Synthesis of Fe–M complexes (M = Mo, Mn, Fe, Co, Ni, Zn, Cd, Hg) using *trans*-Fe(EtPhPpy)₂(CO)₃ as an organometallic tridentate ligand Molecular structures of (CO)₃Fe(μ-EtPhPpy)₂Mo(CO)₃ and (CO)₃Fe(μ-EtPhPpy)₂Cd(SCN)₂ (EtPhPpy = 2-(ethylphenylphosphino)pyridine)

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Abstract

trans-Fe(EtPhPpy)₂(CO)₃ reacts with Mo(CO)₆ and M(SCN)₂ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) to form binuclear complexes containing an Fe–M bond. Crystal and molecular structures of the title complexes have been determined by X-ray analysis, which yielded Fe(0)–Mo(0) and Fe(0)–Cd(II) bonded lengths of 2.922(1) Å and 2.648(1) Å respectively. © 1997 Elsevier Science S.A.

Keywords: 2-(Ethylphenylphosphino)pyridine; Heterodinuclear complex; Molecular structure

1. Introduction

There is currently considerable interest in binuclear complexes in which strong interaction takes place between the metal atoms. Many hetero- and homo-binuclear complexes have been prepared using 2-(diphenylphosphino)pyridine (Ph₂Ppy) as a bridging ligand [1]. Previous papers from our laboratories have described the synthesis of binuclear complexes using *trans*-Fe(Ph₂Ppy)₂(CO)₃ [2–4], *trans*-Fe(Ph₂Ppym)₂(CO)₃ (Ph₂Ppym = 2-(diphenylphosphino)pyrimidine) [5] and Fe(Ph₂Ppy-P)(CO)₄ [6] as bidentate or tridentate ligands. We report here the synthesis of a series of Fe–M (M = Mo, 2; Mn, 3; Fe, 4; Co, 5; Ni, 6; Zn, 7; Cd, 8; Hg, 9) complexes using *trans*-Fe(EtPhPpy)₂(CO)₃, 1, as a neutral tridentate ligand.

2. Results and discussion

Reaction of EtPhPLi, which was prepared by the reaction of EtPh₂P with lithium shavings in THF, with 2-chloropyridine led to the formation of a new pyridylphosphine ligand 2-(ethylphenylphosphino)pyridine (EtPhPpy) as an R/S mixture. A new neutral organometallic tridentate ligand *trans*-Fe(EtPhPpy)₂(CO)₃, which is the RS-isomer, was obtained from the reaction of EtPhPpy, NaOH and Fe(CO)₅ in *n*-butanol. The racemic RR/SS diastereomer was also found as a minor product in the reaction mixture but not crystallized with the RS-isomer. Evidence for the formation of the racemic product is provided by the ³¹P{¹H} NMR of the mixture, which exhibits a tiny peak ($\delta = 88.76$ ppm) beside the main peak ($\delta = 92.71$ ppm) assigned to the RS-isomer (Scheme 1).

The IR spectrum of complex 1 shows one intensive carbonyl stretching absorption $\nu(CO)$ at 1865 cm⁻¹ which implies that the local symmetry about the Fe atom is near D_{3h}. A recent study has shown that the basicity of the metal atom in *trans*-Fe(R₃P)₂(CO)₃ depends linearly on the basicity of the phosphine ligand and $\nu(CO)$ [7]. Compared to $\nu(CO) = 1874$ cm⁻¹ for *trans*-Fe(Ph₂Ppy)₂(CO)₃, the smaller $\nu(CO)$ value of compound 1 indicates that the basicity of EtPhPpy is higher than that of Ph₂Ppy, and the Fe(0) atom in 1 has stronger donor properties.

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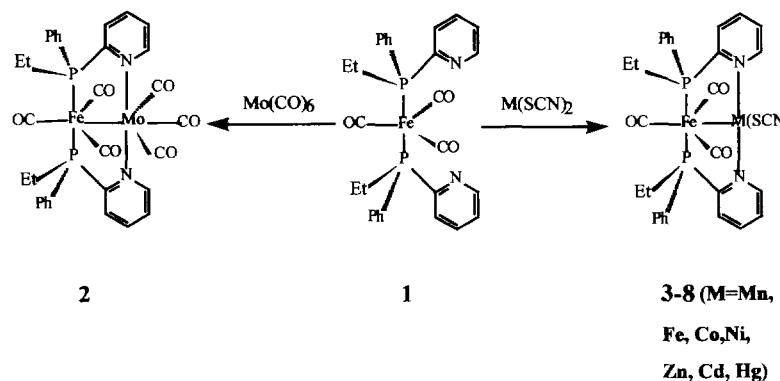
Scheme 1.

