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A Triphosphete and a Spirocyclic Cation with a PP₄ Skeleton and a 10e Spiro P Atom

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A particularly wide variety of suitable redox processes are available for the formation of P–P bonds. For example, from the reaction of white phosphorus with phosphanes and phosphanides Schmidpeter et al. obtained cyclic and acyclic triphosphenium ions containing phosphorus(I) centers with eight electrons.^[11] Diphosphinomethanides are particularly suitable for the synthesis of heterocycles containing a P₃ unit; they can react with PCl₃ to yield heterocycles with eight-,^[11] seven-, or sixmembered rings.^[21] However, in the reaction of PCl₃ with Li[C(PMe₂)₂(SiMe₃)] it was not possible to completely rule out the formation of an as yet unknown four-membered ring system (triphosphete) rather than an eight-membered ring.^[2]

1,2-Diphosphetenes,^[3] 1,2,3-triphosphetenes,^[4] and 1,3diphosphetes^[5] have been known for some time. In order to discover whether an eight- or a four-membered ring was formed, we exchanged the methyl substituents on the phosphorus atoms of the phosphinomethanide for phenyl groups [Eq. (a)]. Indeed,



the four-membered ring compounds 2a,b were obtained as colorless crystals from pentane, and were unequivocally characterized by elemental analysis and by mass and NMR spectra. If 2ais formulated with formal charges, then the phosphanide nature of the divalent phosphorus atom (oxidation state + I) is evident and in agreement with the observed high-field ³¹P NMR shift ($\delta = -86.31$). The course of the reaction can be easily understood in terms of Li/Cl exchange, subsequent elimination of LiCl, and a further substitution step. In this last step the behavior of 2a differs from that of the methylated compound,^[2] because Ph₂P-PPh₂ coupling of the phosphinomethanides as the pertinent redox step is obviously not feasible for steric reasons.^[6]

If SbCl₃ and BiCl₃ are treated with 1 in an analogous manner, then the *P*-chloromethylenephosphorane 3 is obtained along with elemental antimony and bismuth, respectively. An alternative method, based on the Schmidpeter procedure,^[11] yields **2a** from white phosphorus and **1**. Although only produced in moderate yields (30%), it is free of **3**. The stoichiometry was chosen based on the (hypothetical) formation of Li_3P_7 [Eq. (b)].^[7]

 $10/4 P_4 + 3 \text{LiC}(PPh_2)_2(\text{SiMe}_3) \cdot \text{TMEDA} \xrightarrow{\text{THF}} 3 \times 2\alpha + \text{Li}_3P_7$ (b)

X-ray structural analysis^[8] of the isotypic compounds 2a,b revealed that they both crystallize in the space group $P\overline{1}$ and

contain two independent, but very similar molecules in the unit cell (Fig. 1). The fourmembered rings are not completely planar: P3a and As1a project out of the C1a-P1a-P2a plane by 0.148(1) and 0.177(1) Å, respectively. The most striking features are the bond angles P1a-P3a(As1a)-P2a, the smallest found so far for divalent phosphorus (arsenic), and the relatively short nonbonding P1a-P2a distance, particularly in 2a.^[9] The structural parameters, especially the almost identical P1a-P3a(As1a) and P2a-P3a(As1a) bond lengths, suggest a representation as a cyclic bis(ylide) as expressed in the heteropolar notation in Equation (a).^[10] Alternatively, 2a,b can be regarded as an internally donor-stabilized phosphinidene and arsinidene, respectively. Further, a representation derived from a P^I phosphenium ion^[1b] or a phosphanide ion^[11] can also be considered.^[12] Less convincing is a description as a cycloheterobutadiene (cf. ref.[5]) with a $\lambda^5 P - \lambda^3 P(As) \lambda^5 P$



Fig. 1. Crystal structure of 2b (the asymmetric unit contains two molecules that are identical within the limits of error). 2a crystallizes isomorphously (exchange of As1a,b by P3a,b). Selected bond lengths [Å] and angles [°] of molecule a [molecule b] in 2a: P1-P3 2.1489(5) [2.1526(5)], P2-P3 2.1530(6) [2.1488(5)], P1-C1 1.729(1) [1.738(1)], P2-C1 1.738(1) [1.733(1)], P1...P2 2.5483(5) [2.5347(5)]; P1-C1-P2 94.64(7) [93.83(7)], C1-P1-P3 96.44(5) [96.77(5)], C1-P2-P3 96.03(5) [97.07(5)], P1-P3-P2 72.65(2) [72.21(2)]. 2b molecule a [molecule b]: P1-As1 2.2710(7) [2.2729(7)], P2-As1 2.2692(7) [2.2681(7)], P1-C1 1.741(2) [1.740(2)], P2-C1 1.731(2) [1.730(2)], P1...P2 2.6008(9) [2.5868(9)]; P1-C1-P2 97.0(1) [96.4(1)], C1-P1-As1 96.21(8) [96.78(8)], C1-P2-As1 [97.27(8)], 96.59(8) P1-As1-P2 69.90(2) [69.45(2)].

structural element. Another novel feature of 2a,b is that these are the first bis(organo)-substituted examples of 1,3-diphosphonium four-membered rings.^[26]

The small P1a-P3a(As1a)-P2a angle may lead to special reactivity, for example high nucleophilicity. However, large amounts of **2a,b** could not be obtained free of **3**, so that reactions of **2a,b** as nucleophiles have not yet been successful. In order to use this "disadvantage" positively, an equivalent amount of NaBPh₄ was added to the mixture of **2a** and **3** obtained according to Equation (a). Here **3** is converted in situ into the cation **3a**,^[13] which is then attacked by the nucleophilic **2a** to yield the spirocyclic phosphorus(III) cation **4** with a PP₄ backbone [Eq. (c)].



