

Reactions of dithiadiphosphetane disulfides with organonitrogen compounds †

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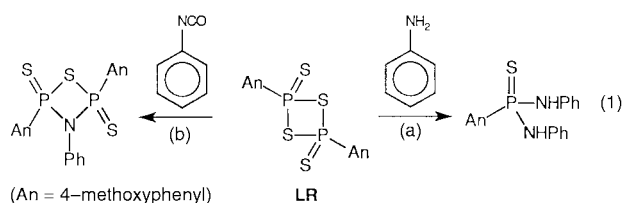
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The reactions of $R^1P(S)_2P(S)R^1$ ($R^1 = \text{ferrocenyl}$) with a range of organic systems containing unsaturated C–N linkages have been studied. Thus treatment with dimethylcyanamide gives a 1,3,5,2-thiazaphosphorine 4-sulfide, whereas reaction with dicarbodiimides gives a thiazadiphosphetane. Furthermore reaction of diphenylurea gives a phenylthiazaphosphetane. Mechanisms for the reactions are proposed and the crystal structures of three selected examples are reported and discussed with reference to the steric effects of the reactants. These reactions provide a new entry into C–P–S–N heterocycles. Cyclic voltammetry studies on a range of ferrocenyl substituted heterocycles were also made.

Organo-phosphorus–sulfur–nitrogen compounds have been investigated as ligands,^{1,2} insecticides,³ fungicides,⁴ herbicides³ and antibacterials.⁵ Since many nitrogen–phosphorus–sulfur compounds have been made from Lawesson's reagent the question of how the presence of a ferrocenyl group would modify the chemistry arose. Another goal was the synthesis of new nitrogen–phosphorus–sulfur compounds from dithiadiphosphetane disulfides.

The reactions of nitrogen compounds with dithiadiphosphetane disulfides include: (i) the reaction with nitrogen nucleophiles, such as the reaction (1a) of aniline with Lawesson's reagent (LR);⁶ (ii) transformations that could be a series of pericyclic reactions, such as the reaction of azides¹ and isocyanates⁷ with dithiadiphosphetane disulfides to give thiazadiphosphetanes, eqn. (1b).

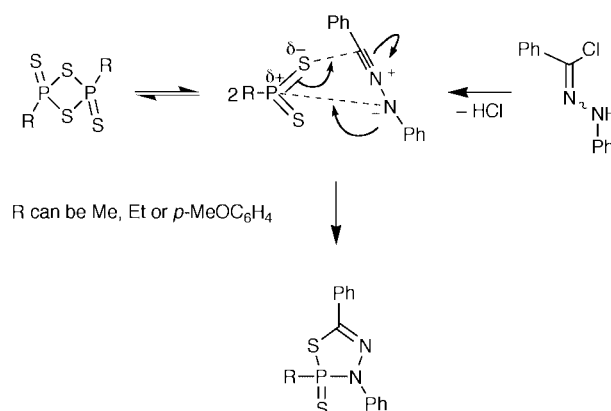


The reaction of 1,3-dipoles with dithiadiphosphetane disulfides affords compounds with five membered rings. An example would be the reaction of Lawesson's reagent with α -chlorobenzaldehyde phenylhydrazone (Scheme 1).⁸ Bent 1,3-dipoles can be treated with Lawesson's reagent to give adducts of the dithiophosphine ylide.⁹

The reaction of a variety of dialkylcyanamides with dithiadiphosphetane disulfides was reported to give 1,3,5,2-thiazadiazaphosphorine sulfides^{10,11} in 100% yield, and this reaction is thought to be stepwise starting with the attack of a cyanide nitrogen on the phosphorus atoms.¹¹ The product of this reaction has been reported to be a plant protection agent.¹⁰

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3419/>

Also available: electrochemical data. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/3419/>, otherwise available from BLDSC (No. SUP 57629, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).



Scheme 1 Reaction of dithiadiphosphetane disulfides with α -chlorobenzaldehyde phenylhydrazone.⁸

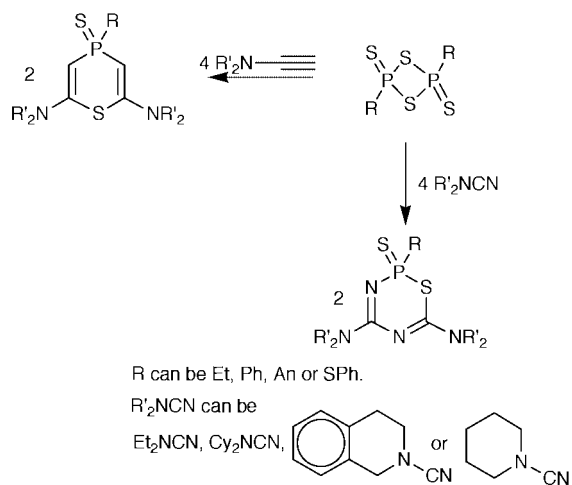
It was decided to repeat this work as the results presented in the literature were not completely convincing. Interestingly the reported formation of the 1,3,5,2-thiazadiazaphosphorines formed from dialkylcyanamides and dithiadiphosphetane disulfides^{10,11} contrasts with the formation of 1,4-thiazaphosphorines from electron-rich alkynes^{12–14} (Scheme 2).

Results and discussion

The synthesis of a 1,3,5,2-thiazadiazaphosphorine ring from diferrocenyl dithiadiphosphetane disulfide and dimethylcyanamide according to eqn. (2) ($R^1 = \text{ferrocenyl}$) was unsuccessful.



However, flash column chromatography gave compound **1** as a bright yellow solid (57%), while the phosphorus chemical shift (δ_P 61.8) is similar to the chemical shifts reported for the 1,3,5,2-thiazadiazaphosphorines (δ 56.5 to 68.5);¹⁰ in the ¹H NMR spectrum instead of 2 distinct methyl environments a single peak (δ_H 3.02) was observed. For a 1,3,5,2-thiazadiazaphosphorine

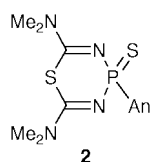


Scheme 2 Reported reactions of LR with electron-rich acetylenes and dialkylcyanamides.^{10–14}

sulfide two environments in the ring and two methyl carbon environments would be expected, but only one environment was found for each of these two types of carbon (δ_C ring 154.7 and δ_C methyl 37.3) suggesting that **1** is either the 1,3,5,4- or 1,2,6,4-thiadiazaphosphorine. The absence of a strong coupling between the phosphorus and the heterocycles carbons suggests that the product is not the 1,2,6,4 isomer.

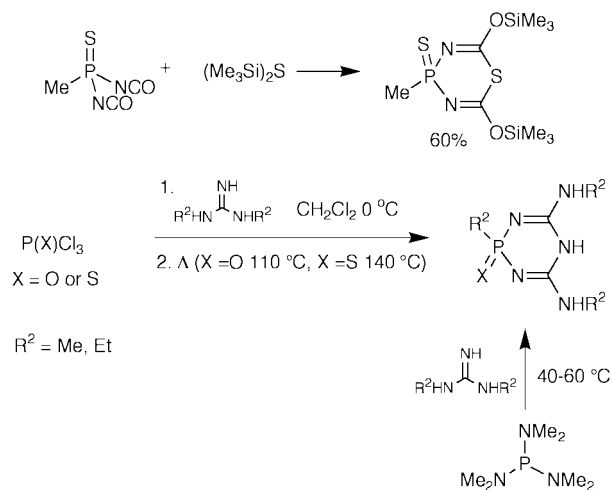
X-Ray crystallography confirmed that this compound is a 1,3,5,4-thiadiazaphosphorine 4-sulfide.¹⁵ The thiadiazaphosphorine is an almost symmetric boat shaped ring, with the sulfur and phosphorus atoms lying 0.48 and 0.30 Å respectively above the C(1)–N(1)–C(2)–N(2) plane, while N(3) and N(4) are 0.16 and 0.25 Å below this plane. The dimethylamino groups are planar suggesting that they are participating in some delocalization. The exocyclic sulfur and the ferrocenyl group occupy approximately axial and equatorial sites. The Cp rings of the ferrocenyl group are twisted by 72° with respect to the C₂N₂ plane of the thiadiazaphosphorine ring. The P=S bond length in **1** is not significantly different to that in R¹₂P₂S₄. Both P–N distances are shorter (mean is 0.144 Å shorter) than the sum of the covalent radii (1.8 Å) suggesting that both bonds have some π character.^{16,17}

The reaction of dimethylcyanamide was repeated for Lawesson's reagent to give a modest yield of the analogous 1,3,5,4-thiadiazaphosphorine **2**. The synthesis of a 1,3,5,4-thia-



diazaphosphorine has previously been reported by the reaction of a *P,P*-diisocyanate with bis(trimethylsilyl) sulfide,¹⁵ and the related heterocyclic system, the triazaphosphorine, has been prepared (Scheme 3).¹⁸

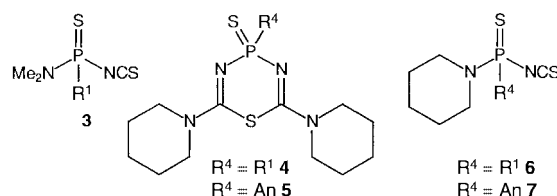
When the reaction of R¹₂P₂S₄ and dimethylcyanamide was repeated on a larger scale and at a lower temperature, besides **1**, a second compound **3** was isolated (15%), as a red oil which on standing became a solid. ³¹P-¹H NMR Spectroscopy indicated this to have a single phosphorus environment (δ_P 67), and ¹H NMR spectroscopy (δ_H 2.6) indicated that the compound has methyl groups where the ³¹P–¹H coupling (14 Hz) was much greater than that in the thiadiazaphosphorine. X-Ray crystallography established the identity of **3**.¹⁵ The P(1)–N(1) bond length is shorter (1.631(4) Å) than P(1)–N(11) (1.700(5) Å), due to differences in the electronegativities of the NMe₂ and NCS groups; the more electron-rich group bonds more strongly



Scheme 3 Synthesis of a thiadiazaphosphorine and triazaphosphorines.

to the phosphorus atom. Atom N(1) is in an almost perfectly planar environment, and this shape, combined with the shortened bond length, does suggest some double bond character of the P(1)–N(1) bond.

To test if the outcome of the reaction is dependent on the nature of the alkyl groups, the reactions of piperidine-1-carbonitrile with R¹₂P₂S₄ and LR were performed. Both gave 1,3,5,4-thiadiazaphosphorines **4** and **5** and *P*-isothiocyanates **6** and **7**. On changing from dimethylamino groups to piperidinyl groups little change was seen in δ_P or $\nu(\text{P}=\text{S})$ values. The ³¹P and ¹H NMR spectra for the thiadiazaphosphorine from LR are identical with those reported¹⁰ suggesting that **4** is the same as that in the original report, though the previous interpretation¹⁰ of the ¹H NMR spectrum is surprising since the ¹³C-¹H NMR spectrum obtained in this work suggests the piperidinyl groups are identical. The NCS group δ_C chemical shifts of **3** and **6** (144 and 145) are similar to that reported for PhNCS (136.0).¹⁹



In the ¹H NMR spectrum of compound **3** the peaks due to the *N*-methyl groups are simple doublets, but in that of **6** a complex multiplet at δ 3.2 is observed. By irradiation of the alkyl proton environment at δ 1.5, the multiplet is simplified to two doublets of doublets (Fig. 1). A geminal coupling (²*J*[¹H–¹H] = 12.6 Hz) between the axial and equatorial protons in the piperidinyl group on atoms 2 and 6 is present, furthermore two different ³¹P–¹H couplings (10.2 and 9.8 Hz) are present. These ³¹P–¹H coupling constants are similar to the coupling constant of **3**. Infrared spectroscopy clearly indicates the presence of an isothiocyanate group in **3**, **6** and **7** ($\nu(\text{NCS})$ 2031 cm⁻¹).

