DALTON

2,4-Diferrocenyl-1,3-dithiadiphosphetane 2,4-disulfide; structure and reactions with catechols and [$PtCl_2(PR_3)_2$] (R = Et or Bu^n)

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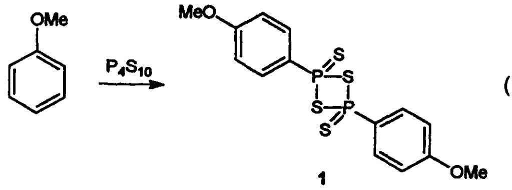
Reaction of ferrocene (or 1,1′-dimethylferrocene) with P_4S_{10} yielded R′P(S)S_2P(S)R′ (R′ = ferrocenyl) (or the analogous dimethylferrocene species). This compound reacted with catechols to form R′P(S)O_2C_2 ring systems and with [$PtCl_2(PR_3)_2$] (R = Et or Bu^n) to give [R′PS_3Pt$(PR_3)_2$]. The new compounds have been characterised spectroscopically with illustrative examples having been fully studied by X-ray crystallography.

The chemistry of P–S heterocyclic systems continues to attract interest since they are important commercially both as bulk materials and in organic synthesis. For example, dithiadiphosphetane disulfides with alkyl, aryl or heteroaryl groups attached to the phosphorus atoms are known, thus reaction (1) of anisole with P_4S_{10} gives 2,4-bis(*p*-methoxyphenyl)-1,3-dithiadiphosphetane disulfide **1** (commonly known as Lawesson's reagent),[1] which is extensively used in synthetic chemistry as a thionation reagent.[2,3] As ferrocene is electron rich and aromatic, its reaction with P_4S_{10} was attempted, to establish if the reaction forming dithiadiphosphetane disulfides such as **1** could be extended to furnish such compounds with a metallocene group in place of the aromatic group. Furthermore, the steric effects of a group intermediate in size between that of phenyl and *tert*-butyl could be investigated. Here, we report the preparation of (η-C_5H_5)Fe(η-C_5H_4)P(S)S_2P(S)(η-C_5H_4)Fe(η-C_5H_5) **2** together with some investigations into its reactions with catechols and with [$PtCl_2(PEt_3)_2$]. The crystal structures of three illustrative compounds have been determined.



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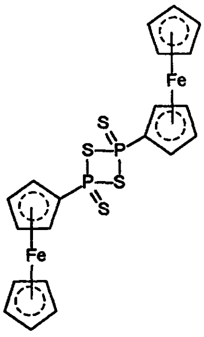
(1)



2

Experimental

All reactions were performed under an inert atmosphere of nitrogen. Reagents were obtained from Aldrich. Xylene was obtained from Fisons and was dried over sodium before use. Hexane, tetrahydrofuran (thf) and diethyl ether were distilled from sodium–benzophenone before use, toluene from sodium. The NMR spectra [$^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$, $CDCl_3$] were recorded using either a JEOL FX90Q or a Bruker 250AX spectrometer, infrared spectra using KBr discs with a Perkin-Elmer system 2000 Fourier-transform spectrometer and mass spectra using a Kratos MS80 instrument or by the national service in Swansea. Microanalyses were carried out by the Loughborough University Chemistry Department.

Preparations

[$(C_{10}H_9Fe)_2P_2S_4$] 2. Ferrocene (5.2 g, 28 mmol) was dissolved in xylenes (50 cm^3) before the addition of P_4S_{10} (3 g, 7 mmol), then refluxed for 30 min before being allowed to cool. After cooling the orange solid was filtered off, washed with toluene and dried *in vacuo*. Yield 5.9 g, 78%. This preparation has been successfully scaled up eight-fold in which case the product was washed with toluene and diethyl ether before being dried. **CAUTION**: care should be exercised with any large-scale synthesis as large volumes of hydrogen sulfide are produced rapidly. This gas should be treated with sodium hypochlorite before release into an effective fume cupboard. Microanalysis found: C, 43.1; H, 2.95. $C_{20}H_{18}Fe_2P_2S_4$ requires C, 42.9; H, 3.25%. Electron impact (EI) mass spectrum: *m/z* 280 ($M \div 2^+$), 248 [($C_{10}H_9Fe$)PS], 217, 184, 147, 121 and 56. IR: 3093w, 3068w, 1407m, 1390m, 1364m, 1349m, 1310m, 1179s, 1169s, 1107m, 1023s, 1001m, 822s, 670s, 620m, 552s, 523s, 488s and 467s cm^{-1}. Decomposes above 165 °C to give a black solid not melting below 240 °C. Low solubility prevented the measurement of NMR spectra.

