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Oxidative Addition of Elemental Sulfur to Phosphenium Centers and the Structure of a Novel Heterobis(spiro)tricyclic Dimer

Neil Burford,* Pierre Losier, Simon Mason, Pradip K. Bakshi, and T. Stanley Cameron*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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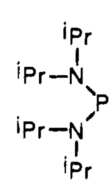
Coordinatively unsaturated centers are attractive synthons due to their potential for simple systematic reaction chemistry as recently demonstrated for carbenes.[1] The phosphorus analogues of carbenes (phosphenium cations) have been known for more than 20 years, and an extensive chemistry has been established.[2] However, it is surprising that some of the more fundamental oxidation reactions that are typical for phosphines[3] have not been reported for phosphenium cations. As part of our studies into the synthetic utility of these important units, we report here the reaction of elemental sulfur with the ionic phosphenium salt $[(^iPr_2N)_2P][AlCl_4]$[4] (**1**) and with the neutral zwitterionic compound 1,3,2,4-diazaphosphoniaaluminatacyclobutane (**2**).[5,6]



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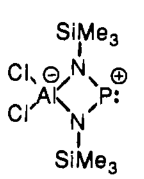

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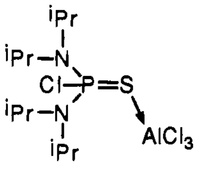
Reactions of **1** (in CH_2Cl_2) and **2** (in toluene) with S_8 each give a single product as shown by ^{31}P NMR spectroscopy. The previously reported[7] thiophosphoryl chloride−aluminum trichloride complex $(^iPr_2N)_2P(Cl)S{\cdot}AlCl_3$ (**3**) (^{31}P: 62 ppm) is formed from **1**,[8] while reaction of **2** gives the new bis(spiro)tricyclodialuminatetraazadithiadiphosphetane **4**(^{31}P: −18 ppm).[9] The slow reaction of **1** (3 weeks) may be due to the steric shielding imposed by the diisopropylamino substituents and contrasts the reaction of the neutral derivative **2**, which occurs within minutes (^{31}P: −18 ppm), with the precipitation of a fine white powder, and proceeds most effectively with compound **2** in excess (2:1). Compound **4** is the major product (>90% observed by ^{31}P NMR spectroscopy: −18 ppm) independent of stoichiometry. Solid state ^{31}P NMR spectra of the bulk precipitate confirm **4** as the single phosphorus containing component (−17 ppm). Solution ^{31}P NMR spectra of the reaction mixtures after 2 weeks reveal a new species (55 ppm) which is formed at the expense of **4**. Nevertheless, toluene solutions of **4** in pure form are indefinitely stable.



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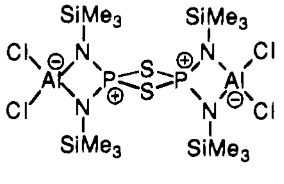

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Compound **4** is readily recrystallized, and the bis(spiro)tricyclic structure (Figure 1) has been confirmed by X-ray crystallography.[10] Spirocyclic geometries are common for phosphorus; however, the bis(spiro) functionality is unusual. The centrosymmetric tricyclic framework has a dithiadiphosphonium bridge as a central feature which is orthogonal to the terminal rings. The geometry of the P_2S_2 ring is typical of

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(1) See, for example: Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992,** *114,* 9725−9726. Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993,** *462,* 13−18. Arduengo, A. J., III; Tamm, M.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994,** *116,* 3625−3626. Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994,** *116,* 4391−4394.

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(8) A suspension of excess S_8 (0.05 g, 1 mmol) in a solution of $[(^iPr_2N)_2P][AlCl_4]$ (0.15 g, 0.37 mmol in 0.5 mL of CH_2Cl_2) was monitored over 3 weeks by ^{31}P NMR: 62 ppm.

(9) A solution of **2** (prepared according to literature[5] sublimed; 0.61 g, 2.0 mmol) in toluene (dried over sodium/benzophenone; 10 mL) was added quickly to a suspension of S_8 (Aldrich, used as received; 0.03 g, 1 mmol) in toluene (5 mL). A white precipitate formed within minutes. After 12 h of stirring at room temperature, the solution was decanted and the solid washed twice by back-distillation. All volatiles were removed *in vacuo*. The white powder was contaminated with a small amount of elemental sulfur (0.26 g, ~76%): ^{31}P NMR (CH_2Cl_2) −18 ppm; solid CP-MAS −17 ppm. Recrystallized from CH_2Cl_2 (68% recovery; approximate solubility 6 mg/mL): mp 174.5−179.0 °C; ^{31}P NMR (CH_2Cl_2) −18 ppm; IR (CsI, Nujol mull) 1258 (s), 1147 (m), 1108 (s), 848 (s), 776 (s), 739 (s), 695 (w), 661 (w), 647 (m), 617 (m), 603 (w), 533 (s), 443 (s), 378 (w), 343 (w) cm^{-1}. Anal. Calcd: C, 21.49; H, 5.41; N, 8.35. Found: C, 21.17; H, 5.38; N, 8.42.

