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Synthesis and structure of $[Fc(RO)PS_2]^-$ complexes

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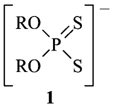
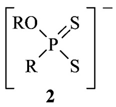
Reaction of $Fc(S)PS_2P(S)Fc$ with NaOR [R = Me, ^{i}Pr] gives the non symmetric phosphonodithioato anions $[Fc(RO)PS_2]^-$ which can be complexed to a range of metals. The square planar NiL_2 complexes adopt two distinct configurations, '*trans*' with the ferrocenyl groups above and below the square plane and '*cis*' with the ferrocenyl groups on the same side of the square plane. There is good evidence that the isomerisation occurs *via* a *cis*-$ML_2(solv)_2$ intermediate. The zinc and cadmium complexes adopt dimeric M_2L_4 structures whilst the PbL_2 complex has a distorted pyramidal structure and forms infinite chains *via* Pb ··· S interactions. All new compounds have been characterised spectroscopically and seven demonstrative X-ray structures are reported.

Organodithio- derivatives of phosphorus have been widely studied since the beginning of the twentieth century.[1] Phosphodithioates, their corresponding acids and metal complexes have been shown to have many commercial applications. Historically compounds of this type have been used as floatation reagents for the recovery of metals from their solutions,[2] additives to lubricant oils,[3] pesticides and for chemical warfare.[4] More recently research has been conducted on attempts to use these compounds to form liquid transition metal complexes, specifically of Pt, for use in the preparation of thin layers by chemical vapour deposition (CVD) or of polymer–inorganic nanocomposites.[5] Other recent papers have looked at the biological and potential medicinal uses of dithiophosphate metal complexes for example it has been shown that tin diphenyldithiophosphinato complexes exhibit considerable antiproliferation activity towards certain leukaemia cells.[6]

There is a great deal of literature available detailing the synthesis, chemistry and structural studies of the complexes of phosphorodithioate (**1**) and dithiophosphinodithioate (**3**) ligands[5–7] including recent work conducted within our laboratory where the thirty year old mystery of the structure of 'basic' zinc *O*,*O'*-dialkyldithiophosphates (ZDDPs) was finally elucidated by X-ray crystallography.[8] The same cannot be said for compounds of phosphonodithioate (**2**) ligands.


1
Phosph**oro**dithioate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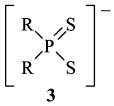
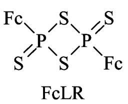

3
Phosph**ino**dithioate

The potentially interesting and varied chemistry of these compounds has been largely overlooked until very recently. Aragoni *et al.* have reported the synthesis and characterisation of several monomeric structures involving two organodithiophosphonate ligands attached to a metal centre (Ni^{2+},$Pd^{2+}$and Pt^{2+}) in a square planar conformation.[9] They have achieved this *via* a ring opening reaction involving the well known thionation compound Lawesson's Reagent. The chemical behaviour of Lawesson's Reagent is well known and has been studied thoroughly for many years.[10]

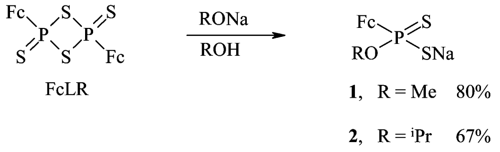

FcLR

By comparison the chemistry of Ferrocenyl Lawesson's Reagent (FcLR) has received little attention. Since the synthesis of FcLR, first published in 1996,[11] the reactivity of FcLR towards organic substrates has been shown to yield a great number of varied P–S–C heterocyclic systems. Cycloaddition reactions of FcLR with a range of organic systems containing unsaturated C–N linkages have been studied and shown to form many new and potentially useful C–P–S–N heterocycles.[12] Studies have also been conducted on the behaviour of FcLR towards unsaturated C–C bonds, reactions with strained bicyclic alkenes *via* simple cycloaddition reactions give rise to a variety of fused 4-membered C_2PS ring containing compounds.[13]

As of yet the metal complexation chemistry of FcLR has been largely overlooked with only a handful of complexes reported.[11] Here we report a route to cleave the dimeric structure of FcLR giving stable phophonodithioate salts for ligation to various metals. Ni, Pd, Pt, Zn, Cd, Hg, Sn and Pb complexes with several phosphonodithioate ligands have been studied by IR, mass spectroscopy, multinuclear NMR and in several cases by X-ray crystallography and have been shown to exhibit a variety of different and interesting binding modes.

Results and discussion

The phosphonodithioate salts **1** and **2** were prepared by the reaction of FcLR with 2 molar equivalents of NaOMe in methanol and NaO^{i}Pr in isopropyl alcohol generating **1** and **2**, respectively, [eqn. (1)].



(1)

FcLR undergoes a ring opening reaction allowing the dimer to be cleaved and the sodium salts **1** and **2** to be isolated as bright yellow powders in high yield. Both salts are soluble in polar solvents such as methanol and acetone but are insoluble in less polar solvents *e.g.* dichloromethane, chloroform *etc.* The two salts are air stable both as solids and in solution. The ^{31}P NMR spectra of **1** and **2** displayed sharp singlets at δ(P) 112.1 and 106.7 ppm, respectively. The ^{1}H NMR and ^{13}C NMR spectra of both compounds were as expected confirming the presence of both the ferrocenyl and alkoxy substituents. The IR spectra clearly shows strong bands at 1181, 1010, 579 and 503 cm^{-1} for **1** and 1175, 1024, 584 and 488 cm^{-1} for **2**, these can be attributed to ν[(P)–O–C], ν[P–O–(C)], $\nu(PS)_{asym}$ and $\nu(PS)_{sym}$ absorptions, respectively.[14] Mass spectrometry showed the parent ions as $(M–Na)^+$ at *m*/*z* 311 and 339, respectively, as expected. Although the microanalysis of **1** and **2** proved to be relatively poor, the purity of both salts was deemed satisfactory for use in further reactions.

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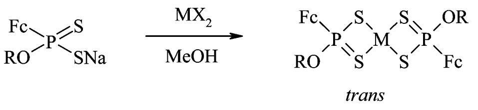
Table 1 Selected bond lengths (Å) and angles (°)

	3m	**3m-*cis***	**4m**	**6m**	**8m**	**10p**
M(1)–S(1)	2.234(1)	2.213(1)	2.344(1)	2.561(2)	2.369(1)	2.736(4)
M(1)–S(2)	2.230(1)	2.221(1)	2.345(1)	2.654(3)	2.419(2)	2.943(4)
M(1)–S(21)	—	—	—	2.560(2)	2.316(1)	2.721(3)
M(1)–S(22)	—	—	—	2.548(3)	2.323(1)	2.950(3)
P(1)–S(1)	2.011(2)	1.988(2)	2.015(1)	2.014(3)	2.002(2)	2.016(5)
P(1)–S(2)	2.004(2)	2.001(2)	2.009(1)	1.995(3)	2.002(2)	1.999(4)
P(21)–S(21)				2.007(3)	1.999(2)	2.017(5)
P(21)–S(22)	—	—	—	1.986(3)	2.010(2)	1.999(4)
P(1)–O(11)	1.581(3)	1.581(2)	1.584(2)	1.588(6)	1.597(3)	1.587(9)
P(21)–O(31)	—	—	—	1.600(5)	1.588(3)	1.577(8)
P(1)–C(1)	1.769(4)	1.766(3)	1.765(3)	1.756(8)	1.762(4)	1.751(12)
P(21)–C(21)	—	—	—	1.759(9)	1.765(4)	1.781(13)
S(1)–M(1)–S(2)	88.20(4)	88.38(5)	84.39(2)	78.51(7)	86.01(5)	71.21(10)
S(1)–P(1)–S(2)	101.40(7)	101.59(6)	103.00(4)	110.88(14)	109.32(8)	111.1(2)
S(21)–M(1)–S(22)	—	—	—	105.32(8)	122.52(5)	71.40(9)
S(22)–P(1)–S(21)	—	—	—	116.08(15)	114.51(8)	111.3(2)