[$(C_{12}H_{13}Fe)_2P_2S_4$] 3. 1,1′-Dimethylferrocene (0.92 g, 4.3 mmol) was dissolved in xylenes (9 cm^3); to this was added P_4S_{10} (0.46 g, 1.0 mmol). The reaction mixture was heated under reflux for 2 min before the addition of more xylene (9 cm^3). Heating/stirring was continued for 13 min after which time the reaction was allowed to cool. The resultant blood-red solution was filtered to remove a small trace of a green solid. Hexane (5 cm^5) was used to wash the green solid and this washing was added to the filtrate. More hexane (5 cm^3) was added to the filtrate which was then cooled to − 18 °C for 3 h. Compound **3** was filtered off and washed with hexane (10 cm^3). Yield 0.28 g, 11% (Found: C, 46.4; H, 3.8. $C_{24}H_{26}Fe_2P_2S_4$ requires C, 46.8; H, 4.3%). Positive-ion (EI) mass spectrum: *m/z* 308 ($M/2^+$), 245 and 198. NMR: ^1H, complex group of multiplets present from δ 4.8 to 4.0, 2.0(s) and 1.9(s); $^{31}P-\{^1H\}$, δ 16.9. IR: 3075w, 2947m, 2918m, 1475w, 1451w, 1382m, 1305w, 1251m, 1187w, 1097m, 1039m, 829m, 680s, 646m and 469s cm^{-1}.

2-(1,1′-Dimethylferrocen-3-yl)-4-(*p*-methoxyphenyl)-1,3-dithiadiphosphetane disulfide 4 within an NMR tube. An equimolar solution of compounds **1** and **3** (2.0 mg) was made in $CDCl_3$

and the ^{31}P-{^{1}H} NMR spectrum was recorded: δ 15.6 (**1**), 16.9 (**3**), 15.8, 16.4 (AX) $^2J(^{31}P–^{31}P)$ 7 Hz; the AX system accounted for *ca.* 30% of the total intensity.

$[(C_{10}H_9Fe)(o\text{-}C_6H_4O_2)PS]$ 5. Catechol (1.3 g, 12 mmol) was placed in a flask with toluene (200 cm^3), and the flask was fitted with a Soxhlet head containing a thimble containing compound **2** (3.2 g, 5.7 mmol). The flask was heated so that **2** was extracted from the Soxhlet apparatus until the extract was no longer coloured, *i.e.* all **2** had been added to the reaction mixture. Cooling to room temperature and removal of toluene gave a crude orange material. The solid was extracted with hexane and the extract was filtered through a pad of Al_2O_3 (active basic Brockman grade I). Evaporation of the solvent *in vacuo* gave the final product as an orange solid. On storage or even brief exposure to air it darkened to black. Yield 134 mg, 24%. Crystals for X-ray crystallography were obtained from light petroleum (b.p. = 60–80 °C). EI mass spectrum: *m*/*z* 356 (M^+), 291 $(M - C_5H_5)^+$, 290, 186, 139, 121, 69 and 56. NMR: ^{1}H, δ 7.1 (m), 6.8 (m), 4.54 (d), 4.4 (s) and 4.2 (s); ^{13}C-{^{1}H}, δ 123.2, 122.4, 116.0, 112.4 and 72.7 (m); ^{31}P-{^{1}H}, δ 113 (s). IR 3095w, 1478s, 1412m, 1390m, 1366w, 1350w, 1230s, 1188s, 1106m, 1095m, 1028s, 1009m, 1002m, 924w, 903m, 858s, 837s, 815m, 780m, 770m, 741s, 710s, 606m, 540m, 495m and 479m cm^{-1}.

