

Directional $\text{Fe}-\text{C}\equiv\text{O}\cdots\text{S}$ intermolecular interaction leading to chain-like crystal packing in binuclear $\text{Fe(0)}-\text{M(II)}$ ($\text{M} = \text{Hg}, \text{Cd}$) complexes with 2-(diphenylphosphino)thiazole

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Abstract

A new thiazole-based phosphine ligand was designed to construct heterobinuclear complexes $(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{PNS})_2\text{MX}_2$ ($\text{M} = \text{Hg}, \text{X} = \text{SCN}; \text{M} = \text{Cd}, \text{X} = \text{I}; \text{Ph}_2\text{PNS} = 2\text{-(diphenylphosphino)thiazole}$), in which weak $\text{Fe}-\text{C}\equiv\text{O}\cdots\text{S}$ intermolecular interaction led to chain-like molecular packing in the solid state. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Intermolecular interaction; Thiazole-based phosphine ligand; Crystal packing; Heterobinuclear complex

1. Introduction

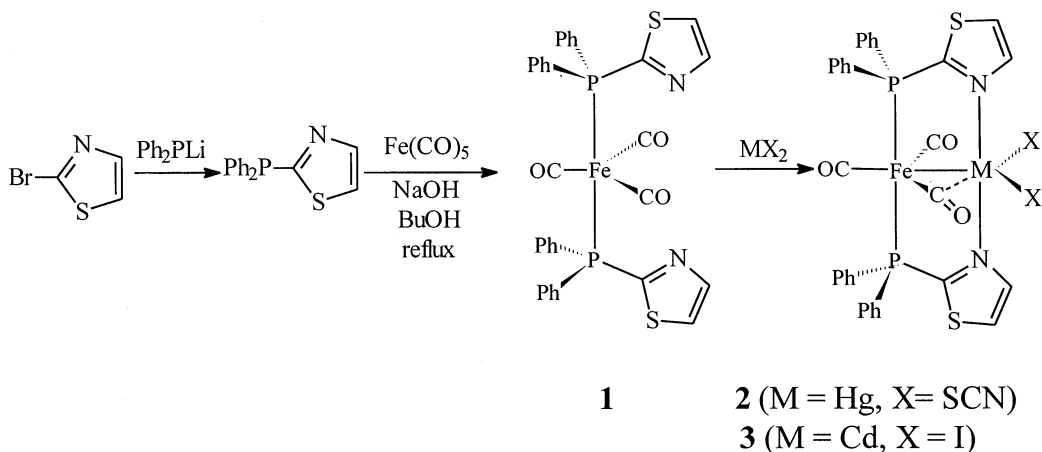
Solid-state molecular processes and reactivity, intermolecular interaction, and packing modes in organic materials have been the subject of much work and constitute the subject matter of continuing investigation [1–8]. The predictable self-organization of molecules into one-, two, or three-dimensional networks is of the utmost importance in crystal engineering. For such rational design, hydrogen bonding has been the most commonly used supramolecular cement, yet in its absence weaker interactions such as $\text{CH}\cdots\text{O}$, $\text{CH}\cdots\text{N}$, $\text{I}\cdots\text{I}$, $\text{O}\cdots\text{I}$, $\text{N}\cdots\text{Cl}$, or even $\text{C}\cdots\text{H}$ and $\text{C}\cdots\text{C}$ can be utilized [6]. In contrast, comparatively little has been done in the field of organometallic crystal engineering, in spite of increasing current interest in the solid-state behavior of organometallic compounds [9].

The formation of a crystalline solid is a process of molecular aggregation that depends primarily on the number and type of atoms, overall molecular volume

and shape, charge distribution in the molecule, and nature of intermolecular interaction ([9]b). The controlled aggregation of organometallic molecules into directional crystal packing arrangements through weak intermolecular interaction other than hydrogen bonding poses an interesting problem. A feasible approach involves the design of an organometallic compound which possesses specific interaction sites, such that intermolecular interaction occurs in a logical fashion to form an ordered molecular assembly in the crystalline state.

