Binuclear complexes containing an iron(I)–mercury(I) bond from oxidation of trans-[Fe(CO)₂(CS₂)(Ph₂Ppy-P)₂] with HgX₂ (Ph₂Ppy = 2-(diphenylphosphino)pyridine, X = Cl, SCN)

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Abstract

trans-[Fe(CO)₂(CS₂)(Ph₂Ppy-P)₂] reacts with HgX₂ (X = Cl, SCN) in dichloromethane at room temperature to give heterodinuclear complexes XFe(CO)₂(μ-Ph₂Ppy)₂HgX (X = SCN, 1; X = Cl, 2) containing an iron(I)–mercury(I) bond. The Fe(I)–Hg(I) bond length as determined by X-ray analysis is 2.527(2) Å for 1 and 2.529(1) Å for 2.
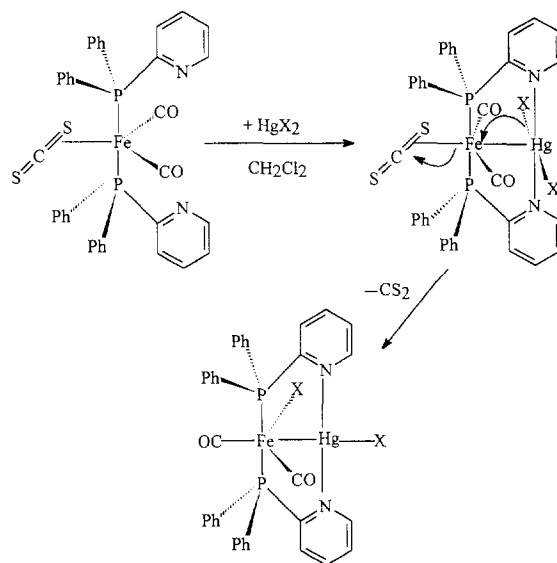
Keywords: Oxidation elimination; Heterobimetallics; Iron carbonyl; Mercury (I); Phosphine; Crystal structure

1. Introduction

Synthetic and structural aspects of the chemistry of complexes containing directly bonded iron and mercury atoms are of continuing intrest [1–4]. Heterodinuclear complexes of this type have been synthesized by two reaction routes. One is an addition reaction in which an iron(0) complex acts as a two-electron donor ligand [5,6]. By this method, several iron(0)–mercury(II) complexes have been obtained in our laboratories using organometallic iron(0) polydentate ligands [7–9]. The other involves displacement of anionic ligands, in which halides of mercury complexes are most commonly displaced by organoiron anionic ligands, such as [Fe(CO)₃{Si(OMe)₃}(dppm-P)]⁻ [10–12]. On the other hand, very few reactions are known in which iron(0) complexes are oxidized by complexes of mercury(II) [13]. We report here the synthesis and X-ray crystal structures of heterodinuclear iron(I)–mercury(I) complexes XFe(CO)₂(μ-Ph₂Ppy)₂HgX (X = SCN, 1; X = Cl, 2) whose formation involves an oxidation elimination process.

2. Results and discussion

The reaction of trans-[Fe(CO)₂(CS₂)(Ph₂Ppy-P)₂] with HgX₂ (X = Cl, SCN) was carried out in

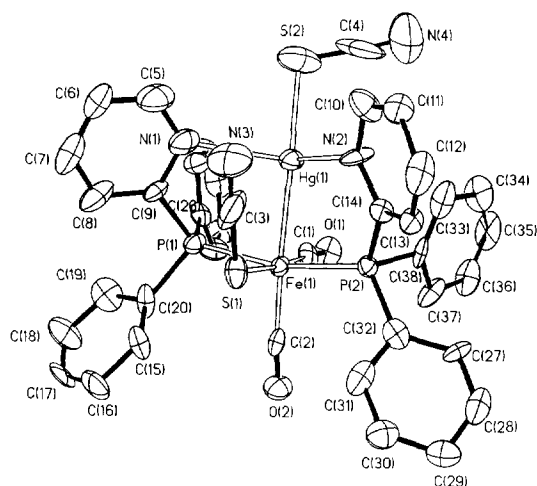
X = SCN, 1; X = Cl, 2.