$[(C_{10}H_9Fe)(3,5\text{-}Bu^t{}_2C_6H_2O_2)PS]$ 6. This compound was prepared in a similar fashion to that of **5**. 3,5-Di-*tert*-butylcatechol (0.53 g, 2.3 mmol) was treated with **2** (0.63 g, 1.1 mmol) in toluene (50 cm^3). After removal of the solvent, and storage at −18 °C, the resulting solid was recrystallised from light petroleum (to remove the residual di-*tert*-butylcatechol) to yield an orange product, 0.225 g (21%). On standing this darkened to brown. NMR: ^{31}P-{^{1}H}, δ 113 (s); ^{1}H, δ 7.0 (3 H, unresolved m), 4.65–4.45 (poorly resolved m with s at 4.4, 9 H), 1.45 (16 H, s) and 1.30 (15 H, s). IR: 1720w, 1655w, 1624m, 1588m, 1561w, 1519w, 1485s, 1466m, 1446m, 1412s, 1392m, 1365m, 1352w, 1319m, 1283m, 1264m, 1228s, 1188s, 1153m, 1089m, 1051w, 1026s, 1004m, 975s, 935w, 903m, 860vs, 822s, 804m, 788s, 736s, 706s, 643m, 635m, 623w, 594m, 536w, 526w, 493s, 445m, 419w, 410w, 343w and 323w cm^{-1}. Positive-ion EI mass spectrum: *m*/*z* 468 (M^+), 403, 316, 267, 217, 186, 155, 113, 70, 51, 41 and 31; molecular ion at *m*/*z* 468.0976 ($^{12}C_{24}{}^1H_{29}{}^{56}Fe^{16}O_2{}^{31}P^{32}S_2$ requires 468.09748).

$[(C_{10}H_9Fe)P(S_3)Pt(PEt_3)_2]$ 7. Compound **2** (18.9 mg, 34 mmol) and $[PtCl_2(PEt_3)_2]$ (17 mg, 34 mmol) were stirred together overnight in deoxygenated thf (1 cm^3) before the addition of deoxygenated hexane (5 cm^3). The resulting solid was allowed to settle before removal of the supernatant. After washing with more hexane the solid was dried *in vacuo*. Yield 23 mg, 91%. NMR: ^{31}P, δ 3.3 [^1J(Pt–P) 3108] and 92.0 [^2J(Pt–P) 215 Hz]; ^{1}H, δ 4.73 (m), 4.31 (s), 4.30 (m), 1.91 (m) and 1.16 (m). IR: 3094w, 3079w, 2961s, 2930m, 2875m, 1451m, 1412m, 1370w, 1349w, 1312w, 1255w, 1237w, 1187w, 1164m, 1106m, 1034s, 1015s, 1002w, 892w, 883w, 858w, 834w, 822s, 806w, 771m, 754s, 745s, 726m, 709m, 666vs, 634m, 571w, 559m, 542m, 507w, 493s, 445m, 424m, 402w, 382m, 339m, 312w, 296w and 287w. FAB mass spectrum: *m*/*z* 767 ($[M + Na]^+$) and 743 (M^+); expected isotopic distributions observed. Crystals suitable for X-ray studies were obtained from dichloromethane–toluene.

$[(C_{10}H_9Fe)P(S_3)Pt(PBu^n{}_3)_2]$ 8. The reaction of $[PtCl_2(PBu^n{}_3)_2]$ (15 mg, 22.4 mmol) and **2** (13 mg, 23.2 mmol) in thf (1 cm^3) gave an orange solution. Addition of hexane (2 cm^3) gave $[(C_{10}H_9Fe)P(S_3)Pt(PBu_3{}^n)_2]$ as a yellow solid, which was washed with hexane and dried *in vacuo*. Yield 15 mg, 16.5 mmol (74%) (Found: C, 44.3; H, 6.4. $C_{34}H_{63}FeP_3PtS_3$ requires C, 44.8; H, 6.95%). NMR: ^{31}P-{^{1}H}, δ 90.7 [$^2J(^{31}P–Pt)$ = 206]; and 4.4 [$^1J(^{31}P–Pt)$ = 3103]; ^{1}H NMR, δ 4.7 (poorly resolved m), 4.36 and 4.3 (poorly resolved m) (total for ferrocenyl area 9 H), 1.8 (br), 1.4 (br) and 0.95 (t, 7.0 Hz). IR: 3099m, 2956s, 2927s, 2867m, 1462m, 1407m, 1379w, 1209w, 1167m, 1093m, 1050w, 1017m, 967w, 904m, 815m, 799m, 773w, 720m, 666vs, 542m, 490m, 463w, 402w, 377w, 341w and 310w cm^{-1}. FAB mass spectrum: *m*/*z* 911, 726, 694, 663, 595, 571, 537, 459, 335, 279 and 203; expected isotopic distributions observed.

