Phosphorus–sulfur–nitrogen heterocycles from diferrocenyl dithiadiphosphetane disulfide

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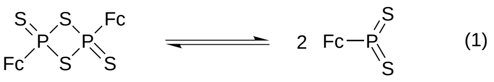
FcP(S)S$_2$P(S)Fc undergoes cycloaddition reactions with C–N bonds to generate C–P–N rings including the novel, boat shaped, PN$_2$C$_2$S system as well as four-membered P$_2$CN rings.

Cycloaddition reactions provide one of the most exciting entries into heterocyclic compounds. We have recently developed[1] a facile synthesis of FcP(S)S$_2$P(S)Fc **1** (Fc = ferrocenyl) which can be considered as consisting of two FcPS$_2$ units (capable of a wide range of cycloaddition reactions) in solution [eqn. (1)].



(1)

Very few cycloaddition reactions of phosphetane disulfides have been described, though some reactions of Lawesson's reagent **2** with amines,[2] ureas[3] and cyanamides[4] to form sulfur–phosphorus–nitrogen compounds are known. Here we describe the results of our studies into the reactions of cyanamides, and related systems with **1**. The first example of the synthesis (and X-ray structure) of a PN$_2$C$_2$S is reported together with a novel, readily generalised, synthesis of the P$_2$SN ring system.

Thus, the reaction of **1** with dimethylcyanamide gives *P*-ferrocenyl 2,6-bis(dimethylamino)1,3,5,4-thiadiazaphosphorine-4-sulfide **3** in good yield and *P*-ferrocenyl *P*-dimethylamino thiophosphoroisothiocyanate **4** in lower yield.† Both **3** and **4** displayed the expected spectroscopic properties. The X-ray structure‡ of **3** (Fig. 1) confirms the identity of the heterocycle, the PC$_2$N$_2$S ring adopts a distorted boat conformation with the P and S(2) atoms at the prow and stern of the boat. The P and S(2) atoms lie 0.48 and 0.30 Å, respectively above the C(1)N(1)C(2)N(2) mean plane [max. deviation 0.007 Å for C(1)] with the C(1)C(2)S(2) and PN(1)N(2) planes being inclined by 15.7 and 30.0°, respectively, to this plane. Within the six-membered ring the bond lengths are in accord with the localised structure drawn in Scheme 1, *i.e.* short C–N bonds [C(1)–N(1) 1.289(6), C(2)–N(2) 1.290(6) Å] and 'normal' single P–N and C–S bond lengths. The angles at the ring nitrogen atoms are close to trigonal whilst the C(1)–S(2)–C(2) angle is significantly contracted at 101.0(2)° and the N(1)–P(1)–N(2) is close to tetrahedral [108.2(2)°]. The exocyclic P=S and ferrocenyl groups occupy (approximate) axial and equatorial sites whilst the NMe$_2$ groups are only slightly out of the central C$_2$N$_2$ plane of the ring [N(3) and N(4) lie 0.16 and 0.25 Å below the C$_2$N$_2$ plane and on the opposite side to S(2) and P(1)]. The coplanarity of the NMe$_2$ groups is accompanied by short C–N bond lengths [C(2)–N(4) 1.365(6), C(1)–N(3) 1.335(6) Å] suggesting some degree of delocalisation in this part of the molecule. The cyclopentadienyl rings in the ferrocenyl group are twisted by *ca.* 72° with respect to (w.r.t.) the C$_2$N$_2$ ring plane. In the structure of **4** (Fig. 2)‡ the phosphorus centre is approximately tetra-