With this strategy in mind, we synthesized the new phosphine ligand 2-(diphenylphosphino)thiazole (Ph_2PNS), which contains potential P, N and S donor atoms (Scheme 1). It was anticipated that the rigid, short-bite *P,N*-donor set would function as a bridging ligand to form binuclear complexes consolidated by a metal–metal bond, making the exposed S atom available for directed intermolecular interaction. Here we report the weak $\text{Fe}-\text{C}\equiv\text{O}\cdots\text{S}$ intermolecular interaction which leads to aggregation of molecules into zigzag chains in the crystal structures of new binuclear $\text{Fe(0)}-\text{M(II)}$ complexes $(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{PNS})_2\text{MX}_2$ ($\text{M} = \text{Hg}, \text{X} = \text{SCN}; \text{M} = \text{Cd}, \text{X} = \text{I}$).

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Scheme 1.

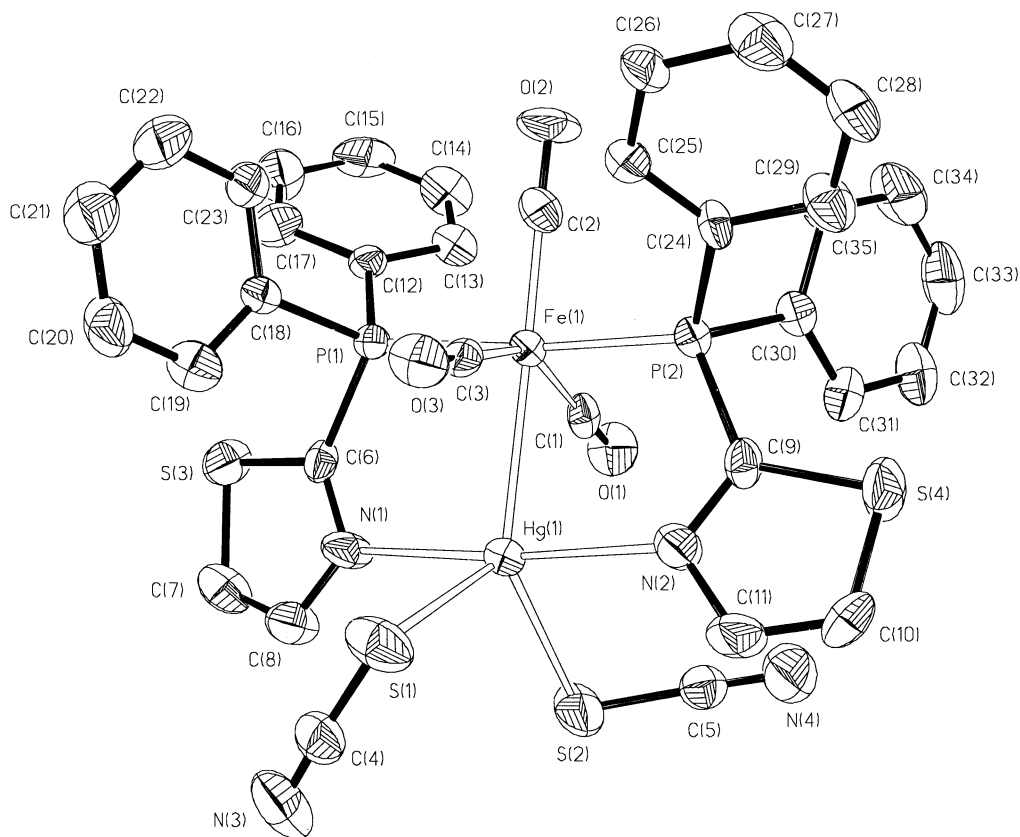


Fig. 1. Perspective view (35% thermal ellipsoids) of complex **2**. Selected bond lengths (Å) and angle (°): Fe(1)–Hg(1) 2.653(1), Fe(1)–P(1) 2.225(3), Fe(1)–P(2) 2.257(3), Fe(1)–C(1) 1.821(9), Fe(1)–C(2) 1.808(10), Fe(1)–C(3) 1.811(9), Hg(1)–S(1) 2.560(4), Hg(1)–S(2) 