Group 10 metals (Ni, Pd and Pt) in the oxidation state 2+ were stirred at room temperature in methanol with two equivalents of phosphonodithioate salt to yield complexes of the type ML_2 ($L = [Fc(OR)PS_2]^-$), (**3**–**5**) [eqn. (2)],



$MX_2 = NiCl_2$, $Pd(PhCN)_2Cl_2$ and $Pt(PhCN)_2Cl_2$ (2)

M	=		R	=			R	=		
		Ni			Me,	**3m**			^{i}Pr,	**3p**
		Pd			Me,	**4m**			^{i}Pr,	**4p**
		Pt			Me,	**5m**			^{i}Pr,	**5p**

with the exception of Ni^{2+} with **2** which required refluxing in order to achieve reaction. The metal complexes were isolated in varying yields (48–87%) as either brown, orange or yellow powders. All are air stable and soluble in both dichloromethane and chloroform. The ^{31}P NMR spectra of **3m** and **3p** display sharp singlets at δ(P) 110.1 and 102.8 ppm, respectively, showing that complexation has little effect on the chemical shift. In the cases of compounds **4m**, **4p**, **5m** and **5p** each spectrum contains a pair of singlets of roughly equal intensity indicating the presence of isomeric forms which we believe to be *cis* and *trans* isomers, *i.e.* ferrocenyl groups on the same side of the molecule – *cis*, on the opposite – *trans*. The presence of two distinct isomers in solution is further substantiated by ^{1}H and ^{13}C NMR, **3m** and **3p** show exactly the same pattern as their corresponding "free phosphonodithioate salts". However in the case of **4m**, **4p**, **5m** and **5p** each spectrum contains the expected ^{1}H and ^{13}C NMR patterns observed for the "free salts", but each set of resonances is accompanied by a second set of matching peaks that are very close in chemical shift indicating the presence in solution of two very similar species. IR spectra of compounds **3**–**5** were virtually unchanged by complexation and in all cases mass spectrometry found the expected $(M)^+$.

The X-ray structures of **3m** and **4m** (Fig. 1, Table 1) are isomorphous and reveal square planar geometry about the metal centre with symmetric MS_2P rings [*i.e.* ion contrast to some dithiophosphates which are reported to have unsymmetrical P–S bond lengths[6]]. The ferrocenyl groups of the two ligands are arranged above and below the metal coordination plane in a '*trans*' arrangement.

As mentioned above we detected two isomers from several of the reactions. We speculated that the isomers would be a consequence of the relative arrangement of the ferrocenyl groups. Furthermore, several papers have been published reporting the chemistry of metal dithiophosphate complexes towards coordinating bases.[15] Small bases, *e.g.* pyridine, 3-picoline and benzimidazole, have been shown to bind to nickel dithiophosphate complexes to form pseudo-octohedral structures.[15] We treated **3m** with pyridine and were able to crystallise two products [eqn. (3)].

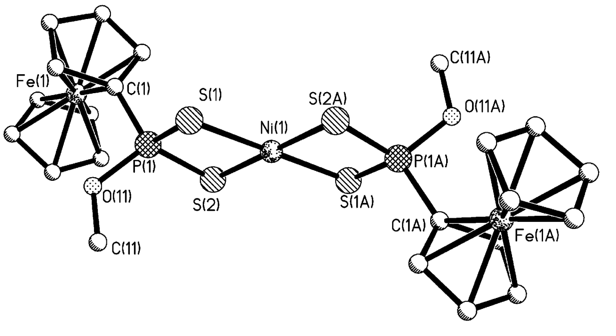
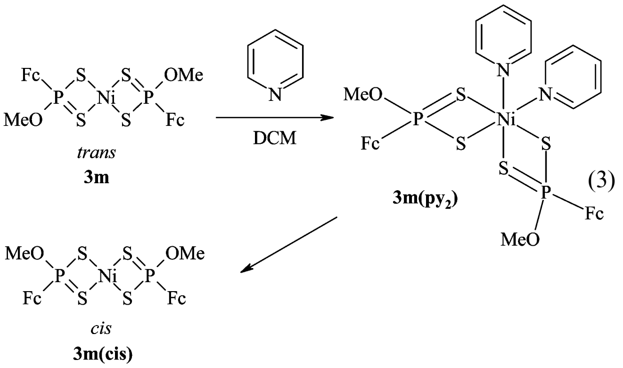


Fig. 1 The X-ray structure of **3m**, the structure of **4m** is isomorphous and is not reproduced.



(3)

Slow evaporation from an acetone solution yielded dark brown crystals of the *cis* isomer of **3m** suitable for X-ray analysis while slow evaporation from dichloromethane yielded very poor quality green crystals of **3mpy$_2$**. The X-ray structure of **3m-*cis*** (Fig. 2) reveals square planar geometry about the nickel centre with the configurational change having little effect on the coordination bondlengths and angles. The structure of **3mpy$_2$** is of very poor quality, despite collecting data on five different crystals at a variety of temperatures. Although not amenable to complete refinement the structure does confirm the *cis* arrangement of the pyridine groups (Fig. 3) and thus represents a mechanistic pathway for the isomerisation in these ML_2 complexes.

Group 12 metals (Zn, Cd and Hg) in the oxidation state 2+ were either stirred at room temperature or refluxed in the

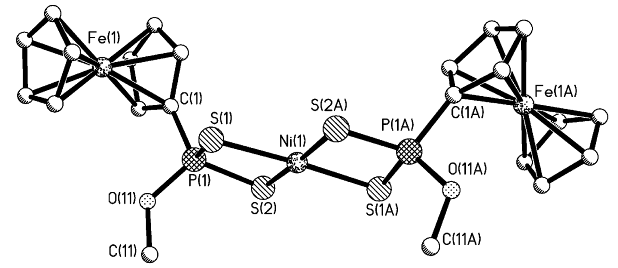


Fig. 2 The X-ray structure of the **3m-*cis*** isomer.

