Letter

Synthesis and structure of new eight-membered Si—O—$\lambda^5\sigma^4$—P heterocycles

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The reaction of $Bu^t_2Si(OLi)_2$ **1** with $PhPOCl_2$ or of $Ph_2Si(OLi)_2$ with $POCl_3$ in a 1 : 1 molar ratio leads to the formation of the 1,3,3,7-tetraoxa-2,6-disila-4,8-$\lambda^5\sigma^4$-diphosphacyclooctanes **5** and **9**, respectively. An X-ray structure analysis shows **5** to contain an eight-membered $Si_2O_4P_2$ ring in the chair conformation. The Si—O (1.65 Å) and P—O 1.57 Å bond lengths in the ring lie within the typical range; the terminal P═O oxygen centres are in an axial position and oriented *trans* with respect to the central Si_2O_4 plane.

Metallasiloxanes, containing a metal—oxygen—silicon linkage, have been extensively explored,[1–23] mainly owing to two reasons: (*i*) to attempt the synthesis of siloxane polymers with special properties by incorporating different metal atoms in the siloxane chains and (*ii*) to compare the properties of metal siloxides with metal alkoxides.

Although heterosiloxanes containing phosphorus atoms have been studied already, many of them are intractable polymers. Of the molecular species, which have been described, the large majority are derivatives of the monodentate triorganosiloxy ligands (—$OSiR_3$).[24–26] Exceptions to this group are two eight-membered heterocycles with an Si_3O_4-λ^5P or Si_2O_4-λ^5P_2 skeleton, the syntheses and properties of which were reported by Graalman *et al.*[27] and Kerger and Kohlass,[28] respectively. In neither case were the molecules structurally characterised. As part of a study of the bonding characteristics of phosphorus—siloxane ring systems, we present in this study a simple and convenient synthesis of two new eight-membered Si_2O_4-λ^5P_2 heterocycles and report the structure of one of them.

Syntheses and Characterisation

In order to prepare heterocycle **5**, $Bu^t_2Si(OH)_2$ (**1**)[29] is first converted into the lithiumsilanolate **3**. This is subsequently reacted with phenyldichlorophosphane, **4**, giving **5** in good yields. In the same manner, the related compound **9** is formed according to reaction (2) when the freshly prepared diphenylsilanolate **7** is condensed with phosphorylchloride **8** (Scheme 1).

Reaction (2) was followed by ^{31}P NMR spectroscopy. Remarkably, although the reaction was not performed under high dilution conditions, after four hours of stirring at ambient temperature only one singlet at 3.7 ppm assigned to **9** was detected, shifted by about 30 ppm to lower frequencies from the resonance of compound **8** (34.7 ppm). The resonance signal of **5** is observed at −4.9 ppm.

After isolation and crystallisation, compounds **5** and **9** were characterised by different spectroscopic methods. In the infrared spectra, intensive bands at 1041 and 1032 cm^{-1} are assigned to the Si—O—P stretching vibrations of **5** and **9**, respectively.[30] A band at 531 cm^{-1} in the IR spectrum of **9** is assigned to the stretching vibration of the P—Cl bond.

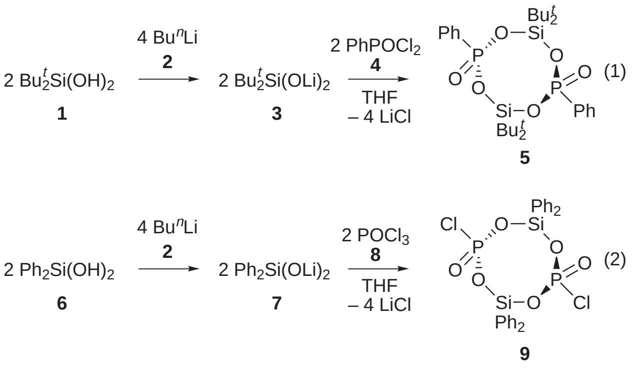
In the EI mass spectra of **5** and **9** peaks of the molecular ions at *m*/*z* 597 and 595 are observed with 10% and 100% intensities, respectively. The base peak at *m*/*z* 539 in the mass spectrum of **5** corresponds to $[M - Bu^t]^+$.

