 2.055(4)$ Å. In the cadmium(II) complex, one tertiary N atom coordinates to the Cd atom at $\text{Cd-N1} = 2.481(3)$ Å, but only a weak interaction of 2.730 Å exists between the Hg and a N atom in the isomorphous mercury(II) complex. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphine; Iron(0); Hetero-binuclear complex; Polydentate ligand; Metal–metal bond

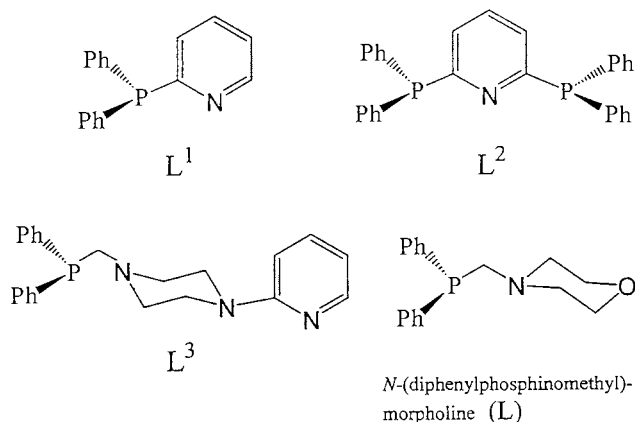
1. Introduction

In the past two decades, hetero- and homo-binuclear organometallic compounds containing a metal–metal bond have been subjected to extensive investigation owing to interest in their unique structures, reactivities and spectroscopic properties [1]. Hemilabile bridging ligands such as 2-(diphenylphosphino)pyridine (L^1) and 2,6-bis(diphenylphosphino)pyridine (L^2) [2] were used widely to bind different metal atoms, as *electronic differentiation* [3] associated with the hard and soft donor atoms dic-

tates their unique reactivities and coordination modes. However, the non-rigid ligands $\text{Ph}_2\text{PCH}_2\text{NPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{NPh}$ only exhibit a monodentate *P*-coordination mode to form mononuclear Rh, Au, and Cu complexes [4]. The reason they do not function as a bidentate ligand is attributed to the nearly planar configuration around the tertiary amino nitrogen atom, which precludes its coordination to a metal center, as revealed by the structures of $\text{Rh}(\text{Ph}_2\text{PCH}_2\text{NPh}_2)_2(\text{CO})\text{Cl}$, $\text{Au}[(\text{Ph}_2\text{PCH}_2\text{NPh}_2)_2]\text{Cl}$ and $\text{Cu}[(\text{Ph}_2\text{PCH}_2\text{NPh}_2)_2]\text{Cl}$ [4]. In our previous work, we replaced the phenylamino or diphenylamino group by a pyridyl piperazine ring to ensure that the proximal tertiary amino nitrogen atom has a pyramidal configuration in the resulting non-rigid *P,N*-phosphine ligand (L^3) and reported the synthesis and structure of its binuclear silver(I) and mononuclear iron(0) complexes [5].

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However, the polydentate organometallic ligand $trans\text{-Fe}(\text{CO})_3(L^3)_2$ does not readily form hereto-binuclear complexes containing a $\text{Fe}^0 \rightarrow \text{M}^{n+}$ bond because the coordination ability of pyridine is stronger than that of a tertiary amine. Therefore, we replaced the pyridylpiperazine group in L^3 by morpholine to form N -(diphenylphosphinomethyl)morpholine (L), and then used it to synthesize the new organometallic tridentate ligand $trans\text{-Fe}(\text{CO})_3(L)_2$, whose reactivity and hetero-binuclear complexes with Group 11 and 12 metals are reported here (Scheme 1).

2. Results and discussion

Heating a mixture of diphenylphosphine, morpholine and paraformaldehyde in toluene in a manner similar to that devised by Maier yielded a colorless solution [6], from which L was obtained as colorless crystals after evaporation and crystallization from ethanol. Compared to (diphenylphosphino)(diphenylamino)methane, this P,N -phosphine ligand has a pyramidal nitrogen atom seated at the bridge head of the morpholine ring, which can readily coordinate to a metal center with its lone-pair electrons.