$[(C_{10}H_9Fe)P(S_3)Pt(dppe)]$ 9 (dppe = $Ph_2PCH_2CH_2PPh_2$). This compound was obtained as above (Found: C, 47.2; H, 3.6. $C_{36}H_{33}FeP_3PtS_3$ requires C, 47.7; H, 3.7%). NMR: ^{31}P-{^{1}H}, δ 42.05 [$^1J(^{31}P–Pt)$ = 3132.0] and 97.72 [$^2J(^{31}P–Pt)$ = 228.8 Hz]; ^{1}H, δ 7.7 (br), 7.5 (br), 4.7 (poorly resolved m), 4.3 (poorly resolved m) and 4.2 (s). IR: 3074w, 3050m, 2956s, 2925s, 2867w, 1483m, 1435s, 1409m, 1166m, 1105s, 1018m, 998m, 879w, 822s (br), 748m (br), 716s, 706s, 692vs, 665vs, 534vs, 486s, 378w and 343w cm^{-1}. FAB mass spectrum: *m*/*z* 1026, 928, 906 (M^+), 890 ($[M - 16]^+$), 873, 840, 823, 777, 745, 720, 704, 688, 672, 657, 639, 625, 593, 515, 499, 485, 467, 453, 423, 409, 377, 334, and 302; in addition to a large number of peaks below 300.

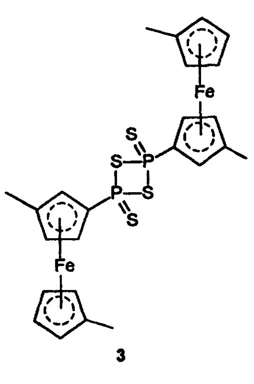
Crystallography

Details of the data collections and refinements are summarised in Table 1. Data were collected using Cu-Kα (λ = 1.541 78 Å) radiation and ω scans with a Rigaku AFC7S diffractometer. Intensities were corrected for Lorentz-polarisation and for absorption effects (DIFABS).[4] The structures were solved by the heavy atom method.[5] In all cases all of the non-hydrogen atoms were refined anisotropically, The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on *F* using teXsan.[6]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/196.

Results and Discussion

The reaction of P_4S_{10} with ferrocene in hot xylene gives compound **2** in good yield. However at higher temperatures **2** decomposes to give a black insoluble solid (iron sulfide together with other inorganic residues). It is indefinitely stable at room temperature in the solid state and was found to be unexpectedly insoluble in all cold solvents (preventing NMR characterisation), but it can be dissolved in hot toluene or xylene. Often thionations using **1** are carried out in hot solvents so **2** could still be used as a replacement without any great alteration to the experiment. In an attempt to form a more soluble version of **2**, 1,1′-dimethylferrocene was treated with P_4S_{10} in xylene to give the bis(dimethylferrocenyl)dithiadiphosphetane disulfide **3** in low isolated yield (the improved solubility made this compound somewhat harder to isolate). This orange solid is very soluble in



3

Table 1 Selected bond lengths (Å) and angles (°) in compound **2**

P(1)–S(1)	2.134(3)	P(1)–S(1*)	2.101(3)
P(1)–S(2)	1.930(3)	P(1)–C(1)	1.747(8)
P(1)–S(1)–P(1*)	86.9(1)	S(1)–P(1)–S(1*)	93.1(1)
S(1)–P(1)–S(2)	115.2(1)	S(1)–P(1)–C(1)	107.8(3)
S(1')–P(1)–C(1)	106.4(3)	S(1')–P(1)–S(2)	115.9(1)

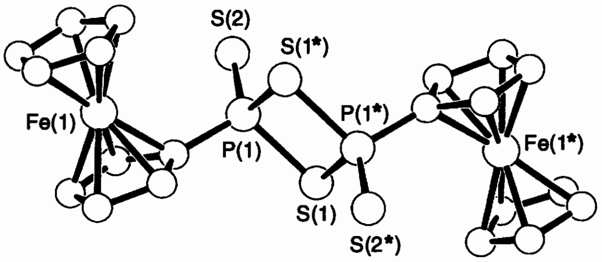
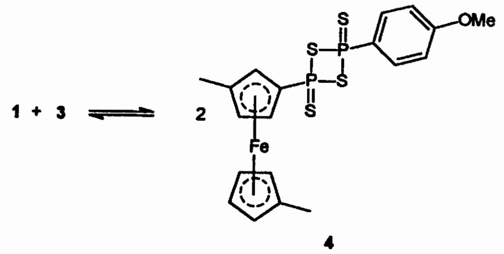


