PERGAMON

Polyhedron 20 (2001) 3189–3200

POLYHEDRON

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Bidentate aryldichalcogenide complexes of [(diphosphino)ferrocene]palladium(II) and [(diphosphino)ferrocene]platinum(II). Synthesis, molecular structures and electrochemistry

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Received 23 April 2001; accepted 30 August 2001

Abstract

A series of homochalcogenide and mixed-chalcogenide ligand complexes of palladium and platinum have been prepared from the reactions of Pd(dppf)Cl_2, (dppf = 1,1′-bis(diphenylphosphino)ferrocene), Pd(dippf)Cl_2 (1,1′-bis(diisopropylphosphino)ferrocene), and Pt(dppf)Cl_2 with 1,2-benzenedithiol (HSC_6H_4SH) (**a**), 3,4-toluenedithiol (HSC_6H_3MeSH) (**b**), 3,6-dichloro-1,2-benzenedithiol ($HSC_6H_2Cl_2SH$) (**c**), 2-mercaptophenol (HSC_6H_4OH) (**d**), thiosalicylic acid ($HSC_6H_4CO_2H$) (**e**) and thionicotinic acid ($HSC_6H_3NCO_2H$) (**f**). Single-crystal X-ray diffraction studies show that all complexes have distorted square-planar geometry. The complexes undergo two quasi-reversible or irreversible one-electron redox processes that involve the chalcogen ligands and diphosphinoferrocene ligands. The oxidation potentials of the chalcogen ligands increase when they bear electron-withdrawing substituents. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aryldichalcogenide complexes; Synthesis; Molecular structures; Electrochemistry

1. Introduction

1,1′-Bis(diphenylphosphino)ferrocene (dppf) first synthesised in 1971 [1], has a coordination chemistry comparable to that of the traditional diphosphino ligands like 1,2-bis(diphenylphosphino)ethane (dppe). Much of this coordination chemistry has been developed over the past 15 years [2]. In some cases dppf has been found to form more stable complexes compared to other diphosphines or monophosphines. For example, attempts by Hor and co-workers to prepare pure $Pd_2(PPh_3)_4(\mu\text{-}S)_2$ were plagued by the lability of the phosphine but a stable $Pd_2(dppf)_2(\mu\text{-}S)_2$ is readily prepared when the PPh_3 is replaced with dppf [3]. Group 10 dppf dichloro compounds, M(dppf)Cl_2, particularly the palladium analogue, have been used in various catalytic reactions. These include the cross-coupling of primary and secondary alkyl Grignard and alkylzinc reagents with organic halides [4]. Pd(dppf)Cl_2 also catalyses the cross-coupling reactions above more selectively than $Pd(PPh_3)_2Cl_2$, Pd(dppe)Cl_2 and Pd(dppm)Cl_2 (dppm = bis(diphenylphosphino)methane) and demonstrates greater potential use of metallocene anchored diphosphino ligand complexes over either bis(-monophosphino) and alkyl bridged diphosphino complexes.

Another area of diphosphino chemistry of Group 10 metals is their complex formation with the organodichalcogenide ligands [5]. This work involved the synthesis and characterisation of the thiolato complexes [5a,b,d–g], as well as studies toward potential applications. For example Sadler and co-workers [5c] showed that M(dppe)(H_2dmsucc-SS′) (M = Ni, Pd, Pt; H_2dmsucc-SS′ = dimercaptosuccinic acid) has anti-

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PII: S0277-5387(01)00923-8

cancer activity. The photophysical properties of the dithiolato complexes M(dppe){S_2C_2(2-quinoxaline)(R)} (M = Ni, Pd, Pt; R = H, Me) have been reported by Pilato and co-workers [5g,h]. Our contribution to this chemistry has focused on the synthesis and reactivity of Ni(dppe) aryldichalcogenide compounds, which centres on investigating the nucleophilic behaviour of the aryldichalcogenide ligands towards SO_2 and acetylenes [6]. We have found that both reversible SO_2 reactions [6a] and cyclotrimerisation of dimethylacetylene dicarboxylate (DMAD) [6b] are facilitated by these compounds. The current report is an extension of the previous work [6a] which replaces dppe as a ligand with the ferrocene anchored diphosphino ligands dppf and dippf (dippf = bis(diisopropylphosphino)ferrocene). Electrochemical studies were also performed to show how changes in metals and ligands would affect the ease of oxidation of complexes.

2. Materials and instrumentation

All solvents were of analytical grade and were used without further purification; however, they were degassed prior to use. The dichloromethane, which was used for the cyclic voltammetry experiments, was refluxed over P_2O_5 twice for 24 h, distilled under nitrogen and stored over molecular sieves. All commercial reagents were ACS reagent grades and were purchased from stated sources: 1,2-benzenedithiol (Fluka), palladium chloride (Next Chimica, South Africa), chlorodiphenylphosphine, chlorodiisopropylphosphine, triethylamine, thiosalicylic acid, 3,6-dichloro-1,2-benzenedithiol and *n*-butyllithium (Aldrich), 3,4-toluenedithiol (Riedel-de-Haën), while 2-mercaptophenol was supplied by Merck. The starting materials, Pd(dppf)Cl_2 [7], Pd(dippf)Cl_2 [8], Pt(cod)Cl_2 (cod = cycloocta-1,5-diene) [9], and Pt(dppf)Cl_2 [10] were prepared by the literature procedures. All the reactions were performed under nitrogen atmosphere using the standard inert atmosphere techniques but the air-stable products were worked-up in air.

^1H and ^{31}P NMR spectra were recorded in a Varian Gemini-2000 NMR spectrometer at 200 and 80.96 MHz, respectively, and referenced to residual $CHCl_3$ for ^1H (δ 7.26) and externally with PPh_3 for ^{31}P (δ − 5.00). IR spectra were recorded in a Perkin–Elmer paragon 1000 PC FTIR spectrometer using Nujol mulls. Mass spectra were recorded in a JEOL JMS-HX EBE spectrometer in the fast atom bombardment (FAB) mode. Elemental analyses were performed inhouse in a Carlo Erba NA 1500 Analyzer.

Cyclic voltammetric measurements were made in a BAS CV-50W electrochemical analyser. The three-electrodes system used were a platinum disc as a working electrode, a platinum wire as an auxiliary electrode and a silver/silver chloride reference electrode. All experiments were carried out under a dry nitrogen atmosphere on sample concentrations of 10^{-3} M, with [n-Bu_4N][BF_4] as the supporting electrolyte (0.10 M) at a scan rate of 100 mV s^{-1}. Potentials were referenced to an internal ferrocene/ferrocenium couple added at the end of each experiment and quoted versus the saturated calomel electrode (SCE) [11].

2.1. Reaction of Pd(dppf)Cl_2 with 1,2-benzenedithiol: formation of Pd(dppf)(SC_6H_4S-o) (**1a**)

A mixture of Pd(dppf)Cl_2 (0.30 g, 0.41 mmol) and 1,2-benzenedithiol (0.058 g, 0.41 mmol) was degassed in a Schlenk tube. Degassed dichloromethane (50 ml) was added, followed by triethylamine (Et_3N) (1 ml). The reddish brown solution turned dark red on adding the Et_3N and was stirred at room temperature (r.t.) for 22 h, after which the mixture was filtered and the product precipitated by adding hexane. The precipitate was isolated by filtration and washed with copious amount of water until the washings gave a negative test for chloride ions. The solid was redissolved in CH_2Cl_2 and dried over anhydrous $MgSO_4$. The filtrate was concentrated to about 15 ml and equal volume of hexane was added to give analytically pure yellowish orange product. Yield = 0.24 g, 67%. *Anal.* Calc. for $C_{40}H_{32}P_2S_2FePd\cdot 1/2CH_2Cl_2$: C, 57.67; H, 3.94. Found: C, 57.65; H, 3.59%. ^1H NMR ($CDCl_3$): δ 7.81 (m, 8H, PC_6H_5), 7.40 (m, 12H, PC_6H_5), 7.10 (dd, $^3J_{HH} = 8.00$ Hz, $^4J_{HH} = 2.00$ Hz, 2H, SC_6H_4S), 6.72 (dd, $^3J_{HH} = 5.90$ Hz, $^4J_{HH} = 3.30$ Hz, 2H, SC_6H_4S), 4.38 (t, $J_{HH} = 2.00$ Hz, 4H, PC_5H_4), 4.20 (t, $J_{HH} = 1.90$ Hz, 4H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 25.08 (s). FAB MS: 799 (M^+, 18). IR (Nujol, cm^{-1}): 1712 w, 1548 m, 1459 w, 1379 s, 1283 w, 1165 w, 1094 m, 1026 w, 812 m, 736 s, 698 s, 631 m, 543 s, 484 s.