Scheme 1.

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Fig. 1. ORTEP view of $(NCS)Fe(CO)_2(\mu\text{-}Ph_2Ppy)_2Hg(SCN)$, **1**. The thermal ellipsoids are drawn at the 35% probability level.

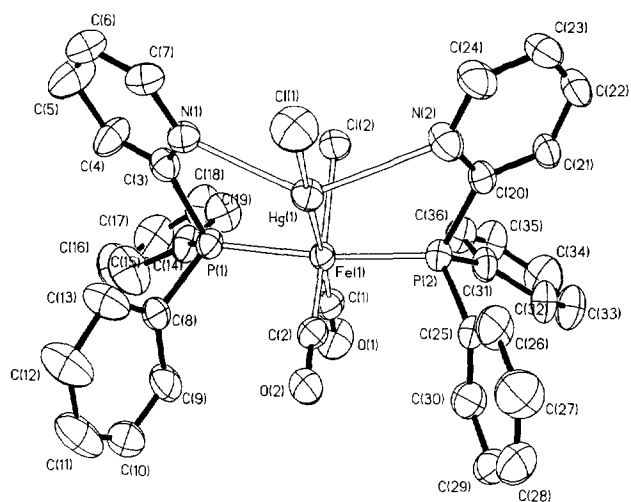Fig. 2. ORTEP view of the $ClFe(CO)_2(\mu\text{-}Ph_2Ppy)_2HgCl$ molecule, **2**, in its 1:1:1 solvate with $CHCl_3$ and CH_3OH. The thermal ellipsoids are drawn at the 35% probability level.

dichloromethane at room temperature. The products $XFe(CO)_2(\mu\text{-}Ph_2Ppy)_2HgX$ (X = Cl, SCN) were obtained in moderate yield as air-stable crystals after solvent evaporation and crystallization from dichloromethane/methanol or chloroform/methanol. The process involves oxidation elimination at the Fe(0) center by the Hg(II) halide/pseudo-halide with simultaneous formation of a metal–metal bond. The first step is mostly likely initiated by tricoordinate attachment of the Fe(0) complex to HgX_2, which is followed by CS_2 elimination with migration of one of the X ligands from Hg to Fe (Scheme 1). This kind of reaction has been reported in the oxidation of Rh [14], Ir [15] and W [16] complexes by complexes of Hg(II).

In the $^{31}P\{^1H\}$ NMR spectra, the two bond coupling $(^{31}P\text{–}Fe\text{–}^{199}Hg)$ is observed for complex **2** and the magnitude of the $^2J(^{31}P\text{–}Fe\text{–}^{199}Hg)$ value is 419 Hz. But for complex **1**, such coupling has not been observed.

The molecular structure of $(NCS)Fe(CO)_2(\mu\text{-}Ph_2Ppy)_2Hg(SCN)$, **1**, is shown in Fig. 1. The iron(I) exhibits octahedral coordination geometry with Hg(1)–Fe(1)–P(1) = 82.3(1)°, Hg(1)–Fe(1)–P(2) = 84.3(1)°, P(1)–Fe(1)–S(1) = 86.7(2)°, P(2)–Fe(1)–S(1) = 89.1(2)°, P(1)–Fe(1)–C(1) = 91.0(3)°, P(2)–Fe(1)–C(1) = 91.9(3)°, P(1)–Fe(1)–C(2) = 97.5(3)°, P(2)–Fe(1)–