The reaction of L with $\text{Fe}(\text{CO})_5$ and KOH in refluxing ethanol afforded a yellow precipitate formulated as $trans\text{-Fe}(\text{CO})_3(L)_2$. The IR spectrum showed intense carbonyl absorption at 1880 cm^{-1} , which implied that the local symmetry about the Fe atom is near D_{3h} . The molecular structure of $trans\text{-Fe}(\text{CO})_3(L)_2$ (**1**) is depicted in Fig. 1 with the atom numbering scheme. Selected bond lengths and angles are listed in Table 1. The coordination environment about the iron atom may be best described as an FeP_2C_3 trigonal bipyramid with two phosphine ligands occupying axial positions and three carbonyl groups lying on the equatorial plane. The P-Fe-P angle of $178.24(3)^\circ$ is comparable to that ($174.2(1)^\circ$) in $trans\text{-Fe}(\text{CO})_3(\text{Ph}_2\text{Ppym})_2$ [7] and that ($177.1(1)^\circ$) in $trans\text{-Fe}(\text{CO})_3(\text{Ph}_2\text{Ppy})_2$ [1d]. The three C-Fe-C angles ($123.25(15)$, $119.30(15)$, and $117.45(15)^\circ$) are not far from the ideal value of 120° .

Reaction of **1** with MX_2 ($\text{M} = \text{Cd}, \text{Hg}; \text{X} = \text{I}$) and $[\text{M}(\text{MeCN})_4]\text{ClO}_4$ ($\text{M} = \text{Ag}, \text{Cu}$) resulted in the formation of binuclear complexes **2–5** in moderate yields. Compared to **1**, the IR $\nu(\text{CO})$ spectra of these binuclear complexes split into three peaks and shift to higher frequencies, which are consistent with both a change in stereochemistry and a decrease in electron density on

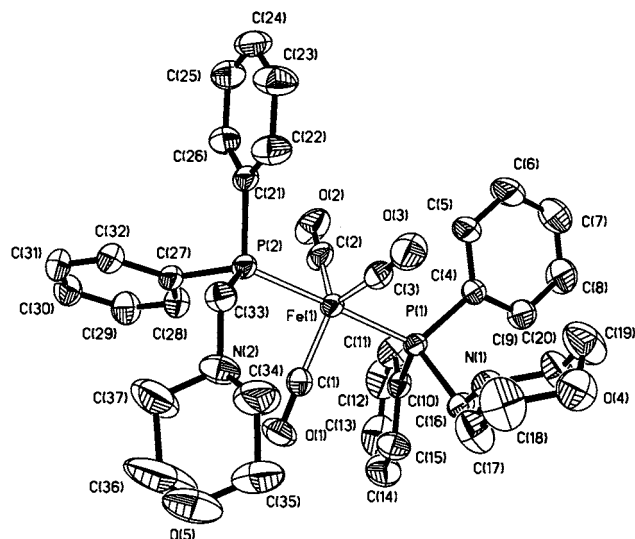
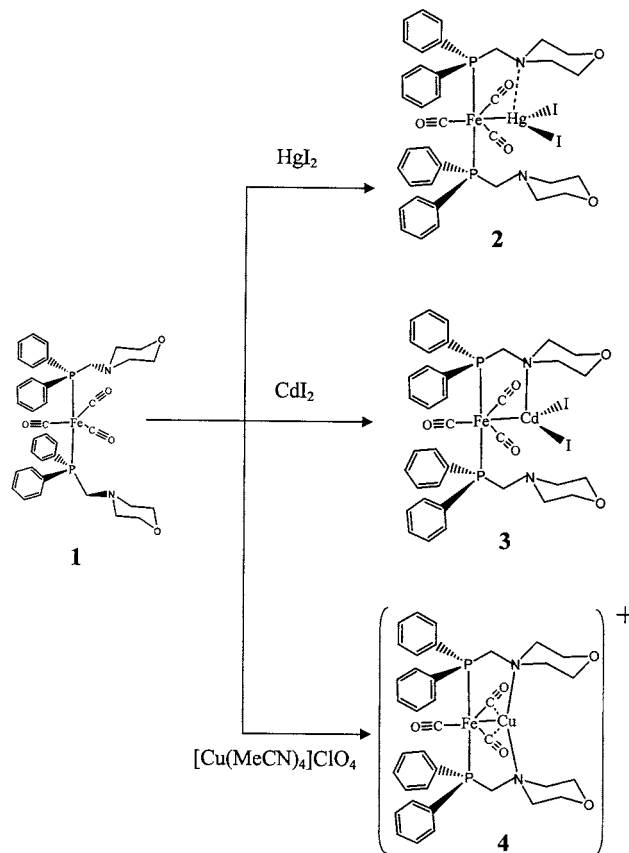


Fig. 1. Perspective view (35% thermal ellipsoids) of $trans\text{-}[\text{Fe}(\mu\text{-L})_2(\text{CO})_3]$ (**1**). In this and all other figures, the hydrogen atoms have been omitted for clarity.

