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Preliminary communication

Sulphurisation reactions of $P_5C_5{}^tBu_5$ and $P_5C_5{}^tBu_5H_2$: crystal and molecular structure of the ethanol adduct of $P_5C_5{}^tBu_5H_2S_3$

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Abstract

Treatment of $P_5C_5{}^tBu_5$, and $P_5C_5{}^tBu_5H_2$ with an excess of sulphur affords the corresponding mono- and trisulphur compounds $P_5C_5{}^tBuS$ and $P_5C_5{}^tBuH_2S_3$, respectively, whose structures have been elucidated by NMR spectroscopy; and in the case of the trisulphur derivative confirmed by a single crystal X-ray study of its EtOH adduct, $P_5C_5{}^tBu_5H_3S_3(OEt)$.

There is considerable current interest in the novel organic chemistry and ligating ability of compounds containing phosphorus–carbon multiple bonds [1,2]. Phosphaalkynes, RC≡P, have played a particularly important role in the development of both these areas [3], and recently their potential as building blocks for the synthesis of cages containing four [4,5], five [5,6], and six [7] phosphorus atoms has been revealed.

Recently, we described (*i*) the oxidative coupling of the $P_2C_3{}^tBu_3$ and $P_3C_2{}^tBu_2$ anions **1** and **2** [7] to give the cage compound **3**, and (*ii*) protonation of a mixture of **1** and **2** [8] to afford the Diels–Alder product $P_5C_5{}^tBu_5H_2$ **4**. We have now found that treatment of **3** and **4** with an excess of sulphur leads to the formation of the colourless monosulphide $P_5C_5{}^tBu_5S$ **5** (80%), and trisulphide $P_5C_5{}^tBu_5H_2S_3$ **6** (76%), respectively (see Scheme 1).

The proposed structure of **5** is based on the observation of the parent ion $m/z = 532$ in the mass spectrum and analysis of its $^{31}P\ \{^1H\}$ NMR spectrum. The latter shows 4 different phosphorus environments. A large chemical shift difference (69 ppm) is observed for the resonance of P(3) in **5** compared with P(3) in **3**, whereas the chemical shifts of the other phosphorus atoms in the molecule remain relatively unchanged on sulphurisation. * The proposed structure of **5** also accounts for the observed increase in the $^1J(P(1)P(3))$ coupling constant (322 Hz in **5**, *cf.* 262 Hz in **3**), which is characteristic of a mixed valence phosphorus compound.

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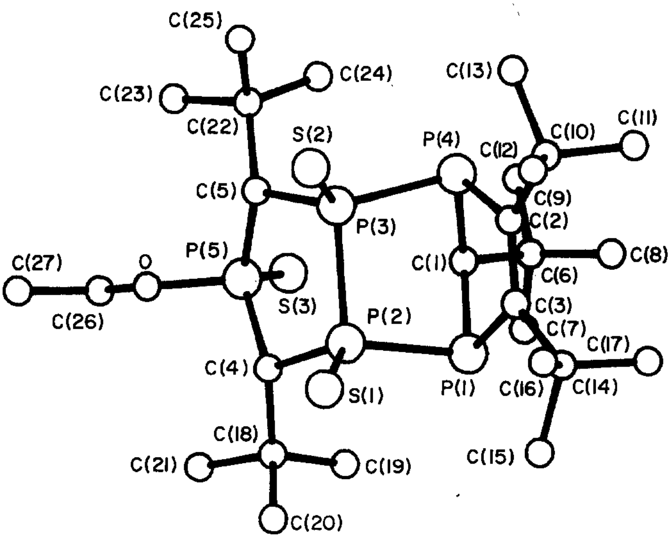

Fig. 1. Molecular structure of 7. Selected bond lengths (Å): S(1)–P(2) 1.946(3), S(3)–P(5) 1.931(4), P(1)–C(1) 1.833(9), P(2)–P(3) 2.238(3), P(3)–P(4) 2.232(3), P(4)–C(1) 1.825(8), P(5)–O 1.617(7), P(5)–C(5) 1.842(10), S(2)–P(3) 1.935(3), P(1)–P(2) 2.219(3), P(1)–C(3) 1.834(10), P(2)–C(4) 1.848(9), P(3)–C(5) 1.867(10), P(4)–C(2) 1.868(10), P(5)–C(4) 1.859(9).

It is remarkable that P(3), which is part of the strained three-membered ring in **3**, is the only P atom to have been sulphurised even though an excess of sulphur was used.

The ^{31}P {^1H} NMR spectrum of the trisulphide **6**, which has also been fully analysed and simulated, is only consistent with a structure in which P(2), P(3), and P(5) are bonded to sulphur. ** Confirmation of the proposed geometry comes from a single crystal X-ray study of the product formed when the sulphurisation reaction of **4** was carried out in ethanol. The molecular structure of the colourless compound $P_5C_5{}^tBu_5H_3S_3(OEt)$ **7**, resulting from addition of EtOH across the P=C double bond of **4**, is shown in Fig. 1. *

These results and related studies by Regitz [3,4] on the $P_4C_4{}^tBu_4$ cluster indicates that a rich chemistry of these novel organophosphorus compounds can be expected.

