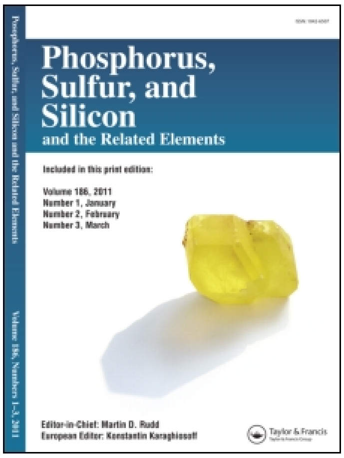

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HETEROCYCLES FROM DIFERROCENYL DITHIADIPHOSPHETANE DISULFIDE

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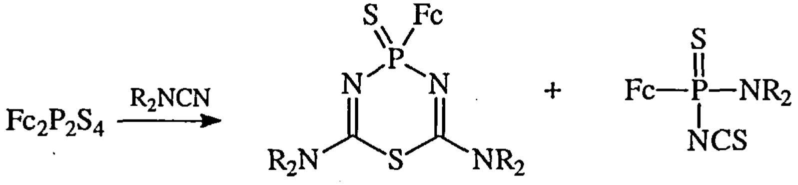
Diferrocenyl dithiadiphosphetane disulfide ($Fc_2P_2S_4$) has been found act as a source of a reactive species, believed to be $FcPS_2$, which reacts with dialkyl cyanamides, imines, aldehydes and strained alkenes to form a variety of phosphorus compounds. These reactions include a convenient route to thiaphosphetanes.

When diferrocenyl dithiadiphosphetane disulfide[1] ($Fc_2P_2S_4$) was combined with piperidine-1-carbonitrile at room temperature a reaction occurs which forms a 1,3,5,4-thiadiazaphosphinane (**1a**) and a *P*-isothiocyanate (**2a**). While treatment of $Fc_2P_2S_4$ with dimethylcyanamide in hot toluene gives **1b** and **2b**,[2,3] Figure 1.



1 2

R_2N	Yield	R_2N	Yield
a. NC_5H_{10}	65%	**a.** NC_5H_{10}	18%
b. NMe_2	60%	**b.** NMe_2	15%

Figure 1.

It is thought that both products are formed via a common intermediate (X), which can either react with a second molecule of the dialkyl cyanamide or rearrange to the *P*-isothiocyanate. To investigate this, to a hot suspension of $Fc_2P_2S_4$ was slowly added dilute solutions of the dialkyl cyanamides. From these reactions the major product isolated (>55%) was **2a** or **2b**. Similar results were obtained with Lawesson's reagent, which are in disagreement with existing work.[4] Treatment of **2b** with Me_2NCN in hot xylenes failed to give **1b**, suggesting an irreversible rearrangement converts X to the *P*-isothiocyanate, Figure 2.

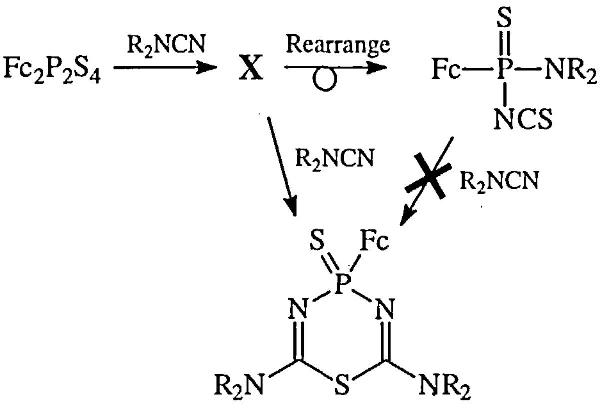
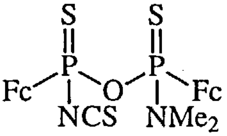


Figure 2.

A third product (**3**) was isolated from the slow treatment of $Fc_2P_2S_4$ with Me_2NCN, **3** contains an oxygen atom and is thought to have formed from a trace of water present in the reaction mixture. Figure 3.



3

Figure 3.

For this compound sequential oxidation of the ferrocenyl groups has been observed by square wave voltammetry,[5] Figure 4.

Square wave voltammogram for **3**.