The presence of sulfur and phosphorus at the 1,4 positions in the thiadiazaphosphorine ring of compound **1** poses a mechanistic challenge. The formation of the **1**(and **4**) together with **3**(and **6**) can be rationalized *via* a thiazaphosphorane intermediate,¹⁵ the first step being a thermal (2 π s + 2 π a) 2 + 2 cycloaddition to give a thiazaphosphetane ring which opens in a 4 π electron process *via* a Möbius transition state. This ring opening process is favoured by the increased ring strain when compared with the thiaphosphetanes, even while the thiaza-

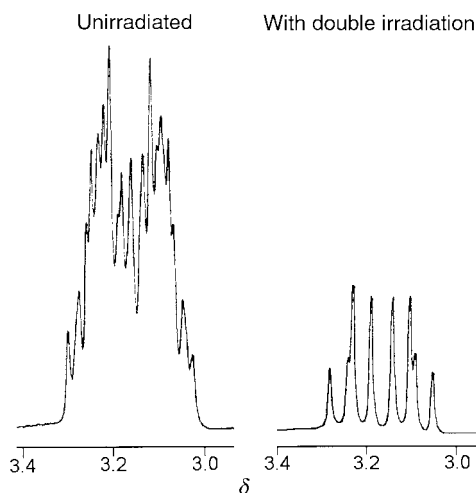
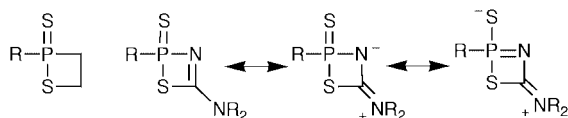


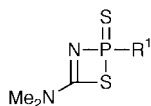
Fig. 1 Part of the ^1H NMR spectrum of compound **6** with and without double irradiation at δ 1.5.



Scheme 4 Resonance forms in thiaphosphetane and thiazaphosphetane rings.

phosphetane is stabilized by resonance (Scheme 4). After the ring opening the intermediate undergoes either a Diels Alder reaction with another molecule of the cyanamide, or a rearrangement to the isothiocyanate.

We postulated that if the formation of compounds **1** and **3** occurred *via* the mechanism in ref. 15 then slow addition of dimethylcyanamide to a hot solution/suspension of a dithiadiphosphetane disulfide would give a greater proportion of **3** in the mixture and indeed when a suspension of $\text{R}^1_2\text{P}_2\text{S}_4$ in refluxing toluene was treated slowly with a dilute solution of Me_2NCN a high yield of **3** and a small yield of **1** was obtained. [A similar experiment was performed where the dimethylcyanamide was replaced by piperidine-1-carbonitrile, to give a 90% yield of the *P*-isothiocyanate **6**.] Besides **1** and **3** an additional product was isolated as a red oil that solidified on standing. According to ^{31}P NMR spectroscopy this solid is a mixture of two compounds, the spectrum consisting of two pairs of doublets, suggesting that two related species are formed. By maintaining a low concentration of the cyanamide, apart from forming **3**, the intermediate thiazaphosphetane has greater opportunity to react with another phosphorus containing compound to give **8** which contains two phosphorus atoms.



After recrystallization one of the two species was obtained as an orange crystalline solid (**8**) [δP_A 81.0, δP_B 52.1, $J(\text{P}_A\text{P}_B) = 44$ Hz]. The mother-liquor was enriched in the second isomer [δP_A 81.0, δP_B 53.2, $J(\text{P}_A\text{P}_B) = 41$ Hz]. The $^2J(^{31}\text{P}-\text{X}-^{31}\text{P})$ coupling constant of 41 Hz is similar to the $^2J(^{31}\text{P}-\text{N}-^{31}\text{P})$ coupling seen in $\text{R}^2\text{P}(\text{E})\text{NHP}(\text{E}')\text{R}^6_2$ (Table 1).^{3,4} According to mass spectrometry (m/z 614, M^+) the molecular formula of **8** is $\text{C}_{23}\text{H}_{24}\text{Fe}_2\text{N}_2\text{OP}_2\text{S}_3$; the oxygen atom originates from a small trace of water in the reaction mixture, or alternatively during the chromatography on silica a hydrolysis or oxidation reaction could have occurred.

The presence of an isothiocyanate was clear from the infrared spectrum, $\nu(\text{NCS})$ 2013 cm^{-1} . A number of alternative structures for the formula $\text{R}^1_2\text{P}_2(\text{NCS})(\text{NMe}_2)\text{OS}_2$ were con-

Table 1 P-P Coupling constants for $\text{R}^5_2\text{P}(\text{E})\text{NHP}(\text{E}')\text{R}^6_2$; L.P. = lone pair

R^5	R^6	E	E'	J/Hz	Ref.
Ph	Ph	O	L.P.	66	3
Ph	Ph	S	L.P.	86	3
Ph	Ph	S	S	27	3
Ph	Ph	Se	L.P.	93	3
Bu	<i>iso</i> -Bu	S	S	26.4	4
Bu	<i>sec</i> -Bu	S	S	30.8	4
<i>iso</i> -Bu	<i>sec</i> -Bu	S	S	30.8	4
EtO	Ph	S	S	22.0	4
EtO	Ph	S	O	17.6	4
EtO	Ph	O	S	3.2	4

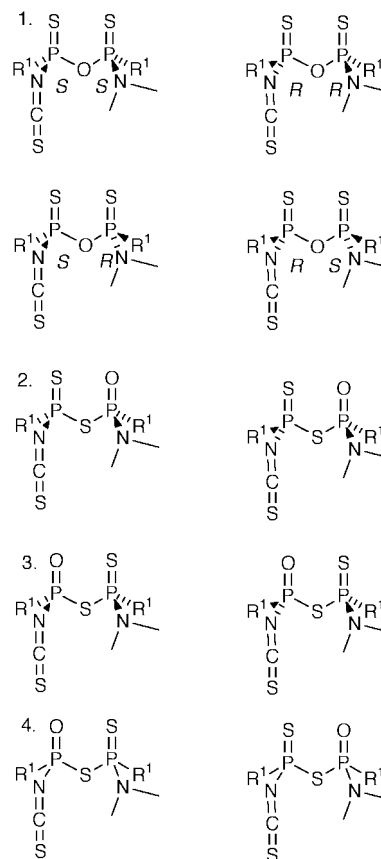


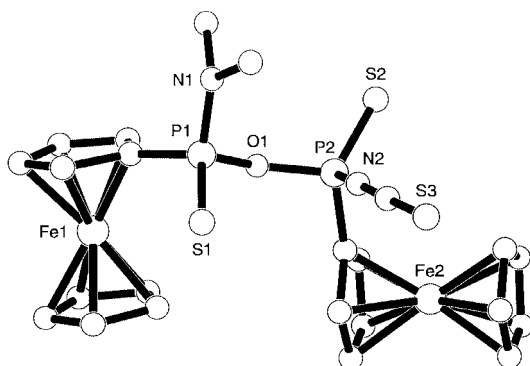
Fig. 2 Possible isomers for the formula $\text{R}^1_2\text{P}_2(\text{NCS})(\text{NMe}_2)\text{OS}_2$ **8**.

sidered. The oxygen atom could bridge the phosphorus atoms (1) or be doubly bonded to either of the phosphorus atoms (2 and 3). The presence of two similar $^{31}\text{P}-\{^1\text{H}\}$ NMR spectra eliminates the possibility of the oxygen being bonded to different phosphorus atoms in the two compounds (4) (Fig. 2). We concluded that two diastereoisomers were formed in approximately equal amounts.

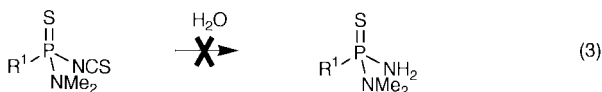
Crystals of compound **8** suitable for X-ray analysis were obtained by slow cooling of a hot solution in ethyl acetate. The analysis revealed a mixture of the *RR* and *SS* diastereoisomers (Fig. 3 and Table 2). The $\text{P}(1)-\text{N}(1)$ and $\text{P}(2)-\text{N}(2)$ lengths are similar to the related bond lengths in **3** $\text{P}(1)-\text{N}(1)$ [1.631(4) Å] and $\text{P}(1)-\text{N}(11)$ [1.700(5) Å]. Like **3**, the nitrogen of the dimethylamino group is almost planar, suggesting some donation of the lone pair electrons to the phosphorus. The molecule is arranged in the solid state with the $\text{P}=\text{S}$ groups approximately *anti* (torsion angle 150.8°).

Table 2 Selected bond lengths (Å) and angles (°) in compound **8**

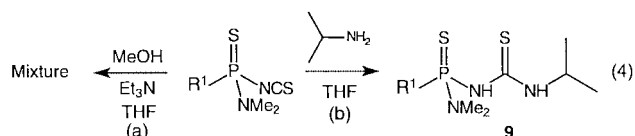
S(1)–P(1)	1.919(2)	P(1)–N(1)	1.623(5)
S(2)–P(2)	1.905(2)	P(2)–N(2)	1.662(5)
P(1)–O(1)	1.632(4)	N(1)–C(1)	1.472(8)
P(2)–O(1)	1.581(4)	N(1)–C(2)	1.459(8)
S(1)–P(1)–O(1)	114.3(2)	O(1)–P(2)–N(2)	102.1(2)
S(1)–P(1)–N(1)	113.7(2)	O(1)–P(2)–C(14)	103.9(2)
S(1)–P(1)–C(4)	115.7(2)	N(2)–P(2)–C(14)	104.5(3)
O(1)–P(1)–N(1)	106.5(2)	P(1)–O(1)–P(2)	137.9(2)
O(1)–P(1)–C(4)	98.1(2)	P(1)–N(1)–C(1)	123.2(5)
N(1)–P(1)–C(4)	107.0(3)	P(1)–N(1)–C(2)	120.0(4)
S(2)–P(2)–O(1)	113.6(2)	C(1)–N(1)–C(2)	113.1(5)
S(2)–P(2)–N(2)	112.9(2)	P(2)–N(2)–C(3)	163.7(6)
S(2)–P(2)–C(14)	118.2(2)		
S(1)–P(1)–P(2)–S(2)	150.8		

**Fig. 3** Molecular structure of compound **8**.

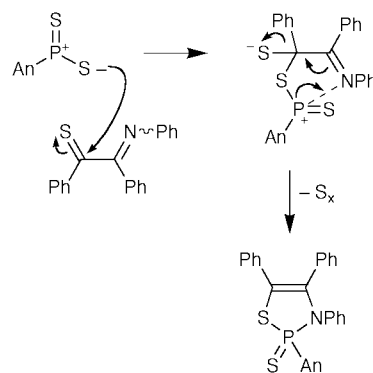
The stability of the isothiocyanates on silica was unexpected but not without precedent.^{19,20} Furthermore we found that treatment of compound **1** with THF–water (80:20 by volume) for 30 d caused little change (TLC) suggesting that the isothiocyanate group has special protection against the action of nucleophiles. Sulfuric acid was added to this mixture and allowed to stand for 8 d with little effect. The starting material was recovered unchanged (88% recovery), eqn. (3).



In contrast to the sluggish reaction of compound **1** and water, its reactions with isopropylamine, (4a), and with methanol/Et₃N, (4b), to give a thiourea derivative **9** occur more rapidly.

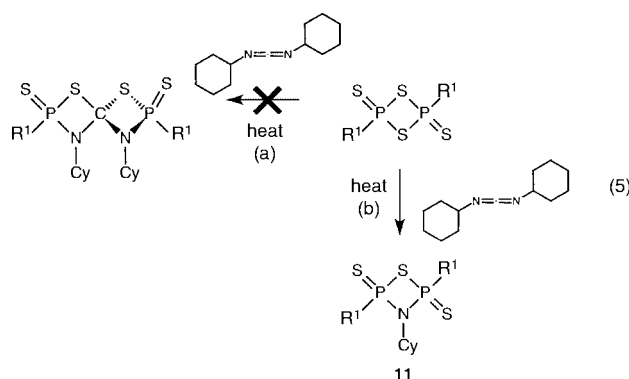


Imines are known to act as dieneophiles in hetero Diels–Alder reactions and such reactions have been used in organic synthesis, e.g. the formation of alkaloids using intramolecular Diels–Alder reactions of imines.²¹ As dithiadiphosphetane disulfides take part in cycloaddition chemistry, the reactions of imines with R¹₂P₂S₄ were considered as a route to new nitrogen–phosphorus compounds. The reaction of LR with benzil monoanils has been reported to give 1,3,2-thiazaphospholine 2-sulfides,²² though the mechanism suggested which requires a sulfide anion to act as a leaving group, and for a three-co-ordinate phosphorus cation to act as a nucleophile (Scheme 5), is surprising. We have previously noted that R¹₂P₂S₄ reacts with *N*-benzylidenebenzylamine to give the

**Scheme 5** Literature mechanism for the formation of 1,3,2-thiazaphospholine 2-sulfides.

1,3,2,4-thiazadiphosphetane 2,4-disulfide R¹P(S)S(NCH₂Ph)-P(S)R¹ **10**.