Table 1
X-ray crystallographic data refinement parameters of the complexes

Complex	1	2-Et ₂ O	3-Et ₂ O	4-H ₂ O	6
Formula	C ₃₇ H ₄₀ FeN ₂ O ₅ P ₂	C ₄₁ H ₅₀ FeHgI ₂ N ₂ O ₆ P ₂	C ₄₁ H ₅₀ FeCdI ₂ N ₂ O ₆ P ₂	C ₃₇ H ₄₂ ClCuFeN ₂ O ₁₀ P ₂	C ₁₇ H ₂₁ HgI ₃ NO ₂ P
Formula weight	710.5	1239.01	1150.82	891.51	883.61
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
Crystal size (mm)	0.30 × 0.20 × 0.20	0.64 × 0.58 × 0.40	0.35 × 0.25 × 0.19	0.34 × 0.29 × 0.20	0.30 × 0.15 × 0.15
<i>a</i> (Å)	10.4174(5)	14.814(4)	14.839(1)	11.2142(13)	9.9782(6)
<i>b</i> (Å)	11.4122(5)	12.580(2)	12.5764(8)	13.6807(16)	10.4880(7)
<i>c</i> (Å)	16.4169(8)	24.847(4)	24.8657(16)	14.3070(17)	11.7326(8)
α (°)	83.323(1)			106.274(2)	78.787(1)
β (°)	84.097(1)	91.225(14)	91.413(1)	107.670(2)	78.499(1)
γ (°)	67.244(1)			94.732(3)	82.836(1)
<i>U</i> (Å ³)	1784.03(14)	4629.4(16)	4639.1(5)	1973.6(4)	1175.49(13)
<i>Z</i>	2	4	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.323	1.778	1.648	1.500	2.496
<i>F</i> (000)	744	2400	2272	920	800
μ (Mo–K α) (mm ⁻¹)	0.556	5.073	2.215	1.113	10.565
Goodness-of-fit	0.963	1.013	0.949	0.971	0.917
Unique reflections	8408	9091	11239	6903	5543
<i>R</i> _{int}	0.0207	0.0603	0.0332	0.0505	0.0276
Observed reflections	5004	5617	7365	4767	3505
Variables (<i>p</i>)	376	448	448	441	203
<i>R</i> ₁ , <i>wR</i> ₂					
[<i>I</i> > 2 σ (<i>I</i>)] ^a	0.049, 0.1289	0.0569, 0.1113	0.0358, 0.0961	0.0673, 0.1819	0.0449, 0.1004
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.086, 0.1475	0.1123, 0.1312	0.0648, 0.1070	0.0925, 0.1985	0.0765, 0.1123

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

the iron(0) atom. The ³¹P{¹H}-NMR spectra of complexes **2–5** at room temperature consist of a singlet, which indicates that both P atoms remain chemically equivalent. The change in δ value also implies the formation of binuclear complexes. For complex **2**, coupling of two bonds (³¹P–Fe–¹⁹⁹Hg) is observed with ²*J*_{P–Fe–Hg} = 177 Hz, and comparable coupling constants have been observed previously in related complexes containing an Fe–Hg bond, for example: Fe(CO)₃(μ -Ph₂Ppy)HgI₂, ²*J*_{P–Fe–Hg} = 190 Hz [1d], and Hg[Fe(CO)₃{Si(OMe)₃}(dppm-p)]₂ (173 Hz) [8]. For complex **3**, the magnitude of the ²*J*(³¹P–Fe–¹¹¹Cd) value is 93 Hz, which is comparable to those observed in *mer*-{[(MeO)₃Si](CO)₃Fe(μ -Ph₂Py)CdBr(4-pic)]} (82 Hz), *mer*-{[(MeO)₃Si](CO)₃Fe(μ -Ph₂Py)₂Cd} (66 Hz) [9], and Fe(CO)₃(μ -Ph₂Ppy)CdCl₂ (34 Hz) [1d].