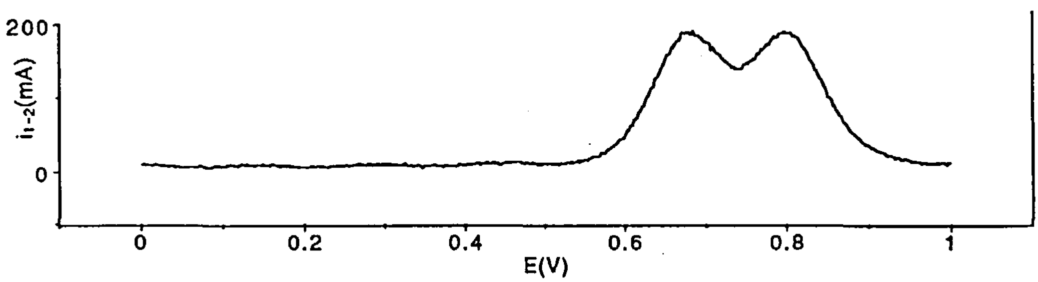


Figure 4.

When an ten-fold excess of norbornadiene was heated (ca. 80°C) with $Fc_2P_2S_4$ a high yield (69%) of a thiaphosphetane (**4**) was isolated,[6] $^{31}P\text{-}\{^{1}H\}$ NMR on the crude product indicated it to be pure, no evidence was obtained for the formation of a *Homo* Diels-Alder product. Treatment of norbornene and hexamethyl dewarbenzene under similar conditions, followed by chromatography and recrystallization gave lower yields (29% and 5%) of thiaphosphetanes **5** and **6**[6], Figure 5.

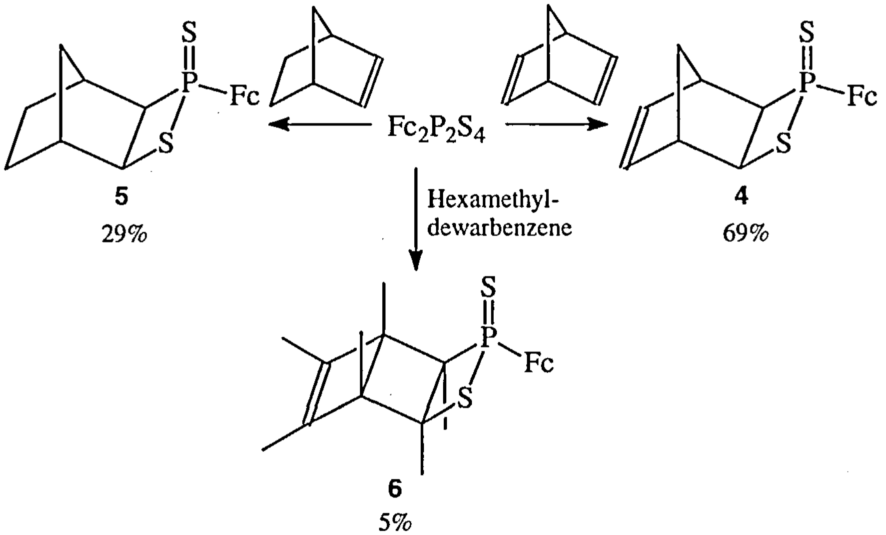


Figure 5.

For **4** and **6**, X-ray crystallography was used to examine the shape of the thiaphosphetane rings. It was found that in **6** the steric repulsion between a methyl group and the exocyclic sulfur causes a distortion away the planar thiaphosphetane ring seen for **4**. Below are partial crystal structures of the two compounds, the ferrocenyl and some methyl groups are omitted for clarity. Figure 6.