Fig. 1 Crystal structure of compound **2**

chloroform and other solvents. The $^{31}\mathrm{P}$ NMR chemical shift is similar to that of **1** (δ 16.9 and 17 respectively) suggesting that the two compounds have similar structures. The $^{1}\mathrm{H}$ NMR spectrum of **3** is more complex than would be expected for a single isomer and we believe that substitution of the $\mathrm{MeC_5H_4}$ ring has occurred at both the 2 and 3 positions to give a number of isomers. The ready formation of **2** and **3** suggests that the synthesis of many related compounds should be possible. The infrared spectra of **2** and **3** contain bands due to the ferrocenyl and dimethylferrocenyl groups as well as the characteristic ν(PS) at 670 and 680 $\mathrm{cm^{-1}}$ respectively.

In the crystal structure of compound **2** (Table 1, Fig. 1) the molecule is disposed about a crystallographic centre of symmetry with the ferrocenyl groups *trans* to each other. The bond lengths and angles are normal and comparable with those in 2,4-dimethyl-1,3-dithiadiphosphetane[7] and 2,4-di-*tert*-butyl-1,3-dithiadiphosphetane disulfide[8] with, as anticipated, the exocyclic (P=S) bonds being substantially shorter [1.930(3) Å] than the ring P–S bonds [2.101(3), 2.134(3) Å]. Within the four-membered ring the P–S–P and S–P–S angles are 86.9(1) and 93.1(1)° respectively. The transannular P ··· P and S ··· S distances are 2.91 and 3.08 Å respectively. The cyclopentadienyl rings of the ferrocenyl group are eclipsed.

Lawesson's reagent has been shown by NMR spectroscopy to undergo reversible dissociation in solution.[9] To establish if this effect could be observed with a diferrocenyldithiadiphosphetane disulfide a $^{31}\mathrm{P}$ NMR spectrum of an equimolar $\mathrm{CDCl_3}$ solution of compounds **1** and **3** was recorded. We observed three species. Apart from signals due to **1** and **3** (δ 15.6 and 16.9 respectively) an AX spectrum [δ 15.8, 16.4, $^{2}J(^{31}\mathrm{P}–^{31}\mathrm{P}) = 7$ Hz] which is readily assigned to the mixed species, 2-(1,1'-dimethylferrocen-3-yl)-4-(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **4** was also observed. The formation of **4** in the NMR tube suggests that in solution both **1** and **3** undergo dissociation to form dithiophosphine ylides which can then reversibly form **4** [equation (2)]. The value of the $^{2}J(^{31}\mathrm{P}–^{31}\mathrm{P})$ coupling constant for **4** is similar to that found for 2,4-(naphthalene-1,8-diyl)dithiadiphosphetane disulfide.[12]



(2)

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Table 2 Selected bond lengths (Å) and angles (°) in compound **5**

P–O(1)	1.636(4)	P–O(2)	1.627(3)
P–S	1.893(2)	P–C(7)	1.761(5)
C(1)–O(1)	1.396(5)	C(2)–O(2)	1.392(6)
C(1)–C(2)	1.373(7)		
C(1)–O(1)–P	110.5(3)	C(2)–O(2)–P	110.3(1)
O(1)–P–O(2)	95.2(2)	O(1)–P–S	114.5(2)
O(2)–P–S	117.0(2)	S–P–C(7)	115.8(2)
O(1)–P–C(7)	105.6(2)	O(2)–P–C(7)	106.2(2)
O(1)–C(1)–C(2)	111.1(5)	O(2)–C(2)–C(1)	112.5(5)

