The new organometallic polydentate ligand
trans-bis(2-(diphenylphosphino) pyrimidine) tricarbonyliron(0) and its
mono-, di- and tridentate coordination modes towards mercury(II)
halide/pseudohalide [1]

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Abstract

A novel organometallic polydentate ligand *trans*-$(CO)_3Fe(Ph_2Ppym)_2$ **1** has been synthesized from the new phosphine ligand Ph_2Ppym (Ph_2Ppym = 2-(diphenylphosphino)pyrimidine) and its structure determined by single crystal X-ray diffraction studies. Four binuclear organometallic Fe–Hg complexes have been prepared from **1** and also fully characterized crystallographically: $\{[(CO)_3Fe(Ph_2Ppym-N,N')_2HgCl_2][(CO)_3Fe(Ph_2Ppym-N)_2HgCl_2]\} \cdot 2CH_2Cl_2 \cdot 0.5MeOH$ (**2**); $[(CO)_3Fe(Ph_2Ppym)_2HgBr_2]$ (**3**); $[(CO)_3Fe(Ph_2Ppym)_2HgI_2]$ (**4**); $[(CO)_3Fe(Ph_2Ppym-N)_2Hg(SCN)_2]$ (**5**). In all these complexes the Fe–Hg distances lying between 2.616(2) and 2.652(2) Å are consistent with the existence of a donor–acceptor metal–metal bond. The crystal structures show that the coordination mode of **1** is greatly influenced by the nature of the anion. In one (**2a**) of the two independent molecules in compound **2**, the Hg(II) atom is coordinated by the Fe(0) atom and nitrogen atoms from both pyrimidyl rings, whereas in the other (**2b**) the Hg(II) atom is coordinated by the Fe(0) atom and only one pyrimidyl nitrogen atom. In compound **5** ligand **1** acts as a bidentate ligand as in **2b**. In compounds **3** and **4** the Hg...N distances of 2.692(7)–2.740(7) Å are significantly longer than the Fe → Hg donor–acceptor bond, and ligand **1** can be considered to act in the monodentate mode. © 1997 Elsevier Science S.A.

Keywords: Iron; Carbonyl; Organoiron complex; Mercury(II) complex; Heterobimetallic complex; Donor–acceptor bonding; 2-(Diphenylphosphino)pyrimidine

1. Introduction

Heterobimetallic complexes have been extensively studied in the past decades owing to their potential use in cooperative activation of carbon oxide substrates by the two metal centres [1–4]. It has long been known that transition metals in low oxidation states have substantial non-bonding electron density resident, and consequently may form a donor bond to another metal atom in a suitable Lewis acid range [5–7].

Recently, the common effects of basic metals and phosphine bridging ligands on the formation of binuclear complexes have been reviewed [8,9]. A variety of homo- and heterobinuclear complexes have been synthesized by employing 2-(diphenylphospino)pyridine, Ph_2Ppy, as a bridging ligand through oxidative addition [10] or condensation [11]. The compound *trans*-$(CO)_3Fe(Ph_2Ppy)_2$, with one basic iron centre and two pyridyl nitrogen atoms, is structurally analogous to terpyridine which acts as a mono-, bi- or tridentate ligand [12]. Functioning as a neutral organometallic tridentate ligand, it has been used as a precursor in the convenient synthesis of a series of homo- and heterobinuclear complexes, each containing a donor–acceptor metal–metal bond [3,13].

In a previous paper, a series of heterobimetallic complexes with the tridentate organometallic ligand *trans*-$(CO)_3Fe(Ph_2Ppy)$ was synthesized and their cat-

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alytic activity for carbonylation of ethanol to form ethyl propionate was studied. It has been found that in this catalytic reaction such systems involve a synergistic interaction [3]. However, the coordination behaviour of trans-$(CO)_3Fe(Ph_2Ppy)_2$ towards different metals, as well as the relationship between the catalytic activity of its binuclear complexes and their structures, are still unclear, although a few crystal structures of this series of complexes have been determined [3,13].

In the present paper we report the preparation and characterization of a new phosphine bridging ligand, 2-(diphenylphosphino)pyrimidine (Ph_2Ppym), and its iron tricarbonyl derivative trans-$(CO)_3Fe(Ph_2Ppym)_2$ 1. Here we adopt pyrimidine, a weaker base than pyridine, as a bridging ligand in order to study the influence of the basicity of the nitrogen atom on both the structures of the binuclear compounds and their catalytic activity. Four heterobinuclear complexes of HgX_2 (X = Cl, Br, I and SCN) with this new neutral organometallic tridentate ligand, $(CO)_3Fe(Ph_2Ppym)_2HgX_2$ (2–5); have been prepared and their structures determined by single crystal X-ray analysis. In all these complexes the Fe–Hg distance lies in the range 2.616(2)–2.652(2) Å, which indicates the presence of a donor–acceptor metal–metal bond. The coordination behaviour of lig-

and 1 towards mercury(II) changes when different halide/pseudohalide anions are attached to the mercury(II) atom. The interaction between the mercury(II) and pyrimidyl nitrogen atoms decreases significantly in the order Cl > SCN > Br > I for compounds 2, 5, 3 and 4; in the case of isomorphous 3 and 4, the Hg...N distance of 2.692(7)–2.756(7) Å indicates that only weak interactions exist between the mercury(II) and nitrogen atoms. However, the Fe–Hg bond lengths in 2–5 vary over a narrow range of 2.616(2)–2.652(2) Å, showing that the Fe–Hg bond is mainly formed by direct electron donation from Fe(0) to Hg(II).

2. Experimental section

All reactions were performed under a nitrogen atmosphere using standard Schlenck techniques. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled before use. Other solvents and chemicals were used as purchased without further purification. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer. The proton NMR spectrum was measured on a Bruker Cryospec WM 250 (250 MHz).

Table 1
Crystallographic data for compounds 1–5 (L = Ph_2Ppym)

	trans-Fe$(CO)_3L_2$	[FeHg$(CO)_3L_2Cl_2]_2$ $\cdot 2CH_2Cl_2 \cdot 0.5$ MeOH	[FeHg$(CO)_3L_2Br_2$]	[FeHg$(CO)_3L_2I_2$]	[FeHg$(CO)_3L_2(SCN)_2$]
	1	2	3	4	5
M	668.4	2065.6	1028.8	1122.8	985.1
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Crystal size (mm³)	0.15 × 0.40 × 0.40	0.15 × 0.40 × 0.50	0.25 × 0.30 × 0.30	0.10 × 0.20 × 0.40	0.30 × 0.30 × 0.50
a (Å)	9.424(2)	12.428(1)	13.767(1)	13.856(1)	16.355(3)
b (Å)	11.270(2)	13.420(1)	14.123(1)	14.114(1)	13.631(3)
c (Å)	16.970(3)	25.607(1)	19.019(1)	19.559(1)	17.777(4)
α (deg)	101.29(3)	87.14(1)	90	90	90
β (deg)	93.39(3)	80.60(1)	102.75(1)	102.69(1)	109.54(3)
γ (deg)	112.94(3)	84.35(1)	90	90	90
U (Å³)	1609(1)	4191(2)	3607(1)	3731(1)	3735(2)
Z	2	2	4	4	4
D_c (g cm⁻³)	1.379	1.637	1.895	1.998	1.752
F(000)	688	2018	1976	2120	1928
μ (cm⁻¹)	6.10	43.76	69.99	62.78	47.37
Transmission coefficients	0.61–1.00	*	*	*	*
$2\theta_{max}$ (deg)	55.0	55.2	55.2	55.2	55.2
No. of data collected	7372	14410	6909	7400	7384
No. of data used, n	3440[$F > 4\sigma(F)$]	9320[$F > 4\sigma(F)$]	2968[$F > 6\sigma(F)$]	4519[$F > 6\sigma(F)$]	5803[$F > 4\sigma(F)$]
No. of variables, p	407	941	434	434	467
R	0.071	0.051	0.069	0.069	0.044
R'	0.083	0.063	0.085	0.094	0.053
S	0.84	1.16	1.64	1.35	1.11

$R = \Sigma\Delta/\Sigma|F_0|$, $R' = [\Sigma w\Delta^2/\Sigma|F_0|^2]^{1/2}$ and $S = [w\Delta^2/(n-p)]^{1/2}$ where $w = [\sigma^2(F_0) + K|F_0|^2]^{-1}$, $\Delta = ||F_0| - |F_c||$; $10^5 K = 10, 50, 50, 10$ and 50 for complexes 1, 2, 3, 4 and 5 respectively. Extinction parameter $\chi = 0.00096, 0.00013, 0.00017, 0.00023$ and 0.00017 for complexes 1, 2, 3, 4 and 5 respectively where $F_{corr} = F_c(1 + 0.002 \chi F_c^2/\sin 2\theta)^{-1/4}$.
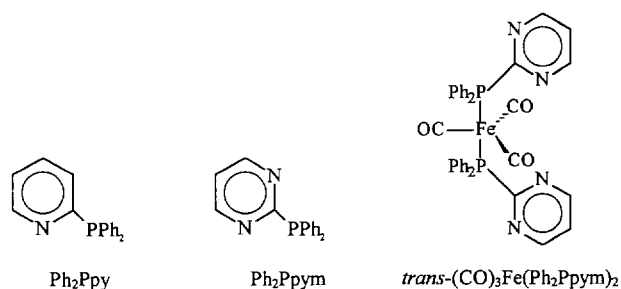* Absorption corrections applied by correlation of symmetry-equivalent reflections.