Reaction of *trans*-Fe(EtPhPpy)$_2$(CO)$_3$ with Mo(CO)$_6$ in refluxing benzene resulted in the formation of (OC)$_3$Fe(μ-EtPhPpy)$_2$Mo(CO)$_3$, **2**, whose IR spectrum shows extensive absorption bands (1830–2017 cm^{-1}) in the range of terminal carbonyl stretching vibration. The ^{31}P{^{1}H} NMR spectra exhibits one peak at $\delta =$ 78.35 ppm which is consistent with the chemical equivalence of the two phosphorus atoms.

An ORTEP drawing and atom numbering of the binuclear molecule **2** is shown in Fig. 1. A crystallographic mirror plane contains the metal atoms and four carbonyl groups. The Fe(0) and Mo(0) centers are bridged by two EtPhPpy ligands and a metal–metal bond, such that two P atoms coordinated to Fe are trans to each other, whereas two N atoms coordinated to Mo are cis to each other. The O(4), C(4), Mo(1), Fe(1), C(2) and O(2) atoms are almost collinear. The Fe–Mo distance of 2.922(1) Å is shorter than that of Mo(η^6-C$_6$H$_6$)(μ-η^5,η^3-azulene)Fe(CO)$_3$ 3.092(1) Å [8], but is longer

than those found in the complexes (OC)$_2$MoCp(μ-Tol)Fe(CO)$_4$, 2.823(1) Å [9], (OC)$_2$MoCp(μ-η^2-SCC$_6$H$_4$Me-4)Fe(CO)$_3$, 2.765(1) Å [10], (OC)$_4$Mo(μ-Ph$_2$P)$_2$Fe(CO)$_3$, 2.854(1) Å [11]. The Mo–N bond distance of 2.327(4) Å is comparable to those found in the complexes Mo(CO)$_3$(dien), 2.32(3) Å [12], Mo(CO)$_4${P(OMe)$_3$}(pip), 2.341(5) Å [13]. The Mo–C distances 1.922(7) Å, 1.934(6) Å are shorter than those of (OC)$_2$MoCp(μ-Tol)Fe(CO)$_4$, 1.973(7), 1.952(7) Å [9], (OC)$_2$MoCp(μ-η^2-SCC$_6$H$_4$Me-4)Fe(CO)$_3$, 2.163(2), 1.974(2) Å [10] and (OC)$_4$Mo(μ-Ph$_2$P)$_2$Fe(CO)$_3$, 2.012(7), 2.025(8), 2.045(7), 2.059(7) Å [11].

Under mild conditions, reaction of complex **1** with M(SCN)$_2$ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) resulted in the formation of binuclear complexes containing Fe(0)–M(II) bonds in moderate yields. Compared to complex **1**, the IR ν(CO) spectra of these binuclear complexes split into three peaks and shift to higher frequencies, which is consistent with both a change in stereochemistry and decrease in electron density on the Fe(0) atom.

The ^{31}P{^{1}H} NMR spectra of complexes **3–7** 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 **8**, coupling of two bonds (^{31}P–Fe–^{111}Cd, ^{113}Cd) is observed with $^2J_{P-Fe-Cd} =$ 36 Hz, which is comparable to those observed in *mer*-[{(MeO)$_3$Si}(CO)$_3$Fe(μ-Ph$_2$Ppy)]$_2$Cd, $^2J_{P-Fe-Cd} =$ 66 Hz, and *mer*-[{(MeO)$_3$Si}(CO)$_3$Fe(μ-Ph$_2$Ppy)CdBr(4-pic)], $^2J_{P-Fe-Cd} =$ 82 Hz [14]. For complex **9**, the magnitude of the $^2J($^{31}P–Fe–^{199}Hg) value is 235 Hz, and comparable coupling constants have been previously observed in some complexes containing an Fe–Hg bond, for example Hg[Fe(CO)$_3$(SiMePh$_2$)(PR$_3$)]$_2$ (R = Me, Bu, $^2J_{P-Fe-Hg}$ = 240, 205 Hz) [15], and Hg[Fe(CO)$_3${Si(OMe)$_3$}(dppm-P)]$_2$ ($^2J_{P-Fe-Hg} =$ 173 Hz) [16].

