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To cite this Article Foreman, Mark R. S. J. , Slawin, Alexandra M. Z. and Woollins, J. Derek (1997) 'Heterocycles from Diferrocenyl Dithiadiphosphetane Disulfide', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 469-472 To link to this Article: DOI: 10.1080/10426509708545661

URL: http://dx.doi.org/10.1080/10426509708545661

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# HETEROCYCLES FROM DIFERROCENYL DITHIADIPHOSPHETANE DISULFIDE

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Diferrocenyl dithiadiphosphetane disulfide (Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub>) has been found act as a source of a reactive species, believed to be FcPS<sub>2</sub>, 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<sup>1</sup> (Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub>) 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<sub>2</sub>P<sub>2</sub>S<sub>4</sub> with dimethylcyanamide in hot toluene gives 1b and 2b,<sup>2,3</sup> Figure 1.

Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub> 
$$\xrightarrow{R_2NCN}$$
  $\xrightarrow{N}$   $\xrightarrow{$ 

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. 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.

Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub> 
$$\xrightarrow{R_2NCN}$$
 X  $\xrightarrow{Rearrange}$  Fc—P—NR<sub>2</sub>
NCS

R<sub>2</sub>NCN

S Fc

NR<sub>2</sub>NCN

R<sub>2</sub>NCN

R<sub>2</sub>NCN

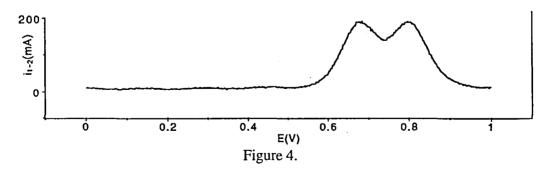
R<sub>2</sub>NCN

R<sub>2</sub>NCN

A third product (3) was isolated from the slow treatment of Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub> with Me<sub>2</sub>NCN, 3 contains an oxygen atom and is thought to have formed from a trace of water present in the reaction mixture. Figure 3.

For this compound sequential oxidation of the ferrocenyl groups has been observed by square wave voltammetry,<sup>5</sup> Figure 4.

### Square wave voltammogram for 3.



When an ten-fold excess of norbornadiene was heated (ca.  $80^{\circ}$ C) with  $Fc_2P_2S_4$  a high yield (69%) of a thiaphosphetane (4) was isolated,  $^{6}$   $^{31}P-\{^{1}H\}$  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.

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.

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.

RCHO 
$$\xrightarrow{Fc_2P_2S_4}$$
 RCHS  $\xrightarrow{Fc_2P_2S_4}$  S Fc

 $\xrightarrow{-Fc_3P_3O_3S_3}$  R is phenyl or *tert*-butyl

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.

Fc<sub>2</sub>P<sub>2</sub>S<sub>4</sub> PhCH<sub>2</sub>NCHPh 
$$\begin{bmatrix} S & NCH_2Ph \\ Fc \end{bmatrix}$$
 +  $\begin{bmatrix} PhCHS \end{bmatrix}$  FcPS<sub>2</sub>  $\begin{bmatrix} FcPS_2 & FcPS_2 \end{bmatrix}$  FcPS<sub>2</sub>  $\begin{bmatrix} S & Fc & Ph & S & S \\ Ph & S & Ph & S & Fc \end{bmatrix}$  Figure 8.

#### References and notes.

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