ORTEP drawings with atom numbering for compounds **2–4** are shown in Figs. 2–4, respectively. Selected bond lengths and angles are listed in Table 2. Complexes **2–4** display a distorted octahedral geometry about the Fe atom, in which the FeP₂ unit is nearly linear with a P(1)–Fe–P(2) angle close to 180°, and three CO moieties and M lie in a plane perpendicular to the FeP₂ axis. In complex **2**, the Hg atom is only three-coordinated with a Fe–Hg distance of 2.6596(13) Å, which is comparable to those of the Fe(0) → Hg(II) dative bond in Fe(CO)₃(μ -Ph₂Ppy)₂Hg(SCN)₂ (2.648(3) Å) [10], Fe(CO)₃(μ -Ph₂Ppy)₂HgI₂ (2.678(2) Å) [1d], and Fe(CO)₃(μ -Ph-MePpy)₂Hg(μ -Cl)₂HgCl₂ (2.592(4) Å) [11]. The Hg–N distances are 2.730 and 3.753 Å, which

means only one nitrogen atom has a weak interaction with the mercury atom (the distance of 2.730 Å is longer than those in the range of 2.26–2.56 Å for mercury–tertiary amine complexes [12]). In complex **3**, the Cd atom is four-coordinated with a Fe–Cd = 2.7369(6) Å, which is comparable to those of the Fe(0) → Cd(II) dative bond in related complexes: Fe(CO)₃(μ -Ph₂Ppym)₂CdX₂ (X = Cl, Br, I, SCN) (2.701(1)–2.818(1) Å) [13], Fe(CO)₃(μ -Ph₂Ptaz)₂CdI₂

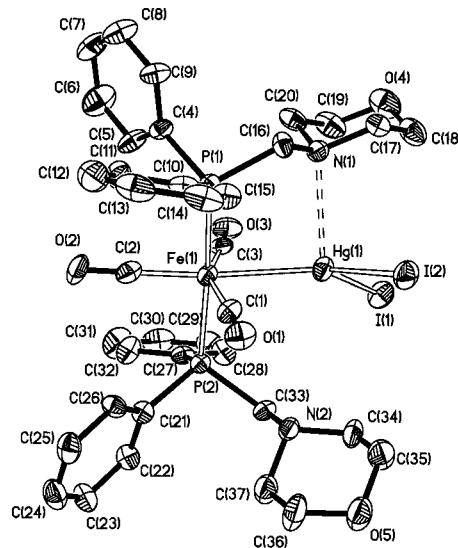


Fig. 2. Perspective view (35% thermal ellipsoids) of [Fe(μ -L)₂(CO)₃HgI₂] (**2**).

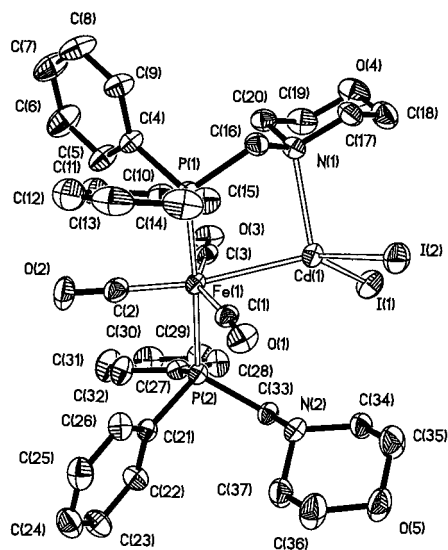


Fig. 3. Perspective view (35% thermal ellipsoids) of $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{CdI}_2]$ (**3**).

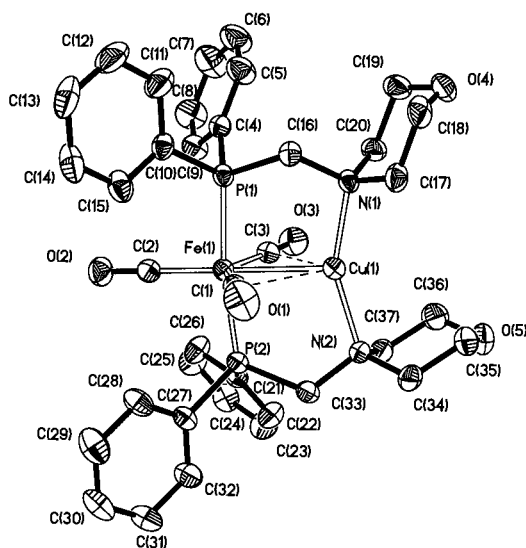


Fig. 4. Perspective view (35% thermal ellipsoids) of the $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{Cu}]^+$ cation in **4**.

