Novel 1,2-thiaphosphetanes from diferrocenyldithiadiphosphetane disulfide

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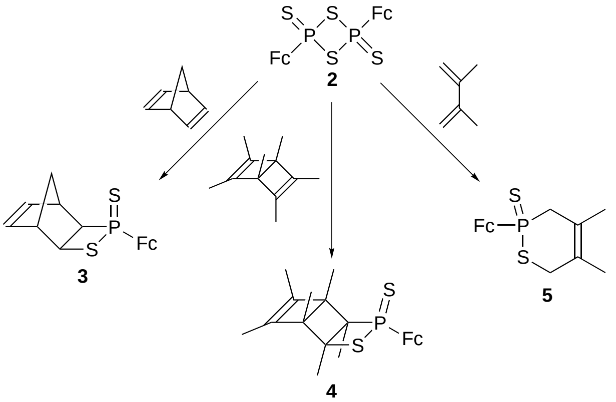
Diferrocenyldithiadiphosphetane disulfide reacts with bicyclic dienes to form four- and six-membered PS containing rings which are crystallographically characterised.

We have recently reported on the synthesis[1] of a ferrocene analogue of Lawesson's reagent [p-(MeO)$C_6H_4P(S)S_2P(S)$-C_6H_4(OMe)] **1**. These types of system are used as reagents in thionation reactions but their potential in the formation of new heterocycles is less well developed although some reactions of **1** with 1,3-dienes to give Diels–Alder adducts at moderate temperatures have been described.[2] Lawesson's reagent has been reported to react with alkenes at high temperature to give anti-sludge additives for engine oils[3] and ferrocene derivatives have been studied as additives for fuels.[4] There have only been a few reports on the isolation of RPS_2 systems (R = 'supermesityl')[5] but from NMR studies[1] we have speculated on the transitory existence of RPS_2 in **1** and **2**. This observation has led us to investigate the cycloaddition chemistry of **2** and here we describe preliminary investigations into the low temperature reactions of alkenes with **2** together with the X-ray crystal structures of three new organophosphorus–sulfur heterocycles, which are the first examples of these ring types to be characterised crystallographically.[6]

The reactions are shown in Scheme 1. Treatment of **2** with norbornadiene at 80 °C leads to 4-ferrocenyl-3-thia-$4\lambda^5$-phosphatricyclo[4.2.1.$0^{2,5}$]non-7-ene 4-sulfide **3** in high yield (69%).‡ The X-ray structure§ of **3** reveals (Fig. 1) it to be the *exo*-isomer. The C_2PS (thiaphosphorane) ring is close to planar [max. deviation from the PSC_2 mean plane 0.043(6) and −0.050(6) Å for C(16) and C(11) respectively]. The P=S and P–S bond lengths are similar to those in **2** whilst P(1)–C(16)



