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The reaction of dithiadiphosphetane disulfides with dienes, alkenes and thioaldehydes

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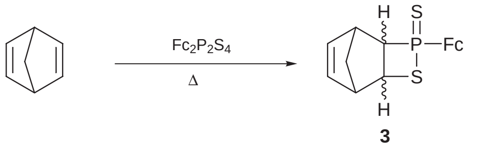
Ferrocenyl dithiadiphosphetane disulfide behaves as RPS_2 in simple cycloaddition reactions. Reactions with norbornadiene, norbornene and hexamethyl dewar benzene all give rise to fused 4-membered C_2PS ring compounds. Reaction with 2,3-dimethylbutadiene gave a simple Diels–Alder adduct which undergoes further reaction with BuLi and RX to yield $FcP(S)(SR)(C_6H_9)$ (R = CH_2Ph, *o*-$MeC_6H_4CH_2$, 2,4-dinitrophenyl). A trithiaphosphorinane was obtained when $Fc_2P_2S_4$ was reacted with benzaldehyde or trimethylacetaldehyde. Reaction of $Fc_2P_2S_4$ with $PhCH_2N{=}CHPh$ gave a dithiophospholane and a thiazadiphosphetane disulfide. The new compounds have been characterised spectroscopically with illustrative examples having been studied by X-ray crystallography.

Cyclic P–S systems continue to attract interest since these heterocycles are important commercially both as bulk materials and in organic synthesis, *e.g.* 2,4-bis(*p*-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide **1** (commonly known as Lawesson's reagent, LR),[1] which is extensively used in synthetic chemistry as a thioanation reagent.[2,3] We recently reported the preparation[4] of FcP(S)S$_2$P(S)Fc **2** together with some preliminary investigations into its reactions with unsaturated systems.[5,6] Here we describe the reactions of **1** and **2** (and some solubilised analogues) with a range of unsaturated systems. The new compounds have been characterised spectroscopically and in several cases by X-ray crystallography.

Results and discussion

The reaction of dithiadiphosphetane disulfides ($R_2P_2S_4$) with alkenes has been used in the synthesis of antisludge agents for use in engine oils.[7] We selected norbornadiene (bicyclo[2.2.1]-hepta-2,5-diene) NBD as a substrate for reactions with dithiadiphosphetane disulfide. The ring strain present was expected to increase the reactivity of the C=C double bonds and furthermore homo Diels–Alder reactions are possible with this diene.

The reaction of NBD with $Fc_2P_2S_4$ for 16 hours at 80 °C gave **3** [δ_P 64, ν(P=S) 631 cm^{-1}] as a racemic mixture (eqn. (1)). No attempt was made to separate the enantiomers or to devise a stereoselective synthesis. **3** Was found by ^{13}C-{^1H} and ^1H NMR spectroscopy to be the tricyclo product (thiaphosphetane) formed by the [2 + 2] reaction of the alkene with a dithiophosphine ylide. The formation of **3** is the most straightforward synthesis of the 1,2-thiaphosphetane ring known though a fluoro substituted ring has been prepared by two routes using a sulfur halide or a bis-TMS sulfide.[8] Using a COSY spectrum the majority of the proton NMR spectrum of **3** was assigned whilst $^1H/^{13}C$ correlation allowed identification of the carbon atoms that are in the thiaphosphetane ring (Fig. 1) and a double irradiation ^1H experiment identified the geminal coupling between the protons on C(9). The ^1H–^1H COSY spectrum (d_8-toluene) suggests that the two thiaphosphetane proton environments are coincidental. The EI mass spectrum for **3** contains a strong molecular ion (as did the other thiaphosphetanes formed from norbornadiene/norbornene, *vide infra*) and a peak at *m*/*z* 280, which is due to the $FcPS_2$ ion obtained by a [2 + 2] cycloelimination.



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(1)

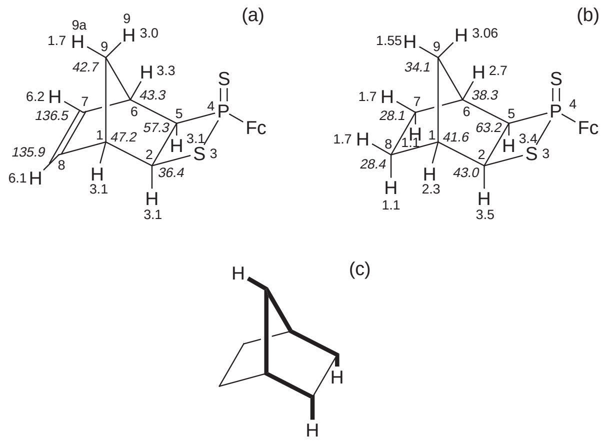


Fig. 1 (a) Atom numbering with ^1H (Roman type) and ^{13}C (italics) NMR spectroscopy assignments for: (a) and **3**, (b) **6**, (c) long range ^4J coupling in **6**.

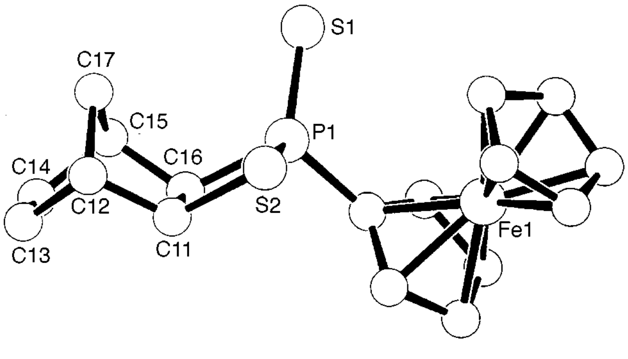


Fig. 2 Molecular structure of **3** in the crystal.

While exo [2 + 2] cycloadditions to norbornadiene are well known, the possibility of either an *endo* [2 + 2] cycloaddition or a homo Diels–Alder reaction followed by a rearrangement could not be discounted. In the solid state **3** (Fig. 2 and Table 1)

Table 1 Selected bond lengths (Å) and angles (°) in **3**

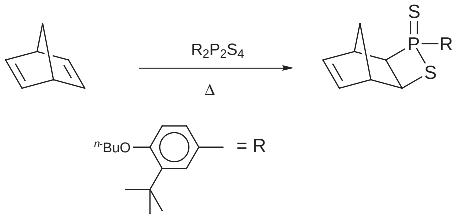
S(1)–P(1)	1.940(2)	C(11)–C(16)	1.585(7)
S(2)–C(11)	1.850(6)	S(2)–P(1)	2.102(2)
P(1)–C(16)	1.847(6)	P(1)–C(1)	1.800(6)
S(1)–P(1)–S(2)	122.0(1)	S(2)–C(11)–C(16)	100.3(4)
P(1)–S(2)–C(11)	80.1(2)	P(1)–C(16)–C(11)	95.7(4)
S(1)–P(1)–C(1)	114.1(2)	S(1)–P(1)–C(16)	118.9(2)
S(2)–P(1)–C(16)	83.8(2)		

Table 2 Selected bond lengths (Å) and angles (°) in **7**

S(1)–P(1)	1.931(1)	P(1)–C(1)	1.785(4)
S(2)–P(1)	2.095(1)	P(1)–C(11)	1.844(4)
S(2)–C(12)	1.880(3)	C(11)–C(12)	1.588(4)
P(1)–S(2)–C(12)	79.9(1)	P(1)–C(11)–C(12)	96.0(2)
S(2)–P(1)–C(11)	83.7(1)	C(11)–P(1)–S(1)	122.4(1)
S(2)–C(12)–C(11)	98.5(2)	S(1)–P(1)–S(2)	122.9(1)

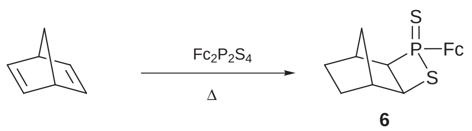
exists as the *exo* isomer. The intra-ring P–S bond length [S(2)–P(1) 2.102(2) Å] is slightly shorter than those in $Fc_2P_2S_4$ [mean 2.118(4) Å] though the P=S bond length [1.940(2) Å] is not significantly different. The P(1)–S(2)–C(11) [80.1(2)°] and S(2)–P(1)–C(16) [83.8(2)°] angles are significantly reduced from a tetrahedral arrangement as a consequence of four membered ring formation with the P(1)–C(16)–C(11) and S(12)–C(11)–C(16) angles being 95.7(4) and 100.3(4)° respectively. The thiaphosphetane ring is close to planar [max. dev. from the P(1)–C(11)–C(16)–S(2) mean plane is 0.05 Å].

We tested the generality of the reaction using LR with NBD which gave a white solid **4** (δ_P 62.6), whilst the more soluble dithiadiphosphetane disulfide Fc*R (Fc*R = dimethylferrocenyl analogue of FcR) also reacted with NBD in $CDCl_3$ at room temperature, giving (within 14 hours) the [2 + 2] adduct. Similarly the reaction of bis(4-butoxy-3-*tert*-butylphenyl)dithiadiphosphetane disulfide with NBD gave **5** (δ_P 63.9) (eqn. (2)), which was very soluble in most organic solvents.



(2)

To further investigate the scope of this type of reaction, norbornene was reacted with $Fc_2P_2S_4$ to give a low yield of a waxy orange solid **6** (δ_P 66.4) (eqn. (3)) formed by a [2 + 2] reaction of the alkene with the dithiophosphine ylide.

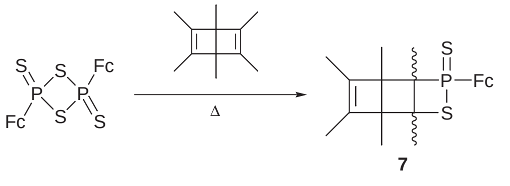


(3)

6

NOE experiments on **6** did not reveal whether the compound exists as the *exo* or *endo* isomer because several of the proton environments overlap. The extremely complex nature of the spectrum prevented measurement of the ^1H–^1H coupling constants. In the ^1H COSY spectrum cross peaks from 3.1 to 1.1 ppm and 1.6 to 3.4/3.5 were clearly seen. The presence of these peaks is consistent with the *exo* isomer. Similar cross peaks are present in the ^1H COSY spectrum for **3**. Fig. 1 illustrates the long range coupling which is found in the rigid bicyclic system.