All complexes were prepared and worked-up in a similar manner as described for the reaction of Pd(dppf)Cl_2 with 1,2-benzenedithiol above.

2.2. Reaction of Pd(dppf)Cl_2 and 3,4-toluenedithiol: formation of Pd(dppf)(SC_6H_3MeS-o) (**1b**)

Yield = 0.24 g, 71%. *Anal.* Calc. for $C_{41}H_{34}P_2S_2FePd\cdot CH_2Cl_2$: C, 56.05; H, 4.03. Found: C, 55.49; H, 3.66%. ^1H NMR ($CDCl_3$): δ 7.80 (m, 8H, PC_6H_5), 7.52 (m, 12H, PC_6H_5), 6.98 (d, $J_{HH} = 8.00$ Hz, 1H, SC_6H_3MeS), 6.92 (s, 1H, SC_6H_3MeS), 6.76 (dd, $^3J_{HH} = 8.00$ Hz, $^4J_{HH} = 1.20$ Hz, 1H, SC_6H_3MeS), 4.37 (m, 4H, PC_5H_4), 4.19 (m, 4H, PC_5H_4), 2.13 (s, 3H, SC_6H_3MeS). $^{31}P\{^1H\}$ NMR: δ 24.97 (s). FAB MS: 813 (M^+, 20). IR (Nujol, cm^{-1}): 1464 w, 1434 m, 1371 m, 1308 m, 1257 s, 1173 w, 1089 s, 1035 w, 997 m, 820 s, 732 s, 677 s, 635 s, 547 s, 484 s, 463 s, 433 s.

2.3. Reaction of Pd(dppf)Cl_2 with 3,6-dichloro-1,2-benzenedithiol: formation of Pd(dppf)($SC_6H_2Cl_2S$-o) (*1c*)

Yield = 0.21 g, 59%. *Anal.* Calc. for $C_{40}H_{30}P_2S_2Cl_2FePd$: C, 55.22; H, 3.48. Found: C, 55.43; H, 3.34%. ^1H NMR ($CDCl_3$): δ 7.79 (m, 8H, PC_6H_5), 7.40 (m, 12H, PC_6H_5), 6.82 (s, 2H, $SC_6H_2Cl_2S$), 4.41 (t, $J_{HH} = 1.60$ Hz, 4H, PC_5H_4), 4.23 (d, $J_{HH} = 1.60$ Hz, 4H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 25.48 (s). FAB MS: 869 (M^+, 37). IR (Nujol, cm^{-1}): 1707 w, 1464 m, 1375 s, 1304 w, 1270 w, 1157 m, 820 m, 749 m, 694 s, 639 m, 538 s, 459 s.

2.4. Reaction of Pd(dppf)Cl_2 with 2-mercaptophenol: formation of Pd(dppf)(OC_6H_4S-o) (*1d*)

Yield = 0.22 g, 69%. *Anal.* Calc. for $C_{40}H_{32}OP_2SFePd$: C, 61.20; H, 4.12. Found: C, 60.66; H, 3.75%. ^1H NMR ($CDCl_3$): δ 8.00 (m, 4H, PC_6H_5), 7.69 (m, 4H, PC_6H_5), 7.41(m, 6H, PC_6H_5), 7.31(m, 6H, PC_6H_5), 7.02 (d, $J_{HH} = 7.60$ Hz, 1H, OC_6H_4S), 6.70 (t, $J_{HH} = 7.50$ Hz, 1H, OC_6H_4S), 6.40 (t, $J_{HH} = 6.80$ Hz, 1H, OC_6H_5), 6.25 (d, $J_{HH} = 8.20$ Hz, 1H, OC_6H_4S), 4.71 (q, $J_{HH} = 3.80$ Hz, $J_{HH} = 2.00$ Hz, 2H, PC_5H_4), 4.50 (s, 2H, PC_5H_4); 4.28 (s, 2H, PC_5H_4), 3.77 (q, $J_{HH} = 3.80$ Hz, $J_{HH} = 1.80$ Hz, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 39.53 (d, 1P, P *trans* S, $J_{PP} = 27.45$ Hz), 21.98 (d, 1P, P *trans* O, $J_{PP} = 27.45$ Hz). FAB MS: 783 (M^+, 15). IR (Nujol, cm^{-1}): 1464 w, 1379 m, 1274 s, 1164 m, 1094 w, 1022 w, 736 s, 719 s, 690 m, 547 s, 480 s.

2.5. Reaction of Pd(dppf)Cl_2 with thiosalicylic acid: formation of Pd(dppf)($SC_6H_4CO_2$-o) (*1e*)

Yield = 0.20 g, 60%. *Anal.* Calc. for $C_{41}H_{32}O_2P_2SFePd \cdot 1/2CH_2Cl_2$: C, 58.27; H, 3.89. Found: C, 58.05; H, 3.78%. ^1H NMR ($CDCl_3$): δ 7.82 (m, 10H, PC_6H_5), 7.44 (m, 10H, PC_6H_5), 7.00 (m, 4H, $SC_6H_4CO_2$), 4.63 (q, $J_{HH} = 3.7$ Hz, 2H, PC_5H_4), 4.48 (s, 2H, PC_5H_4), 4.31 (s, 2H, PC_5H_4), 3.84 (q, $J_{HH} = 3.7$ Hz, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 37.88 (d, 1P, P *trans* S, $J_{PP} = 29.35$ Hz), 22.67 (d, 1P, P *trans* O, $J_{PP} = 29.35$ Hz). FAB MS: 812 (M^+, 35). IR (Nujol, cm^{-1}): 1716 w, 1590 w, 1464 w, 1384 m, 1350 w, 1169 m, 1098 m, 1035 m, 854 w, 744 s, 690 s, 635 m, 547 s, 467 s.

2.6. Reaction of Pd(dppf)Cl_2 with 2-mercaptonicotinic acid: formation of Pd(dppf)($SC_5H_3NCO_2$-o) (*1f*)

Yield = 0.18 g, 53%. *Anal.* Calc. for $C_{40}H_{31}NO_2P_2SFePd$: C, 59.02; H, 3.85; N, 1.72. Found: C, 59.26; H, 3.64; N, 1.68%. ^1H NMR ($CDCl_3$): δ 8.25 (m, 2H, $SC_5H_3NCO_2$), 8.04 (m, 4H, PC_6H_5), 7.69 (m, 6H, PC_6H_5), 7.51 (m, 6H, PC_6H_5), 7.31 (m, 4H, PC_6H_5), 6.89 (m, 1H, $SC_5H_3NCO_2$), 4.49 (q, $J_{HH} = 1.80$ Hz, 2H, PC_5H_4), 4.56 (s, 2H, PC_5H_4), 4.28 (s, 2H, PC_5H_4), 3.64 (q, $J_{HH} = 2.00$ Hz, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 39.53 (d, 1P, P *trans* S, $J_{PP} = 29.55$ Hz), 21.94 (d, 1P, P *trans* O, $J_{PP} = 29.55$ Hz). FAB MS: 813 (M^+, 74). IR (Nujol, cm^{-1}): 3441 w, 1607 w, 1468 w, 1375 w, 1304 m, 1169 m, 1094 s, 997 s, 850 w, 749 s, 673 s, 679 m, 555 s, 484 s.

