PAPER

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Synthesis and characterisation of disulfides and esters derived from their sodium organodithiophosphonate salts†

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Reaction of $Fc(S)PS_2P(S)Fc$ and $An(S)PS_2P(S)An$ with NaOR [R = Me, Et, ^{i}Pr] gives the non symmetric sodium phosphonodithioate salts $Fc(RO)PS_2Na$ and $An(RO)PS_2Na$ respectively (An = anisyl, Fc = ferrocenyl). These salts can be oxidised by I_2, activated by KI, to form organodithiophosphono disulfides of the type $(R(R'O)P(S)–S–S–P(S)(OR')R)$. Reactions of these salts with 2,4-dinitrosulfenyl chloride form organodithiophosphono disulfides of the type [R(R′O)P(S)–S–S–R]. These sodium salts can also react with benzyl bromide to form *S*-alkyl *O*-alkyl 4-methoxyphenyldithiophosphonate esters and *S*-alkyl *O*-alkyl ferrocenyldithiophosphonate esters. All new compounds have been characterised spectroscopically and seven demonstrative X-ray structures are reported.

Introduction

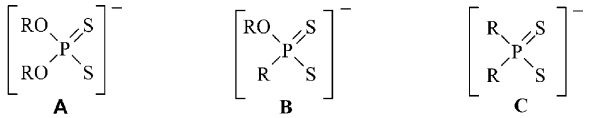
Phosphodithioates, their corresponding acids and metal complexes have been used in many commercial applications. Since the beginning of the twentieth century, compounds of this type have been used as flotation reagents,[1] additives to lubricant oils,[2] pesticides and for chemical warfare.[3]

Recent studies on phosphodithioate compounds have focused largely on the use of these as ligands for metal complexation.[4] The ability of phosphodithioates to form organic compounds has been largely overlooked, although this area would benefit greatly from the use of modern techniques *e.g.* crystallography and NMR spectroscopy.

Phosphodithioates can be used in the synthesis of disulfides; these can be two dithiophosphate groups joined by a disulfide bridge (–P–S–S–P–) or one dithiophosphate group attached *via* a disulfide bridge to an organic substituent *e.g.* an aliphatic or aromatic moiety (–P–S–S–R). Compounds of the former type have been the subjects of some recent reports;[5] the structures have been elucidated using spectroscopic techniques and in a handful of cases their X-ray structures have been obtained.[5a–c] One compound has a very useful application in biological chemistry. Oligo(nucleoside phosphorothioate)s are amongst the most promising of the nucleotide analogues which have been tested as antisense modulators of gene expression, bis(*O*, *O*-diisopropoxy phosphinothioyl) disulfide has been shown to be a highly efficient sulfurizing reagent for cost-effective synthesis of oligo(nucleoside phosphorothioate)s.[5d] It is relatively inexpensive to prepare, easy to handle, highly efficient and can be stored in air for several months.

Few studies of disulfides of the type (–P–S–S–R) have been conducted in recent years. Almost twenty years ago Shabana *et al.* published studies containing a few of these compounds with their ^{31}P NMR chemical shifts and very little other experimental data.[6] Other publications concerning these disulfides were published in the 1960's and early 1970's and, although very useful, contain very little spectroscopic information.[7]

Esters of *O*,*O*-dialkyl and *O*,*O*-dialkoxy phosphodithioic acids (–P–S–R) have also been of importance because of their use as lubricant additives and as insecticides of low mammalian toxicity.[8] They have been synthesized *via* several methods, the addition of *O*,*O*-dialkyl and *O*,*O*-dialkoxy phosphodithioic acids to C=C double bonds,[8a,9] cleaving the S–S bridge of the aforementioned phosphodithioate disulfides with organometallic reagents such as butyl lithium or Grignard reagents[5h,10] and also by reacting alkali metal or ammonium salts of *O*, *O*-dialkyl and *O*,*O*-dialkoxy phosphodithioic acids with alkyl halides.[10] A recent publication has detailed another successful route using phosphorothioylsulfenyl halides (phosphinesulfenyl halide *P*-sulfides), $(RO)_2PS(=S)X$ (X = Cl, Br, I),[11] in the past this route had been found to be problematic due to the thermal instability of the halides and difficult synthesis. The vast majority of the phosphodithioate disulfides and esters discussed contain either phosphorodithioate (**A**) or phosphinodithioate (**C**) phosphorus centres. Literature detailing the synthesis, chemistry and structural behaviour of the complexes of phosphorodithioate (**A**) and phosphinodithioate ligands (**C**) is plentiful and widely available.[4a–d] Due to synthetic difficulties, compounds containing phosphonodithioate ligands (**B**) have received little attention.



Interest in phosphonodithioate (**B**) derivatives has increased in recent years. Aragoni *et al.* have reported the synthesis and characterisation of several square planar complexes of alkoxy(4-methoxyphenyl)dithiophosphonate ligands with group 10 metal centres (Ni, Pd and Pt).[4f] They achieved this *via* a ring opening reaction of the well known and well studied[12] thionation compound Lawesson's Reagent. The dimeric Lawesson's Reagent is cleaved by nucleophilic attack conducted by sodium alkoxides to form sodium alkoxy(4-methoxyphenyl)dithiophosphonate salts, which can be further reacted to form metal complexes. A similiar method was employed by Özcan *et al.* in

† Electronic supplementary information (ESI) available: syntheses and spectroscopic data. See http://www.rsc.org/suppdata/nj/b4/b406007e/

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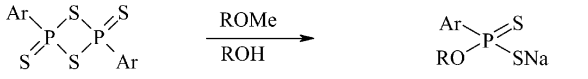
the formation of bis[*O*-2,4-di-tert-butylphenyl(4-methoxyphenyl)dithiophosphoato] nickel(II), an analogous compound containing a bulky sterically protecting substituent.[4g] We have extended this work on alkoxy(4-methoxyphenyl)dithiophosphonate ligands, within our laboratory, to include complexes of group 12 (Zn, Cd, Hg) and group 14 (Sn and Pb) metal centres exhibiting a range of different structural motifs.[13]

We have also recently described the synthesis, full characterisation and crystallographic structural study of alkoxy(ferrocenyl)dithiophosphato complexes[4e,14] which were synthesised using sodium alkoxy(ferrocenyl)dithiophosphonate salts obtained from the cleavage of Ferrocenyl Lawesson's Reagent, a less well studied[15] analogue of Lawesson's Reagent. Stable complexes exhibiting varied structural types were also formed using group 10, 12 and 14 metals in an analogous manner.[4e,14]

The use of these phosphonodithioate ligands as synthons for main group organic chemistry has been largely overlooked. Here we report the use of sodium alkoxy(4-methoxyphenyl) dithiophosphonate and sodium alkoxy(ferrocenyl)dithiophosphonate salts in the formation of disulfides, of both (–P–S–S–P–) and (–P–S–S–R) types, *S*-alkyl *O*-alkyl 4-methoxyphenyldithiophosphonate and *S*-alkyl *O*-alkyl ferrocenyldithiophosphonate esters.