In contrast to NBD we found that cyclohexene does not react with $Fc_2P_2S_4$ suggesting that only ring strained alkenes can react under these mild conditions. However, hexamethyl dewar benzene does react with $Fc_2P_2S_4$ (eqn. (4)) to give the tricyclo product **7** [ν(P=S) 699 cm^{-1}, δ_P 68.4] which has a ^1H NMR spectrum that contains six peaks due to the methyl groups and a ^{13}C-{^1H} NMR spectrum that clearly shows the presence of two alkene environments at 146.4 and 140.1 ppm, thus ruling out the possibility of a homo Diels–Alder reaction. Like **3**, **7** was formed as a racemic mixture.



(4)

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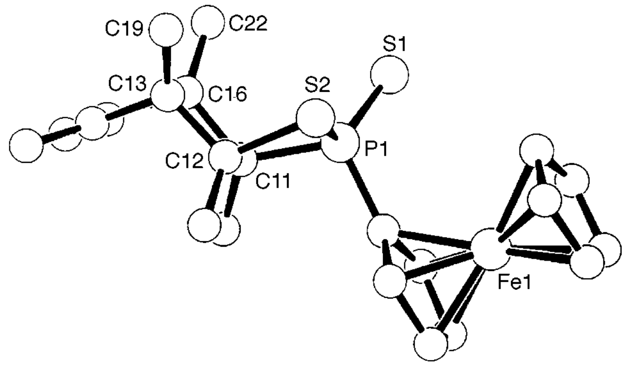
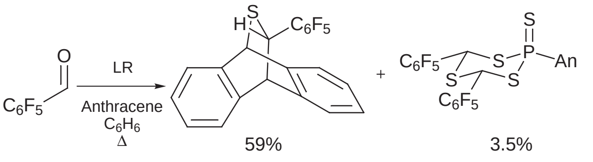


Fig. 3 Molecular structure of **7** in the crystal.

X-Ray crystallography reveals that **7** exists as the *exo* isomer (Fig. 3, Table 2) in the solid state. In the thiaphosphetane ring the P–S, P–C and C–C bond lengths in **7** are similar to those in **3**, though the C–S distance in **7** [1.880(3)] is slightly longer than that in **3** [1.850(6) Å]. Furthermore the ring in **7** is slightly less planar than that in **3**, C(11) and C(12) lie +0.14 and −0.14 Å from the P(2)–S(2)–C(11)–C(12) mean plane. The P(1)–S(2)–C(12) angle in **7** [79.9(1)] is similar to the corresponding angle in **3** [80.1(2)] though the C(11)–P(1)–S(1) angle in **7** [122.4(1)] is larger than the corresponding angle in **3** [118.9°] as a consequence of the steric effect of the methyl group (C22).

Diels–Alder reactions of selenoketones,[9] tellurocarbonyls[10] and thioaldehydes[11,12] have been used to trap these reactive molecules. Thioaldehydes can be regenerated by a retro Diels–Alder reaction, enabling these adducts to be used as a storage system for the reactive molecules.[12] In addition to acting as dienophiles, thioketones are also known to take part in Diels–Alder reactions as heterodienes.[13–15] Simple 1,3-dienes are known to react with dithiadiphosphetane disulfides,[16–18] though the mechanism suggested for the reaction is inconsistent with the generally accepted one for Diels–Alder reactions.[17] LR has previously been found to react with the anthracene present in benzene to form a thioaldehyde adduct (eqn. (5)).[19] However,



(5)

we did not observe any reaction of anthracene with $Fc_2P_2S_4$ in hot xylenes. This was not entirely surprising as anthracene is an unreactive 1,3-diene when its Diels–Alder reactivity is compared with an open chain 1,3-diene.

In comparison with anthracene and the products from the bicyclic alkenes, we found that the reaction of 2,3-dimethylbutadiene with $Fc_2P_2S_4$ gives a high yield of the Diels–Alder adduct **8** (δ_P 69.2, ν(P=S) 666 cm^{-1}) (eqn. (6)) as a racemic mixture. However, when the naphthalene analogue NpP_2S_4 was

Table 3 Selected bond lengths (Å) and angles (°) in **8**

S(1)–P(1)	1.994(3)	P(1)–C(14)	1.816(8)
S(2)–P(1)	2.086(4)	C(11)–C(12)	1.588(4)
S(2)–C(11)	1.840(9)		
S(2)–P(1)–C(14)	101.6(3)	C(12)–C(13)–C(14)	118.1(8)
S(2)–P(1)–C(1)	106.5(3)	P(1)–S(2)–C(11)	100.4(4)
C(1)–P(1)–C(14)	106.0(4)	S(1)–P(1)–S(2)	114.7(2)
P(1)–S(2)–C(11)	100.4(4)	S(1)–P(1)–C(1)	112.5(3)
S(2)–C(11)–C(12)	112.4(6)	S(1)–P(1)–C(14)	114.5(3)

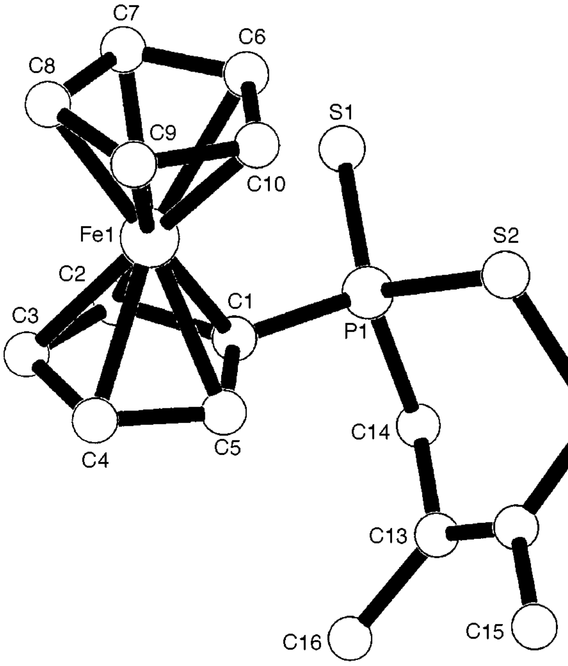
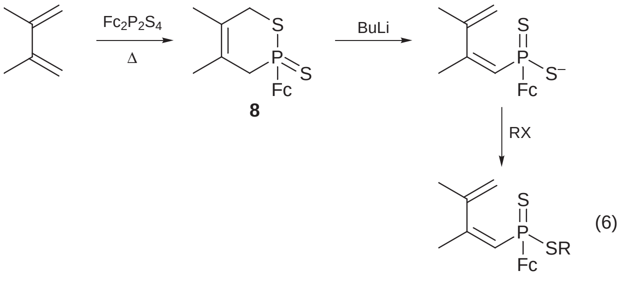


Fig. 4 Molecular structure of **8** in the crystal.



(6)

10 R = CH_2Ph
11 R = *o*-$MeC_6H_4CH_2$
12 R = 2,4-dinitrophenyl

treated with 2,3-dimethylbutadiene no reaction occurred, which is consistent with the hypothesis that the diene reacts with the dithiophosphine ylide and not with the dithiadiphosphetane disulfide.

The phosphorus–sulfur bond lengths of **8** are not significantly different from those in **3**. In the solid state **8** has a pseudo boat shaped C_4PS ring (Fig. 4 and Table 3). The P–S bond length in **8** [2.086(4)] is similar to those in **3** [2.102(2) Å] and **7** [2.095(1) Å] and the C–S distance [1.840(9)] is similar to that in **3** [1.850(6) Å]. The C(14)–P(1)–S(2)–C(11) plane is inclined by 123° to the C(14)–C(13)–C(12)–C(11) plane.

The Diels–Alder reaction normally involves the frontier orbitals (HOMOs and LUMOs). However, in this case it is likely that the HOMO (non-bonding orbital) is not involved; instead it is likely that the lowest occupied π orbital is replacing it in the reaction (Fig. 5). A related compound **9**, which is similar to **8** but with the endocyclic sulfur missing, has been reported (eqn. (7)).[20]

Table 4 Selected bond lengths (Å) and angles (°) in **10**

S(1)–P(1)	1.946(2)	P(1)–C(1)	1.774(6)
S(2)–P(1)	2.108(2)	P(1)–C(18)	1.787(6)
S(2)–C(11)	1.812(7)		
S(2)–P(1)–C(18)	101.9(2)	S(1)–P(1)–C(1)	115.8(2)
C(1)–P(1)–C(18)	108.8(3)	S(1)–P(1)–C(18)	114.3(2)
P(1)–S(2)–C(11)	101.4(2)	S(2)–P(1)–C(1)	99.6(2)
S(1)–P(1)–S(2)	114.8(1)		

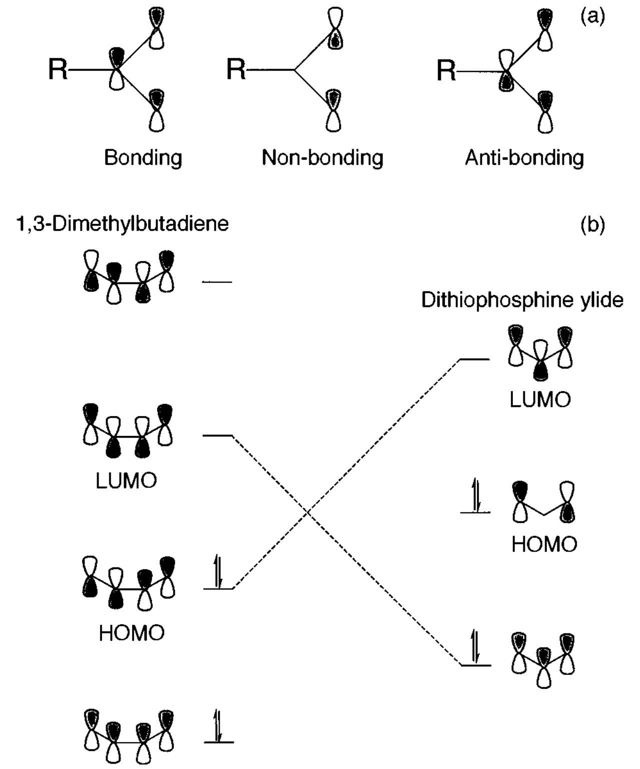
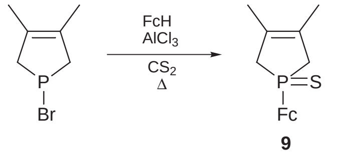


Fig. 5 (a) Molecular orbitals in a dithiophosphine ylide. (b) The π-orbitals on the atoms taking part in the Diels–Alder reaction.