2.7. Reaction of Pd(dippf)Cl_2 with 1,2-benzenedithiol: formation of Pd(dippf)(SC_6H_4S-o) (*2a*)

A mixture of Pd(dippf)Cl_2 (0.50 g, 0.839 mmol) and 1,2-benzenedithiol (0.119 g, 0.839 mmol) was degassed in a Schlenk tube. Degassed dichloromethane (50 ml) and Et_3N (1 ml) were added sequentially and the solution was stirred at r.t. for 3 h and filtered. The filtrate was concentrated to about 20 ml and addition of 10 ml hexane precipitated the by-product, Et_3NHCl which was filtered. Addition of excess hexane to the filtrate gave the crude product, which was recrystallised from CH_2Cl_2/hexane to give dark orange **2a**. Yield = 0.29 g, 52%. *Anal.* Calc. for $C_{28}H_{40}P_2S_2FePd$: C, 50.57; H, 6.06. Found: C, 51.11; H, 6.01%. ^1H NMR ($CDCl_3$): δ 7.40 (dd, $^3J_{HH} = 4.85$ Hz, $^4J_{HH} = 3.10$ Hz, 2H, SC_6H_4S), 6.88 (dd, $^3J_{HH} = 5.90$ Hz, $^4J_{HH} = 3.20$ Hz, 2H, SC_6H_4S), 4.48 (m, 8H, PC_5H_4), 2.64 (m, 4H, $PCH(CH_3)_2$), 1.48 (m, 12H $PCH(CH_3)_2$), 1.19 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 47.19 (s). FAB MS: 664 (M^+, 15). IR (Nujol, cm^{-1}): 1556 m, 1014 m, 1287 m, 1245 m, 1199 m, 1165 s, 1102 s, 1080 w, 1030 s, 934 w, 887 w, 829 m, 736 s, 656 w, 627 s, 538 m.

A similar procedure was used to prepare the remaining dippf complexes.

2.8. Reaction of Pd(dippf)Cl_2 with 3,4-toluenedithiol: formation of Pd(dippf)(SC_6H_3MeS-o) (*2b*)

The product was isolated as an orange solid. Yield = 0.32 g, 56%. *Anal.* Calc. for $C_{29}H_{42}P_2S_2FePd \cdot CH_2Cl_2$: C, 47.17; H, 5.81. Found: C, 46.75; H, 5.77%. ^1H NMR ($CDCl_3$): δ 7.28 (d, $J = 7.00$ Hz, 1H, SC_6H_3MeS), 7.22 (s, 1H, SC_6H_3MeS), 6.70 (dd, $^3J_{HH} = 8.00$ Hz, $^4J_{HH} = 1.40$ Hz, 1H, SC_6H_3MeS), 4.49 (s, 4H, PC_5H_4), 4.46 (s, 4H, PC_5H_4), 2.64 (m, 4H, $PCH(CH_3)_2$), 2.24 (s, 3H, SC_6H_3MeS), 1.47 (m, 12H, $PCH(CH_3)_2$), 1.18 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 42.15 (d, 1P, $J_{PP} = 18.30$ Hz), 41.87 (d, 1P, $J_{PP} = 18.30$ Hz). FAB MS: 680 (M^+, 100). IR (Nujol, cm^{-1}): 1383 w, 1285 w, 1262 w, 1245 w, 1195 w, 1159 m, 1116 m, 1066 w, 1035 w, 970 w, 930 w, 879 m, 865 m, 850 m, 813 s, 793 s, 731 s, 700 m, 653 s, 626 s, 540 s.

2.9. Reaction of Pd(dippf)Cl_2 with 3,6-dichloro-1,2-benzenedithiol: formation of Pd(dippf)($SC_6H_2Cl_2S$-o) (*2c*)

The product was obtained as a yellow solid. Yield = 0.30 g, 49%. *Anal.* Calc. for $C_{28}H_{38}Cl_2P_2S_2FePd$: C, 45.86; H, 5.22. Found: C, 46.04; H, 5.38%. ^{1}H NMR ($CDCl_3$): δ 6.97 (s, 2H, $SC_6H_2Cl_2S$), 4.51 (s, 4H, PC_5H_4), 4.49 (d, 4H, $J_{HH} = 3.20$ Hz, PC_5H_4), 2.68 (m, 4H, $PCH(CH_3)_2$), 1.49 (m, 12H, $PCH(CH_3)_2$), 1.20 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 41.92 (s). FAB MS: 734 (M^+, 46). IR (Nujol, cm^{-1}): 1527 w, 1379 w, 1342 w, 1274 m, 1194 w, 1169 s, 1068 s, 1035 s, 963 w, 892 w, 816 m, 774 m, 728 m, 652 m, 623 s, 597 m.

2.10. Reaction of Pd(dippf)Cl$_2$ with 2-mercaptophenol: formation of Pd(dippf)(OC$_6$H$_4$S-o) ***(2d)***

The product was isolated as a shinny dark brown solid. Yield = 0.38 g, 70%. *Anal.* Calc. for $C_{28}H_{40}OP_2SFePd\cdot 1/2CH_2Cl_2$: C, 49.51; H, 5.98. Found: C, 49.25; H, 6.21%. ^{1}H NMR ($CDCl_3$): δ 7.35 (d, $J_{HH} = 8.4$ Hz, 1H, OC_6H_4S), 7.01 (d, $J_{HH} = 7.6$ Hz, 1H, OC_6H_4S), 6.82 (t, $J_{HH} = 8.20$ Hz, 1H, OC_6H_4S), 6.54 (t, $J_{HH} = 8.20$ Hz, 1H, OC_6H_4), 4.54 (s, 4H, PC_5H_4), 4.46 (s, 4H, PC_5H_4), 2.36 (m, 4H, $PCH(CH_3)_2$), 1.42 (m, 12H, $PCH(CH_3)_2$), 1.20 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 55.18 (d, 1P, P *trans* S, $J_{PP} = 12.14$ Hz); 48.28 (d, 1P, P *trans* O, $J_{PP} = 12.14$ Hz). FAB MS: 648 (M^+, 28). IR (Nujol, cm^{-1}): 2621 w, 1581 w, 1548 w, 1379 s, 1274 s, 1169 s, 1119 w, 1030 s, 934 w, 883 m, 850 m, 803 m, 732 s, 698 s, 652 m, 628 m, 602 m.

2.11. Reaction of Pd(dippf)Cl$_2$ with thiosalicylic acid: formation of Pd(dippf)(SC$_6$H$_4$CO$_2$-o) ***(2e)***

The product was isolated as a brown oil and kept at − 15 °C to solidify. Yield = 0.57 g, 68%. *Anal.* Calc. for $C_{29}H_{40}O_2P_2SFePd$: C, 51.46; H, 5.96. Found: C, 51.02; H, 6.94%. ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 2H, $SC_6H_4CO_2$), 7.01 (m, 2H, $SC_6H_4CO_2$), 4.50 (m, 8H, PC_5H_4), 2.80 (m, 4H, $PCH(CH_3)_2$), 1.49 (m, 2H, $PCH(CH_3)_2$), 1.20 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 59.16 (d, 1P, P *trans* S, $J_{PP} = 11.17$ Hz); 51.63 (d, 1P, P *trans* O, $J_{PP} = 11.17$ Hz). FAB MS: 677 (M^+, 66). IR (Nujol, cm^{-1}): 2730 w, 2593 w, 2347 w, 1678 m, 1581 m, 1464 s, 1379 s, 1300 w, 1236 w, 1165 m, 1030 s, 934 w, 879 w, 837 w, 791 w, 740 w, 652 m, 625 m.