Results and discussion

The phosphonodithioate salts **1** and **2** were prepared using the literature procedures.[4e,f,13,14] Lawesson's Reagent and Ferrocenyl Lawesson's Reagent were refluxed with 2 molar equivalents of NaOMe in methanol to give salts **1m** and **2m** respectively. Phosphonodithioate salts **1e**, **1p**, **2e** and **2p** were also formed from the reaction of Lawesson's Reagent or Ferrocenyl Lawesson's Reagent with the corresponding sodium alkoxide, but in these cases the sodium alkoxide was prepared from the reaction of sodium metal and the corresponding alcohol and used directly in the alcohol solution, [eqn. (1)].

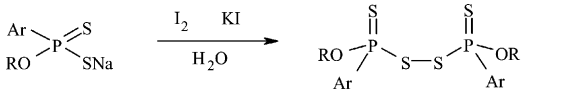


(1)

Ar = An R = Me, **1m** R = Et, **1e** R = ^{i}Pr, **1p**
Fc Me, **2m** Et, **2e** ^{i}Pr, **2p**

Cleavage of these dimers generates the sodium phosphonodithioate salts as either white **1** or dark yellow **2** powders in high yield (An = anisyl, Fc = ferrocenyl). The salts are soluble in polar solvents such as alcohols and acetone but are insoluble in less polar solvents *e.g.* dichloromethane, chloroform, hexane *etc*. All of the above salts were found to be air stable both as solids and in solution. All spectra (^{31}P, ^{1}H, ^{13}C NMR, IR and mass spectrometry) were in accord with literature values.

The dithiophosphonodisulfides **3** and **4** were prepared by the reaction of I_2, activated by KI, with phosphonodithioate salts **1** and **2** in aqueous solution [eqn. (2)].



(2)

Ar = An R = Me, **3m** R = Et, **3e** R = ^{i}Pr, **3p**
Fc Me, **4m** Et, **4e** ^{i}Pr, **4p**

The disulfides **3m** and **3e** were obtained as colourless oils; **3p** was obtained as a white solid and **4m**, **4e** and **4p** as yellow solids. All are air stable and soluble in both dichloromethane and chloroform. The ^{31}P spectra contain a pair of sharp singlets of approximately equal intensity in the range δ(P) 89.2 –98.3 ppm. This result would indicate the presence of two distinct isomeric forms, but in this case we believe these to be due to chirality since the sodium salts **1** and **2** each possess a chiral centre at the phosphorus atom. When the sulfur–sulfur bridge is formed, the phosphorus atom can have either *R* or *S* orientation, allowing two distinct isomers to be formed—where both phosphorus atoms have the same orientation (*R*–*R*, *S*–*S*) or have different orientations (*R*–*S*). The ^{1}H and ^{13}C spectra clearly show the presence of both the aromatic and alkoxy substituents displaying the expected coupling constants. The IR spectra of the disulfides **3** and **4** showed one significant difference from the starting sodium salts, the appearance of an ν(S–S) absorption from the disulfide bridge in the range 488–492 cm^{-1}. In all cases mass spectrometry found the expected $(M)^{+}$.

The X-ray structure of **3p** (see Fig. 1) shows that the compound crystallizes with two isomeric independent molecules present within the unit cell. Both isomers display the same

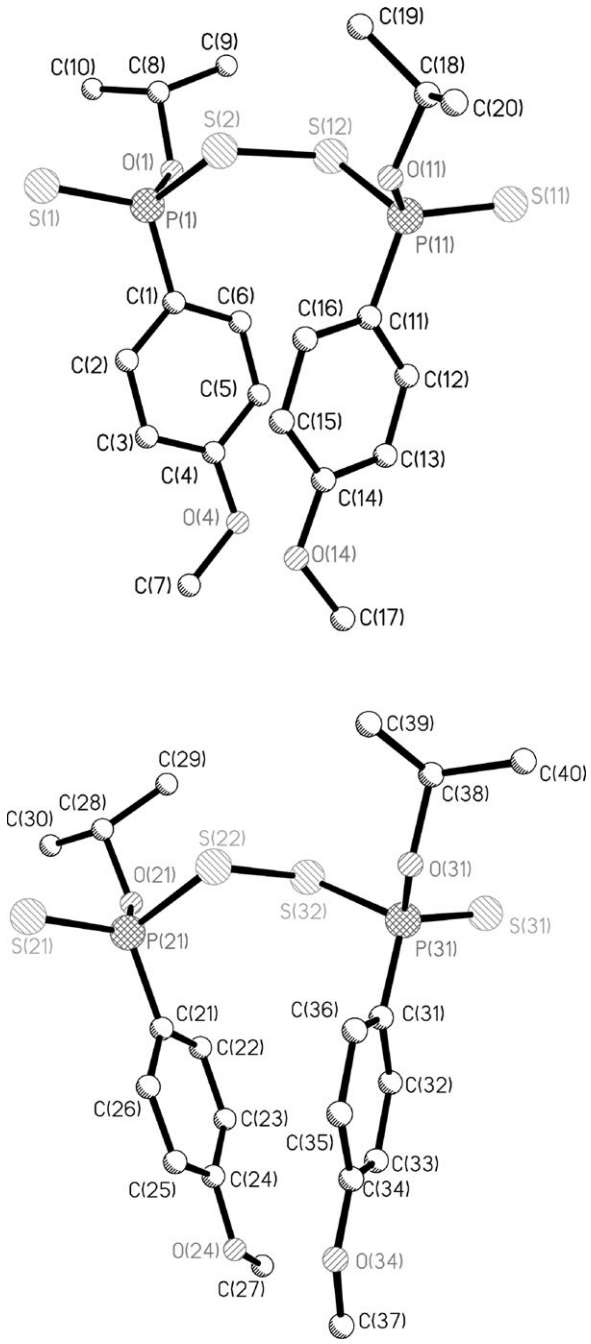
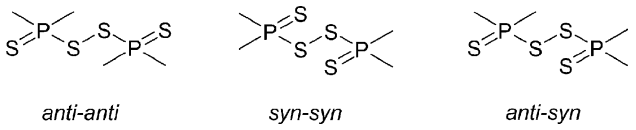


Fig. 1 The X-ray structure of **3p**, all hydrogen atoms are omitted for clarity. Both isomers are illustrated. Upper diagram, isomer (a); lower diagram isomer (b).

geometry in terms of the P_2S_4 backbone of the molecules. Other studies[5a] have shown that this P_2S_4 backbone can adopt several different geometries, *anti–anti* where both sulfurs not involved in the disulfide bridge point away from the disulfide bridge, *syn–syn* where both point towards the disulfide bridge or *anti–syn* where one points towards while the other points away.



