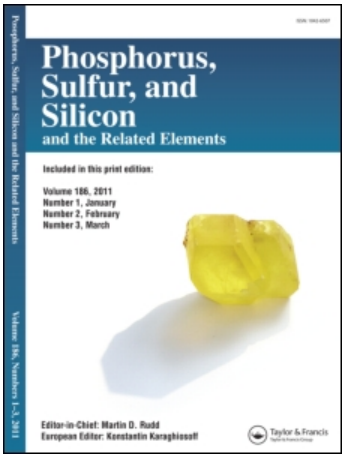

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Communication

THE FIRST X-RAY STRUCTURE OF A CLASSICAL λ^2-BISAMINO-PHOSPHENIUM CATION WITHOUT CATION-ANION INTERACTIONS

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This paper is dedicated to Prof. Dr. R. Schumann on the occasion of his 60th birthday

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Reaction of the cyclic compound (Bu^t)N—Si(Me)$_2$—N(Bu^t)—P(Cl) with Na(BPh$_4$) yields the corresponding λ^2-phospheniumtetraphenylborate salt, the structure of which is determined by X-ray crystallography and shows no cation-anion interactions [shortest intermolecular distance P—C 3.48 Å, intramolecular: P—N 1.623(3) Å, Si—N 1.774(3) Å].

Key words: Two coordinate phosphorus in the crystal, phosphenium cation, X-ray structure.

Since more than 30 years syntheses, structures and reactivities of low valent λ^2-phosphenium-cations have been intensively investigated.[1,2] The special interest in these species lies in their carbene analogous structure and behavior.[3] Due to the facile synthesis, the electron-rich tetrachloroaluminate and triflate anions have been exclusively used as counterions to the phosphenium cations.[1,2] The stability of these phosphenium salts has been in part attributed to the interaction of the lone pair(s) of the anion with the electrophilic phosphenium centre. In order to verify this statement, N. Burford *et al.* in 1992 tried for the first time to introduce the electron-poor BPh_4^- anion as a counterion in these systems.[4] The corresponding λ^2-phosphenium-tetraphenylborate **1** could be prepared successfully [Equation (1)][4] by chloride abstraction from the sterically hindered bis(diisopropylamino)chlorophosphane with Na(BPh$_4$).

$$[(Pr^i)_2N]_2P(Cl) + Na(BPh_4) \rightarrow \underset{\mathbf{1}}{[(Pr^i)_2N]_2P^+(BPh_4)^-} + NaCl \qquad (1)$$

1 reacts in a solution of CH_2Cl_2(or $CHCl_3$) in several hours partly by oxidative addition (insertion) into the C—Cl bond of the solvent affording the λ^4-phosphoniumtetraphenylborate **2** [Equation (2)].[4]

$$\mathbf{1} + CH_2Cl_2 \rightarrow \underset{\mathbf{2}}{\{[(Pr^i)_2N]_2P[Cl(CH_2Cl)]\}^+(BPh_4)^-} + \text{other unidentified products} \qquad (2)$$

The attempts to prepare a sterically less hindered phospheniumtetraphenylborate resulted only in the isolation of the phenylphosphane **3** [Equation (3)].[5]

$$(Me)N\overline{—CH_2—CH_2—N(Me)—P}(Cl) + Na(BPh_4) \rightarrow (Me)N\overline{—CH_2—CH_2—N(Me)—P}(Ph)\cdot BPh_3 + NaCl \quad (3)$$

3

Until now this specific reactivity has not been observed before and can be explained by the high nucleophilicity of the λ^2-phosphenium centre caused by the lack of stabilizing cation-anion interactions.[6]

We describe here a new approach of the synthesis of a cation-anion system which does not degrade. The sterically hindered 1,3-di-*tert*-butyl-4,4-dimethyl-[1,3,4,2λ^2]-diazasilaphosphetidinium cation, which was previously prepared with tetrachloroaluminate[6] and triflate[7] as anion, can be obtained as its tetraphenylborate salt **4** by treatment of its chloro-precursor[8] with $Na(BPh_4)$ [Equation (4)].

$$(Bu^t)N\overline{—Si(Me)_2—N(Bu^t)—P}(Cl) + Na(BPh_4) \rightarrow (Bu^t)N\overline{—Si(Me)_2—N(Bu^t)—P}^+(BPh_4)^- + NaCl \quad (4)$$

4

In a solution of CH_2Cl_2, **4** decomposes in the same way as **1**. However, **4** could be isolated in crystalline form, could be dissolved in acetonitrile and first signs of decomposition were observed in this solution only after several days.

The ^{31}P NMR spectrum shows one sharp signal at δ = 348 ppm [low-field shift relative to the $(AlCl_4)^-$ and $(OSO_2CF_3)^-$ salt] and one signal in the ^1H NMR

