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Coordination of a tripodal phosphine sulphide P_2S towards various transition metal ions

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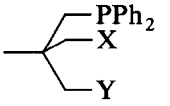
Abstract

The coordination chemistry of a tripodal phosphine thioether, 2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane (P_2S), towards Fe^{II}, Ni^{II}, Pd^{II}, Pt^{II}, Co^{II}, Rh^{I} was investigated. The ligand reacts with $CpFe(CO)_2I$, $NiCl_2$, $PdCl_2(CH_3CN)_2$, K_2PtCl_4, $CoCl_2$, $[(NBD)RhCl]_2$ and $(NBD)_2RhBF_4$[NBD = 2,5-norbornadiene] to give the respective complexes. The tripodal ligand behaves as tridentate in $[(P,P',S\text{-}P_2S)FeCp]PF_6$ and $[(P,P',S\text{-}P_2S)Rh(NBD)]BF_4$, but as bidentate in the other complexes. Crystal structures of $[P,P',S\text{-}(P_2S)FeCp]PF_6$ (**2a**) and $[P,P'\text{-}(P_2S)]NiI_2$ (**5**) have been determined.

1. Introduction

Polydentate phosphines incorporating mixed donor atoms with consequent modified reactivity of the metal ion have received attention recently. Our research on synthesis of tripodal phosphines containing different donor atoms **1** and on their coordination chemistry has shown that the tripodal ligand **1** can function in bidentate or tridentate mode [1–6]. The thermal reaction of **1** with group VI metal hexacarbonyls produced bidentate complexes, except that the tridentate complex was formed when (η^6-cycloheptatriene)$W(CO)_3$ was used [7]. Additionally, sulphur donors exchanged in the complex of (**1d**)$PdCl_2$ due to the weak coordinating ability of thioether [2]. The use of a sulphur donor in **1a** as a bridging atom to construct polymeric copper(I) complexes was investigated previously [6]. To continue research in this field, we report the coordination behaviour of **1a** (P_2S) with various transition metal ions.



1a X = PPh_2, Y = SPh
b X = PPh_2, Y = OMe
c X = PPh_2, Y = NEt_2
d X = SPh, Y = SPh
e X = SPh, Y = NEt_2

2. Results and discussion

2.1. *Iron complex.*

The photochemical substitution of $CpFe(CO)_2I$ with the tripodal ligand P_2S in benzene solution leads to the formation of $[P,P',S\text{-}(P_2S)FeCp]^+I^-$ (**2**) in 92% yield. The spectral and analysis data are shown in Table 1. The 1:1 electrolyte nature of **2** is established by the measurement of conductivity in acetone (121.6 Ω^{-1} cm^2 mol^{-1}). The detailed structure is further confirmed by single crystal structure analysis of $[P,P',S\text{-}(P_2S)FeCp]^+PF_6^-$ (**2a**), which was obtained by the anionic metathesis of **2** with ammonium hexafluorophosphate. The atomic coordinates of **2a** are listed in Table 2 and an ORTEP plot is shown in Fig. 1. Bond distances of Fe–S (2.26 Å) and Fe–P (average 2.21 Å) are all in the normal range. Bond angles P1–Fe–P2 (90.75°), P1–Fe–S (84.93°), and P2–Fe–S (92.31°) are close to 90° (Table 3) indicating the octahedral geometry around the metal centre (viewing cyclopentadienyl as tridentate). The slightly smaller size of the P1–Fe–S angle than of P2–Fe–S is presumably due to the relief of steric hindrance of the phenylthio and diphenylphosphino moieties (P2). The average Fe–C distance 2.09 Å is typical for the Cp–Fe moiety. The dihedral angles of the three six member chelate rings (Table 4) indicate they are all in a twist-boat conformation as indicated by the characteristic four positive and two negative values. Complex **2** exhibits a distinct singlet shift for the methyl group at $\delta = 1.49$, which provides a defini-

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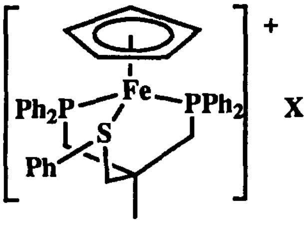
tive characteristic to identity P_2S as being either bidentate or tridentate in complexes (Table 5).

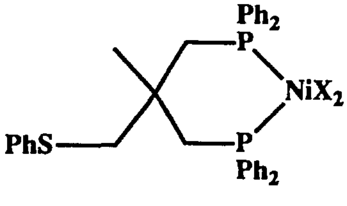


2 X = I
2a X = PF_6

When the reaction of **1a** with $CpFe(CO)_2I$ is thermal, in acetonitrile, rather than photochemical, a mixture of **2**, $[P,P'\text{-}(P_2S)]FeCpI$ and $[\{P,P'\text{-}(P_2S)\}FeCp(CO)]^+I^-$ results, identified from infrared and NMR spectra. However, the separation of three species has not yet proved possible.

2.2. Nickel complexes

Reactions of the tripodal ligand P_2S with equimolar NiX_2 (X = Cl, Br, I) in dichloromethane at room temperature give the desired complexes of the type $[P,P'\text{-}(P_2S)NiX_2]$ {X = Cl, **3**; Br, **4**; I, **5**}, in which P_2S exhibits a bidentate mode of coordination. The physical and spectral data of these complexes are listed in Table 1. In the case of complex **5**, a crystal of X-ray quality was obtained by recrystallization from diethyl ether and dichloromethane, and its ORTEP plot is given in Fig. 2. The final non-hydrogen atomic coordinates and selected bond distance and bond angles of **5** are listed in Tables 6 and 7, respectively.