Scheme 1

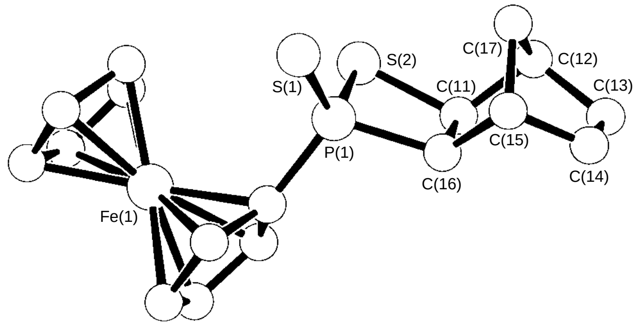


Fig. 1 The X-ray structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–S(1) 1.940(2), P(1)–S(2) 2.102(2), P(1)–C(16) 1.847(6), P(1)–C(1) 1.800(6), S(2)–C(11) 1.850(6), C(11)–C(16) 1.585(7), C(11)–C(12) 1.535(8), C(12)–C(13) 1.520(8), C(13)–C(14) 1.321(8), C(14)–C(15) 1.487(9), C(15)–C(16) 1.523(8), C(12)–C(17) 1.564(9), C(15)–C(17) 1.548(8), S(1)–P(1)–S(2) 122.0(1), S(1)–P(1)–C(1) 114.1(2), S(1)–P(1)–C(16) 118.9(2), S(2)–P(1)–C(1) 104.9(2), S(2)–P(1)–C(16) 83.8(2), C(1)–P(1)–C(16) 109.0(3), P(1)–S(2)–C(11) 80.1(2), S(2)–C(11)–C(16) 100.3(4), P(1)–C(16)–C(11) 95.7(4).

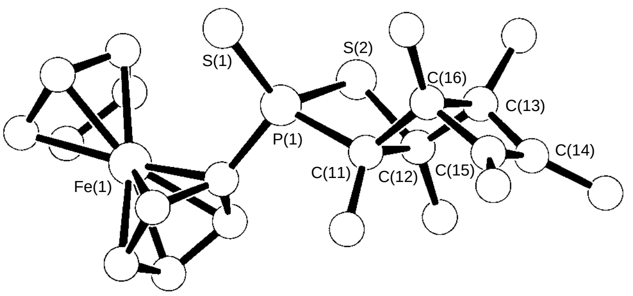


Fig. 2 The X-ray structure of **4**. Selected bond lengths (Å) and angles (°): P(1)–S(1) 1.931(1), P(1)–S(2) 2.095(1), S(2)–C(12) 1.880(5), C(11)–C(12) 1.588(4), P(1)–C(11) 1.844(4), C(12)–C(13) 1.538(5), C(13)–C(14) 1.520(5), C(14)–C(15) 1.322(5), C(15)–C(16) 1.520(5), C(16)–C(11) 1.578(5), C(13)–C(16) 1.584(5), S(1)–P(1)–S(2) 122.9(1), S(1)–P(1)–C(1) 112.3(1), S(1)–P(1)–C(11) 122.4(1), S(2)–P(1)–C(1) 104.7(1), S(2)–P(1)–C(11) 83.7(1) C(1)–P(1)–C(11) 106.6(2), P(1)–S(2)–C(12) 79.9(1), S(2)–C(12)–C(11) 98.5(2).

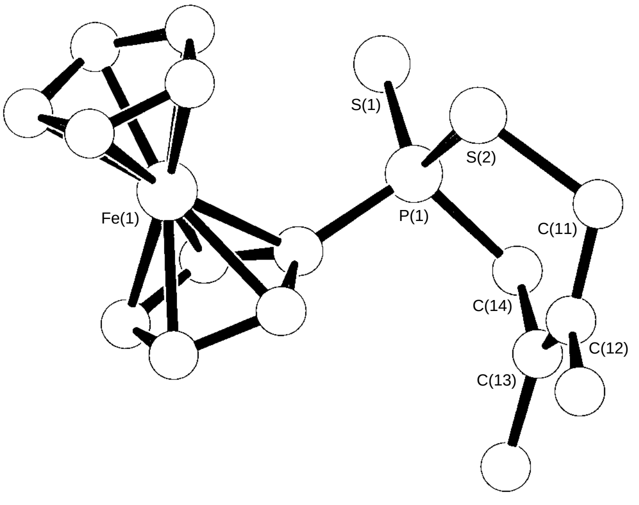


Fig. 3 The X-ray structure of **5**. Selected bond lengths (Å) and angles (°): P(1)–S(1) 1.944(3), P(1)–S(2) 2.086(4), S(2)–C(11) 1.840(9), C(11)–C(12) 1.50(1), C(12)–C(13) 1.31(1), C(13)–C(14) 1.52(1), P(1)–C(14) 1.816(8), S(1)–P(1)–S(2) 1147.7(2), S(1)–P(1)–C(1) 112.5(3), S(1)–P(1)–C(14) 114.5(3), S(2)–P(1)–C(14) 101.6(3), S(2)–P(1)–C(1) 106.5(3), C(1)–P(1)–C(14) 106.0(4), P(1)–S(2)–C(11) 100.4(4), S(2)–C(11)–C(12) 112.4(6), C(11)–C(12)–C(14) 120.6(8), P(1)–C(14)–C(13) 111.4(6), C(12)–C(13)–C(14) 118.1(8).

