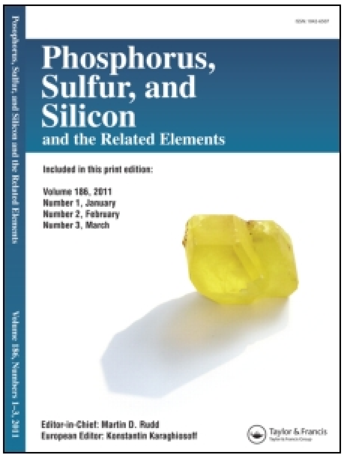

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Gloede, J. , Ozegowski, S. , Weber, D. and Habicher, W. D.(2003) 'A Hexacoordinated P-Bridged Calixarene Derivative -- Phosphorylation of p-tert -Butylthiacalix[4]arene', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 4, 923 — 927

To link to this Article: DOI: 10.1080/10426500307805

URL: http://dx.doi.org/10.1080/10426500307805

Phosphorus, Sulfur and Silicon, 2003, Vol. 178:923–927
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1042-6507/03 $12.00 + .00
DOI: 10.1080/10426500390198165

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A HEXACOORDINATED P-BRIDGED CALIXARENE DERIVATIVE — PHOSPHORYLATION OF *p-tert*-BUTYLTHIACALIX[4]ARENE

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(Received November 9, 2000; accepted March 19, 2001)

p-tert-*Butylthiacalix[4]arene (**1**) reacts with phosphorus pentachloride under participation of the sulfur atoms to a hexacoordinated phosphorus derivative (**2**) of the thiacalixarene. Hydrolysis of **2** leads to the twofold 1,2-bridged thiacalixarene bis(chlorophosphate) **3**.*

Keywords: Hexacoordinated phosphorus derivatives; P-bridged calixarenes; phosphorylation; thiacalix[4]arenes

The phosphorylation of calixarenes and their complexation behaviour were intensively investigated during the last few years.[1] The phosphorylation of *p-tert*-butylcalix[4]arene with phosphorus pentachloride led to the chlorophosphoniumsalt **A**.[2] The corresponding calix[6]- and calix[8]arenes reacted in an analogous way.[2,3] Recently, the phosphorylation of *p-tert*-butylthiacalix[4]arene (**1**) with phosphorus trichloride followed by the oxidation with air giving the chlorophosphate **B** was described.[4] The structures of the two compounds **A** and **B** were established by x-ray analysis.[4,5]

Our interest was focused on the question whether the reaction of **1** with PCl_5 also results in an *O*-phosphorylation or whether the sulfur atoms of the macrocyclic ring are attacked by PCl_5.

In analogy to the former described reactions, *p-tert*-butylthiacalix[4]arene (**1**) was treated with phosphorus pentachloride. The reaction was monitored by ^{31}P NMR. The detected signal at −133 ppm is consistent with a hexacoordinated phosphorus compound. The thus formed

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We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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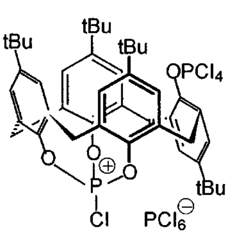
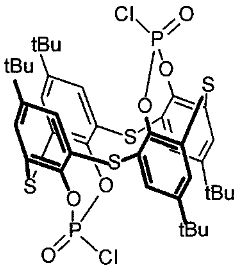
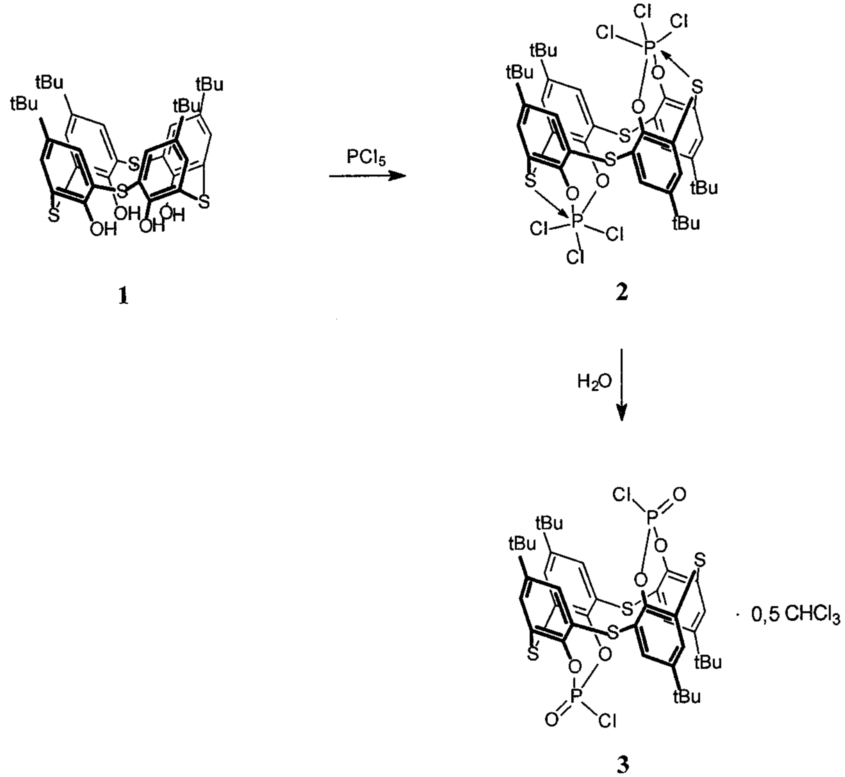