3, X = Cl
4, X = Br
5, X = I
6, X = CO

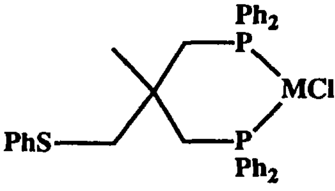
The molecular structure of **5** is quite similar to that of $(P_2O)NiCl_2$, where P_2O = 2,2-bis(diphenylphosphinomethyl)-1-methoxypropane [3]. Nickel metal is bonded in square-planar NiP_2I_2 fashion. The average bond distances Ni–P and Ni–I are 2.18 and 2.52 Å respectively, which are within the normal range. The distortion of P1–Ni–P2 (95.5(4)°) away from 90° is presumably due to the relief of the steric congestion of two diphenylphosphino moieties. The conformation of the chelate ring adopts a near half-chair form as indicated by the small dihedral angles of C3–P2–Ni–P1 and P2–Ni–P1–C1 (Table 4). The preferred conformation in **5** is the consequence of minimization of the eclipsed interaction of phenyl groups and iodides.

The diamagnetic properties of **3** and **4**, similar to those of **5** in the solid state, suggest the geometry of both complexes to be square-planar. But one question to be addressed here is whether such a geometry for $[P,P'\text{-}(P_2S)NiX_2]$ still applies in solution. It has been reported [8] that $[(dppp)NiX_2]$ exhibited equilibrium between square-planar and tetrahedral species in solution. Complexes **3**, **4** and **5** appear to have similar behaviour, as they all have the characteristic electronic absorptions around 820 nm in dichloromethane solution (Table 1) which are indicative of the presence of tetrahedral species [8,9], *i.e.* the nature of $(P_2S)NiX_2$ in solution is similar to that of $[(dppp)NiX_2]$.

Reduction of $[P,P'\text{-}(P_2S)NiX_2]$ with zinc powder in the presence of carbon monoxide produces the corresponding dicarbonyl complex $[P,P'\text{-}(P_2S)Ni(CO)_2]$ (**6**) in high yield. The ^{31}P NMR spectrum of **6** consists only of a singlet at 15.7 ppm, suggesting both phosphorus atoms coordinate to the metal centre. The infrared absorptions at 1996 and 1937 cm^{-1} are typical for $L_2Ni(CO)_2$ [10]. Both spectral and elemental analysis (Table 1) confirm the structure of **6**, clearly eliminating the possibility of formation of $[P,P',S\text{-}(P_2S)Ni(CO)]$. The tripodal ligand P_2S only behaves as a bidentate in the series of nickel complexes.

2.3. Palladium and platinum complexes

$P,P'\text{-}(P_2S)PdCl_2$ (**7**) was readily obtained from the substitution of $(CH_3CN)_2PdCl_2$ with P_2S in dichloromethane, while $P,P'\text{-}(P_2S)PtCl_2$ (**8**) is produced from the reaction of K_2PtCl_4 with the tripodal ligand under phase transfer catalysis conditions. The single absorption in ^{31}P NMR spectra of both **7** and **8** at 19.24 and 0.62(J(Pt–P) = 3432 Hz) respectively indicates that both phosphorus donors of P_2S coordinate to the metal centres. Again, P_2S acts in bidentate mode in these complexes. Unlike (**1d**) $PdCl_2$ [2], complexes **7** and **8** do not show intramolecular donor exchange.



7, M = Pd
8, M = Pt
9, M = Co

TABLE 1. Physical and spectral data

Complex	Colour	m.p. (dec.) (°C)	^{31}P NMR	UV/VIS	Elemental analyses
2	brown	152–155	53.96	–	$C_{40}H_{39}IP_2S$ Fe C, 59.86 (60.32); H, 4.49 (4.93)
2a	dark red	215–220	54.98	–	$C_{40}H_{39}F_6P_3S$ Fe C, 58.99 (58.98); H, 4.94 (4.82)
3	orange	138–141	30.29	828 (ϵ = 0), 466 (ϵ = 1130), 306 (ϵ = 11440), 284 (ϵ = 23300), 262 (ϵ = 28700), 238 (ϵ = 19100),	$C_{35}H_{34}Cl_2P_2SNi$ C, 61.36(61.98); H, 5.45(5.15)
4	red	138–142	–	817 (ϵ = 24), 486 (ϵ = 2263), 402 (ϵ = 1540), 312 (ϵ = 21300), 262 (ϵ = 40200), 244 (ϵ = 32400)	$C_{35}H_{34}Br_2P_2SNi$ C, 55.26(54.79); H, 4.77(4.47)
5	purple	144–147	–	818 (ϵ = 51), 550 (ϵ = 590), 364 (ϵ = 2610), 296 (ϵ = 11000), 258 (ϵ = 16000), 236 (ϵ = 17800)	$C_{35}H_{34}I_2P_2SNi$ C, 48.38(48.81); H, 3.71(3.98)
6	white	103–107	15.70	–	$C_{37}H_{34}O_2P_2SNi$ C, 67.28(66.99); H, 5.29(5.17)
7	white	220–226	19.24		$C_{35}H_{34}Cl_2P_2SPd$ C, 57.22(57.90); H, 4.57(4.72)
8	white	219–224	0.62 [J(Pt–P) = 3432 Hz]	–	$C_{35}H_{34}Cl_2P_2SPt$ C, 51.25(51.60); H, 4.03(4.20)
9	blue	127–130	–	722 (ϵ = 120), 648 (ϵ = 203) 594 (ϵ = 210), 258 (ϵ = 8011) 238 (ϵ = 7040)	$C_{35}H_{34}Cl_2P_2SCo$ C, 62.12(61.96); H, 4.90(5.05)
10	orange	100–104	30.67 [J(Rh–P) = 150 Hz] 10.83 [J(Rh–P) = 118 Hz]		$C_{36}H_{34}ClOP_2SRh$ C, 60.07(60.47); H, 4.52(4.79)
11	yellow	154–156 [a]	21.07 [J(Rh–P) = 128 Hz]	–	$C_{42}H_{42}ClP_2SRh$ C, 65.18(64.74); H, 5.60(5.43)
12	yellow	154–156 [a]	20.92 [J(Rh–P) = 128 Hz]	–	$C_{42}H_{42}ClP_2SRh$ C, 65.18(64.74); H, 5.60(5.43)
13	yellow	158–162	15.73 [J(Rh–P) = 126 Hz]		$C_{42}H_{42}BF_4P_2SRh$ C, 60.24(60.74); H, 4.91(5.09)

[a] The mixture of **11** and **12**.