Table 1
Crystal and structural data for **1** and **2** · $CHCl_3$ · CH_3OH

formula	$C_{38}H_{28}FeHgN_4O_2P_2S_2$ (**1**)	$C_{38}H_{33}Cl_5FeHgN_2O_3P_2$ (**2** · $CHCl_3$ · CH_3OH)
MW	955.1	1035.98
space group	$P2_1/c$ (No. 14)	$P1$ (No. 2)
unit-cell dimensions		
a (Å)	11.425(1)	10.062(1)
b (Å)	22.177(1)	12.928(1)
c (Å)	14.822(1)	17.337(1)
α (deg)	90	77.31(1)
β (deg)	90.62(1)	81.82(1)
γ (deg)	90	78.18(1)
V (Å^3)	3755.3(4)	2142.3(11)
Z	4	2
d_{calc} (g cm^{-3})	1.689	1.642
radiation	Mo $K\alpha$	Mo $K\alpha$
scan mode	ω–2θ	ω–2θ
$2\theta_{max}$	4–50°	3–55°
no. of unique reflections	7578	7575
no. of observed reflections	2304	5828
no. of variables, p	452	544
R_F	0.049	0.051
R_{wF}^2	0.051	0.069

Table 2
Atomic coordinates ($\times 10^5$ for Hg, Fe, $\times 10^4$ for others) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^4$ for Hg, Fe, $\text{Å}^2 \times 10^3$ for others) % of complex **1**

Atom	x	y	z	U_{eq}
Hg(1)	64280(7)	9200(3)	76145(5)	489(2)
Fe(1)	84316(20)	10439(9)	69336(13)	342(3)
P(1)	8455(3)	21(2)	7067(3)	43(1)
P(2)	8067(3)	2039(2)	7074(3)	37(1)
S(1)	9447(4)	1069(2)	8336(3)	55(1)
S(2)	4348(4)	675(3)	7936(3)	110(1)
O(1)	7007(5)	997(4)	5265(4)	64(1)
O(2)	10505(5)	1180(4)	5853(4)	63(1)
N(1)	7086(5)	−31(4)	8530(5)	73(1)
N(2)	6602(5)	1894(4)	8479(4)	58(1)
N(3)	8095(5)	1098(5)	9916(4)	106(1)
N(4)	3371(5)	1764(5)	7855(5)	220(1)
C(1)	7559(5)	996(4)	5944(5)	49(1)
C(2)	9747(5)	1120(4)	6295(5)	42(1)
C(3)	8674(5)	1070(4)	9196(5)	148(1)
C(4)	3774(5)	1287(5)	7837(5)	147(1)
C(5)	6801(5)	−188(5)	9411(5)	99(1)
C(6)	7419(5)	−593(5)	9891(5)	120(1)
C(7)	8420(5)	−834(5)	9496(5)	102(1)
C(8)	8730(5)	−704(4)	8634(5)	84(1)
C(9)	8087(5)	−249(4)	8184(5)	44(1)
C(10)	5984(5)	2024(4)	9225(5)	74(1)
C(11)	6272(5)	2523(4)	9717(5)	79(1)
C(12)	7288(5)	2875(4)	9438(5)	79(1)
C(13)	7819(5)	2759(4)	8666(5)	56(1)
C(14)	7451(5)	2281(4)	8170(4)	43(1)
C(15)	10845(5)	−149(4)	7075(5)	81(1)
C(16)	11929(5)	−486(4)	6995(5)	105(1)
C(17)	11808(5)	−1061(5)	6658(5)	86(1)
C(18)	10840(5)	−1324(4)	6447(5)	87(1)
C(19)	9805(5)	−980(4)	6537(5)	81(1)
C(20)	9834(5)	−377(4)	6814(5)	53(1)
C(21)	6328(5)	−574(4)	6540(5)	58(1)
C(22)	5578(5)	−764(4)	5959(5)	62(1)
C(23)	5755(5)	−790(4)	5060(5)	87(1)
C(24)	6859(5)	−574(4)	4761(5)	64(1)
C(25)	7639(5)	−354(4)	5380(5)	65(1)
C(26)	7394(5)	−334(4)	6323(5)	45(1)
C(27)	9118(5)	3153(4)	6600(5)	48(1)
C(28)	10042(5)	3514(4)	6505(5)	68(1)
C(29)	11187(5)	3379(4)	6710(5)	72(1)
C(30)	11301(5)	2804(4)	7096(5)	64(1)
C(31)	10387(5)	2398(4)	7165(5)	65(1)
C(32)	9272(5)	2566(4)	6995(5)	50(1)
C(33)	5901(5)	2415(4)	6437(5)	90(1)
C(34)	5132(5)	2596(4)	5680(5)	94(1)
C(35)	5467(5)	2650(4)	4872(5)	96(1)
C(36)	6548(5)	2561(4)	4688(5)	75(1)
C(37)	7430(5)	2377(4)	5365(5)	59(1)
C(38)	7065(5)	2329(4)	6235(5)	53(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