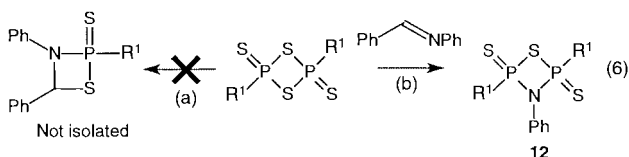
Simple imines formed from aliphatic aldehydes and amines are subject to polymerization and hydrolysis. Imines with aromatic groups attached to the nitrogen or the imine carbon are more stable and less reactive. Owing to the high temperature needed to dissolve the insoluble dithiadiphosphetane disulfides, it was decided to use these less reactive imines as they were expected to survive the harsh conditions. The reaction of dicyclohexylcarbodiimide with R¹₂P₂S₄ was performed with the intention of preparing a pair of thiazaphosphetane rings fused at the carbon to give a spiro system, eqn. (5a). It was hoped the



steric bulk of the cyclohexyl groups would give steric protection to the heterocycle. The reaction was carried out and a small yield of an orange compound **11** was obtained (δ_p 61.0, m/z 625), eqn. (5b). Proton and ¹³C-¹H} NMR spectroscopy revealed the presence of both ferrocenyl and cyclohexyl groups (δ_H 3.3). On irradiation of the alkyl peak at δ 1.5 the complex multiplet at δ 3.3 becomes a simple triplet, showing coupling (³ J [³¹P–¹H] = 19 Hz) of the proton environment to two phosphorus atoms, supporting the thiazadiphosphetane structure **11**.

It was hoped that by the reaction (6a) of *N*-benzylideneaniline with R¹₂P₂S₄ a thiazaphosphorane would be obtained since the two phenyl groups would provide both electronic and steric stabilization. However although a solid product was isolated (δ_p 64.2) spectroscopy revealed this to be a thiazadiphosphorane **12**, eqn. (6b).

The X-ray analyses of compounds **10–12** (Fig. 4, Table 3) reveal that in all three structures the two ferrocenyl groups are arranged *trans* to each other which can be rationalized on steric



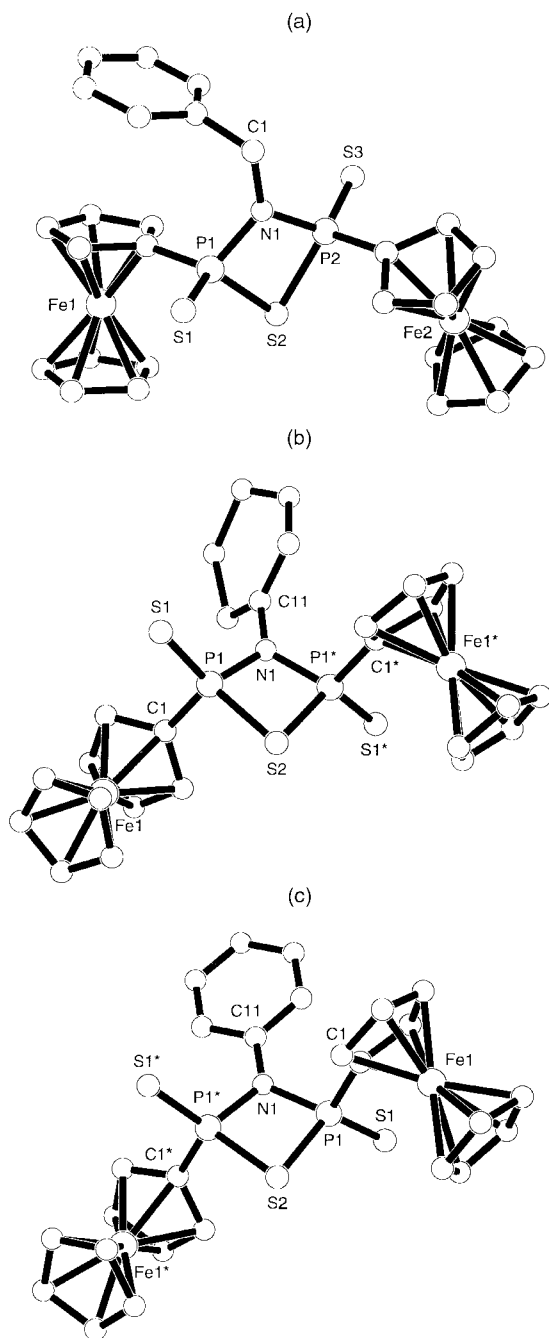


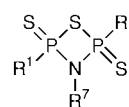
Fig. 4 Molecular structures of compounds (a) **10**, (b) **11** and (c) **12**.

grounds. Compared with $R^1_2P_2S_4$ rotation about the C–P bonds has occurred to increase the distance from the iron atoms to the NR groups in **10–12**. The $P(1) \cdots P(1^*)$ separations (2.69–2.67 Å) are smaller than that in $R^1_2P_2S_4$ (3.08 Å) and the $S(2) \cdots N(1)$ (2.65–2.61 Å) distances are smaller than the $S(1) \cdots S(1^*)$ distance in $R^1_2P_2S_4$ (2.91 Å). These differences are due to the relatively short and strong P–N bonds pulling the two phosphorus atoms closer to each other. The P(1)–S(2) and P(2)–S(2) bond lengths in **10–12** are shorter than the mean P–S bond length in $R^1_2P_2S_4$ whilst the P=S distances are not significantly different to those in $R^1_2P_2S_4$.

The formation of compound **11** can be rationalized by the mechanism in Scheme 6.

The reaction of LR with DCC was carried out on a large scale. After recrystallization of the thiazadiphosphetane **14**⁷ the mother-liquor was distilled to give a good yield of cyclohexyl isothiocyanate, eqn. (7). The isolation of the cyclohexyl isothiocyanate (identified by IR, GCMS and NMR spectroscopy) provides further evidence for the above mechanism.

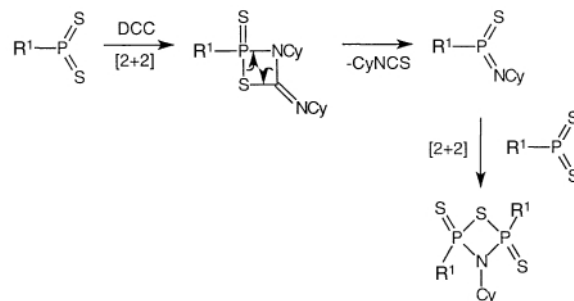
Table 3 Selected bond lengths (Å) and angles (°) for thiazadiphosphetane disulfides



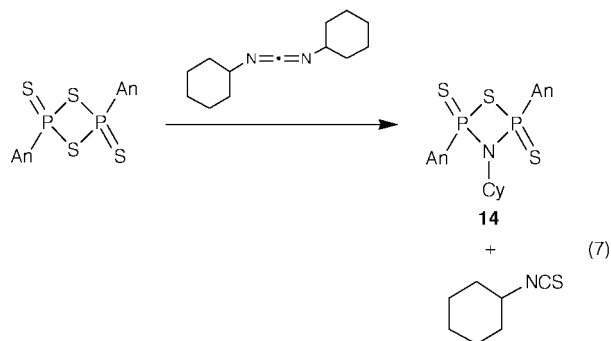
$R^7 = PhCH_2$ **10**, Cy **11**, Ph **12** or Me **13**

	10	11 ^a	12 ^a	13 ²³
S(1)–P(1)	1.918(4)	1.918(3)	1.917(3)	1.950(16)
S(2)–P(1)	2.110(4)	2.095(3)	2.098(3)	2.121(7)
P(1)–N(1)	1.661(8)	1.675(5)	1.704(5)	1.689(5)
P(1)–C(1)	1.790(0)	1.785(6)	1.789(5)	1.818(4)
S(2)–P(2)	2.108(4)			
S(3)–P(2)	1.925(4)			
P(2)–N(1)	1.680(7)			
P(2)–C(21)	1.781(9)			
N(1)–C	1.47(1)	1.44(1)	1.40(1)	1.517(20)
P \cdots P	2.69	2.67	2.69	2.69
N(1) \cdots S(2)	2.61	2.64	2.65	2.65
P(1)–S(2)–P(2)	79.3(1)	79.0(2)	79.9(2)	79.1(2)
S(1)–P(1)–S(2)	119.3(2)	119.9(1)	120.1(1)	
S(1)–P(1)–N(1)	117.3(3)	116.7(2)	116.5(2)	
S(2)–P(1)–N(1)	86.8(3)	87.9(2)	87.8(2)	87.4(3)
P(1)–N(1)–P(2)	107.4(5)	105.3(5)	104.5(4)	
S(2)–P(2)–S(3)	120.4(2)			
S(3)–P(2)–N(1)	117.8(3)			
S(3)–P(2)–C(21)	107.3(4)			
S(2)–P(2)–N(1)	86.4(3)			
S(2)–P(2)–C(21)	107.3(4)			

^a Compounds **11** and **12** contain crystallographic twofold axes and thus no parameters for atom P(2) are reported.



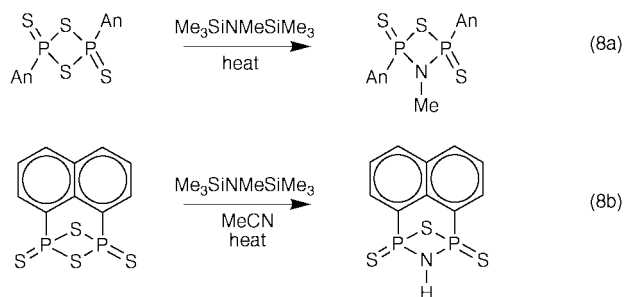
Scheme 6 Mechanism for the formation of compound **11**. DCC = Dicyclohexylcarbodiimide.



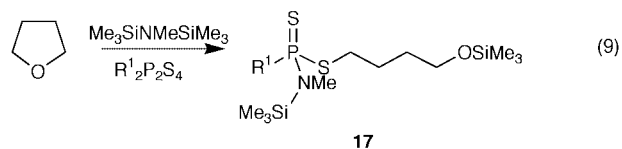
To investigate the effect of increasing the steric bulk around the nitrogen atom we treated $R^1_2P_2S_4$ and *N*-benzylidene-2,4-dimethylaniline, to give after purification, the expected thiazadiphosphetane **15**. The reactions of *N*-benzylidene-2,6-dimethylaniline and *N*-benzylidene-1-phenylethylamine with $R^1_2P_2S_4$ were also attempted, but these gave intractable mixtures from which no pure product could be isolated. However the reaction of 2,6-dimethylaniline did give the thiazadiphosphetane **16** in low yield. The formation of this product does

offer a new route to these heterocycles. As imines react with $R^1_2P_2S_4$ to form thiazadiphosphetane disulfides, the reaction of triphenylphosphine *N*-phenylimine with $R^1_2P_2S_4$ was attempted. While a good yield of triphenylphosphine sulfide was isolated, no other phosphorus compound was obtained from the intractable mixture of *P*-ferrocenyl compounds.