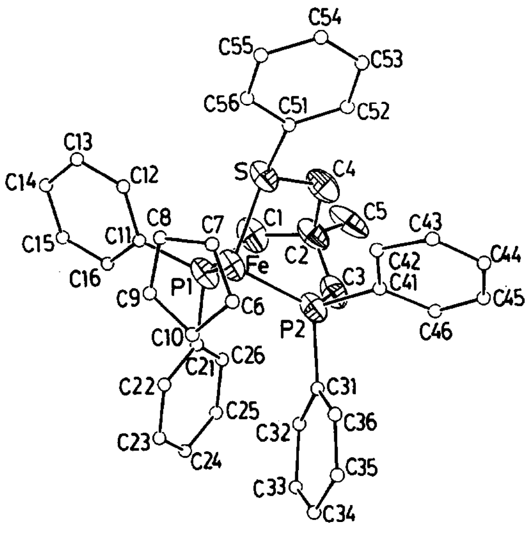


Fig. 1. ORTEP drawing of complex **2a**. C11–C56 atoms are all refined anisotropically. For a clear view, all these atoms are drawn as simple circles.

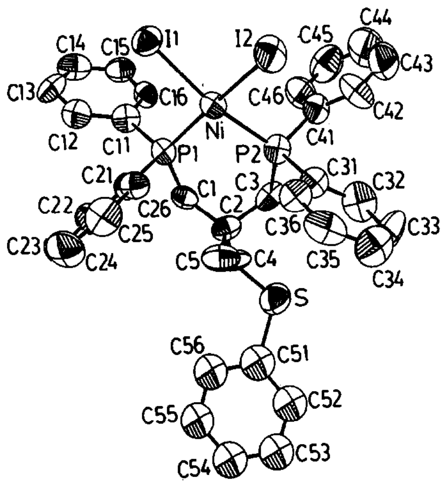


Fig. 2. ORTEP drawing of complex **5**.

TABLE 2. Atomic coordinates and thermal parameters of **2a**

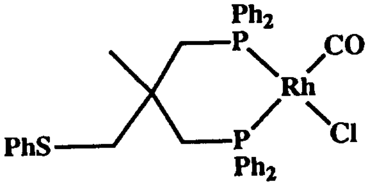
Atom	x	y	z	B_{iso}
Fe	0.62506(17)	0.06436(13)	0.79523(13)	3.44(10)
P1	0.6000(3)	−0.05529(25)	0.83490(24)	3.66(22)
P2	0.7736(3)	0.03997(25)	0.8141(3)	3.77(22)
S	0.5927(3)	0.01387(24)	0.66555(24)	3.87(22)
C1	0.6330(12)	−0.1285(8)	0.7658(9)	4.4(9)
C2	0.7163(11)	−0.1023(8)	0.7302(9)	4.2(9)
C3	0.7953(11)	−0.0636(9)	0.7954(9)	4.3(9)
C4	0.6837(11)	−0.0517(9)	0.6545(9)	4.4(9)
C5	0.7604(13)	−0.1782(9)	0.7020(9)	5.3(11)
C6	0.6521(11)	0.1802(9)	0.8266(9)	4.4(9)
C7	0.5778(11)	0.1774(9)	0.7620(9)	4.6(9)
C8	0.5058(12)	0.1338(9)	0.7840(9)	4.6(9)
C9	0.5394(11)	0.1112(9)	0.8655(9)	4.6(9)
C10	0.6308(11)	0.1371(9)	0.8958(9)	4.1(8)
C11	0.4797(11)	−0.0865(8)	0.8268(8)	3.5(8)
C12	0.4103(11)	−0.0633(10)	0.7580(9)	4.6(9)
C13	0.3213(11)	−0.0903(9)	0.7468(9)	4.8(10)
C14	0.2997(11)	−0.1412(10)	0.8050(10)	5.0(10)
C15	0.3684(12)	−0.1643(9)	0.8722(9)	4.8(10)
C16	0.4557(11)	−0.1370(9)	0.8832(9)	4.3(9)
C21	0.6551(10)	−0.0846(8)	0.9423(9)	3.8(8)
C22	0.6437(11)	−0.0369(9)	1.0066(9)	4.3(9)
C23	0.6852(11)	−0.0564(10)	1.0862(9)	5.0(10)
C24	0.7371(12)	−0.1228(10)	1.1045(9)	5.4(10)
C25	0.7489(12)	−0.1700(10)	1.0427(10)	5.6(10)
C26	0.7070(12)	−0.1510(9)	0.9613(9)	4.8(10)
C31	0.8477(10)	0.0647(9)	0.9165(8)	4.0(8)
C32	0.8592(11)	0.0132(11)	0.9820(10)	5.7(11)
C33	0.9078(11)	0.0426(13)	1.0647(10)	8.4(14)
C34	0.9469(12)	0.1110(12)	1.0759(11)	7.7(13)
C35	0.9391(15)	0.1571(10)	1.0052(13)	9.0(14)
C36	0.8857(15)	0.1359(10)	0.9299(10)	7.5(14)
C41	0.8392(11)	0.0908(9)	0.7494(9)	4.2(9)
C42	0.9338(11)	0.0720(11)	0.7554(11)	6.6(11)
C43	0.9817(12)	0.1120(12)	0.7093(12)	8.4(14)
C44	0.9446(13)	0.1719(12)	0.6577(12)	8.4(14)
C45	0.8546(13)	0.1895(10)	0.6499(10)	6.2(11)
C46	0.7971(12)	0.1504(9)	0.6938(10)	4.7(10)
C51	0.5800(10)	0.0787(8)	0.5804(8)	3.9(8)
C52	0.6415(12)	0.0845(10)	0.5276(9)	5.8(11)
C53	0.6213(13)	0.1381(10)	0.4616(10)	6.1(11)
C54	0.5469(13)	0.1815(10)	0.4466(9)	5.7(11)
C55	0.4841(13)	0.1737(10)	0.4984(11)	5.5(10)
C56	0.5017(11)	0.1234(9)	0.5624(9)	4.4(9)
P	0.2256(4)	0.3761(3)	0.0972(3)	6.0(3)
F1	0.2524(12)	0.3516(9)	0.0190(8)	15.2(12)
F2	0.2062(11)	0.3992(10)	0.1772(9)	18.8(14)
F3	0.3031(9)	0.3258(8)	0.1443(9)	13.8(11)
F4	0.1484(12)	0.4282(9)	0.0539(11)	20.4(14)
F5	0.1603(9)	0.3065(8)	0.0844(10)	15.0(12)
F6	0.2945(9)	0.444(7)	0.1066(8)	11.3(9)
C61	0.08167	0.64834	0.11788	5.53
C62	0.14167	0.68652	0.13366	5.53
C63	0.08316	0.60517	0.04843	5.53
C64	0.02500	0.62494	0.15208	5.53