($\text{Ph}_2\text{Ptaz} = 2$ -diphenylphosphinothiazole) (2.812(1) Å) [14]. The Cd–N distances are 2.481(3) and 3.968 Å, indicating that only one nitrogen atom is coordinated to the cadmium atom. Complex **4** consists of a packing of hetero-binuclear cations, discrete perchlorate anions and lattice water molecules. The Fe–Cu distance of 2.550(1) Å falls within the range of 2.394–2.580 Å reported for polynuclear complexes containing an Fe–Cu bond [15]. The Cu(I) atom exhibits three coordination, which is different from related four-coordinate complexes: the N1–Cu1–N2 angle of 154.36(16)° is larger than those of $[\text{Fe}(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})_2\text{Cu}(\text{Me}_2\text{CO})]^+$ (123.6(4)°) and $[\text{Fe}(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})_2\text{Cu}(\text{H}_2\text{O})]^+$

(135.0(2)°) [11]. That the coordination modes of the two nitrogen atoms in **2–4** differ with different metal cations may be explained by the Lewis acid–base concept. The tertiary amino nitrogen atom is a hard base whose coordinated ability decreases with increasing softness of the Lewis acid ($\text{Hg}(\text{II}) > \text{Cd}(\text{II}) > \text{Cu}(\text{I})$) (Fig. 5).

Complex **6** is a salt isolated from the mother liquor of $\text{Fe}(\text{CO})_3(\mu\text{-L})_2\text{HgI}_2$. The P atom of L is converted to oxidation state +5 and the N atom becomes protonated. The resulting centrosymmetric cationic moieties are linked into cyclic dimers through normal N–H⋯O hydrogen bonds of length $\text{N}\cdots\text{O} = 2.706$ Å. The anionic part consists of a centrosymmetric $[\text{Hg}_2\text{I}_6]^{2-}$ dimer consolidated by two bridging iodide ions.

In summary, we have taken advantage of the coordination ability of the tertiary amino nitrogen atom of the morpholine fragment in the non-rigid *P,N*-phosphine ligand L to induce selective coordination of the new organometallic ligand *trans*- $\text{Fe}(\text{CO})_3(\mu\text{-L})_2$ toward Group 11 and 12 metal ions in the formation of hetero-binuclear $\text{Fe}^0 \rightarrow \text{M}^{n+}$ complexes.

3. Experimental

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Shimadzu 435 spectrometer as KBr discs. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on an AC-P200 spectrometer at 81.03 MHz using H_3PO_4 as the external standard and CDCl_3 as the solvent. The ligand L was prepared by a procedure similar to that of L^3 [5].

3.1. Synthetic procedure

3.1.1. *trans*- $[\text{Fe}(\text{CO})_3(\text{L})_2]$ (**1**)

This compound was prepared by the published procedure for *trans*- $[\text{Fe}(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})_2]$ [10] and single crystals were recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$. (Yield 65%. Found: C, 62.50; H, 5.52; N, 3.72. Calc. for $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_5\text{P}_2\text{Fe}$: C, 62.54; H, 5.67; N, 3.94%). IR $\nu(\text{CO})$: 1880s cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ -NMR(CDCl_3 , 298 K): $\delta = 66.18$ ppm.

3.1.2. $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{HgI}_2]$ (**2**)

HgI_2 (0.078 g, 0.17 mmol) was added to a solution of **1** (0.1 g, 0.14 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 2 h at room temperature (r.t.). The solution was filtered and the filtrate concentrated. *n*-Hexane was added to give a yellow solid (0.14 g, 83%). (Found: C, 38.00; H, 3.76; N, 2.18. Calc. for $\text{C}_{39}\text{H}_{40}\text{N}_2\text{O}_5\text{P}_2\text{FeI}_2\text{Hg}$: C, 38.15; H, 3.46; N, 2.40%). IR $\nu(\text{CO})$: 2010m, 1970s cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 ,