It has been shown that changes in the configuration can result in alteration of the P–S bond lengths. *Anti* geometries result in short (*ca.* 2.1 Å) P–S bonds, distortion from *anti* geometries causes P–S bond length elongation. Both isomers of **3p** display *anti–anti* geometry with S–S–P=S torsion angles of −171.21(3) and −170.28(3)° for (a) and −173.52(3) and −172.28(2)° for (b). The P–S bond lengths are short (2.1154(7) and 2.1022(7) Å) as expected, with S–S bond lengths of 2.0849(7) and 2.0831(7) Å respectively. These lengths and angles are consistent with literature values for disulfides of this type with *anti–anti* configuration.[5a] Both isomers have another common structural feature, the anisyl groups adopt an eclipsed geometry (with respect to the P–P vector) but contain subtle differences. For isomer (a) the distance between the centres of the rings is 3.70(1) Å and the deviation from parallel is 11°, while for (b) the distance between the centre of the rings is larger 3.83(1) Å with a larger angle of deviation (19°). These subtle differences arise from the structural differences between the two isomeric forms. The isomerisation arises from the differing geometries of the *p*-OMe group of the anisyl rings. In the case of isomer (a) the *p*-OMe groups are on opposite sides of the molecule with respect to the P–P vector, allowing the molecule to have approximate 2-fold rotational symmetry. In the case of isomer (b) the *p*-OMe groups are on the same side of the molecule breaking the rotational symmetry. The extra steric bulk resulting from both *p*-OMe groups residing on the same side of the molecule may cause the anisyl rings to be further apart and hence deviate further from parallel.

The X-ray structure of **4m** was also obtained (see Fig. 2). Like both isomers of **3p**, **4m** also adopts an *anti–anti* geometry with S–S–P=S torsion angles of −174.25(5)° (the molecule has crystallographic 2-fold symmetry). The P–S bond lengths are short (2.0995(13) Å) as expected whilst the S–S bond length is 2.0746(19) Å. Unlike both isomers of **3p**, the aromatic (ferrocenyl) substituents of **4m** do not exhibit an eclipsed structure with respect to the P–P vector. The ferrocenyl groups adopt a non-eclipsed geometry allowing them to be a much greater distance apart.

The structure of **4p** (see Fig. 3) is very similar to that of **3p**. The molecule adopts an *anti–anti* geometry with S–S–P=S torsion angles of −177.10(5)°, contains P–S bond lengths of 2.087(12) Å and an S–S bond lengths of 2.0808(18) Å. Like **3p**, **4p** also adopts an eclipsed structure with the two substituted cyclopentadiene rings of the ferrocenyl groups arranging themselves to face each other. The centres of the rings are 3.78(1) Å apart with a deviation of 15° from parallel.

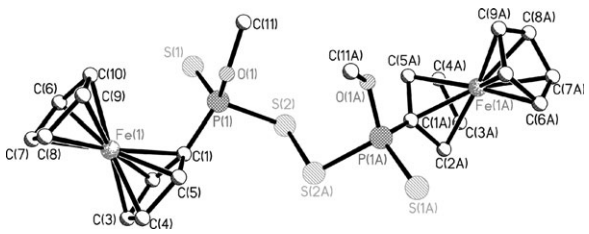


Fig. 2 The X-ray structure of **4m**, all hydrogen atoms are omitted for clarity.

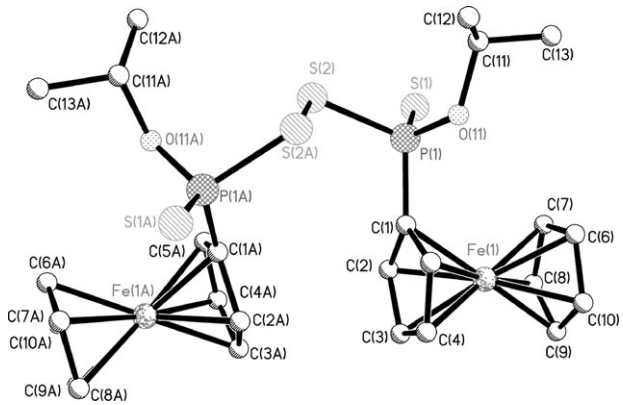
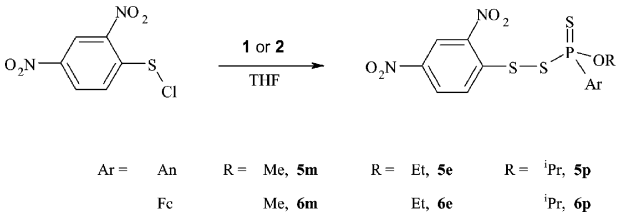


Fig. 3 The X-ray structure of **4p**, all hydrogen atoms are omitted for clarity.

Dithiophosphonodisulfides **5** and **6** were prepared by the reaction of sodium salts **1** and **2** with 2,4-dinitrosulfenyl chloride in tetrahydrofuran [eqn. (3)].



(3)

Disulfides **5** were obtained as greenish yellow solids while **6** were obtained as red solids. All are air stable and soluble in both dichloromethane and chloroform. The ^{31}P spectrum of each contains a sharp singlet in the range δ(P) 85.1–95.2 ppm. The ^{1}H and ^{13}C spectra confirm the presence of the 2,4-dinitrophenyl group as well as the aromatic and alkoxy substituents on the phosphorus centre. The IR spectra of the disulfides **5** and **6** showed the appearance of the ν(S–S) absorption from the disulfide bridge, in the range 478–499 cm^{-1}, as well as the appearance of the two distinct nitro environments, $\nu(NO_2)_{asymm}$ 1596–1593 and 1527–1523, $\nu(NO_2)_{symm}$ 1391–1384 and 1342–1338. In all cases mass spectrometry found the expected $(M)^+$.