Ph2Ppy   Ph2Ppym   trans-(CO)3Fe(Ph2Ppym)2

Table 2

Atomic coordinates ($\times 10^5$ for Fe, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\mathring{A}^2 \times 10^4$ for Fe, $\mathring{A}^2 \times 10^3$ for other atoms) for complex **1**

Atom	x	y	z	U_{eq}
Fe(1)	23279(11)	751(9)	25662(5)	598(4)
C(1)	1364(9)	−836(7)	3241(4)	75(3)
O(1)	730(7)	−1474(6)	3680(4)	103(3)
C(2)	1476(10)	834(7)	2002(5)	93(4)
O(2)	920(9)	1386(6)	1658(5)	144(4)
C(3)	4216(9)	166(6)	2497(3)	64(3)
O(3)	5472(7)	241(6)	2461(3)	91(3)
P(1)	1277(2)	−1709(2)	1559(1)	61(1)
N(1)	2799(10)	−3094(7)	2060(5)	114(4)
C(4)	2925(15)	−4206(12)	2183(7)	124(7)
C(5)	1750(19)	−5349(11)	2037(8)	127(7)
C(6)	394(19)	−5408(13)	1735(13)	197(11)
N(2)	172(12)	−4311(9)	1614(8)	155(6)
C(7)	1409(9)	−3207(7)	1755(4)	70(3)
C(8)	−1726(9)	−1931(8)	1722(5)	86(4)
C(9)	−3281(11)	−2350(11)	1474(8)	114(6)
C(10)	−3923(13)	−3117(14)	702(10)	154(8)
C(11)	−3025(13)	−3477(17)	207(8)	183(9)
C(12)	−1496(11)	−3078(12)	454(6)	139(6)
C(13)	−804(8)	−2264(7)	1219(4)	78(3)
C(14)	2820(19)	−2291(16)	310(6)	167(11)
C(15)	3410(26)	−2180(26)	−404(9)	251(21)
C(16)	3300(19)	−1376(22)	−789(10)	177(12)
C(17)	2469(23)	−677(17)	−541(10)	171(11)
C(18)	1878(17)	−748(12)	210(7)	146(8)
C(19)	2089(8)	−1613(7)	610(4)	73(3)
P(2)	3218(2)	1934(2)	3521(1)	62(1)
N(3)	5069(10)	3381(8)	2539(5)	107(4)
C(20)	6289(11)	4507(9)	2407(6)	103(5)
C(21)	7213(11)	5520(9)	3042(7)	105(5)
C(22)	6976(12)	5467(9)	3818(6)	100(5)
N(4)	5799(9)	4391(8)	3982(5)	108(4)
C(23)	4842(8)	3350(7)	3337(4)	65(3)
C(24)	2109(10)	3899(8)	3918(5)	86(4)
C(25)	960(13)	4343(10)	4046(7)	115(6)
C(26)	−499(15)	3515(14)	4022(8)	130(7)
C(27)	−802(14)	2233(13)	3875(12)	197(10)
C(28)	288(13)	1756(10)	3734(11)	171(8)
C(29)	1774(10)	2609(8)	3758(4)	79(4)
C(30)	5398(10)	1883(8)	4639(5)	88(4)
C(31)	5918(18)	1741(11)	5372(9)	144(7)
C(32)	4946(30)	1501(14)	5939(9)	175(13)
C(33)	3525(26)	1384(14)	5767(8)	161(11)
C(34)	2996(13)	1540(9)	5049(5)	101(5)
C(35)	3930(10)	1790(7)	4515(4)	78(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^5$ for Hg and Fe, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\mathring{A}^2 \times 10^4$ for Hg and Fe, $\mathring{A}^2 \times 10^3$ for other atoms) for complex **2**

Atom	x	y	z	U_{eq}
Molecule 2a				
Hg(1)	35874(4)	30218(3)	7581(2)	455(2)
Fe(1)	23329(13)	15867(10)	6417(5)	368(3)
Cl(1A)	5619(3)	3094(2)	472(1)	72(1)
Cl(2A)	3065(3)	4675(2)	1139(2)	83(1)
P(1A)	2464(2)	923(2)	1459(1)	41(1)
P(2A)	2062(2)	2082(2)	−186(1)	40(1)
C(1A)	1402(6)	2615(5)	902(3)	42(1)
O(1A)	756(5)	3246(5)	1067(3)	63(1)
C(2A)	1454(6)	619(6)	597(3)	52(1)
O(2A)	882(6)	12(5)	570(3)	73(1)
C(3A)	3723(7)	1149(5)	406(4)	50(1)
O(3A)	4650(6)	876(5)	249(3)	85(1)
C(4A)	3662(6)	1163(5)	1758(3)	49(1)
N(1A)	4145(6)	1963(5)	1599(3)	53(1)
C(5A)	4982(7)	2183(6)	1849(4)	68(1)
C(6A)	5284(6)	1566(6)	2262(4)	59(1)
C(7A)	4736(7)	734(6)	2396(4)	61(1)
N(2A)	3899(6)	523(5)	2154(3)	57(1)
N(3A)	3436(7)	3563(6)	−250(4)	110(1)
C(8A)	2962(7)	2995(5)	−538(3)	52(1)
N(4A)	3101(7)	3062(6)	−1053(4)	112(1)
C(9A)	3862(8)	3686(7)	−1272(5)	204(1)
C(10A)	4254(7)	4320(6)	−1038(4)	77(1)
C(11A)	4141(7)	4192(7)	−515(5)	143(1)
C(12A)	1511(7)	2123(6)	2301(4)	68(1)
C(13A)	635(7)	2571(7)	2628(4)	89(1)
C(14A)	−374(7)	2280(7)	2644(4)	123(1)
C(15A)	−572(7)	1542(7)	2311(4)	103(1)
C(16A)	272(7)	1122(7)	1982(4)	77(1)
C(17A)	1344(6)	1414(5)	1955(3)	42(1)
C(18A)	3153(7)	−980(6)	1112(4)	68(1)
C(19A)	3206(7)	−2021(6)	1114(4)	81(1)
C(20A)	2631(7)	−2517(6)	1521(5)	90(1)
C(21A)	1997(7)	−1996(6)	1934(5)	95(1)
C(22A)	1941(7)	−950(6)	1927(4)	60(1)
C(23A)	2501(6)	−434(5)	1508(3)	48(1)
C(24A)	−179(7)	2088(6)	−118(4)	68(1)
C(25A)	−1258(7)	2486(6)	−126(5)	85(1)
C(26A)	−1425(7)	3514(7)	−256(4)	81(1)
C(27A)	−588(7)	4075(6)	−358(4)	73(1)
C(28A)	481(7)	3677(6)	−332(3)	56(1)
C(29A)	700(6)	2670(5)	−221(3)	45(1)
C(30A)	2835(7)	175(6)	−590(4)	63(1)
C(31A)	2917(7)	−580(6)	−954(4)	80(1)
C(32A)	2427(7)	−435(6)	−1376(4)	72(1)
C(33A)	1819(7)	473(6)	−1468(4)	78(1)
C(34A)	1739(7)	1228(6)	−1109(4)	59(1)
C(35A)	2199(6)	1075(6)	−661(3)	48(1)
Molecule 2b				
Hg(2)	67241(4)	88644(3)	35036(2)	492(2)
Fe(2)	81518(13)	73609(10)	36653(5)	405(4)
Cl(1B)	7096(3)	10507(3)	3070(2)	93(1)
Cl(2B)	4699(3)	9023(3)	3703(1)	78(1)
P(1B)	7596(2)	6402(2)	3075(1)	43(1)
P(2B)	8790(2)	8279(2)	4249(1)	43(1)
C(1B)	8856(6)	8069(6)	3126(3)	52(1)
O(1B)	9341(6)	8475(5)	2771(3)	72(1)
C(2B)	9213(7)	6387(6)	3759(4)	59(1)

Table 3 (continued)