(7)

Diels–Alder adducts of other dithiophosphine ylides were reported to undergo ring opening when treated with sodium hydride and the resulting anions were quenched with carbon electrophiles to give S-aryl and S-alkyl dithiophosphates.[17] We found that treatment of **8** with BuLi in THF followed by the addition of benzyl bromides or 2,4-dinitrochlorobenzene gives moderate yields of similar compounds **10**, **11** and **12**. The X-ray structure of **10** reveals that the carbon–carbon double bond α,β to the phosphorus has *Z* stereochemistry (Fig. 6, Table 4) suggesting it was formed from a sulfur anion where this *cis* relationship exists. However, the isolated yield is not 100% and it would be unreasonable to assume that only one ring opening process is in operation, and the observed product may simply be kinetically controlled. It was hoped that the terminal sulfur would interact with the 2,3-dimethylbut-1,3-dien-1-yl group to give a possible homo aromatic ring. In the X-ray structure no inter or intra molecular interactions were observed between the terminal sulfur and the dienyl group. The bond between the 2 and 3 carbons has rotated and the sp^2 carbons are not coplanar. While the P=S and C–P bond lengths are not significantly different from the Diels–Alder adduct **8**, the P–S bond in

Table 5 Selected bond lengths (Å) and angles (°) for **13** and **14**

	13	**14**
S(1)–P(1)	1.937(2)	1.938(1)
S(2)–P(1)	2.102(2)	2.091(1)
S(6)–P(1)	2.086(2)	2.081(1)
S(2)–C(3)	1.841(4)	1.855(3)
S(4)–C(3)	1.815(5)	1.820(4)
S(4)–C(5)	1.795(5)	1.814(3)
S(6)–C(5)	1.847(5)	1.848(3)
P(1)–S(2)–C(3)	97.8(2)	98.34(11)
C(3)–S(4)–C(5)	105.1(2)	101.0(2)
P(1)–S(6)–C(5)	98.0(2)	99.33(11)
S(1)–P(1)–S(2)	112.58(8)	114.48(6)
S(1)–P(1)–S(6)	115.25(9)	115.35(6)
S(2)–P(1)–S(6)	103.84(7)	104.80(6)
S(2)–C(3)–S(4)	113.9(3)	111.9(2)
S(2)–C(3)–C(7)	110.1(3)	110.2(2)
S(4)–C(3)–C(7)	106.0(3)	111.2(2)
S(4)–C(5)–S(6)	116.4(3)	112.9(2)

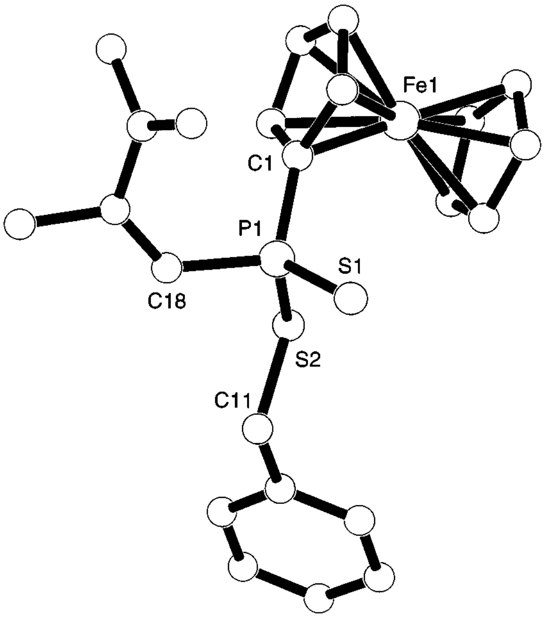
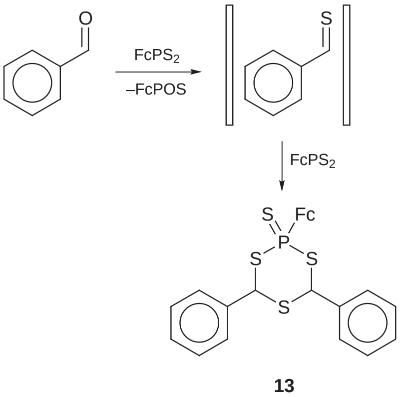


Fig. 6 Molecular structure of **10** in the crystal.

10 is longer. Like **8**, **10** was formed as a racemic mixture and no attempts were made to separate the enantiomers or devise a stereoselective synthesis.

It was anticipated that treatment of benzaldehyde with $Fc_2P_2S_4$ would give the highly unstable thioaldehyde, which would undergo further transformations. C–P–S heterocycles are accessible using LR in high yields.[19,21,22] As expected when $Fc_2P_2S_4$ is reacted with benzaldehyde, the trithiaphosphorinane **13** (δ_P 72.0) is obtained in low yield (reaction conditions were not optimised) (eqn. (8)). When the reaction was performed with trimethylacetaldehyde the analogous ^{t}Bu product **14** (δ_P 72.3) was obtained.



(8)

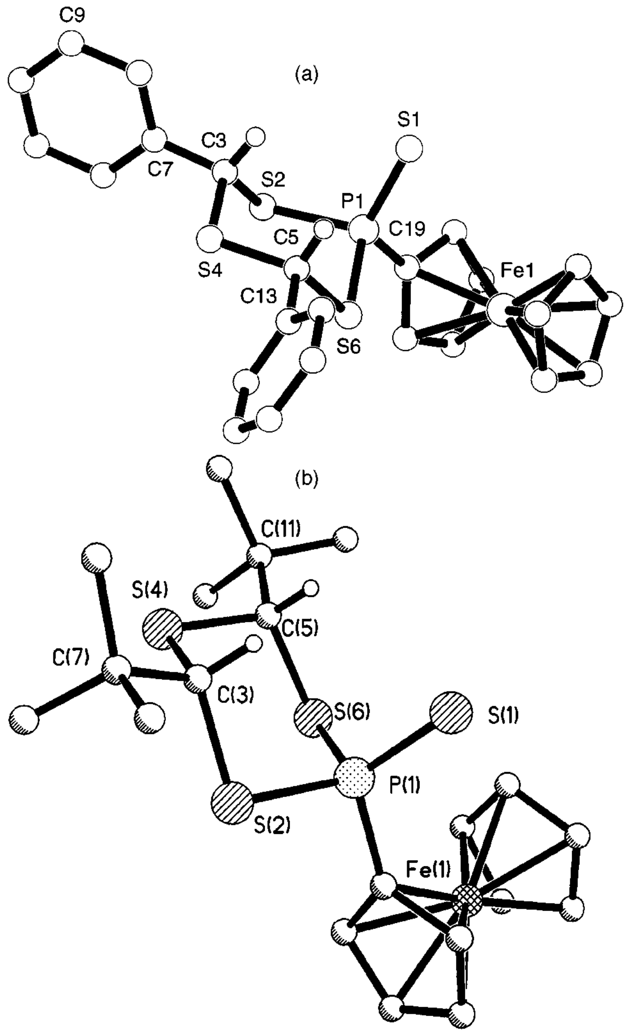


Fig. 7 Molecular structure of (a) **13** and (b) **14** in the crystal illustrating the regularity of the chair conformation in these two structures.

The X-ray structures of **13** and **14** reveal (Fig. 7 and Table 5) that the C_2PS_3 ring adopts a chair conformation with the phenyl/butyl groups being equatorial. The six membered chair-like rings are quite regular, thus for example, for the C(3)–C(5)–S(2)–S(6) mean planes P(1) and S(4) lie 1.20/1.15 and −0.92/−1.04 Å in **13**/**14** whilst for S(4)–S(2)–P(1)–C(5) C(3) lies 0.92/0.98 and S(6) lies −1.13/−1.1 Å from the mean plane. Examination of the crude product mixtures by ^{31}P-{^{1}H} NMR spectroscopy indicated that no other isomer was present in any significant amount.

After investigating the reaction of thioaldehydes with $Fc_2P_2S_4$ when the thione is generated rapidly, an attempt to react $Fc_2P_2S_4$ with thiobenzaldehyde where the thioaldehyde is slowly formed *in situ* was made. Since nitrogen is 'softer' than oxygen and the steric hindrance is slightly greater around the carbon of an imine when compared with the carbonyl carbon, the reaction of an imine was chosen as a means for slowly forming thiobenzaldehyde at an elevated temperature. To this end $Fc_2P_2S_4$ and $PhCH_2N{=}CHPh$ were heated together (45 hours). After repeated chromatography and recrystallisation a small yield of a product **15** (δ_P 86.3) whose ^{1}H NMR spectrum has a complex aromatic area, and a doublet (δ_H 5.21, *J* 14 Hz) outside the ferrocenyl region was obtained. In the ^{13}C NMR spectrum of **15** only one carbon environment, other than those due to phenyl and ferrocenyl groups, was present indicating that the product cannot be a thiazaphosphetane, as this would have two ^{1}H and ^{13}C signals outside the ferrocenyl and aromatic areas.