The X-ray structures of **5m** and **5e** were obtained (see Fig. 4). Both molecules adopt similar structural motifs; the disulfide bridge allows the molecule to curve round with the aromatic rings facing each other, with S–S–C angles of 104.22(7) and 105.59(6)° respectively. In both cases there is only a 9° deviation from the rings being parallel to each other. The rings are 3.59(1) and 3.63(1) Å apart for **5m** and **5e** respectively, indicating the presence of long range π–π interactions. Changing from **5m** to the ethyl analogue, **5e**, does not significantly alter the P–S and S–S bond lengths within the molecule. The P–S bond lengths are 2.1199(8) and 2.1247(8) Å respectively; these are slightly longer than those for disulfides **3p**, **4m** and **4p**, as a consequence of the shortening of the S–S disulfide bridge. The S–S distance has decreased from *ca.* 2.08 Å (for **3p**, **4m** and **4p**) to 2.0640(8) and 2.0567(8) Å for **5m** and **5e** respectively, due to the change in bound substituent from phosphonodithioate to 2,4-dinitrophenyl. There is one significant structural difference between **5m** and **5e**, the orientation of the *p*-OMe of the anisyl groups. Both lie in the plane of the attached aromatic ring but point in opposite directions, for **5e** this forces the *p*-OMe to be closer to the nitro groups of the neighbouring ring; this may be the reason that **5e** has a slightly longer π–π distance (+0.04 Å).

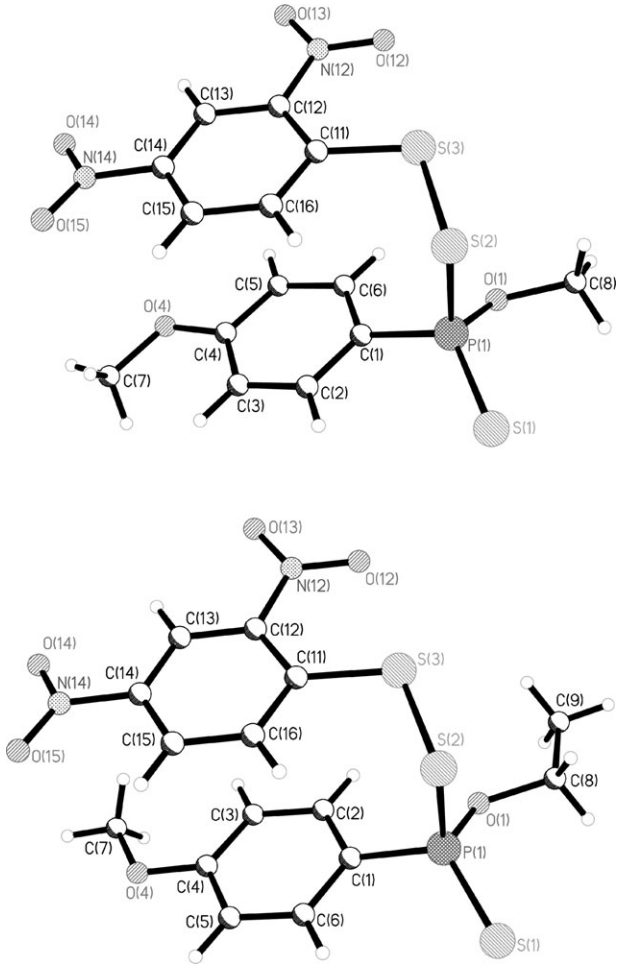


Fig. 4 Upper diagram, the X-ray structure of **5m**; lower diagram, the X-ray structure of **5e**.

6m, the ferrocenyl analogue of **5m**, adopts a very similar structure to that of **5m** and **5e** (see Fig. 5). The molecule exhibits the same S–S–C curve, with an angle of 103.3(3)°. The π–π distance (3.76(1) Å) is slightly longer and the deviation from parallelism (13°) is a little larger. Both P–S (2.115(3) Å) and S–S (2.056(3) Å) bond lengths are not significantly different to those in **5m** and **5e**.

S-alkyl *O*-alkyl 4-methoxyphenyldithiophosphonate **7** and *S*-alkyl *O*-alkyl ferrocenyldithiophosphonate esters **8** were prepared by the reaction of sodium salts **1** and **2** with benzyl bromide in methanol [eqn. (4)].

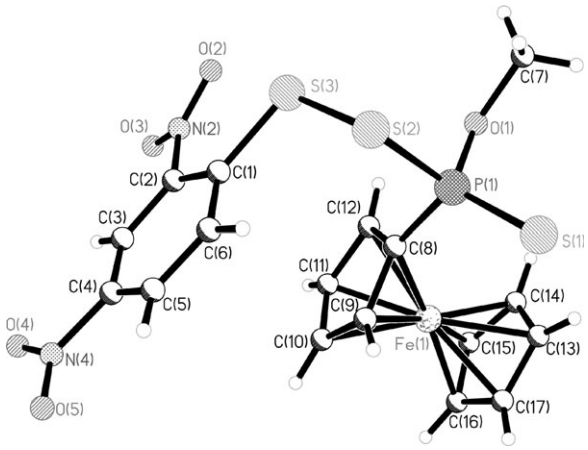
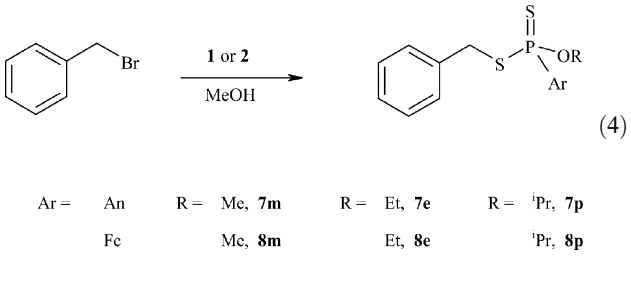


Fig. 5 The X-ray structure of **6m**.



(4)

Ar = An R = Me, **7m** R = Et, **7e** R = ^{i}Pr, **7p**

Fc Me, **8m** Et, **8e** ^{i}Pr, **8p**

The esters **7** were obtained as colourless oils, **8** were obtained as orange oils with the exception of **8p**, an orange solid. All are air stable and soluble in both dichloromethane and chloroform. The ^{31}P spectrum of each contains a sharp singlet in the range δ(P) 93.6–101.1 ppm. The ^{1}H and ^{13}C spectra confirm the presence the aromatic and alkoxy substituents on the phosphorus centre. The chemical shifts of the benzyl group are obvious in the ^{1}H and ^{13}C spectra and the sulfur–carbon linkage is confirmed by the appearance of ^{31}P–^{13}C and ^{31}P–^{1}H coupling to the benzyl CH_2 bridging carbon. The IR spectra of the disulfides **5** and **6** showed no significant differences from the starting sodium salts and in all cases mass spectrometry found the expected $(M)^{+}$.