2.535(4), Hg(1)–N(1) 2.700(8), Hg(1)–N(2) 2.647(8), P(1)–Fe(1)–P(2) 174.4(1), Hg(1)–Fe(1)–C(2) 179.0(3), C(1)–Fe(1)–C(3) 147.4(4), Fe(1)–Hg(1)–S(1) 123.0(1), Fe(1)–Hg(1)–S(2) 130.9(1), S(1)–Hg(1)–S(2) 106.1(1), N(1)–Hg(1)–N(2) 175.3(3)°.

2. Results and discussion

Treatment of Ph_2PLi (prepared by the reaction of Ph_3P with lithium metal in THF) with 2-bromothiazole yielded the desired thiazole-based phosphinyl ligand Ph_2PNS , which was reacted with $\text{Fe}(\text{CO})_5$ and NaOH in refluxing *n*-butanol to afford a yellow precipitate formulated as *trans*-

$\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PNS})_2$, **1**. Its IR spectrum showed an intense carbonyl absorption at 1874 cm^{-1} , which implies that the local symmetry about the iron(0) atom is near D_{3h} .

Reaction of **1** with solid MX_2 gave addition products $(\text{CO})_3\text{Fe}(\mu\text{-Ph}_2\text{PNS})_2\text{MX}_2$ (M = Hg, X = SCN, **2**; M = Cd, X = I, **3**), the structures of which were determined by single crystal X-ray analysis.

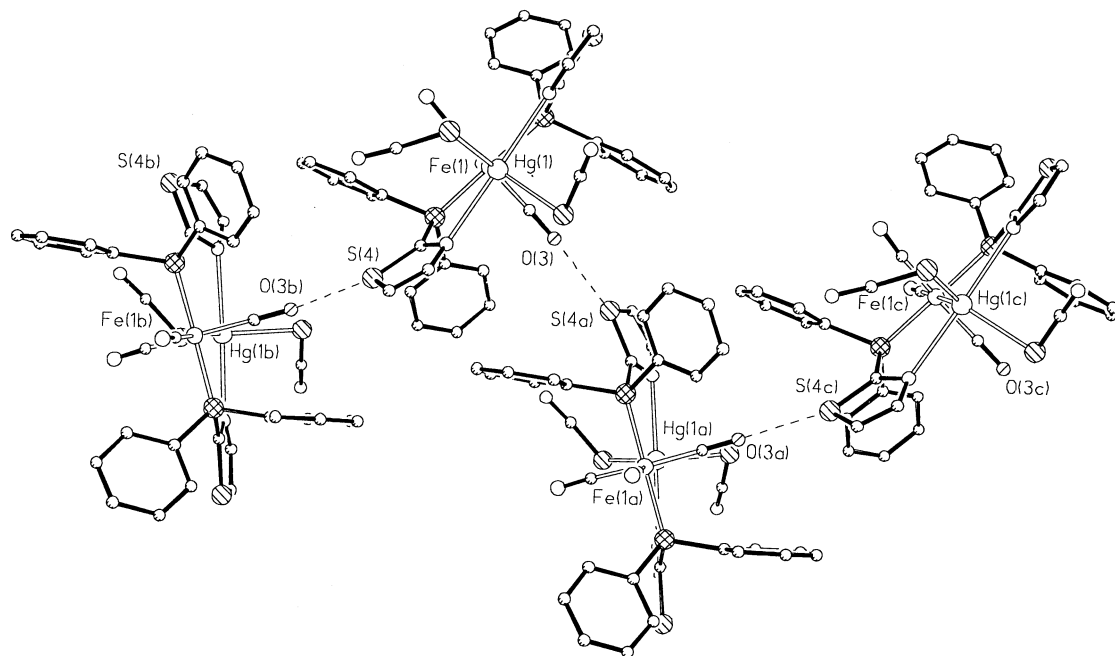


Fig. 2. Zigzag chain structure of complex **2** connected by weak intermolecular Fe–C≡O...S interaction.