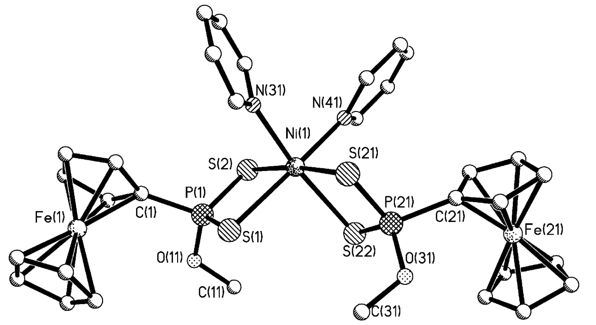
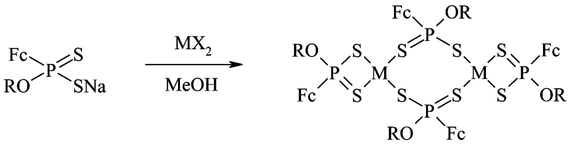


Fig. 3 The partially refined X-ray structure of **3mpy2**. Poor crystal quality prevented full refinement and the structure is only suitable for establishing gross structure/connectivity.

methanol with two equivalents of phosphonodithioate salt to yield complexes of the type M_2L_4(L = $[Fc(OR)PS_2]^-$) (**6**–**8**) [eqn. (4)].



(4)

$MX_2 = ZnCl_2, Cd(CH_3COO)_2.2H_2O$ and $HgCl_2$

M =		R =		R =	
Cd		Me, **6m**		^{i}Pr, **6p**	
Hg		Me, **7m**		^{i}Pr, **7p**	
Zn		Me, **8m**		^{i}Pr, **8p**	

It has been shown in the literature that group 12 metal complexes of phosphorodithioate and phophinodithioate ligands can exhibit dimeric structures.[7c,f,h] This dimeric structure consists of an eight membered $M_2P_2S_4$ ring with two ligands being bidentate with both sulfurs bound to one metal atom and the other two acting as bridging ligands with their sulfur atoms binding to two different metal atoms.

The metal complexes were isolated as yellow powders in high yields (70–95%), with the exception of **8p** which was considerably lower (39%). All were air stable and soluble in both dichloromethane and chloroform. The ^{31}P, ^{1}H and ^{13}C NMR spectra of all these complexes followed exactly the same pattern as **3m** and **3p**. The ^{31}P spectra all showed distinct sharp singlets with chemical shifts in the range δ(P) 101 to 113 ppm. This would indicate that in solution these complexes do not behave as simple dimers as we would expect to see two distinct phosphorus environments of equal intensity for each complex. The same question arose in earlier studies of phophorodithioate and phophinodithioate complexes of group 12 metal where it was postulated that there is an equilibrium present where the molecule rapidly interchanges between a monomeric and dimeric structure.[16] This equilibrium must be faster than the NMR timescale hence we see an average of the signals giving us singlets in our spectra.

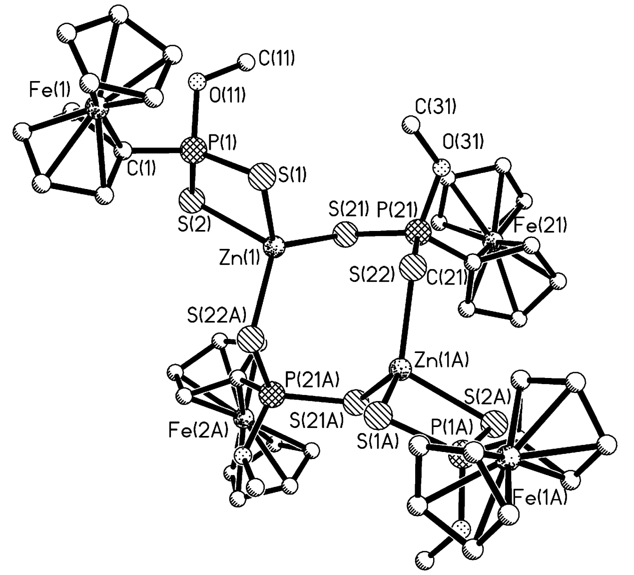
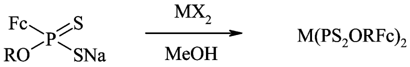


Fig. 4 The X-ray structure of **8m**; the cadmium analogue, **6m**, is structurally closely related and is not illustrated.

As was the case for **3**–**5**, the IR spectra of compounds **6**–**8** were virtually unchanged by complexation. In the mass spectra of **6**–**8** the expected $(M)^+$ ion could not be found, the most prominent fragments were the loss of one phosphonodithioate ligand, $(M–Fc(OR)PS_2)^+$ and $(1/2M)^+$.The structures of **6m** and **8m** were determined and confirmed the dimeric nature of the complexes in the solid state, with the structures being closely related to the symmetric $Zn_2[S_2P(OBu)_2]_4$ which we have described previously.[8]

Similar reactions to those described above carried out with two of the group 14 metals (Sn^{2+} and Pb^{2+}) giving yellow powders in high yields [eqn. (5)].



$MX_2 = SnCl_2, Pb(CH_3COO)_2.3H_2O$ (5)

M =		R =		R =	
Sn		Me, **9m**		^{i}Pr,	**9p**
Pb		Me, **10m**		^{i}Pr,	**10p**

As with phosphonodithioate complexes of the group 12 metals the ^{31}P, ^{1}H and ^{13}C NMR spectra were analogous to those of **3m** and **3p** and the IR spectra were very similar. As in the case of **6**–**8**, in the mass spectra of **9m**, **9p**, **10m** and **10p** the most prominent fragments were again the loss of one phophonodithioate ligand, $(M–Fc(OR)PS_2)^+$ and $(1/2M)^+$, indicating the presence of a dimeric structure in solution. This is surprising as **10p** has been shown crystallographically to be a monomer suggesting that in these cases a more complicated equilibrium than that postulated for **6**–**8** may be occurring in solution.

Very few tin compounds of this type have been investigated, only one compound has been studied by single X-ray crystallography, $[Sn\{(OPh)_2PS_2\}_2]_2$, exhibiting a dimeric structure similar to **6m** and **8m** (Fig. 4). Several structures of lead phosphorodithioate complexes have been determined, $[Pb\{(OR)_2PS_2\}_2]_n$, with R = Et,[17,18] ^{i}Pr,[19] Bu[18] and Ph,[18] each with a different stuctural motif. Bis(diethylphosphorodithioato)lead exhibits a structure of the same type as **10p**, the structure is built up of distorted tetragonal pyramids, with the apical lead atom 1.41 Å above the basal S_4 plane and the ligands anisobidentate. The molecules are linked by Pb ··· S interactions [Pb(1) ··· S(2A) 3.892(3), Pb(1) ··· S(22B) 4.039(4) Å] to form chains running along the *b* axis (Fig. 5).