Table 6 Selected bond lengths (Å) and angles (°) in **15**

S(1)–P(1)	2.905(2)	S(2)–C(2)	1.832(4)
S(2)–P(1)	2.089(2)	C(1)–C(2)	1.540(5)
S(3)–P(1)	1.938(2)	P(1)–C(15)	1.778(4)
S(1)–C(1)	1.836(4)		
S(2)–P(1)–C(15)	109.6(1)	S(1)–P(1)–S(2)	99.20(6)
S(1)–C(1)–C(2)	108.6(2)	S(1)–P(1)–S(3)	118.18(7)
S(2)–C(2)–C(1)	111.7(3)	S(2)–P(1)–S(3)	112.20(7)
P(1)–S(1)–C(1)	101.0(1)	S(3)–P(1)–C(15)	112.7(1)
P(1)–S(2)–C(2)	97.3(1)	S(1)–P(1)–C(15)	103.9(1)

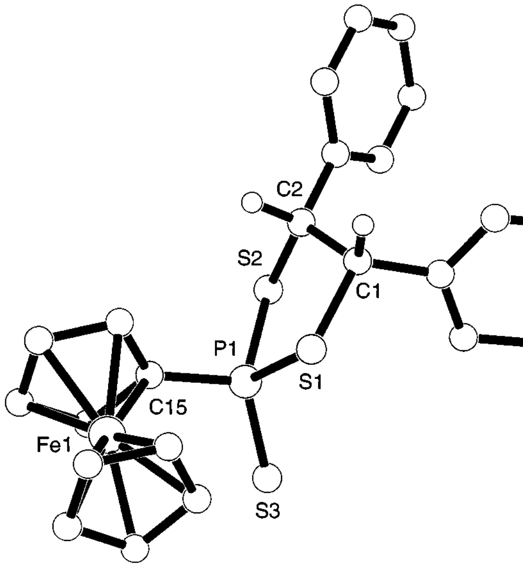
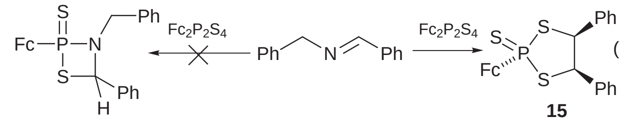


Fig. 8 Molecular structure of **15** in the crystal.



(9)

15

Considering the ^{1}H and ^{13}C NMR spectroscopic data and the molecular ion at *m*/*z* 492 ($^{12}C_{24}{}^{1}H_{23}{}^{56}Fe^{31}P^{32}S_3$) the structure **15** containing a dithiophospholane ring was assigned (eqn. (9)). If the phenyl groups of **15** are arranged *cis* to each other, one of the phenyls could be equatorial while the other would be axial, making the two potentially inequivalent by NMR spectroscopy, depending on the rate of change from one conformation to the other.

X-Ray crystallography reveals the compound to be a C_2PS_2 heterocycle (Fig. 8, Table 6). The mean P–S and C–S bond lengths in **15** are not significantly different from the mean bond lengths in the trithiaphosphinanes **13** and **14**. The mean S–P–S(3) angle of 115.2(1) is larger than the corresponding angle in the diphenyl trithiaphosphinane **13** but it is not significantly different from the mean angle in the di-*tert*-butyl trithiaphosphinane **14**. While the P–S bond lengths of **15** are similar to those found for two thiadiphospholanes with tri- and tetracoordinate phosphorus[23,24] (respectively 2.087(2) and 2.09 Å), the P–S bond lengths in **15** are shorter than those found in two thiadiphospholanes with penta-coordinate phosphorus atoms (mean P–S lengths of 2.134 and 2.142 Å).[25,26] The PS_2C_2 ring in **15** adopts a classic puckered geometry with P(1)–S(1)–S(2)–C(1) forming a planar fragment and C(2) lying 0.76 Å out of this plane. The phenyl substituents in **15** are on the same side of the five-membered ring [C(3)–C(1)–C(2)–C(9) torsion angle 46°]. The most likely source of the phenyl groups found in **15** is the thiobenzaldehyde assumed to be the sulfur containing side product from the formation of the nitrogen phosphorus compounds (Fig. 9). The formation of this heterocycle did pose a mechanistic challenge, as a C–C bond is formed and **15** cannot be rationalised as being an adduct of thiobenzaldehyde and the dithiophosphine ylide. One suggestion as to the mechanism would be the [2 + 2] cycloaddition of thiobenzaldehyde with the dithiophosphine ylide followed by a second [2 + 2] cycloaddition. After the second cycloaddition an atom of sulfur is eliminated from the molecule to give **15**. A precedent for the final step (loss of a sulfur atom) can be taken from the reaction of dimethyl dithiadiphosphetane disulfide with trimethylsilyl azide.[17]

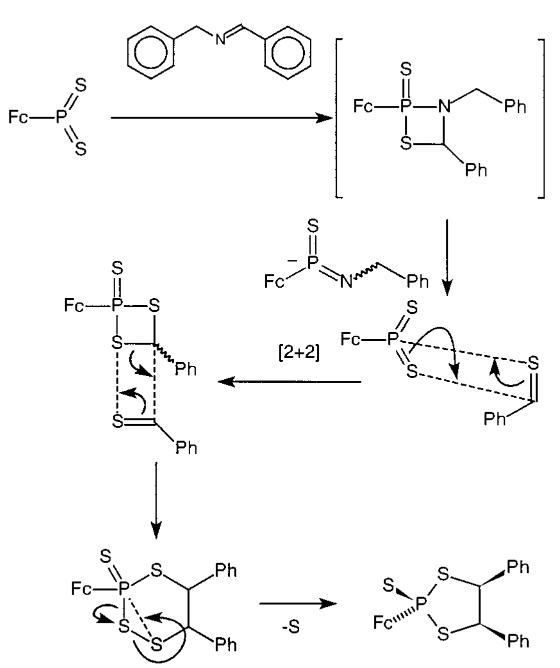
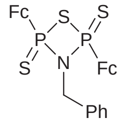


Fig. 9 Possible mechanism for the formation of **15** from $Fc_2P_2S_4$.

The reaction of $Fc_2P_2S_4$ and $PhCH_2N{=}CHPh$ gave a second isolated product which from ^{1}H NMR has only one phenyl group environment and other than the phenyl and ferrocenyl groups, the only feature present was a poorly resolved multiplet (δ_H 4.16). From NMR spectral data and as a molecular ion was found at *m*/*z* 633 in the FAB MS, a thiazadiphosphetane disulfide structure **16** (δ_P 65.1) was assigned.



16

The benzyl CH_2 protons (δ_H 4.16) are expected to give rise to a 1:2:1 triplet in the ^{1}H NMR spectrum, but a more complex system consisting of a sharp single peak with a doublet on either side was observed. A $^{1}H/^{13}C$ correlation confirmed that this complex peak was due to the benzylic protons. At lower temperature the multiplet due to the benzylic protons was seen to broaden when compared with the rest of the spectrum. This indicates that a slow rotation is occurring about the nitrogen–carbon bond. This rotation could not be frozen out at 233 K, nor was any change to this peak observed on heating to 363 K (90 °C in d_8-toluene). It is likely that the two benzylic protons are experiencing through space effects because they are at different distances from the ferrocenyl groups and the sulfur atoms. Because of slow rotation about the P–C bonds, four different proton environments and five carbon environments are seen in the NMR spectra for the substituted Cp ring.

The X-ray structure of **16** (Table 7, Fig. 10) reveals an almost perfectly planar P_2SN ring [max. dev. from the P(1)–P(2)–S(2)–N(1) mean plane 0.36 Å for N(1)] with the carbon substituent on the nitrogen atom lying only 0.09 Å out of the plane of the

Table 7 Selected bond lengths (Å) and angles (°) in **16**

P(1)–S(1)	1.918(4)	P(1)–S(2)	2.110(4)
P(2)–S(3)	1.925(4)	P(2)–S(2)	2.108(4)
P(1)–N(1)	1.661(8)	P(2)–N(1)	1.680(7)
P(1)–S(2)–P(2)	79.3(1)	S(1)–P(1)–S(2)	119.3(2)
S(1)–P(1)–N(1)	117.3(3)	S(2)–P(1)–N(1)	86.8(3)
S(2)–P(2)–S(3)	120.4(2)	S(2)–P(2)–N(1)	86.4(3)
S(3)–P(2)–N(1)	117.8(3)	P(1)–N(1)–P(2)	107.4(5)

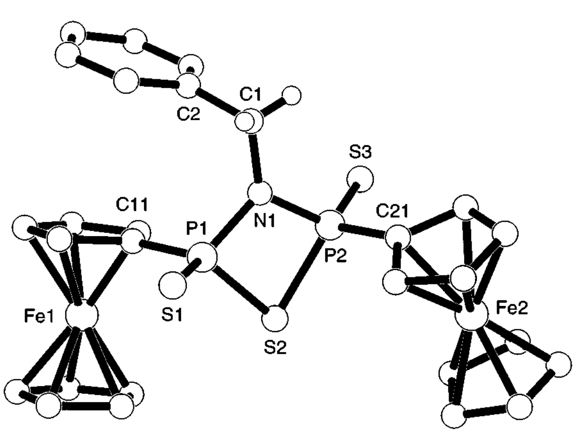


Fig. 10 Molecular structure of **16** in the crystal.

ring. Interestingly it appears that the benzyl group exerts a steric effect on S(1) which is 1.48 Å out of the P_2SN plane whereas S(2) lies −1.41 Å on the opposite side of the ring.

Experimental

All reactions were performed under an inert atmosphere of nitrogen. Reagents were purchased from Aldrich. Xylene was obtained from Fisons and was dried over sodium before use. Hexane, THF and diethyl ether were distilled from sodium/benzophenone before use. Toluene was distilled from sodium before use. NMR spectra [^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H}, $CDCl_3$] were recorded using either a JEOL FX90Q or a Bruker 250AX spectrometer. LR, $Fc_2P_2S_4$ and $Fc^*{}_2P_2S_4$ were prepared as previously described.[4] Infrared spectra were obtained using KBr discs with a Perkin-Elmer system 2000 FT-IR. Mass spectra were obtained using a Kratos MS80 or by the National Service in Swansea. Microanalyses were carried out by the Loughborough University Chemistry Department service. Electrochemical results are reported with respect to SCE.