Atom	x	y	z	U_{eq}
O(2B)	9904(6)	5772(5)	3823(3)	86(1)
C(3B)	6960(6)	7127(6)	4127(4)	53(1)
O(3B)	6227(6)	6995(5)	4420(3)	77(1)
C(4B)	6472(6)	6983(5)	2761(3)	41(1)
N(1B)	5427(7)	6700(6)	2907(4)	82(1)
C(5B)	4596(7)	7216(6)	2682(4)	76(1)
C(6B)	4775(7)	7980(6)	2329(4)	74(1)
C(7B)	5831(7)	8294(6)	2185(4)	70(1)
N(2B)	6691(7)	7794(6)	2411(4)	83(1)
N(3B)	6933(6)	9568(5)	4373(3)	63(1)
C(8B)	7875(6)	9383(5)	4545(3)	48(1)
N(4B)	8207(6)	9838(6)	4924(4)	85(1)
C(9B)	7548(7)	10599(7)	5140(4)	85(1)
C(10B)	6571(7)	10873(6)	4969(4)	85(1)
C(11B)	6271(7)	10333(7)	4589(4)	89(1)
C(12B)	7288(6)	4782(6)	3784(4)	79(1)
C(13B)	7005(7)	3754(7)	3916(5)	106(1)
C(14B)	6725(7)	3187(6)	3571(6)	123(1)
C(15B)	6611(7)	3586(7)	3083(5)	100(1)
C(16B)	6864(7)	4579(6)	2918(5)	88(1)
C(17B)	7183(7)	5160(6)	3291(4)	61(1)
C(18B)	8861(8)	6753(7)	2099(5)	46(1)
C(19B)	9866(8)	6567(8)	1681(6)	62(1)
C(20B)	10403(7)	5548(7)	1724(4)	84(1)
C(21B)	10127(8)	4980(8)	2133(6)	63(1)
C(22B)	9308(8)	5188(7)	2557(5)	42(1)
C(23B)	8695(6)	6093(6)	2524(3)	51(1)
C(18C)	8392(8)	5976(8)	2070(7)	84(1)
C(19C)	9327(8)	5678(8)	1644(7)	123(1)
C(21C)	10568(8)	5533(8)	2259(7)	103(1)
C(22C)	9744(8)	5830(8)	2650(6)	61(1)
C(24B)	9994(7)	9829(6)	3720(4)	77(1)
C(25B)	10912(7)	10176(7)	3441(4)	86(1)
C(26B)	11874(7)	9618(7)	3362(4)	86(1)
Molecule 2b				
C(27B)	1190(7)	8622(7)	3545(4)	86(1)
C(28B)	11021(7)	8240(6)	3833(4)	62(1)
C(29B)	10010(6)	8834(6)	3928(3)	51(1)
C(30B)	9859(7)	8048(6)	5122(4)	74(1)
C(31B)	10176(7)	7560(7)	5581(4)	89(1)
C(32B)	9875(7)	6681(7)	5735(4)	87(1)
C(33B)	9129(7)	6215(6)	5472(4)	83(1)
C(34B)	8810(7)	6701(6)	5018(4)	69(1)
C(35B)	9211(7)	7613(6)	4831(3)	53(1)
CH_2Cl_2 *solvate molecules*				
C(36)	3462(8)	1485(6)	3915(3)	202(1)
Cl(3A)	3894(4)	2063(4)	4412(2)	139(1)
Cl(3B)	3045(5)	2258(5)	3433(2)	206(1)
C(37)	6295(7)	3856(6)	5764(4)	133(1)
Cl(4A)	7538(6)	3636(6)	5359(3)	146(1)
Cl(4B)	5853(7)	5096(6)	5643(5)	230(1)
C(38)	2727(7)	4590(8)	2563(5)	178(1)
Cl(5A)	4122(6)	4507(6)	2513(4)	180(1)
Cl(5B)	2214(7)	5401(7)	3069(5)	219(1)
MeOH solvate molecule				
C(39)	7923(7)	3538(7)	1317(5)	87(1)
O(4)	6871(7)	3388(7)	1476(6)	111(1)

Table 4

Atomic coordinates ($\times 10^5$ for Hg, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\mathring{A}^2 \times 10^4$ for Hg, $\mathring{A}^2 \times 10^3$ for other atoms) for complex **3**

Atom	x	y	z	U_{eq}
Hg(1)	46469(7)	23111(7)	12822(4)	505(1)
Br(1)	2931(2)	2138(2)	412(1)	86(1)
Br(2)	6024(2)	2440(2)	529(1)	76(1)
Fe(1)	5066(2)	2363(2)	2701(1)	39(1)
C(1)	5296(9)	2381(9)	3650(8)	49(1)
O(1)	5438(8)	2352(8)	4270(6)	73(1)
C(2)	6082(9)	3002(9)	2463(8)	54(1)
O(2)	6715(7)	3425(8)	2334(7)	72(1)
C(3)	3890(9)	1694(9)	2443(8)	53(1)
O(3)	3200(8)	1287(8)	2354(7)	78(1)
P(1)	5946(3)	1004(4)	2761(3)	40(1)
N(1)	4965(8)	419(8)	1449(7)	50(1)
C(4)	4835(10)	−183(9)	855(8)	73(1)
C(5)	5517(9)	−882(9)	835(8)	76(1)
C(6)	6306(10)	−966(10)	1372(8)	88(1)
N(2)	6403(8)	−429(8)	1921(7)	61(1)
C(7)	5754(9)	249(9)	1935(8)	50(1)
C(8)	4944(9)	112(9)	3728(8)	51(1)
C(9)	4780(9)	−598(9)	4173(8)	71(1)
C(10)	5381(10)	−1286(9)	4372(7)	75(1)
C(11)	6256(9)	−1342(9)	4084(8)	62(1)
C(12)	6458(9)	−618(9)	3558(8)	62(1)
C(13)	5750(9)	131(9)	3384(7)	43(1)
C(14)	7733(10)	1315(10)	3693(9)	87(1)
C(15)	8779(9)	1467(9)	3870(9)	78(1)
C(16)	9324(10)	1502(9)	3319(9)	104(1)
C(17)	8853(9)	1448(9)	2616(9)	64(1)
C(18)	7825(9)	1271(9)	2426(8)	58(1)
C(19)	7294(9)	1205(9)	2983(7)	41(1)
P(2)	4216(4)	3728(4)	2704(3)	41(1)
N(3)	4338(9)	4234(8)	1345(7)	64(1)
C(20)	3056(10)	5620(10)	1206(9)	119(1)
C(21)	3436(10)	5461(10)	651(8)	88(1)
C(22)	4099(10)	4719(10)	736(8)	113(1)
N(4)	3246(9)	5109(9)	1839(8)	74(1)
C(23)	3892(9)	4449(9)	1834(8)	59(1)
C(24)	2924(10)	3500(10)	3611(8)	98(1)
C(25)	2000(9)	3332(10)	3789(9)	117(1)
C(26)	1231(9)	3127(10)	3209(9)	106(1)
C(27)	1226(10)	3173(10)	2464(10)	134(1)
C(28)	2180(9)	3341(9)	2356(8)	66(1)
C(29)	2970(9)	3544(9)	2888(8)	47(1)
C(30)	4179(10)	5392(9)	3507(8)	75(1)
C(31)	4590(10)	6073(10)	3979(9)	123(1)
C(32)	5670(10)	5992(9)	4319(8)	86(1)
C(33)	6115(10)	5229(10)	4176(9)	106(1)
C(34)	5775(9)	4596(9)	3701(7)	56(1)
C(35)	4785(9)	4631(8)	3353(7)	39(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Note to Table 3:
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Atoms C(18B)–C(23B) and C(18C)–C(23C) represent a two-fold disordered phenyl group and each has a site occupancy of 0.5. Atoms C(37)–Cl(4B) and C(38)–Cl(5B) represent a two-fold disordered CH_2Cl_2 molecule and each has a site occupancy of 0.5. Atoms C(39) and O(4) represent a two-fold disordered MeOH molecule and each has a site occupancy of 0.5.

2.1. Synthesis of 2-(diphenylphosphino)pyrimidine (Ph₂Ppym)

Triphenylphosphine (26.3 g, 0.10 mol) was dissolved in 80 cm³ of anhydrous THF, to which Li (1.8 g, 0.26 mol) was added. After stirring overnight, the unreacted Li was filtered off, and 9 cm³ of 2,2-dimethylchloro-

Table 5
Atomic coordinates ($\times 10^5$ for Hg, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\text{Å}^2 \times 10^4$ for Hg, $\text{Å}^2 \times 10^3$ for other atoms) for complex **4**

Atom	x	y	z	U_{eq}
Hg(1)	46328(5)	22844(5)	13033(3)	426(2)
I(1)	2792(1)	2101(1)	428(1)	73(1)
I(2)	6100(1)	2411(1)	534(1)	65(1)
Fe(1)	5050(2)	2350(2)	2699(1)	32(1)
C(1)	5268(7)	2379(7)	3634(6)	41(1)
O(1)	5404(7)	2365(7)	4235(5)	67(1)
C(2)	6066(7)	2977(6)	2466(6)	41(1)
O(2)	6717(7)	3403(6)	2342(5)	61(1)
C(3)	3889(7)	1699(7)	2451(6)	36(1)
O(3)	3160(7)	1310(6)	2345(6)	77(1)
P(1)	5915(3)	982(3)	2775(2)	35(1)
N(1)	4989(7)	413(7)	1464(6)	50(1)
C(4)	4929(7)	−186(7)	907(7)	57(1)
C(5)	5582(8)	−867(7)	882(7)	60(1)
C(6)	6346(8)	−979(8)	1463(7)	72(1)
N(2)	6430(7)	−452(7)	1992(7)	77(1)
C(7)	5782(7)	222(7)	1967(6)	47(1)
C(8)	4817(7)	132(7)	3703(6)	49(1)
C(9)	4679(7)	−563(7)	4118(7)	72(1)
C(10)	5397(8)	−1271(7)	4358(7)	73(1)
C(11)	6100(8)	−1342(7)	4079(7)	71(1)
C(12)	6348(8)	−657(7)	3569(7)	69(1)
C(13)	5658(7)	97(7)	3392(6)	37(1)
C(14)	7649(8)	1286(7)	3688(7)	69(1)
C(15)	8725(7)	1437(8)	3860(7)	71(1)
C(16)	9213(8)	1501(7)	3377(7)	74(1)
C(17)	8821(8)	1461(7)	2654(7)	74(1)
C(18)	7781(7)	1270(7)	2489(7)	58(1)
C(19)	7264(7)	1168(7)	2989(6)	43(1)
P(2)	4229(3)	3734(3)	2699(2)	35(1)
N(3)	4377(7)	4199(7)	1372(6)	61(1)
C(20)	2985(8)	5638(8)	1257(7)	119(1)
C(21)	3427(8)	5397(7)	680(7)	71(1)
C(22)	4102(8)	4700(7)	783(7)	136(1)
N(4)	3244(7)	5122(7)	1841(7)	72(1)
C(23)	3911(7)	4445(7)	1869(7)	49(1)
C(24)	2987(7)	3538(7)	3606(7)	57(1)
C(25)	1977(8)	3372(8)	3730(7)	94(1)
C(26)	1175(7)	3184(8)	3157(7)	77(1)
C(27)	1269(8)	3196(8)	2537(8)	97(1)
C(28)	2208(7)	3350(7)	2340(7)	64(1)
C(29)	3008(7)	3570(7)	2902(6)	42(1)
C(30)	4264(7)	5423(7)	3446(7)	60(1)
C(31)	4748(8)	6072(7)	3974(7)	93(1)
C(32)	5727(8)	6014(7)	4300(7)	71(1)
C(33)	6199(8)	5259(8)	4135(7)	91(1)
C(34)	5823(7)	4564(8)	3652(7)	63(1)
C(35)	4818(7)	4643(7)	3328(6)	46(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6
Atomic coordinates ($\times 10^5$ for Hg and Fe, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\text{Å}^2 \times 10^4$ for Hg and Fe, $\text{Å}^2 \times 10^3$ for other atoms) for complex **5**