An ORTEP drawing and atom numbering of compound **8** is shown in Fig. 2. The distorted octahedral environ-
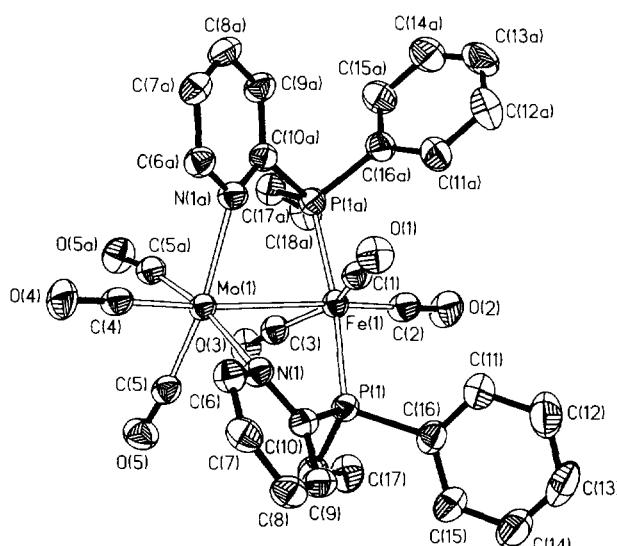
Fig. 1. Perspective view of (CO)$_3$Fe(μ-EtPhPpy)$_2$Mo(CO)$_3$, **2**, in its 2:1 solvate with toluene. The thermal ellipsoids are drawn at the 35% probability level. The atoms Mo(1), Fe(1), C(1), O(1), C(2), O(2), C(3), O(3), C(4) and O(4) lie on a crystallographic mirror plane.
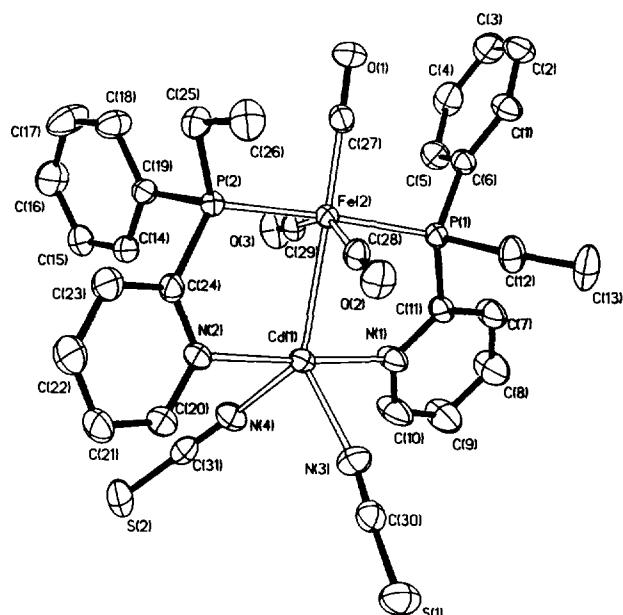
Fig. 2. Perspective view of $(CO)_3Fe(\mu$-EtPhPpy$)_2Cd(SCN)_2$, **8**. The thermal ellipsoids are drawn at the 35% probability level.

ment about the Fe atom consists of the Cd(II) atom, two P atoms and three carbon atoms of terminal carbonyls. The Cd atom exhibits a distorted trigonal bipyramidal configuration, in which two pyridine nitrogen atoms occupy the axial position and the Fe, N(3) and N(4) atoms lie in the equatorial plane. The SCN$^-$ ligand is bonded to the Cd(II) atom in the isothiocyanate mode rather than a thiocyanate one. The two pyridine nitrogen atoms remain trans, which is different from that of complex **2**. The Fe–Cd bond distance, 2.684(1) Å, is

similar to that of mer-[{(MeO)$_3$Si}(CO)$_3$Fe(μ-Ph$_2$Ppy)]$_2$Cd, 2.6970(5) Å [14], and is longer than those found in mer-[{(MeO)$_3$Si}(CO)$_3$Fe(μ-dppm)]$_2$Cd, 2.624(2) Å [17], mer-[(Ph$_2$HP)(Ph$_3$Si)(CO)$_3$FeCd(μ-Br)$_2$], 2.540(3) Å [14], and [{CdFe(CO)$_4$}$_4$], 2.559(2)–2.565(2) Å [18].

3. Experimental

3.1. Physical measurements

Microanalyses for C, H and N were carried out in the Department of Chemistry, Brunel University, Uxbridge, UK. Infrared spectra (KBr disc) were recorded with a Shimadzu 435 spectrophotometer. An AC-P200 NMR spectrometer was used to record ^{31}P{^{1}H} spectra at 81.03 MHz (CDCl$_3$, external standard: H$_3$PO$_4$ and 298 K).

3.2. Synthesis of the compounds

All preparations were carried out under nitrogen using Schlenk techniques. The solvents were purified by standard procedures. Ph$_2$PEt was synthesized by the published method [19].