2.12. Reaction of Pd(dippf)Cl$_2$ with 2-mercaptonicotinic acid: formation of Pd(dippf)(SC$_5$H$_3$NCO$_2$-o) ***(2f)***

The product was isolated as a yellowish orange solid. Yield = 0.45 g, 79%. *Anal.* Calc. for $C_{28}H_{39}NO_2P_2SFePd\cdot 1/2CH_2Cl_2$: C, 49.19; H, 6.00; N, 1.94. Found: C, 48.81; H, 6.30; N, 2.11%. ^{1}H NMR ($CDCl_3$): δ 8.35 (m, 2H, $SC_5H_3NCO_2$), 7.01 (dd, $^3J_{HH} = 4.90$ Hz, $^4J_{HH} = 1.80$ Hz, 1H, $SC_5H_3NCO_2$), 4.53 (m, 8H, C_5H_4), 2.83 (m, 4H, $PCH(CH_3)_2$), 1.51 (m, 12H, $PCH(CH_3)_2$), 1.23 (m, 12H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 59.66 (d, 1P, P *trans* S, $J_{PP} = 12.71$ Hz); 52.34 (d, 1P, P *trans* O, $J_{PP} = 12.71$ Hz). FAB MS: 678 (M^+, 29). IR (Nujol, cm^{-1}): 1720 w, 1602 w, 1560 m, 1459 m, 1375 s, 1249 m, 1165 m, 1077 w, 1043 s, 934 w, 883 m, 770 s, 719 s, 656 m, 606 s.

Synthetic procedure for the platinum complexes was similar to that of the palladium analogues.

2.13. Reaction of Pt(dppf)Cl$_2$ with 1,2-benzenedithiol: formation of Pt(dppf)(SC$_6$H$_4$S-o) ***(3a)***

The product was obtained as a yellowish solid. Yield = 0.32 g, 73%. *Anal.* Calc. for $C_{40}H_{32}P_2S_2FePt\cdot CH_2Cl_2$: C, 50.52; H, 3.52. Found: C, 50.11; H, 3.02%. ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 8H, PC_6H_5), 7.41 (m, 12H, PC_6H_5), 7.27 (m, 2H, SC_6H_4S), 6.68 (m, 2H, SC_6H_4S), 4.36 (s, 4H, PC_5H_4), 4.23 (d, $J_{HH} = 1.8$ Hz, 4H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 22.82 (s), 2P, ($J_{Pt–P} = 1471$ Hz). FAB MS: 889 (M^+, 85). IR (Nujol, cm^{-1}): 1556 m, 1410 m, 1287 m, 1199 m, 1165 s, 1102 s, 1080 w, 1030 s, 934 w, 887 w, 829 m, 736 s, 656 w, 627 s, 538 m.

2.14. Reaction of Pt(dppf)Cl$_2$ with 3,4-toluenedithiol: formation of Pt(dppf)(SC$_6$H$_3$MeS-o) ***(3b)***

The product was isolated as a yellow solid. Yield = 0.40 g, 54%. *Anal.* Calc. for $C_{41}H_{34}P_2S_2FePt\cdot 1/2CH_2Cl_2$: C, 52.68; H, 3.73. Found: C, 52.76; H, 3.85%. ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 8H, PC_6H_5), 7.39 (m, 12H, PC_6H_5), 7.14 (d, $J_{HH} = 7.60$ Hz, 1H, SC_6H_3MeS), 7.08 (s, 1H, SC_6H_3MeS), 6.50 (dd, $^3J_{HH} = 7.60$ Hz, $^4J_{HH} = 1.30$ Hz, 1H, SC_6H_3MeS), 4.35 (s, 4H, PC_5H_4), 4.22 (s, 4H, PC_5H_4), 2.15 (s, 3H, SC_6H_3MeS). $^{31}P\{^1H\}$ NMR: δ 22.83 (s), 2P, ($J_{Pt–P} = 1471$ Hz). FAB MS: 904 (M^+, 96). IR (Nujol, cm^{-1}): 1463 m, 1387 s, 1308 w, 1295 w, 1264 m, 1171 m, 1096 s, 1034 m, 1003 w, 821 m, 724 s, 698 s, 636 m, 561 s.

2.15. Reaction of Pt(dppf)Cl$_2$ with 3,6-dichloro-1,2-benzenedithiol: formation of Pt(dppf)(SC$_6$H$_2$Cl$_2$S-o) ***(3c)***

The product was isolated as a yellowish green solid. Yield = 0.26 g, 55%. *Anal.* Calc. for $C_{40}H_{30}Cl_2P_2S_2FePt$: C, 50.12; H, 3.15. Found: C, 50.41; H, 3.42%. ^{1}H NMR ($CDCl_3$): δ 7.80 (m, 8H, PC_6H_5), 7.39 (m, 12H, PC_6H_5), 6.80 (s, 2H, $SC_6H_2Cl_2S$), 4.38 (s, 4H, PC_5H_4), 4.25 (s, 4H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 22.52 (s), 2P, ($J_{Pt–P} = 1466$ Hz). FAB MS: 958 (M^+, 100). IR (Nujol, cm^{-1}): 1526 w, 1471 m, 1379 m, 1334 m, 1272 s, 1171 m, 1096 s, 1069 s, 1029 m, 1007 m, 830 s, 751 m, 711 s, 636 s, 561 s.

2.16. *Reaction of Pt(dppf)Cl_2 with 2-mercaptophenol: formation of Pt(dppf)(OC_6H_4S-o)* ***(3d)***

The product was isolated as a yellow solid. Yield = 0.22 g, 51%. *Anal.* Calc. for $C_{40}H_{32}OP_2SFePt\cdot 1/2CH_2Cl_2$: C, 53.10; H, 3.63. Found: C, 53.51; H, 3.77%. ^1H NMR ($CDCl_3$): δ 7.94 (m, 4H, PC_6H_5), 7.71 (m, 4H, PC_6H_5), 7.34 (m, 12H, PC_6H_5), 7.11 (d, $J_{HH} = 8.40$ Hz, 1H, OC_6H_4S), 6.62 (t, $J_{HH} = 7.80$ Hz, 1H, OC_6H_4S), 6.40 (t, $J_{HH} = 7.80$ Hz, 1H, OC_6H_4S), 6.31 (d, $J_{HH} = 8.40$ Hz, 1H, OC_6H_4S), 4.62 (q, $J_{HH} = 1.80$ Hz, $J_{HH} = 3.80$ Hz, 2H, PC_5H_4), 4.45 (s, 2H, PC_5H_4), 4.28 (s, 2H, PC_5H_4), 3.91 (q, $J_{HH} = 1.80$ Hz, $J_{HH} = 3.80$ Hz, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 26.40 (d, 1P, P *trans* S, $J_{PP} = 22.30$ Hz, $J_{Pt–P} = 1504$ Hz); 13.08 (d, 1P, P *trans* O, $J_{PP} = 22.30$ Hz, $J_{Pt–P} = 1749$ Hz). FAB MS: 873 (M^+, 40). IR (Nujol, cm^{-1}): 1560 m, 1272 m, 1237 m, 1184 s, 1096 s, 1025 m, 998 w, 848 m, 746 s, 693 s, 640 s, 567 s.

2.17. *Reaction of Pt(dppf)Cl_2 with thiosalicylic acid: formation of Pt(dppf)($SC_6H_4CO_2$-o)* ***(3e)***

The product was isolated as a yellow solid. Yield = 0.26 g, 59%. *Anal.* Calc. for $C_{41}H_{32}O_2P_2SFePt$: C, 54.62; H, 3.58. Found: C, 55.22; H, 3.81%. ^1H NMR ($CDCl_3$): δ 7.82 (m, 8H, PC_6H_5), 7.40 (m, 12H, PC_6H_5), 7.09 (m, 2H, $SC_6H_4CO_2$), 6.98 (m, 2H, $SC_6H_4CO_2$), 4.58 (q, $J_{HH} = 3.80$ Hz, 2H, PC_5H_4), 4.45 (s, 2H, PC_5H_4), 4.30 (s, 2H, PC_5H_4), 3.90 (q, $J_{HH} = 3.80$ Hz, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 26.87 (d, 1P, P *trans* S, $J_{PP} = 22.59$ Hz, $J_{Pt–P} = 1472$ Hz); 14.27 (d, 1P, P *trans* O, $J_{PP} = 22.59$ Hz, $J_{Pt–P} = 1982$ Hz). FAB MS: 902 (M^+, 45). IR (Nujol, cm^{-1}): 1617 m, 1595 w, 1330 w, 1175 m, 1131 m, 1100 s, 1034 m, 1007 m, 830 w, 746 s, 698 s, 636 m, 561 s.