The X-ray structure of **8p** was obtained (see Fig. 6). The molecule does not exhibit a curved structure like **5m** or **5e** but instead adopts a more linear structure allowing the aromatic groups to be well separated. The P–S bond length (2.0768(6) Å) is consistent with the other compounds in this paper. The bridging S–C bond length, 1.8416(18) Å, is consistent with S–C bond lengths known[16] and is considerably shorter than the disulfide bridge S–S bond lengths we have reported. The angle between the S–C and the C-1 of the phenyl ring, S(2)–C(14)–C(15), is 107.65°. This is significantly larger than the equivalent S–S–C angles displayed for **5m**, **5e** and **6m** (103.3–105.59°), which is not unexpected as carbon compounds generally adopt more strictly tetrahedral conformations than their sulfur analogues. This larger angle, coupled with the shorter bridge length, may be the reason why the molecule does not display any π–π interactions.

This work clearly demonstrates the use of sodium alkoxy(4-methoxyphenyl)dithiophosphonate and sodium alkoxy(ferrocenyl)dithiophosphonate salts in the preparation of organodithiophosphono disulfides, of both (–P–S–S–P–) and (–P–S–S–R) types, *S*-alkyl *O*-alkyl 4-methoxyphenyldithiophosphonate and *S*-alkyl *O*-alkyl ferrocenyldithiophosphonate esters.

Experimental

General

Unless otherwise stated, operations were carried out under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The phosphonodithioate salts **1**

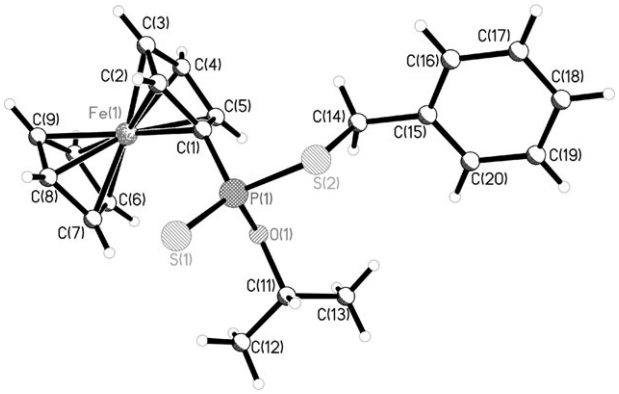


Fig. 6 The X-ray structure of **8p**.

and **2**[4e,f,13,14] and Ferrocenyl Lawesson's Reagent[15] were prepared using literature procedures. All other reagents were purchased from either Aldrich, Acros or Lancaster and used as received. Infrared spectra were recorded as either Nujol mulls or KBr discs in the range 4000–250 cm^{-1} on a PerkinElmer System 2000 Fourier-transform spectrometer. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded using a JEOL DELTA GSX 270 FT NMR spectrometer. Microanalyses were performed by the University of St. Andrews' microanalysis service. Mass spectra were recorded by the Swansea mass spectrometry service.

Six typical syntheses are described below. The remaining syntheses and spectroscopic data are available as electronic supplementary information.†

Bis[(ethoxy)-4-methoxyphenylthiophosphono] disulfide (3e)

A solution of KI (1 g, 6.029 mmol) in H_2O (9 cm^3) was added to I_2 (0.141 g, 0.555 mmol) and stirred until I_2 completely dissolved. This solution was added dropwise to a solution of **1e** (0.300 g, 1.110 mmol) in H_2O (20 cm^3). A white suspension formed immediately and was stirred for a further 1 h to ensure complete reaction. The solvent was removed under reduced pressure, the resulting yellow oil was redissolved in dichloromethane and filtered through a small Celite plug. The solvent was removed under reduced pressure to give a colourless oil (0.235 g, 86%). Found (calc. for $C_{18}H_{24}O_4P_4S_4$): C 44.11 (43.72), H 4.77 (4.90), S 25.33 (25.89)%.

Isomer (a). ^{31}P NMR ($CDCl_3$) δ: 90.1. ^{1}H NMR ($CDCl_3$) δ: 7.74 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.1 Hz, $^{3}J(^{1}H–^{1}H)$ 9.3 Hz, *o*-AnH), 6.87 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.9 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-AnH), 4.22 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 1.8 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 3.80 (s, 3H, AnOMe), 1.30 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 163.6 (d, $^{4}J(^{31}P–^{13}C)$ 3.0 Hz, *p*-AnC), 133.8 (d, $^{3}J(^{31}P–^{13}C)$ 12.8 Hz, *m*-AnC), 125.0 (d, $^{1}J(^{31}P–^{13}C)$ 130.1 Hz, An C-1), 114.3 (d, $^{2}J(^{31}P–^{13}C)$ 16.6 Hz, *o*-AnC), 62.6 (d, $^{2}J(^{31}P–^{13}C)$ 7.5 Hz, CH_2), 56.0 (s, $AnOCH_3$), 16.3 (d, $^{3}J(^{31}P–^{13}C)$ 8.3 Hz, CH_3).

Isomer (b). ^{31}P NMR ($CDCl_3$) δ: 89.2. ^{1}H NMR ($CDCl_3$) δ:7.54 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-AnH), 6.65 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.9 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-AnH), 4.06 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 1.8 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 3.80 (s, 3H, AnOMe), 1.17 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 163.4 (d, $^{4}J(^{31}P–^{13}C)$ 3.0 Hz, *p*-AnC), 133.7 (d, $^{3}J(^{31}P–^{13}C)$ 12.8 Hz, *m*-AnC), 123.8 (d, $^{1}J(^{31}P–^{13}C)$ 131.3 Hz, An C-1), 114.0 (d, $^{2}J(^{31}P–^{13}C)$ 16.6 Hz, *o*-AnC), 62.6 (d, $^{2}J(^{31}P–^{13}C)$ 7.5 Hz, CH_2), 55.8 (s, $AnOCH_3$), 16.3 (d, $^{3}J(^{31}P–^{13}C)$ 8.3 Hz, CH_3).