3.3. Preparation of EtPhPpy

Lithium (1.60 g, 0.23 mol) was finely cut and added to a solution of Ph$_2$PEt (21.40 g, 0.10 mol) in 100 ml THF. The mixture was stirred at room temperature (RT)

Table 1
Crystal data and structure refinement parameters for $2 \cdot \frac{1}{2}C_7H_8$ and **8**

Formulae	$C_{32}H_{28}N_2O_6P_2FeMo \cdot \frac{1}{2}C_7H_8$ $(2 \cdot \frac{1}{2}C_7H_8)$	$C_{31}H_{28}N_4O_3P_2S_2CdFe$ (**8**)
MW	796.4	798.9
Space group	$P2_1/m$ (No. 11)	$P2_1/n$ (No. 14)
Cell dimensions		
a (Å)	7.881(1)	17.279(1)
b (Å)	15.535(1)	12.437(1)
c (Å)	16.157(1)	18.017(1)
β (deg)	102.97(1)	116.99(1)
V (Å^3)	1928(1)	3450(2)
Z	2	4
d_{calcd} (g cm^{-3})	1.372	1.538
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
Goodness-of-fit index	2.84	1.43
No. of unique reflections	4092	7027
No. of observed reflections		
($|F| \geq 4\sigma(F)$)	2768	5455
No. of variables, p	238	398
weighting scheme $w^{-1} = \sigma^2(F) + gF^2$	$g = 0.0002$	$g = 0.00001$
R_F	0.049	0.052
R_{wF}^2	0.069	0.063

for 6 h, after which the solution was transferred to another flask with a cannula. Then 2-chloro-2-methyl-propane (9.25 g, 0.10 mol) in 20 ml THF was added dropwise at 0 °C, after which the mixture was stirred at RT for 1 h. Then the mixture was cooled to 0 °C, and 2-chloropyridine (11.30 g, 0.10 mol) in 20 ml THF was added dropwise, and the resulting solution was stirred at 50 °C for 5 h. The solvent was almost completely removed and 100 ml of distilled water and 100 ml of CH_2Cl_2 were added to the mixture. The organic layer was separated and the aqueous layer extracted twice with CH_2Cl_2 (2 × 20 ml). The organic fraction collected was dried with anhydrous Na_2SO_4 overnight and then fractionated (134–138 °C/1 mmHg) to give a colorless liquid. (11.80 g, yield 55%). The product was contaminated by a trace amount of Ph_2PEt as observed from TLC, but this has no effect on subsequent reactions.

3.4. Preparation of trans-Fe(EtPhPpy)₂(CO)₃, 1

This compound was synthesized by the analogous method described [2]. Yield: yellow microcrystal, 72%. $^{31}P\{^1H\}$ NMR: $\delta = 92.71$ ppm. Anal. Calcd. for $C_{29}H_{28}FeN_2O_3P_2$: C, 61.06; H, 4.95; N, 4.91. Found: C, 61.32; H, 5.06; N, 4.86. IR ν(CO): 1951, 1865 cm^{-1}.

3.5. Preparation of (CO)₃Fe(μ-EtPhPpy)₂Mo(CO)₃, 2

A solution of compound 1 (0.29 g, 0.50 mmol) and $Mo(CO)_6$ (0.16 g, 0.6 mmol) in benzene (20 ml) was heated under refluxing for 3 h. After the solution was cooled to 10 °C, the red solid was precipitated. This was collected by filtration and washed with benzene and diethyl ether, then re-crystallized with toluene and dried in vacuum. Yield: 0.23 g, 58%. $^{31}P\{^1H\}$ NMR: $\delta = 78.35$ ppm. Anal. Calcd. for $2 \cdot \frac{1}{2}C_7H_8$ $C_{35.5}H_{32}FeMoN_2O_6P_2$: C, 53.49; H, 4.02; N, 3.51. Found: C, 53.43; H, 4.09; N, 3.52. IR ν(CO): 2017, 1986, 1954, 1903, 1867, 1830 cm^{-1}.

3.6. Preparation of (CO)₃Fe(μ-EtPhPpy)₂Mn(SCN)₂ (M = Mn, 3; Fe, 4; Co, 5; Ni, 6)

To a solution of complex 1 (0.29 g, 0.50 mmol) in 20 ml dichloromethane was added solid $M(SCN)_2$ (0.60 mmol). The mixture was stirred at RT for 8 h. After filtration, the filtrate was concentrated to about 5 ml, then diethyl ether was added to give a precipitate. The precipitate was filtered and dried in vacuum.

Complex 3. Yield: pale yellow powder, 0.25 g, 67%. $^{31}P\{^1H\}$ NMR: $\delta = 42.80$ ppm. Anal. Calcd. for $C_{31}H_{28}FeMnN_4O_3P_2S_2$: C, 50.22; H, 3.81; N, 7.56. Found: C, 50.26; H, 3.86; N, 7.58. IR ν(CO): 2000, 1923, 1882 cm^{-1}.