C(2) = 96.5(3)°; the mercury(I) atom exhibits distorted tetrahedral coordination geometry with Fe(1)–Hg(1)–N(1) = 92.2(1)°, Fe(1)–Hg(1)–N(2) = 92.5(1)°, S(1)–Hg(1)–N(1) = 89.7(2)°, S(2)–Hg(1)–N(2) = 99.2(2)°, N(1)–Hg(1)–N(2) = 114.0(2)°. Both thiocyanato ligands bond the metal through the S atom. The C(2), Fe(1), Hg(1) and S(2) atoms are almost collinear, with

Hg(1)–Fe(1)–C(2) = 171.7(2)° and Fe(1)–Hg(1)–S(2) = 166.2(1)°. The Fe(1)–Hg(1) distance, 2.527(2) Å, is comparable to those of the Fe(0)–Hg(I) complex $(CO)_4Fe(HgBr)_2$, 2.515 Å (average) [17], and that of the Fe(I)–Hg(I) binuclear complex $(CO)_3(PMe_3)(Ph_2MeSi)FeHgBr$, 2.515(3) Å [18], but much shorter than the Fe(0) → Hg(II) dative bond in

Table 3

Atomic coordinates ($\times 10^5$ for Hg and Fe atoms, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^4$ for Hg and Fe atoms, $\mathring{A}^2 \times 10^3$ for other atoms) of complex $\mathbf{2} \cdot CHCl_3 \cdot CH_3OH$