From these data, it was concluded that compounds **5** and **9** correspond to eight-membered $Si_2O_4P_2$ heterocycles. In particular, the synthesis of **9** is noteworthy as it is easily prepared from readily available chemicals and still contains reactive P—Cl groups that may be further derivatised.

Crystal Structure of 5

In order to confirm the structure of compounds **5** and **9** as eight-membered 1,3,3,7-tetraoxa-2,6-disila-4,8-$\lambda^5\sigma^4$-diphosphacyclooctanes, we performed an X-ray analysis of **5**. Suitable colourless crystals of **5** were obtained by recrystallisation from toluene, *n*-pentane or diethyl ether at −18 °C. The result is shown in Fig. 1; selected bond lengths and angles are listed in Table 1.

To our knowledge structural details of Si_2O_4-$\lambda^5\sigma^4P_2$ heterocycles have not been elucidated before. The $Si_2O_4P_2$ centrosymmetric ring adopts a chair conformation. The phosphorus atoms deviate by 0.634 Å from the best plane through the two silicon and four oxygen centres [deviations from that plane are: Si 0.021 Å, O(2) −0.020 Å, O(3) 0.019 Å]. The dihedral angle formed by the intersection of this central Si_2O_4 plane and the PO_2 planes is 40.4°. The silicon as well as the phosphorus centres are slightly distorted from tetrahedral co-



Scheme 1

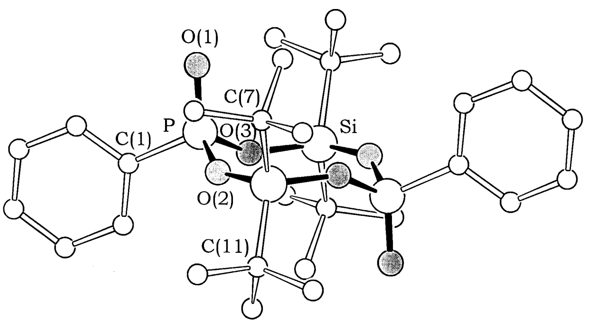


Fig. 1 Molecular structure of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 1.

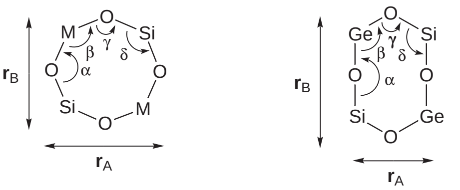
ordination; the inner ring O—Si—O [107.1(2)°] and O—P—O [102.8(2)°] angles deviate only a little from the ideal values. The angles at the oxygen centres O(2) and O(3) are, as expected, quite large [148.8(2)° and 146.1(2)°]. The phenyl rings at the phosphorus centres bind in an equatorial position while the terminal oxygen centres O(1) and O(1A) bind axially and in a *trans* position with respect to the central Si_2O_4 plane. The Si—O bond lengths [1.646(3) Å] are comparable to those found in other heterocycles.[31,32] The terminal P=O(1) [1.449(3) Å], as well as the other P—O distances [1.571(3) Å], lie within the range expected for phosphates.[33]

