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The First Example of a $\sigma^2\lambda^2$-Dioxaphosphenium Cation, Stabilized by an Intramolecular Dative $P^+ \leftarrow S$ Bond[§]

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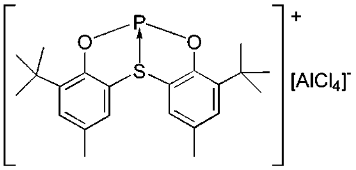
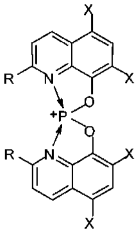
ABSTRACT



The first example of a $\sigma^2\lambda^2$-dioxaphosphenium cation 5 bearing dioxathiophosphocin ring systems stabilized by an intramolecular dative $P^+ \leftarrow S$ bond and its reactivity with pyridine and cycloaddition reaction with 2,3-dimethylbutadiene are reported.

The phosphorus analogues of carbens, known as phosphenium cations, are reactive species. Many reactions can be attributed to the electrophilic character of these cations. Moreover the dative action by the lone pair provides an unusual reactivity and permits the cation to exhibit rich coordination chemistry. Over 50 phosphenium cations have been identified in solution, and some of them have also been isolated and comprehensively characterized.[1]

In most cases the phosphenium ion stabilization is achieved either by interaction with a directly attached donor atom[1,2] (P−N) or by intramolecular dative P ← X bonds.[2,3] Unlike diazaphosphenium ions dioxa derivatives are very unstable. Until now only a few examples of such cations stabilized by intramolecular $P^+ \leftarrow N$ interactions are known. The first of them were derivatives of 8-hydroxyquinolines (**1**) with a chloride anion as a counterion that was observed in equilibrium at low temperature (−60 °C).[4] The second one, compound **2**, was identified as chloride and tetraphenylborate.[5]



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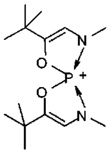

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The dioxathiophosphocin ring system is a suitable model compound to study dative P−S bonds. Sulfur donor atom interaction at phosphorus has been found to increase in the order phosphates < phosphites < oxyphosphoranes and to depend on phosphorus atom electrophilicity.[6] Obviously, the phosphorus atom positively charged in dioxaphosphenium

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[§] Dedicated to Prof. Dr. Giesbert Grossmann on the occasion of his 70th birthday.

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(1) (a) Cowley, A. N.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Sanchez, M.; Maziers, M. R.; Lamande, L.; Wolf R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Georg Thieme Verlag: Stuttgart, 1990; p 129.

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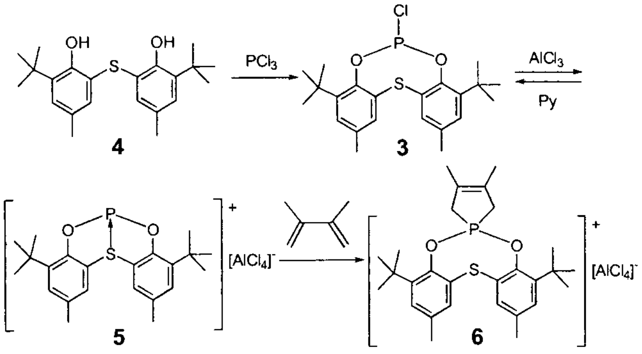
ions possesses higher electrophilicity than in the above-mentioned organophosphorus compounds. So, the stabilization of a two-coordinated phosphorus atom by the intramolecular donor action of sulfur can be expected. Moreover, such a cycle is included in recently synthesized P(III) derivatives[7] of *p*-*tert*-butyl thiacalix[4]arene.[8] The transformation of these compounds into phosphenium cations can extend the synthetic possibilities for further modification of the thiacalix[4]arene platform and for the design of novel macrocyclic receptors.

The general route to phosphenium ions by aluminum chloride promoted halide ion abstraction[1] from the corresponding chlorophosphite precursor **3** has been used. Chlorophosphite **3** was prepared by the reaction of PCl_3 with 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) **4** used as model compound of thiacalix[4]arene. It was found that the best yield and purity of product **3** can be achieved using a slightly modified literature procedure [9] (an excess of PCl_3 in *p*-xylene without base at elevated temperature).[10] In the ^{31}P NMR spectrum of the reaction mixture and also of the isolated product only one resonance at δ 169 ppm is observed.[11] The comparison with the literature value of δ 168.4 [6a] for this compound confirms the formation of the cyclic chlorophosphite **3** (Scheme 1). The treatment of chlorophosphite **3** in $CDCl_3$ solution with solid anhydrous $AlCl_3$ yields a single product that shows an intense (100%) peak in the MALDI-TOF-MS spectrum at *m*/*z* 388 and one resonance at δ 153 ppm in the ^{31}P NMR spectrum of the reaction mixture.

Scheme 1



Phosphorus chemical shifts of phosphenium ions are usually in the range of +500 to +200 ppm.[1] However, the formation of dative bonds leads to an upfield shift. For example, for compound **1** $\delta_P = 117$ ppm (X = Br) and 92 ppm (X = H) and for compound **2** $\delta_P = 103.5$ ppm for both chloride or tetraphenylborate were found. So the phosphorus chemical shift observed for compound **5** is in a good agreement with literature data for dioxaphosphenium cations stabilized by an intramolecular dative bond. The phosphenium ion formation is also confirmed by the ^{27}Al NMR spectrum. The chemical shift at 104 ppm (relative to $[Al(H_2O)_6]^{3+}$) corresponds to the value earlier reported[1] for the anion $[AlCl_4]^-$. The proposed structure is also supported by ^1H and ^{13}C NMR data.[12]

Cation **5** exhibits a remarkable stability. It is stable in chloroform solution at room temperature (!) for 2 weeks (in inert atmosphere). This indicates the existence of the stabilizing $P^+{-}S$ interactions. So, the dative $P^+{-}S$ interactions in the dioxathiophosphocin ring systems play a major role in the stabilization of **5**.