Pale yellow crystals of 4-BPh₄ were obtained from THF. Xray structural analysis^[14] confirmed the structure deduced from the ³¹P{¹H} NMR spectrum (see below) (Fig. 2). As in phosphonium ions, the central phosphorus atom is tetravalent; however, it does not have a (distorted) tetrahedral environment, but exhibits a distorted pseudo-trigonal-bipyramidal frame-

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Fig. 2. Crystal structure of 4. a) Front view, b) side view. Selected bond lengths [Å] and angles [°]: P-P1 2.4077(8), P-P2 P-P3 2.4616(9), P1-C1 2.2009(9), P-P4 1.712(2), P2-C1 1.737(2), P3-C2 1.718(2), P4-C2 1.733(2); P1-P-P2 71.15(3), P1-P-P3 125.12(4), P1-P-P4 107.81(3), P2-P-P3 107.22(3), P2-P-P4 176.41(3), P3-P-P4 70.41(3), P-P1-C1 93.97(8), P-P2-C1 86.46(8), P-P3-C2 95.06(8), P-P4-C2 85.98(9), P1-C1-P2 102.3(1), P3-C2-P4 102.8(1).

work (Fig. 2a,b). The free equatorial position indicates the presence of a lone pair. Thus 4 can be included in a series, in general terms, of electronically isovalent element(II) compounds $E[C(PMe_2)_2(SiMe_3)]_2$ 5 (E = Si,^[15] Ge,^[16] Sn,^[17] Pb^[18]), with a formal isoelectronic exchange of Si by P⁺. Therefore, following this type of notation, 4 can be regarded as a double phosphane adduct of a phosphenium ion (in short, a ten-electron phosphenium ion). In contrast to simple phosphenium ions (e.g. $[(R_2N)_2P]^+$, six electrons^[19a]) or simple base adducts of ions of the type $[R_3N-PR'_2]X^{[19b, 20]}$ and $[R_3P-PR'_2]X^{[21]}$ (eight electrons), the chelate function of the two diphosphinomethanide ligands in 4 leads to ten electrons on the central P atom.^[22] Therefore, it is possible to describe 4 as a tetraonio-substituted phosphoranide^[23] with partial charge compensation by two internal carbanion functions. Although the phosphenium formalism represents the charge correctly and establishes the analogy to the systems listed above, the phosphoranide formalism describes the nature of the central phosphorus atom more accurately. Therefore, both representations are useful and should be used in conjunction.

As in the compounds 5, the axial P–P bonds in 4 are not only longer than the equatorial P–P bonds, which are both equal in length, but they also differ slightly. The bond length differences $\Delta d P-P_{ax}$ and P–P_{eq} (0.21 and 0.26 Å, ca. 8%) lie in the usual range for this geometry.

The chelate four-membered rings are not planar here either; the deviation of C1 from the P1-P-P2 plane amounts to

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0.480(2), that of C2 from the P3-P-P4 plane, 0.467(3) Å. However, at both C1 and C2 the sum of the angles is 360°. The ring strain in the two chelate four-membered rings in 4 has a different effect on the bond angles than that expressed in compounds 5. Not only the P2-P-P4 but also the P1-P-P3 angles are greatly expanded. Thus the P2-P-P4 axis is almost linear, whilst P1 and P3 are very clearly distorted out of the equatorial "plane" of the pseudo-trigonal-bipyramidal framework. The reason for this could lie in the interactions of the bulky phenyl groups (methyl groups in 5).

The ³¹P{¹H} NMR spectra of **4** in solution reveal a rapid scrambling of the equatorial and axial positions at room temperature. The signal of the central phosphorus atom is, as in **2a**, shifted to high field ($\delta = -76.26$). The average "coupling constant" ¹J(P,P) of 137.3 Hz is about half of that found in **2a**. On cooling to -107 °C this scrambling process is essentially frozen; an A₂B₂M spin system can be observed.

Tetravalent phosphorus(III) compounds, in which the phosphorus has ten electrons with one lone pair, have only been achieved with phosphoranide ions.^[23] Compound 4 is novel as an illustration of one of the possible types of bonding in P-P systems.^[24] PP_4 skeletons—be they cationic, neutral, or anionic—have not been detected to date. The formation of the novel type of structure in 4 is obviously a consequence of the nucleophilic behavior of the triphosphete **2a** and the amphiphilic character of "diphosphino carbocations" such as **3a**.