3: Reaction of $Fc_2P_2S_4$ and NBD

Into a thick walled glass tube were placed $Fc_2P_2S_4$ (3.1 g, 5.5 mmol) and NBD (5 ml, 4.3 g, 46 mmol), the reaction mixture was cooled to −196 °C before all air was removed. The tube was sealed and allowed to warm to room temperature before being heated to *ca.* 80 °C (16 hours) with stirring of the reaction mixture. The red brown reaction mixture was allowed to cool to room temperature before the excess NBD was removed using a high vacuum line to yield a brown tar that solidified to give **3** as a yellow solid (2.82 g, 7.6 mmol, 69% isolated). This solid was found to be insoluble in ether, but to be soluble in chloroform and dichloromethane. This solid may be recrystallised from ethyl acetate. δ_P ($CDCl_3$) 64. δ_C ($CDCl_3$) 136.5 [d, *J*(PC) 15 Hz], 135.9, 73.5 [d, *J*(PC) 16 Hz], 72.4 (m), 70.0, 57.3 [d, *J*(PC) 53 Hz], 47.2, 43.3, 42.7 and 36.4 [d, *J*(PC) 7 Hz]. δ_H ($CDCl_3$) 6.3 (2H, m), 4.7 (2H, m), 4.6 (2H, m), 4.2 (4H, s), 3.0 (5H, m) and 1.6 [1H, d, ^2J(^{1}H–^{1}H) = 9.8 Hz]. On irradiation of the doublet at 1.6 ppm, part of the complex peak at 3.0 ppm changed from a doublet to a singlet. ^{1}H ($CDCl_3$) COSY δ 6.15 [3.27], 6.10 [3.06], 4.74 [4.54], 3.26 [2.97], 3.26 [1.70], 3.13 [1.70], 3.08 [1.70] and 2.97 [1.70]. ^{1}H/^{13}C ($CDCl_3$) correlation ^{1}H δ [^{13}C δ] 6.2 [136.5], 6.1 [135.9], 4.7 [73.5], 4.7 [72.4], 4.5 [72.4], 4.2 [70.0], 3.1 [57.3], 3.1 [47.2], 3.3 [43.3], 3.0 [42.7], 1.6 [42.7] and 3.1 [36.4]. δ_H (Toluene-d_8) 5.68 (m), 4.07 (m), 4.61 (m), 4.22 (m), 4.17 (s), 3.15 (d, 9.7 Hz), 3.07 (m), 2.6 (m) and 1.5 (d, 9.7 Hz). On heating to 90 °C (363 K) no change was observed in the spectrum. On irradiation of the peak at 1.50 the doublet at 3.15 ppm becomes a singlet. ^{1}H COSY (Toluene-d_8) δ_1 [δ_2] 5.68 [3.07], 5.68 [2.59], 4.70 [4.16], 4.62 [4.21], 3.15 [2.59], 3.15 [1.50], 3.07 [2.59] and 2.59 [1.50]. δ_C (Toluene-d_8) (δ range 100–0 ppm) 74.4 [d, *J*(PC) 15.7 Hz], 72.8 [d, *J*(PC) 14.5 Hz], 72.4 [d, *J*(PC) 11.3 Hz], 70.4, 57.8 [d, *J*(PC) 53 Hz], 47.6 [d, *J*(PC) 2 Hz], 43.8 [d, *J*(PC) 3 Hz], 43.1 and 36.4 [d, *J*(PC) 7.4 Hz]. IR (cm^{-1}) 3126w, 3106w, 3094w, 3068m, 3061m, 3000m, 2982s, 2969s, 2956s, 2882w, 1787w, 1551w, 1542w, 1459m, 1409m, 1390m, 1365m, 1350w, 1319s, 1279m, 1256m, 1222w, 1178s, 1170s, 1149m, 1107m, 1064w, 1056w, 1034m, 1019s, 1007s, 976m, 939m, 926m, 911w, 897w, 862m, 829s, 818s, 785s, 766s, 753s, 713s, 686m, 631vs, 535m, 490s, 276s, 444m, 400w, 365w, 348m and 326m. MS(EI+) *m*/*z* 372 (M$^+$), 280 ($FcPS_2$), 248, 217, 184, 155, 121, 91, 69, 51 and 31 (Found: C, 54.6; H, 4.4; N, 0.1. $C_{17}H_{17}FePS_2$ requires C, 54.8; H, 4.6; N, 0.0%). Mp 120–121.5 °C. CV 0.70 V and reversible.

4: The reaction of LR with NBD

The reaction of LR (1.86 g, 4.6 mmol) with excess NBD (5 ml, 4.2 g, 46 mmol) was carried out in the same manner as above, to give, after removal of solvent and recrystallisation from ethyl acetate, a while solid (0.879 g). The solid when examined by ^{1}H NMR spectroscopy was found to be contaminated with ethyl acetate. The product was dissolved in CH_2Cl_2 (3 ml) and to this was added ether (4 ml) followed by trituration to give **4** as a white solid (0.364 g, 1.2 mmol, 13%). After re-examination with ^{1}H NMR spectroscopy the compound was now found to be free of ethyl acetate. MS(EI+) *m*/*z* 294 (M$^+$), 228, 202 (M − H_2S_2)$^+$, 202 (M − C_7H_8)$^+$, 165, 139, 91, 66 (H_2S_2), 39. δ_C 136.5 [d, *J*(PC) 15 Hz], 135.8 [d, *J*(PC) 1.8 Hz], 133.4 [d, *J*(PC) 14 Hz], 113.9 [d, *J*(PC) 14 Hz], 57.0, 56.1, 56.4, 47.4, 43.8, 42.8 (CH_2) and 36.8 [d, *J*(PC) 8 Hz]. δ_H 8.1 {2H, dd, [^3J(^{31}P–^{1}H) = 14 Hz, ^3J(^{1}H–^{1}H) = 8.8 Hz]}, 7.0 (2H, m), 6.7 (2H, m), 3.9 (4H, s), 3.3–3.0 (6H, m), 1.7 (2H, d). δ_P 62.55. IR (cm^{-1}) 3055w, 2985s, 2836m, 1589s, 1564m, 1495m, 1479w, 1463m, 1450w, 1439m, 1406m, 1320m, 1308m, 1292s, 1276m, 1259s, 1221w, 1180s, 1146m, 1100s, 1023s, 989w, 928m, 906w, 895w, 865w, 835s, 816m, 800m, 787s, 766s, 750s, 702s, 688m, 654s, 628m, 614s, 530s, 519m, 507m, 464m, 414m, 341m (Found: C, 57.0; H, 5.1; N, 0.0. $C_{14}H_{15}OPS_2$ requires C, 57.2; H, 5.1; N, 0.0%). Mp 161–162 °C.

Room temperature reaction of $Fc^*{}_2P_2S_4$ and NBD (Fc* = 1,1-dimethylferrocene)

$Fc^*{}_2P_2S_4$ (22 mg, 36 μmol) was dissolved in $CDCl_3$ and a drop of NBD was added to the NMR tube, after 4.5 hours the signal due to **12** at 18 ppm was replaced by a peak at 64.1 ppm. The reaction mixture was evaporated down to a red tar (31 mg) which even after drying in high vacuum overnight retained some NBD. δ_P 64.1. δ_H 6.1 (2H, m), 4.6 to 4.0 (9H, m), 3.4 to 2.8 (4H, m) and 2.0 (8H, complex). IR (thin film) (cm^{-1}) 3064m, 2974s, 1567w, 1543m, 1474m, 1455s, 1387s, 1312m, 1282m, 1251s, 1229m, 1184m, 1148w, 1096s, 1039s, 980m, 940m, 895w, 868s, 832s, 789m, 765m, 754m, 730s, 703s, 658m, 631s, 540w, 523w, 490s and 444w. MS(EI+) *m*/*z* Molecular ion found at 400.0174 [$^{12}C_{19}{}^1H_{21}{}^{56}Fe^{31}P^{32}S_2$ requires 400.01713 (error of 0.6 ppm)].

5: The reaction of bis(4-butoxy-3-*tert*-butylphenyl)dithiadiphosphetane disulfide with NBD

Bis(4-butoxy-3-*tert*-butylphenyl)dithiadiphosphetane disulfide (1.13 g, 1.88 mmol) and NBD (4.1 ml, 3.5 g, 37.6 mmol) were reacted in the same manner as above. After being allowed to cool the solvent was removed *in vacuo* forming a gelatinous solid. This was dissolved in ether (4 ml) which after removal of ether gave a waxy solid. A sample was withdrawn for ^{31}P NMR spectroscopy (71 mg). δ_P 73.9. δ_C 161.8 (quat), 144.1 (impurity), 138.8 [d, J(PC) 3 Hz, quat], 137.3 [d, J(PC) 15 Hz], 136.6, 131.9 [d, J(PC) 14 Hz], 130.9 [d, J(PC) 14 Hz], 127.6 [d, J(PC) 77 Hz, quat], 112.1 [d, J(PC) 15 Hz], 76.0 (impurity), 68.6 (CH_2), 57.6, 57.1, 50.9 (impurity), 48.0 [d, J(PC) 32 Hz], 44.2 [d, J(PC) 2.4 Hz], 43.5 [d, J(PC) 21 Hz, CH_2], 37.5 [d, J(PC) 8 Hz], 35.9 (quat), 32.0 (CH_2), 30.2, 20.2 (CH_2), 14.5. IR (cm^{-1}) 3124w, 2962s, 1587s, 1563m, 1543w, 1455s (cluster of lines), 1394s (pair of lines), 1360s, 1321s, 1202s, 1186s, 1149s, 1091s, 1067m, 1023s, 1008s, 978m, 836s, 810s, 789s, 766s, 729s, 703s, 687m, 662m, 624s, 596m, 583m, 510s, 475s, 428s. The product was washed with petrol. After the removal of the petrol extract, the gummy residue was then allowed to stand in high vacuum to give **5** as a white solid (0.352 g, 897 µmol, 24%). δ_H 8.1 {dd, [$^4J(^1H–^1H) = 2.3$ Hz, $^3J(^{31}P–^1H) = 15.0$ Hz]}, 7.9 {ddd, [$^4J(^1H–^1H) = 2.3$ Hz, $^3J(^{31}P–^1H) = 13.4$ Hz, $^3J(^1H–^1H) = 8.5$ Hz]}, 6.9 {dd, [$^3J(^1H–^1H) = 8.5$ Hz, $^4J(^1H–^{31}P) = 3.4$ Hz]}, 6.0 (m), 4.0 (t, 6.4 Hz), 3.2 (m), 3.0 (m), 1.8 (m), 1.6 (d, 9.6 Hz), 1.5 (m), 1.3 (s), 0.9 (t, 7.4 Hz), 0.8 (m). ^{1}H COSY δ_1 (δ_2) 8.1 (6.9), 6.0 (3.2), 6.0 (3.0), 4.0 (1.8), 3.2 (3.0), 3.0 (1.6), 1.8 (1.5) and 1.5 (0.9). MS(EI) *m*/*z* 392, 326, 300, 262, 229, 207, 151, 124, 91, 66, 57 and 41. Molecular ion found at *m*/*z* 392.1400 ($^{12}C_{21}{}^1H_{29}{}^{16}O^{32}S_2{}^{31}P$ requires *m*/*z* 392.1397 (0.6 ppm error)). Mp 66–71 °C to a colourless tar.