Complex 4. Yield: orange powder, 0.22 g, 59%. $^{31}P\{^1H\}$ NMR: $\delta = 43.37$ ppm. Anal. Calcd. for $C_{31}H_{28}Fe_2N_4O_3P_2S_2$: C, 50.15; H, 3.80; N, 7.55. Found: C, 50.37; H, 4.03; N, 7.49. IR, ν(CO): 2004, 1925, 1870 cm^{-1}.

Complex 5. Yield: green powder, 0.18 g, 49%. $^{31}P\{^1H\}$ NMR: $\delta = 43.23$ ppm. Anal. Calcd. for $C_{31}H_{28}CoFeN_4O_3P_2S_2$: C, 50.69; H, 3.84; N, 7.68. Found: C, 49.93; H, 3.86; N, 7.49. IR, ν(CO): 2005, 1932, 1884 cm^{-1}.

Complex 6. Yield: brown powder, 0.25 g, 67%. $^{31}P\{^1H\}$ NMR: $\delta = 42.70$ ppm. Anal. Calcd. for $C_{31}H_{28}FeN_4NiO_3P_2S_2$: C, 49.97; H, 3.79; N, 7.48. Found: C, 50.11; H, 3.76; N, 7.37. IR, ν(CO): 2004, 1930, 1868 cm^{-1}.

Table 2
Atomic coordinates of complex $2 \cdot \frac{1}{2}C_7H_8$ (×10⁵ for Mo, Fe and P atoms, ×10⁴ for other atoms) and equivalent isotropic displacement coefficients (Å² ×10⁴ for Mo, Fe and P atoms, Å² ×10³ for other atoms)

Atoms	X	Y	Z	U_{eq}
Mo(1)	22156(8)	25000	6934(1)	414(2)
Fe(1)	37598(13)	25000	25152(6)	435(3)
P(1)	35198(2)	10804(8)	24078(8)	463(4)
O(1)	73(7)	2500	2613(4)	65(2)
O(2)	5904(10)	2500	4243(4)	88(3)
O(3)	6569(8)	2500	1588(3)	66(2)
O(4)	−134(9)	2500	−1122(3)	80(3)
O(5)	4490(5)	1259(3)	−96(3)	68(2)
N(1)	685(5)	1353(3)	1100(2)	45(1)
C(1)	1479(11)	2500	2562(5)	52(3)
C(2)	5045(11)	2500	3573(5)	57(3)
C(3)	5334(10)	2500	1872(4)	49(3)
C(4)	719(10)	2500	−424(4)	49(3)
C(5)	3615(7)	1684(3)	235(3)	49(2)
C(6)	−900(7)	1152(3)	615(3)	50(2)
C(7)	−1638(7)	350(3)	610(3)	54(2)
C(8)	−740(8)	−291(3)	1114(3)	60(2)
C(9)	840(8)	−84(3)	1641(3)	59(2)
C(10)	1516(7)	746(3)	1637(3)	46(2)
C(11)	2337(10)	871(4)	3899(4)	76(3)
C(12)	1991(11)	412(5)	4583(4)	93(3)
C(13)	2549(12)	−379(5)	4739(4)	91(3)
C(14)	3428(11)	−763(5)	4229(5)	93(3)
C(15)	3787(10)	−325(4)	3538(4)	77(3)
C(16)	3214(8)	492(4)	3365(3)	56(2)
C(17)	5259(7)	479(4)	2090(3)	60(2)
C(18)	7024(8)	567(5)	2742(4)	78(3)
C(19)	4117(24)	2500	6576(10)	99(7)
C(20)	2610(29)	2500	5950(10)	152(11)
C(21)	975(25)	2500	6141(14)	169(13)
C(22)	859(25)	2500	6988(16)	221(19)
C(23)	2371(27)	2500	7622(12)	186(15)
C(24)	3991(25)	2500	7432(10)	167(14)
C(25)	5607(28)	2500	8113(12)	144(11)

Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The carbon atoms C(19) to C(25) of the toluene solvated molecule have only 1/2 site occupancy (multiplicity = 1/4).

3.7. Preparation of (CO)₃Fe(μ-EtPhPpy)₂M(SCN)₂ (M = Zn,7; Cd, 8; Hg, 9)

To a solution of complex **1** (0.29 g, 0.50 mmol) in 20 ml dichloromethane and 10 ml methanol was added solid M(SCN)₂ (0.60 mmol). The mixture was stirred at RT for 4 h. After filtration, the filtrate was concentrated to about 15 ml, then cooled to −30 °C for 20 h to give microcrystals. The crystals were filtered and dried in vacuum.