Atom	x	y	z	U_{eq}
Hg(1)	79216(3)	50617(3)	−20526(3)	515(1)
Fe(1)	66386(11)	68837(9)	−26684(7)	432(2)
Cl(1)	9101(3)	3274(2)	−1474(2)	81(1)
Cl(2)	8735(2)	7107(2)	−3421(1)	61(1)
P(1)	7318(2)	7572(2)	−1732(1)	49(1)
P(2)	6211(2)	6108(2)	−3638(1)	47(1)
C(1)	5561(4)	8144(4)	−3018(3)	58(1)
O(1)	4772(4)	8885(3)	−3194(3)	87(1)
C(2)	5329(4)	6378(4)	−2015(3)	61(1)
O(2)	4475(4)	6057(3)	−1591(3)	76(1)
N(1)	9439(4)	5968(3)	−1364(3)	56(1)
C(3)	9033(4)	7010(4)	−1410(3)	56(1)
C(4)	9775(4)	7625(4)	−1163(4)	81(1)
C(5)	11006(4)	7074(4)	−825(4)	106(1)
C(6)	11405(4)	6013(4)	−759(4)	79(1)
C(7)	10601(4)	5511(4)	−1056(3)	62(1)
C(8)	6266(4)	7379(4)	−788(3)	55(1)
C(9)	4917(4)	7851(4)	−735(4)	88(1)
C(10)	4092(4)	7692(4)	−41(4)	100(1)
C(11)	4497(4)	6999(4)	599(4)	102(1)
C(12)	5838(4)	6490(4)	575(4)	104(1)
C(13)	6738(4)	6686(4)	−120(4)	84(1)
N(2)	8357(4)	4452(4)	−3467(3)	65(1)
C(14)	7336(4)	9008(4)	−1959(3)	63(1)
C(15)	7032(4)	9635(4)	−1386(4)	115(1)
C(16)	7086(4)	10741(4)	−1588(4)	126(1)
C(17)	7568(4)	11204(4)	−2328(4)	109(1)
C(18)	7989(4)	10559(4)	−2873(4)	103(1)
C(19)	7813(4)	9494(4)	−2702(4)	87(1)
C(20)	7555(4)	5099(4)	−4011(3)	47(1)
C(21)	7777(4)	4958(4)	−4789(3)	64(1)
C(22)	8825(4)	4137(4)	−4987(4)	77(1)
C(23)	9574(4)	3492(4)	−4444(4)	78(1)
C(24)	9318(4)	3649(4)	−3685(4)	74(1)
C(25)	4770(4)	5403(4)	−3322(3)	53(1)
C(26)	4939(4)	4305(4)	−3094(4)	77(1)
C(27)	3847(4)	3775(4)	−2808(4)	104(1)
C(28)	2587(4)	4358(4)	−2752(4)	96(1)
C(29)	2347(4)	5457(4)	−2966(3)	80(1)
C(30)	3479(4)	6010(4)	−3254(3)	73(1)
C(31)	5725(4)	7036(4)	−4551(3)	58(1)
C(32)	4744(4)	6914(4)	−5007(3)	74(1)
C(33)	4379(4)	7659(4)	−5666(4)	90(1)
C(34)	5003(4)	8479(4)	−5914(4)	105(1)
C(35)	5978(4)	8657(4)	−5504(4)	87(1)
C(36)	6333(4)	7955(4)	−4842(3)	69(1)
C(37)	8319(4)	8961(4)	1443(3)	117(1)
Cl(3)	9044(4)	9653(4)	496(4)	142(1)
Cl(4)	8142(4)	9788(4)	2103(4)	153(1)
Cl(5)	6660(4)	8916(4)	1228(4)	134(1)
Cl(3′)	9033(4)	9920(4)	856(4)	144(1)
Cl(4′)	8133(4)	8810(4)	2445(3)	141(1)
Cl(5′)	7346(4)	8390(4)	1013(4)	134(1)
Cl(3″)	8751(4)	10214(4)	1411(4)	154(1)
Cl(4″)	7230(4)	8819(4)	2344(4)	159(1)
Cl(5″)	7384(4)	9084(4)	648(4)	161(1)
C(39)	9042(4)	−46(4)	3655(4)	85(1)
O(4)	9248(4)	−533(4)	4474(4)	127(1)
O(3)	10733(4)	−308(4)	4921(4)	131(1)
C(38)	11760(4)	−1200(4)	5260(4)	79(1)

Table 4
Selected bond lengths (Å) and angles (°) in complex 1

Hg(1)–Fe(1)	2.527(2)	P(1)–C(9)	1.813(8)
Hg(1)–S(2)	2.489(5)	P(1)–C(20)	1.848(8)
Hg(1)–N(1)	2.613(8)	P(1)–C(26)	1.810(8)
Hg(1)–N(2)	2.519(8)	P(2)–C(14)	1.856(8)
Fe(1)–P(1)	2.277(4)	P(2)–C(32)	1.811(8)
Fe(1)–P(2)	2.255(4)	P(2)–C(38)	1.801(8)
Fe(1)–S(1)	2.370(4)	S(1)–C(3)	1.558(8)
Fe(1)–C(1)	1.767(7)	S(2)–C(4)	1.514(12)
Fe(1)–C(2)	1.793(6)	O(1)–C(1)	1.182(9)
		O(2)–C(2)	1.099(8)
Fe(1)–Hg(1)–S(2)	166.2(1)		
Fe(1)–Hg(1)–N(1)	92.2(1)	P(2)–Fe(1)–S(1)	89.1(2)
S(2)–Hg(1)–N(1)	89.7(2)	Hg(1)–Fe(1)–C(1)	79.6(2)
Fe(1)–Hg(1)–N(2)	92.5(1)	P(1)–Fe(1)–C(1)	91.0(3)
S(2)–Hg(1)–N(2)	99.2(2)	P(2)–Fe(1)–C(1)	91.9(3)
N(1)–Hg(1)–N(2)	114.0(2)	S(1)–Fe(1)–C(1)	174.5(3)
Hg(1)–Fe(1)–P(1)	82.3(1)	Hg(1)–Fe(1)–C(2)	171.7(2)
Hg(1)–Fe(1)–P(2)	84.3(1)	P(1)–Fe(1)–C(2)	97.5(3)
P(1)–Fe(1)–P(2)	165.6(2)	P(2)–Fe(1)–C(2)	96.5(3)
Hg(1)–Fe(1)–S(1)	95.1(1)	S(1)–Fe(1)–C(2)	93.2(2)
P(1)–Fe(1)–S(1)	86.7(2)	C(1)–Fe(1)–C(2)	92.1(3)