Atom	x	y	z	U_{eq}
Hg(1)	54003(2)	66838(2)	25388(1)	418(1)
S(1)	3781(1)	6314(2)	2014(2)	80(1)
C(4)	3750(5)	5134(8)	1961(6)	72(4)
N(5)	3703(6)	4284(8)	1923(8)	132(6)
S(2)	5848(3)	7390(4)	1423(3)	67(1)
C(5)	5301(11)	6844(13)	679(11)	49(4)
N(6)	5035(12)	6270(13)	189(10)	78(4)
S(2')	5511(3)	7730(3)	1362(3)	55(1)
C(5')	4977(16)	7043(17)	644(15)	77(6)
N(6')	4491(18)	6712(19)	89(17)	140(9)
Fe(1)	64395(5)	66638(7)	40457(5)	319(3)
C(1)	6991(4)	7302(5)	3470(4)	45(3)
O(1)	7378(3)	7725(4)	3148(3)	65(2)
C(2)	5488(4)	5987(5)	4053(4)	39(2)
O(2)	4920(3)	5519(4)	4068(3)	57(2)
C(3)	7179(5)	6672(5)	5039(4)	46(3)
O(3)	7661(4)	6691(4)	5681(3)	77(3)
P(1)	7053(1)	5232(1)	3885(1)	34(1)
N(1)	5950(4)	4912(4)	2370(3)	52(2)
C(6)	5577(5)	4355(7)	1720(5)	60(3)
C(7)	5664(5)	3361(6)	1757(5)	58(3)
C(8)	6137(5)	2961(6)	2464(5)	58(4)
N(2)	6534(4)	3487(4)	3124(4)	47(2)
C(9)	6428(4)	4454(5)	3033(4)	38(2)
C(10)	6892(5)	4439(6)	5288(4)	52(3)
C(11)	7105(6)	3786(7)	5927(5)	66(4)
C(12)	7752(5)	3093(6)	6014(5)	64(4)
C(13)	8194(5)	3061(6)	5476(5)	57(3)
C(14)	7985(5)	3702(5)	4836(5)	49(3)
C(15)	7327(4)	4397(5)	4741(4)	38(2)
C(16)	8780(4)	5767(6)	4288(5)	56(3)
C(17)	9581(5)	5866(6)	4193(6)	63(4)
C(18)	9684(5)	5550(6)	3493(6)	64(4)
C(19)	9006(5)	5156(7)	2902(5)	67(4)
C(20)	8198(5)	5058(6)	3000(4)	53(3)
C(21)	8074(4)	5362(5)	3691(4)	39(2)
P(2)	5907(1)	8080(1)	4378(1)	34(1)
N(3)	4737(4)	8525(5)	2958(4)	59(3)
C(22)	3949(6)	8790(7)	2461(5)	76(4)
C(23)	3261(5)	8941(7)	2720(6)	75(4)
C(24)	3418(5)	8860(7)	3526(6)	69(4)
N(4)	4210(4)	8610(5)	4049(4)	58(3)
C(25)	4812(4)	8436(5)	3721(4)	40(2)
C(26)	6133(5)	10095(6)	4264(5)	56(3)
C(27)	6608(7)	10939(7)	4263(6)	75(4)
C(28)	7479(7)	10883(7)	4392(6)	82(5)
C(29)	7896(6)	9991(7)	4558(6)	74(4)
C(30)	7433(5)	9145(6)	4575(5)	58(3)
C(31)	6537(4)	9182(5)	4400(4)	40(2)
C(32)	6312(5)	8559(6)	5985(4)	58(3)
C(33)	6277(7)	8431(7)	6750(5)	77(4)
C(34)	5747(6)	7753(8)	6888(5)	73(4)
C(35)	5249(7)	7168(8)	6276(5)	79(4)
C(36)	5270(5)	7311(7)	5512(5)	66(4)
C(37)	5814(4)	7999(5)	5371(4)	43(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
Atoms S(2)–N(6) and S(2')–N(6') represent a two-fold disordered SCN⁻ group and each has a site occupancy of 0.5.

ethane was added to decompose the phenyllithium formed. A solution of 2-chloropyrimidine (11.5 g, 0.10 mol) in 50 cm^3 of THF was added dropwise to the mixture at −5°C with stirring. After the mixture had been stirred continuously at 45°C for 4 h, the solvent was removed under reduced pressure and the residue poured into distilled water. The solid product was recrystallized from CH$_2$Cl$_2$/MeOH twice. The colourless crystalline solid formed was collected and dried in air (18.5 g, 70%), m.p. 121–123°C. ^{1}H NMR (CDCl$_3$, TMS) δ 8.69 (2H, d, $J = 4.7$), 7.55–7.34 (10H, m), 7.12 (1H, dt, $J = 4.7$, 1.1).

2.2. Synthesis of trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ 1

Sodium hydroxide (1.5 g, 37.5 mmol) was ground and dissolved in *n*-butanol (80 cm^3), to which Fe(CO)$_5$ (2.1 cm^3, 16 mmol) was added. After the mixture was stirred for 30 min at ambient temperature, Ph$_2$Ppym (7.5 g, 28.3 mmol) was added. The mixture was refluxed for 4 h, then cooled to room temperature and filtered. The product obtained was dissolved in CH$_2$Cl$_2$ and filtered to remove the insoluble solid. Methanol was added to the filtrate and the solvent was removed under reduced pressure to give an orange crystalline solid which was collected. Recrystallization from CH$_2$Cl$_2$/ MeOH afforded the orange complex 1 (8.2 g, 86%).

2.3. Synthesis of [(CO)$_3$Fe(Ph$_2$Ppym-N,N')$_2$HgCl$_2$]-[(CO)$_3$Fe(Ph$_2$Ppym-N)$_2$HgCl$_2$] · 2CH$_2$Cl$_2$ · 0.5 MeOH 2

trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ (0.334 g, 0.5 mmol) and HgCl$_2$ (0.14 g, 0.5 mmol) were dissolved in 10 cm^3 of CH$_2$Cl$_2$. After stirring for 2 h at ambient temperature, the solvent was removed under reduced pressure. The solid obtained was dissolved in CH$_2$Cl$_2$ (ca. 5 cm^3) and filtered. MeOH was allowed to diffuse into the filtrate, and pale yellow block-like crystals of complex 2 were

formed after one day at ambient temperature (0.20 g, 42%).

2.4. Synthesis of [(CO)$_3$Fe(Ph$_2$Ppym)$_2$HgBr$_2$] 3

trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ (0.334 g, 0.5 mmol) and HgBr$_2$ (0.18 g, 0.5 mmol) were dissolved in CH$_2$Cl$_2$ (15 cm^3) and stirred for 2 h at ambient temperature. Diffusion of MeOH into the mixture yielded pale yellow prismatic crystals of 3 (27 g, 53%).

2.5. Synthesis of [(CO)$_3$Fe(Ph$_2$Ppym)$_2$HgI$_2$] 4

trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ (0.334 g, 0.5 mmol) and HgI$_2$ (0.23 g, 0.5 mmol) were dissolved in CH$_2$Cl$_2$ (25 cm^3) and stirred for 2 h at ambient temerature. Diffusion of MeOH into the mixture gave yellow prismatic crystals of 4 (0.31 g, 55%).

2.6. Synthesis of [(CO)$_3$Fe(Ph$_2$Ppym-N)$_2$Hg(SCN)$_2$] 5

trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ (0.334 g, 0.5 mmol) and Hg(SCN)$_2$ (0.16 g, 0.5 mmol) were dissolved in CH$_2$Cl$_2$ (10 cm^3). After stirring for 2 h at ambient temperature, the solvent was removed under reduced pressure. The solid obtained was dissolved in CH$_2$Cl$_2$ (ca. 5 cm^3) and filtered. Diffusion of MeOH into the filtrate yielded pale yellow block-like crystals of complex 5 (0.29 g, 60%).