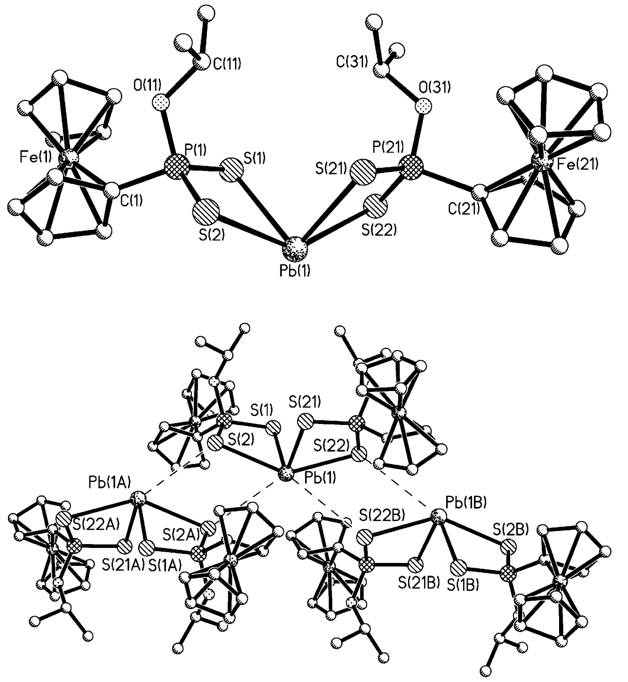


Fig. 5 The X-ray structure of **10p**. Upper diagram, single molecule; lower diagram, chain like packing in the solid state.

This work clearly demonstrates the versatile coordination behaviour of the $[Fc(RO)PS_2]^-$ ligand.

Experimental

General

Unless otherwise stated, operations were carried out under an oxygen-free nitrogen atmosphere using predried solvents and standard schlenk techniques. $Pd(PhCN)_2Cl_2$,[20] $Pt(PhCN)_2Cl_2$[21] and Ferrocenyl Lawesson's Reagent[11] (FcLR) were prepared using literature procedures. All other reagents were used as purchased from either Aldrich, Acros or Lancaster and used as received. Infrared spectra were recorded as KBr discs in the range 4000–250 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^1H, ^{31}P and ^{13}C NMR spectra were recorded using a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalyses were performed by the University of St. Andrews microanalysis service. Mass spectra were recorded by both the University of St. Andrews mass spectrometry service and the Swansea mass spectrometry service. We are grateful to Johnson Matthey PLC for the loan of precious metals.

Synthesis

(Methoxy)ferrocenylphosphonodithioate sodium salt (1). A mixture of MeONa (0.19 g, 3.57 mmol) and FcLR (1 g, 1.79 mmol) in methanol was refluxed for 17 h. The resulting brown–orange solution was filtered through a small celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to *ca.* 5 cm^3 and a 50 : 50 diethyl ether–hexane mixture (40 cm^3) was added to precipitate the product as a bright yellow solid (0.951 g, 79.7%). Found (Calc. for $C_{11}H_{12}NaOFePS_2$): C 37.13 (39.54), H 3.71 (3.62), S 17.77 (19.19)%. ^{31}P NMR (methanol D_3) δ: 112.1. ^1H NMR (methanol D_3) δ: 4.51 (m, 2H, Fc substituted ring), 4.24 (s, 5H, Fc unsubstituted ring), 4.21 (m, 2H, Fc substituted ring), 3.42 (d, 3H, $^3J(^{31}P–^1H)$ 14.6 Hz, CH_3. ^{13}C NMR (methanol D_3). ^{13}C NMR (methanol D_3) δ: 87.4 (d, $^1J(^{31}P–^{13}C)$ 124.9 Hz, Fc substituted ring C-1), 73.3 (d, $^2J(^{31}P–^{13}C)$ 14.4 Hz, Fc substituted ring), 71.7 (s, Fc unsubstituted ring), 71.3 (d, $^3J(^{31}P–^{13}C)$ 11.1 Hz, Fc substituted ring), 51.4 (d, $^2J(^{31}P–^{13}C)$ 6.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1181 (m), 1010 (s), 579 (s) and 503 (s). Mass Spec (ESI): $(M–Na)^+$ 311.

(Isopropoxy)ferrocenylphosphonodithioate sodium salt (2). Small pieces of sodium (0.15 g, 6.52 mmol) were stirred in propan-2-ol (20 cm^3) with gentle heating until fully dissolved. To this solution FcLr (1.46 g, 3.26 mmol) was added and heated to reflux for 15 h. The resulting brown–orange solution was filtered through a small celite pad. The filtrate was concentrated under vacuum to *ca.* 5 cm^3, hexane (30 cm^3) was added and the mixture was cooled to 5 °C for 18 h to precipitate the product as a bright yellow solid (1.572 g, 66.5%). Found (Calc. for $C_{13}H_{16}NaOFePS_2$): C 44.90 (43.11), H 5.40 (4.45), S 16.14 (17.71)%. ^{31}P NMR (methanol D_3) δ: 106.7. ^1H NMR (methanol D_3) δ: 4.69 (dsept = septet of doublets, 1H, $^3J(^{31}P–^1H)$ 2.2 Hz, $^3J(^1H–^1H)$ 6.2 Hz, CH), 4.57 (m, 2H, Fc substituted ring), 4.27 (s, 5H, Fc unsubstituted ring), 4.24 (m, 2H, Fc substituted ring), 1.14 (d, 6H, $^4J(^{31}P–^1H)$ 6.2 Hz, CH_3). ^{13}C NMR (methanol D_3) δ: 87.4 (d, $^1J(^{31}P–^{13}C)$ 123.5 Hz, Fc substituted ring C-1), 71.4 (d, $^2J(^{31}P–^{13}C)$ 14.2 Hz, Fc substituted ring), 69.9 (s, Fc unsubstituted ring), 69.4 (d, $^3J(^{31}P–^{13}C)$ 11.4 Hz, Fc substituted ring), 68.0 (d, $^2J(^{31}P–^{13}C)$ 7.3 Hz, CH), 23.3 (d, $^3J(^{31}P–^{13}C)$ 4.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1175 (m), 1024 (m), 584 (m) and 488 (s). Mass Spec (ESI): $(M–Na)^+$ 339.

Bis[(methoxy)ferrocenylphosphonodithioato]Ni (3m). $NiCl_2$ (0.018 g, 0.139 mmol) was added to a flask containing salt **1** (0.092 g, 0.275 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate red precipitate formed. The reaction mixture was stirred for a further 20 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a brown–red solid (0.044 g, 48%). Dark brown crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane solution. Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Ni$): C 39.12 (38.83), H 3.22 (3.55), S 18.96 (18.83)%. ^{31}P NMR ($CDCl_3$) δ: 110.1. ^1H NMR ($CDCl_3$) δ: 4.69 (m, 2H, Fc substituted ring), 4.50 (m, 2H, Fc substituted ring), 4.44 (s, 5H, Fc unsubstituted ring), 3.96 (d, 3H, $^3J(^{31}P–^1H)$ 15.1 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 79.1 (d, $^1J(^{31}P–^{13}C)$ 124.6 Hz, Fc substituted ring C-1), 71.8 (d, $^3J(^{31}P–^{13}C)$ 12.5 Hz, Fc substituted ring), 71.1 (d, $^2J(^{31}P–^{13}C)$ 16.6 Hz, Fc substituted ring), 70.4 (s, Fc unsubstituted ring), 52.1 (d, $^2J(^{31}P–^{13}C)$ 6.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1185 (s), 1020 (s), 601 (s) and 492 (m). Mass Spec (EI+): $(M)^+$ 680.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Ni (3p). $NiCl_2$ (0.012 g, 0.093 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, no immediate reaction occurred. The reaction mixture was refluxed for 1.5 h resulting in a brown solution. The solvent was removed under reduced pressure, the resulting orange–brown solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and a 50 : 50 diethyl ether–hexane mixture (15 cm^3) was added to precipitate the product as a brown solid (0.053 g, 87%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Ni$): C 42.14 (42.36), H 4.09 (4.38), S 17.16 (17.40)%. ^{31}P NMR ($CDCl_3$) δ: 102.8. ^1H NMR ($CDCl_3$) δ: 5.23 (dsept, 1H, $^3J(^{31}P–^1H)$ 2.2 Hz, $^3J(^1H–^1H)$ 6.2 Hz, CH), 4.71 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.40 (s, 5H, Fc unsubstituted ring), 1.42 (d, 6H, $^3J(^1H–^1H)$ 6.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 79.9 (d, $^1J(^{31}P–^{13}C)$ 126.1 Hz, Fc substituted ring C-1), 71.9 (d, $^2J(^{31}P–^{13}C)$ 13.1 Hz, Fc substituted ring), 71.7 (d, $^3J(^{31}P–^{13}C)$ 13.1 Hz, Fc substituted ring), 71.7 (d, $^2J(^{31}P–^{13}C)$ 7.5 Hz, CH), 70.6 (s, Fc unsubstituted ring), 24.8 (d, $^3J(^{31}P–^{13}C)$ 4.6 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1187 (m), 1030 (m), 595 (s) and 492 (m). Mass Spec (EI+): $(M)^+$ 736.