Experimental Procedure

All work was carried out under exclusion of air and moisture in an inert atmosphere of N_2 .

2a: To a solution of 1[25] (2.66 g, 4.6 mmol) in 30 mL of THF at -78 °C was added PCl₃ (0.15 mL, 1.72 mmol) by pipette. The mixture was slowly warmed to room temperature and stirred for 12 h before the solvent was removed in vacuo. The residual orange foam was extracted with pentane (2 × 40 mL). Slow evaporation of the combined pentane extracts at room temperature furnished orange crystals of 24 (0.31 g, 37%). ³¹P{¹H} NMR (C₆D₆, 20 °C): AB₂ spin system: $\delta P_A = -86.31$; $\delta P_B = 20.18$; $J(P_A, P_B) = 261.0$ Hz. MS(CI): $m/z = 487 (M^+ + 1, 100\%)$. ³¹P NMR spectroscopy of the remaining oil indicates 3 along with HC(PPh₂)₂(SiMe₃). ³³P{¹H} NMR (C₆D₆, 20 °C) of 3: AB spin system: $\delta P_A = 0.15$; $\delta P_B = 70.15 (J = 164.0$ Hz).

2b: To a solution of **1** (1.76 g, 3.04 mmol) in 30 mL of THF at -90 °C was added dropwise AsCl₃ (0.11 mL, 1.31 mmol) in 15 mL of THF. The mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was evaporated in vacuo and the residue extracted with pentane (3 × 30 mL). Evaporation of the combined pentane extracts at room temperature yielded a precipitate of product **2b** as a red crystalline solid (0.32 g, 46%). ³¹P{³H} NMR (C₆D₆, 20 °C): δ P: -0.51, s. MS(CI): m/z = 530 (M^{+} , 100%).

4-BF₄: To a mixture of **3** (0.403 g, 0.82 mmol) and **2a** (0.398 g, 0.82 mmol) in 35 mL of THF at -78 °C was added dry NaBPh₄ (0.281 g, 0.82 mmol). The mixture was warmed to room temperature and stirred for 10 h before the solvent was removed by evaporation (room temperature)). Extraction with pentane gave traces of **3** and HC(PPh₂)₂(SiMe₃). Extraction with THF yielded a yellow-orange oil, which when left to stand for 5 d at room temperature gave a precipitate of orange crystals of **4** (0.40 g, 39 %). ³¹P¹H} NMR (C₆D₆ + THF, 20 °C): AB₄ spin system: $\delta P_A = -76.26$, $\delta P_B = 37.73$, $J(P_A, P_B) = 137.3$ Hz; (C₆D₅CD₃ + THF, -107 °C): A₂B₂M spin system: $\delta P_A = 44.39$; $\delta P_B = 26.25$; $\delta P_M = -83.71$; $J(P_A, P_B) = 172.0$ Hz, $J(P_A, P_M) = 86.0$ Hz, $J(P_B, P_M) = 172.0$ Hz.

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- [14] Crystal structure determination of 4-BPh₄: crystals of were obtained by recrystallization from THF. C₈₀H₇₈BP₃Si₂, monoclinic, space group P2₁/c, a = 14.817(1), b = 18.639(1), c = 25.665(2) Å, β = 94.08(1)°, V = 7070.0(8) Å³, Z = 4, ρ_{calcd} = 1.185 g cm⁻³, Mo_{Ka} radiation (λ = 0.71073 Å), μ(Mo_{Ka}) = 20.6 cm⁻¹. 12.373 independent reflections measured with ω scans at 68(2) °C in the 2θ range [°] 3-50. Structure solution using direct methods, refinement of the positional parameters of all the non-hydrogen atoms with anisotropic thermal parameters, hydrogen atoms on calculated positions with U_H = 1.2-1.5 U_{eq.C}. Refinement of the positional parameters with SHELXL-93 versus F². R = 0.0403, R_w = 0.0950 for 8783 structural factors F₀ ≥ 4 σ(F₀)] and 799 variables. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59325.
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Donor/Acceptor Complexes in Hydrogen-Bonded Networks: pH-Dependent Self-Organization**

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Donor/acceptor complexes $\{D^{\delta^+} \cdots A^{\delta^-}\}^{[1, 2]}$ between donor molecules of low ionization energy, which also function as Lewis bases, nucleophiles, or reducing reagents, and electrondeficient acceptor molecules with their properties as Lewis acids, electrophiles, or oxidizing reagents are kept together by weak Coulomb interactions and can be intermediates in microscopic pathways of substitution or redox reactions.^[1d, 2] Their fascinating color is due to the long-wavelength excitation into short-lived charge transfer (CT) states {D⁺···A⁻}.^[1a] Structural analysis of mixed-stack aggregates between six-membered ring donors and acceptors, which can be specifically crystallized,^[2c-g] proves that in their ground states, all bond lengths and angles of the components remain unchanged on π -complexation. Attempts to increase the π -interaction by shortening the donor ··· acceptor distance, thereby generating recognizable structure perturbations, have been the starting point for the

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