2.7. Structure determination of complexes 1–5

Information concerning X-ray data collection and structure refinement is summarized in Table 1. The intensities of 1 were collected at 290 K in the ω-scan mode [14] on a Rigaku AFC7 four-circle diffractometer using Mo K α radiation ($\lambda = 0.71073$ 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 reflec-

Table 7
Selected bond lengths (Å) and angles (deg)

Fe(1)–C(1)	1.746(8)	Fe(1)–C(2)	1.75(1)
Fe(1)–C(3)	1.754(9)	Fe(1)–P(1)	2.202(2)
Fe(1)–P(2)	2.204(2)	C(1)–O(1)	1.16(1)
C(2)–O(2)	1.17(1)	C(3)–O(3)	1.16(1)
P(1)–C(7)	1.831(9)	P(2)–C(23)	1.826(6)
C(1)–Fe(1)–C(2)	122.6(4)	C(1)–Fe(1)–C(3)	114.7(4)
C(2)–Fe(1)–C(3)	122.6(4)	C(1)–Fe(1)–P(1)	90.3(2)
C(2)–Fe(1)–P(1)	87.3(2)	C(3)–Fe(1)–P(1)	92.6(2)
C(1)–Fe(1)–P(2)	91.4(2)	C(2)–Fe(1)–P(2)	87.2(2)
C(3)–Fe(1)–P(2)	91.8(2)	P(1)–Fe(1)–P(2)	174.2(1)
Fe(1)–C(1)–O(1)	178.0(8)	Fe(1)–C(2)–O(2)	176.8(7)
Fe(1)–C(3)–O(3)	179.0(6)	P(1)–C(7)–N(1)	117.1(5)
P(1)–C(7)–N(2)	120.2(8)	P(2)–C(23)–N(3)	118.3(4)
P(2)–C(23)–N(4)	120.6(6)		

tions. 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-scan was applied to the raw intensities in data processing.

The intensity data of complexes 2–5 were collected at 290 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å, 50 kV, 90 mA) ($2\theta_{max} = 55°$, 36 6° oscillation frames in the range 0–180°, exposure 12 min. per frame for 2 and 3; 33 5° oscillation frames in the range 0–160°, exposure 15 min. per frame for 4 36 5° oscillation frames in the range 0–180°, exposure 10 min. per frame for 5) [15].

The structures of all five complexes were solved by direct methods. All non-hydrogen atoms other than the solvated MeOH molecule and the disordered carbon atoms of one phenyl group in 1, and one of the SCN⁻ group which exhibits two-fold disorder in 5, were refined anisotropically by full-matrix least-squares. 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. In one independent molecule of complex 2 (2b), one of the phenyl groups exhibits two-fold orientational disorder, and an occu-

Table 8
Selected bond lengths (Å) and angles (deg) for complex 2

Molecule 2a			
Hg(1)–Fe(1)	2.651(2)	Hg(1)–Cl(1A)	2.522(3)
Hg(1)–Cl(2A)	2.454(3)	Hg(1)–C(3A)	2.692(8)
Hg(1)–N(1A)	2.669(8)	Hg(1)–N(3A)	2.677(9)
Fe(1)–P(1A)	2.257(3)	Fe(1)–P(2A)	2.257(3)
Fe(1)–C(1A)	1.792(7)	Fe(1)–C(2A)	1.797(9)
Fe(1)–C(3A)	1.785(8)	C(1A)–O(1A)	1.154(9)
C(2A)–O(2A)	1.144(11)	C(3A)–O(3A)	1.185(10)
P(1A)–C(4A)	1.842(9)	P(2A)–C(8A)	1.842(8)
Fe(1)–Hg(1)–Cl(1A)	129.7(1)	Fe(1)–Hg(1)–Cl(2A)	129.2(1)
Cl(1A)–Hg(1)–Cl(2A)	101.1(1)	Fe(1)–Hg(1)–N(1A)	87.3(2)
Cl(1A)–Hg(1)–N(1A)	85.2(2)	Cl(2A)–Hg(1)–N(1A)	100.7(2)
C(3A)–Hg(1)–N(1A)	79.5(2)	Fe(1)–Hg(1)–N(3A)	86.0(2)
Cl(1A)–Hg(1)–N(3A)	85.1(2)	Cl(2A)–Hg(1)–N(3A)	97.7(2)
C(3A)–Hg(1)–N(3A)	83.8(3)	N(1A)–Hg(1)–N(3A)	160.6(2)
Hg(1)–Fe(1)–P(1A)	92.1(1)	Hg(1)–Fe(1)–P(2A)	95.6(1)
P(1A)–Fe(1)–P(2A)	172.3(1)	Hg(1)–Fe(1)–C(1A)	74.8(3)
Hg(1)–Fe(1)–C(2A)	177.2(3)	Hg(1)–Fe(1)–C(3A)	71.7(3)
C(1A)–Fe(1)–C(3A)	146.5(4)	C(2A)–Fe(1)–C(3A)	110.0(4)
Fe(1)–P(1A)–C(4A)	118.1(3)	Fe(1)–P(2A)–C(8A)	116.9(3)
Fe(1)–C(1A)–O(1A)	176.2(7)	Fe(1)–C(2A)–O(2A)	179.0(7)
Hg(1)–C(3A)–O(3A)	109.7(6)	Hg(1)–C(3A)–Fe(1)	69.2(2)
Fe(1)–C(3A)–O(3A)	178.8(7)	P(1A)–C(4A)–N(1A)	117.9(6)
Hg(1)–N(1A)–C(4A)	119.2(6)	Hg(1)–N(3A)–C(8A)	120.0(6)
P(2A)–C(8A)–N(3A)	117.9(7)	P(2A)–C(8A)–N(4A)	119.3(7)
Molecule 2b			
Hg(2)–Fe(2)	2.616(2)	Hg(2)–Cl(1B)	2.468(3)
Hg(2)–Cl(2B)	2.475(3)	Hg(2)–N(3B)	2.522(8)
Fe(2)–P(1B)	2.266(3)	Fe(2)–P(2B)	2.268(3)
Fe(2)–C(1B)	1.793(8)	Fe(2)–C(2B)	1.799(8)
Fe(2)–C(3B)	1.781(8)	C(1B)–O(1B)	1.151(10)
C(2B)–O(2B)	1.158(10)	C(3B)–O(3B)	1.105(10)
P(1B)–C(4B)	1.814(8)	P(2B)–C(8B)	1.887(8)
Fe(2)–Hg(2)–Cl(1B)	127.4(1)	Fe(2)–Hg(2)–Cl(2B)	130.6(1)
Cl(1B)–Hg(2)–Cl(2B)	101.9(1)	Fe(2)–Hg(2)–N(3B)	89.6(2)
Cl(1B)–Hg(2)–N(3B)	88.7(2)	Cl(2B)–Hg(2)–N(3B)	93.6(2)
P(1B)–Fe(2)–P(2B)	177.2(1)	Hg(2)–Fe(2)–C(1B)	76.1(2)
Hg(2)–Fe(2)–C(2B)	175.7(3)	Hg(2)–Fe(2)–C(3B)	75.7(3)
C(1B)–Fe(2)–C(2B)	100.2(4)	C(1B)–Fe(2)–C(3B)	151.7(4)
C(2B)–Fe(2)–C(3B)	108.1(4)	Fe(2)–P(1B)–C(4B)	114.8(3)
Fe(2)–P(2B)–C(8B)	118.0(3)	Fe(2)–C(1B)–O(1B)	176.3(7)
Fe(2)–C(2B)–O(2B)	178.9(9)	Fe(2)–C(3B)–O(3B)	178.6(9)
P(1B)–C(4B)–N(1B)	120.9(6)	Hg(2)–N(3B)–C(8B)	118.7(5)
P(2B)–C(8B)–N(3B)	115.8(6)		

Table 9
Selected bond lengths (Å) and angles (deg) for complexes **3** and **4** (X = Br for **3**, I for **4**)

Hg(1)–X(1)	2.579(3)	2.755(2)	Hg(1)–X(2)	2.622(3)	2.788(2)
Hg(1)–Fe(1)	2.633(3)	2.665(2)	Fe(1)–C(1)	1.76(1)	1.79(1)
Fe(1)–C(2)	1.81(1)	1.80(1)	Fe(1)–C(3)	1.84(1)	1.823(9)
Fe(1)–P(1)	2.259(6)	2.260(4)	Fe(1)–P(2)	2.256(6)	2.260(4)
C(1)–O(1)	1.15(1)	1.15(1)	C(2)–O(2)	1.13(1)	1.15(1)
C(3)–O(3)	1.09(1)	1.13(1)	P(1)–C(7)	1.87(1)	1.89(1)
P(2)–C(23)	1.91(1)	1.88(1)			
X(1)–Hg(1)–X(2)	109.0(1)	110.9(1)	X(1)–Hg(1)–Fe(1)	128.5(1)	127.1(1)
X(2)–Hg(1)–Fe(1)	122.5(1)	122.1(1)	Hg(1)–F(1)–C(1)	177.7(4)	177.2(3)
Hg(1)–Fe(1)–C(2)	76.3(5)	76.3(4)	Hg(1)–F(1)–C(3)	74.5(5)	74.3(4)
C(1)–Fe(1)–C(2)	105.9(6)	106.3(5)	C(1)–Fe(1)–C(3)	103.3(6)	103.0(5)
C(2)–Fe(1)–C(3)	150.8(7)	150.7(5)	Hg(1)–Fe(1)–P(1)	91.3(2)	91.7(1)
Hg(1)–Fe(1)–P(2)	91.7(1)	91.9(1)	P(1)–Fe(1)–P(2)	177.0(2)	176.2(2)
Fe(1)–C(1)–O(1)	177(1)	176.2(2)	Fe(1)–C(2)–O(2)	178(1)	177.7(9)
Fe(1)–C(3)–O(3)	174(1)	177.0(9)	Fe(1)–P(1)–C(7)	117.8(4)	118.6(3)
P(1)–C(7)–N(1)	116(1)	114.6(3)	Fe(1)–P(2)–C(23)	118.4(5)	119.0(4)
P(2)–C(23)–N(3)	117(1)	115.8(7)			

pancy factor of 0.5 was assigned to each orientation of the rigid phenyl group in refinement.