2.4. Cobalt complex

Complexation of $CoCl_2$ with equimolar tripodal ligand **1a** in butyl alcohol results in the formation of P,P'-$(P_2S)CoCl_2$ (**9**). Such a complex appears not to be an electrolyte in acetone, and this is quite different from the dimeric species $[(P,P',P''\text{-}P_3)CoCl]_2(BPh_4)_2$ where $P_3 = CH_3C(CH_2PPh_2)_3$ [11], but is identical to that of $(P,P'\text{-}P_3)CoCl_2$ [12]. Besides, both the magnetic moment (4.16 BM) and electronic absorption (Table 1) for **9**, which are essentially similar to those of $(dppp)CoCl_2$ [13] and $(P,P'\text{-}P_3)CoCl_2$ [12], reflect the cobalt centre having the CoP_2Cl_2 core in a tetrahedral geometry, *i.e.* the sulphur donor in **1a** remains uncoordinated.

2.5. Rhodium complexes

$[P,P'(P_2S)Rh(CO)Cl]$ (**10**) is prepared from the reaction of tripodal ligand with dimeric $[Rh(CO)_2Cl]_2$ in acetone. Complex **10** appears to be a non-electrolyte in acetone. Thus the coordination around rhodium is square-planar with a carbonyl, a chloride and a biphosphine from the tripodal ligand that are *cis* to each other; this structure is further confirmed by the following spectral data. Infrared absorption at 2012 cm^{-1} clearly shows the existence of Rh–CO. The ^{31}P NMR spectrum of **10** shows two sets of doublets of doublets at 30.68 (J(Rh–P) = 150 Hz, J(P–P) = 54 Hz) and 10.83(J(Rh–P) = 118 Hz, J(P–P) = 54 Hz). The downfield shift is from the phosphorus donor *trans* to chloride ligand, whereas that upfield is from the one *trans* to carbonyl ligand. The larger J(Rh–P) is another indication of phosphorus *trans* to the chloride ligand [14].



10

Treatment of $[(NBD)RhCl]_2$ with one equivalent of P_2S gives a stereo-isomeric mixture of penta-coordinate rhodium(I) complex **11** and **12** in a ratio of 6:4. Although separation of **11** and **12** is not yet possible, the characterization of both complexes was achieved

TABLE 3. Selected bond distances (Å) and angles (°)

Fe–P1	2.222(5)	P1–Fe–P2	90.75(18)
Fe–P2	2.191(5)	P1–Fe–S	84.93(16)
Fe–S	2.262(5)	P2–Fe–S	92.32(17)
Fe–C6	2.078(15)	P1–Fe–C6	148.6(4)
Fe–C7	2.100(15)	P1–Fe–C7	150.5(5)
Fe–C8	2.106(16)	P1–Fe–C8	110.9(5)
Fe–C9	2.080(14)	P1–Fe–C9	91.5(4)
Fe–C10	2.071(14)	P1–Fe–C10	107.5(4)

TABLE 4. Dihedral angles along the chelate rings for **2a** and **5**

Complex **2a**						Complex **5**	
Fe–P1–C1–C2–C3–P2		Fe–P1–C1–C2–C4–S		Fe–P2–C3–C2–C4–S		Ni–P1–C1–C2–C3–P2	
Fe–P1–C1–C2	32.3(6)	Fe–P1–C1–C2	32.3(6)	Fe–P2–C3–C2	41.6(6)	Ni–P1–C1–C2	40(1)
P1–C1–C2–C3	43.3(7)	P1–C1–C2–C4	−83.5(11)	P2–C3–C2–C4	−88.7(11)	P1–C1–C2–C3	−67(2)
C1–C2–C3–P2	−81.1(10)	C1–C2–C4–S	39.1(7)	C3–C2–C4–S	45.2(8)	C1–C2–C3–P2	67(2)
C2–C3–P2–Fe	30.3(6)	C2–C4–S–Fe	41.6(6)	C2–C4–S–Fe	30.3(6)	C2–C3–P2–Ni	−40(2)
C3–P2–Fe–P1	30.4(5)	C4–S–Fe–P1	−68.7(5)	C4–S–Fe–P2	−54.5(5)	C3–P2–Ni–P1	9(1)
P2–Fe–P1–C1	−60.9(5)	S–Fe–P1–C1	31.4(5)	S–Fe–P2–C3	21.8(5)	P2–Ni–P1–C1	−10(1)