Bis[(methoxy)ferrocenylphosphonodithioato]Pd (4m). Method (a): K_2PdCl_2 (0.03 g, 0.092 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, no immediate reaction occured. The reaction mixture was stirred for 1 h and an orange precipitate was obvious. The solvent was removed under reduced pressure, the resulting orange solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and a 50 : 50 diethyl ether–hexane mixture (15 cm^3) was added to precipitate the product as an orange solid (0.035 g, 53%).

Method (b): $PdCl_2(PhCN)_2$ (0.035 g, 0.092 mmol) was added to a flask containing salt **1** (0.06 g, 0.092 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate brown precipitate formed. The reaction mixture was stirred for a further 10 min to ensure completion. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a brown solid (0.047 g, 72%).

Red crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane solution. Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Pd$): C 36.37 (36.26), H 3.01 (3.32), S 17.14 (17.60)%.

Isomer (a). ^{31}P NMR (CDCl$_3$) δ: 123.7. ^{1}H NMR (CDCl$_3$) δ: 4.67 (m, 2H, Fc substituted ring), 4.47 (m, 2H, Fc substituted ring), 4.40 (s, 5H, Fc unsubstituted ring), 3.92 (d, 3H, ^3J(^{31}P–^{1}H) 6.7 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.4 (d, ^1J(^{31}P–^{13}C) 125.6 Hz, Fc substituted ring C-1), 71.8 (m, Fc substituted ring), 71.5 (m, Fc substituted ring), 52.5 (d, ^2J(^{31}P–^{13}C) 6.2 Hz, CH$_3$).

Isomer (b). ^{31}P NMR (CDCl$_3$) δ: 122.8. ^{1}H NMR (CDCl$_3$) δ: 4.65 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.37 (s, 5H, Fc unsubstituted ring), 3.72 (d, 3H, ^3J(^{31}P–^{1}H) 7.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.3 (d, ^1J(^{31}P–^{13}C) 126.6 Hz, Fc substituted ring C-1), 71.3 (m, Fc substituted ring), 71.5 (m, Fc unsubstituted ring), 52.4 (d, ^2J(^{31}P–^{13}C) 6.2 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1185 (m), 1028 (s), 595 (vs) and 501 (m). Mass Spec (FAB): (M)$^+$ 728.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Pd (4p). $PdCl_2$-(PhCN) (0.034 g, 0.089 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate brown precipitate formed. The reaction mixture was stirred for a further 20 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a brown solid (0.055 g, 84%).

Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Pd$): C 39.46 (39.79), H 3.72 (4.11), S 15.84 (16.34)%.

Isomer (a). ^{31}P NMR (CDCl$_3$) δ: 116.5. ^{1}H NMR (CDCl$_3$) δ: 5.07 (m, 1H, CH), 4.68 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.36 (s, 5H, Fc unsubstituted ring), 1.43 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.1 (d, ^1J(^{31}P–^{13}C) 128.2 Hz, Fc substituted ring C-1), 71.7 (m, Fc substituted ring), 71.5 (m, Fc substituted ring), 71.2 (d, ^2J(^{31}P–^{13}C) 7.2 Hz, CH), 70.3 (s, Fc unsubstituted ring), 24.6 (d, ^3J(^{31}P–^{13}C) 4.2 Hz, CH$_3$).

Isomer (b). ^{31}P NMR (CDCl$_3$) δ: 115.2. ^{1}H NMR (CDCl$_3$) δ: 5.07 (m, 1H, CH), 4.63 (m, 2H, Fc substituted ring), 4.41 (m, 2H, Fc substituted ring), 4.34 (s, 5H, Fc unsubstituted ring), 1.40 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.9 (d, ^1J(^{31}P–^{13}C) 129.6 Hz, Fc substituted ring C-1), 71.7 (m, Fc substituted ring), 71.5 (m, Fc substituted ring), 71.2 (d, ^2J(^{31}P–^{13}C) 7.3 Hz, CH), 70.3 (s, Fc unsubstituted ring), 24.5 (d, ^3J(^{31}P–^{13}C) 4.1 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1187 (m), 1028 (m), 590 (vs) and 493 (m). Mass Spec (EI+): (M)$^+$ 784.

Bis[(methoxy)ferrocenylphosphonodithioato]Pt (5m). $PtCl_2$-(PhCN)$_2$ (0.043 g, 0.091 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 10 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.056 g, 76%). Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Pt$): C 32.62 (32.33), H 2.95 (2.96), S 15.80 (15.69).

Isomer (a). ^{31}P NMR (CDCl$_3$) δ: 123.23 (s, ^2J ^{31}P–^{195}Pt 382 Hz). ^{1}H NMR (CDCl$_3$) δ: 4.71 (m, 2H, Fc substituted ring), 4.48 (m, 2H, Fc substituted ring), 4.38 (s, 5H, Fc unsubstituted ring), 4.02 (d, 3H, ^3J(^{31}P–^{1}H) 3.7 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.2 (d, ^1J(^{31}P–^{13}C) 120.4 Hz, Fc substituted ring C-1), 72.0 (d, ^3J(^{31}P–^{13}C) 13.5 Hz, Fc substituted ring), 71.4 (d, ^2J(^{31}P–^{13}C) 16.6 Hz, Fc substituted ring), 70.4 (s, Fc unsubstituted ring), 52.8 (d, ^2J(^{31}P–^{13}C) 6.2 Hz, CH$_3$).