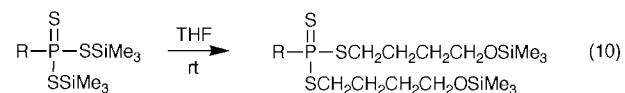
The reactions of heptamethyl- and hexamethyl-disilazane with LR, eqn. (8a),²⁴ NpP_2S_4 , eqn. (8b)²⁵ and $MeONpP_2S_4$ ²⁵



have been reported to give thiazadiphosphetane disulfides. We found that the reaction of $R^1_2P_2S_4$ with heptamethyldisilazane in dichloromethane gives a mixture of products including traces of a malodorous substance [thought to be bis(trimethylsilyl) sulfide] which could not be removed. The experiment was repeated using THF in place of dichloromethane, and after chromatography and removal of solvent a heavy red oil **17** (δ_p 82.7) was obtained. Compound **17** is a 1:1:1 adduct of *P*-ferrocenyldithiophosphine ylide, THF and heptamethyldisilazane, eqn. (9), and we assume is obtained *via* an *S*-



trimethylsilyl compound that is initially formed from $R^1_2P_2S_4$ and heptamethyldisilazane. This reaction is similar to that of *P*-organotrithiophosphonic acid *S,S'*-trimethylsilyl ester with THF to form *P*-organotrithiophosphonic acid *S,S'*-bis(4-trimethylsilyloxybutyl) esters, eqn. (10).²⁶



R can be methyl or *tert*-butyl

The reaction of 1,3-diphenylurea with LR was reported to give $ArP(S)(NHPh)_2$.⁶ We found that using $R^1_2P_2S_4$ this reaction gives, besides the diamide **18** (δ_p 54.5), the thiazadiphosphorane **12**. Close examination of the infrared spectrum of $R^1_2P(S)(NHPh)_2$ **18** reveals the presence of two different NH stretches. One is sharp [$\nu(NH)$ 3382 cm^{-1}] while the other [$\nu(NH)$ 3243 cm^{-1}] is broader suggesting that in the solid some NH groups are involved in hydrogen bonding. X-Ray crystallography reveals (Fig. 5 and Table 4) that in the solid state **18** forms hydrogen bonded dimers, using an amine proton of one molecule and the thiophosphoryl group of another.

The mechanism by which 1,3-diphenylurea and $R^1_2P_2S_4$ form compound **12** is not clear. Conversion of the diphenylurea into the thiourea, followed by loss of hydrogen sulfide, would give diphenylcarbodiimide. The reaction of the carbodiimide with $R^1_2P_2S_4$ could be a reasonable route to **12** (Scheme 7). Both carbon–nitrogen bond cleavage and nitrogen–phosphorus bond formation are required. One possible mechanism would require the reversible dissociation of *N,N'*-diphenylurea (or *N,N'*-

Table 4 Selected bond lengths (Å) and angles (°) in compound **18**

S(1)–P(1)	1.941(2)	P(1)–C(1)	1.779(5)
P(1)–N(11)	1.662(4)	N(17)–S(1*)	3.416(4)
P(1)–N(17)	1.649(4)		
S(1)–P(1)–N(11)	117.0(2)	N(11)–P(1)–C(1)	99.6(2)
S(1)–P(1)–N(17)	108.1(1)	N(17)–P(1)–C(1)	113.0(2)
S(1)–P(1)–C(1)	112.6(2)	P(1)–N(11)–C(11)	127.2(3)
N(11)–P(1)–N(17)	106.4(2)	P(1)–N(17)–C(17)	130.7(3)

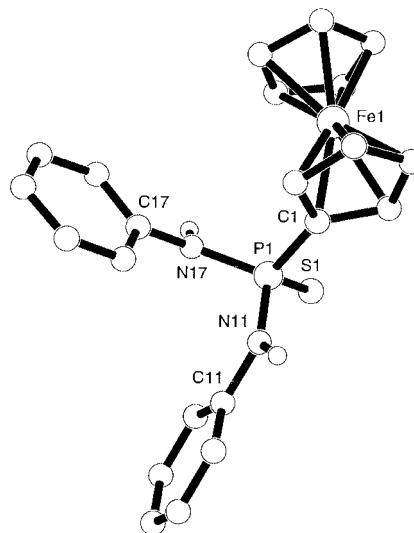
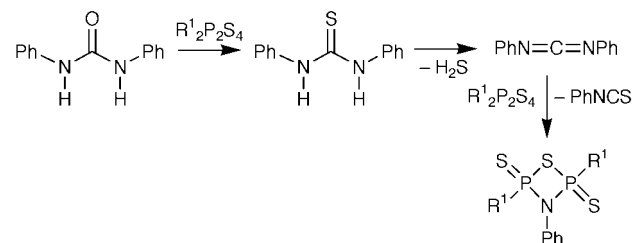


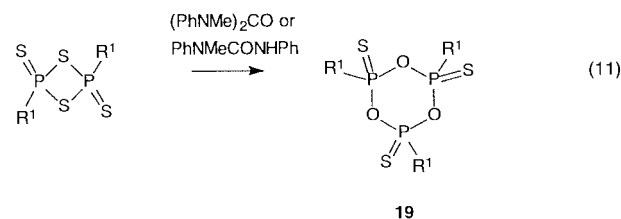
Fig. 5 Molecular structure of compound **18**.



Scheme 7 A mechanism for the formation of compound **12**.

diphenylthiourea) to phenyl isocyanate (or phenyl isothiocyanate) and aniline; both the aniline and the isocyanate could take part in reactions.

Further to examine the reactions of ureas with $R^1_2P_2S_4$, *N,N'*-dimethyl-*N,N'*-diphenylurea and *N*-methyl-*N,N'*-diphenylurea were treated with $R^1_2P_2S_4$. No nitrogen–phosphorus compounds were isolated, but instead a R^1 POS trimer **19**, eqn. (11). Compound **19** is a likely phosphorus–oxygen



containing side product formed in thionation reactions. This outcome is consistent with the hypothesis of the carbodiimide being required as an intermediate. The presence of even one methyl group will prevent the formation of any diphenylcarbodiimide, and also make thionation of the urea more likely by slightly increasing the electron density of the carbonyl oxygen.

The $^{31}P\{-^1H\}$ spectrum of compound **19** appears (Fig. 6) to be an AMN system in which no coupling between the M and N

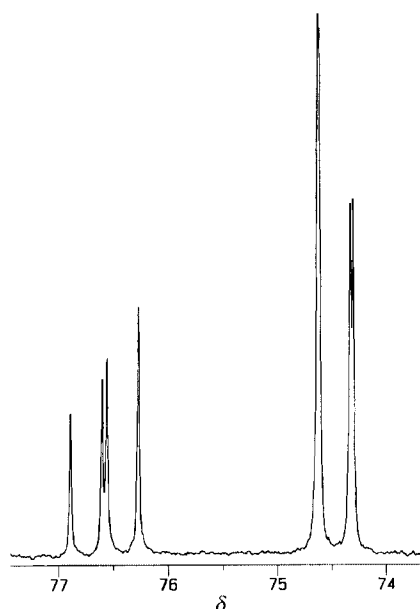
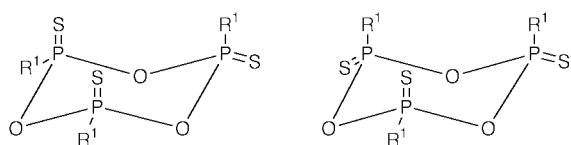


Fig. 6 The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of compound **19**.

environments is observed. However simulation with *geNMR* suggests the spectrum to be an AB_2 system with second order effects exerting a strong influence. This spectrum contrasts with the single environment (δ_{P} 72) reported for 2,4,6-tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulfide,²⁷ which has been found by X-ray crystallography to have two aromatic groups on one side of the ring with the third on the other side. For such a compound an AX_2 system could be expected in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum, but the molecule could be flipping from one conformation to another. ^1H NMR spectroscopy upon **19** reveals two ferrocenyl groups in a 1:2 intensity ratio suggesting that the isolated compound is one of two isomers. The conformation on the left with fewer bulky ferrocenyl groups in the axial positions is likely to have the lower energy.



The electronic effects of the phosphorus portions of the molecules on the ferrocene moiety were investigated using cyclic and square wave voltammetry. From literature data for ferrocenes with chalcogen or phosphorus substituents^{28,29} it was anticipated that the phosphorus substituents examined here would withdraw electronic charge and stabilize the ferrocenes to oxidation. This is the case for all molecules (SUP 57629), replacement of the sulfurs on the phosphorus with more electronegative atoms (C, N, O) leading to a further general increase in the redox potential of the ferrocene moiety. Changes in the P=S distance and stretching frequency of the molecules were not significant enough to allow correlation with the redox potentials. Likewise, there was no clear relationship between the ^{31}P NMR chemical shift and the redox potentials.

In contrast with measurements for bis(dimethylferrocenyl)-dithiadiphosphetane disulfide, where a single redox couple ($E_{\text{r}} = 0.62$ V vs. SSCE) is observed, cyclic voltammograms for the diferrocenylthiazadiphosphetane disulfides revealed two overlapping redox waves. Here, the nitrogen atom permits communication between the two ferrocenes. The ferrocenium radical cation produced on oxidation of the first ferrocene

withdraws electronic charge, leading to a shift in the redox potential of the second ferrocene moiety. The overlapping redox waves were resolvable using square wave voltammetry, the differences (ΔE range = 60–90 mV) in the redox potentials being small in comparison to those of biferrocene **205** ($\Delta E = 330$ mV)³⁰ which has direct linkages between the ferrocenyl moieties.

Experimental

Reagents came from Aldrich. Solvents were dried using standard procedures. ^{31}P NMR spectra were recorded in CDCl_3 and are referenced to 85% H_3PO_4 .

Synthesis of compound 1

To $\text{R}^1_2\text{P}_2\text{S}_4$ (1.079 g, 1.93 mmol) was added dimethylcyanamide (0.7 ml); after stirring to mix the reactants no reaction was seen to occur. Within a minute of the mixture being heated in a 140 °C oil-bath a violent reaction was observed. The tube was withdrawn from the oil-bath and allowed to cool for several minutes before being replaced in the oil-bath for 4 min of heating. The reaction mixture was then allowed to cool to room temperature, before the products were recrystallized from a small volume of toluene to give a brown product (1.385 g). This solid was examined by ^{31}P NMR spectroscopy and found to contain paramagnetic material. Chromatography on silica followed by removal of the solvent gave **1** as an orange-yellow solid (0.924 g, 2.2 mmol, 57%). By cooling a hot toluene solution a crystal was obtained. δ_{P} 61.82. δ_{H} 4.46 (m) and 4.28 (m) (9 H in total), and 3.02 (12 H). δ_{C} 154.7 (quat), 80.7 [d, $^1J(^{31}\text{P}\text{--}^{13}\text{C})$ 168, quat], 71.6 [d, $J(\text{PC})$ 14.9], 70.5 [d, $J(\text{PC})$ 12.7 Hz], 70.1, and 37.3. IR: 2927m, 1618s, 1547s, 1442m, 1358m, 1253m, 1190m, 1180m, 1105m, 1055w, 1022m, 997w, 954s, 937m, 861s, 847m, 821m, 680s, 641m, 575m, 510m, 492w, 473m, 417w, and 330w cm^{-1} . MS(EI+): m/z 420 (M^+), 280 (FcPS_2)⁺, 248 (FcPS)⁺, 217 (FcS)⁺, 184, 121, 69, 51 and 31. mp 150 °C (decomp.) (Found: C, 45.5; H, 4.8; N, 13.1. $\text{C}_{16}\text{H}_{21}\text{FeN}_4\text{PS}_2$ requires C, 45.7; H, 5.0; N, 13.3%).

Low temperature synthesis of compounds 1 and 3

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (0.494 g, 0.882 mmol) was suspended in toluene (10 ml), to which was added dimethylcyanamide (0.5 ml, 0.43 g, 6.2 mmol). This mixture was slowly brought to reflux. After 8 min almost all the $\text{R}^1_2\text{P}_2\text{S}_4$ was absent (TLC). This mixture was allowed to cool to room temperature and stand for 3 d. Flash column chromatography gave a red oil **3** (0.144 g, 0.411 mmol, 23%) and compound **1** as a yellow solid (0.449 g, 1.07 mmol, 61%). Compound **3** (120 mg) was heated under reflux in xylene for three hours, during which the mixture became very dark and cloudy. A black solid formed; after filtration through a short pad of Al_2O_3 a pale orange solution was obtained. After removal of the solvent an orange oil remained (24 mg) which according to ^{31}P NMR spectroscopy was almost pure **3**. δ_{P} 67.8.