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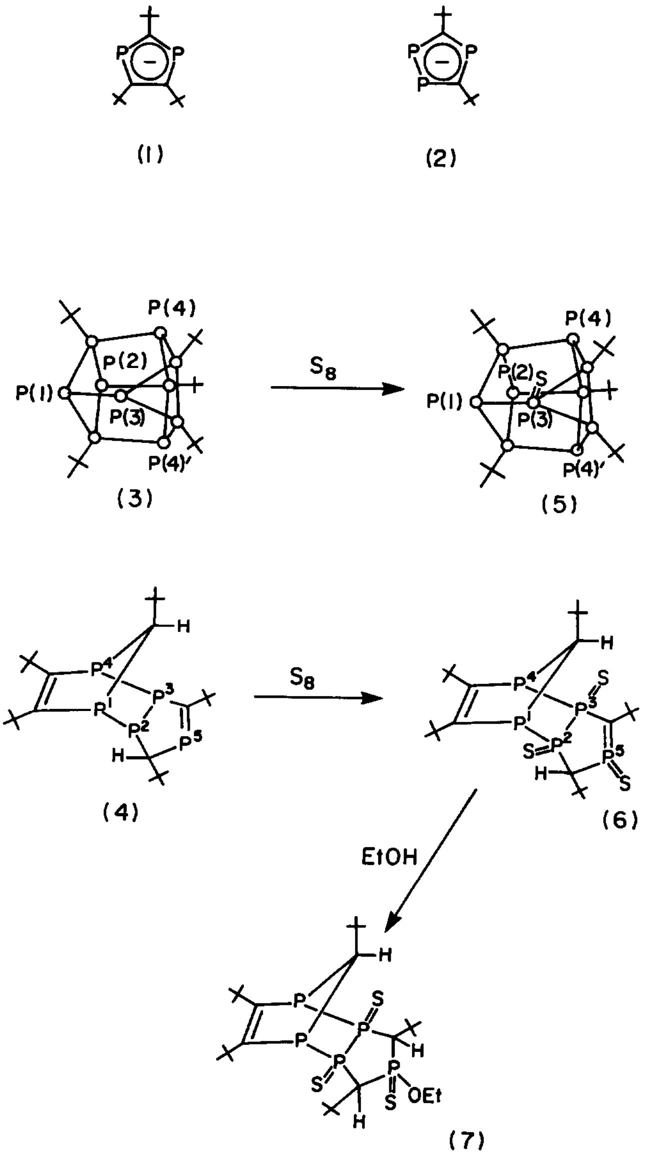
* ^{31}P {^1H} NMR **5**, ppm rel. H_3PO_4. $\delta_{P(1)}$ 160.3, $\delta_{P(2)}$ 54.8, $\delta_{P(3)}$ 69.0 ppm, $\delta_{P(4)}$ 221.6; $J_{1,3}$ 322.2, $J_{1,3}$ 27.2, $J_{1,4}$ 27.1, $J_{3,4}$ 12.2, $J_{1,2}$ 0, $J_{2,3}$ 11.1 Hz. MS: m/z 532 (M^+), 469 $(^tBu_5C_5P_4)^+$, 331 $(^tBu_3C_3P_4)^+$, 263 $(^tBu_2C_2P_2H)^+$, 231 $(^tBu_2C_2P_3)^+$. ^{31}P {^1H} NMR **6**: $\delta_{P(1)}$ 99.2, $\delta_{P(2)}$ −63.7, $\delta_{P(3)}$ 60.5; $\delta_{P(4)}$ 67.2; $\delta_{P(5)}$ 99.1; $J_{1,2}$ 317.8, $J_{1,3}$ 0, $J_{1,4}$ 19.1, $J_{1,5}$ 7.8, $J_{2,3}$ 7.8, $J_{2,3}$ 295.4, $J_{2,4}$ 5.7, $J_{2,4}$ 5.1, $J_{2,5}$ 21.7, $J_{2,5}$ 21.7, $J_{3,4}$ 335.9, $J_{3,5}$ 42.7, $J_{4,5}$ 0 Hz.

** Crystal data for **7**. $C_{27}H_{53}OP_5S_3$, $M = 644.8$, monoclinic, $P2_1/c$, $a = 15.088(4)$, $b = 12.927(3)$, $c = 17.879(2)$ Å, $\beta = 95.68(2)°$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 4.5$ cm^{-1}, 2193 reflexions with $F^2 > 3\sigma F^2$ were used in the refinement. ($R = 0.059$, $R_w = 0.074$). Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.



Scheme 1.

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