Isomer (b). ^{31}P NMR (CDCl$_3$) δ: 120.16 (s, ^2J ^{31}P–^{195}Pt 387 Hz). ^{1}H NMR (CDCl$_3$) δ: 4.69 (m, 2H, Fc substituted ring), 4.45 (m, 2H, Fc substituted ring), 4.36 (s, 5H, Fc unsubstituted ring), 3.96 (d, 3H, ^3J(^{31}P–^{1}H) 3.46 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.8 (d, ^1J(^{31}P–^{13}C) 120.4 Hz, Fc substituted ring C-1), 71.8 (d, ^3J(^{31}P–^{13}C) 13.5 Hz, Fc substituted ring), 71.2 (d, ^2J(^{31}P–^{13}C) 16.6 Hz, Fc substituted ring), 70.4 (s, Fc unsubstituted ring), 52.7 (d, ^2J(^{31}P–^{13}C) 6.2 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1182 (m), 1026 (s), 595 (vs) and 502 (m). Mass Spec (FAB): (M)$^+$ 817.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Pt (5p). $PtCl_2$-(PhCN)$_2$ (0.042 g, 0.089 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, no immediate reaction occurred. The reaction mixture was refluxed for 10 min resulting in a yellow solution containing a yellow precipitate. The solvent was removed under reduced pressure, the resulting yellow solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and a 50 : 50 diethyl ether–hexane mixture (15 cm^3) was added to precipitate the product as a yellow solid (0.035 g, 48%).

Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Pt$): C 35.89 (35.75), H 3.19 (3.69), S 14.02 (14.68)%.

Isomer (a). ^{31}P NMR (CDCl$_3$) δ: 114.55 (s, ^2J ^{31}P–^{195}Pt 382 Hz). ^{1}H NMR (CDCl$_3$) δ: 5.25 (dsept, 1H, ^3J(^{31}P–^{1}H) 2.0 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 4.71 (m, 2H, Fc substituted ring), 4.45 (m, 2H, Fc substituted ring), 4.34 (s, 5H, Fc unsubstituted ring), 1.45 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.7 (d, ^1J(^{31}P–^{13}C) 130.6 Hz, Fc substituted ring C-1), 71.7 (d, ^2J(^{31}P–^{13}C) 13.3 Hz, Fc substituted ring), 71.5 (d, ^3J(^{31}P–^{13}C) 16.4 Hz, Fc substituted ring), 71.2 (d, ^2J(^{31}P–^{13}C) 7.6 Hz, CH), 70.3 (s, Fc unsubstituted ring), 24.5 (d, ^3J(^{31}P–^{13}C) 4.2 Hz, CH$_3$).

Isomer (b). ^{31}P NMR (CDCl$_3$) δ: 110.81. (s, ^2J ^{31}P–^{195}Pt 387 Hz). ^{1}H NMR (CDCl$_3$) δ: 5.25 (dsept, 1H, ^3J(^{31}P–^{1}H) 2.0 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 4.70 (m, 2H, Fc substituted ring), 4.43 (m, 2H, Fc substituted ring), 4.33 (s, 5H, Fc unsubstituted ring), 1.44 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.5 (d, ^1J(^{31}P–^{13}C) 129.4 Hz, Fc substituted ring C-1), 71.6 (d, ^2J(^{31}P–^{13}C) 13.5 Hz, Fc substituted ring), 71.4 (d, ^3J(^{31}P–^{13}C) 16.6 Hz, Fc substituted ring), 71.2 (d, ^2J(^{31}P–^{13}C) 6.8 Hz, CH), 70.3 (s, Fc unsubstituted ring), 24.4 (d, ^3J(^{31}P–^{13}C) 4.1 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1187 (m), 1028 (m), 589 (vs) and 493 (m). Mass Spec (EI+): (M)$^+$ 873.

Bis[(methoxy)ferrocenylphosphonodithioato]Cd (6m). $(CH_3COO)_2Cd\cdot 2H_2O$ (0.024 g, 0.090 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 1 h to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.046 g, 70%).

Yellow crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane solution. Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Cd$): C 35.96 (35.96), H 3.12 (3.29), S 17.17 (17.45)%.

^{31}P NMR (CDCl$_3$) δ: 112.99. ^{1}H NMR (CDCl$_3$) δ: 4.67 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.35 (s, 5H, Fc unsubstituted ring), 3.87 (d, 3H, $^3J(^{31}P–^1H)$ 15.6 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.02 (d, $^1J(^{31}P–^{13}C)$ 132.6 Hz, Fc substituted ring C-1), 71.12 (m, Fc substituted ring), 70.78 (m, Fc substituted ring), 70.02 (s, Fc unsubstituted ring), 52.14 (d, $^2J(^{31}P–^{13}C)$ 7.2 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1184 (m), 1022 (vs), 581 (m) and 504 (m). Mass Spec (MALDI): (1/2M)$^+$ 736, (M–FeS$_2$-PC$_{11}$H$_{12}$O)$^+$ 1158.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Cd (6p). (CH$_3$-COO)$_2$Cd·2H$_2$O (0.024 g, 0.090 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, no immediate reaction occurred. The reaction mixture was refluxed for 1.5 h resulting in a yellow solution. The solvent was removed under reduced pressure, the resulting yellow solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and a 50 : 50 diethyl ether–hexane mixture (15 cm^3) was added to precipitate the product as a yellow solid (0.053 g, 80%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Cd$): C 39.30 (39.49), H 4.08 (4.08), S 15.80 (16.22)%. ^{31}P NMR (CDCl$_3$) δ: 105.76. ^{1}H NMR (CDCl$_3$) δ: 5.23 (dsept, 1H, $^3J(^{31}P–^1H)$ 2.73 Hz, $^3J(^1H–^1H)$ 6.19 Hz, CH), 4.66 (m, 2H, Fc substituted ring), 4.39 (m, 2H, Fc substituted ring), 4.33 (s, 5H, Fc unsubstituted ring), 1.38 (d, 6H, $^3J(^1H–^1H)$ 6.19 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 81.1 (d, $^1J(^{31}P–^{13}C)$ 129.8 Hz, Fc substituted ring C-1), 71.8 (d, $^2J(^{31}P–^{13}C)$ 16.6 Hz, Fc substituted ring), 71.7 (d, $^2J(^{31}P–^{13}C)$ 7.3 Hz, CH), 71.4 (d, $^3J(^{31}P–^{13}C)$ 12.5 Hz, Fc substituted ring), 70.6 (s, Fc unsubstituted ring), 24.2 (d, $^3J(^{31}P–^{13}C)$ 4.2 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1184 (m), 1027 (m), 577 (s) and 493 (m). Mass Spec (MALDI): (1/2M)$^+$ 792.