It is interesting to compare the main structural features of $Si_2O_4M_2$ rings obtained for comparable heterocycles containing boron,[32] germanium,[32] titanium[31] or zirconium[31] centres instead of the phosphorus centres in **5** (Scheme 2, Table 2). The $Si_2O_4B_2$ heterocycle is folded, as observed in **5** though to a lesser extent (intersection of the Si_2O_4 and BO_2 planes is 19.3°), while all other cycles (M = Ge, Ti, Zr) are planar. With the notable exception of the mixed silicon/germanium heterocycle the bond angles at the oxygen centres do not differ by more than about 10°, leading to rather symmetrically shaped eight-membered ring systems as expressed by the r_A/r_B ratios (0.89–0.97). In the germanium compound these angles are quite different ($\Delta = 32°$), which leads to an elongated $Si_2O_4Ge_2$ ring structure ($r_A/r_B = 0.75$). The inner ring angles β and δ at the metallic centres show the expected values; they vary between 103° and 112° for centres in a tetrahedral coordination sphere (M = Ti, Ge, P), 122° for a centre in a trigonal planar coordination sphere (M = B) and 99° for zirconium in an octahedral coordination environment. The diameters r_A and r_B of the heterocycles compare well with the cavity of the twelve-membered crown ether 12-crown-4 (approximately 3.5 Å). Hence, these heterocycles may be suitable ligands for small ions like Li^+. Furthermore, heterocycles **5** and **9** contain terminal P=O groups as further Lewis basic sites. Since the Lewis acidic λ^5, σ^4-phosphorus centres, as well as the silicon centres, may undergo expansion of their valence spheres to become penta- or even hexa-coordinated, these heterocycles may serve as multifunctional complexing agents for cations as well as anions. These issues, as well as more in-depth studies to understand the influence of silicium centres on the shape of these heterocycles, are under current investigation.

Table 1 Selected bond lengths/Å and angles/° for **5**

Si—O(3)[a]	1.643(3)	P—O(1)	1.449(3)
Si—O(2)	1.649(3)	P—O(2)	1.567(3)
Si—C(7)	1.863(5)	P—O(3)	1.575(3)
Si—C(11)	1.869(4)	P—C(1)	1.779(4)
O(3)[a]—Si—O(2)	107.1(2)	O(1)—P—O(3)	114.6(2)
O(3)[a]—Si—C(7)	105.3(2)	O(2)—P—O(3)	102.8(2)
O(2)—Si—C(7)	110.2(2)	O(1)—P—C(1)	113.0(2)
O(3)[a]—Si—C(11)	108.9(2)	O(2)—P—C(1)	105.3(2)
O(2)—Si—C(11)	105.1(2)	O(3)—P—C(1)	104.8(2)
C(7)—Si—C(11)	119.7(2)	P—O(2)—Si	148.8(2)
O(1)—P—O(2)	115.2(2)	P—O(3)—Si[a]	146.1(2)

[a] Symmetry transformation used to generate equivalent atoms: $-x$, $-y$, $-z$.



Scheme 2

Experimental

All experiments were carried under an atmosphere of dry oxygen-free nitrogen. Solvents were dried over molecular sieves and distilled prior to use. $Bu^t_2Si(OH)_2$ (**1**) was prepared according to a method described by Weidenbruch *et al.*,[29] diphenylsilanol (**6**), $PhPOCl_2$ (**4**) and $POCl_3$ (**8**) were purchased from Aldrich. NMR spectra were recorded on a Brucker WP 300 spectrometer. Chemical shifts are referenced against internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). IR and Raman spectra were recorded on Bomen MB-100 or Dilor XY multi-canal spectrometers, respectively; the latter used a 514.32 nm argon ion laser for excitation. Chemical ionisation (CI) mass spectra were run on a Nermag R10-10B spectrometer.

Synthesis of 5

Bu^nLi (1.6 M; 7.5 ml, 6.00 mmol) in *n*-hexane was added dropwise at room temperature to a solution of 1.156 g (6.57 mmol) of $Bu^tSi(OH)_2$ in 15 ml of toluene. To complete the lithiation, the solution was heated at 80 °C for 20 min, then 1.17 g (6 mmol) of $PhPOCl_2$ in toluene (15 ml) were added dropwise. The mixture was kept for one additional hour at 60 °C. After cooling to room temperature, the solution was filtered through Celite. All volatiles were removed *in vacuo* to afford a white solid, which was purified by crystallisation from pentane to give colourless crystals of **5**. Yield: 1.52 g (85%), mp 272 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -3.6$ (s). ^1H NMR (C_6D_6): $\delta = 0.9$ (s, 36H, CH_3), 7.0 (m, 10H, C_6H_5). IR (KBr): 1261s, 1132s, 1041vs, 938w, 831s, 737w, 664.4s, 545vs cm^{-1}. MS: *m/z*