Table 1

Selected intermolecular O...S distances and C≡O...S angles in some sulfur-containing iron carbonyl complexes

Compound	O...S (Å)	C≡O...S (°)	Reference
[Fe ₃ (CO) ₉ (μ ₃ -S)(μ ₃ -PPh)]	3.300	138.6	[18]
[(μ-η ² -SCSMe ₂)Fe ₂ (CO) ₆]	3.259	147.8	[19]
[(μ-CH ₃ C(O)CH ₂ SCHS)Fe ₂ (CO) ₆]	3.261	148.0	[20]
[{SC(Ph)C(O)SMe}Fe ₂ (CO) ₆]	3.225	133.7	[21]
[{μ-CF ₃ CC(CF ₃)S}Fe ₂ (CO) ₆]	3.162	133.6	[22]
[(μ-Sme) ₂ (μ-C ₂ F ₄)Fe ₂ (CO) ₆]	3.265	132.5	[23]
[Fe(CO) ₃ {η ³ -CH ₃ SC(S)PCy ₃ }CF ₃ SO ₃]	3.156	127.7	[24]
[(CO) ₈ Fe ₃ (=CNH ₂)(μ ₃ -S)(μ ₃ -P ⁱ Pr)]	3.258	148.6	[25]
[Fe ₂ (CO) ₅ {P(OMe) ₃ }{(μ-CF ₃ CC(CF ₃)S)}]	3.180	143.7	[26]
[(CO) ₃ Fe(μ-Ph ₂ PNS) ₂ Hg(SCN) ₂], 2	3.149	144.7	This work
[(CO) ₃ Fe(μ-Ph ₂ PNS) ₂ CdI ₂], 3	3.276	136.2	This work

As anticipated, in complex **2** a pair of Ph₂PNS ligands bridge between metal centers via coordination by their P,N-donor sets with the S atoms uncoordinated (Fig. 1). The iron(0) atom exhibits distorted octahedral coordination geometry with P(1)–Fe(1)–P(2) = 174.4(1), Hg(1)–Fe(1)–C(2) = 179.0(3) and C(1)–Fe(1)–C(3) = 147.4(4)°. The Hg(II) atom exhibits distorted trigonal bipyramidal coordination geometry with Fe(1)–Hg(1)–S(1) = 123.0(1), Fe(1)–Hg(1)–S(2) = 130.9(1), S(1)–Hg(1)–S(2) = 106.1(1) and N(1)–Hg(1)–N(2) = 175.3(3)°. The two phosphine ligands coordinate to the mercury atom through the N rather than the S atoms, while both thiocyanato ligands function as donors through their S terminals. The Fe(1)–Hg(1) distance, 2.653(1), is comparable to those of the Fe(0)→Hg(II) dative bond in related complexes: Fe(CO)₃(μ-Ph₂Ppy)₂Hg(SCN)₂ (2.648(3) [10], Fe(CO)₃–

(μ-Ph₂Ppy)₂HgI₂ (2.678(2)) [11] and Fe(CO)₃(μ-Ph-MePpy)₂Hg(μ-Cl)₂HgCl₂ (2.592(4) Å) [12], but much longer than that (avg. 2.515 Å) of the Fe(0)–Hg(I) complex (CO)₄Fe(HgBr)₂, [13] and those of the Fe(I)–Hg(I) binuclear complexes (CO)₃(PMe₃)(Ph₂MeSi)Fe–HgBr (2.515(3) Å) [14] and (NCS)Fe(CO)₃(μ-Ph₂Ppy)₂Hg(SCN) (2.527(2) Å) [15]. The measured Fe–P, Fe–C, Hg–N and Hg–S distances of **2** are not significantly different from the corresponding distances observed in Fe(CO)₃(μ-Ph₂Ppy)₂Hg(SCN)₂ and (NCS)Fe(CO)₃(μ-Ph₂Ppy)₂Hg(SCN).