Table 3 Selected bond lengths (Å) and angles (°) in compound **7**

Pt–S(1)	2.367(3)	Pt–S(2)	2.360(3)
Pt–P(2)	2.227(3)	Pt–P(3)	2.267(4)
S(1)–P(1)	2.049(5)	S(2)–P(1)	2.068(4)
S(3)–P(1)	1.934(5)	C(1)–P(1)	1.78(1)
S(1)–Pt–S(3)	81.6(1)	S(1)–Pt–P(3)	90.8(1)
S(1)–Pt–P(3)	167.2(1)	S(2)–Pt–P(2)	86.2(1)
S(2)–Pt–P(3)	172.4(1)	P(2)–Pt–P(3)	101.4(1)
Pt–S(1)–P(1)	89.8(1)	Pt–S(2)–P(1)	89.5(1)
S(1)–P(1)–S(2)	97.2(2)	S(1)–P(1)–S(3)	118.2(2)
S(1)–P(1)–C(1)	107.3(5)	S(2)–P(1)–S(3)	114.7(2)
S(2)–P(1)–C(1)	108.0(5)	S(3)–P(1)–C(1)	110.4(5)

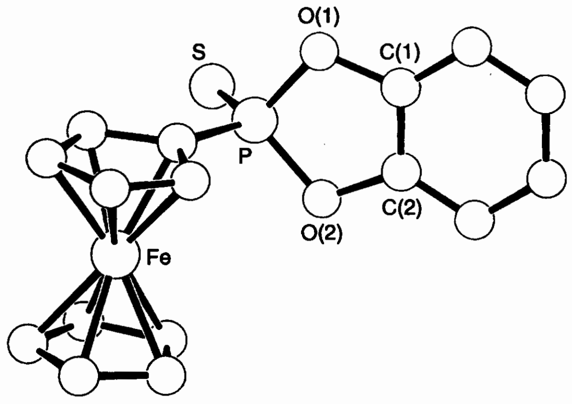
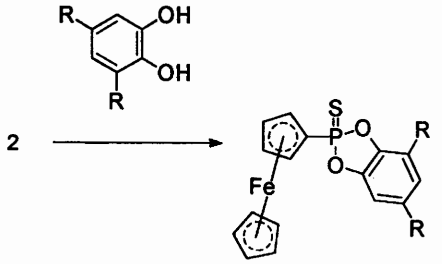


Fig. 2 Crystal structure of compound **5**

Treatment of compound **2** with catechol gives a mixture of products. However if the reaction is performed in boiling toluene, with slow addition of **2**, then **5** is obtained in moderate (28%) yield, equation (3). The $^{31}\mathrm{P}$ NMR spectrum of **5** is a simple singlet (δ 113) and mass spectroscopy suggests the presence of a compound with a molecular weight of 356 ($\mathrm{C_{16}H_{13}FeO_2PS}$). The crystal structure of **5** reveals (Table 2, Fig. 2) that **2** has undergone a ring-cleavage reaction to give a $\mathrm{C_2O_2(PS)}$ ring, in contrast to the naphthalene analogue which formed a $\mathrm{C_2O_2P_2S}$ ring.[10] In **5** the $\mathrm{C_2O_2P}$ is almost perfectly



5 R = H
6 R = Bu^t

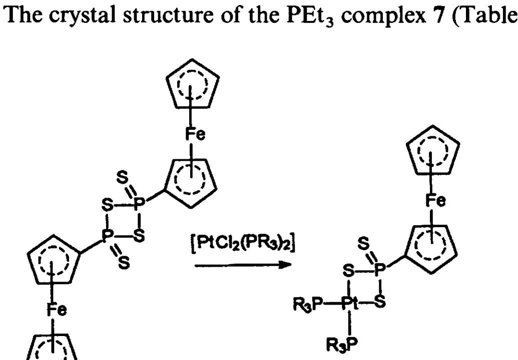
Table 4 Details of the data collections and refinements for compounds **2**, **5** and **7**