2.18. *Reaction of Pt(dppf)Cl_2 with 2-mercaptonicotinic acid: formation of Pt(dppf)($SC_6H_3NCO_2$-o)* ***(3f)***

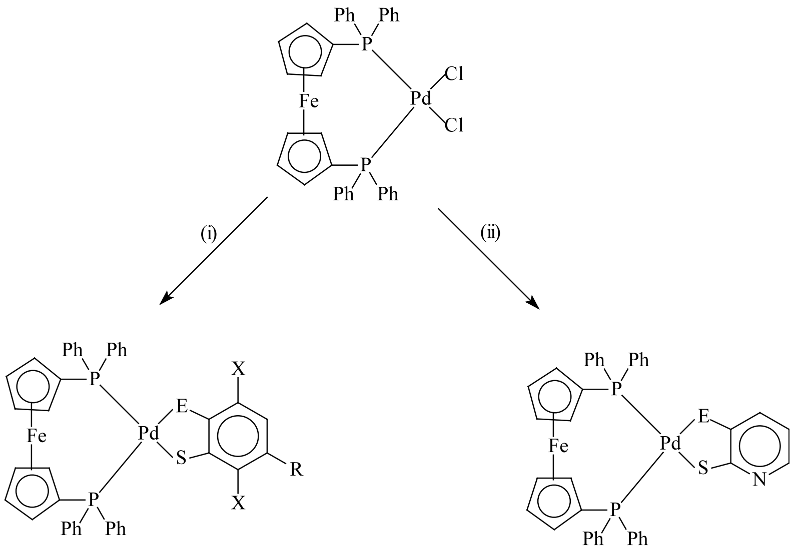
The product was isolated as a yellow solid. Yield = 0.25 g, 57%. *Anal.* Calc. for $C_{40}H_{31}NO_2P_2SFePt$: C, 53.23; H, 3.46; N, 1.55. Found: C, 52.90; H, 3.24; N, 1.50%. ^1H NMR ($CDCl_3$): δ 8.27 (m, 1H, $SC_6H_4NCO_2$), 7.91 (m, 4H, PC_6H_5), 7.53 (m, 16H, PC_6H_5), 6.90 (m, 1H, $SC_6H_3NCO_2$), 6.37 (m, 1H, $SC_6H_4NCO_2$), 4.82 (m, 2H, PC_5H_4), 4.59 (s, 2H, PC_5H_4), 4.29 (s, 2H, PC_5H_4), 3.70 (m, 2H, PC_5H_4). $^{31}P\{^1H\}$ NMR: δ 25.80 (d, 1P, P *trans* S, $J_{PP} = 23.80$ Hz, $J_{Pt–P} = 1472.26$ Hz); 15.03 (d, 1P, P *trans* O, $J_{PP} = 23.80$ Hz, $J_{Pt-P} = 1973.80$ Hz). MS (FAB): 902 (M^+, 65). IR (Nujol, cm^{-1}): 1626 w, 1578 w, 1330 w, 1171 m, 1153 s, 1091 m, 1025 s, 994 m, 861 m, 830 s, 746 s, 689 s, 640 s, 561 s.

2.19. *X-ray crystal structures of* ***1a***, ***2a***, ***2b***, ***3a*** *and* ***3b***

Crystal evaluation and data collection were performed in a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation. Processing parameters

Table 1
Crystal data and structure refinement parameters for **1a**, **2a**, **2b**, **3a** and **3d**

	1a·$CHCl_3$	**2a**	**2b**·CH_2Cl_2	**3a**·CH_2Cl_2	**3d**
Empirical formula	$C_{41}H_{33}Cl_3P_2S_2FePd$	$C_{28}H_{40}P_2S_2FePd$	$C_{30}H_{46}Cl_2P_2S_2FePd$	$C_{41}H_{34}Cl_2P_2S_2FePt$	$C_{40}H_{32}OP_2SFePt$
Formula weight	920.33	664.91	765.88	974.58	873.60
Temperature (K)	293(2)	173(2)	173(2)	173(2)	173(2)
Crystal size (mm)	0.24 × 0.20 × 0.17	0.40 × 0.30 × 0.10	0.17 × 0.17 × 0.17	0.20 × 0.20 × 0.20	0.40 × 0.30 × 0.30
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$Pca2_1$	$P2_1/c$
Unit cell dimensions					
a (Å)	14.474(3)	11.0673(7)	18.790(2)	20.2023(9)	10.1134(6)
b (Å)	13.431(3)	14.6503(9)	9.4199(7)	13.2890(6)	18.5641(10)
c (Å)	20.209(4)	18.0601(11)	20.055(2)	27.2748(12)	17.9553(10)
β (°)	104.28(3)		111.73(3)	90	99.6916(10)
V (Å^3)	3807.5(13)	2928.3(3)	3297.5(5)	7322.4(6)	3322.9(3)
Z	4	4	4	8	4
D_{calc} (Mg m^{-3})	1.606	1.508	1.543	1.768	1.746
θ Range	2.57–27.46	1.79–26.37	2.51–27.48	1.49–28.29	1.59–26.37
Total number of reflections	27 868	34 296	15 619	48 562	18 588
Number of independent reflections	8346	5988	7536	15 952	6661
	[$R_{int} = 0.0434$]	[$R_{int} = 0.0321$]	[$R_{int} = 0.0357$]	[$R_{int} = 0.0286$]	[$R_{int} = 0.0261$]
μ (Mo Kα) (mm^{-1})	1.288	1.377	1.391	4.591	4.834
R	0.0310	0.0262	0.0365	0.0220	0.0237
Rw	0.0647	0.0606	0.0792	0.0424	0.0480
Goodness-of-fit	1.033	1.041	1.040	1.018	1.004



R	X	E	Compound
H	H	S	**1a**
Me	H	S	**1b**
H	Cl	S	**1c**
H	H	O	**1d**
H	H	CO_2	**1e**
H	H	CO_2	**1f**

Scheme 1. (i) Et_3N, 1,2-$(HS)C_6H_3R(EH)$, (E = S, R = H, Me; R = H, E = O, CO_2), E_t3N, 1,2-$(HS)C_6H_2Cl_2(SH)$; (ii) Et_3N, 1,2-$(HS)C_5NH_3(CO_2H)$.

are given in Table 1. In each case an absorption correction was based on a fitting function to the empirical transmission surface as sampled by multiple equivalent measurements [12]. All crystal structures were solved by the direct methods and refined against F^2 using SHELXTL version 5.1 [13]. All non-hydrogen atoms were refined with anisotropic displacement coefficient.

3. Results and discussion

3.1. Synthesis and characterisation

The reactions of M(dppf)Cl_2 (M = Pd, Pt) and Pd(dippf)Cl_2 with various aryldichalcogen compounds proceeded smoothly in the presence of the base Et_3N, at r.t. in dichloromethane. This is illustrated in Scheme 1 using Pd(dppf)Cl_2 as an example. The air-stable products were isolated in moderate to good yields as microcrystalline solids. Some of these solids contained crystallisation solvent in the lattice as was confirmed by microanalysis and for **1a**, **2b** and **3a** by single-crystal X-ray crystallography. It is not uncommon for this type of compounds to co-crystallise with solvents as further proven by Cullen and co-workers for Pd(dppf)Cl_2 [8].

The Pd and Pt complexes with thiosalicylic acid ligands were recently reported by Henderson and co-workers [14], however, our synthetic route produces higher yields. Complex **1e** was isolated by Henderson and co-workers in 36% yield by reacting Pd(dppf)Cl_2 with thiosalicylic acid in ethanol and with pyridine as a base, whilst we obtained a yield of 60% by our procedure.