Reaction of LR and dimethylcyanamide to give compound 2

To LR (2.4 g, 5.9 mmol) was added toluene (22 ml) and dimethylcyanamide (3 ml, 2.6 g, 37 mmol). This mixture was stirred as it was heated until it started to reflux. Shortly after starting the heating the LR dissolved to give a clear solution which then became cloudy again. The mixture was heated under reflux for 30 min before being allowed to cool to room temperature. The white solid was collected by filtration and washed with a little toluene, before being dried in high vacuum to give compound **2** as a white solid (1.9 g, 5.6 mmol, 47%). δ_{P} 58.2. δ_{H} 7.8 (2 H, m), 6.8 (2 H, m), 3.75 (3 H), and 3.1 (s). δ_{C} 162.0, 155.8, 132.7 [d, $J(\text{PC})$ 12], 130 [d, $^1J(\text{PC})$ 154], 113.6 [d, $J(\text{PC})$

16 Hz], 55.7 and 37.8. IR: 1627s, 1571m, 1551s, 1501m, 1442m, 1425m, 1205m, 1361m, 1304m, 1291m, 1258s, 1190m, 1181m, 1116s, 1059m, 1022m, 950s, 871s, 844s, 828w, 802m, 720w, 691s, 638m, 627m, 588m, 541m, 529m, 496w, 478m, 439m, 413m, and 401w cm^{-1} . MS(EI⁺): *m/z* 342(M⁺), 272(M - Me₂NCN), 202(M - 2Me₂NCN), 171, 155, 139, 133, 123, 107, 95, 77, 70, 69, 63, and 44. Molecular ion found at *m/z* 342.0746 (¹²C₁₃¹H₁₉¹⁴N₄¹⁶O³¹P³²S₂ requires 342.07379, error 2.4 ppm). mp >190 °C (Found: C, 45.3; H, 5.2; N, 17.5. C₁₃H₁₉N₄OPS₂ requires C, 45.6; H, 5.6; N, 16.4%). For a second sample results were: C, 46.6; H, 5.7; N, 16.4%.

Preparation of compound 3

The reaction of R¹₂P₂S₄ and dimethylcyanamide was repeated on a larger scale (2.91 g, 10.4 mmol and 1.7 ml, 1.5 g, 21 mmol in toluene (50 ml)). The reaction mixture was allowed to cool before the addition of light petroleum (bp 40–60 °C; 40 ml) to precipitate out **1**. After filtration and removal of solvent a red oil remained. This was purified by flash column chromatography (petroleum–toluene 75:25) to give compound **3** as a red oil (0.57 g, 1.6 mmol, 15%) which crystallized on standing. δ_{P} 67. δ_{H} 4.6 (m), 4.4 (m) and 4.3 (s) (total integration of signals between δ 4 and 5: 9 H) and 2.6 [6 H, d, ³*J*(PH) = 14 Hz]. δ_{C} 144.4 (quat), 75.4 [d, ¹*J*(PC) = 91, quat], 72.0 [d, ²*J*(PC) = 21 Hz], 71.2 to 70.3 (m), 69.9 (s) and 36.3 (s). IR: 3098m, 2997w, 2941s, 2885s, 2845m, 2805m, 2553w, 2031vs, 1649m, 1455m, 1413m, 1388w, 1368w, 1351w, 1309m, 1279s, 1183s, 1107m, 1059m, 1029s, 1001 (sh), 977s, 897w, 823s, 743s, 671s, 627m, 556m, 494s, 478s and 448s cm^{-1} . MS(FAB): *m/z* 373(minor), 350(M⁺), 318(M - S), 306, 292(M - NCS), 285, 274, 260, 248, 186, 165, 128, 121, and 108. MS(EI⁺): *m/z* 350(M⁺), 348, 318 (M - S), 306, 292, 285, 274, 260, 248, 217, 186, 171, 128, 121, 108, 96, 75, 60 and 44. Molecular ion found at *m/z* 349.9767 (¹²C₁₃¹H₁₅¹⁴N₂⁵⁶Fe³¹P³²S₂ requires 349.97633 (1.1 ppm error) (Found: C, 44.9; H, 4.1; N, 8.1. C₁₃H₁₅FeN₂PS₂ requires C, 44.6; H, 4.3; N, 8.0%).

The reaction of R¹₂P₂S₄ and piperidine-1-carbonitrile to give compounds 4 and 6

To piperidine-1-carbonitrile (2.0 ml, 1.9 g, 17.5 mmol) was added to R¹₂P₂S₄ (2.45 g, 4.38 mmol) to give a red mud-like mass, to which was added a little toluene. This mixture was heated in a bath (110 °C) for 2 min. After cooling, light petroleum was added and the tube shaken. This reaction mixture was seen to thicken before crystallization to give a red solid. This was recrystallized from toluene (12 ml) to give an orange solid **4** (2.42 g, 4.84 mmol, 55%) and a red tar. The recrystallized **4** retained a trace of toluene, detected by ¹H NMR spectroscopy, even after prolonged drying in high vacuum so a sample of **4** was dissolved in a little CDCl₃ before removal of all solvent in high vacuum to give a sample for examination by ¹H NMR spectroscopy. δ_{P} 61.6. δ_{H} 4.5 (2 H, m), 4.33 (7 H, s), 3.70 (8.7 H, t, *J* 5.1 Hz) and 1.6 (13.6 H, m). δ_{C} 71.5 (d, *J* 15), 70.4 (d, *J* 12 Hz), 70.0, 46.3 (CH₂), 25.7 (CH₂), and 24.6 (CH₂). IR (Nujol mull): 3092m, 1599s, 1532s, 1495m, 1464s, 1447s, 1413m, 1399m, 1378m, 1365m, 1351m, 1318w, 1285w, 1240s, 1208s, 1186m, 1178m, 1123s, 1106m, 1081w, 1062w, 1020s, 1002s, 994s, 948s, 938s, 884s, 852s, 836m, 806s, 795m, 728s, 694m, 674s, 645s, 621s, 589m, 540w, 502m, 486m, 464w, 455w, 421w, 409m, 380w, 349w and 326w cm^{-1} . mp 160 °C (decomp.) (Found: C, 52.8; H, 5.8; N, 11.0; S, 12.8. C₂₂H₂₉FeN₄PS₂ requires C, 52.8; H, 5.8; N, 11.2; S, 12.8%).

The red tar was subjected to flash column chromatography on silica (24 g, hexane–CH₂Cl₂ then CH₂Cl₂ then ethyl acetate) to give three different orange fractions. The first fraction after removal of solvent furnished ferrocenyl isothiocyanato(piperidino)phosphine sulfide **6** as a red oil (0.63 g, 1.6 mmol, 18%), pure by GCMS. δ_{P} 63.3. δ_{H} 4.65 (m), 4.55 (m), 4.49 (m), 4.40 (s) (integration for 4.7 to 4.3: 9 H), 3.2 (7 H, m) and 1.5 (11 H, m).

When the peak at δ 1.5 was irradiated in a double irradiation experiment the peak at δ 3.2 changed to a pair of doublets of doublets: ²*J*(HH) = 12.6, ³*J*(PH) = 10.2 Hz for the peak centred at δ 3.2, ³*J*(PH) = 9.8 Hz for the peak centred at δ 3.1. δ_{C} 145.0 [d, *J*(PC) 2.5], 75.8 [d, *J*(PC) 162 Hz], 72.9 to 71.4 (m), 70.9 (s), 46.1, 25.9, 25.8, and 24.4. IR: 3098m, 2936s, 2852s, 2022vs, 1463m, 1450m, 1442m, 1413m, 1387w, 1369m, 1335m, 1311w, 1278m, 1259w, 1205s, 1184s, 1160s, 1107s, 1066s, 1027s, 1003m, 952s, 896w, 850m, 825s, 730s, 678s, 628m, 559m, 491s, 477s, and 446s cm^{-1} . MS(EI⁺): *m/z* 390, 332, 307, 274, 248, 186, 146, 121, and 84. Molecular ion found at *m/z* 390.0074 (¹²C₁₆¹H₁₉–Fe¹⁴N₂³¹P³²S₂ requires 390.0076, error 0.7 ppm) (Found: C, 48.8; H, 4.9; N, 7.3; S, 16.5. C₁₆H₁₉FeN₂PS₂ requires C, 49.3; H, 4.9; N, 7.2; S, 16.4%). The second fraction was an intractable mixture, while the third was compound **4** (454 mg, 0.91 mmol, 10%).

The reaction of R¹₂P₂S₄ with slow addition of piperidine-1-carbonitrile to give compound 6

The compound of R¹₂P₂S₄ (9.84 g, 17.6 mmol) was suspended in toluene (80 ml) and heated to reflux before piperidine-1-carbonitrile (8.1 ml, 7.7 g, 70 mmol) in toluene (80 ml) was added dropwise over 3 h. This mixture was maintained at reflux during the addition, R¹₂P₂S₄ dissolving to give a deep red solution as the piperidine-1-carbonitrile was added. The mixture was allowed to cool before filtration. After removal of solvent the mixture was subject to flash column chromatography (100 g SiO₂, 1 L 20% CH₂Cl₂ in light petroleum, 1 L 30% CH₂Cl₂ followed by 500 ml 50% CH₂Cl₂) to give **6** (12.36 g, 35.15 mmol, 90%).

Reaction of piperidine-1-carbonitrile and LR to give compounds 5 and 7

The compound LR (0.970 g, 2.4 mmol) was treated with piperidine-1-carbonitrile (1.2 ml, 1.1 g, 9.9 mmol). The mixture was stirred for 40 min before being heated in an oil-bath (140 °C for one minute) and then allowed to cool to give a jelly-like mass. This was insoluble in cold toluene giving after recrystallization from toluene a white solid (1.19 g, 2.8 mmol, 59%) impure according to ¹H NMR spectroscopy. The solid was subjected to a second recrystallization from toluene to give **5** (0.73 g, 1.7 mmol, 36%). δ_{P} 58.1. δ_{H} 7.9 [2 H, dd (8.7 and 14 Hz)], 6.9 (2 H, m), 3.8 (s) and 3.6 (m) (11.6 H), 3.1 (1 H, m) and 1.6 (15 H, m). ¹H–¹H COSY: δ 1 [δ 2] 7.9 [6.9], 3.6 [1.6] and 3.1 [1.6]. δ_{C} 154.4 (quat), 132.2 [d, *J*(PC) 12], 113.2 [d, *J*(PC) 15 Hz], 55.2, 50 (minor peak, CH₂), 46.3 (CH₂), 25.6 (CH₂) and 24.6 (CH₂). ¹³C–¹H Correlation: ¹H δ [¹³C δ] 7.9 [132], 6.9 [113], 3.8 [55], 3.1 [50], 3.6 [46], 1.6 [26] and 1.6 [25]. MS(EI): *m/z* 422 (M⁺ very weak), 316, 279, 254, 222, 196, 171, 139, 110, 84, 63 and 42. Molecular ion found at *m/z* 422.1368 (¹²C₁₉¹H₂₇¹⁴N₄¹⁶O³¹P³²S₂ requires 422.13638 error 0.9 ppm). CV: irreversible oxidation, measured by square wave voltammetry at 0.67 V.