The obtained compound **5** shows a reactivity typical for phosphenium ions.[1] It reacts with pyridine via chloride transfer to the phosphenium cation yielding immediately chlorophosphite **3** and the stable [Py → $AlCl_3$] adduct (Scheme 1).[13] Furthermore, phosphenium cations usually act as dienophiles toward 1,3-dienes. It was displayed by the

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(10) **Modified Synthetic Procedure for 3.** A mixture of 1 g (2.7 mmol) of 2,2-thiobis(4-methyl-6-*tert*-butylphenol) and 0.6 mL (6.1 mmol) of PCl_3 in 3 mL of xylene was stirred at 80 °C for 1 h in an inert atmosphere. The stirred mixture was then gradually heated to 120 °C over a period of 1 h, and the temperature was increased by 10 °C steps every hour up to 150 °C. The resulting mixture was cooled to 50 °C, the excess of PCl_3 and the solvent were removed in vacuo, the residue was diluted with 6 mL of heptane, and a colorless crystalline precipitate was dried in vacuo at 70 °C. This method gives a quantitative yield of **3**, mp 174 °C. The product obtained was used without further purification. According to spectral data the purity of product **3** is higher than 98%. Spectral data of **3**: ^1H NMR ($CDCl_3$) δ 1.33 s (18H, $6CH_3$), 2.19 s (6H, $2CH_3$), 7.06 s (2H, AR), 7.22 (2H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.74; 29.82; 35.12; 121.47; 130.10; 132.66; 133.47; 140.91; 153.36 (d, $^2J_{PC} = 12.8$ Hz).

(11) The NMR experiments were performed on a Bruker DRX-300 spectrometer operating at 300.13 MHz (^1H), 75.475 MHz (^{13}C), and 121.49 MHz (^{31}P) and a Bruker DRX-500 at 130.31 MHz (^{27}Al). The spectra were recorded at ambient temperature in $CDCl_3$ solution using solvent signals as internal standard for ^1H NMR and ^{13}C NMR. For ^{31}P NMR 85% H_3PO_4 was used as external standard, and $Al[(H_2O)_6]^{3+}$ for ^{27}Al NMR. The molecular mass spectra were recorded on a Kratos Compact MALDI II mass spectrometer.

(12) **Reaction of 3 with $AlCl_3$.** Compound **3** (0.75 mmol) was dissolved in 5 mL of $CDCl_3$, and then 0.85 mmol of anhydrous aluminum chloride was added. After stirring for 10−15 min the resulting solution was subjected to NMR studies: ^1H NMR ($CDCl_3$) δ 1.36 s (18H, $6CH_3$), 2.41 s (6H, $2CH_3$), 7.36 s (2H, Ar), 7.65 (2H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.21; 29.16; 35.61; 116.69; 126.07; 134.22; 138.37; 140.56; 156.06 (d, $^2J_{PC} = 18.1$ Hz).

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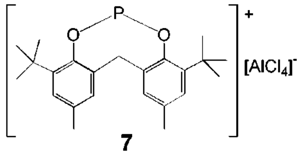
fast exothermic reaction of cation **5** with 2,3-dimethylbutadiene (Scheme 1). Only the signal of **6** at δ_P 93 ppm appears in the ^{31}P NMR spectrum after mixing of the reagents.[14] This value is in a good agreement with the phosphorus chemical shifts of the reaction products of the different 1,3-dienes with $[(R_2N)_2P]^+[AlCl_4]^-$, which are in the range of 69−88 ppm.[15] Obviously, the displacement of one or two nitrogen atoms for the more electronegative ones (O, Cl) have to result in the low field shift. For example, the reaction of the chlorophosphenium ion $[(R_2N)(Cl)P]^+$ and 2,3-dimethylbutadiene leads to corresponding 3-phospholenium cation with δ_P 93.4 ppm.[15b] Thus, ^{31}P NMR as well as ^{1}H NMR spectra[14] of the reaction mixture is entirely consistent with the 3-phospholenium ion structure **6**.

Of particular interest in the present context is a comparison of stability and spectral characteristics of **5** with those of **7**, which has related composition but lacks the possibility of donor coordination. Unfortunately, the corresponding chlorophosphite precursor is easily decomposed in the solution[6c] and our attempts to synthesize and to identify an individual phosphenium cation **7** were unsuccessful.



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In summary, the synthesis of the first dioxaphosphenium ion stabilized by an intramolecular dative P$^+$ ← S bond has been achieved, and its reactivity as usual phosphenium cation has been demonstrated.

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(14) **Reaction of 5 with 2,3-Dimethylbutadiene.** The solution of 0.5 mmol of 2,3-dimethylbutadiene in 5 mL of $CDCl_3$ was added at the ambient temperature to a solution of 0.5 mmol of compound **5** in 2 mL of $CDCl_3$. A fast exothermic reaction immediately proceeded; the temperature of the reaction mixture increased up to 60 °C. After cooling to room temperature the resulting solution was subjected to NMR analysis. Spectral data of **6**: ^{1}H NMR ($CDCl_3$) δ 1.38 s (18H, $(CH_3)_3C$), 1.77 s (3H, CH_3), 1.89 s (3H, CH_3), 2.44 s (6H, CH_3−Ar), 2.80−3.07 br (4H, CH_2), 7.38 s (2H, Ar), 7.69 (2H, Ar).

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