The slightly shorter Hg(1)⋯C(3) distance of 2.748(9) Å, as compared to 2.780(9) Å for Hg(1)⋯C(1), is suggestive of a weak interaction between the mercury atom and the C(3)–O(3) carbonyl group, although it cannot be construed as a semi-bridging bonding mode [16]. Most interestingly, this weak intermolecular inter-

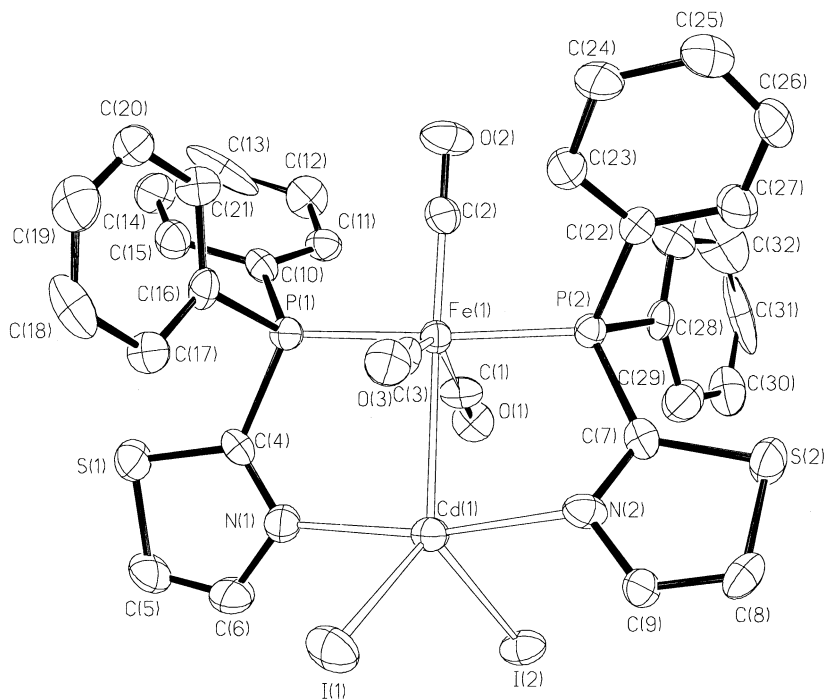


Fig. 3. Perspective view (35% thermal ellipsoids) of complex **3**. Selected bond lengths (Å) and angle (°): Fe(1)–Cd(1) 2.812(1), Fe(1)–P(1) 2.226(1), Fe(1)–P(2) 2.224(1), Fe(1)–C(1) 1.802(4), Fe(1)–C(2) 1.789(4), Fe(1)–C(3) 1.786(4), Cd(1)–I(1) 2.789(1), Cd(1)–I(2) 2.763(1), Cd(1)–N(1) 2.488(4), Cd(1)–N(2) 2.497(4); P(1)–Fe(1)–P(2) 176.6(1), Cd(1)–Fe(1)–C(2) 177.8(2), C(1)–Fe(1)–C(3) 144.0(2), Fe(1)–Hg(1)–I(1) 121.0(1), Fe(1)–Hg(1)–I(2) 128.2(1), I(1)–Cd(1)–I(2) 110.8(1), N(1)–Cd(1)–N(2) 168.9(1)°.

action in turn accounts for the selectivity of the related carbonyl group in weak intermolecular Fe–C≡O⋯S interaction. The basicity of CO increases on going from the terminal to the bridging mode so that the involvement of the latter in intermolecular interaction is enhanced.