The mother-liquors from the recrystallizations were combined and subjected to flash column chromatography to give after removal of solvent compound **7** as a colourless heavy oil (0.304 g, 0.97 mmol, 20%). δ_{P} 60.2. δ_{H} 7.8 (2 H, m), 6.9 (2 H, m), 3.8 (3 H, s), 3.2 (5 H, m) and 1.6 (8 H, m). When the peak at δ 1.6 was irradiated the peak at δ 3.2 changed to a pair of doublets of doublets, ²*J*(HH) = 12.7 and ³*J*(PH) = 10.0 Hz for the proton resonance centred at δ 3.25 while for the resonance centred at δ 3.11 ³*J*(PH) = 9.2 Hz. δ_{C} 163 (quat), 132 [d, *J*(PC) 13], 114 [d, *J*(PC) 16 Hz], 56, 50 (minor peak, CH₂), 46 (CH₂), 25.8 (CH₂), 25.7 (CH₂) and 24 (CH₂). IR: 3068w, 3005m, 2938s, 2852s, 2210m, 2031m, 1965vs, 1596s, 1570m, 1502s, 1462m, 1451m, 1442m, 1408m, 1375m, 1335w, 1307m, 1296s, 1259s, 1205s, 1181s, 1160s, 1118s, 1065s, 1026s, 990w, 953s, 904w, 853m, 830s, 804s, 735s, 712m, 689s, 640m, 620s, 527m, 500m, 467m, 443w, 425w, and 392w cm^{-1} . MS (EI⁺): *m/z* 312, 279, 254, 238, 196, 171, 139, 110, 84, 59, 42 and 28. Molecular

ion found at m/z 312.0523 ($^{12}\text{C}_{13}^{1}\text{H}_{17}^{14}\text{N}_2^{16}\text{O}^{31}\text{P}^{32}\text{S}_2$ requires 312.05199, error 1.1 ppm).

The reaction of $\text{R}^1_2\text{P}_2\text{S}_4$ with slow addition of dimethylcyanamide: formation of compound 8

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (9.6 g, 17.1 mmol) was suspended in toluene (100 ml) and heated to reflux before dimethylcyanamide (6 ml, 5.2 g, 74.7 ml) dissolved in toluene (100 ml) was added dropwise over 1 h. This mixture was maintained at reflux during the addition; the $\text{R}^1_2\text{P}_2\text{S}_4$ dissolved to give a deep red solution as the dimethylcyanamide was added. The mixture was allowed to cool before filtration. After removal of solvent the mixture was subjected to flash column chromatography (100 g SiO_2 , elution with 500 ml 20% CH_2Cl_2 in light petroleum, 1 L 30% CH_2Cl_2 , 500 ml 40% CH_2Cl_2 , 500 ml CH_2Cl_2 and 1 L 10% ethyl acetate in CH_2Cl_2) to give **1** (4.08 g, 9.72 mmol, 28%) and **3** (6.82 g, 19.5 mmol, 57%) identical to that from the above experiment. Another fraction was collected which on removal of solvent gave a red oil that later solidified. δ_{p} 81.0 (d, J 42), 80.6 (d, J 44 Hz) and 52.6 (m). This red solid was recrystallized from hot ethyl acetate (8 ml) to give **8** as an orange crystalline solid (81 mg, 132 μmol , 1%). By slow cooling of a hot solution, in ethyl acetate, crystals were obtained. δ_{p} 81.0 [d, $^3J(\text{PP}) = 44$] and 52.1 [d, $^3J(\text{PP}) = 44$ Hz]. δ_{H} 4.85 (m), 4.74 (m), 4.56 (m), 4.41 (s), 4.34 (m), 4.24 (s) (integration for the ferrocenyl area: 18 H) and 2.80 (7 H, d, J 13 Hz). δ_{C} 73.3 [d, $J(\text{PC})$ 22], 72.6 to 71.1 (m), 70.8, 70.5 [d, $J(\text{PC})$ 12 Hz], 70.5 and 37.7. IR: 3110w, 3092m, 3082m, 2933m, 2882w, 2844m, 2810w, 2079s, 2013vs, 1475w, 1453m, 1435w, 1410m, 1387w, 1366m, 1348w, 1311w, 1287m, 1188s, 1178s, 1106m, 1061w, 1053w, 1028s, 1000 (sh), 958s, 919vs, 896 (sh), 859w, 847w, 825s, 810 (sh), 736vs, 691s, 636w, 625m, 602w, 568s, 519 (sh), 500m, 489m, 465m, 425m, 382w, 366m, 341w, 329w, and 303w cm^{-1} . MS(FAB): m/z 637 (M + Na), 614 (M^+), 350, and 292 (isotropic distribution correct for $\text{C}_{23}\text{H}_{24}\text{Fe}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_3$). MS(ES^+): m/z 637 (M + Na), 615 (MH), and 292. MS(ES^-): m/z 672, 659, 645 (M + OMe), 631 (M + OH), 572, 381, and 335 (Found: C, 43.3; H, 3.8; N, 4.2. $\text{C}_{23}\text{H}_{24}\text{Fe}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_3$ requires C, 45.0; H, 3.9; N, 4.6%). mp 151–153 °C to a red tar that decomposes to a black tar on heating to 180 °C.

The mother-liquor from the first recrystallization was examined by ^{31}P NMR spectroscopy; in addition to the isomer isolated above a second compound was present. The isomers were present in a 2:1 ratio, the minor component being that isolated above. δ_{p} 81.0 (d, J 41) and 53.2 (d, J 41 Hz).

Treatment of compound 1 with an excess of isopropylamine to give 9

To compound **1** (351 mg, 1 mmol) in THF (15 ml) was added isopropylamine (7 ml, 4.9 g, 82 mmol). This mixture was allowed to stand overnight before the removal of all volatile compounds. TLC indicated the absence of **1**. After dissolving the residue in diethyl ether (28 ml) followed by washing with water (12 ml) the ether extract was dried with MgSO_4 ; after filtration and evaporation a red solid was obtained. This was applied to a flash column (CH_2Cl_2 followed by ethyl acetate 25% in CH_2Cl_2) after evaporation a red solid was obtained. Further flash column chromatography on the solid (40% CH_2Cl_2 in light petroleum, CH_2Cl_2 followed by 20% ethyl acetate in CH_2Cl_2), followed by evaporation, gave **9** as an orange solid (0.324 g, 0.69 mmol, 69%). δ_{p} 61.6. δ_{H} 4.66 (1 H, m), 4.44 (1 H, m), 4.30 (2 H, m), 4.25 (5 H, s), 3.9 (2 H, br), 2.45 [6 H, d(14 Hz)] and 1.28 (13 H, m). IR: 3396m, 3263m, 2194w, 3150 (sh), 3089w, 3037w, 2981 (sh), 2967s, 2930m, 2864m, 2824w, 2784w, 1613s, 1536s, 1471m, 1435m, 1413w, 1388m, 1367m, 1342m, 1312w, 1294w, 1260w, 1080m, 1170m, 1140w, 1120w, 1106w, 1049w, 1023m, 1001w, 971 (sh), 959m, 900w, 872w, 852w, 823m, 814w, 774m, 720w, 700m, 637m, 611m, 570w, 492m, 464w, 440w, and 339w cm^{-1} . MS(ES^+): 435, 436, 869, 870, and 891. MS(ES^-): m/z 433 and 434.

The reaction of N -benzylidenebenzylamine with $\text{R}^1_2\text{P}_2\text{S}_4$ to give compound 10

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (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 h. After cooling this mixture was filtered through a silica pad and the pad 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 light petroleum 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 light petroleum) gave after removal of solvent 3-benzyl-2,4-diferrocenyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide **10** as an orange solid (0.489 g, 772 μmol , 10%), mp ca. 150–160 °C (Found: C, 52.0; H, 4.1; N, 2.3; S, 15.4. $\text{C}_{27}\text{H}_{25}\text{Fe}_2\text{NP}_2\text{S}_3$ requires C, 51.2; H, 3.9; N, 2.2; S, 15.2%). IR: 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 cm^{-1} . δ_{p} 65.1. δ_{H} 7.2 (2 H, m), 7.0 (3 H, m), 4.89 (2 H, m), 4.68 (2 H, m), 4.55 (2 H, m), 4.44 (2 H, m), 4.33 (10 H, s) and 4.16 (2 H, s). δ_{C} 129.1, 127.9, 127.3, 76.5 [d, $J(\text{PC})$ 20], 73.5 [d, $J(\text{PC})$ 14], 72.2 [d, $J(\text{PC})$ 14], 71.6 [d, $J(\text{PC})$ 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]. MS(FAB): m/z 656 (M + Na), 634 (MH), 633 (M^+), 617, 601, 568, 513, 492, and 353.

The reaction of $\text{R}^1_2\text{P}_2\text{S}_4$ and dicyclohexylcarbodiimide to form compound 11

Dicyclohexylcarbodiimide (0.72 g, 3.5 mmol) and $\text{R}^1_2\text{P}_2\text{S}_4$ (1.9 g, 3.4 mmol) were placed in toluene (10 ml) and heated to reflux for 7 d. The toluene soluble compounds were transferred to a flask and the solvent was removed to give a brown tar. This was subjected to flash column chromatography (light petroleum–ether 9:2) to give after removal of solvent an orange solid (0.43 g). δ ^{31}P - $\{^1\text{H}\}$ minor peaks at 94 and 58.8, major peak at 60.9. On heating with ethyl acetate the orange solid was insoluble in the hot solvent, and on cooling no additional solid was precipitated after the addition of ethanol. The orange solid was collected by filtration and dried (77 mg, 101 mmol, 3%). This solid is 2,4-diferrocenyl-3-cyclohexyl-1,3,2,4-thiazadiphosphorane 2,4-disulfide **11**. δ_{p} 61.0. δ_{H} 4.96 (m), 4.88 (m), 4.61 (m), 4.55 (m) and 4.36 (s) (integration for the ferrocenyl area: 9.0 H), 3.3 (br m), 1.55 (m) and 0.97 (m) (combined integration of the last two peaks: 10.3 H). On irradiation of the peak at δ 1.55 the resonance δ 3.3 changed to a broad 1:2:1 triplet like peak (lines observed at δ 3.35, 3.27, and 3.19). On repeating this experiment at 233 K (–40 °C) this triplet appears to be sharper. δ_{C} 76.7 (d, J 20 Hz), 73.7 (m), 72 (m), 70.4, 57.8, 33.1 (CH_2), 32.2 (m, CH_2), 25.7 (CH_2), 25.3 (CH_2), and 24.9 (CH_2). IR: 3087m, 2929s, 2849s, 1448w, 1438w, 1407w, 1387w, 1364w, 1304w, 1266w, 1247w, 1191m, 1179m, 1171m, 1128m, 1106m, 1053w, 1033m, 1022m, 1001m, 936m, 914m, 873m, 864m, 844m, 821m, 746m, 701s, 679s, 617w, 535w, 519m, 492s, 456s, 409m, 349m and 325w cm^{-1} . MS(EI^+): m/z 444, 248, 186, 121 and 56. MS(FAB): m/z 625 (M^+), 538 and 346 (Found: C, 49.1; H, 4.5; N, 2.2. $\text{C}_{26}\text{H}_{29}\text{Fe}_2\text{NP}_2\text{S}_3$ requires C, 49.9; H, 4.6; N, 2.2%), decomposes above 220 °C to a black solid which does not melt below 280 °C.

The reaction of $\text{R}^1_2\text{P}_2\text{S}_4$ with $\text{PhCH}=\text{NPh}$ to give compound 12

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (3.0 g, 5.36 mmol) and $\text{PhCH}=\text{NPh}$ (2 g, 11.0 mmol) were heated at reflux in toluene (150 ml) for

16 h. According to TLC very little chemical change occurred. After about 8 h of heating under reflux, xylenes (100 ml) were added and the mixture was heated under reflux (64 h) before being allowed to cool. It was filtered through a pad of silica and the pad was washed with CH_2Cl_2 (50 ml). Removal of solvent from the combined filtrates in vacuum gave a red oil (8 g). This on standing showed some signs of crystallization; It was applied to a silica column (83 g) and eluted (500 ml of 40% CH_2Cl_2 in light petroleum followed by 500 ml of CH_2Cl_2). The red eluted liquid was combined and the solvent removed in vacuum to give a red solid. This was heated with ethyl acetate (160 ml) and the resulting mixture of red liquid and orange solid allowed to cool to room temperature. The inside of the flask was scratched and the mixture cooled in a freezer overnight. The orange solid was collected by filtration and washed with ethyl acetate (10 ml) to give orange microcrystals (0.97 g, 1.57 mmol, 29%) of **12**. δ_{P} 64.2. δ_{H} 7.2 (5 H, m), 5.00 (1 H, m), 4.87 (1 H, m), 4.66 (m) and 4.57 (m) (combined integration height of the last two peaks: 3 H) and 4.28 (6 H, s). δ_{C} 136.3 (quat), 129.2, 127.2, 126.4 (m), 78.6 (d, J 118 Hz), 76.1 (m), 74.0 (m), 72.7 (m), 72.1 (m), and 70.6 (s). IR: 3097m, 1736w, 1594m, 1497m, 1490m, 1407w, 1389w, 1363w, 1341w, 1304w, 1247s, 1191w, 1173s, 1106m, 1079w, 1034m, 1025s, 1001w, 944s, 909s, 880s, 867m, 845m, 825s, 751s, 736w, 690vs, 670m, 613w, 522s, 489s, 464s, and 412w cm^{-1} . MS(FAB): m/z 642, 619, 505, 498, 481, 451, 433, 421, 391, 377, 361, 305, 243, 217, 204, 154, 146, 136, and many peaks below 136 (Found: C, 50.3; H, 3.7; N, 2.3. $\text{C}_{26}\text{H}_{23}\text{Fe}_2\text{NP}_2\text{S}_3$ requires C, 50.4; H, 3.7; N, 2.2%), mp 180 °C, decomposes to a black solid not melting below 300 °C.