(10) Crystal data for compound **4**: $C_{12}H_{36}Al_2Cl_4N_4P_2Si_4S_2$, M = 670.62, monoclinic, space group = $P2_1/n$, a = 6.599(3) Å, b = 12.602(2) Å, c = 20.070(2) Å, β = 96.02(2)°, V = 1659.8(8) Å^3, Z = 2, D_c = 1.342(6) g/cm^3, $F(000)$ = 696. Crystals were selected and mounted in Pyrex capillaries in a drybox. Unit cell parameters were obtained from the setting angles of 24 accurately centered reflections in the range 38.31 > 2θ > 44.35°; the choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structure. Data were collected on a crystal of dimensions 0.5 × 0.1 × 0.1 mm^3 at room temperature on a Rigaku AFC5R diffractometer (Mo Kα, λ = 0.710 69 Å, graphite monochromator) using the $\omega/2\theta$ scan technique. The stability of the crystals was monitored using three standard reflections; no significant decay was observed. Data were corrected for Lorentz and polarization effects. An empirical absorption (ψ scan) was applied with the transmission factor ranging from 0.94 to 1.00. Scattering factors were corrected for anomalous dispersion. The structure was solved by direct methods. Hydrogen atoms were placed in their geometrically calculated positions (C−H = 1.08 Å), kept fixed during refinement, and assigned fixed isotropic temperature factors of 1.2 times the B_{eq} of the carbon atom to which each was bonded. The models were refined using full-matrix least-squares techniques based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight is defined as unity. All calculations were performed using TEXSAN. Further details are available as supplementary material.

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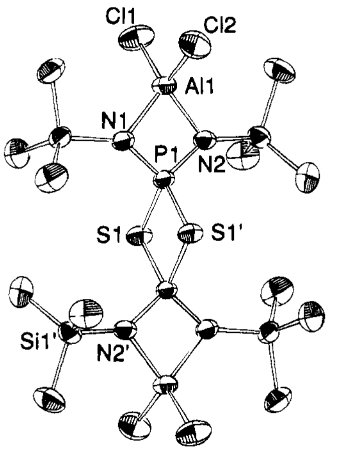
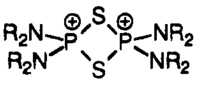


Figure 1. ORTEP view of compound **4**. Selected parameters: P1–S1, 2.120(2) Å; P1–S1', 2.119(2) Å; P1–N1, 1.593(3) Å; P1–N2, 1.598(3) Å; S1–P1–S1', 92.39(6)°; P1–S1–P1', 87.61(6)°; N1–P1–N2, 99.5(2)°.

dithiadiphosphetane[11,12] or dithiaphosphonium **5**[7]systems with single P–S bonds [2.120(2) and 2.119(2) Å; cf. (PhS)$_3$P, 2.122(8) Å].[13] The terminal heterocycles are structurally similar to **2**.[6]



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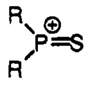

6a R = ^{i}Pr$_2$N

6b R = Me$_3$SiN-Al(Cl)$_2$-NSiMe$_3$

Compounds **3** and **4** represent simple one-atom (Staudinger-type)[14] oxidative addition products of the phosphenium center but are structural alternatives to the tricoordinate thioxophosphonium **6**. Compound **3** can also be generated directly from the reaction of a thiophosphoryl chloride with AlCl$_3$,[7] and this illustrates the thermodynamic preference for this covalent structure over the isomeric ionic (**6a**) AlCl$_4$. Diethylamino and dimethylamino derivatives of **3**, which are less sterically restricted, form the same covalent structures in solution but are in equilibrium with the ionic dithiadiphosphonium **5** bis(tetrachloroaluminate) in the solid state.[7] The heterospirocycle **4** is a neutral zwitterionic analogue of **5** and can be viewed as a dimer of the zwitterionic thioxophosphonium **6b**. Consequently, the structure of **4** is consistent with the thermodynamic instability of tricoordinate thioxo-[7] and iminophosphonium species.[15,16]

The dimerization of **6b** is reminiscent of the behavior of thioxophosphoranes involving small substituents,[17] and the hemihelical geometry of heterocyclic rings in **4** is novel. Moreover, it is interesting to note that, unlike the dithiadiphosphonium **5** cations reported earlier,[7] **4** maintains the same structure in solution and solid state, as there are no obvious structural alternatives other than a monomeric system containing the elusive tricoordinate thioxophosphonium center.

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Supplementary Material Available: Tables of crystallographic experimental data, atomic coordinates, temperature factors, bond lengths, bond angles, and torsion or conformation angles (6 pages). Ordering information is given on any current masthead page.

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