Table 2
Selected bond lengths (Å) and angles (°) for the complexes

Complex 1			
Fe(1)–P(1)	2.2010(7)	Fe(1)–P(2)	2.2064(7)
Fe(1)–C(1)	1.771(3)	Fe(1)–C(2)	1.772(3)
Fe(1)–C(3)	1.767(4)		
P(1)–Fe(1)–P(2)	178.24(3)	C(1)–Fe(1)–P(1)	87.53(9)
C(2)–Fe(1)–P(1)	91.49(9)	C(3)–Fe(1)–P(1)	91.4(1)
C(1)–Fe(1)–P(2)	91.14(9)	C(2)–Fe(1)–P(2)	90.16(9)
C(3)–Fe(1)–P(2)	88.4(1)	C(1)–Fe(1)–C(2)	119.3(2)
C(1)–Fe(1)–C(3)	123.3(2)	C(2)–Fe(1)–C(3)	117.5(2)
C(1)–Fe(1)–P(1)	87.53(9)	C(2)–Fe(1)–P(1)	91.49(9)
C(3)–Fe(1)–P(1)	91.4(1)	C(1)–Fe(1)–P(2)	91.14(9)
C(2)–Fe(1)–P(2)	90.16(9)	C(3)–Fe(1)–P(2)	88.4(1)
O(1)–C(1)–Fe(1)	176.4(3)	O(2)–C(2)–Fe(1)	179.6(3)
O(3)–C(3)–Fe(1)	177.0(3)		
Complex 2·Et₂O			
Hg(1)–Fe(1)	2.665(1)	Hg(1)–I(1)	2.7748(8)
Hg(1)–I(2)	2.7907(7)	Fe(1)–C(1)	1.803(9)
Fe(1)–C(2)	1.79(1)	Fe(1)–C(3)	1.80(1)
Fe(1)–P(1)	2.276(3)	Fe(1)–P(2)	2.273(3)
C(1)–O(1)	1.14(1)	C(2)–O(2)	1.15(1)
C(3)–O(3)	1.14(1)		
Hg(1)–Fe(1)–P(1)	87.52(7)	Hg(1)–Fe(1)–P(2)	95.41(7)
Hg(1)–Fe(1)–C	79.2(3)	Hg(1)–Fe(1)–C(2)	174.7(3)
Hg(1)–Fe(1)–C(3)	74.2(3)	Fe(1)–Hg(1)–I(1)	126.45(3)
Fe(1)–Hg(1)–I(2)	122.12(3)	I(1)–Hg(1)–I(2)	107.90(2)
C(1)–Fe(1)–C(2)	103.5(4)	C(1)–Fe(1)–C(3)	153.0(4)
C(2)–Fe(1)–C(3)	103.4(4)	P(1)–Fe(1)–C(1)	90.2(3)
P(1)–Fe(1)–C(2)	87.9(3)	P(1)–Fe(1)–C(3)	93.0(3)
P(2)–Fe(1)–C(1)	88.8(3)	P(2)–Fe(1)–C(2)	89.3(3)
P(2)–Fe(1)–C(3)	89.3(3)	P(1)–Fe(1)–P(2)	176.7(1)
O(1)–C(1)–Fe(1)	175.3(9)	O(2)–C(2)–Fe(1)	178.9(9)
O(3)–C(3)–Fe(1)	175.5(9)		
Complex 3·Et₂O			
Cd(1)–Fe(1)	2.7369(6)	Cd(1)–N(1)	2.481(3)
Cd(1)–I(1)	2.7628(4)	Cd(1)–I(2)	2.7698(4)
Fe(1)–P(1)	2.261(1)	Fe(1)–P(2)	2.266(1)
Fe(1)–C(1)	1.809(4)	Fe(1)–C(2)	1.784(4)
Fe(1)–C(3)	1.794(4)	C(1)–O(1)	1.138(5)
C(2)–O(2)	1.150(5)	C(3)–O(3)	1.144(5)
Cd(1)–Fe(1)–P(1)	84.61(3)	Cd(1)–Fe(1)–P(2)	98.99(3)
Cd(1)–Fe(1)–C(1)	78.4(1)	Cd(1)–Fe(1)–C(2)	171.0(1)
Cd(1)–Fe(1)–C(3)	72.2(1)	Cd(1)–N(1)–C(16)	99.7(2)
Fe(1)–Cd(1)–I(1)	122.65(2)	Fe(1)–Cd(1)–I(2)	119.84(2)
N(1)–Cd(1)–Fe(1)	92.97(7)	N(1)–Cd(1)–I(1)	113.47(7)
N(1)–Cd(1)–I(2)	93.87(7)	I(1)–Cd(1)–I(2)	108.52(1)
C(1)–Fe(1)–C(2)	105.8(2)	C(1)–Fe(1)–C(3)	149.8(2)
C(2)–Fe(1)–C(3)	104.2(2)	P(1)–Fe(1)–C(1)	90.0(1)
P(1)–Fe(1)–C(2)	87.4(1)	P(1)–Fe(1)–C(3)	94.2(1)
P(2)–Fe(1)–C(1)	88.8(1)	P(2)–Fe(1)–C(2)	89.2(1)
P(2)–Fe(1)–C(3)	88.9(1)	P(1)–Fe(1)–P(2)	175.90(4)
O(1)–C(1)–Fe(1)	173.8(4)	O(2)–C(2)–Fe(1)	179.0(4)
O(3)–C(3)–Fe(1)	174.7(4)		
Complex 4·H₂O			
Cu(1)–Fe(1)	2.550(1)	Cu(1)–N(2)	2.055(4)
Fe(1)–P(1)	2.214(1)	Fe(1)–P(2)	2.214(1)
Fe(1)–C(1)	1.780(6)	Fe(1)–C(2)	1.766(5)
Fe(1)–C(3)	1.789(6)	C(1)–O(1)	1.143(7)
C(2)–O(2)	1.152(6)	C(3)–O(3)	1.150(7)
Cu(1)–Fe(1)–P(1)	85.54(4)	Cu(1)–Fe(1)–P(2)	85.84(4)