Bis[(methoxy)ferrocenylphosphonodithioato]Hg (7m). HgCl$_2$ (0.025 g, 0.092 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 15 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a bright yellow powder (0.054 g, 73%). Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Hg$): C 31.52 (32.11), H 2.92 (2.94), S 15.97 (15.59)%. ^{31}P NMR (CDCl$_3$) δ: 110.67. ^{1}H NMR (CDCl$_3$) δ: 4.66 (m, 2H, Fc substituted ring), 4.46 (m, 2H, Fc substituted ring), 4.34 (s, 5H, Fc unsubstituted ring), 4.00 (d, 3H, $^3J(^{31}P–^1H)$ 15.83 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.88 (d, $^1J(^{31}P–^{13}C)$ 134.9 Hz, Fc substituted ring C-1), 71.76 (m, Fc substituted ring), 71.56 (m, Fc substituted ring), 70.52 (s, Fc unsubstituted ring), 52.32 (d, $^2J(^{31}P–^{13}C)$ 7.3 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1182 (m), 1029 (vs), 577 (s) and 499 (s). Mass Spec (MALDI): (1/2M)$^+$ 824, (M–FeS$_2$-PC$_{11}$H$_{12}$O)$^+$ 1335.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Hg (7p). HgCl$_2$ (0.024 g, 0.088 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 45 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a bright yellow powder (0.07 g, 95%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Hg$): C 34.91 (35.53), H 3.21 (3.67), S 14.04 (14.59)%. ^{31}P NMR (CDCl$_3$) δ: 105.31. ^{1}H NMR (CDCl$_3$) δ: 5.22 (dsept, 1H, $^3J(^{31}P–^1H)$ 2.47 Hz, $^3J(^1H–^1H)$ 6.19 Hz, CH), 4.66 (m, 2H, Fc substituted ring), 4.46 (m, 2H, Fc substituted ring), 4.31 (s, 5H, Fc unsubstituted ring), 1.45 (d, 6H, $^3J(^1H–^1H)$ 6.19 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.0 (d, $^1J(^{31}P–^{13}C)$ 133.9 Hz, Fc substituted ring C-1), 72.7 (d, $^2J(^{31}P–^{13}C)$ 7.3 Hz, CH), 72.0 (broad s, Fc substituted ring), 71.7 (d, $^3J(^{31}P–^{13}C)$ 13.1 Hz, Fc substituted ring), 70.8 (s, Fc unsubstituted ring), 24.3 (d, $^3J(^{31}P–^{13}C)$ 4.2 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1182 (s), 1026 (s), 570 (s) and 489 (m). Mass Spec (MALDI): (1/2M)$^+$ 880, (M–FeS$_2$PC$_{13}$H$_{16}$O)$^+$ 1420.

Bis[(methoxy)ferrocenylphosphonodithioato]Zn (8m). ZnCl$_2$ (0.013 g, 0.095 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 40 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.039 g, 63%). Orange crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Zn$): C 38.43 (38.42), H 3.27 (3.52), S 17.92 (17.65)%. ^{31}P NMR (CDCl$_3$) δ: 107.09. ^{1}H NMR (CDCl$_3$) δ: 4.66 (m, 2H, Fc substituted ring), 4.46 (m, 2H, Fc substituted ring), 4.34 (s, 5H, Fc unsubstituted ring), 3.92 (d, 3H, $^3J(^{31}P–^1H)$ 15.8 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 79.18 (d, $^1J(^{31}P–^{13}C)$ 133.90 Hz, Fc substituted ring C-1), 71.70 (d,$^3J(^{31}P–^{13}C)$ 12.45 Hz, Fc substituted ring), 71.50 (d,$^2J(^{31}P–^{13}C)$ 15.57 Hz Fc substituted ring), 70.60 (s, Fc unsubstituted ring), 52.27 (d, $^2J(^{31}P–^{13}C)$ 6.23 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1185 (m), 1028 (vs), 591 (vs) and 500 (s). Mass Spec (MALDI): (1/2M)$^+$ 686, (M–FeS$_2$PC$_{11}$-H$_{12}$O)$^+$ 1065.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Zn (8p). ZnCl$_2$ (0.012 g, 0.088 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, no immediate reaction occurred. The reaction mixture was refluxed for 1.5 h resulting in a yellow solution. The solvent was removed under reduced pressure, the resulting yellow solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and a 50 : 50 diethyl ether–hexane mixture (15 cm^3) was added to precipitate the product as a yellow solid (0.024 g, 39%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Zn$): C 42.11 (41.98), H 4.33 (4.34), S 16.64 (17.24)%. ^{31}P NMR (CDCl$_3$) δ: 101.89. ^{1}H NMR (CDCl$_3$) δ: 5.05 (dsept, 1H, $^3J(^{31}P–^1H)$ 2.2 Hz, $^3J(^1H–^1H)$ 5.76 Hz, CH), 4.65 (m, 2H, Fc substituted ring), 4.42 (m, 2H, Fc substituted ring), 4.32 (s, 5H, Fc unsubstituted ring), 1.37 (d, 6H, $^3J(^1H–^1H)$ 5.76 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 80.5 (d, $^1J(^{31}P–^{13}C)$ 134.9 Hz, Fc substituted ring C-1), 71.7 (d, $^2J(^{31}P–^{13}C)$ 16.2 Hz, Fc substituted ring), 71.5 (d, $^2J(^{31}P–^{13}C)$ 7.3 Hz, CH), 71.3 (d, $^3J(^{31}P–^{13}C)$ 12.5 Hz, Fc substituted ring), 70.5 (s, Fc unsubstituted ring), 24.8 (d, $^3J(^{31}P–^{13}C)$ 4.6 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1185 (m), 1027 (s), 581 (s) and 493 (m). Mass Spec (MALDI): (1/2M)$^+$ 742.

Bis[(methoxy)ferrocenylphosphonodithioato]Sn (9m). SnCl$_2$ (0.017 g, 0.09 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate bright yellow precipitate formed. The reaction mixture was stirred for a further 10 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a bright yellow powder (0.048 g, 72%). Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Sn$): C 34.74 (35.66), H 2.90 (3.26), S 17.52 (17.31)%. ^{31}P NMR (CDCl$_3$) δ: 98.46. ^{1}H NMR (CDCl$_3$) δ: 4.63 (m, 2H, Fc substituted ring), 4.42 (m, 2H, Fc substituted ring), 4.32 (s, 5H, Fc unsubstituted ring), 3.90 (d, 3H, $^3J(^{31}P–^1H)$ 15.59 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 81.9 (d, $^1J(^{31}P–^{13}C)$ 138.1

Hz, Fc substituted ring C-1), 71.3 (d, $^3J(^{31}P–^{13}C)$ 13.5 Hz, Fc substituted ring), 71.0 (d, $^2J(^{31}P–^{13}C)$ 16.6 Hz, Fc substituted ring), 70.3 (s, Fc unsubstituted ring), 51.9 (d, $^2J(^{31}P–^{13}C)$ 6.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1185 (m), 1028 (vs), 580 (vs) and 502 (s). Mass Spec (MALDI): (1/2M)$^+$ 742, (M–$FeS_2PC_{11}H_{12}O$)$^+$ 1203.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Sn (9p). $SnCl_2$ (0.017 g, 0.09 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), methanol (10 cm^3) was added and after approx 30 s stirring a yellow precipitate formed. The reaction mixture was stirred for a further 45 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.045 g, 68%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Sn$): C 39.47 (39.18), H 3.75 (4.05), S 16.15 (16.09)%. ^{31}P NMR ($CDCl_3$) δ: 89.59. ^1H NMR ($CDCl_3$) δ: 5.22 (dsept, 1H, $^3J(^{31}P–^1H)$ 2.47 Hz, $^3J(^1H–^1H)$ 6.19 Hz, CH), 4.70 (m, 2H, Fc substituted ring), 4.53 (m, 2H, Fc substituted ring), 4.38 (s, 5H, Fc unsubstituted ring), 1.48 (d, 6H, $^3J(^1H–^1H)$ 6.19 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 79.1 (d, $^1J(^{31}P–^{13}C)$ 128.7 Hz, Fc substituted ring C-1), 71.7 (d, $^2J(^{31}P–^{13}C)$ 16.3 Hz, Fc substituted ring), 71.0 (d, $^3J(^{31}P–^{13}C)$ 12.7 Hz, Fc substituted ring), 70.4 (d, $^2J(^{31}P–^{13}C)$ 6.2 Hz, CH), 70.2 (s, Fc unsubstituted ring), 24.4 (d, $^3J(^{31}P–^{13}C)$ 4.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1186 (m), 1025 (m), 582 (s) and 492 (m). Mass Spec (MALDI): (1/2M)$^+$ 796.