Reaction of LR and dicyclohexylcarbodiimide to give compound 14

The compound LR (6.9 g, 17 mmol) and dicyclohexylcarbodiimide (3.8 g, 18 mmol) were heated in refluxing toluene (*ca.* 60 ml) for 6 d. After filtration, the filtrate was diluted with light petroleum (bp 60–80 °C, 55 ml). The addition of this light petroleum caused very little precipitation of solid. After removal of all the solvent in vacuum, recrystallization from ethyl acetate (30 ml) gave 2,4-bis(4-methoxyphenyl)-3-cyclohexyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide **14** as a white solid (2.28 g, 4.9 mmol, 29%). $\delta^{13}\text{C}$ - $\{^1\text{H}\}$, 163.5 (quat), 135.2 (m), 129.4 (quat), 127.7 (quat), 114.0 (m), 58.8, 55.5, 33.2 (CH_2), 32.5 (m, CH_2), and 25 (m, CH_2). $\delta^1\text{H}$ 8.4 [3H, dd, $^3J(\text{PH}) = 16$, $^3J(\text{HH}) = 8.8$], 7.0 [4 H, dd, $^4J(\text{PH}) = 3.4$ and $^3J(\text{HH}) = 8.8$ Hz], 3.91 (6 H, s), 3.4 (1 H, s), 1.7 to 0.9 (12 H, m). IR: 3067w, 3004m, 2932s, 2856s, 1591s, 1567m, 1497s, 1461 (sh), 1449s, 1410m, 1374w, 1349w, 1309m, 1293m, 1261s, 1180m, 1153w, 1101s, 1051w, 1023m, 997w, 932s, 915m, 890w, 877s, 852m, 829s, 815m, 800m, 749m, 697s, 645w, 627m, 613s, 549s, 514w, 501s, 471w, 426s, 385m, 342w and 282w cm^{-1} . MS(FAB): 492 (M + Na), 470 (M + H), 438 (M + H - S), 354, 277, 267, 234, 203, and 186. (M + H peak has isotropic distribution expected for $\text{C}_{20}\text{H}_{26}\text{NO}_2\text{P}_2$) (Found: C, 51.0; H, 5.0; N, 3.4. $\text{C}_{20}\text{H}_{25}\text{NO}_2\text{P}_2\text{S}_3$ requires C, 51.2; H, 5.4; N, 3.0%).

After removal of the ethyl acetate from the mother-liquor the orange tar that remained was distilled (3 mbar, 100–180 °C air-bath temperature) to give a colourless liquid (1.95 g, 14 mmol, 81%). IR (thin film): 2937s, 2858m, 2186s, 2102vs, 2062s, 1450m, 1362m, 986w, 927m, 892w, 801w, and 641w cm^{-1} . δ_{H} 3.7 (1 H, m) and 1.9 to 1.3 (11 H, m). δ_{C} 55.3, 33.1 (CH_2), 25.0 (CH_2), and 23.2 (CH_2). GCMS: single compound with a retention time of 10.776 min MS (EI): m/z 141, 98, 83, 82, 67, 55, 41, and 39.

The reaction of $\text{R}^1_2\text{P}_2\text{S}_4$ with $\text{PhCH}=\text{NH}(\text{C}_6\text{H}_3\text{Me}_2-2,4)$ to form compound 15

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (4.27 g, 7.63 mmol) and $\text{PhCH}=\text{NH}(\text{C}_6\text{H}_3\text{Me}_2-2,4)$ (1.6 g) were heated in toluene (70 ml) and

xylenes (80 ml) for three days. After cooling the mixture was filtered through a SiO_2 pad. This pad was washed with CH_2Cl_2 (4×50 ml) and these washings were combined with the filtrate. The solvents were removed in vacuum to give a red oil (5.5 g). Chromatography (64 g SiO_2 , elution with 500 ml of 20% CH_2Cl_2 , 30% CH_2Cl_2 , 40% CH_2Cl_2 in light petroleum followed by 500 ml CH_2Cl_2) gave two orange fractions. On removal of solvent the first fraction gave an orange solid which on extraction with hot ethyl acetate (*ca.* 10 ml) followed by cooling gave 3-(2,4-dimethylphenyl)-2,4-diferrocenyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide **15** as an orange solid (548 mg, 0.847 mmol, 11%). δ_{P} 66.9. δ_{C} 139.4 (m, quat), 139.2 (m, quat), 132.4, 131.6 (m), 127.3, 74.2 (d, J 13.6), 73.1 (d, J 13.4), 72.4 (br d, J 15.7 Hz), 71.0, 21.5, and 19.5. The aromatic area was re-examined with reduced sweep width: δ 139.44 (t, J 3.6), 139.20 (t, J 3.1), 132.43, 132.41, 131.63 (t, J 4.0 Hz) and 127.32. δ_{H} 6.79 (1 H), 6.64 (2 H), 5.04 (m, 2 H), 4.64 (m, 2 H), 4.59 (m, 2 H), 4.48 (m, 2 H), 4.30 (s, 10 H), 2.10 (s, 3 H) and 1.93 (s, 3 H). IR: 3096m, 3085m, 2958m, 2919m, 2857m, 1497m, 1451w, 1409m, 1390w, 1377w, 1365w, 1349w, 1309w, 1257m, 1226m, 1193w, 1179s, 1129w, 1107w, 1058w, 1024s, 1005m, 952s, 914s, 888s, 864m, 825m, 811m, 801w, 734w, 714s, 687vs, 630m, 603w, 576w, 552m, 511 (sh), 503 (sh), 486m, 473 (sh), 486m, 473w, 460s, 451s, 408m, 365w and 355w cm^{-1} . MS(FAB): m/z 647 (M^+) and 367 (Found: C, 52.2; H, 4.3; N, 2.2; S, 15.0. $\text{C}_{28}\text{H}_{27}\text{Fe}_2\text{NP}_2\text{S}_3$ requires C, 52.0; H, 4.2; N, 2.2; S, 14.9%).

The reaction of $\text{R}^1_2\text{P}_2\text{S}_4$ with 2,6-dimethylaniline to form compound 16

The compound $\text{R}^1_2\text{P}_2\text{S}_4$ (2.77 g, 4.94 mmol) and 2,6-dimethylaniline (5.25 ml, 5.2 g, 43 mmol) were mixed. After stirring at room temperature (30 min) xylene (150 ml) was added and this mixture heated under nitrogen (19 h) before being allowed to cool. The mixture was filtered through a SiO_2 pad which was then washed with CH_2Cl_2 (2 portions of 50 ml). The filtrate was evaporated to give a blood red oil which was applied to a flash column (SiO_2 70 g). Elution with light petroleum (300 ml) followed by 20% CH_2Cl_2 in light petroleum (500 ml) and 30% CH_2Cl_2 in light petroleum (500 ml) gave fractions which according to TLC contained an orange product. These fractions were combined and the solvent removed in vacuum to give an orange tar like solid. Recrystallization from ethyl acetate (90 ml) gave an orange solid (0.26 g). To the mother-liquor was added methanol (100 ml) to give a second crop of orange microcrystals. Both crops were combined and recrystallized from ethyl acetate to give 3-(2,6-dimethylphenyl)-2,4-diferrocenyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide **16** as an orange solid (471 mg, 0.728 mmol, 15%). δ_{P} 63.9. δ_{H} 6.97 (1 H, m), 6.84 (2 H, d, J 7.5 Hz), 5.14 (2 H, m), 4.74 (2 H, m), 4.61 (4 H, m), 4.38 (10 H, s) and 2.05 (6 H, s). δ_{C} 140.7 (m), 129.0 (t, J 0.6 Hz), 128.3 (m), 77.0 (m), 73.3 (m), 70.8 (s) and 21.1 (s). IR: 1465m, 1409m, 1390w, 1381w, 1364w, 1311w, 1260w, 1197s, 1180s, 1170s, 1106m, 1056w, 1023s, 1003m, 946m, 907s, 883vs, 869w, 834w, 824s, 776m, 719s, 683vs, 630w, 582w, 558w, 532s, 491s, 457vs, 410m, and 342m cm^{-1} . MS(FAB): m/z 647 (M^+), 582, 367, 302, 280, 248 and 217 (for M^+ the expected isotropic distribution was observed) (Found: C, 51.3; H, 4.2; N, 1.8. $\text{C}_{28}\text{H}_{27}\text{Fe}_2\text{NP}_2\text{S}_3$ requires C, 51.9; H, 4.2; N, 2.2%).

The reaction of heptamethyldisilazane, tetrahydrofuran and $\text{R}^1_2\text{P}_2\text{S}_4$ to form compound 17

Compound $\text{R}^1_2\text{P}_2\text{S}_4$ (719 mg, 1.28 mmol), heptamethyldisilazane (0.5 ml, 0.4 g, 2.29 mmol) and THF (2 ml, 1.8 g, 25 mmol) were heated together in a sealed tube in an oil-bath (50–70 °C) for 5 h, to give a dark red solution. This was allowed to stand for 10 h before the removal of all volatile material in vacuum. **CAUTION:** bis(trimethylsilyl) sulfide has an extremely strong unpleasant smell like that of butanethiol.

When evaporating any reaction mixture which might contain it a high vacuum line fitted with a trap cooled by liquid nitrogen should be used. After the evaporation, while the trap contents are still frozen, sodium hypochlorite solution should be added and allowed to stand.

This tar was found to be soluble in light petroleum, chloroform, and ethyl acetate. After being dissolved in light petroleum it was filtered through Al_2O_3 , the Al_2O_3 pad washed with light petroleum until the filtrate was no longer orange (*ca.* 50 ml used). Evaporation of the light petroleum gave compound **17** as a syrup like orange oil (803 mg, 1.52 mmol, 66%) which, on standing, solidified. δ_{H} 4.62 (m), 4.47 (m), 4.37 (m), 4.34 (m), 4.28 (s) (total integration for δ 4.7 to 4.2 is 9 H), 3.59 (2 H, t, J 6.1 Hz), 2.9 (2 H, m), 2.4 [3 H, d, $^3J(\text{PH}) = 16$ Hz], 1.7 (4 H, m), 0.28 (9 H, s) and 0.09 (8 H, s). $\delta^{31}\text{P}-\{\text{H}\}$ 82.7. $\delta^{13}\text{C}-\{\text{H}\}$ 58.9 (CH_2), 30.1, 28.6 (CH_2), 26.5 (CH_2), 23.4 (CH_2), 0.0 and -3.8 . $^{13}\text{C}-^1\text{H}$ Correlation (^{13}C δ 10–70, ^1H 1.0–5.0): $\delta^{13}\text{C}$ ($\delta^1\text{H}$) 58.9 (3.6), 30.1 (2.4), 28.6 (1.7), 26.5 (2.9), and 23.4 (1.7). IR: 3100m, 2953s, 2907s, 2864s, 2817m, 1452m, 1436m, 1412m, 1387m, 1368w, 1299w, 1261 (sh), 1250s, 1196 (sh), 1180s, 1170s, 1100s, 1063s, 1027s, 1003m, 964m, 903s, 882s, 843s, 759s, 736s, 701s, 691 (sh), 645m and 628s cm^{-1} . MS(FAB): m/z 527 (M^+), expected isotropic distribution observed for molecular ion. mp 44–46 °C.