The ^1H and ^{31}P NMR spectra of the products reported are consistent with two equivalent phosphorus atoms in the complexes that have dithiolato ligands. When the complexes had hetero chalcogen atoms in the ligands, the effect of the two magnetically inequivalent phosphorus atoms of the phosphine could be seen in both the ^1H and ^{31}P NMR spectra. This is indicative of the *trans*-influence of the sulfur and the oxygen atoms on the phosphorus atoms of the dppf. All complexes of the ligands SC_6H_4O-*o*, $SC_6H_4CO_2$-*o* and $SC_6H_3NCO_2$-*o* showed two doublets in their ^{31}P NMR spectra of a typical AX spin pattern, except for Pt(dppf)($SC_6H_4CO_2$) and Pt(dppf)($SC_6H_3NCO_2$) which displayed six doublets in their spectra. Other AX ^{31}P NMR spin patterns that are the result of *trans*-influence can be found in Ni(dppe)(SC_6H_4O), Ni(dppe)(SC_6H_4-CO_2), Ni(dppe)($SC_6H_3NCO_2$) [6b,c], [Ni(dippe)(SR)-

$(CN^tBu)]^+$ [5f], Pd(dppf)($SC_6H_4CO_2$) and Pt(dppf)($SC_6H_4CO_2$) [14]. In the Pt complexes, Pt(dppf)($CH{=}CHC_6H_4OCH_3$)Br and Pt(dppf)($CH{=}CHC_6H_4OCH_3$)(C_6H_5) [15], Pt–P coupling constants are used as an indicator of *trans*-influence [16]. We found ^{31}P NMR coupling constants for **3d**–**f** in the range reported for *cis*-phosphino platinum complexes [17] and show that ^{31}P NMR spectroscopy is a good measure of *trans*-influence for the complexes reported.

3.2. Molecular structures of **1a**, **2a**, **2b**, **3a** and **3d**

Complexes **1a**, **2a**, **2b**, **3a** and **3d** were characterised by single-crystal X-ray crystallographic analyses. Three of the complexes (**1a**, **2b** and **3a**) contained crystallisation solvent in the lattice (Table 1). Complex **1a** was crystallised by slow evaporation of the NMR solution of **1a** that was used to run ^{1}H NMR spectrum. The other four complexes were crystallised by layering from a mixture of CH_2Cl_2/hexane (2:1) at − 15 °C.

Crystallographic information for compounds **1a**, **2a**, **2b**, **3a** and **3d** is given in Table 1. Their ORTEP diagrams are shown in Figs. 1–5, and selected bond distances and angles are given in Tables 2–6. In all complexes the Pd and Pt atoms exhibit square-planar geometry with *cis*-S–M–S angles ranging from 87.09(3) to 88.34(3)° for Pd and 85.89(7) to 88.26(4)° for Pt. The *cis*-P–M–P angles are found to be between 97.24(3) and 102.44(3)° for the Pd and 96.19(3)° for the Pt complexes. The dippf complexes have large P–M–P angles and are among the largest bite angles for the diphosphinoferrocene complexes. Some examples of wide bite angles are found in Pt(dppf)(η^2-dba) (dba = dibenzylideneacetone) (100.72(3)°) [18], Pt(dppf)Me_2 (100.77(3)°) [19], Pd(dippf)(SC_6H_5)$_2$ (101.09(2)°) [20] and Pt(nppf)Cl_2 (nppf = 1,1′-bis(naphthylphosphino)ferrocene) (102.97(5)°) [21]. The latter has the largest P–M–P bite angle reported to date, which has been attributed to the steric strain of the naphthyl group. Consequently, the larger bite angle for **2a** (102.44(3)°) and **2b** (101.88(3)°) could be the effect of the more bulky isopropyl group in these compounds. The substantial P–Pd–P bite angles in **2a** and **2b** cause concomitant reduction of the S–Pd–S angles to 87.09(3) and 87.30(3)°, respectively, compared to the corresponding angle in **1a** (88.34(3)°).

The Pd–P bond distances in **1a**, **2a** and **2b** are similar, with one bond out of the two in each compound slightly longer. The Pd–P bond distances in **1a**, **2a** and **2b** are slightly longer than the average Pd–P bond length obtained by averaging 2422 Pd–P bond distances reported in the Cambridge Structural Database (CSD) [22]. In contrast, the Pt–P bond distances in **3a** are closer to the normal distance of 2.9 Å (mean value for 5404 bond distances extracted from the CSD) [22], while the Pt–P bond distances in **3d** had two sets of values, both shorter than normal. For the phosphorus atom *trans* to the sulfur atom in **3d**, the Pt–P bond distance is 2.2888(9) Å and the Pt–P bond distance of the phosphorus atom *trans* to the oxygen atom in this complex is 2.2259(8) Å. Thus the *trans*-influence of the

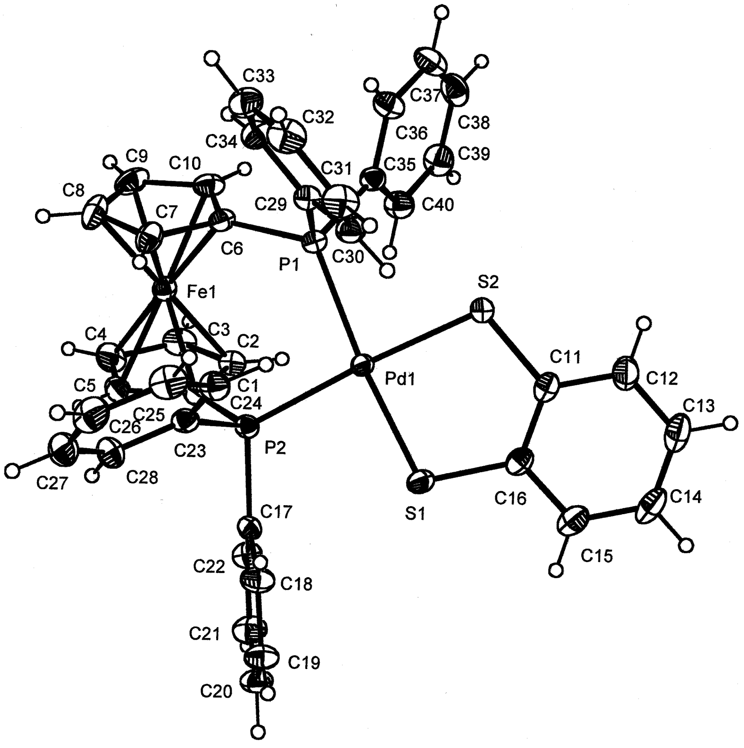


Fig. 1. ORTEP diagram of **1a**.

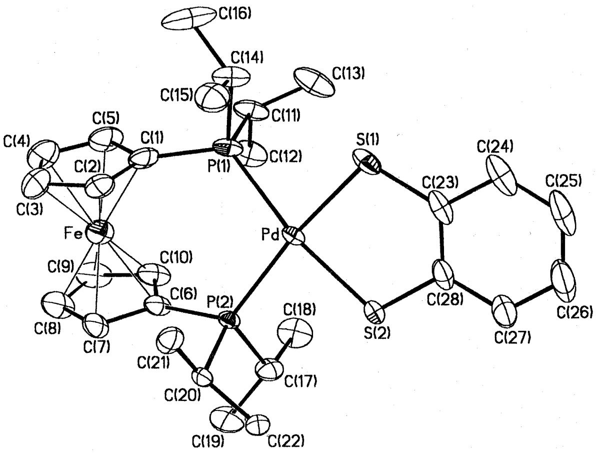


Fig. 2. ORTEP diagram of **2a**.

oxygen atom is similar to the trend found in Pt($SC_6H_4CO_2$-*o*)(PPh_3)$_2$ (Pt–P *trans* to sulfur (2.3027(11) Å) and Pt–P *trans* to oxygen (2.2502(11) Å) [15].