related complexes: $Fe(CO)_3(\mu-Ph_2Ppy)_2Hg(SCN)_2$, 2.648(3) Å [7]; $Fe(CO)_3(\mu-Ph_2Ppy)_2HgI_2$, 2.678(2) Å [8]; $Fe(CO)_3(\mu-PhMePpy)_2Hg(\mu-Cl)_2HgCl_2$, 2.592(4) Å [9]. The measured Fe–P, Fe–C, Hg–N and Hg–S distances of 1 are not greatly different from the corresponding distances of $Fe(CO)_3(\mu-Ph_2Ppy)_2Hg(SCN)_2$.

The binuclear molecule 2 (Fig. 2) is isostructural with 1 and has virtually the same Fe(I)–Hg(I) bond distance at 2.529(1) Å. The Fe–Cl distance, 2.354(2) Å, and the Hg–Cl distance, 2.440(2) Å, are comparable to those of $ClFe(CO)_3(\mu-Pchx_2)Pt(PEt_3)$ (chx = cyclohexyl), 2.376(2) Å [19] and $ClW(CO)_3(bipy)HgCl$, 2.36(2) Å [20] respectively.

3. Experimental

3.1. Synthesis

All reactions were carried out under nitrogen using Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Shimadzu 435 spectrometer as KBr discs. The $^{31}P\{^1H\}$ 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 solvent. trans-$[Fe(CO)_2(CS_2)(Ph_2Ppy-P)_2]$ were prepared similarly by the published procedure [21].

3.1.1. Preparation of (NCS)Fe(CO)₂(μ-Ph₂Ppy)₂Hg(SCN), 1

$Hg(SCN)_2$ (0.16 g, 0.5 mmol) was added to a solution of trans-$[Fe(CO)_2(CS_2)(Ph_2Ppy-P)_2]$ (0.36 g, 0.5 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature for 12 h and filtered. The filtrate was concentrated and diethyl ether was added to give a yellow precipitate. Yellow crystals were obtained from dichloromethane/methanol. Yield: 0.32 g (67.0%). Anal. Found: C, 48.45; H, 3.29, N, 5.56. $C_{38}H_{28}FeHgN_4O_2P_2S_2$ Calc.: C, 47.74; H, 2.96; N, 5.86%. IR (νCO): 1983.0, 1942.0 cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl₃, 200 MHz, 298 K): $\delta = 70.00$ ppm.

3.1.2. Preparation of ClFe(CO)₂(μ-Ph₂Ppy)₂HgCl, 2

The above procedure was repeated starting with $HgCl_2$ (0.14 g, 0.5 mmol), and compound 2 was recrystallized from chloroform/methanol to give a 1:1:1 solvate. Yield: orange crystals 0.37 g (63.6%). Anal. Found: C, 43.43; H, 2.86; N, 2.62. $C_{36}H_{28}Cl_2FeHgN_2O_2P_2 \cdot CHCl_3 \cdot CH_3OH$ Calc.: C, 43.97; H, 3.16; N, 2.70%. IR (νCO): 1989.7, 1939.8 cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl₃, 200 MHz, 298 K): $\delta = 72.02$ ppm, ^2J(P–Fe–^{199}Hg) = 419 Hz.