Selected IR data (KBr) ν/cm^{-1}: 1181 (s), 1026 (s), 678 (m), 530 (m), 488 (m). MS (ES+): $(1/2M)^+$ 247, $(M)^+$ 495, $(M + Na)^+$ 517.

Bis[(ethoxy)ferrocenylthiophosphono] disulfide (4e)

A solution of KI (1 g, 6.029 mmol) in H_2O (9 cm^3) was added to I_2 (0.109 g, 0.431 mmol) and stirred until I_2 completely dissolved. This solution was added dropwise to a solution of **2e** (0.300 g, 0.862 mmol) in H_2O (20 cm^3). An obvious yellow precipitate formed immediately and was stirred for a further 25 mins to ensure complete reaction. The product was collected by suction filtration, washed with methanol (2×10 cm^3) and dried *in vacuo* to give a mustard yellow powder (0.246 g, 88%). Found (calc. for $C_{24}H_{28}O_2Fe_2P_2S_4$): C 44.33 (44.31), H 4.05 (4.34), S 19.19 (19.68)%.

Isomer (a). ^{31}P NMR ($CDCl_3$) δ: 94.6. ^{1}H NMR ($CDCl_3$) δ: 4.60 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.25 (s, 5H, Fc unsubstituted ring), 3.98 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 3.3 Hz, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_2), 1.35 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 75.7 (d, $^{1}J(^{31}P–^{13}C)$ 140.4 Hz, Fc substituted ring C-1), 73.1 (m, Fc substituted ring), 72.5 (m, Fc substituted ring), 70.9 (s, Fc unsubstituted ring), 61.9 (d, $^{2}J(^{31}P–^{13}C)$ 6.6 Hz, CH_2), 16.6 (broad s, CH_3).

Isomer (b). ^{31}P NMR ($CDCl_3$) δ: 93.0. ^{1}H NMR ($CDCl_3$) δ 4.57 (m, 2H, Fc substituted ring), 4.41 (m, 2H, Fc substituted ring), 4.18 (s, 5H, Fc unsubstituted ring), 3.52 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 2.7 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 1.21 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 75.6 (d, $^{1}J(^{31}P–^{13}C)$ 144.3 Hz, Fc substituted ring C-1), 72.8 (m, Fc substituted ring), 72.2 (m, Fc substituted ring), 70.8 (s, Fc unsubstituted ring), 61.8 (d, $^{2}J(^{31}P–^{13}C)$ 6.6 Hz, CH_2), 16.5 (broad s, CH_3).

Selected IR data (KBr) ν/cm^{-1}: 1184 (m), 1023 (s), 664 (s), 536 (s), 491 (m). MS (MALDI): $(M)^+$ 650.

2,4-Dinitrophenyl 4-methoxyphenyl(ethoxy)thiophosphonyl disulfide (5e)

2,4-Dinitrosulfenyl chloride (0.087 g, 0.370 mmol) was added to a flask containing salt **1e** (0.100 g, 0.370 mmol). Upon addition of tetrahydrofuran (10 cm^3), with stirring, an immediate cloudy yellow solution is formed. The reaction mixture was stirred for 1 h resulting in a yellow/green solution. The solvent was removed under reduced pressure, the resulting green oily solid was redissolved in dichloromethane and filtered through a small Celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3, hexane was added and cooled to 5 °C for 2 h to precipitate the product as a bright green solid. (0.108 g, 65%). Yellow crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (calc. for $C_{15}H_{15}O_6N_2PS_3$): C 40.44 (40.36), H 3.55 (3.39), N 5.99 (6.28), S 21.02 (21.51)%. ^{31}P NMR ($CDCl_3$) δ: 87.2. ^{1}H NMR ($CDCl_3$) δ: 8.87 (d, 1H, $^{4}J(^{1}H–^{1}H)$ 2.5 Hz, Ph H-3), 8.00 (dd, 1H, $^{4}J(^{1}H–^{1}H)$ 2.5 Hz, $^{3}J(^{1}H–^{1}H)$ 9.1 Hz, Ph H-5), 7.77 (d, 1H, $^{3}J(^{1}H–^{1}H)$ 9.2 Hz, Ph H-6), 7.69 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 13.6 Hz, $^{3}J(^{1}H–^{1}H)$ 8.9 Hz, *o*-AnH), 6.62 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 4.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-AnH), 4.44 (dq, 1H, $^{3}J(^{31}P–^{1}H)$ 2.9 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 4.28 (dq, 1H, $^{3}J(^{31}P–^{1}H)$ 2.9 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 3.69 (s, 3H, AnOMe), 1.46 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz. ^{13}C NMR ($CDCl_3$) δ: 163.6 (d, $^{6}J(^{31}P–^{13}C)$ 4.2 Hz, *p*-AnC), 145.2 (s, Ph C-4), 144.9 (s, Ph C-1), 144.1 (s, Ph C-2), 133.4 (d, $^{3}J(^{31}P–^{13}C)$ 13.5 Hz, *m*-AnC), 129.6 (s, Ph C-3), 126.6 (s, Ph C-5), 123.1 (d, $^{1}J(^{31}P–^{13}C)$ 131.8 Hz, An C-1), 120.8 (s, Ph C-6), 113.7 (d, $^{2}J(^{31}P–^{13}C)$ 16.6 Hz, *o*-AnC), 63.1 (d, ^{2}J ($^{31}P–^{13}C$) 6.2 Hz, CH_2), 55.5 (s, AnOMe), 16.1 (d, ^{3}J ($^{31}P–^{13}C$) 8.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1595 (vs), 1523 (s), 1389 (m), 1339 (vs), 1183 (m), 1015 (s), 672 (m), 532 (m), 491 (m). MS (ES+): $(M - S_2C_6H_3(NO_2)_2)^+$ 215, $(M)^+$ 446.