The Pd–S bond distances in **1a**, **2a** and **2b** are similar to the average Pd–S bond distance 2.30(3) Å obtained by averaging 340 corresponding distances in complexes reported to the CSD [22]. Similarly, the Pt–S bond distances in **3a** are in good agreement with the Pd–S bond lengths in **1a**, **2a** and **2b**. However, these are shorter than Pt–S bonds reported for Pt($SC_6H_4CO_2$-*o*)(PPh_3)$_2$ (2.322(2) Å) [14] and Pt($SC_6H_4CO_2$-*o*)(PPh_3)(XyNC) (Xy = 2,6-xylyl) (2.3395(8) Å) [23]. Henderson et al. ascribe this to the high *trans*-influence of PPh_3 as compared to the low *trans*-influence of pyridine in Pt($SC_6H_4CO_2$-*o*)(PPh_3)(py) (Pt–S = 2.255(3) Å) [23]. The *trans*-influence of dppf could lie between that of PPh_3 and py and hence the intermediate value of Pt–S observed for **3d**. In all complexes the ferrocenyl moiety is typical, with the cyclopentadienyl rings in near perfect staggered conformation.

3.3. Electrochemistry of complexes

Cyclic voltammetry, using a three-electrode cell, was used to investigate the electrochemistry of all the complexes synthesised, cycling between − 1.0 and 1.6 V. Both negative and positive scans from 0.0 V were performed. Typical voltammograms are shown in Fig. 6. There are two main redox processes that were observed in the cyclic voltammetry of all complexes. The first redox processes were quasi-reversible peaks between 0.3 and 1.1 V (Table 7). These had anodic–cathodic current ratios in the range 1.2–1.5. The second redox processes were at more positive potentials between 0.8 and 1.3 V. The two electrochemical processes described above were established as one-electron processes [24]. The former redox process is ligand-based as with similar potentials as the free ligands. Bowmaker et al. reports similar electrochemical behaviour by M(dppe)($S_2C_2Ph_2$) (M = Ni, Pd, Pt) and Ni(dppe)-(SC_6H_3MeS) [25]. In complexes containing homoleptic sulfur ligands (**1a**–**c**, **2a**–**c**, **3a**–**c**) the ease of oxidation was **b** > **a** > **c**. This conforms to the effect of either an electron-releasing group (**b**) or an electron-withdrawing group (**c**) on the ligand. The remaining three sets of complexes had heterolytic ligands that contain oxygen

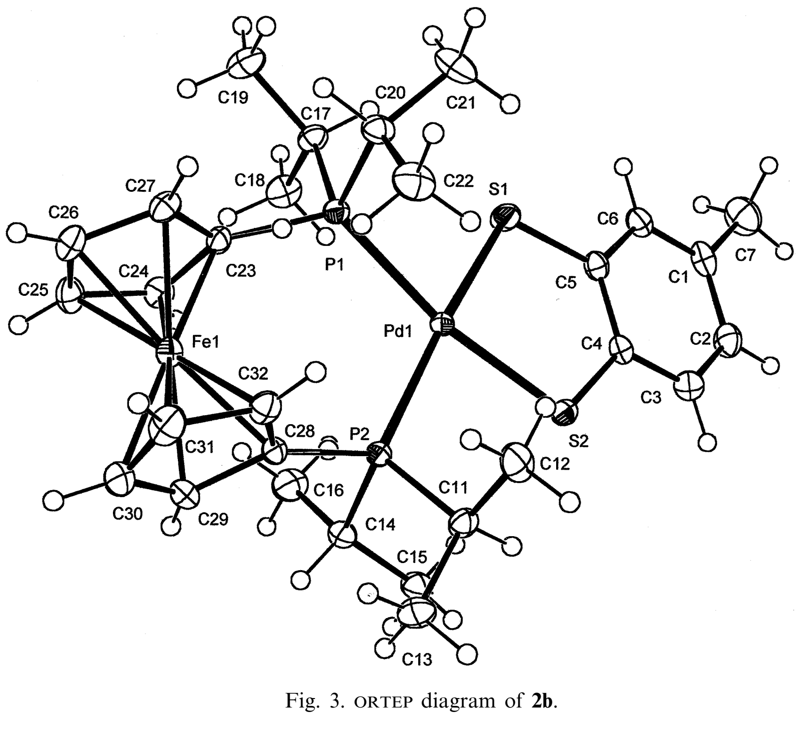


Fig. 3. ORTEP diagram of **2b**.

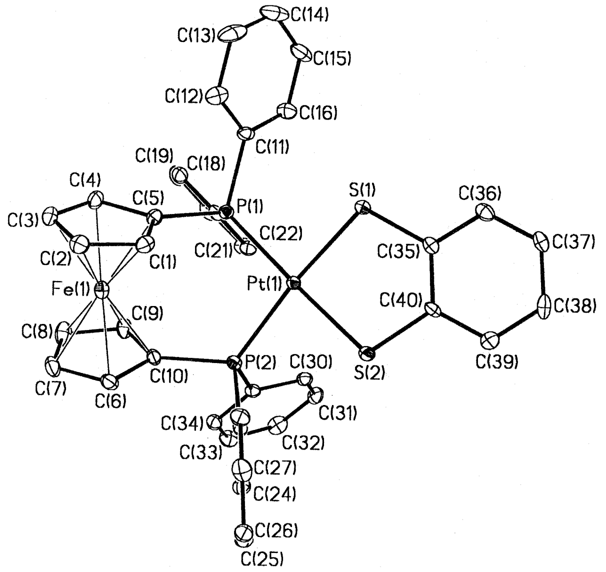


Fig. 4. ORTEP diagram of **3a**.

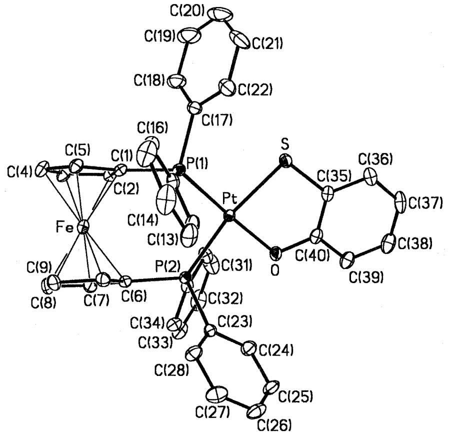


Fig. 5. ORTEP diagram of **3d**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1a**

Bond lengths			
Pd–S(1)	2.2963(8)	Pd–S(2)	2.3043(8)
Pd–P(1)	2.3298(9)	Pd–P(2)	2.3126(7)
P(1)–C(6)	1.815(2)	P(2)–C(1)	1.797(2)
S(1)–C(16)	1.762(3)	S(2)–C(11)	1.757(2)
Bond angles			
S(1)–Pd–S(2)	88.34(3)	S(1)–Pd–P(2)	88.12(3)
S(2)–Pd–P(1)	86.31(3)	P(2)–Pd–P(1)	97.24(3)
S(1)–Pd–P(1)	174.40(2)	S(2)–Pd–P(2)	176.45(2)

and sulfur, all with the oxygen and the sulfur atoms bound to the metals. Where there was a simple oxygen atom involved, as in **1d**, **2d** and **3d**, the anodic peaks were at lower potentials than the peaks for the homoleptic sulfur compounds. However, for complexes featuring a carbonyl functional group (**1e**, **1f**, **2e**, **2f**, **3e**, **3f**), anodic peaks were as high as those found in the **c** series.