Bis[(methoxy)ferrocenylphosphonodithioato]Pb (10m). $(CH_3COO)_2Pb\cdot 3H_2O$ (0.034 g, 0.09 mmol) was added to a flask containing salt **1** (0.06 g, 0.18 mmol), upon addition of methanol (10 cm^3), with stirring, an immediate yellow precipitate formed. The reaction mixture was stirred for a further 30 min to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.061 g, 82%). Found (Calc. for $C_{22}H_{24}O_2Fe_2P_2S_4Pb$): C 31.67 (31.85), H 2.61 (2.92), S 15.02 (15.46)%. ^{31}P NMR ($CDCl_3$) δ: 104.23. ^1H NMR ($CDCl_3$) δ: 4.64 (m, 2H, Fc substituted ring), 4.41 (m, 2H, Fc substituted ring), 4.31 (s, 5H, Fc unsubstituted ring), 3.88 (d, 3H, $^3J(^{31}P–^1H)$ 15.83 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 80.9 (d, $^1J(^{31}P–^{13}C)$ 127.7 Hz, Fc substituted ring C-1), 71.2 (d, $^3J(^{31}P–^{13}C)$ 12.5 Hz, Fc substituted ring), 70.8 (d, $^2J(^{31}P–^{13}C)$ 17.7 Hz, Fc substituted ring), 70.3 (s, Fc unsubstituted ring), 51.7 (d, $^2J(^{31}P–^{13}C)$ 6.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1184 (m), 1029 (vs), 588 (s) and 501 (m). Mass Spec (MALDI): (1/2M)$^+$ 830, (M–$FeS_2PC_{11}H_{12}O$)$^+$ 1349.

Bis[(isopropoxy)ferrocenylphosphonodithioato]Pb (10p). $(CH_3COO)_2Pb\cdot 3H_2O$ (0.034 g, 0.09 mmol) was added to a flask containing salt **2** (0.06 g, 0.177 mmol), upon addition of methanol (10 cm^3), with stirring, some immediate yellow precipitate formed. The reaction mixture was refluxed for 10 min resulting in a yellow solution containing a yellow precipitate. The product was collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow powder (0.062 g, 83%). Found (Calc. for $C_{26}H_{32}O_2Fe_2P_2S_4Pb$): C 35.57 (35.26), H 3.48 (3.64), S 14.62 (14.48)%. ^{31}P NMR ($CDCl_3$) δ: 97.73. ^1H NMR ($CDCl_3$) δ: 5.11 (dsept, 1H, $^3J(^{31}P–^1H)$ 3.22 Hz, $^3J(^1H–^1H)$ 5.94 Hz, CH), 4.61 (m, 2H, Fc substituted ring), 4.38 (m, 2H, Fc substituted ring), 4.30 (s, 5H, Fc unsubstituted ring), 1.41 (d, 6H, $^3J(^1H–^1H)$ 5.94 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 85.3 (d, $^1J(^{31}P–^{13}C)$ 138.1 Hz, Fc substituted ring C-1), 71.1 (d, $^3J(^{31}P–^{13}C)$ 13.5 Hz, Fc substituted ring), 70.8 (d, $^2J(^{31}P–^{13}C)$ 16.6 Hz, Fc substituted ring), 70.4 (d, $^2J(^{31}P–^{13}C)$ 6.2 Hz, CH), 70.3 (s, Fc unsubstituted ring), 24.7 (d, $^3J(^{31}P–^{13}C)$ 4.2 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1180 (m), 1025 (m), 576 (s) and 492 (m). Mass Spec (MALDI): (1/2M)$^+$ 886, (M–$FeS_2PC_{13}H_{16}O$)$^+$ 1433.

Table 2 Details of the X-ray data collections and refinements

Compound	**3m**	**3m-*cis***	**4m**	**6m**	**8m**	**10p**
Empirical formula	$C_{22}H_{24}Fe_2NiO_2P_2S_4$	$C_{22}H_{24}Fe_2NiO_2P_2S_4$	$C_{22}H_{24}Fe_2PdO_2P_2S_4$	$C_{44}H_{48}Fe_4O_4P_4S_8Cd_2$	$C_{44}H_{48}Fe_4O_4P_4S_8Zn_2$	$C_{26}H_{32}Fe_2O_2P_2S_4Pb$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*2(1)/*n*	*I*2/*a*	*P*2(1)/*n*	*P*2(1)/*c*	*C*2/*c*	$P\bar{1}$
a/Å	6.8818(16)	13.906(4)	6.9328(15)	12.842(5)	21.750(6)	10.4327(10)
b/Å	16.902(4)	9.6511(16)	17.093(4)	16.296(6)	10.3711(13)	11.5696(11)
c/Å	10.762(3)	19.517(5)	10.767(2)	13.563(5)	24.319(4)	15.0558(13)
β/°	95.415(5)	98.17(3)	95.283(4)	113.698(7)	96.286(7)	109.647(1)
U/Å^3	1246.2(5)	2592.8(10)	1270.5(5)	2599.1(17)	5452.5(19)	1627.4(3)
Z	2	4	2	4	4	1
M	681.00	681.00	728.69	1469.38	1375.32	688.4
μ/mm^{-1}	2.380	2.288	2.302	2.376	2.365	6.417
Measured reflections	5309	4523	5322	10939	10329	8510
Independent reflections (R_{int})	1769(0.0419)	1781(0.0438)	1788(0.0254)	3694(0.1549)	4621(0.0386)	5362(0.0442)
Final R_1, ωR_2 [$I > 2\sigma(I)$]	0.0310, 0.0597	0.0349, 0.0623	0.0208, 0.0520	0.0460, 0.0736	0.0465, 0.0831	0.0604, 0.1363

X-Ray crystallography

Tables 1 and 2 list details of data collections and refinements. For, **3m-*cis***, **8m** and **10p**, data were collected at room temperature using Mo Kα radiation with a Rigaku Mercury system and for **3m**, **3mpy$_2$**, **4m** and **6m** at 125 K using a Bruker SMART system. Several crystals of **3mpy$_2$** were examined; as a transient intermediate this proved extremely difficult to crystallise and poor crystal quality precluded any significant refinement of the structure; only the metal atoms were refined anisotropically; the structure is thus only of use for defining the connectivity of the atoms and no crystal data is provided. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[22]

CCDC reference numbers 212462–212468.

See http://www.rsc.org/suppdata/dt/b3/b306387a/ for crystallographic data in CIF or other electronic format.

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