6: Reaction of norbornene with $Fc_2P_2S_4$

$Fc_2P_2S_4$ (1.1 g, 2.0 mmol), norbornene (4.1 g, 44 mmol) and toluene (8 ml) were heated together in a sealed tube at *ca.* 80 °C for 63 hours before being allowed to cool. After removal of the volatile organics in high vacuum a red oil remained (2.26 g), this was subject to purification by flash column chromatography on silica (eluting with petrol before 20% CH_2Cl_2 in petrol) to give a red oil which on storage in a freezer crystallised (1.58 g). This was then recrystallised from ethyl acetate (5 ml) and dried in high vacuum to give **6** as an orange crystalline solid (431 mg, 1.2 mmol, 29%). Both samples were identical by NMR spectroscopy. δ_P 66.4. δ_C 73.5 [d, J(PC) 15 Hz], 72.4 (m), 70.0, 63.2 [d, J(PC) 57 Hz], 43.0 [d, J(PC) 12 Hz], 41.6 [d, J(PC) 2.5 Hz], 38.3 [d, J(PC) 3.4 Hz], 34.1, 28.4 and 28.1 (m). δ_H 4.7 (m), 4.5 (m), 4.2 (s). Overall integration for the ferrocenyl area is 13H. 3.45 (m), 3.29 (m) combined integration of these two peaks is 3.86H, 2.99 (2H, m), 2.63 (1.6H, m), 2.31 (d), 1.99 (Impurity), 1.6 (m) and 1.1 (m). Total integration for the area 2.4–0.9 17.8H. ^{1}H–^{1}H COSY δ 3.5 [3.3], 3.5 [1.5], 3.3 [1.5], 3.0 [2.6], 3.0 [1.5], 3.0 [1.2], 3.0 [1.0], 2.6 [1.6], 2.3 [1.7], 2.3 [1.5] and 1.6 [1.1]. Cross peaks due to the ferrocenyl group have been ignored here. ^{1}H NOESY 3.4 [3.3], 3.4 [3.0]w, 3.4 [1.5]w, 3.3 [1.5]w, 3.0 [2.25]w, 3.0 [1.5], 2.6 [1.6]w, 2.3 [1.7]w, 2.3 [1.5]w and 1.7 [1.1]w. ^{13}C/^{1}H Correlation ^{1}H δ [^{13}C δ], 4.73 [73.4], 4.79 [72.5], 4.53 [72.3], 4.29 [70.0], 3.38 [63.2], 3.52 [43.0], 2.34 [41.6], 2.70 [38.3], 3.06 [34.1], 1.55 [34.1], 1.66 [28.4], 1.12 [28.4], 1.66 [28.1] and 1.12 [28.1]. δ_C 73.5 (d, J 15 Hz), 72.4 (m), 70.0, 63.2 (d, J 57 Hz), 43.0 (d, J 12 Hz), 41.6 (d, J 2.5 Hz), 38.3 (d, J 3.4 Hz), 34.1, 28.4 and 28.1 multiplets. δ_H (d_8-Toluene) 4.73 (1H, m), 4.66 (1H, m), 4.24 (m), 4.17 (m), 4.17 (s). Total integration for peaks at 4.24 and 4.17 ppm is 7H, 3.24 (1H, d, 10.6 Hz), 3.0 to 2.8 (2H, m), 2.55 (1H, d, 10.9 Hz), 1.94 (1H, br, s), 1.4 to 1.1 (3H, m) and 0.8 to 0.6 (2H, m). IR (cm^{-1}) 3079m, 2951s, 2866s, 1474w, 1410m, 1388w, 1364w, 1347w, 1308m, 1295m, 1249m, 1213w, 1198m, 1188m, 1179s, 1170s, 1138m, 1111w, 1104m, 1055w, 1048w, 1034m, 1018s, 1005m, 963w, 940w, 920w, 892w, 865w, 842s, 823s, 806s, 779s, 752m, 730s, 680w, 648s, 621s, 600m, 530s, 495s, 482s, 456s, 376m and 324w. MS(EI+) *m*/*z* 374 M$^+$, 280 $(M - C_7H_{10})^+$, 217 $(FcS)^+$, 184, 155, 121, 84, 66, 47 and 31 (Found: C, 54.2; H, 4.9; N, 0.1. $C_{17}H_{19}FePS_2$ requires C, 54.5; H, 5.1; N, 0.0%). CV, reversible redox couple at 0.67 V relative to a SCE. Mp 101–112 °C to an orange tar.

Synthesis of *P*-ferrocenyl-1,2,5,6,7,8-hexamethyl-3-thia-4-phosphatricyclo[4.2.0.0^{2,5}]oct-7-ene-4-sulfide 7

Inside a sealed tube was heated 1,2,3,4,5,6-hexamethylbicyclo-[2.2.0]hexa-2,5-diene (hexamethyl dewar benzene) (1.2 ml, 1 g, 6.2 mmol), $Fc_2P_2S_4$ (1 g, 3.6 mmol) and toluene (5 ml) in an oil bath at 70–80 °C overnight before being allowed to cool. The reaction mixture was filtered through an Al_2O_3 pad, CH_2Cl_2 (20 ml) was used to rinse the Al_2O_3 and this extract was combined with the filtrate. Removal of the solvents from the combined filtrates gave an orange oil (3 g). Chromatography on silica (30 g using 200 ml 10% toluene, 200 ml 20% toluene, 200 ml 25% toluene followed by 200 ml 20% EtOAc all in petrol) gave an orange fraction. Removal of solvents from this fraction gave a red tar (0.741 g), recrystallisation from ethyl acetate (*ca.* 7 ml) gave **7** as an orange solid (166 mg, 376 mmol, 5%). δ_P 68.4. δ_H 4.74 (1H, m), 4.64 (1H, m), 4.54 (1H, m), 4.49 (1H, m), 4.33 (5H, s), 1.73 (3H, s), 1.58 (s) and 1.16 (s) total of (6H), 1.44 (3H, s), 1.35 (3H, s), 0.97 [3H, d, J(PH) 24 Hz]. δ_C 146.4, 140.1, 81 [d, $^1J(^{31}P–^{13}C) = 75$ Hz], 76.0 [d, $^2J(^{31}P–^{13}C) = 15$ Hz], 72.4 [d, $^3J(^{31}P–^{13}C) = 11$ Hz], 72 (m), 70.2, 65 [d, $^1J(^{31}P–^{13}C) = 50$ Hz], 57.2 (m), 56.4 (m), 55.0 (m), 20.8 (m), 16.3, 12.3 [d, J(PC) 7 Hz], 11.7, 11.2 and 10.7. ^{1}H/^{13}C Correlation ^{1}H δ [^{13}C δ] 4.74 [76], 4.64 [72], 4.54 [72.4], 4.49 [72], 4.33 [70.2], 1.73 [12.3], 1.58 [10.7], 1.16 [11.2], 1.44 [20.8], 1.35 [11.7] and 0.97 [16.3]. Mp 154–157 °C. CV, almost reversible couple showing slow electron transfer. With a scan rate of 200 mV s^{-1} the redox couple is 0.65 V (Found: C, 59.7; H, 6.1; N, 0.0; S, 14.1. $C_{22}H_{27}FePS_2$ requires C, 59.8; H, 6.1; N, 0.0; S, 14.5%). MS(EI+) *m*/*z* 442, 280, 248, 186, 162, 147, 121 and 91. Molecular ion found at *m*/*z* 442.0641 ($^{12}C_{22}{}^1H_{27}{}^{31}P^{32}S_2$ requires *m*/*z* 442.0641, within 0.0 ppm). MS(FAB+) *m*/*z* 442, 280, 248, 217 and 163. The predicted isotropic distribution was observed for the molecular ion. IR (cm^{-1}) 3095m, 2909s, 2855s, 1655w, 1444m, 1408w, 1387m, 1374m, 1307w, 1283w, 1185w, 1167s, 1106m, 1066m, 1026s, 1000m, 903w, 838m, 814s, 759w, 720s, 699s, 650m, 626m, 536s, 508s, 485m, 456s, 421w, 396w, 349m.

8: Reaction of $Fc_2P_2S_4$ and 2,3-dimethylbutadiene

$Fc_2P_2S_4$ (0.925 g, 1.65 mmol) and 2,3-dimethylbutadiene (3.7 ml, 2.7 g, 33 mmol) were heated together overnight at 87–90 °C. After being allowed to cool the tube contained an orange solid mixed with excess diene. The excess diene was removed in vacuum and then the solid **8** (1.03 g, 2.8 mmol, 86%) was scraped out of the tube. By the slow cooling of a hot solution in ethyl acetate, a crystal suitable for X-ray crystallography was obtained. δ_P 69.2. δ_C 130.6, 127.4, 73.6, 72.5, 72.2, 71.7, 70.0, 46.7 (d, 46 Hz, CH_2), 34.9 (CH_2), 21.0 and 19.2. δ_H 4.63 (1H, m), 4.37 (2H, m), 4.28 (5H, s), 4.17 (1H, m), 3.57 (1H, m), 3.12 [1H, dd, $^2J(^1H–^{31}P) = 21.5$ Hz, $^2J(^1H–^1H) = 14.1$ Hz], 2.82 (2H, m), 1.82 [4H, d, $^4J(^{31}P–^1H) = 5.4$ Hz] and 1.56 (5H, s). IR (cm^{-1}) 3077m, 2887s, 2857s, 1656m, 1439m, 1407w, 1399w, 1384m, 1363w, 1306w, 1292m, 1262w, 1221m, 1186m, 1167s, 1115w, 1104m, 1058m, 1024s, 1000m, 926w, 890w, 863w, 849w, 831s, 820s, 741m, 718m, 680s, 666s, 620m, 583m, 527m, 499s, 481s, 431s, 395m, 368w, 332m, 310w. MS(EI) *m*/*z* 362(M$^+$), 280($FcPS_2$), 248(FcPS), 217(FcS), 184, 155, 121, 82(C_6H_{10}), 67, 51 and 39 (Found: C, 52.7; H, 5.1; N, 0.2. $C_{16}H_{19}FePS_2$ requires C, 53.0; H, 5.3; N, 0.0%). Redox couple is 0.66 V, and reversible. Mp 141–143 °C to an orange oil that decomposes above 188 °C to a black tar.