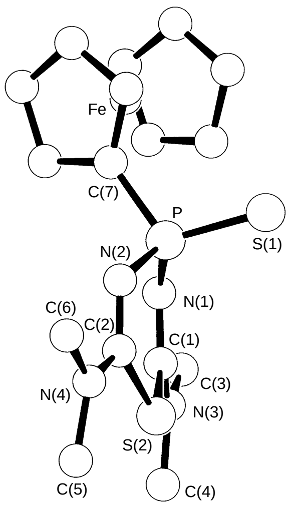
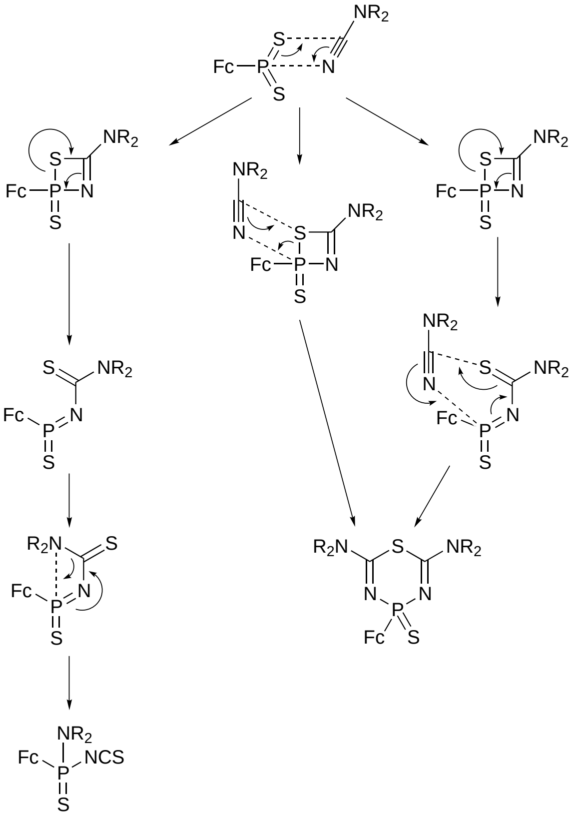


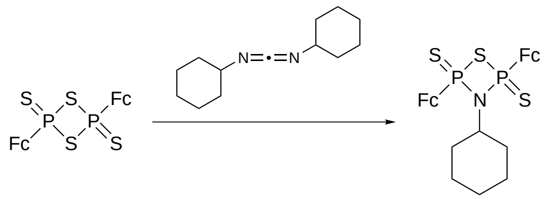
Fig. 1 X-Ray crystal structure of **3**. Important bond lengths (Å) and angles (°): P–N(1) 1.648(6), P–N(2) 1.664(4), P–S(1) 1.941(2), P(1)–C(7) 1.783(5), N(1)–C(1) 1.289(6), N(2)–C(2) 1.290(6), C(1)–S(2) 1.788(5), C(2)–S(2) 1.771(5), C(1)–N(3) 1.335(6), C(2)–N(4) 1.365(6); N(1)–P–N(2) 108.2(2), P–N(1)–C(1) 122.6(4), P–N(2)–C(2) 121.0(4), N(1)–C(1)–S(2) 125.4(5), N(2)–C(2)–S(2) 127.3(4), C(1)–S(2)–C(2) 101.0(2), S(1)–P–C(7) 111.1(2), N(1)–P–S(1) 114.6(1), N(2)–P–S(1) 113.6(2), N(1)–P–C(7) 104.4(4), N(2)–P–C(7) 103.9(2).



Scheme 1

hedral, interestingly P–N(1) is substantially shorter [1.631(4) Å] than P–N(11) [1.700(5) Å] reflecting the difference in electronegativities of the NMe_2 and NCS groups. The formation of these products presents a challenge mechanistically; we believe that a series of [2 + 2] reactions are a reasonable explanation for the formation of **3** and **4** (Scheme 1).

The reaction of dicyclohexylcarbodimide with **1** gives [eqn. (2)] 2,4-diferrocenyl-3-cyclohexyl-1,3,2,4-thiaazadiphosphorine-2,4-disulfide **5**.† Alternatively reaction of **1** with *N*-(benzylidene)aniline yields the phenyl analogue **6**.† Compounds **5** and **6** display the expected spectroscopic properties. There are only two previous reported examples[5,6] of the crystallographic characterisation of the RP(S)SNP(S)R rings. The X-ray structures‡ of **5** and **6** are isomorphous and we shall only discuss **6**. The molecule (Fig. 3) has crystallographic twofold symmetry and the central P_2NS ring is thus flat with the S(1) and S(1*) atoms lying on opposite sides of the ring. Within the rings the bond lengths are appropriate for P–N and P–S single bonds whilst the internal ring angles [S(2)–P(1)–N(1) 87.8(2), P(1)–N(1)–P(1*) 104.5(4), P(1)–S(2)–P(1*) 79.9(2)°] indicate substantial ring strain. The phenyl substituent is twisted by *ca.* 14° w.r.t. the P_2NS plane in **6**.