	2	**5**	**7**
Empirical formula	$C_{20}H_{18}Fe_2P_2S_4$	$C_{16}H_{13}FeO_2PS$	$C_{22}H_{39}FeP_3PtS_3$
M	560.2	356.2	743.6
Colour, habit	Orange, needle	Orange, plate	Yellow, hexagon
Crystal size/mm	0.08 × 0.08 × 0.33	0.11 × 0.05 × 0.05	0.32 × 0.35 × 0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	6.431(4)	13.816(2)	15.515(5)
b/Å	12.616(3)	7.402(4)	10.817(10)
c/Å	13.461(3)	16.215(2)	17.167(13)
β/°	93.62(3)	113.05(1)	98.90(5)
U/Å^3	1090	1526	2846
Z	2[a]	4	4
D_c/Mg m^{-3}	1.71	1.55	1.74
μ(Cu-Kα)/mm^{-1}	15.7	10.2	17.0
F(000)	568	728	1472
Independent reflections (R_{int})	1719(0.091)	2483(0.082)	4479(0.078)
Observed reflections [$I > 3.0\sigma(I)$]	959	1345	2815
No. parameters refined	128	191	272
Data : parameter ratio	7.5:1	7.0:1	10.3:1
Minimum, maximum transmission	0.65, 1.0	0.82, 1.0	0.60, 1.0
p in weighting scheme[b]	0.009	0.001	0.001
Final R,R'	0.040, 0.044	0.038, 0.024	0.045, 0.039
Largest Δ/σ	0.00	0.07	0.81
Largest difference peak, hole/e Å^{-3}	0.33, −0.30	0.25, −0.24	0.96, −2.59[c]

[a] The molecule is disposed about a crystallographic centre of symmetry. [b] Weighting scheme of form $w^{-1} = \sigma^2(F) + pF^2$. [c] The largest difference peak is located close to the platinum atom.

planar [maximum deviation from the mean plane 0.04 Å for C(1)] and is coplanar with the aryl ring, though the C–O [C(1)–O(1) 1.396(5), C(2)–O(2) 1.392(6) Å] and P–O distances [1.636(4), 1.627(3) Å] do not suggest any degree of delocalisation in the C_2O_2P ring. The exocyclic P=S distance is reduced compared to that in **2** [1.930(3) in **2** and 1.893(2) Å in **5**]. The cyclopentadienyl rings in the ferrocenyl group are eclipsed and almost perfectly orthogonal (85°) with respect to the C_2O_2P ring. Heating **2** with 3,5-di-*tert*-butylcatechol gives **6** which has an identical phosphorus chemical shift (δ 113) to that of **5** suggesting that it is isostructural. The IR and other data are in accord with this view. On standing both **5** and **6** decompose to form highly coloured species which have low solubilities in non-polar solvents.

We have previously shown that Lawesson's reagent reacts with bis(phosphine)platinum dichloride complexes[11] to form chelate complexes of the $[RPS_3]^{2-}$ anion. Treatment of **2** with bis(trialkylphosphine)platinum dichloride results in similar products, with asymmetric cleavage of the P_2S_2 ring [equation (4)]. The crystal structure of the PEt_3 complex **7** (Table 3, Fig. 3) reveals that the $[RPS_3]^{2-}$ (R = ferrocenyl) anion co-ordinates through two of its sulfur atoms to form a PtS_2P ring. The platinum centre is slightly distorted from square planar with the Pt atom lying 0.05 Å from the mean plane of its substituents. Within the PtS_2P ring the P–S bond lengths [P(1)–S(1) 2.049(5), P(1)–S(2) 2.068(4) Å] indicate substantial π delocalisation whilst the exocyclic P=S distance [1.934(5) Å] is reasonable for a formal P=S double bond. The Pt–P distances are normal whilst the Pt–S distances [Pt–S(1) 2.367(3), Pt–S(2) 2.360(3) Å] are similar to those in $[Pt\{(MeOC_6H_4)PS_3\}(PPh_3)_2]$.[11a] The PtS_2P ring is slightly hinged with the PtS_2 and PS_2 planes being inclined by 15° with respect to each other. The transannular Pt ··· P and S ··· S distances are 3.13 and 3.09 Å respectively. As was the case in **5**, the cyclopentadienyl rings are eclipsed and close to orthogonal with respect to the co-ordination plane (85°).



(4)

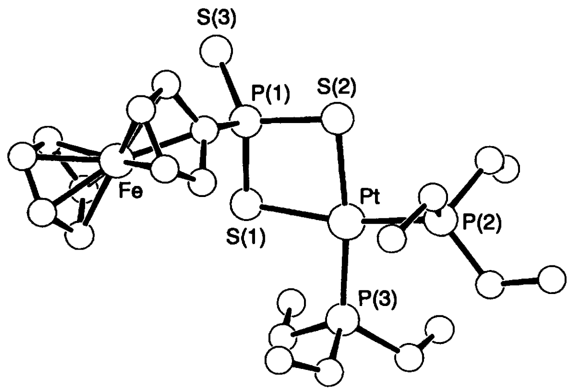


Fig. 3 Crystal structure of compound **7**

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