Table 2 (Continued)

Cu(1)–Fe(1)–C(1)	67.9(2)	Cu(1)–Fe(1)–C(2)	179.9(2)
Cu(1)–Fe(1)–C(3)	67.7(2)	Cu(1)–N(1)–C(16)	109.5(3)
Cu(1)–N(2)–C(33)	108.2(3)	C(1)–Fe(1)–C(2)	112.1(3)
C(2)–Fe(1)–C(3)	112.3(3)	C(1)–Fe(1)–C(3)	135.6(3)
P(1)–Fe(1)–C(1)	87.3(2)	P(1)–Fe(1)–C(2)	94.3(2)
P(1)–Fe(1)–C(3)	89.2(2)	P(2)–Fe(1)–C(1)	88.3(2)
P(2)–Fe(1)–C(2)	94.3(2)	P(2)–Fe(1)–C(3)	88.7(2)
P(1)–Fe(1)–P(2)	171.29(6)	N(1)–Cu(1)–N(2)	154.4(2)
N(1)–Cu(1)–Fe(1)	103.0(1)	N(2)–Cu(1)–Fe(1)	102.7(1)
N(1)–Cu(1)–C(1)	98.2(2)	N(1)–Cu(1)–C(3)	101.1(2)
N(2)–Cu(1)–C(1)	101.4(2)	N(2)–Cu(1)–C(3)	97.6(2)
C(1)–Cu(1)–C(3)	82.8(2)	O(1)–C(1)–Fe(1)	177.4(5)
O(2)–C(2)–Fe(1)	179.4(5)	O(3)–C(3)–Fe(1)	177.4(5)
Complex 6			
Hg(1)–I(1)	2.6582(7)	Hg(1)–I(2)	2.9169(7)
Hg(1)–I(3)	2.7049(7)	Hg(1)–I(2) # 1	2.9531(7)
I(2)–Hg(1) # 1	2.9531(7)	P(1)–O(1)	1.488(5)
I(1)–Hg(1)–I(2)	109.76(2)	I(1)–Hg(1)–I(3)	124.03(3)
I(2)–Hg(1)–I(3)	106.06(2)	I(1)–Hg(1)–I(2) # 1	105.25(2)
I(3)–Hg(1)–I(2) # 1	111.44(2)	I(2)–Hg(1)–I(2) # 1	97.02(2)
Hg(1)–I(2)–Hg(1) # 1	82.98(2)		

298 K): $\delta = 58.41$ ppm. $J_{\text{Hg-P}} = 88.5$ Hz. Recrystallization of **2** in $\text{CHCl}_3\text{-Et}_2\text{O}$ yielded yellow crystals of **2·Et₂O** for X-ray analysis.

3.1.3. $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{CdI}_2]$ (**3**)

CdI_2 (0.063 g, 0.17 mmol) was added to a solution of **1** (0.1 g, 0.14 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 2 h at r.t. The solution was filtered and the filtrate concentrated. Ether was added to give yellow crystals of **3·Et₂O** (0.104 g, 65%). (Found: C, 42.68; H, 4.35; N, 2.44. Calc. for $\text{C}_{41}\text{H}_{50}\text{N}_2\text{O}_6\text{P}_2\text{FeI}_2\text{Cd}$: C, 42.79; H, 4.38; N, 2.43%). IR $\nu(\text{CO})$: 2000m, 1958s, 1936s cm^{-1} . $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3 , 298 K): $\delta = 58.64$ ppm. $J_{\text{Cd-P}} = 93$ Hz.