A



B

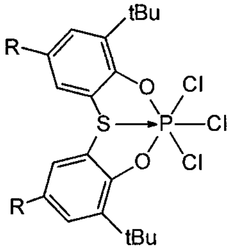
intermediate **2** was not isolated. We assign to this compound the structure shown in Scheme 1. Indeed the hydrolysis of **2** led to the bridged *p-tert*-butylthiacalix[4]arene bis(chlorophosphate) **3**. The NMR data of this compound are nearly identical with those of the recently reported flattened 1,2-alternate compound **B**.[4] Both compounds show a signal at −4 ppm in the ^{31}P NMR spectrum. Due to the synthetic pathway,



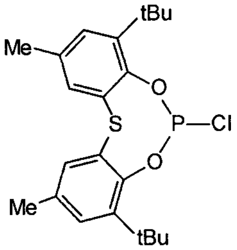
SCHEME 1

compound **B** encloses half of a molecule of *p*-bromotoluene, while compound **3** includes half of a molecule of chloroform.

Note, the ^{31}P signal of another phosphorus compound with a "hexacoordinated phosphorus via donor action,"[6] namely **4a** (δ – 134 ppm), is very close to that of **2**.[7*]



4



5

a R = tBu ; **b** R = Me

These findings confirm the structure for **2**. Two sulfur atoms of the macrocyclic system are involved in the reaction of thiacalix[4]arene (**1**) with phosphorus pentachloride. They stabilize the trichlorodioxyphosphorane systems and prevent reaction of the chlorine atoms with a third hydroxyl group as observed in analogous reactions with sulfur-free calixarenes.[2] Compound **2** constitutes the first example of a calixarene molecule containing two hexacoordinated phosphorus atoms ($\sigma^6\lambda^5$-P-atoms).[†,§]

EXPERIMENTAL

Reaction of *p-tert*-Butylthiacalix[4]arene (1) with PCl$_5$

A solution of **1** (144 mg, 0.2 mmol) and PCl$_5$ (124 mg, 0.6 mmol) in dry chloroform (10 ml) was refluxed under argon for 1 h. After cooling to room temperature the solution was measured by NMR spectroscopy. **2**:

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[*] Monitoring the reaction of 3,3′-di-*tert*-butyl-5,5′-dimethyl-2,2′-dihydroxydiphenylsulfide with PCl$_5$ showed a signal at −132,5 ppm, that we assigned to the derivative **4b**. Furthermore, a signal was found at 170 ppm corresponding to the tricoordinated chloride **5**. The latter results from a side-reaction (e.g., chlorination of the sulfide), which was not further investigated.
The chemical shift in ref. 7 refers to the isolated solid, and not to the reaction mixture.

[†] A calixarene derivative with hexacoordinated phosphorus atom synthesised from *p-tert*-butylcalix[4]arene and P(NMe$_2$)$_3$ has already been described, but it has a $\sigma^6\lambda^3$-P-atom.[8]

^{31}P-NMR: -133 ppm, contaminated with traces of **3** (-3.7 ppm) and $POCl_3$ (4 ppm).

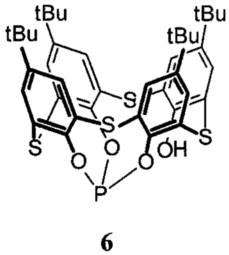
p-tert-Butylthiacalix[4]arene bis(chlorophosphate) (3)

The above mentioned solution was evaporated in vacuo and water (10 ml) was added. The mixture was stirred at room temperature for 2 h and concentrated in vacuo. The residue was treated with ethanol, shortly refluxed and the unsoluble solid was removed by filtration. It was then purified by column chromatography (Silicagel 60, $CHCl_3$/*n*-hexane). **3**: 100 mg (57% yield); m.p.: 435–436°C; ^{31}P-NMR: -3.7 ppm; FAB-MS (m/z) 881; $C_{40}H_{44}Cl_2O_6P_2S_4 \cdot 0{,}5\ CHCl_3$ (941,6) Calcd.: C 51.66, H 4.76, Cl 13.18%, Found:. C 51.54, H 4.54, Cl 13.60%; after drying (12 h, 150°C, 0,1 torr) $C_{40}H_{44}Cl_2O_6P_2S_4$ (881,9) Calcd.: Cl 8,04%, Found: Cl 8,36%.