2,4-Dinitrophenyl ferrocenyl(ethoxy)thiophosphonyl disulfide (6e)

2,4-Dinitrosulfenyl chloride (0.067 g, 0.287 mmol) was added to a flask containing salt **2e** (0.100 g, 0.287 mmol). Upon addition of tetrahydrofuran (10 cm^3), with stirring, an immediate dark orange solution is formed. The reaction mixture was stirred for 1 h resulting in a red solution. The solvent was removed under reduced pressure, the resulting red oil was redissolved in dichloromethane and filtered through a small Celite plug. The filtrate was concentrated under vacuum to *ca.* 2 cm^3 and hexane was added to precipitate the product as a red/orange solid. (0.109 g, 73%) Found (calc. for $C_{18}H_{17}O_5FeN_2PS_3$): C 41.60 (41.23), H 2.98 (3.27), N 4.89 (5.35), S 18.34 (18.31)%. ^{31}P NMR ($CDCl_3$) δ: 91.8. ^{1}H NMR ($CDCl_3$) δ: 8.88 (d, 1H, $^{4}J(^{1}H–^{1}H)$ 2.2 Hz, Ph H-3), 8.04 (dd, 1H, $^{4}J(^{1}H–^{1}H)$ 2.2 Hz, $^{3}J(^{1}H–^{1}H)$ 9.1 Hz, Ph H-5), 7.86 (d, 1H, $^{3}J(^{1}H–^{1}H)$

9.2 Hz, Ph H-6), 4.47 (m, 2H, Fc substituted ring), 4.27 (m, 2H, Fc substituted ring), 4.24 (s, 5H, Fc unsubstituted ring), 4.18 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 1.8 Hz, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_2), 1.46 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 145.2 (s, Ph C-4), 144.9 (s, Ph C-1), 144.3 (s, Ph C-2), 129.9 (s, Ph C-3), 126.6 (s, Ph C-5), 120.8 (s, Ph C-6), 79.9 (d, $^{1}J(^{31}P–^{13}C)$ 134.9 Hz, Fc substituted ring C-1), 71.8 (d, $^{2}J(^{31}P–^{13}C)$ 13.8 Hz, Fc substituted ring), 71.6 (d, $^{2}J(^{31}P–^{13}C)$ 12.2 Hz, Fc substituted ring), 70.5 (s, Fc unsubstituted ring), 63.1 (d, ^{2}J ($^{31}P–^{13}C$) 7.2 Hz, CH_2), 16.3 (d, $^{3}J(^{31}P–^{13}C)$ 8.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1593 (s), 1527 (s), 1387 (m), 1338 (vs), 1177 (m), 1020 (s), 667 (m), 540 (m), 498 (m). MS (EI+): $(M - S_2C_6H_3(NO_2)_2)^+$ 293, $(M)^+$ 524.

S-Benzyl *O*-ethyl 4-methoxyphenyldithiophosphonate (7e)

Salt **1e** (0.126 g, 0.468 mmol) in methanol (4 cm^{-3}) was added to benzyl bromide (0.080 g, 0.468 mmol) in methanol (10 cm^{-3}) and stirred for 1 h resulting in a colourless solution. The solvent was removed under reduced pressure, the resulting colourless oil was redissolved in dichloromethane and filtered through a small Celite plug. The solvent was again removed under reduced pressure to yield a colourless oil (0.128 g, 81%). Found (calc. for $C_{16}H_{19}O_2PS_2$): C 56.74 (56.80), H 5.57 (5.66), S 18.44 (18.92)%. ^{31}P NMR ($CDCl_3$) δ: 94.6. ^{1}H NMR ($CDCl_3$) δ: 7.86 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 13.8 Hz, $^{3}J(^{1}H–^{1}H)$ 8.9 Hz, *o*-AnH), 7.21 (m, 5H, Ph), 6.94 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.5 Hz, $^{3}J(^{1}H–^{1}H)$ 8.9 Hz, *m*-AnH), 4.19 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 2.4 Hz, $^{3}J(^{1}H–^{1}H)$ 3.6 Hz, OCH_2), 3.96 (d, 1H, ^{3}J ($^{31}P–^{1}H$) 3.2 Hz, SCH_2), 3.90 (d, 1H, ^{3}J ($^{31}P–^{1}H$) 2.7 Hz, SCH_2), 3.83 (s, 3H, AnOMe), 1.28 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 162.9 (d, ^{6}J ($^{31}P–^{13}C$) 3.1 Hz, *p*-AnC), 137.2 (d, $^{3}J(^{31}P–^{13}C)$ 5.2 Hz, Ph C-1), 132.8 (d, ^{3}J ($^{31}P–^{13}C$) 13.5 Hz, *m*-AnC), 129.0 (s, Ph C-3), 128.6 (s, Ph C-4), 127.5 (s, Ph C-2), 126.7 (d, ^{1}J ($^{31}P–^{13}C$) 128.7 Hz, An C-1), 114.1 (d, ^{2}J ($^{31}P–^{13}C$) 15.6 Hz, *o*-AnC), 64.0 (d, ^{2}J ($^{31}P–^{13}C$) 6.2 Hz, OCH_2), 55.6 (s, AnOMe), 38.0 (d, $^{2}J(^{31}P–^{13}C)$ 4.2 Hz, SCH_2), 16.1 (d, ^{2}J ($^{31}P–^{13}C$) 8.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1184 (s), 1027 (s), 671 (m), 549 (m). MS (EI+): $(M)^+$ 338.

S-Benzyl *O*-ethyl ferrocenyldithiophosphonate (8e)

Salt **2e** (0.116 g, 0.333 mmol) in methanol (4 cm^{-3}) was added to benzyl bromide (0.057 g, 0.333 mmol) in methanol (10 cm^{-3}) and stirred for 1 h resulting in a yellow solution. The solvent was removed under reduced pressure, the resulting orange oil was redissolved in dichloromethane and filtered through a small Celite plug. The solvent was again removed under reduced pressure to yield an orange oil (0.107 g, 77%). Found (calc. for $C_{19}H_{21}OFePS_2$): C 54.90 (54.81), H 5.04 (5.09), S 14.86 (15.37)%. ^{31}P NMR ($CDCl_3$) δ: 97.7. ^{1}H NMR ($CDCl_3$) δ: 7.26 (m, 5H, Ph), 4.58 (m, 2H, Fc substituted ring), 4.44 (m, 2H, Fc substituted ring), 4.32 (s, 5H, Fc unsubstituted ring), 4.21 (dq, 1H, $^{3}J(^{31}P–^{1}H)$ 1.8 Hz, $^{3}J(^{1}H–^{1}H)$ 3.5 Hz, OCH_2), 4.00 (d, 2H, ^{3}J ($^{31}P–^{1}H$) 13.9 Hz, SCH_2), 3.84 (dq, 1H, $^{3}J(^{31}P–^{1}H)$ 1.7 Hz, $^{3}J(^{1}H–^{1}H)$ 3.6 Hz, OCH_2), 1.29 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 137.6 (d, $^{3}J(^{31}P–^{13}C)$ 3.8 Hz, Ph C-1), 129.0 (s, Ph C-3), 128.6 (s, Ph C-4), 127.3 (s, Ph C-2), 77.9 (d, $^{1}J(^{31}P–^{13}C)$ 141.2 Hz, Fc substituted ring C-1), 71.8 (m, Fc substituted ring), 71.3 (m, Fc substituted ring), 70.5 (s, Fc unsubstituted ring), 61.3 (d, ^{2}J ($^{31}P–^{13}C$) 7.6