3.2. X-ray crystallography

Intensity data were collected in the variable ω-scan mode on a four-circle diffractometer (Rigaku AFC7R)

Notes to Table 3:
Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
The site occupancy factor (s.o.f.) = 0.5 for atoms C(38), C(39), O(3) and O(4) of the disordered methanol molecules, and s.o.f. = 0.33 for atoms Cl(3) to Cl(5″) of the three-fold disordered chloroform molecule.

Table 5
Selected bond lengths (Å) and angles (°) in complex **2** · $CHCl_3$ · CH_3OH

Fe(1)–Hg(1)	2.529(1)	P(1)–C(3)	1.843(5)
Fe(1)–Cl(2)	2.354(2)	P(1)–C(8)	1.816(5)
Fe(1)–P(1)	2.257(3)	P(1)–C(14)	1.815(5)
Fe(1)–P(2)	2.267(3)	P(2)–C(20)	1.830(5)
Fe(1)–C(1)	1.797(4)	P(2)–C(25)	1.824(5)
Fe(1)–C(2)	1.747(4)	P(2)–C(31)	1.825(5)
Hg(1)–Cl(1)	2.440(2)	C(1)–O(1)	1.127(5)
Hg(1)–N(1)	2.644(5)	C(2)–O(2)	1.133(6)
Hg(1)–N(2)	2.689(6)		
		Hg(1)–Fe(1)–C(2)	79.9(1)
Hg(1)–Fe(1)–Cl(2)	84.9(1)	Cl(2)–Fe(1)–C(2)	164.7(2)
Hg(1)–Fe(1)–P(1)	88.0(1)	P(1)–Fe(1)–C(2)	92.7(2)
Cl(2)–Fe(1)–P(1)	87.7(1)	P(2)–Fe(1)–C(2)	91.6(2)
Hg(1)–Fe(1)–P(2)	87.9(1)	C(1)–Fe(1)–C(2)	93.4(2)
Cl(2)–Fe(1)–P(2)	86.9(1)	Fe(1)–Hg(1)–Cl(1)	177.9(1)
P(1)–Fe(1)–P(2)	173.4(1)	Fe(1)–Hg(1)–N(1)	91.4(1)
Hg(1)–Fe(1)–C(1)	173.2(2)	Cl(1)–Hg(1)–N(1)	90.6(1)
Cl(2)–Fe(1)–C(1)	101.9(2)	Fe(1)–Hg(1)–N(2)	90.7(1)
P(1)–Fe(1)–C(1)	91.3(2)	Cl(1)–Hg(1)–N(2)	88.2(1)
P(2)–Fe(1)–C(1)	93.4(2)	N(1)–Hg(1)–N(2)	130.5(1)

using Mo Kα radiation (λ = 0.71073 Å, 50 kV, 90 mA) at 294 K. For each compound, determination of the crystal class, orientation matrix, and unit-cell parameters were performed according to established procedures [22]. Unit-cell parameters were calculated from least-squares fitting of 2θ angles for 20–25 reflections. Crystal stability was monitored by recording three check reflections at intervals of 150 data measurements, and no significant variation was detected. The raw data were processed with a learn-profile procedure [23], and empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the the ψ-scan data of selected strong reflections over a range of 2θ angles [24].

The crystal structure of compound **1** was determined by the direct method which yielded the positions of all non-hydrogen atoms. The structure of **2** · $CHCl_3$ · CH_3OH was solved with the Patterson superposition method, and subsequent difference Fourier syntheses were employed to locate the remaining non-hydrogen atoms which did not show up in the initial structure. All the non-hydrogen atoms were refined on *F* data anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement on the *F* data.

All computations were performed on an IBM-compatible 486 PC with the SHELTX-PC program package [25]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incoporated [26].

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3. Selected bond distances and angles are given in Tables 4 and 5 respectively.

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