All calculations were carried out on a PC 486 using the SHELXTL/PC program package [16]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [17]. Final atomic coordinates and equivalent isotropic thermal parameters for the five crystal structures, along with their estimated standard deviations, are listed in Tables 2–6. Selected bond lengths and angles are presented in Tables 7–10.

For all the compounds supplementary material has been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Reaction of Ph$_2$PLi and 2-chloropyrimidine led to the formation of the new phosphine ligand 2-(diphenylphosphino)pyrimidine, Ph$_2$Ppym. Further reaction of

Table 10
Selected bond lengths (Å) and angles (deg) for complex **5**

Hg(1)–S(1)	2.546(2)	Hg(1)–S(2)	2.523(6)
Hg(1)–Fe(1)	2.649(1)	Hg(1)–C(1)	2.709(6)
Hg(1)–N(1)	2.628(6)	Fe(1)–C(1)	1.798(8)
Fe(1)–C(2)	1.812(7)	Fe(1)–C(3)	1.776(7)
Fe(1)–P(1)	2.256(2)	Fe(1)–P(2)	2.276(2)
C(1)–O(1)	1.141(9)	C(2)–O(2)	1.135(9)
C(3)–O(3)	1.149(8)	P(1)–C(9)	1.851(6)
P(2)–C(25)	1.847(6)		
S(1)–Hg(1)–S(2)	109.1(1)	S(1)–Hg(1)–Fe(1)	127.2(1)
S(2)–Hg(1)–Fe(1)	122.8(1)	S(1)–Hg(1)–C(1)	162.5(2)
S(2)–Hg(1)–C(1)	83.7(2)	Fe(1)–Hg(1)–C(1)	39.2(2)
S(1)–Hg(1)–N(1)	97.4(1)	S(2)–Hg(1)–N(1)	93.5(2)
Fe(1)–Hg(1)–N(1)	88.7(1)	Hg(1)–S(1)–C(4)	103.2(3)
Hg(1)–S(2)–C(5)	104.8(8)	Hg(1)–Fe(1)–C(1)	72.2(2)
Hg(1)–Fe(1)–C(2)	75.5(2)	Hg(1)–Fe(1)–C(3)	177.1(3)
C(1)–Fe(1)–C(2)	147.7(3)	C(1)–Fe(1)–C(3)	105.0(3)
C(2)–Fe(1)–C(3)	107.2(3)	Hg(1)–Fe(1)–P(1)	92.5(1)
Hg(1)–Fe(1)–P(2)	94.7(1)	Hg(1)–C(1)–O(1)	115.5(5)
Fe(1)–C(1)–O(1)	175.8(6)	Fe(1)–C(2)–O(2)	176.4(6)
Fe(1)–C(3)–O(3)	179.0(7)	Fe(1)–P(1)–C(9)	116.8(2)
Hg(1)–N(1)–C(9)	116.9(5)	P(1)–C(9)–N(1)	117.1(5)
Fe(1)–P(2)–C(25)	115.7(2)	P(2)–C(25)–N(3)	114.1(6)

Table 11
Infrared carbonyl absorption spectra for complexes 1–5

Compound		$\nu(CO)(cm^{-1})$
trans-Fe(CO)$_3$(Ph$_2$Ppym)$_2$	1	1875
[(CO)$_3$Fe(Ph$_2$Ppym)$_2$HgCl$_2$]$_2$ · 2CH$_2$Cl$_2$ · 0.5MeOH	2	2031, 1974, 1895
(CO)$_3$Fe(Ph$_2$Ppym)$_2$HgBr$_2$	3	2036, 1976, 1894
(CO)$_3$Fe(Ph$_2$Ppym)$_2$HgI$_2$	4	2032, 1977, 1895
(CO)$_3$Fe(Ph$_2$Ppym)$_2$Hg(SCN)$_2$	5	2041, 1977, 1896

Ph$_2$Ppym with Fe(CO)$_5$ and NaOH in *n*-butanol afforded an orange complex formulated as *trans*-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ (**1**) in good yield (80%). With this new organometallic polydentate ligand four iron(0)–mercury(II) heterobimetallic complexes **2–5** were prepared and their crystal structure determined.

3.1. IR spectra of complexes 1–5

The carbonyl stretching frequencies of compounds **1–5** are listed in Table 11. The IR spectra of **1** show one intense carbonyl stretching absorption at $\nu(CO) = 1875 \ cm^{-1}$ which implies that the local symmetry about the Fe atom is D_{3h}. A recent study has shown that the basicity of the metal atom in *trans*-(CO)$_3$Fe(R$_3$P)$_2$ depends linearly on the basicity of the phosphine ligand and the carbonyl stretching frequency $\nu(CO)$ [18]. The virtually identical $\nu(CO)$ values of compound **1** and *trans*-(CO)$_3$Fe(Ph$_2$Ppy)$_2$ (1874 cm^{-1}) [3] indicate that Ph$_2$Ppym and Ph$_2$Ppy have the same basicity, as do the Fe atoms in these two complexes, although pyrimidine has two basic nitrogen atoms and pyridine has only one. The IR spectra for all four bimetallic complexes **2–5** are typical, all exhibiting three $\nu(CO)$ vibrations that shift

to higher frequencies are compared with $\nu(CO)$ for **1**. In contrast, similar $\nu(CO)$ vibrations for complexes **2–4** indicate that the choice of anion has little influence on the Fe → Hg donor–acceptor bond.

3.2. Crystal structure of trans-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ 1

As illustrated in Fig. 1, the coordination environment about the iron atom may best be described as an FeP$_2$C$_3$ trigonal bipyramid with two phosphine ligands occupying axial positions and three carbonyl groups lying on the equatorial plane. The phenyl and pyrimidyl groups of each phosphine ligand are staggered with respect to the planar (CO)$_3$Fe fragment, so that the molecule nearly attains idealized D_{3h} symmetry, which is consistent with the observed IR data.

The Fe–P distances of 2.202(2) and 2.204(2) Å are the same as those [2.202(1) and 2.206(1) Å] found in *trans*-(CO)$_3$Fe(Ph$_2$Ppy)$_2$ [3], but the Fe–C distances of 1.748(8), 1.749(10) and 1.753(9) Å are somewhat shorter than those found in *trans*-(CO)$_3$Fe(Ph$_2$Ppy)$_2$ [av. 1.782 Å] [3]. The P–Fe–P angle of 174.2(1)°, which is smaller than that found in *trans*-(CO)$_3$Fe(Ph$_2$Ppy)$_2$ [177.08(7)°], deviates significantly from linearity. Unlike *trans*-
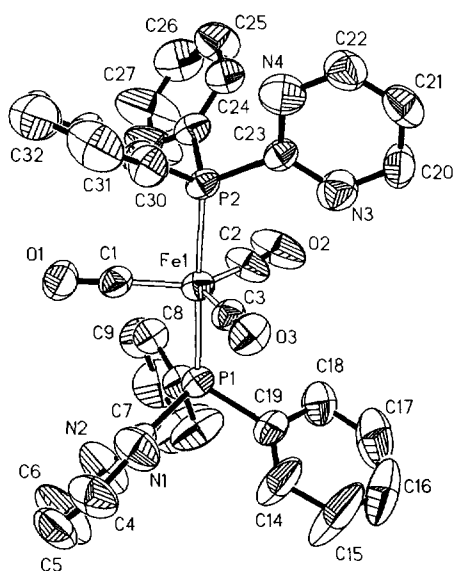
Fig. 1. Molecular structure and atom numbering of *trans*-(CO)$_3$Fe(Ph$_2$Ppym)$_2$ **1**. The thermal ellipsoids are drawn at the 35% probability level.