Complex **7**. Yield: pale yellow microcrystals, 0.26 g, 70%. $^{31}P\{^1H\}$ NMR: $\delta = 80.50$ ppm. Anal. Calcd. for

Table 3
Atomic coordinates of complex **8** ($\times 10^5$ for Cd and Fe atoms, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^4$ for Cd and Fe atoms, $\mathring{A}^2 \times 10^3$ for other atoms)

Atoms	X	Y	Z	U_{eq}
Cd(1)	67229(3)	15673(4)	87830(3)	496(2)
Fe(2)	54897(5)	1505(6)	78563(4)	386(3)
P(1)	6329(1)	−1161(1)	8692(1)	43(1)
P(2)	4724(1)	1522(1)	7059(1)	42(1)
C(1)	5474(5)	−3137(5)	8294(3)	61(3)
C(2)	4908(6)	−3895(6)	8349(5)	83(4)
C(3)	4551(5)	−3747(7)	8883(7)	88(4)
C(4)	4744(5)	−2868(7)	9363(5)	77(4)
C(5)	5319(5)	−2108(6)	9338(4)	64(3)
C(6)	5689(4)	−2238(5)	8811(3)	48(2)
C(7)	7404(5)	−1501(6)	10416(4)	79(3)
C(8)	7972(7)	−1147(8)	11194(5)	111(5)
C(9)	8148(7)	−68(8)	11333(5)	116(5)
C(10)	7768(7)	616(7)	10667(5)	102(4)
C(11)	7050(4)	−769(5)	9770(4)	56(3)
N(1)	7235(4)	280(4)	9894(3)	68(2)
C(12)	7071(5)	−1785(6)	8346(5)	67(3)
C(13)	7664(7)	−2687(8)	8884(6)	97(5)
C(14)	4382(4)	2884(5)	8105(4)	53(2)
C(15)	3871(5)	3388(6)	8409(4)	60(3)
C(16)	2998(6)	3253(8)	8025(6)	86(4)
C(17)	2626(5)	2580(10)	7339(6)	100(5)
C(18)	3123(5)	2057(7)	7037(5)	72(3)
C(19)	4021(4)	2208(5)	7415(3)	45(2)
C(20)	6536(5)	3776(6)	7687(4)	63(3)
C(21)	6255(5)	4514(6)	7077(5)	73(4)
C(22)	5500(6)	4312(7)	6377(5)	87(4)
C(23)	5041(5)	3394(6)	6321(5)	73(3)
C(24)	5354(4)	2676(5)	6998(4)	49(2)
N(2)	6115(3)	2862(4)	7668(3)	51(2)
C(25)	4015(4)	1177(6)	5980(3)	55(3)
C(26)	4455(6)	663(7)	5516(4)	74(3)
C(27)	4641(4)	−775(5)	7257(4)	52(3)
O(1)	4086(3)	−1348(4)	6886(3)	78(2)
C(28)	6168(4)	222(5)	7356(3)	51(2)
O(2)	6599(3)	252(4)	7016(3)	71(2)
C(29)	5218(4)	518(5)	8668(4)	52(3)
O(3)	5022(4)	703(4)	9181(3)	77(3)
N(3)	8065(4)	1749(6)	8908(5)	80(3)
C(30)	8697(5)	1995(6)	8921(4)	61(3)
S(1)	9623(2)	2295(2)	8955(2)	87(1)
N(4)	6744(4)	2880(5)	9642(3)	66(3)
C(31)	6762(4)	3769(6)	9820(4)	57(3)
S(2)	6804(2)	5009(2)	10109(2)	91(1)

Table 4
Selected bond lengths (Å) and angles (deg) in complex $2 \cdot \frac{1}{2}C_7H_8$

Mo(1)–Fe(1)	2.922(1)	Fe(1)–C(2)	1.781(7)
Mo(1)–N(1)	2.327(4)	Fe(1)–C(3)	1.788(9)
Mo(1)–C(4)	1.922(7)	O(1)–C(1)	1.129(11)
Mo(1)–C(5)	1.934(6)	O(2)–C(2)	1.141(9)
Fe(1)–P(1)	2.217(1)	O(3)–C(3)	1.165(11)
Fe(1)–C(1)	1.816(9)	O(4)–C(4)	1.176(8)
		O(5)–C(5)	1.167(7)
Fe(1)–Mo(1)–N(1)	80.8(1)		
Fe(1)–Mo(1)–C(4)	167.2(2)	P(1)–Fe(1)–C(2)	95.5(1)
N(1)–Mo(1)–C(4)	91.0(2)	C(1)–Fe(1)–C(2)	108.3(4)
Fe(1)–Mo(1)–C(5)	104.0(1)	Mo(1)–Fe(1)–C(3)	66.5(2)
N(1)–Mo(1)–C(5)	89.0(2)	P(1)–Fe(1)–C(3)	90.7(1)
C(4)–Mo(1)–C(5)	85.5(2)	C(1)–Fe(1)–C(3)	147.9(3)
N(1)–Mo(1)–N(1a)	99.8(2)	C(2)–Fe(1)–C(3)	103.8(4)
C(5)–Mo(1)–N(1a)	170.5(2)	P(1)–Fe(1)–P(1a)	168.3(1)
C(5)–Mo(1)–C(5a)	81.9(3)	Fe(1)–C(1)–O(1)	178.3(7)
Mo(1)–Fe(1)–P(1)	85.0(1)	Fe(1)–C(2)–O(2)	178.3(8)
Mo(1)–Fe(1)–C(1)	81.4(2)	Fe(1)–C(3)–O(3)	168.1(6)
P(1)–Fe(1)–C(1)	86.3(1)	Mo(1)–C(4)–O(4)	177.2(7)
Mo(1)–Fe(1)–C(2)	170.3(3)	Mo(1)–C(5)–O(5)	173.0(5)