Reaction of $\text{R}_2^1\text{P}_2\text{S}_4$ with (*N,N'*-diphenylurea) to form compounds **12** and **18**

The compound $\text{R}_2^1\text{P}_2\text{S}_4$ (2.8 g, 4.9 mmol) and *N,N'*-diphenylurea (2.0 g, 9.4 mmol) were refluxed in xylene (100 ml) (17 h) before being allowed to cool. Filtration through silica, followed by washing the silica pad with CH_2Cl_2 , gave on evaporation a brown tar (3.6 g). Flash column chromatography on silica (38 g, elution with light petroleum– CH_2Cl_2) gave an orange material **12** (225 mg, 316 μmol , 3%). δ_{P} 64.3. δ_{H} 7.19 (m) and 7.16 (4 H, m), 4.93 (1 H, m), 4.80 (1 H, m), 4.58 (1 H, m), 4.50 (1 H, m) and 4.21 (5 H, s). IR: 3098m, 1594m, 1497m, 1491m, 1247s, 1180s, 1173s, 1106m, 1034m, 1025s, 943s, 909s, 881s, 867w, 845w, 825m, 751m, 736w, 690vs, 670m, 618w, 522m, 489s, 405s, 412w, 359w, and 336w cm^{-1} . mp 180 °C (decomp.). This solid is slightly impure 2,4-diferrocenyl-3-phenyl-1,3,2,4-thiazadiphosphetane 2,4-disulfide. Almost all the solid was dissolved in ethyl acetate and the resulting solution allowed to cool to give red crystals.

Further elution with CH_2Cl_2 –light petroleum mixtures gave more orange fractions, and evaporation gave an orange solid **18** (674 mg). This was recrystallized from ethyl acetate to give after drying two crops of an orange yellow solid (222 and 123 mg). δ_{H} 7.2 (m), 7.0 (t), 5.2 (d), 4.65 (m), 4.42 (m), 4.34 (s), 4.13 (q), 2.05 (s) and 1.26 (t). IR: 3367m, 3289m, 3247s, 3042m, 1722s, 1654w, 1599s, 1498s, 1400s, 1321w, 1281s, 1240m, 1226s, 1175m, 1108w, 1077w, 1029s, 999m, 943s, 910s, 894m, 856w, 840w, 826m, 799m, 772w, 756s, 746s, 694s, 676s, 637w and 617w cm^{-1} .

This solid contained ethyl acetate, to remove this it was recrystallized from toluene to give an orange yellow solid (230 mg, 532 μmol , 6%). δ_{P} 54.5. δ_{H} 7.2 (8 H, m), 7.0 (2 H, t), 5.2 (2 H, d, J 12 Hz), 4.65 (2 H, m), 4.42 (2 H, m) and 4.34 (3 H, s). δ_{C} 139.6 (quat), 129.2, 122.6, 119.5 (d, J 6), 72.3 (d, J 14), 71.4 (d, J 12 Hz), and 70.2. IR (KBr): 3382s, 3243s (br), 3087w, 3042w, 3019w, 1599s, 1496s, 1474sm, 1401m, 1383s, 1324w, 1301 (sh), 1283s, 1225m, 1192w, 1179 (sh), 1172m, 1106w, 1078w, 1031m, 1000w, 948s, 915s, 892m, 829m, 791w, 753s, 694s, 674s, 637w, 616w, 599m, 578w, 564w, 524w, 501w, 488m, 474s, 437 (sh), 417m, 390w and 356w cm^{-1} . IR (CH_2Cl_2): 3388m, 1605s, 1503m, 1387m and 1271m cm^{-1} . MS(EI): m/z 432 (M^+), 340 ($\text{M} - \text{PhNH}_2$), 274, 248, 217, 186, 155, 122, and 93. Molecular ion at m/z 432.0512 ($^{12}\text{C}_{22}^1\text{H}_{21}^{56}\text{Fe}^{14}\text{N}_2^{31}\text{P}^{32}\text{S}$ requires 432.05120 (within 0.1 ppm)) (Found: C, 60.4; H, 4.6; N, 6.3. $\text{C}_{22}\text{H}_{21}\text{Fe}_2\text{N}_2\text{PS}$ requires C, 56.9; H, 4.6; N, 6.0%).

The reaction of $\text{R}_2^1\text{P}_2\text{S}_4$ with *N,N'*-dimethyl-*N,N'*-diphenylurea to form compound **19**

N,N'-Dimethyl-*N,N'*-diphenylurea (2.6 g, 11 mmol) was dissolved in xylenes (150 ml); to this was added $\text{R}_2^1\text{P}_2\text{S}_4$ (3 g, 5.4 mmol). This mixture was refluxed for 17 h. After being allowed to cool the xylene was removed in vacuum to give a red tar that was subjected to flash column chromatography on silica (50 g, 500 ml 20% CHCl_3 in light petroleum (bp 60–80 °C), 500 ml of 50% CHCl_3 in light petroleum followed by CHCl_3). An orange fraction was collected, which after removal of the solvent gave a red oil. This red oil became a solid that was then recrystallized from ethyl acetate to give compound **19** as an orange powder (257 mg, 324 μmol , 9%). δ_{P} 76.59 [dd, $^2J(\text{PP}) = 54$ and $^2J(\text{PP}) = 46$], 74.47 [d, $^2J(\text{PP}) = 53$] and 74.48 [d, $^2J(\text{PP}) = 47$ Hz]. δ_{H} 4.96 (2 H, m), 4.85 (2 H, m), 4.60 (2 H, m), 4.54 (2 H, m), 4.47 (2 H, m), 4.40 (2 H, m), 4.35 (5 H, s), and 4.25 (10 H, s). δ_{C} 74.0 to 72.9 (m), 72.2 (m) and 71.1 (s). MS(FAB): m/z 792(M^+), and 727 ($\text{M} - \text{C}_5\text{H}_5$) (expected isotropic distribution observed for M^+). IR: 3095m, 1412m, 1391w, 1370w, 1351w, 1316w, 1191s, 1107m, 1057w, 1029m, 1000w, 942vs, 894s, 865w, 841 (sh), 822m, 798m, 758s, 680m, 666m, 488m, 471s, 428m, 403w and 341w cm^{-1} . mp 233–235 °C, melts with decomposition (Found: C, 45.3; H, 3.6; N, 0.0; S, 11.8. $\text{C}_{10}\text{H}_9\text{FeOPS}$ requires C, 45.5; H, 3.4; N, 0.0; S, 12.1%).

The synthesis of *N*-methyl-*N,N'*-diphenylurea

Phenyl isocyanate (46 ml, 50 g, 420 mmol) was added cautiously, over 30 min, to *N*-methylaniline (50 ml, 49.5 g, 462 mmol) dissolved in CH_2Cl_2 (50 ml). An exothermic reaction occurred and the phenyl isocyanate added at such a rate to maintain a gentle reflux. After stirring for 30 min, the CH_2Cl_2 was removed in vacuum to give an off white solid. This was recrystallized from hot ethanol (10 ml) before being stirred with hot light petroleum (bp 60–80 °C fraction) (500 ml). After cooling the white solid was filtered off and dried in vacuum to give *N*-methyl-*N,N'*-diphenylurea (82.5 g, 365 mmol, 94%). δ_{H} 7.47 (t, J 7.4), 7.3 (m) (combined integration for the multiplets and the triplet: 9 H), 6.99 (1 H, t, J 5.8 Hz), 6.3 (1 H, br) and 3.32 (3 H, s). $\delta^{13}\text{C}-\{\text{H}\}$ 154.4 (quat), 143.0 (quat), 139.0 (quat), 130.3, 128.8, 127.8, 127.4, 122.8, 119.3, and 37.3. **CAUTION:** phenyl isocyanate is toxic and a strong irritant. All contact should be avoided and care taken to decontaminate glassware before cleaning. Small traces of PhNCO can be destroyed using ethanol.

The reaction of $\text{R}_2^1\text{P}_2\text{S}_4$ with *N*-methyl-*N,N'*-diphenylurea

N-Methyl-*N,N'*-diphenylurea (4 g, 17.7 mmol) and $\text{R}_2^1\text{P}_2\text{S}_4$ (5.24 g, 9.4 mmol) in xylenes (150 ml) were refluxed (17 h). After cooling, chromatography on SiO_2 (97 g, elution with 300 ml light petroleum, 1 L 40% CH_2Cl_2 in light petroleum, 500 ml CH_2Cl_2 , and 500 ml 20% ethyl acetate in CH_2Cl_2), followed by recrystallization from ethyl acetate (50 ml) gave compound **19** as an orange powder (1.38 g, 1.74 mmol, 29%). $^{31}\text{P}-\{\text{H}\}$ and ^1H NMR spectra identical with those of the product *N,N'*-dimethyl-*N,N'*-diphenylurea.

Electrochemical measurements

Cyclic voltammograms, 20–200 mV s^{-1} , were recorded at 22 ± 1 °C using an EG & G Princeton Applied Research (PAR) Model 173 potentiostat interfaced to a MacLab/2e and operated using EChem software (ADInstruments Ltd) with a Macintosh LC computer. No IR compensation was employed. Square wave voltammograms were recorded, as appropriate, to resolve overlapping redox waves. A three compartment electrochemical cell was employed, with a platinum wire (0.32 cm^2 surface area) working electrode, a platinum-mesh counter electrode, and a Radiometer sodium chloride saturated calomel

Table 5 Details of the crystal data and refinements for compounds **8**, **10** and **18**

	8	10	18
Formula	C ₂₃ H ₂₄ Fe ₂ N ₂ OP ₂ S ₃	C ₂₇ H ₂₅ Fe ₂ NP ₂ S ₃	C ₂₂ H ₂₁ FeN ₂ PS
Formula weight	614.3	633.3	432.2
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>n</i>
<i>a</i> /Å	11.776(3)	7.347(2)	9.568(2)
<i>b</i> /Å	12.172(2)	14.262(3)	12.6641(9)
<i>c</i> /Å	9.949(1)	25.660(2)	16.383(2)
α /°	106.28(1)	—	—
β /°	108.82(1)	95.75(1)	92.24(1)
γ /°	80.96(2)	—	—
<i>V</i> /Å ³	1292	2575	1984
<i>Z</i>	2	4	4
<i>D</i> _c /Mg m ⁻³	1.58	1.572	1.45
μ /mm ⁻¹	12.6	12.15	7.9
Reflections	4066	4198	3319
Observed reflections (<i>I</i> > 2.0σ(<i>I</i>))	2599	2100 (<i>I</i> > 3.00σ(<i>I</i>))	1832
Final <i>R</i> , <i>R</i> '	0.042, 0.039	0.060, 0.058	0.041, 0.035

reference electrode (SSCE). The platinum wire working electrode was pretreated before measurements by anodization, then cathodization (1 min each at 100 mA in 1 mol dm⁻³ sulfuric acid) followed by washing with deionized water, then acetonitrile and finally air dried. All measurements were made using nitrogen purged acetonitrile solutions containing 0.001 mol dm⁻³ of each ferrocenyl compound and 0.2 mol dm⁻³ Bu₄NClO₄ supporting electrolyte.

Formal redox potentials were calculated from cyclic voltammograms as $E_f = (E_{pc} + E_{pa})$ where E_{pc} = cathodic peak potential and E_{pa} = anodic peak potential. For diferrocenes formal redox potentials can be interpreted as averages of the values of the two ferrocene groups. Ferrocene ($E_f = 0.40$ V vs. SSCE) was used as both a reference and as a test compound.

Crystallography

Details of the data collections and refinements are summarized in Table 5, experimental details have been previously reported¹⁵ for compounds **1**, **3**, **11** and **12**. For **8**, **10** and **18** data were collected at 298 K using copper radiation and ω scans with a Rigaku AFC7S diffractometer. Intensities were corrected for Lorentz-polarization and for absorption effects. 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 idealized. Refinements were by full-matrix least squares based on *F* using TEXSAN.³¹

CCDC reference number 186/1625.

See <http://www.rsc.org/suppdata/dt/1999/3419/> for crystallographic files in .cif format.

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