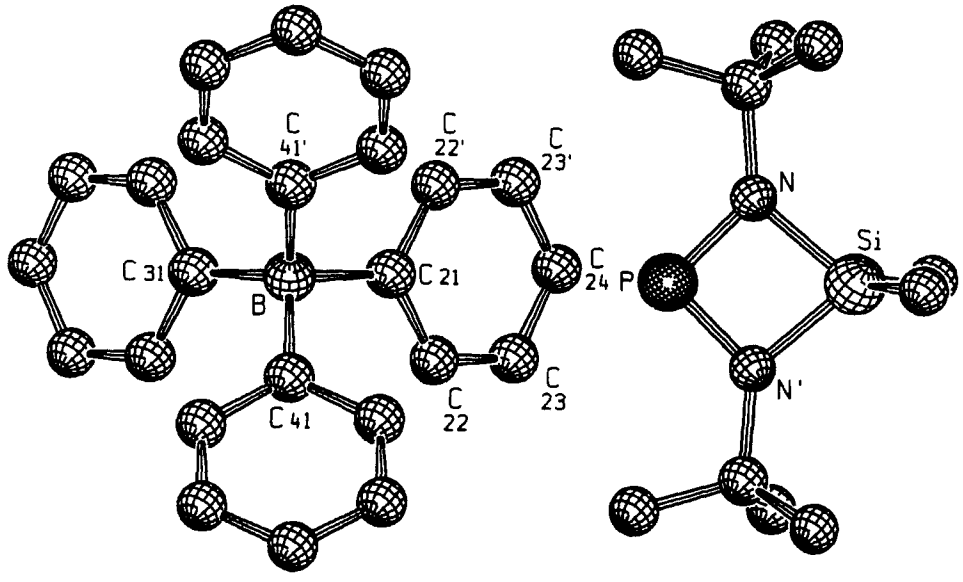

FIGURE 1 The structure of **4** with atomic labelling (the dashed labels identify atoms which are related by a mirror plane). Hydrogen atoms have been omitted for clarity. Some important bond lengths (Å): P—N 1.623(3), Si—N 1.774(3), B—C(21) 1.648(8), B—C(31) 1.629(8), B—C(41) 1.645(5), P—C(21) 3.90, P—(C22) 3.77, P—C(23) 3.59, P—C(24) 3.48. Some important bond angles (°): N'—P—N 89.6(2), N'—Si—N 80.2(2), C(21)—B—C(31) 104.1(4), C(21)—B—C(41) 111.4(3), C(31)—B—C(41) 113.2(3), C(41)—B—C(41)' 103.8(4).

spectrum for the *tert*-butyl and the methyl hydrogen atoms. Together with the ^{13}C and ^{29}Si NMR data, compound **4** can be clearly identified and seems to be highly symmetric in solution.

An X-ray structure determination of **4** gives more insight in the structure of the salt and the cation-anion interactions (Figure 1). The ion pair has a symmetry plane, occupied by the atoms C(10), C(20), Si, P, B, C(21), C(24), C(31) and C(34). The central cationic four membered NSiNP ring is planar. The Si—N (Si—N 1.774(3) Å) and the P—N (P—N 1.623(3) Å) bonds are shortened by about 0.02 Å as compared with the tetrachloroaluminate salt.[6] As in the NSiNP rings P is coordinated by *two* chemically equivalent nitrogen atoms and the P—N bonds lie generally at the upper limit of experimentally determined P=N double bond distances in $\lambda^3\sigma^2$ iminophosphanes.[9] The comparison to the aluminate salt reveal the increase of the positive charge density in the cationic unit in **4**. The shortest P—C distance (P—C(24) 3.48 Å) lies outside bonding interactions or η^6-coordination,[10,11] thus the tetraphenylborate anion shows no unusual distortion (approximately similar B—C distances, see caption to Figure 1).

These facts are in accord with no important cation-anion interactions in **4**. It possesses an ionic structure with completely separated cations and anions.

EXPERIMENTAL

A suspension of $Na(BPh_4)$ was added to $(Bu^t)\overline{N—Si(Me)_2—N(Bu^t)—P(Cl)}^8$ in dichloromethane and stirred for 12 h. After separation of NaCl by filtration, 6.5% of **4** was isolated by slow removal of the solvent in vacuo and washing with *n*-hexane. mp above 250°C, (Anal. Calcd.: C 74.2, H 8.1, N 5.1, Found: C 72.5, H 7.9, N 5.1). NMR (ppm): δ ^1H, 0.75 (s), 1.38 (d) ($^4J_{PH}$ = 1.4 Hz), 6.83–7.02 (m), 7.24–7.30 (m), $^{13}C\{^1H\}$, 2.2 (d) ($^4J_{PC}$ = 2.0 Hz), 32.0 (d) ($^3J_{PC}$ = 7.3 Hz), 57.2 ($^2J_{PC}$ = 6.3 Hz), 123.1 (s), 126.9 (m), 137.1 (m), 163.7–166.6 (m), $^{29}Si\{^1H\}$,δ = 43.9 (d) ($^2J_{PSI}$ = 4.1 Hz), ^{31}P,δ = 348.0 (s).

Crystal data for $C_{34}H_{44}BN_2PSi$: M = 550.58, orthorhombic, a = 18.795(24), b = 16.603 (15), c = 10.353(14) Å, V = 3231(7) Å^3, space group Pnma, Z = 4, D_c = 1.132 g cm^{-3}, F(000) = 1184, μ (Mo-Kα) = 1.47 cm^{-1}. The alternative space group $Pn2_1a$ has been ruled out by comparative refinements. 2194 data were recorded on a Siemens Stoe AED 2 diffractometer using a graphite monochromator, Mo-Kα radiation and ω-θ-scan. 1224 [$I > 2\sigma(I)$] reflections were classified as observed. The structure was solved by direct methods[12] and refined by full matrix least squares on all F_0^2 data.[13] The final R, wR indices [$I > 2\sigma(I)$] were 0.0481 and 0.0949 for 234 parameters [non-hydrogen atoms anisotropic, hydrogen atoms in ideal positions, C—H (aliphatic) = 0.96 Å, all other without restrictions but with a common U_{iso} value of each group]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Fachinformationszentrum (FIZ) Karlsruhe, and can be ordered on quoting the authors, the journal and the depository number, CSD-401829.

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