[1.847(6) Å] and S(2)–C(11) [1.850(6) Å] are relatively long single bonds. The phosphorus centre is somewhat distorted from tetrahedral, in part because of the reduced angles within the PSC_2 ring. The exocyclic sulfur is pointing up (in the same direction as the CH_2 of the tricyclic system). No trace could be found of any homo-Diels–Alder adduct in the reaction products.

Reaction of **2** and hexamethyl Dewar benzene in toluene at 80 °C gives 4-ferrocenyl-1,2,5,6,7,8-hexamethyl-3-thia-4λ^5-phosphatricyclo[4.2.0.0^{2,5}]oct-7-ene 4-sulfide **4** after chromatography and recrystallisation.‡ The X-ray structure§ of **4** reveals (Fig. 2) it to be the *exo*-isomer. The bond lengths and angles in **4** display similar trends to those in **3** although the PSC_2 ring is less planar than that in **3** [maximum deviation from the PSC_2 mean plane 0.14(1) and −0.14(1) Å for C(12) and C(11) respectively]. The difference may be a consequence of the steric repulsion between the exocyclic methyl groups and the P=S in **4**. Like **3** the phosphorus centre is distorted with reduced angles within the PSC_2 ring.

Treatment of **2** with 2,3-dimethylbutadiene at *ca.* 80 °C gave 2-ferrocenyl-4,5-dimethyl-1-thia-2λ^5-phosphacyclohex-4-ene 2-sulfide **5** in high yield (86%). The thiaphosphorinine ring in **5** has a pseudo boat conformation (Fig. 3) with the P(1)–S(2)–C(11)–C(14) and C(11)–C(12)–C(13)–C(14) mean planes are inclined by 123° to each other. The bond lengths at phosphorus and sulfur are similar to those in **3** and **4** with, as expected, significantly less angular deviations about the phosphorus centres.

The new compounds described here illustrate the ability of **1** to behave as a source of PS_2 in ring forming reactions as well as providing the first structure determinations on two heterocyclic systems. Reactions with other multiple bonds are in progress.

Footnotes

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‡ Satisfactory C, H microanalyses/accurate mass spectral data were obtained for all new compounds. *Selected spectroscopic data* for **3**: mp 120–121.5 °C; δ_P 64.0; δ_C 136.5 (d, $J[^{31}P–^{13}C]$ 15 Hz), 135.9, 73.5 (d, $J[^{31}P–^{13}C]$ 16 Hz), 72.4 (m), 70.0, 57.3 (d, $J[^{31}P–^{13}C]$ 53 Hz), 47.2, 43.3, 42.7, 36.4 (d, $J[^{31}P–^{13}C]$ 7 Hz). δ_H 6.3 (m, 2 H), 4.7 (d, *J* 9.5 Hz, 2 H), 4.6 (m, 2 H), 4.2 (s, 4 H), 3.0 (m, 5 H), 1.6 (d, *J* 9.8 Hz); MS(EI$^+$) *m/z* 372 (M$^+$), 280 ($FcPS_2$), 248, 217, 184, 155, 121.