The ring opening of 8 with BuLi followed by alkylation with benzyl bromide to give *P*-ferrocenyl-*P*-benzylthio-*P*-2,3-dimethylbut-1,3-dien-1-ylphosphine sulfide 10

To **8** (1.04 g, 2.87 mmol) was added THF (40 ml). The resulting solution was deoxygenated by bubbling nitrogen gas through it. To the mixture was added a solution of BuLi in hexanes (2 ml of a 1.5 M solution, 3.0 mmol) at room temperature, 40 min later the mixture was brought to reflux for 30 min before being allowed to cool to room temperature. Benzyl bromide (0.34 ml, 0.49 g, 2.9 mmol) was added to the mixture and this was then heated under reflux for 90 min before being allowed to cool. The THF/hexanes were removed in vacuum to give an orange tar. To this was added water (0.5 ml) and then ether (30 ml), this dark green mixture was then dried with $MgSO_4$ before being filtered through $MgSO_4$. The ether was removed in vacuum, and the solid was dried in high vacuum. The solid was recrystallised from ethyl acetate to give **10** as an orange solid (0.58 g, 1.28 mmol, 44%). Some **10** was dissolved in the minimum volume of hot ethyl acetate and allowed to cool very slowly before being allowed to stand undisturbed for many days. Much of **10** decomposed to a brown solid but a crystal suitable for an X-ray structure was obtained. δ_P 51.3. δ_H 7.2 (4H, m), 5.9 [1H, d, ${}^3J({}^{31}P-{}^1H) = 26$ Hz], 5.0 (1H, s), 4.9 (1H, s), 4.52 (1H, m), 4.44 (1H, m), 4.36 (2H, m), 4.2 (5H, s), 4.1 (2H, m), 1.9 (3H, s), 1.7 (3H, s). On closer examination of the peak at 4.1 ppm, it appears to be a pair of doublets that are poorly resolved. δ_C 158 (quat), 141 (quat), 129, 128, 127, 123, 121, 116 (CH_2), 72 (m), 70 (Cp), 36, 26 [d, *J*(PC) 18 Hz] and 21. IR (cm^{-1}) 1649w, 1632w, 1597m, 1492m, 1452m, 1427m, 1409m, 1384m, 1372m, 1365m, 1350w, 1312w, 1244w, 1231m, 1193m, 1177s, 1168s, 1135w, 1107s, 1067m, 1051w, 1031m, 1019s, 1001m, 946w, 901s, 843m, 831w, 823s, 794s, 774m, 729m, 705s, 693s, 658s, 621s, 593m, 569m, 521m, 504m, 492s, 484s, 475s, 455s, 415w, 385w, 373m, 333w and 321w. Mp 100–104 °C. MS(EI+) *m/z* 452 (M$^+$), 330 $(M - C_7H_6S)^+$, 314 $(M - C_8H_{10}S)$, 248, 232, 217, 186, 155, 121, 91, 65, 51, 39 and 31. Molecular ion found at *m/z* 412.0173, ${}^{12}C_{23}{}^1H_{25}{}^{56}Fe^{31}P^{32}S_2$ requires *m/z* 452.04842 (error of 0.4 ppm) (Found: C, 61.0; H, 5.4; N, 0.0. $C_{23}H_{25}FePS_2$ requires C, 61.1; H, 5.6; N, 0.0%). CV reversible redox couple at 0.66 V.

Synthesis of 11

The above synthesis was repeated using **8** (0.50 g) and 1-methyl-2-bromomethylbenzene (0.18 ml, 0.26 g, 1.4 mmol) in place of the benzyl bromide to furnish *P*-ferrocenyl-*P*-(2-methylphenyl)-methylthio-*P*-2,3-dimethylbuta-1,3-dien-1-yl phosphine sulfide (**11**) as an orange solid (152 mg, 326 mmol, 23%) after recrystallisation. In this experiment Celite was used as a filter aid for the filtration of the ether solution of the raw product. The recrystallised product contained a small trace of impurities including a trace of ethyl acetate even after drying in high vacuum, so a second recrystallisation was done, followed by dissolving the product in $CDCl_3$ before removal of solvent in vacuum to yield an orange solid (89 mg, 191 μmol, 14%). δ_P 51.3. δ_C 158.7, 143.7, 137.5, 130.8, 130.7, 128.0, 126.5, 122.9, 122.0, 116.7 (CH_2), 73 to 71 (m), 70.7 (s, Cp), 34.7 (CH_2), 26.7 [d, *J*(PC) 19 Hz], 21.9 and 19.7. δ_H 7.2 (m), 7.0 (m) the total integration for the aromatic area is (5H), 5.9 [1H, d, ${}^2J({}^1H-{}^{31}P) = 25$ Hz], 5.0 (1H, s), 4.9 (1H, s), 4.6 (1H, s), 4.5 (1H, s), 4.4 (2H, m), 4.2 (5H, s), 4.0 (2H, m), 2.3 (3H, s), 1.9 (3H, s), 1.7 (3H, s). IR (cm^{-1}) 3086m, 2975s, 2950s, 2916s, 2850m, 1596m, 1492m, 1430m, 1411m, 1384w, 1233w, 1168s, 1108m, 1049w, 1031m, 1019s, 1002m, 903s, 851w, 841w, 822s, 793m, 774w, 732s, 689s, 658s, 620s, 593m, 565m, 536m, 520m, 490s, 456s and 445m. Mp 105–110 °C. MS(EI) *m/z* 466 (M$^+$), 331, 328, 296, 248, 217, 186, 144, 129, 105, and 91. Molecular ion found at *m/z* 466.0641, ${}^{12}C_{24}{}^1H_{27}{}^{56}Fe^{31}P^{32}S_2$ requires *m/z* 466.0641 (within 0.1 ppm) (Found: C, 60.7; H, 5.8. $C_{24}H_{27}FePS_2$ requires C, 61.8; H, 5.8%).

Synthesis of *P*-ferrocenyl-*P*-(2,3-dimethylbuta-1,3-dien-1-yl)-*P*-2,4-dinitrophenylthiophosphine sulfide 12

The above synthesis was repeated using **8** (0.601 g, 1.66 mmol), with 1-chloro-2,4-dinitrobenzene (0.5 g, 2.5 mmol) being used instead of a benzyl halide. After 1 hour of reflux following the addition of the dinitrochlorobenzene a small sample was tested with water, no green compounds were formed. After removal of all solvent, the red product was dissolved in hot ethyl acetate before being allowed to cool, after filtration a red solid was obtained by the removal of the ethyl acetate. This solid was washed with ether (50 ml) to give a copper coloured solid (0.411 g, 778 μmol, 47%). This solid was dissolved in dichloromethane to form an almost black solution to which was added ether to give **12** as a copper coloured solid (218 mg, 413 μmol, 25%). δ_P 60.0. δ_H 8.59, 8.31 total for the last two peaks (3H), 6.0 [1H, d, ${}^2J({}^{31}P-{}^1H) = 28$ Hz], 5.09 and 5.01 the total of the last two peaks is (3H), 4.5 to 4.3 (m), 4.28 (s). Integration total for ferrocenyl area (4.5–4.2) is 9H, 2.08 (4H, s), 1.89 (4H, s). IR (cm^{-1}) 3098m, 3078m, 2975w, 2915w, 2854w, 1595m, 1541s, 1524s, 1459w, 1438w, 1410w, 1350s, 1194w, 1172m, 1106m, 1038m, 1023m, 914w, 901s, 831s, 760m, 739s, 703m, 662w, 638m, 619w, 571w, 522w, 498m, 466m, 456m. MS(EI) *m/z* 528 (M$^+$), 364, 329, and many ions below 290. Molecular ion found at *m/z* 528.0028, ${}^{12}C_{22}{}^1H_{21}{}^{56}Fe^{14}N_2{}^{16}O_4{}^{31}P^{32}S_2$ requires 528.0029 (error of 0.2 ppm). Reversible redox couple at 0.69 V.

13: The reaction of benzaldehyde with $Fc_2P_2S_4$

$Fc_2P_2S_4$ (4.09 g, 14.6 mmol) and benzaldehyde (1 ml, 1 g, 9.7 mmol) were heated under reflux in xylenes (50 ml) for 30 minutes. After cooling and stirring overnight the mixture was applied to a flash column (50 g SiO_2). This column was eluted with 100 ml petrol, 500 ml 40% CH_2Cl_2 in petrol, 500 ml CH_2Cl_2 in petrol followed by 750 ml CH_2Cl_2. The first orange group of fractions were combined and evaporated to form an orange solid (2.8 g). Examination of this solid with ${}^{31}P$-{${}^1H$} NMR spectroscopy reveals the presence of $Fc_3P_3O_3S_3$ and another phosphorus compound. This solid was heated with ethyl acetate (50 ml) and allowed to cool before being collected by filtration. This solid was then recrystallised from ethyl acetate (*ca.* 110 ml) to give **13** as an orange solid (574 mg, 1.10 mmol, 8%). δ_P 72.0. δ_H 7.5 (4H, m), 7.4 (6H, m), 6.25 [2H, d, ${}^3J({}^{31}P-{}^1H) = 10$ Hz], 4.88 (2H, m), 4.62 (2H, m) and 4.43 (5H, s). δ_C 129.2, 129.1, 128.0, 72.5 (d, 13 Hz), 71.8 (d, 16 Hz), 70.6 and 58.0. IR (cm^{-1}) 3083m, 3026m, 2916m, 1801w, 1736w, 1595w, 1582w, 1492m, 1452m, 1408m, 1386w, 1363m, 1348w, 1332w, 1238w, 1192m, 1177s, 1169s, 1107m, 1072m, 1052w, 1027s, 1002m, 915w, 897w, 842m, 828s, 797w, 781m, 724s, 703vs, 666s, 614m, 682m, 537s, 515s, 487s, 473s, 400w, 323m, 302w, 285w, 260w, 252m and 241w. CV Redox couple at 0.76 V showing slight signs of slow electron transfer. MS (FAB) *m/z* 524, 490, 413, 402, 391, 371, 349, 315, 303, 280 and 259. The expected isotropic distribution was observed for the molecular ion. Mp 189–190 °C (Found: C, 55.5; H, 3.8; N, 0.0. $C_{24}H_{21}FePS_4$ requires C, 55.0; H, 4.0; N, 0.0%).