Fig. 2. Molecular structure and atom numbering of [(CO)$_3$Fe-(Ph$_2$Ppym-*N*,*N'*)$_2$HgCl$_2$] **2a**. The thermal ellipsoids are drawn at the 35% probability level.
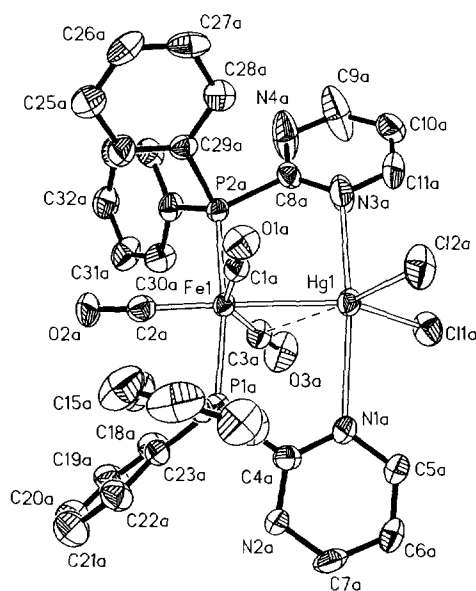
Fig. 3. Molecular structure and atom numbering of [(CO)₃Fe-(Ph₂Ppym-*N*)₂HgCl₂] **2b**. The thermal ellipsoids are drawn at the 35% probability level.
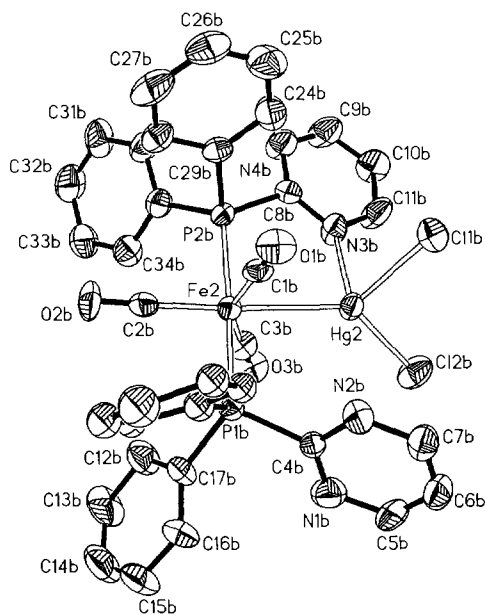

Fig. 5. Molecular structure and atom numbering of [(CO)₃Fe-(Ph₂Ppym)₂HgI₂] **4**. The thermal ellipsoids are drawn at the 35% probability level.

$(CO)_3Fe(Ph_2Ppy)_2$ in which the three C–Fe–C angles are all nearly 120°, in compound **1** C(1)–Fe(1)–C(3) = 114.7(4)° is much smaller than the other two C–Fe–C angles [122.6(4)°].

The pyrimidyl rings in **1** are differentiated from the phenyl rings on the basis of the thermal parameters of the nitrogen and carbon atoms, and also on the relevant bond distances and angles.

3.3. Crystal structures of $(CO)_3Fe(Ph_2Ppym)_2HgX_2$ (X = Cl, Br, I, SCN) 2–5

As depicted in Figs. 2–6, all four complexes contain a heterobinuclear core and the 18-electron neutral complex *trans*-$(CO)_3Fe(Ph_2Ppym)_2$ acts as a donor ligand towards the mercury(II) atom of HgX_2 via an iron–mercury bond of length 2.616(2)–2.652(2) Å. A com-

Fig. 4. Molecular structure and atom numbering of [(CO)₃Fe-(Ph₂Ppym)₂HgBr₂] **3**. The thermal ellipsoids are drawn at the 35% probability level.
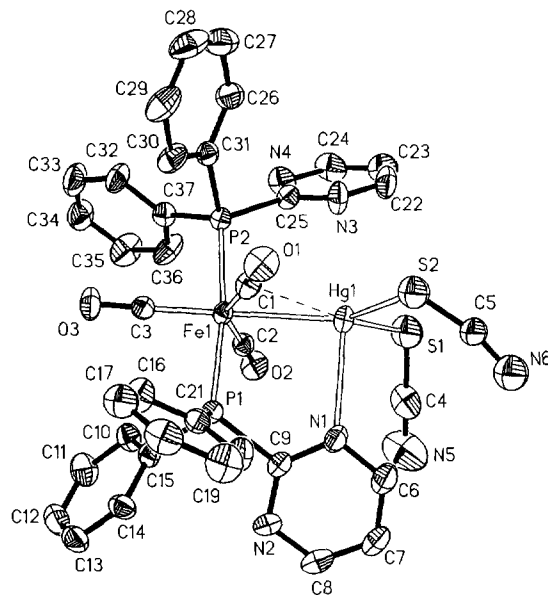
Fig. 6. Molecular structure and atom numbering of [(CO)₃Fe-(Ph₂Ppym-*N*)₂Hg(SCN)₂] **5**. One of the two components of a disordered SCN group is omitted for clarity. The thermal ellipsoids are drawn at the 35% probability level.

parison of the Fe–Hg bond lengths in these compounds with those in related compounds in the literature is shown in Table 12.

The C–Fe–C angle between the two carbonyl groups adjacent to the HgX_2 unit is enlarged to 146.5(4)–151.7(4)°, which is consistent with the expected repulsion by the Fe → Hg bond pair. The remote carbonyl group is nearly collinear with the two metal atoms. However, the deviation of the mercury(II) atom from the FeC_3 plane differs significantly for compounds 2–5, being 0.128(4), 0.128(4), 0.020(4), 0.028(6) and 0.020(1) Å, respectively. The Fe–P and Fe–C bond distances [av. Fe–P 2.257(3) Å in 2a, 2.267(3) Å in 2b, 2.258(6) Å in 3, 2.260(4) Å in 4 and 2.266(2) Å in 5; av. Fe–C 1.791(8) Å in 2a, 1.791(8) Å in 2b, 1.80(1) Å in 3, 1.81(1) Å in 4 and 1.795(7) Å in 5] are considerably longer than those found in *trans*-$(CO)_3Fe(Ph_2Ppym)_2$ (1) [av. Fe–P, 2.203(2) Å; Fe–C, 1.750(9) Å] as the formation of the Fe → Hg donor–acceptor bond in complexes 2–5 reduces the electron density on iron and consequently weakens these bonds.

The coordination geometry of the mercury(II) atom and ligation behaviour of the pyrimidyl groups in complexes 2–5 are of interest. In complex 2, there exist two crystallographically independent $(CO)_3Fe(Ph_2Ppym)_2$-$HgCl_2$ molecules (2a and 2b). In molecule 2a (Fig. 2) the Fe–Hg bond length is 2.652(2) Å; the angle between the $HgCl_2$ and FeC_3 planes is 4.6°, i.e. the Fe(1), Hg(1), Cl(1a), Cl(2a), and C(1a)–C(3a) atoms are approximately coplanar. The Hg–N distances are 2.669(8) and 2.677(9) Å, which are much longer than the average Hg–N distance (2.117 Å) [19] found in mercury pyrimidyl complexes. However, according to the criterion of Grdenić [20] and Canty and Deacon [21], that there is effective coordination between Hg and L when the condition $D(Hg–L) < R(Hg) + R(L)$ (where R = van der Waals radii) is fulfilled, the pyrimidyl nitrogen atoms in 2a can be considered to ligate the mercury (II)

atom effectively since the Hg–N distances well meet this condition [$R(Hg)$ = 1.73 Å, $R(N)$ = 1.5 Å] [20–22]. In addition, the N–Hg–N angle is 160.6(2)° and the dihedral angles between the HgX_2 plane and each of the two pyrimidyl rings are 75.3° and 64.7° respectively, so that the Hg atom is displaced by 0.189(5) Å from the plane of one pyrimidyl ring [N(1)–C(4A)] and by 0.780(5) Å from the other [N(3A)–C(11A)]. The coordination pattern is similar to that in the analogous terpyridine compound [$MeHg(Et_3terpy)]NO_3$ [terpy = 2,2′:6′,2″-terpyridine] [23], in which the mercury(II) atom is strongly bonded to one nitrogen donor at 2.26(2) Å and loosely to the other two nitrogen atoms at 2.51(2) and 2.61(2) Å, lying nearly in one pyridyl plane and out of the other two pyridyl planes by 0.886(1) and 1.032(1) Å respectively. So the compound 1 acts likewise as a tridentate ligand.

Another noteworthy feature of 2a is that one carbonyl group leans towards the mercury(II) atom [Hg(1)–Fe–C(1a) = 74.8(3)°, Hg–Fe–C(3a) = 71.7(3)°]. The Hg(1)...C(3a) distance of 2.692(8) Å is suggestive of a weak interaction between the mercury(II) atom and the carbonyl group, although it cannot be construed as a semi-bridging bonding mode as in Cotton's description [24].