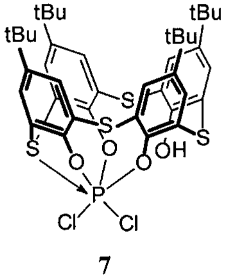
Reaction of 3,3′-di-*tert*-Butyl-5,5′-dimethyl-2,2′-dihydroxydiphenylsulfide with PCl_5

A solution of 3,3′-di-*tert*-butyl-5,5′-dimethyl-2,2′-dihydroxydiphenylsulfide (360 mg, 1 mmol) and PCl_5 (208 mg, 1 mmol) in dry toluene (10 ml) was refluxed for 4 h. After cooling to room temperature the solution was measured by NMR spectroscopy. ^{31}P NMR: 170 ppm (**5**; lit.[10] 168.4 ppm); -132.5 ppm (**4b**), (ratio 2,5:1).

[§] Chlorination of the bridged *p-tert*-butylthiacalix[4]arene phosphite **6** provided the hexacoordinated compound **7** as shown by ^{31}P NMR spectroscopy ($\delta - 129$ ppm).



6



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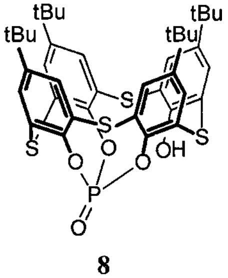

8

The hydrolysis of **7** gives the thiacalixarene phosphate **8**[9] in 78% yield. The analogous sulfur-free calixarene derivative was found to have a partial cone conformation,[8] while a *cone* conformation has been proposed for compound **8**.

Our first report was a poster with the title “P-Containing Hexacoordinated Thiacalixarene Derivatives” at the International Symposium, “Molecular Design and Synthesis of Supramolecular Architectures,” Kazan (Tartarstan/Russia), Sept. 22–24, 2000, *Abstracts*, p. 39.

REFERENCES

[1] a) J. Gloede, *Phosphorus, Sulfur, and Silicon*, **127,** 97 (1997); b) I. Neda, T. Kaukorat, and R. Schmutzler, *Main Group Chemistry News*, **6** (1998), Nr.2–3, p. 4; c) I. S. Antipin, E. Kh. Kazakova, W. D. Habicher, and A. I. Konovalov, *Russian Chem. Rev.*, **67,** 905 (1998); d) C. Wieser-Jeunesse, D. Matt, M. R. Yaftian, M. Burgard, and J. M. Harrowfield, *C. R. Acad. Sci. Paris*, 479 (1998).

[2] a) J. Gloede, B. Costisella, M. Ramm, and R. Bienert, *Phosphorus, Sulfur, and Silicon,* **84,** 217 (1993); b) J. Gloede and I. Keitel, *Phosphorus, Sulfur, and Silicon*, **104,** 103 (1995).

[3] J. Gloede, S. Ozegowski, D. Matt, and A. De Cian, *Tetrahedron Lett.*, **42,** 9139 (2001).

[4] I. S. Antipin, I. I. Stoikov, A. T. Gubaidullin, I. A. Litvinov, D. Weber, W. D. Habicher, and A. I. Konovalov, *Tetrahedron Lett.*, **40,** 8461 (1999).

[5] H. Thönnessen, P. G. Jones, R. Schmutzler, and J. Gloede, *Acta Cryst.*, **C 53,** 1310 (1997).

[6] R. R. Holmes, *Main Group Chemistry News*, **6** (1998), Nr.1, p. 6.

[7] C. Y. Wong, R. McDonald, R. C. Cavell, *Inorg. Chem.*, **35,** 325 (1996).

[8] a) D. V. Khasnis and M. Lattman, *J. Amer. Chem. Soc.*, **112,** 9422 (1990); b) D. V. Khasnis, J. M. Burton, M. Lattman, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, **1991,** 562; c) D. V. Khasnis, J. M. Burton, J. D. McNeil, C. J. Santini, H. Zhang, and M. Lattman, *Inorg. Chem.*, **33,** 2657 (1994).

[9] D. Weber, M. Gruner, and W.D. Habicher, personal comm.

[10] D. J. Sherlock, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *J. Amer. Chem. Soc.*, **119,** 1317 (1997).