(2)

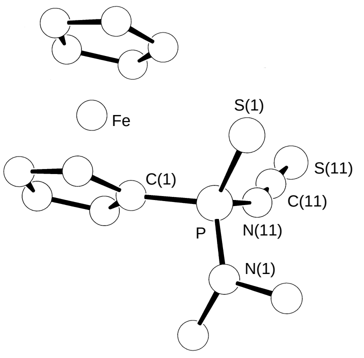


Fig. 2 X-Ray crystal structure of **4**. Important bond lengths (Å) and angles (°): P–C(1) 1.766(5), P–S(1) 1.914(2), P–N(1) 1.631(4), P–N(11) 1.700(5), N(11)–C(11) 1.166(6), C(11)–S(11) 1.538(7); C(1)–P–S(1) 116.7(2), C(1)–P–N(1) 107.3(2), C(1)–P–N(11) 101.2(2), N(1)–P–S(1) 113.2(2), N(1)–P–N(11) 104.9(3), N(11)–P–S(1) 113.2(2), P–N(11)–C(11) 156.5(6), N(11)–C(11)–S(11) 177.1(6).

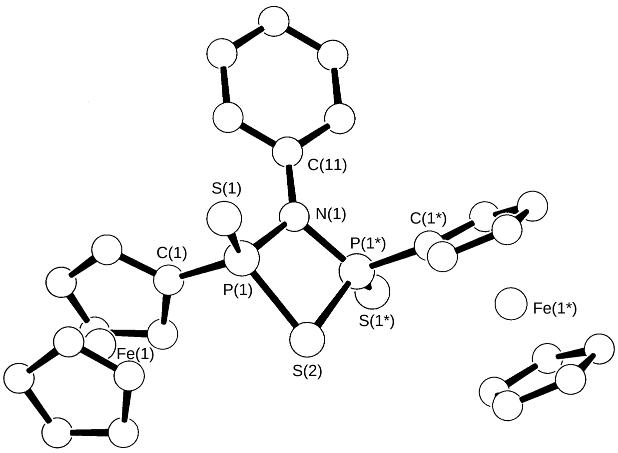


Fig. 3 X-Ray structure of **6**, **5** is isomorphous (and is not illustrated). Important bond lengths (Å) and angles (°) with values for **5** given in square brackets: P(1)–C(1) 1.789(5) [1.785(6)], P(1)–S(1) 1.917(3) [1.918(3)], P(1)–S(2) 2.098(3) [2.095(3)], P(1)–N(1) 1.704(5) [1.675(5)]; C(1)–P(1)–S(1) 114.3(3) [114.1(2)], C(1)–P(1)–N(1) 108.4(3) [109.2(2)], C(1)–P(1)–S(2) 106.6(3) [105.9(3)], S(1)–P(1)–S(2) 120.1(1) [119.9(1)], S(1)–P(1)–N(1) 116.5(2) [116.7(2)], S(2)–P(2)–N(1) 87.8(2) [87.9(2)], P(1)–N(1)–P(1*) 104.5(4) [105.3(5)], P(1)–S(2)–P(1*) 79.9(2) [79.0(2)].

Footnotes

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† **3** and **4**: **1** (2.91 g, 5.2 mmol) and dimethylcyanamide (1.5 g, 21 mmol) were refluxed together in toluene (50 ml) for 8 min. Silica gel chromatography using firstly light petroleum–toluene and then CH_2Cl_2 as the eluent gave **3** and **4** (2.6 g, 60 and 0.57 g 15% yields respectively).