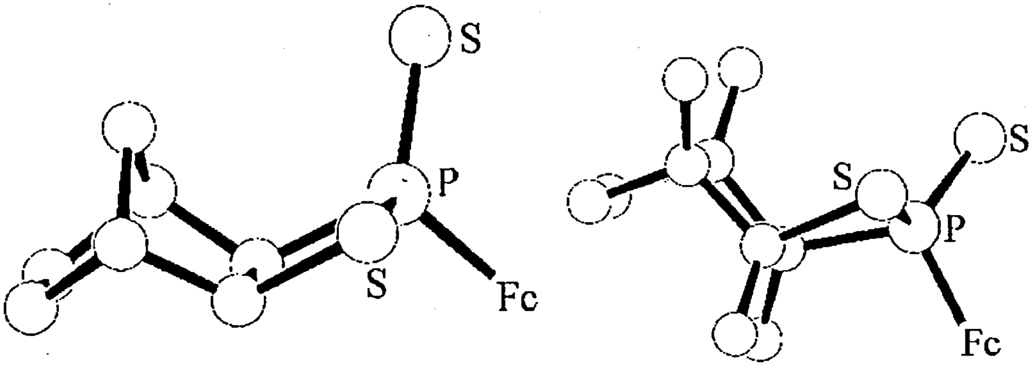


Figure 6.

It was found that treatment of $Fc_2P_2S_4$ with 0.66 eqv. of an aldehyde gave in low yields of trithiaphosphinanes (**7a/7b**) mixed with triferrocenyl trioxatriphosphinane trisulfide (**8**), recrystallization from ethyl acetate rendered pure the trithiaphosphinanes. It is believed that the action of $Fc_2P_2S_4$ on the aldehyde forms **8** and the thioaldehyde which then reacts with more $Fc_2P_2S_4$' to form the trithiaphosphinane. This second reaction is likely to be a multistage reaction as for three molecules to react together in one step is unlikely, Figure 7.

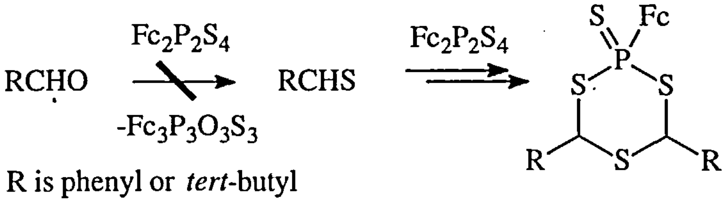


Figure 7.

When $Fc_2P_2S_4$ is treated with *N*-benzylidene benzyl amine a complex mixture of products is formed, from which was isolated a thiazadiphosphetane disulfide and a dithiaphospholane. The formation of the thiazadiphosphetane disulfide can be rationalised as a product formed by the exchange of a sulfur for the =NBn group followed by another step. While the dithiaphospholane is formed by the action of thiobenzaldehyde on $Fc_2P_2S_4$, Figure 8.

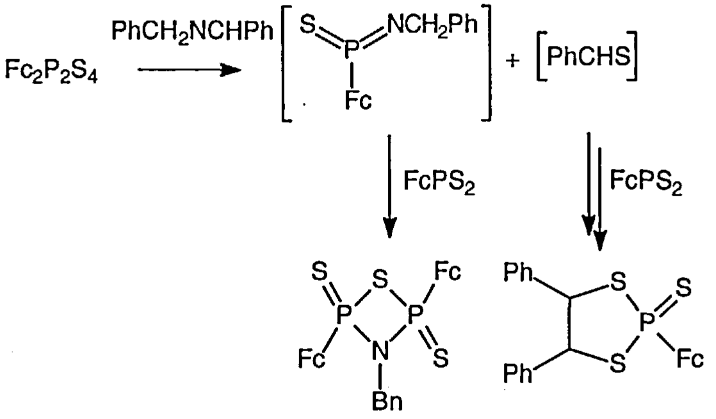


Figure 8.

References and notes.

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2. Satisfactory microanalyses, spectral and electrochemical data were obtained for all new compounds.

3. M.R.S.J. Foreman, A.M.Z. Slawin and J.D. Woollins, *J. Chem. Soc. Chem. Commun.* In press.

4. A. Schmidpeter and N. Schindler, *Angew. Chem.*, *Int. Ed. Engl.*, 1968, 943.

5. Electrochemical experiments were performed in the presence of 0.2 M $[Bu_4N][ClO_4]$ in acetonitrile, thanks to Dr Roger J. Mortimer for his help with electrochemistry.

6. M.R.S.J. Foreman, A.M.Z. Slawin and J.D. Woollins, *J. Chem. Soc. Chem. Commun.* 1997, 855.