unambiguously from their spectral and elemental data (Table 1). The tripodal ligand P_2S still remains as a bidentate in the complexes **11** and **12**. The difference between **11** and **12** is the orientation of phenylthiomethyl group and chloride along the chelate ring. In our previous investigation [15] of both *syn*- and *anti-fac*-[*P*,*P*′-(P_2S)Mn(CO)$_3$Br] (**14**), the ^{1}H NMR chemical shift of the methyl group was found to be a unique characteristic for the differentiation of such stereoisomers, which is also applied in this rhodium complex. The down-field ^{1}H NMR shift of methyl group ($\delta = 1.25$) of **12** is due to the group being deposited at axial orientation of the chelate ring [15]. Despite the *trans* influence of ligands, the coupling constant of rhodium–phosphorus, however, has been a characteristic feature for distinguishing the coordination number around the metal [16,17]. The increase of coordination number is in agreement with the decrease of coupling constant *J*(Rh–P). Indeed, the coupling constants (*J*(Rh–P) = 128 Hz) for **11** and **12** are analogous to those of known five-coordinate species [16,17].

Addition of **1a** to a dichloromethane solution of [(NBD)$_2$Rh]$^+$BF$_4^-$ yields the complex [*P*,*P*′,*S*-(P_2S)Rh(NBD)]$^+$BF$_4^-$ (**13**), which is another example of **1a** acting in a tridentate mode. Elemental analysis and measurement of the conductivity (145 Ω^{-1} cm^2 mol^{-1}) of **13** in acetone confirm respectively the molecular formula and the nature of the 1:1 electrolyte of this complex. Analysis of complex **13** by ^{1}H NMR spectroscopy reveals that chemical shifts of the methyl group ($\delta = 1.43$) and the methylene group ($\delta = 3.00$) adjacent to sulphur are fairly down-field compared to those in **11** or **12**. These evidences indicate that the sulphur donor of P_2S is coordinated to the metal centre in **13**, which is essentially similar to what is seen in [(η^3-P_3)Rh(NBD)][CF$_3$SO$_3$] [18]. The Rh–P coupling constant ($J = 126$ Hz) for **13** also suggests such species to have a five-coordinate geometry.

TABLE 5. The ^{1}H NMR chemical shifts of methyl groups in various complexes containing tripodal ligand P_2S

Complex	Coordination mode of tripodal ligand	Chemical shift δ of methyl group	Ref.
2	terdentate	1.49	This work
3	bidentate	0.58	This work
4	bidentate	0.54	This work
5	bidentate	0.55	This work
6	bidentate	0.53	This work
7	bidentate	0.51	This work
8	bidentate	0.54	This work
10	bidentate	0.63	This work
11	bidentate	0.04	This work
12	bidentate	1.25	This work
13	terdentate	1.43	This work
[*P*,*P*′,*S*-(**1a**)]W(CO)$_3$	terdentate	1.28	7
[*P*,*P*′-(**1a**)]W(CO)$_4$	bidentate	0.71	1
[*P*,*P*′-(**1a**)]Mo(CO)$_4$	bidentate	0.70	1
[*P*,*P*′-(**1a**)]Cr(CO)$_4$	bidentate	0.70	1
syn-fac-[*P*,*P*′-(**1a**)]Mn(CO)$_3$Br	bidentate	0.36	15
anti-fac-[*P*,*P*′-(**1a**)]Mn(CO)$_3$Br	bidentate	1.13	15
[{*P*,*P*′,*S*-(**1a**)}Mn(CO)$_3$]PF$_6$	terdentate	1.60	7