As seen from Fig. 2, weak intermolecular Fe–C≡O⋯S interaction resulted in the formation of an infinite zigzag chain structure, with an O⋯S distance of 3.149(9) Å and a C≡O⋯S angle of 144.7(9)°. Although the O⋯S distance is only slightly shorter than the sum of the van der Waals radii of the O and S atoms (1.52 + 1.80 = 3.32 Å), the stabilizing Fe–C≡O⋯S interaction is in good agreement with the well-established soft intermolecular C≡N⋯S interaction in organic systems with an angle of about 145° [17]. The observed O⋯S distance and C≡O⋯S angle in **2** are consistent with those of several known sulfur-containing iron carbonyl complexes, which were obtained from a search of the Cambridge Structural Database (Table 1), although to our knowledge the directionality characteristics of this type of intermolecular interaction has not been discussed in the literature.

The molecular structure of binuclear compound **3** (Fig. 3) is similar to that of **2** with substitution of the Hg(NCS)₂ fragment by CdI₂, yielding an Fe(0)–Cd(II) bond distance of 2.811(1) Å. The weak intermolecular Fe–C≡O⋯S interaction likewise leads to an infinite zigzag chain structure, with an O⋯S distance of 3.276(9)

Å and a C≡O⋯S angle of 136.2(9)°.

In summary, we have taken advantage of the specific donor sites of the new phosphine ligand Ph₂PNS in a rational design of crystal packing in organometallic systems. The bridging *P,N*-donor set is used to form binuclear Fe(0)–M(II) complexes with metal–metal bonding, while the weak Fe–C≡O⋯S intermolecular interaction leads to chain structures in the solid state. The CO basicity determines the effectiveness and directionality of this type of weak interaction, which is consistently non-linear with C≡O⋯S angles in the range 136–144° for a variety of known crystal structures.

3. Experimental section

3.1. General procedure, measurement, and materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. The ¹H-NMR spectra were recorded on a Bruker-300 NMR spectrometer using Si(Me₄) as the external standard and CDCl₃ as solvent. The ³¹P{¹H}-NMR spectra were recorded on a Bruker-500 NMR spectrometer at 202.45 MHz using 85% H₃PO₄ as the external standard and CDCl₃ as solvent. The solvents were purified by standard methods. IR spectra were measured on a Perkin Elmer 1600 spectrometer.

Table 2
Crystal data for **2** and **3**

Formula	C ₃₅ H ₂₄ FeHgN ₄ O ₃ P ₂ S ₄ (2)	C ₃₃ H ₂₄ CdFeI ₂ N ₂ O ₃ P ₂ S ₂ (3)
Formula weight	995.2	1044.66
Temperature (K)	294	294
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ (no. 19)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
Unit-cell dimensions		
<i>a</i> (Å)	13.993(2)	13.758(3)
<i>b</i> (Å)	14.036(2)	14.110(3)
<i>c</i> (Å)	19.143(1)	19.104(4)
β (°)	90	91.58(3)
<i>V</i> (Å ³)	3760(2)	3707.2
<i>Z</i>	4	4
<i>F</i> (000)	1944	2016
<i>D</i> _{calc.} (g cm ^{−3})	1.758	1.875
λ , Å (Mo–K α)	0.71073	0.71073
μ (cm ^{−1})	4.812	2.844
Collection range	2 θ = 3–52°	2 θ = 3–50°
Goodness-of-fit index	1.12	0.76
Number of unique reflections	4115	5557
Number of observed reflection ($ F \geq 4\sigma(F)$)	2982	2825
Number of variables, <i>p</i>	452	415
<i>R</i> _{<i>f</i>} ^a	0.034	0.085
<i>R</i> _{<i>wF</i>} ^b	0.065	0.124

^a $R_f = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$.

^b $R_{wF}^2 = [\Sigma w(|F_o| - |F_c|)^2] / [\Sigma w|F_o|^2]^{1/2}$.