In molecule 2b (Fig. 3), the Fe–Hg bond length is 2.616(2) Å which is 0.036 Å shorter than in 2a, and the dihedral angle between the $HgCl_2$ and FeC_3 planes is 22.4°. The Hg(2)–N(3b) distance of 2.522(8) Å is significantly shorter than the corresponding value in 2a, and the mercury atom is displaced from the plane of the pyrimidyl ring by 0.62(4) Å. The Hg...N distances involving the nitrogen atoms of the other pyrimidyl ring are 3.216(8) and 3.941(8) Å respectively, and the dihedral angle between the pyrimidyl rings is 96.7°. Thus the second pyrimidyl ring does not participate in coordination; however, there may still exist a secondary interaction between its π orbital and the 6p orbital of Hg

Table 12
Fe–Hg bond distances in some related complexes

Complex		Fe–Hg (Å)	Reference
$(CO)_3Fe(\mu$-$Ph_2Ppy)_2Hg(SCN)_2$		2.648(1)	[3]
$(CO)_3Fe(\mu$-$Ph_2Ppy)_2HgI_2$		2.678(1)	[13]
$Fe(CO)_4(HgClpy)_2$		2.553	[26]
$[Fe(CO)_4(HgCl)(HgCl_2)]^-$		2.516, 2.560	[27]
$Hg[Fe(CO)_2(NO)(PEt_3)]_2$		2.534	[28]
$Fe(CO)_4(HgBr)_2$		2.44, 2.59	[29]
$Fe(CO)_4(HgSCN)_2$		2.506	[30]
$(OC)_3(Me_3P)(Ph_2MeSi)FeHgBr$		2.515	[31]
$Hg[Fe\{Si(OMe)_3\}(CO)_3(dppm-P)]_2$		2.574, 2.576	[32]
$Hg\{Fe_2CO(\mu_3$-$COMe)(CO)_7(\eta$-$C_5H_5)\}_2$		2.727(1), 2.735(1)	
		2.729(1), 2.726(1)	[33]
$[(CO)_3Fe(Ph_2Ppym)_2HgCl_2]_2 \cdot 2CH_2Cl_2 \cdot 0.5MeOH$	2	2.651(2), 2.616(2)	This work
$(CO)_3Fe(Ph_2Ppym)_2HgBr_2$	3	2.633(3)	This work
$(CO)_3Fe(Ph_2Ppym)_2HgI_2$	4	2.665(2)	This work
$(CO)_3Fe(Ph_2Ppym)_2Hg(SCN)_2$	5	2.649(1)	This work

[21,25]. In the present case compound **1** acts as a bidentate ligand. Furthermore, the Hg...C distances [Hg(2)...C(1B), Hg(2)...C(3B)] of 2.794(8) and 2.778(8) Å, and the Hg–Fe–C angles [Hg(2)–Fe(2)–C(1B), Hg(2)–Fe(2)–C(3B)] of 76.1(2)° and 75.7(3)° respectively, indicate that no carbonyl group leans towards the mercury atom as observed in complex **2a**.

$(CO)_3Fe(Ph_2Ppym)_2HgBr_2$ **3** (Fig. 4) and $(CO)_3Fe(Ph_2Ppym)_2HgI_2$ **4** (Fig. 5) are isostructural, with Fe–Hg distances of 2.632(3) and 2.665(2) Å respectively. In both complexes the mercury atom lies in the FeC_3 plane with a deviation of 0.020(4) Å for **3** and 0.028(6) Å for **4**. The dihedral angles between FeC_3 and HgX_2 planes are 25.8° and 25.5° for X = Br (**3**), and X = I (**4**) respectively. The interaction between mercury and nitrogen atoms seems to be more complicated: the Hg–N distances of 2.715(8) and 2.756(8) Å in complex **3** and 2.692(8) and 2.733(8) Å in complex **4** respectively well satisfy the condition $D(Hg–N) < R(Hg) + R(N) = 3.23$ Å, but the displacements of the mercury atom from the mean plane of individual pyrimidyl rings [1.448(5) and 1.596(8) Å in **3**; 1.502(5) and 1.560(5) Å in **4** respectively] indicate that orbital overlap between the mercury and nitrogen atoms are not so efficient. Presumably there is only weak interaction between the Hg and N atoms, and so compound **1** may be better regarded as a monodentate ligand in both **3** and **4**.

The Hg...C distances are 2.78(1) and 2.82(1) Å in **3** and 2.79(1) and 2.84(2) Å in **4** respectively; the Hg–Fe–C angles are 74.5(5)° and 76.3(5)° in **3** and 74.3(4)° and 76.3(4)° in **4** respectively. As is the case in complex **2b**, no significant interaction exists between any carbonyl group and the mercury atom in either complex.

In complex **5** (Fig. 6), the Fe–Hg bond distance is 2.649(1) Å, which is the same as that in $(CO)_3Fe(Ph_2Ppy-N)_2Hg(SCN)_2$ [3]. The Hg...N distances of 2.628(6) and 2.927(6) Å are somewhat longer than those in $(CO)_3Fe(Ph_2Ppy-N)_2Hg(SCN)_2$ [2.595(6), 2.867(6) Å] [3], which may be attributed to the fact that pyrimidine is a weaker base than pyridine. A comparison of the displacements of the mercury atom from the plane of each of the pyrimidyl rings [0.878(5), 2.209(5) Å] indicates that one pyrimidyl group coordinates efficiently to the mercury atom, but the other only interacts weakly with it. Thus in this case compound **1** acts as a bidentate ligand as in molecule **2b**.

In complex **5**, the Hg...C distances are 2.709(6) and 2.812(6) Å and the Hg–Fe–C angles are 72.2(2) and 75.5(2)° respectively, which are similar to those found in the related complex $(CO)_3Fe(Ph_2Ppy-N)_2Hg(SCN)_2$ [Hg...C 2.709(6), 2.750(6) Å; Hg–Fe–C 72.2(2), 74.4(3)°] [3]. A weak interaction exists between the mercury atom and one carbonyl group, as observed in molecule **2a**.

The X-ray crystal structures of the four binuclear

compounds show that the nature of the anion has little influence on the Fe → Hg bond length, but greatly affects the coordination behaviour of the neutral organometallic ligand trans-$(CO)_3Fe(Ph_2Ppym)_2$ (**1**) to mercury(II). In complex **2**, ligand **1** acts in tridentate and bidentate modes in two independent molecules. In complex **5**, compound **1** acts as a bidentate ligand as in **2b**. In complexes **3** and **4**, compound **1** acts as a monodentate ligand as only a weak interaction exists between mercury(II) and pyrimidyl nitrogen atoms. It is believed that the metal–metal bond in these complexes is formed mainly by electron donation from the Fe(0) atom to the Hg(II) atom, and not effected by the rigidity requirement of the bridge ligand.

In molecule **2a** and **5**, one carbonyl group leans towards the mercury atom, and there is some weak interaction between them. Such interaction may be important for the catalytic activity of this type of compound in the carbonylation of ethanol forming ethyl propionate according to the proposed mechanism of the catalytic reaction [3].

From Table 12 it is seen that the Fe–Hg distances in the complexes **2–5** are similar to those in $(CO)_3Fe(Ph_2Ppy-N)_2Hg(SCN)_2$ [3] and $(CO)_3Fe(Ph_2-Ppy)2HgI_2$ [13], but longer than those in $Fe(CO)_4(HgClpy)_2$ [26], $[Fe(CO)_4(HgCl)(HgCl_2)]^-$ [27], $Hg[Fe(CO)_2(NO)(PEt_3)]_2$ [28], $Fe(CO)_4(HgBr)_2$ [29], $Fe(CO)_4(HgSCN)_2$ [30], $(OC)_3(Me_3P)-(Ph_2MeSi)FeHgBr$ [31], and $Hg[Fe\{Si(OMe)_3\}(CO)_3-(dppm-P)]_2$ [32] in which the Fe–Hg bond is best regarded as covalent rather than donor–acceptor. However, they are shorter than those [2.726(1)–2.735(1) Å] found in $[Hg\{FeCO(\mu_3-COMe)(CO)_7(\eta-C_5H_5)\}]_2$ [33].

Normally, a bond will be formed, according to Pearson's acid–base theory [34], when the Lewis acid strength of the electron acceptor is close to the Lewis base strength of the electron donor. The ligand will be deformed to adjust its base strength in order to match the acid strength of the metal, otherwise the bonding is unfavourable when the difference between the acid strength and base strength is large. However the coordination of a ligand to a metal centre will change the acid strength of the metal ion, such that the strength will be reduced if the base strength of the ligand is high and vice versa [35]. Since mercury(II) is a soft acid and the hardness of Lewis bases Cl^-, Br^- and I^- varies in the order $Cl^- > Br^- > I^-$, the softness of mercury(II) in the HgX_2 moiety increases in the order $HgCl_2 < HgBr_2 < HgI_2$. When the organometallic tridentate ligand trans-$(CO)_3Fe(Ph_2Ppym)_2$ coordinates to HgX_2, the difference Δ of the base strength of the pyrimidyl nitrogen atom and the acid strength of the mercury(II) atom increases in the order **2 < 3 < 4**. Based on the molecular structures of **2–4**, Δ takes a critical value in compound **2** since it allows the mercury(II) atom to coordinate with either one pyrimidyl nitrogen atom or two.

With increasing Δ it is expected that the bonding interaction between nitrogen and mercury will be reduced, which is consistent with the coordination modes in complexes 2–4. The behaviour of the SCN^- anion is an anomaly. Generally the softness of SCN^- is similar to that of I^-, but it behaves like Cl^- in this series of complexes, and its apparent hardness seems to fit in the order $Cl^- < SCN^- < Br^- < I^-$.

4. Conclusion

This work has shown that the new organometallic complex $trans$-$(CO)_3Fe(Ph_2Ppym)_2$, similar to terpyridine, can act as a mono-, bi-, or tridentate ligand towards HgX_2 $(X = Cl, Br, I, SCN)$. The Fe–Hg metal–metal bond in the complexes 2–5 is mainly formed by direct electron donation from Fe(0) to Hg(II), but not effected by the rigidity requirement of the bridge ligand. Modification of the molecular structure by the use of different halide/pseudohalide anions is attributed to the difference of the acid strength of mercury(II) and the base strength of the nitrogen atoms from the bridging ligand.

Acknowledgements

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