TABLE 6. Atomic coordinates and thermal parameters of **5**

Atom	*x*	*y*	*z*	B_{iso}
Ni	0.31786(13)	0.51628(13)	0.07254(8)	3.73(13)
I1	0.36493(9)	0.61721(8)	0.04853(5)	5.55(8)
I2	0.25393(3)	0.51548(10)	0.00642(5)	6.89(10)
P1	0.3868(3)	0.5127(3)	0.12284(17)	3.8(3)
P2	0.2633(3)	0.4390(3)	0.09570(17)	4.3(3)
S	0.3160(9)	0.2988(9)	0.2117(6)	7.0(10)
S1A (0.5) [a]	0.4033(17)	0.3438(16)	0.2284(10)	6.0(18)
S1B (0.25) [a]	0.3845(17)	0.2901(16)	0.1319(10)	5.7(16)
S1C (0.25) [a]	0.4427(21)	0.3246(19)	0.1510(11)	7.7(23)
C1	0.3740(10)	0.4622(10)	0.1688(6)	4.1(10)
C2	0.3459(11)	0.3984(10)	0.1628(6)	4.3(11)
C3	0.2792(11)	0.4055(10)	0.1481(6)	4.2(11)
C4	0.3448(13)	0.3071(11)	0.2070(7)	6.0(13)
C5	0.3847(13)	0.3602(11)	0.1302(8)	6.2(14)
C11	0.3994(10)	0.5850(10)	0.1506(6)	4.3(11)
C12	0.4551(11)	0.6181(11)	0.1485(6)	4.7(11)
C13	0.4615(12)	0.6727(10)	0.1688(7)	5.2(13)
C14	0.4132(12)	0.6965(11)	0.1912(7)	5.6(13)
C15	0.3584(11)	0.6657(10)	0.1925(7)	5.0(12)
C16	0.3517(10)	0.6105(10)	0.1728(6)	4.2(10)
C21	0.4589(10)	0.4872(10)	0.1021(6)	3.9(10)
C22	0.5122(11)	0.4805(11)	0.1275(7)	5.0(12)
C23	0.5687(11)	0.4577(12)	0.1106(8)	5.8(14)
C24	0.5714(13)	0.4411(13)	0.0692(9)	7.1(15)
C25	0.5199(12)	0.4470(12)	0.0447(7)	6.1(14)
C26	0.4638(10)	0.4690(10)	0.0592(7)	4.3(10)
C31	0.2603(11)	0.3714(10)	0.0622(7)	4.6(11)
C32	0.2162(13)	0.3257(14)	0.0698(8)	6.9(15)
C33	0.2164(16)	0.2705(13)	0.0463(9)	8.4(18)
C34	0.2573(15)	0.2598(14)	0.0161(8)	7.4(17)
C35	0.3024(13)	0.3043(13)	0.0099(7)	6.7(14)
C36	0.3036(11)	0.3597(11)	0.0326(7)	5.1(12)
C41	0.1855(11)	0.4647(10)	0.1036(7)	4.7(11)
C42	0.1389(12)	0.4514(14)	0.0776(8)	6.7(15)
C43	0.0800(15)	0.4724(15)	0.0844(10)	8.9(19)
C44	0.0691(15)	0.5114(16)	0.1200(12)	10.0(22)
C45	0.1175(15)	0.5253(14)	0.1444(10)	8.4(18)
C46	0.1752(12)	0.5038(13)	0.1367(9)	6.5(15)
C51 (0.5) [a]	0.37666	0.23914	0.22077	7.90
C52 (0.5) [a]	0.36339	0.17380	0.22662	7.90
C53 (0.5) [a]	0.40910	0.12910	0.23360	7.90
C54 (0.5) [a]	0.46810	0.14970	0.23480	7.90
C55 (0.5) [a]	0.48400	0.21370	0.22920	7.90
C56 (0.5) [a]	0.43832	0.25835	0.22216	7.90
O	0.5473(18)	0.2616(21)	0.0573(14)	21.9(16)

[a] Occupancy.

TABLE 7. Selected bond distances (Å) and bond angles (°) for **5**

Ni–I1	2.530(3)	I1–Ni–I2	88.68(10)
Ni–I2	2.514(3)	I1–Ni–P1	88.59(19)
Ni–P1	2.187(6)	I1–Ni–P2	170.06(22)
Ni–P2	2.178(7)	12-Ni–P1	170.04(20)
P1–C1	1.844(21)	I2–Bi–P2	88.68(19)
P2–C3	1.846(21)	P1–Ni–P2	95.56(24)

3. Conclusion

The tripodal ligand P_2S can behave either as bidentate or tridentate when coordinating to metal complexes, as illustrated in a series of complexes by spectral and crystallographic studies. In the case of the bidentate mode of P_2S, the sulphur donor always remains uncoordinated, indicating that the interaction of the metal with the sulphur donor is weaker than that with phosphorus. The labile natures of the sulphur donor in **2** and **13** are currently under investigation.

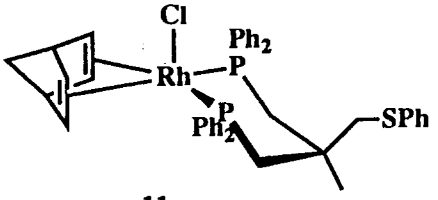
4. Experimental details

4.1. General

^1H and ^{31}P NMR spectra were determined on a Bruker AC-E 200 or AM-300WB spectrometer. Chemical shifts are given in parts per million relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted.

Infrared and UV/VIS spectra were obtained on Perkin–Elmer 983G and Perkin–Elmer Lambda 3B instruments respectively. Elemental analyses were made on a Perkin–Elmer 240C instrument. All reactions, manipulations and purification steps involving phosphines were performed under dry nitrogen. The photochemical apparatus was a 450 W Conrad–Hanovia medium-pressure mercury lamp (Ace Glass).

The tripodal ligand P_2S was synthesized as described previously [1]. Elemental analyses and some spectral data are in Table 1.



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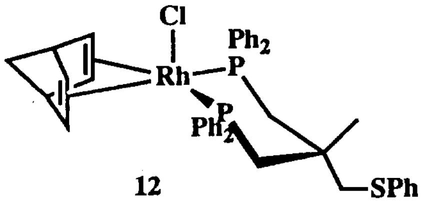

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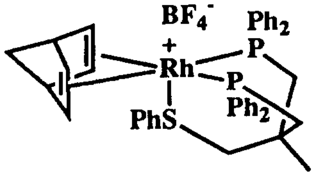

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4.2. *Cyclopentadienyl{P,P′,S-[2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane]}iron(II) iodide* (**2**)

A mixture of $CpFe(CO)_2I$ (58.7 mg, 0.193 mmol) and **1a** (105.9 mg, 0.193 mmol) in benzene (20 ml) was placed in a Pyrex flask (50 ml) and was photolyzed at room temperature for 7 h. After removal of solvents the residue was chromatographed on silica with elution of acetone/dichloromethane (3:7). The eluent was concentrated to give **2** as a brown solid (141.4 mg, 92%): ^1H NMR δ 7.62–6.94 (m, 25H), 4.31 (t, $J = 1$ Hz, 5H), 2.59 (s, 2H), 2.49 (dd, $J = 16.8$ Hz, 2H), 2.30 (dd, $J = 16.9$ Hz, 2H), 1.49 (t, $J = 3$ Hz, 3H); conductivity (acetone), 121.6 Ω^{-1} cm^2 mol^{-1}.