3.1.4. $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{Cu}]\text{ClO}_4$ (**4**)

$\text{Cu}[(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (0.056 g, 0.17 mmol) was added to a solution of **1** (0.1 g, 0.14 mmol) in dichloromethane (10 cm^3). The mixture was stirred for 2 h at r.t. The solution was filtered and the filtrate concentrated. Ether was added to give yellow crystals of **4·H₂O** (0.090 g, 72%). (Found: C, 49.49; H, 4.58; N, 3.82. Calc. for $\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_{10}\text{P}_2\text{FeClCu}$: C, 49.84; H, 4.75; N, 3.14%). IR $\nu(\text{CO})$: 1980m, 1912s, 1865s cm^{-1} . $^{31}\text{P}\{\text{H}\}$ -NMR (CDCl_3 , 298 K): $\delta = 70.67$ ppm.

3.1.5. $[\text{Fe}(\mu\text{-L})_2(\text{CO})_3\text{AgClO}_4]$ (**5**)

$\text{Ag}[(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (0.064 g, 0.17 mmol) was added to a solution of **1** (0.1 g, 0.14 mmol) in dichloromethane (10 cm^3). The mixture was stirred for 20 min at r.t. The solution was filtered and the filtrate concentrated. Ether was added to give yellow crystals of **5·H₂O** (0.076 g, 58%). (Found: C, 47.79; H, 5.17; N,

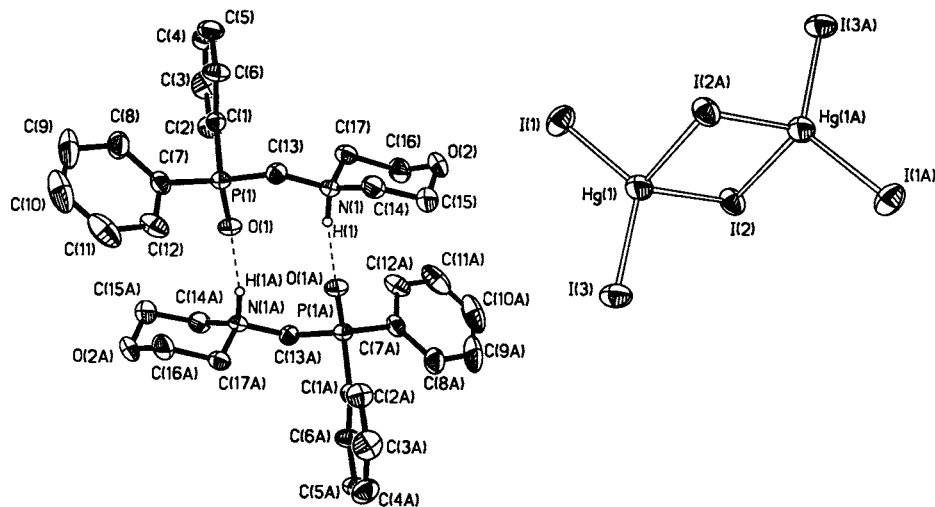


Fig. 5. Perspective view (35% thermal ellipsoids) of the dimeric cationic and anionic species in compound **6**. The N–H \cdots O hydrogen bonds are represented by broken lines.

3.14. Calc. for $C_{37}H_{42}N_2O_{10}P_2FeClAg$: C, 47.49; H, 4.52; N, 2.99%. IR $\nu(CO)$: 1990m, 1920s, 1885s cm^{-1} . $^{31}P\{^1H\}$ -NMR ($CDCl_3$, 298 K): $\delta = 70.67$ ppm.

3.2. X-ray crystallography

Intensity data for complexes **1**, **3**·Et₂O, **4**·H₂O and **6** were collected at 293 K on a Bruker Smart CCD 1000 diffractometer system using Mo–K α radiation ($\lambda = 0.71073$ Å; frames of oscillation range 0.3°; 50 kV, 30 mA; $2\theta_{max} = 56^\circ$ (for **4**·H₂O, $2\theta_{max} = 50^\circ$)). The data for **2**·Et₂O was collected at 293 K in the variable ω -scan mode on a Siemens R3m/V four-circle diffractometer using Mo–K α radiation (50 kV, 30 mA; $2\theta_{max} = 52^\circ$). The crystal structures were determined by direct methods and refined by full-matrix least-squares using the SHELXTL-PC program package [16]. Non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 140767–140771. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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