Table 1 Selected bond lengths (Å) and angles (°) for **3p**, **4m**, and **4p**

	3p	4m	4p
S(2)–S(12)/S(2A)	2.0849(7)	2.0746(19)	2.0808(18)
P(1)–S(2)	2.1154(7)	2.0995(13)	2.1087(12)
P(1)–S(1)	1.9303(7)	1.9203(14)	1.9289(13)
P(1)–O(1)/O(11)	1.5831(13)	1.580(2)	1.578(2)
P(1)–C(1)	1.7805(17)	1.764(3)	1.771(3)
P(1)–S(2)–S(12)	104.65(3)	104.28(5)	102.73(6)
C(1)–P(1)–S(2)/S(2A)	110.46(6)	107.79(11)	110.08(11)

Table 2 Selected bond lengths (Å) and angles (°) for **5m**, **5e**, **6m**, and **8p**

	5m	5e	6m	8p
S(2)–S(3)	2.0640(8)	2.0567(8)	2.056(3)	—
P(1)–S(2)	2.1199(8)	2.1247(8)	2.115(3)	2.0768(6)
P(1)–S(1)	1.9291(8)	1.9231(7)	1.907(3)	1.9342(6)
P(1)–O(1)	1.5797(14)	1.5880(13)	1.574(4)	1.5880(11)
P(1)–C(1)	1.7868(19)	1.7866(17)	—	1.7848(15)
P(1)–C(8)	—	—	1.759(6)	—
S(3)–C(11)	1.775(2)	1.7789(17)	—	—
S(3)–C(1)	—	—	1.776(6)	—
S(2)–C(14)	—	—	—	1.8416(18)
P(1)–S(2)–S(3)	104.36(3)	102.42(3)	100.70(12)	—
S(2)–P(1)–C(1)	107.83(6)	106.10(6)	—	107.83(5)
S(2)–S(3)–C(11)	104.22(7)	105.59(6)	—	—
C(1)–S(3)–S(2)	—	—	103.3(3)	—
S(2)–P(1)–C(8)	—	—	106.44(19)	—
P(1)–S(2)–C(14)	—	—	—	101.85(6)

Table 3 Details of the X-ray data collections and refinements for compounds **3p**, **4m**, and **4p**

Compound	3p	4m	4p
Empirical formula	$C_{20}H_{28}O_4P_2S_4$	$C_{22}H_{24}Fe_2O_2P_2S_4$	$C_{26}H_{32}Fe_2O_2P_2S_4$
Crystal colour, habit	Colourless, needle	Orange, prism	Orange, prism
Crystal dimensions/mm	$0.15 \times 0.1 \times 0.01$	$0.3 \times 0.1 \times 0.01$	$0.1 \times 0.1 \times 0.03$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pca2_1$	$C2/c$	$Pccn$
a/Å	13.0578(14)	30.209(9)	24.880(7)
b/Å	12.8267(14)	7.430(3)	6.4620(19)
c/Å	30.749(3)	11.365(2)	17.898(5)
α/°	90	90	90
β/°	90	99.838(9)	90
γ/°	90	90	90
U/Å^3	5150.1(10)	2513.3(14)	2877.6(15)
Z	8	4	4
M	522.60	622.29	678.40
D_c/g cm^{-3}	1.348	1.633	1.566
μ/mm^{-1}	0.517	2.288	1.433
$F(000)$	2192	1272	1400
Measured reflections	31 641	4487	13 630
Independent reflections (R_{int})	9365 (0.0189)	1928 (0.0312)	2601 (0.0835)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0208, 0.0529	0.0350, 0.0731	0.0406, 0.0815

Table 4 Details of the X-ray data collections and refinements for compounds **5m**, **5e**, **6m** and **8p**

Compound	5m	5e	6m	8p
Empirical formula	$C_{14}H_{13}N_2O_6PS_3$	$C_{15}H_{15}N_2O_6PS_3$	$C_{17}H_{15}FeN_2O_5PS_3$	$C_{20}H_{23}FeOPS_2$
Crystal colour, habit	Yellow, block	Yellow, block	Red, prism	Orange, prism
Crystal dimensions/mm	$0.18 \times 0.1 \times 0.07$	$0.18 \times 0.1 \times 0.03$	$0.10 \times 0.05 \times 0.05$	$0.12 \times 0.1 \times 0.03$
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.4150(11)	7.137(2)	7.089(4)	14.411(2)
b/Å	10.9049(16)	10.767(3)	10.648(6)	12.2057(17)
c/Å	11.8459(18)	13.652(4)	14.773(10)	11.3570(16)
α/°	101.672(2)	109.796(4)	88.56(7)	90
β/°	105.307(2)	90.755(5)	76.45(7)	96.061(2)
γ/°	100.104(2)	104.339(5)	77.84(6)	90
U/Å^3	877.8(2)	950.8(5)	1059.4(11)	1986.5(5)
Z	2	2	2	4
M	432.41	446.44	510.31	430.32
D_c/g cm^{-3}	1.636	1.559	1.600	1.439
μ/mm^{-1}	0.549	0.509	1.114	1.055
$F(000)$	444	460	520	896
Measured reflections	5551	5491	3852	10 502
Independent reflections (R_{int})	3109 (0.0109)	3372 (0.0128)	2661 (0.0319)	3583 (0.0182)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0316, 0.0805	0.0314, 0.0841	0.0476, 0.0828	0.0238, 0.0570

Hz, OCH_2), 37.9 (d, $^2J(^{31}P–^{13}C)$ 3.1 Hz, SCH_2), 16.2 (d, $^2J(^{31}P–^{13}C)$ 8.1 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1180 (s), 1028 (s), 687 (m), 560 (m). MS (EI+): $(M)^+$ 416.

X-Ray crystallography

Tables 1 and 2 list selected bond lengths and angles determined from X-ray crystallographic studies. Tables 3 and 4 list details of the data collections and refinements.‡ For **4m** and **6m** data were collected at room temperature using Mo Kα radiation with a Rigaku Mercury system, and for **3m**, **4p**, **5m**, **5e** and **8p** at 125 K using a Bruker SMART system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL[17]

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