3.2. Preparation of Ph₂PNS

Lithium strips (0.8 g, 230 mmol) was finely cut and added to a solution of Ph₃P (13.2 g, 50 mmol) in 100 ml THF. The mixture was stirred at room temperature (r.t.) for 6 h, after which the solution was transferred to another flask with a canula. Then 2-chloro-2-methylpropane (4.6 g, 50 mmol) in 20 ml THF was added dropwise at 0°C to remove PhLi, after which the mixture was stirred at r.t. for 1 h. Then the mixture was cooled to −78°C, 2-bromothiazole (8.2 g, 50 mmol) in 20 ml THF was added dropwise, and the resulting solution warmed to r.t. slowly and stirred for another 5 h. After the solvent was nearly completely removed, 100 ml of distilled water and 100 ml of CH₂Cl₂ was added to the mixture. The organic layer was separated and the aqueous layer extracted twice with CH₂Cl₂ (2 × 20 ml). The organic fraction collected was dried with anhydrous Na₂SO₄ overnight and then fractionated (128–32°C, 1 mmHg) to give a colorless liquid (6.80 g yield: 51%, ³¹P{H}-NMR: δ = −2.7 ppm), which was purified by column chromatography.

3.3. Preparation of *trans*-Fe(Ph₂PNS)₂(CO)₃, **1**

This compound was synthesized by the method used for *trans*-Fe(Ph₂Ppy)₂(CO)₃ as described previously [10]. Yield: yellow microcrystals, 70% yield.

Anal. Calc. for C₃₃H₂₄FeN₂O₃P₂S₂: C, 58.42; H, 3.59; N, 4.13. Found: C, 58.23; H, 3.50; N, 4.09. ³¹P{H}-NMR: δ = 75.4 ppm. IR ν (CO): 1879 cm^{−1}.

3.4. Reaction of *trans*-Fe(Ph₂PNS)₂(CO)₃ with Hg(SCN)₂

To a solution of complex **1** (0.34 g, 0.50 mmol) in 20 ml dichloromethane was added solid (0.19 g, 0.6 mmol) Hg(SCN)₂. The mixture was stirred at r.t. for 4 h. After filtration, the filtrate was concentrated to about 15 ml, then cooled to −30°C for 20 h to give microcrystals of **2**. Yield: orange crystals, 0.37 g, 74%. Anal. Calc. for C₃₅H₂₄FeHgN₄O₃P₂S₄: C, 42.24; H, 2.43; N, 5.63. Found: C, 42.08; H, 2.46; N, 5.60. ³¹P{H}-NMR: δ = 62.9 ppm. IR, ν (CO): 2029, 1976, 1965 cm^{−1}.

3.5. Reaction of *trans*-Fe(Ph₂PNS)₂(CO)₃ with CdI₂

The above procedure was repeated, except that CdI₂ (0.22 g, 0.60 mmol) was used instead of Hg(SCN)₂. Recrystallization from dichloromethane/methanol gave pale yellow crystals of **3**. Yield: orange microcrystals, 0.32 g, 62% yield. Anal. Calc. for C₃₃H₂₄CdFeI₂N₂O₃P₂S₂: C, 37.94; H, 2.32; N, 2.68. Found: C, 37.60; H, 2.34; N, 2.62. ³¹P{H}-NMR: δ = 71.9 ppm. IR, ν (CO): 2015, 1940, 1886 cm^{−1}.

3.6. X-ray crystallography

Orange crystals of **2** and pale yellow crystals of **3** were grown in a 1:1 mixture of dichloromethane and methanol. The intensity data of **2** and **3** were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\min} = 4$, $2\theta_{\max} = 52$, 5° oscillation frames in the range of 0 – 180° , exposure 8 min per frame) [27]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program [28]. The crystal structures were determined by direct methods and 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 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^2 data.

All computation were performed on an IBM-compatible 486 PC with the SHELXL-PC program package [29]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [30].

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 2.

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