5: *N,N′*-Dicyclohexylcarbodiimide (0.72 g, 3.5 mmol) and **1** (1.9 g, 3.4 mmol) were refluxed in toluene (10 ml) for 7 days. After removal of solvent and chromatography (light petroleum) an orange solid was obtained. This was washed with boiling ethyl acetate to give after filtration **5** (77 mg, 101 μmol, 3%) as a orange solid.

6: **1** (3.0 g, 5.36 mmol) and *N*-(benzylidene)aniline (2.0 g, 11.0 mmol) were refluxed in toluene (150 ml) (24 h). After addition of xylenes (100 ml) the reaction was refluxed for a further 64 h. Chromatography on silica, elution with 500 ml of 40% CH_2Cl_2 in light petroleum followed by 500 ml of CH_2Cl_2, gave a red solid. Recrystallisation from ethyl acetate yielded 0.97 g. 1.57 mmol, 29%.

‡ *Crystal data* Common to all determinations: Diffractometer Rigaku AFC7S $2\theta_{max}$ 120°, Cu-Kα radiation, λ = 1.541 78 Å, T = 296 K, structure solutions by direct methods, refinements employed teXsan. **3**: $C_{16}H_{21}FeN_4PS_2$, M = 420.3, monoclinic, space group $P2_1/c$ (no. 14), a = 13.084(4), b = 7.897(6), c = 18.364(5) Å, β = 97.31(2)°, U = 1882(1) Å^3, D_c = 1.483 g cm^{-3}, Z = 4, 3184 reflections measured, 1820 with $I > 2\sigma(I)$. All non-H atoms refined anisotropically to yield R = 0.040 and R_w = 0.038 for 218 parameters. **4**: $C_{13}H_{15}FeN_2PS_2$, M = 350.2, monoclinic, space group $P2_1/n$ (no. 14), a = 7.6883(9), b = 20.6140(9), c = 9.8804(9) Å, β = 90.700(9)°, U = 1566(2) Å^3, D_c = 1.486 g cm^{-3}, Z = 4, 2162 reflections measured, 1359 with $I > 2\sigma(I)$. All non-H atoms refined anisotropically to yield R = 0.037 and R_w = 0.037 for 173 parameters. **5**: $C_{26}H_{29}Fe_2NPS_3$, M = 625.3, orthorhombic, space group *Pbcn* (no. 60), a = 17.260(5), b = 15.020(3), c = 10.333(4) Å, U = 2678(1) Å^3, D_c 1.550 g cm^{-3}, Z = 4, 2304 reflections measured, 840 with $I > 2\sigma(I)$. The cyclohexyl group was disordered and the two sites were refined anisotropically with 0.6 and 0.4 occupancies, only the H-atoms on the higher occupancy site were included in the refinement. The remaining non-H atoms were refined anisotropically to yield R = 0.041 and R_w = 0.049 for 170 parameters. **6** $C_{26}H_{23}Fe_2NPS_3$, M = 619.3, orthorhombic, space group *Pbcn* (no. 60), a = 16.723(2), b = 14.861(2), c = 10.216(3) Å, U = 2538(1) Å^3, D_c = 1.620 g cm^{-3}, Z = 4, 2186 reflections measured, 948 with $I > 2\sigma(I)$. R = 0.048 and R_w = 0.035 for 152 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/480.

References

1 M. R. StJ. Foreman, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 3653.

2 K. Clausen, A. A. Ei-Barbary and S. O. Lawesson, *Tetrahedron*, 1981, **37**, 1019.

3 A. A. El-Barbary and S. O. Lawesson, *Indian J. Chem. Sect. B*, 1984, **23**, 655.

4 A. Schmidpeter and N. Schindler, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 943.

5 W. Zeiss, H. Jenjes, D. Lux, W. Schwarz and H. Hess, *Z. Naturforsch., Teil B*, 1979, **34**, 1334.

6 C. Donath, B. Wallis, M. Meisel and P. Leibnitz, *Z. Anorg. Allg. Chem.*, 1989, **576**, 33.

Received in Cambridge, UK, 28th April 1997; Com. 7/02857A