$C_{31}H_{28}FeN_4O_3P_2S_2Zn$: C, 49.52; H, 3.77; N, 7.48. Found: C, 48.49; H, 3.82; N, 7.37. IR, ν(CO): 2015, 1940, 1884 cm^{-1}.

Complex **8**. Yield: orange crystals, 0.30 g, 75%. $^{31}P\{^1H\}$ NMR: $\delta = 76.78$ ppm. Anal. Calcd. for $C_{31}H_{28}CdFeN_4O_3P_2S_2$: C, 46.85; H, 3.55; N, 7.04. Found: C, 46.98; H, 3.67; N, 7.37. IR, ν(CO): 2014, 1927, 1868 cm^{-1}.

Complex **9**. Yield: orange microcrystals, 0.32 g, 72%. $^{31}P\{^1H\}$ NMR: $\delta = 66.82$ ppm. Anal. Calcd. for $C_{31}H_{28}FeHgN_4O_3P_2S_2$: C, 41.97; H, 3.18; N, 6.31. Found: C, 41.78; H, 3.28; N, 7.37. IR, ν(CO): 2037, 1966, 1883 cm^{-1}.

3.8. X-ray crystallography

The intensity data of compounds $2 \cdot \frac{1}{2}C_7H_8$ and **8** were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min} = 3°$, $2\theta_{max} = 55°$, 36.5° oscillation frames in the range of 0–180°, exposure 8 min per frame) [20]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting was applied using the ABSCOR program [21].

The crystal structures were determined by direct methods which yielded the positions of all non-hydrogen atoms, and subsequent difference Fourier syntheses were employed to located the remaining non-hydrogen atoms which did not show up in the initial structure. All the non-hydrogen atoms were refined 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

Table 5
Selected bond lengths (Å) and angles (deg) in complex **8**

Cd(1)–Fe(2)	2.684(1)	C(25)–C(26)	1.51(1)
Cd(1)–N(1)	2.397(5)	C(27)–O(1)	1.137(8)
Cd(1)–N(2)	2.412(5)	C(28)–O(2)	1.16(1)
Cd(1)–N(3)	2.238(8)	C(29)–O(3)	1.142(1)
Cd(1)–N(4)	2.239(7)	N(3)–C(30)	1.12(1)
Fe(2)–P(1)	2.247(2)	C(30)–S(1)	1.618(9)
Fe(2)–P(2)	2.235(2)	N(4)–C(31)	1.15(1)
Fe(2)–C(27)	1.790(6)	C(31)–S(2)	1.618(8)
		P(1)–Fe(2)–C(27)	92.3(2)
Fe(2)–Cd(1)–N(1)	88.2(1)	P(2)–Fe(2)–C(27)	91.1(2)
Fe(2)–Cd(1)–N(2)	89.9(1)	Cd(1)–Fe(2)–C(28)	76.3(2)
N(1)–Cd(1)–N(2)	176.1(2)	P(1)–Fe(2)–C(28)	90.2(2)
Fe(2)–Cd(1)–N(3)	128.5(2)	P(2)–Fe(2)–C(28)	88.3(2)
N(1)–Cd(1)–N(3)	90.6(3)	C(27)–Fe(2)–C(28)	105.9(3)
N(2)–Cd(1)–N(3)	93.2(2)	Cd(1)–Fe(2)–C(29)	75.7(2)
Fe(2)–Cd(1)–N(4)	131.9(2)	P(1)–Fe(2)–C(29)	88.1(2)
N(1)–Cd(1)–N(4)	91.4(2)	P(2)–Fe(2)–C(29)	91.8(2)
N(2)–Cd(1)–N(4)	87.3(2)	C(27)–Fe(2)–C(29)	102.2(3)
N(3)–Cd(1)–N(4)	99.5(3)	C(28)–Fe(2)–C(29)	151.9(3)
Cd(1)–Fe(2)–P(1)	88.4(1)	Cd(1)–N(3)–C(30)	169.2(6)
Cd(1)–Fe(2)–P(2)	88.3(1)	N(3)–C(30)–S(1)	177.4(7)
P(1)–Fe(2)–P(2)	176.5(1)	Cd(1)–N(4)–C(31)	152.3(6)
Cd(1)–Fe(2)–C(27)	177.7(3)	N(4)–C(31)–S(2)	177.8(6)