14: The reaction of *tert*-butylaldehyde (pivalaldehyde) with $Fc_2P_2S_4$

$Fc_2P_2S_4$ (6.2 g, 11 mmol) was partially dissolved in hot toluene (50 ml) and allowed to cool before the addition of THF (10 ml) and *tert*-butylaldehyde (1.6 ml, 14.7 mmol). The mixture was slowly brought up to a gentle reflux for 14 hours before being allowed to cool. Before chromatography (74 g SiO_2, 30% CH_2Cl_2 in petrol), after removal of solvent a yellow orange solid remained. This was recrystallised from ethyl acetate. Examination with ${}^{31}P$-{${}^1H$} NMR spectroscopy revealed the presence of $Fc_3P_3O_3S_3$. By cooling a hot solution a crystal suitable for X-ray crystallography was obtained. After two further recrystallisations from ethyl acetate **14** was obtained as a yellow solid (37 mg, 76.4 μmol, 1%). δ_P 72.3. δ_H 5.02 [2H, d, *J*(PH) 11 Hz], 4.85 (2H, m), 4.48 (2H, m), 4.43 (5H, s) and 1.22 (18H, s). δ_C 72.5 to 72.0 (m), 70.7 (s), 68.1 [d, *J*(PC) 2 Hz], 37.5 [d, *J*(PC) 6 Hz] and 28.5. MS(FAB+) *m/z* 484, 452, 401, 280, 248, 217 and 186. Expected isotropic distribution observed for the

Table 8 Details of the crystal data and refinements

Compound	**10**	**13**	**14**	**15**	**16**
Empirical formula	$C_{23}H_{25}PS_2Fe$	$C_{24}H_{21}PS_4Fe$	$C_{20}H_{29}PS_4Fe$	$C_{24}H_{21}PS_3Fe$	$C_{27}H_{25}NP_2S_3Fe_2$
M	452.4	524.5	489.5	492.4	633.3
Colour, habit	Yellow, prism	Yellow, cube	Orange, prism	Yellow, plate	Orange, prism
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1(#2)	*P*-1(#2)	$P2_1/c$	*P*-1(#2)	$P2_1/c$
a/Å	10.7076(9)	11.219(2)	12.059(1)	12.232(1)	7.347(2)
b/Å	11.361(1)	11.614(1)	18.388(1)	14.473(2)	14.262(3)
c/Å	9.533(1)	10.977(2)	11.642(1)	6.750(1)	25.660(2)
α/°	105.700(8)	107.34(1)	90	99.56(1)	90
β/°	94.633(8)	118.54(2)	114.602(1)	92.68(1)	95.75(1)
γ/°	76.127(7)	89.35(1)	90	68.67(1)	90
V/Å^3	1084	1185	2347	1098	2675
Z	2	2	4	2	4
D_c/g cm^{-3}	1.39	1.47	1.37	1.49	1.57
μ/mm^{-1}	8.12	9.1	1.1	8.9	12.1
F(000)	472	540	1016	508	1296
Independent reflections	3232	3729	3151	3262	4194
Observed reflections	1913	2423	3100	2482	2100
Final *R*, *Rw*	0.046, 0.041	0.040, 0.038	0.036, 0.077	0.035, 0.034	0.060, 0.058
Largest Δ/σ	0.16	0.02	—	0.14	0.03
Largest difference peak, hole/e Å^{-3}	0.34, −0.40	0.34, −0.34	0.24, −0.27	0.29, −0.29	0.56, −0.77

molecular ion. IR (cm^{-1}) 3114w, 2957s, 2928m, 2898m, 2864m, 1474m, 1462m, 1411w, 1396m, 1390m, 1367s, 1314w, 1228m, 1200w, 1195w, 1182m, 1172s, 1107m, 1055w, 1029m, 1020m, 1000m, 936w, 912w, 897w, 873w, 842m, 827s, 814w, 778m, 769sh, 735w, 703s, 666vs, 618m, 541m, 530s, 489s, 478s and 330m (Found: C, 49.1; H, 5.9. $C_{20}H_{29}FePS_4$ requires C, 49.6; H, 6.0%).

The reaction of *N*-benzylidenebenzylamine with $Fc_2P_2S_4$

$Fc_2P_2S_4$ (4.4 g, 7.86 mmol) and *N*-benzylidenebenzylamine (1.54 g, 7.89 mmol) were heated in toluene (80 ml) and xylene (80 ml) for 45 hours. After cooling this mixture was filtered through a silica pad and this pad was washed with CH_2Cl_2 until the filtrate was no longer coloured. After removal of solvent, chromatography (60 g silica elution with 1.5 l 40% CH_2Cl_2 in petrol followed by 350 ml CH_2Cl_2) gave fractions containing only two compounds in large amount. Evaporation of these gave a brown solid (2.4 g). This was extracted with hot ethyl acetate before being allowed to cool, to form an orange solid (0.94 g); further chromatography (12 g silica, elution with 500 ml 30% CH_2Cl_2 in petrol) gave, after removal of solvent 3-benzyl-2,4-diferrocenyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide **16** as an orange solid (0.489 g, 772 μmol, 10%). δ_P 65.1. δ_H 7.2 (2H, m), 7.0 (3H, m), 4.89 (2H, m), 4.68 (2H, m), 4.55 (2H, m), 4.44 (2H, m), 4.33 (10H, s), 4.16 (2H, s). δ_C 129.1, 127.9, 127.3, 76.5 [d, *J*(PC) 20 Hz], 73.5 [d, *J*(PC) 14 Hz], 72.2 [d, *J*(PC) 14 Hz], 71.6 [d, *J*(PC) 17 Hz], 70.3 and 46.9 (CH_2). ^1H–^{13}C correlation ^1H δ [^{13}C δ] 7.2 [129.1], 7.0 [127.9], 7.0 [127.3], 4.68 [76.5], 4.55 [73.5], 4.44 [72.2], 4.89 [71.6], 4.33 [70.3] and 4.16 [46.9]. IR (cm^{-1}) 3077w, 3027w, 2919w, 2858w, 1494w, 1455m, 1445w, 1410m, 1390m, 1366m, 1351m, 1315w, 1244m, 1205w, 1195m, 1182s, 1121s, 1105m, 1024s, 998s, 913m, 857s, 843s, 816s, 799s, 768s, 734m, 696m, 681vs, 655m, 613w, 576m, 518m, 504m, 493s, 481m, 462s, 414m, 345w and 329w. CV Reversible couple at 0.80 V, with second waves observed on the leading edges of the couple. MS(FAB) *m*/*z* 656 (M + Na)$^+$, 634 (MH)$^+$, 633 M$^+$, 617, 601, 568, 513, 492 and 353. Mp *ca.* 150–160 °C (Found: C, 52.0; H, 4.1; N, 2.3; S, 15.4. $C_{27}H_{25}Fe_2NP_2S_3$ requires C, 51.2; H, 3.9; N, 2.2; S, 15.2%).

A second fraction that was a mixture of two compounds was then obtained. A third fraction was obtained which is almost pure **15**. Evaporation of this fraction gave **15** as a yellow solid (112 mg, 236 μmol, 1.5%). From a dichloromethane solution orange crystals were obtained, using one of these crystals an X-ray structure was obtained. δ_P 86.3. δ_H 7.1 (10H, m), 5.21 [2H, d, *J*(PH) 14 Hz], 4.77 [2H, d, *J*(PH) 1.5 Hz], 4.54 [2H, d, *J*(PH) 1.5 Hz], 4.32 (5H, s). δ_C 153.4 (quat), 135.5 (quat), 130.0, 128.9, 128.4, 73.5 [d, *J*(PC) 21 Hz], 73.3 [d, *J*(PC) 17 Hz], 71.3 and 67.7. IR (cm^{-1}) 3080m, 3025m, 2923m, 2853m, 1493m, 1449m, 1408w, 1385w, 1366w, 1338w, 1312w, 1284w, 1214w, 1196w, 1183w, 1170s, 1107m, 1076m, 1031m, 1016s, 1007m, 971w, 916w, 887w, 847s, 836m, 827w, 816s, 766s, 757m, 743m, 700s, 692s, 670vs, 644s, 621sh, 598s, 537s, 495s, 479s, 398w, 378w, 363w and 325m. CV, Reversible redox couple at 0.71 V. MS(FAB) *m*/*z* 492 and 391. MS(ES+) *m*/*z* 515 (M + Na)$^+$, 493 (MH)$^+$, 301, 267, 239, 217, 205, 186 and 149. MS(ES−) *m*/*z* 491 (M − H)$^-$ (Found: C, 58.6; H, 4.3; N, 0.0; S, 19.9. $C_{24}H_{21}FePS_3$ requires C, 58.6; H, 4.3; N, 0.0; S, 19.5%).

Crystallography

Details of the data collections and refinements are summarised in Table 1, experimental details have been previously reported for **3**, **7** and **8**.[5] For **10**, **13**, **15** and **16** data were collected using Cu radiation and ω scans with a Rigaku AFC7S diffractometer at 293 K. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or direct methods. 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.[28]

The structure of **14** was obtained using a Siemens SMART diffractometer; a full hemisphere of data was collected with 0.3° 'slices' at room temperature using Mo-Kα radiation. An empirical absorption correction was applied. All of the non-H atoms were refined anisotropically. All calculations employed the SHELXTL program system.[29]

CCDC reference number 186/1312.

See http://www.rsc.org/suppdata/dt/1999/1175/ for crystallographic files in .cif format.

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