Table 2 Comparison of inner ring angles and diameters r_A and r_B, of $Si_2O_4M_2$ heterocycles (M = B, Ge, Ti, Zr, P)

M	α/°	β/°	γ/°	δ/°	r_A/Å	r_B/Å	r_A/r_B
B[a]	149.0	122.0	149.8	111.6	3.52	3.62	0.97
Ge[a]	174.8	112.2	142.9	109.3	3.31	4.41	0.75
Ti[b]	156.1	107.9	169.1	106.5	3.65	4.09	0.89
Zr[b]	169.2	99.6	161.2	109.9	3.84	4.11	0.93
P[c]	146.1	102.8	148.8	107.1	3.47	3.74	0.93

[a] Ref. 31. [b] Ref. 32. [c] This work.

597 ([M + 1]$^+$, 10%), 539 ([M − Bu^t]$^+$, 100%). Anal. calcd for $C_{28}H_{46}O_6P_2Si_2$: C, 56.3; H, 7.8; P, 10.4; found: C, 55.6; H, 7.9; P, 9.7.

Synthesis of 9

The reaction of $P(O)Cl_3$ (2.83 g, 18.33 mmol) with dilithiated diphenylsilanediol (3.95 g, 18.28 mmol) in THF (30 ml) was performed as described for the synthesis of **5**. The dark yellow residue obtained after removal of the volatiles was precipitated in dichloromethane, yielding a yellow solid, and was characterised as compound **9**. Yield (3.75 g, 73%), mp 228 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -4.9$ (s). ^1H NMR (C_6D_6): $\delta = 7.3$ (m, 20H, C_6H_5). IR (KBr): 1594w, 1477m, 1130s, 1040vs, 737s, 545s, 530 m cm^{-1}. MS: m/z 595 ([M + 1]$^+$, 100%). Anal. calcd for $C_{24}H_{20}Cl_2O_6P_2Si_2$: C, 48.6; H, 3.4; Cl, 11.9; P, 10.4; found: C, 50.8; H, 3.4; Cl, 11.9; P, 10.6.

X-ray crystal structure determination

A colourless single crystal (0.68 × 0.61 × 0.49 mm) of **5** ($C_{28}H_{46}O_6P_2Si_2$, $M = 596.77$) was studied at 293 K on a Sot IPDS System ($\mu = 0.242$ mm^{-1}). The refinement in the triclinic space group $P-1$ with one molecule in the unit cell [$a = 8.566(6)$, $b = 10.167(8)$, $c = 10.542(8)$ Å, $\alpha = 102.80(7)$, $\beta = 103.96(6)$, $\gamma = 104.74(7)$°] converged at $R_1 = 0.0535$ (based on F) and $wR_2 = 0.1242$ (based on F^2) for 4648 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the difference Fourier map and refined independently with different isotropic displacement parameters for each group.