4.3. *Cyclopentadienyl{P,P′,S-[2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane]}iron(II) hexafluorophosphate* (**2a**)

A solution of NH_4PF_6 (114.4 mg, 0.70 mmol) in water (1 ml) was added to a solution of **2** (194.3 mg, 0.244 mmol) in acetone (4 ml) with stirring at room temperature. Water (1 ml) was slowly added to the solution and the reaction mixture gave a brown precipitate. The solid was collected and washed with water (2 ml). Recrystallization from acetone/water gave **2a** as a dark red solid (175.2 mg, 88%): ^1H NMR δ 7.79–7.14 (m, 25H), 4.55 (t, $J = 1$ Hz, 5H), 2.75 (s, 2H), 2.67 (dd, $J = 15, 8$ Hz, 2H), 2.40 (dd, $J = 15, 9$ Hz, 2H), 1.45 (t, 3 Hz, 3H); Conductivity (acetone) 128 Ω^{-1} cm^2 mol^{-1}.

4.4. *{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}nickel(II) chloride* (**3**)

A mixture of P_2S (82.6 mg, 0.15 mmol) and $NiCl_2 \cdot$ DME (35.3 mg, 0.16 mmol) (DME = 1,2-dimethoxyethane) in dichloromethane (3.5 ml) was stirred at room temperature overnight. The reaction mixture was filtered and concentrated and the residue dissolved in dichloromethane and benzene. Orange needle crystalline solids were collected as the desired complex (94.9 mg, 93%): ^1H NMR δ 8.16–6.98 (m, 25H), 2.52 (s, 2H), 1.61 (br, m, 4H), 0.58 (s, 3H).

4.5. *{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}nickel(II) bromide* (**4**)

A mixture of P_2S (105.0 mg, 0.191 mmol) and $NiBr_2 \cdot$ DME (62.8 mg, 0.204 mmol) in dichloromethane (8 ml) was stirred at room temperature for 8 h. The volume of solvent was reduced to 4 ml and ether added (4 ml). The red crystalline solid that was precipitated from solution was filtered and dried (132.1 mg, 90%): ^1H NMR δ 8.03–6.94 (m, 25H), 2.39 (s, 2H), 1.56 (br, m, 4H), 0.54 (s, 3H).

4.6. *{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}nickel(II) iodide* (**5**)

In a flask was placed anhydrous nickel iodide (73.4 mg, 0.235 mmol) and P_2S (124.0 mg, 0.226 mmol). Dichloromethane (10 ml) was added and the suspension was stirred for 18 h. After removal of the solvents a mixture of dichloromethane and ether was added to the residue. The desired complex **5** was isolated as a purple crystalline solid (93.4 mg, 48%): ^1H NMR δ 8.30–6.50 (m, 25H), 2.25 (s, 2H), 2.09 (br, m, 4H), 0.55 (s, 3H).

4.7. *Dicarbonyl{P,P′-[2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane]}nickel(0)* (**6**)

CO was bubbled for 3 h through a mixture of **2** (40.7 mg, 0.060 mmol), zinc powder (30 mg, 0.458 mmol) and anhydrous zinc chloride (2.5 mg) in anhydrous acetone (4 ml). The solution changed from red to colourless. Pentane was added to the filtrate to give white precipitates. The white precipitate was collected, washed with pentane and dried under vacuum to give the desired complex **6** (37.0 mg, 93%): IR (ν(CO), acetone) 1996, 1937 cm^{-1}; ^1H NMR δ 7.87–7.24 (m, 25H), 3.04 (s, 2H), 2.83 (dd, $J = 14, 12$ Hz, 2H), 2.40 (dd, $J = 14, 5$ Hz, 2H), 0.53 (s, 3H).

4.8. *{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}palladium(II) chloride* (**7**)

A mixture of P_2S (58.7 mg, 0.11 mmol) and $(PhCN)_2PdCl_2$ (41.6 mg, 0.11 mmol) in dichloromethane (4 ml) was stirred overnight at room temperature. Upon concentration, the crude product was obtained (74.0 mg, 95%) as a pale yellow solid. Recrystallization from dichloromethane and hexane gave the title compound as white needle crystals: ^1H NMR (CD_2Cl_2) δ 8.10–8.03 (m, 4H), 7.79–7.72 (m, 4H), 7.57–7.45 (m, 12H), 7.17–7.15 (m, 3H), 7.03–7.00 (m, 2H), 2.70 (s, 2H), 2.48 (dd, $J = 15$ Hz, J(P–C–H) = 9.6 Hz, 2H), 2.43 (dd, $J = 15$ Hz, J(P–C–H) = 8.4 Hz, 2H), 0.51 (s, 3H).

4.9. *{[P,P′-2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}platinum(II) chloride* (**8**)

A mixture of P_2S (137.8 mg, 0.251 mmol), K_2PtCl_4 (103.9 mg, 0.250 mmol) and tetrabutylammonium bromide (10.2 mg, 0.032 mmol) dispersed in water (10 ml) and dichloromethane (20 ml) was stirred at room temperature overnight. The organic layer was separated and the aqueous layer extracted with dichloromethane (10 ml × 2). The organic extracts were combined, dried and concentrated. The residue was dissolved in dichloromethane (5 ml) and pentane (15 ml) was added. The desired complex **8** precipitated as a white solid: ^1H NMR (CD_2Cl_2) δ 8.10–8.06 (m, 4H), 7.79–7.75 (m, 4H), 7.56–7.46 (m, 12H), 7.21–7.14 (m, 3H), 7.04–7.01 (m, 2H), 2.70 (s, 2H), 2.58 (dd, $J = 15.2$ Hz, J(P–C–H) = 10.9 Hz, 2H), 2.50 (dd, $J = 15.2$ Hz, J(P–C–H) = 9.2 Hz, 2H), 0.54 (s, 3H).