For **4**: δ_P 68.4; δ_C 146.4, 140.1, 81 (d, $^1J[^{31}P–^{13}C]$ 75 Hz), 76.0 (d, $^2J[^{31}P–^{13}C]$ 15 Hz), 72.4 (d, $^3J[^{31}P–^{13}C]$ 11 Hz), 72 (m), 70.2, 65 (d, $^1J[^{31}P–^{13}C]$ 50 Hz), 57.2, 56.4, 55.0, 20.8, 16.3, 12.3 (d, $^3J[^{31}P–^{13}C]$ 7 Hz), 11.7, 11.2 and 10.7; δ_H poorly resolved multiplets at 4.74, 4.64, 4.54 and 4.49 (1 H in each case), 4.33 (s, 5 H), 1.73 (s, 3 H), 1.58 (s, 3 H), 1.44 (s, 3 H), 1.35 (s, 3 H), 1.16 (s, 3 H), 0.97 (d, $^2J[^1H–^{31}P]$ 24 Hz, 3 H); MS(EI$^+$) *m/z* 442 (M$^+$), 280 ($FcPS_2$), 248 (FcPS), 217 (FcS), 162, 147. Found 442.0641, calc. 442.0641. For **5**: δ_P 69.2; δ_C 130.6, 127.4, 73.6, 72.5, 72.2, 71.7, 70.0, 46.7 (d, $^2J[^{31}P–^{13}C]$ 46 Hz, CH_2), 34.9 (CH_2), 21.0, 19.2; δ_H 4.63 (1 H), 4.37 (poorly resolved multiplet, 2 H), 4.28 (5 H) 4.17 (1 H), 3.57 (poorly resolved triplet, 1 H), 3.12 (dd, $^2J[^1H–^{31}P]$ 21.5, $^2J[^1H–^1H]$ 14.1 Hz, 1 H), 2.82 (complex multiplet, 2 H), 1.82 (d, $^4J[^{31}P–^1H]$ 5.4 Hz, 4 H) and 1.56 (5 H). MS(EI$^+$) *m/z* 362(M$^+$), 280($FcPS_2$), 248(FcPS), 217(FcS), 184, 155, 121.

§ *Crystal data*. All measurements were performed at room temperature using a Rigaku AFC7S diffractometer, Cu-Kα radiation, λ = 1.54178 Å, ω-scans (2θ max = 120°). For **3**: $C_{17}H_{17}FePS_2$, M = 372.3 monoclinic, space group $P2_1/c$, a = 11.688(2), b = 9.508(2), c = 14.706(2) Å, β = 104.11(1)°. U = 1585 Å^3, Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 768, μ(Cu-Kα) = 11.0 mm^{-1}. Crystal dimensions 0.10 × 0.21 × 0.30 mm. Of 2670 measured data 2559 were unique and 1996 were observed [$I > 3.0\sigma(I)$]. The structure was solved by the heavy atom method and refined using absorption corrected data (Difabs) with the H-atoms in idealised positions to give R = 0.049 and R_w = 0.046. For **4**: $C_{22}H_{27}FePS_2$, M = 442.4, monoclinic, space group $P2_1/n$, a = 10.616(2), b = 9.604(1), c = 21.033(2) Å, β = 101.26(1)°. U = 2103 Å^3, Z = 4, D_c = 1.40 g cm^{-3}, $F(000)$ = 928, μ(Cu-Kα) = 8.33 mm^{-1}. Crystal dimensions 0.08 × 0.12 × 0.21 mm. Of 3540 measured data 3339 were unique and 2473 were observed [$I > 2.0\sigma(I)$]. The structure was solved by direct methods and refined using absorption corrected data (Difabs) with the H-atoms in idealised positions to give R = 0.038 and R_w = 0.031. For **5**: $C_{16}H_{19}FePS_2$, M = 362.3 monoclinic, space group $P2_1/n$, a = 6.875(3), b = 12.459(4), c = 19.496(6) Å, β = 96.91(3)°. U = 1658 Å^3, Z = 4, D_c = 1.45 g cm^{-3}, $F(000)$ = 752, μ(Cu-Kα) = 10.5 mm^{-1}. Crystal dimensions 0.10 × 0.10 × 0.18 mm. Of 2833 measured data 2708 were unique and 1665 were observed [$I > 3.0\sigma(I)$]. The structure was solved by the heavy atom method and refined to give R = 0.070 and R_w = 0.071. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information to authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/410.

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