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References

1 H. N. Stokes, *Chem. Ber.*, 1891, **24**, 933.
2 (*a*) A. Ladenburg, *Chem. Ber.*, 1871, **4**, 91. (*b*) A. Ladenburg, *Ann. Chem. Pharm.*, 1872, **164**, 300.
3 S. N. Borisov, M. G. Voronkov and E. Y. Lukevits, *Organosilicon Heteropolymers and Hetero Compounds*, Plenum, New York, 1970.
4 J. C. Saam, in *Silicon Based Polymer Science*, ed. J. M. Zeigler and F. W. G. Fearon, Advances in Chemistry 224, American Chemical Society, Washington DC, 1990.
5 Y. I. Yermakov, B. N. Kuznestov and V. A. Zakharov, *Catalysis by Supported Complexes*, Elsevier, New York, 1981.
6 T. Seiyama and K. Tanabe, *New Horizons in Catalysis*, Elsevier, Amsterdam, 1980.
7 F. R. Hartley, *Supported Metal Complexes*, Reidel, Boston, 1985; C. L. Thomas, *Catalytic Process and Proven Catalysts*, Academic, New York, 1970.
8 R. Pearce and W. R. Patterson, *Catalysis and Chemical Process*, Blackie, Glasgow, 1981.
9 *Tailored Metal Catalysts*, ed. Y. Iwasawa, Reidel, Boston, 1986.
10 D. E. Leyden, G. H. Luttrell, A. E. Sloan and N. J. De Angelis, *Anal. Chim. Acta*, 1976, **84**, 97.
11 K. Unger, H. Ruppercht, B. Valentin and W. Kircher, *Drug Dev. Ind. Pharm.*, 1983, **9**, 69.
12 (*a*) E. P. Plueddmann, *Silane Coupling Agents*, Plenum, New York, 982. (*b*) *Silanes and Other Coupling Agents*, ed. K. L. Mittal, VSP, Utrecht, 1992.
13 B. Arkles, *Chemtech*, 1977, **7**, 766.
14 H. Schmidbaur, *Angew. Chem.*, 1965, **77**, 206; *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 201.
15 F. Schindler and H. Schmidbaur, *Angew. Chem.*, 1967, **79**, 697; *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 683.
16 K. A. Andrianov, *Inorg. Macromol. Rev.*, 1970, **1**, 33.
17 M. Baier, P. Bissinger, J. Bluümel and H. Schmidbaur, *Chem. Ber.*, 1993, **126**, 947.
18 A. R. Barron, C. C. Landry, L. K. Cheatham and A. N. MacInnes, *J. Mater. Chem.*, 1991, **1**, 143.
19 A. K. McMullen, T. D. Tilley, A. L. Rheingold and S. J. Geib, *Inorg. Chem.*, 1989, **28**, 3772.
20 G. A. Sigel, R. A. Bartlett, D. Decker, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1987, **26**, 1773.
21 D. C. Hrncir and G. D. Skiles, *J. Mater. Res.*, 1988, **3**, 410.
22 M. G. Voronkov, E. A. Maletina and V. K. Roman, in *Heterosiloxanes*, ed. M. E. Vol'pin and K. Gingild, Soviet Scientific Review Supplement, Series Chemistry, Academic Press, London, 1988, vol. 1.
23 R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205.
24 M. G. Voronkov, S. N. Borisov and E. Y. Lukevits, in *Organosilicon Derivatives of Phosphorus and Silicon*, Plenum, New York, 1971.
25 K. A. Andrianov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 381; translated in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1965, 366.
26 K. A. Andrianov, *Zh. Obshch. Khim.*, 1972, **42**, 850; translated in *J. Gen. Chem. USSR*, 1972, **42**, 840.
27 O. Graalman, M. Meyer and U. Klingebiel, *Z. Anorg. Allg. Chem.*, 1986, **534**, 109.
28 K. Kerger and R. Kohlass, *Z. Anorg. Allg. Chem.*, 1967, **354**, 44.
29 D. Weidenbruch, H. Pesel and D. Van Hieu, *Z. Naturforsch., B*, 1980, **35**, 31.
30 K. A. Andrianov, T. V. Vasil'eva and L. M. Kananashvili, *Izv. An. SSR, Otd. Khim., Nauk*, 1961, 1030.
31 A. Haoudi-Mazzah, A. Mazzah, H.-G. Schmidt, M. Noltemeyer and H. W. Roesky, *Z. Naturforsch., B*, 1991, **46**, 587.
32 A. Mazzah, A. Haoudi-Mazzah, M. Noltemeyer and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 1991, **604**, 93.
33 *International Tables of X-Ray Crystallography*, ed. International Union of Crystallography, The Kynoch Press, Birmingham, UK, 1969, vol. I.

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