4.10. *{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}cobalt (II) chloride* (**9**)

The cobalt complex was prepared by the reaction of $CoCl_2$ (29.5 mg, 0.227 mmol) with P_2S (118 mg, 0.215 mmol) in dichloromethane (8 ml). After stirring at room temperature for 2 h, the reaction mixture was concentrated. Recrystallization from dichloromethane and ether gave the desired complex as a blue crystalline solid (132.7 mg, 91%): conductivity 8.8 Ω^{-1} cm^2 mol^{-1} in acetone; magnetic moment 4.16 μ_B.

4.11. *cis-Chlorocarbonyl{P,P′-[2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane]}rhodium(I)* (**10**)

A solution of $[Rh(CO)_2Cl]_2$ (42.5 mg, 0.219 mmol) and P_2S (120.0 mg, 0.218 mmol) in acetone (3 ml) was stirred at room temperature for 20 min. Pentane (6 ml) was added to the reaction mixture and orange solids formed. The solvent was decanted and the residue washed with pentane (3 ml × 2). The orange solid was collected, dried and identified as the desired complex **10** (148 mg, 95%): IR (υ(CO), acetone) 2012 (s) cm^{-1}; ^{1}H NMR δ 8.11–7.11 (m, 25H), 3.01 (d, $J = 13$ Hz, 1H), 2.97 (d, $J = 13$ Hz, 1H), 2.85–2.39 (m, 4H), 0.63 (s, 3H).

4.12. *[cis- and trans-{P,P′-[2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane]}(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride* (**11** *and* **12**)

A solution of ligand P_2S (95.0 mg, 0.173 mmol) in acetone was added to a solution of $[(NBD)RhCl]_2$ (39.0 mg, 0.169 mmol) in acetone. Yellow precipitates formed immediately. The reaction mixture was centrifuged and the solvent was decanted. The yellow solid was washed with acetone/hexane (3 ml × 2) and dried (110.6 mg, 84%). This product was identified as a mixture of *cis*-form **11** and *trans*-form **12**: conductivity 9.3 Ω^{-1} cm^2 mol^{-1} in acetone; ^{1}H NMR (i) complex **11**: δ 8.90–6.00 (m, 25H), 3.86 (dd, $J = 13$, 8 Hz, 2H), 3.46 (m, 2H), 3.34 (m, 4H), 2.84 (s, 2H), 2.20 (dd, $J = 15$, 13 Hz, 2H), 0.95 (m, 2H), 0.04 (s, 3H). (ii) complex **12**: δ 8.90–6.00 (m, 25H), 3.71 (dd, $J = 14$, 9 Hz, 2H), 3.46 (m, 2H), 3.34 (m, 4H), 2.42 (dd, $J = 15$, 14 Hz, 2H), 1.80 (s, 2H), 1.25 (t, $J = 3$ Hz, 3H), 0.95 (m, 2H).

TABLE 8. Crystal data of **2a** and **5**

Compound	**2a**	**5**
Formula	$FeP_3SC_{43}H_{45}F_6O$	$NiI_2P_2SC_{32}H_{24}O$
FW	872.66	831.06
a, Å	14.833(5)	21.668(5)
b, Å	17.235(5)	–
c, Å	16.577(7)	31.724(11)
β, deg	103.78(3)	–
V, Å^3	4116(3)	14894(6)
Z	4	16
Space group	$P2_1/c$	$I4_1/a$
T, K	298	298
λ, Å	0.71073	0.71073
ρ(calcd), g cm^{-3}	1.405	1.482
μ, cm^{-1}	0.54	2.32
Transm. coeff.	0.93 – 1.0	0.92 – 1.0
No. reflections	7223	4886
No. reflections $I > 2\sigma(I)$	3828	2621
No. variables	461	348
$R(F_o)$	0.095	0.068
$R_w(F_o)$	0.090	0.090
S	5.87	1.11

4.13. *[P,P′-2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropane](bicyclo-[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate* (**13**)

A solution of P_2S (76.8 mg, 0.14 mmol) and $[(NBD)_2Rh]BF_4$ (53.2 mg, 0.14 mmol) in dichloromethane was stirred for 2 h. The reaction mixture was filtered and concentrated. The residue was recrystallized from dichloromethane and hexane to give the rhodium complex as a yellow crystalline solid (108.1 mg, 93%): ^{1}H NMR d 7.56–7.08 (m, 25H), 3.81 (s, 2H), 3.71 (s, 4H), 3.00 (s, 2H), 2.53 (dd, $J = 15.4$ Hz, J(P–C–H) = 10.3 Hz, 2H), 2.35 (dd, $J = 15.4$ Hz, J(P–C–H) = 6.0 Hz, 2H), 1.43 (s, 3H), 1.39 (s, 2H); conductivity 145 Ω^{-1} cm^2 mol^{-1} in acetone.

4.14. *Crystallography*

Cell parameters were determined with a CAD-4 diffractometer at 298 K by a least-squares treatment. Atomic scattering factors were taken from ref. 19. Calculations were performed with the NRCC SDP VAX package [20]. The crystal data of **2a** and **5** are listed in Table 8, and other crystallographic data are available as supplementary material. In the case of **2a**, there is an acetone molecule in the asymmetric unit cell. All atoms of the acetone molecule are designated as C61–C64, because they are difficult to distinguish and cannot be refined. In compound **5**, the phenylthio group is disordered; the occupancies of the disorder sulphur atoms S1A, S1B and S1C are 0.5, 0.25 and 0.25 respectively. The half-occupied phenyl group which attaches to the S1A atom, is designated as C51–C56 and fixed in the refinement. The other quarter-occupied phenyl groups are very diffuse and not located. There is a solvated water molecule in the asymmetric unit cell. Lists of anisotropic thermal parameters, bond distances and angles and structure factors for **2a** and **5** are available from the authors.

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