their parent carbon atoms in the final stage of full-matrix least squares refinement. In $2 \cdot \frac{1}{2}C_7H_8$ both molecular components are located in sites of symmetry m. The toluene solvate molecule exhibits disorder; in the model used for its refinement, all carbon atoms were assigned half site occupancy (multiplicity = 1/4), and the molecule was subjected to soft distance restraints of C–C = 1.39 ± 0.01 and C $\cdots$ C = 2.41 ± 0.01 Å for the aromatic ring, and C–CH$_3$ = 1.50 ± 0.01 Å and C $\cdots$ CH$_3$ = 2.51 ± 0.01 Å for the exocyclic carbon–carbon bond.

All computations were performed on an IBM-compatible 486 PC with the SHELTX-PC program package [22]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [23].

Information and parameters concerning crystallographic data collection and structure refinement of compounds $2 \cdot \frac{1}{2}C_7H_8$ and **8** are 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.

References

[1] Z.Z. Zhang, H. Cheng, Coord. Chem. Rev. 147 (1996) 1.
[2] Z.Z. Zhang, H.P. Xi, W.J. Zhao, K.Y. Jiang, R.J. Wang, H.G. Wang, Y. Wu, J. Organomet. Chem. 454 (1993) 221.
[3] Z.Z. Zhang, H. Cheng, S.M. Kuang, Y.Q. Zhou, Z.X. Liu, J.K. Zhang, H.G. Wang, J. Organomet. Chem. 516 (1996) 1.
[4] S.L. Li, T.C.W. Mak, Z.Z. Zhang, J. Chem. Soc. Dalton Trans. (1996) 3475.
[5] S.L. Li, Z.Z. Zhang, T.C.W. Mak, Inorg. Chim. Acta in press.
[6] S.M. Kuang, L.J. Sun, Z.Z. Zhang, Z.Y. Zhou, B.M. Wu, T.C.W. Mak, Polyhedron 15 (1996) 3417.
[7] J.R. Sowa Jr., V. Zanotti, C. Facchin, R.J. Angelici, J. Am. Chem. Soc. 113 (1991) 9185.
[8] S. Tofke, U. Brhrens, J. Organomet. Chem. 338 (1988) 29.
[9] M.E. Garcia, J.C. Jeffrey, P. Sherwood, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1987) 1209.
[10] P.G. Byrne, M.E. Garcia, J.C. Jeffrey, P. Sherwood, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1987) 1215.
[11] S.L. Li, Z.Z. Zhang, J.C.C. Chan, S.C.F. Au-Yeung, T.C.W. Mak, J. Organomet. Chem. 522 (1996) 155.
[12] F.A. Cotton, R.M. Wing, Inorg. Chem. 4 (1965) 314.
[13] J.L. Atwood, D.J. Darensbourg, Inorg. Chem. 16 (1977) 2314.
[14] G. Reinhard, B. Hirle, U. Schubert, M. Knorr, P. Braunstein, A. Decian, J. Fisher, Inorg. Chem. 32 (1993) 1656.
[15] G. Reinhard, B. Hirle, U. Schubert, J. Organomet. Chem. 427 (1992) 173.
[16] P. Braunstein, M. Knorr, A. Tiripicchio, A. Tiripicchio-Camellini, Inorg. Chem. 31 (1992) 3685.
[17] P. Braunstein, L. Douce, M. Knorr, M. Strampfer, M. Lantranchi, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1992) 331.
[18] R.D. Ernst, T.J. Marks, J.A. Ibers, J. Am. Chem. Soc. 99 (1977) 2090.
[19] V.D. Bianco, S. Doronzo, Inorg. Synth., 16 (1976) 158.
[20] J. Tanner, K.L. Krause, Rigaku J. 4 (1990) 11; Rigaku J. 7 (1990) 28. K.L. Krause, G.N. Phillips Jr., J. Appl. Crystallogr. 25 (1992) 146. M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka, T. Higashi, J. Appl. Crystallogr. 25 (1992) 348.
[21] T. Higashi, ABSCOR—An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rugaku Corporation, Tokyo, 1995.
[22] G.M. Sheldrick, SHELXL PC Manual, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.
[23] J.A. Ibers, W.C. Hamilton, in: International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, UK, 1974 (a) vol. 4, pp. 55, 99, 149; (b) vol. 3, p. 278.