The second centre of redox process was the irreversible oxidation of dppf or dippf, which is very well established as in Pd(dppf)(B_3H_7) [26], Mo(dppf)$(CO)_4$ [27] and Co_3(μ-dppf)(μ-CPh)$(CO)_7$ [28]. In dppf complexes where reversible redox processes are known,

Table 3
Selected bond lengths (Å) and bond angles (°) for **2a**

Bond lengths			
Pd–S(1)	2.3091(8)	Pd–S(2)	2.3048(9)
Pd–P(1)	2.3364(10)	Pd–P(2)	2.3433(8)
P(1)–C(1)	1.802(4)	P(2)–C(6)	1.816(3)
S(1)–C(23)	1.742(3)	S(2)–C(28)	1.749(2)
Bond angles			
S(2)–Pd–S(1)	87.09(3)	S(1)–Pd–P(1)	86.50(3)
S(2)–Pd–P(2)	85.14(3)	P(1)–Pd–P(2)	102.44(3)
S(1)–Pd–P(2)	168.64(3)	S(2)–Pd–P(1)	168.80(3)

Table 4
Selected bond lengths (Å) and bond angles (°) for **2b**

Bond lengths			
Pd–S(1)	2.3005(8)	Pd–S(2)	2.3188(8)
Pd–P(1)	2.3291(9)	Pd–P(2)	2.3329(8)
P(1)–C(6)	1.815(2)	P(2)–C(1)	1.797(2)
S(1)–C(5)	1.752(3)	S(2)–C(4)	1.764(2)
Bond angles			
S(1)–Pd–S(2)	87.30(3)	S(1)–Pd–P(1)	84.94(3)
S(2)–Pd–P(2)	86.67(3)	P(1)–Pd–P(2)	101.88(3)
S(1)–Pd–P(2)	170.66(2)	S(2)–Pd–P(1)	169.41(3)

Table 5
Selected bond lengths (Å) and bond angles (°) for **3a**

Bond lengths			
Pt–S(1)	2.3091(10)	Pt–S(2)	2.3084(10)
Pt–P(1)	2.2882(9)	Pt–P(2)	2.3012(10)
P(1)–C(5)	1.790(4)	P(2)–C(10)	1.821(4)
S(1)–C(35)	1.761(4)	S(2)–C(40)	1.765(4)
Bond angles			
S(1)–Pt–S(2)	88.26(4)	P(1)–Pt–S(1)	89.17(3)
P(2)–Pt–S(2)	86.39(3)	P(1)–Pt–P(2)	96.19(3)
S(1)–Pt–P(2)	174.40(4)	S(2)–Pt–P(1)	177.42(4)

Table 6
Selected bond lengths (Å) and bond angles (°) for **3d**

Bond lengths			
Pt–S	2.2969(9)	Pt–O	2.028(2)
Pt–P(1)	2.2259(8)	Pt–P(2)	2.2888(9)
P(1)–C(1)	1.813(3)	P(2)–C(6)	1.809(3)
S–C(35)	1.760(3)	O–C(40)	1.341(4)
Bond angles			
O–Pt–S	85.89(7)	O–Pt–P(2)	81.52(3)
P(1)–Pt–S	91.51(3)	P(1)–Pt–P(2)	96.19(3)
P(2)–Pt–S	167.26(3)	O–Pt–P(1)	177.08(7)

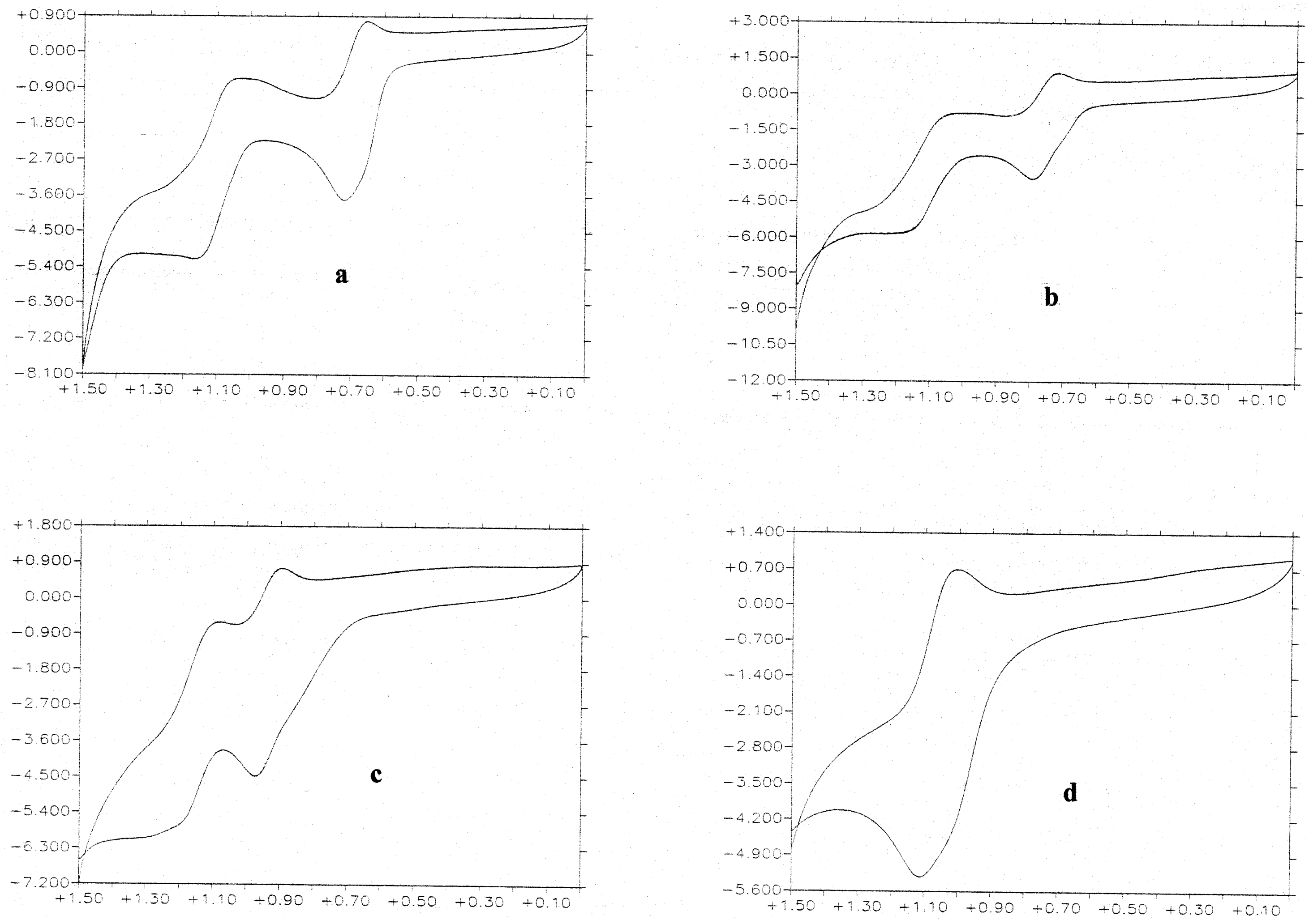


Fig. 6. Cyclic voltammograms of **3b** (a), **3a** (b), **3c** (c) and **3e** (d).

Table 7
Electrochemical data for complexes

Complex	E_c (V) (chalcogenide ligand)	E_a (V) (chalcogenide ligand)	E_c (V) (diphosphino ligand)	E_a (V) (diphosphino ligand)
1a	0.638	0.718	0.954	1.113
1b	0.529	0.663	0.974	1.110
1c	0.870	0.934	1.074	1.315
1d		0.495	1.038	1.225
1e		0.978	1.051	1.172
1f			1.048	1.122
2a	0.643	0.730	0.951	1.080
2b	0.581	0.665	0.933	1.134
2c	0.786	0.881	1.025	1.233
2d	0.387	0.470	0.878	0.900
2e	0.881	0.784	0.955	1.060
2f			0.913	1.034
3a	0.722	0.792	1.050	1.258
3b	0.622	0.686	1.022	1.275
3c	0.899	0.965	1.127	1.227
3d	0.517	0.593	1.022	1.193
3e	0.892	1.012	1.066	1.207
3f			1.018	1.102

$Pd(dppf)Cl_2$ [4] and $Pt(dppf)Cl_2$ [29], the reversible process is associated with the dppf and illustrates that no Pd or Pt redox behaviour was found. Thus it is not surprising that for the complexes reported here only thiolato, dppf or dippf ligand electrochemistry were observed. What is peculiar in our study is the apparent single oxidation peaks found for the complexes of the **f** series. But rotating disc experiments revealed two separate oxidation processes at the observed peak values, implying that the voltammograms were overlapping oxidation peaks from the thiolato ligands and the Pd(dppf) moieties.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 151358–151360 (**2a**, **3a**, **3d**) and 151424 (**1a**), 151425 (**2b**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from the National Research Foundation (NRF), South Africa for this work is gratefully acknowledged. One of us (L.L.M.) wishes to thank the NRF and ESKOM, South Africa, for bursary support. We are also grateful to Dr John Bacsa, University of Cape Town, who determined two of the crystal structures as service.

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