Di(phosphavinyl) Ethers (*2,4*-Diphospha-*3*-oxapentadienes)

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

Hydrolytic cleavage of the *P*-chlorophosphaalkenes $(RMe_2Si)_2C{=}PCl$ (R = Me: **1a**; R = *i*Pr: **1b**) in the presence of triethylamine leads to di(phosphavinyl) ethers (*2,4*-diphospha-*3*-oxapentadienes) $[(RMe_2Si)_2C{=}P]_2O$ (**2a**, **2b**) as main products, accompanied by alkylphosphinic acids $(RMe_2Si)_2(H)CP(H)(O)OH$ (**3a**, **3b**). The hydrolysis of $(PhMe_2Si)_2C{=}PCl$ (**1c**) proceeds less selectively. Reactions with metal oxides under aprotic conditions provide **2a** [impure, from **1a** with $(n\mathrm{Bu}_3Sn)_2O$] and **2b** [from iodophosphaalkene $(i\mathrm{PrMe}_2Si)_2C{=}PI$ with Ag_2O] as oils. ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, however, allow unambiguous characterisation of **2a** and **2b**. Formation mechanisms, structure, and C=P–O π stabilisation of the oxabisphosphaalkene $[(H_3Si)_2C{=}P]_2O$ (**2′**) were studied with DFT methods. The double [2+4] cycloaddition reaction of **2a** with two equivalents of cyclopentadiene leads to the phosphinous anhydride **7** as a mixture of diastereomers whereas the addition of two equivalents of tetrachloro-*o*-benzoquinone proceeds in a diastereoselective fashion. An X-ray crystal structure determination of the resulting oxo-bridged bis(2-phospha-2,5-dioxa-3,4-benzophospholene) derivative **8** revealed the presence of a racemic mixture of *(R,R)*- and *(S,S)*-configurated molecules. The solid state structure of a by-product, bisylphosphonic tetrachlorocatechol monoester $(Me_3Si)_2CH{-}P({=}O)(OH){-}o{-}OC_6Cl_4OH$ **9**, was also determined crystallographically.

Key words: Phosphaalkenes, Di(phosphavinyl) Ethers, Cycloaddition, X-Ray Crystallography, DFT Calculations, Heteronuclear NMR

Introduction

The P–O–P unit is undoubtedly the most common structural motif in phosphorus chemistry. In naturally occurring and anthropogenic phosphorus compounds, $P^{V}OP^{V}$ systems with tetracoordinated phosphorus (such as P_4O_{10} and oligo- or polyphosphates) are the most abundant. Higher coordination numbers (*e. g.* $P^{V}OP^{V}$ with pentacoordinated phosphorus, *e. g.* P_4O_{18}) [1] and lower coordination numbers ($P^{III}OP^{III}$, *e. g.* P_4O_6 and phosphinous anhydrides) [2] have been investigated to a much lesser extent. POP systems involving two-coordinated phosphorus, however, have not appeared in the literature [3]. The only as yet characterised bis-alkylidene POP system was detected as the central di(phosphavinyl) ether ligand ^{t}Bu(H)-CPOPC(H)^{t}Bu of a unique tetranuclear manganese carbonyl complex, derived from the reaction of the methylcyclopentadienylmanganese carbonyl precursor with ^{t}BuCP, apparently in the presence of traces of moisture [4]. Formally, this product can be seen as resulting from the addition of the two O–H bonds of a water molecule, each to one PC triple bond. This elegant access to a doubly unsaturated POP ligand was, however, never reproduced with the metal-free system [3]. Recently we observed that the heavier congeners of doubly unsaturated POP systems, $[(Me_3Si)_2C{=}P]_2S$ (I) and its selenium homologue, are stable compounds that react (i) with $Mo(CO)_4$ to give four-membered chelate complexes contain-

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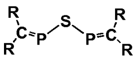

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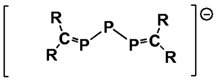

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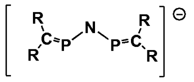

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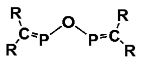

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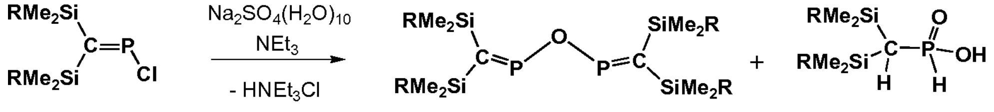


R = Me: **1a**
R = *i*Pr: **1b**
R = Ph: **1c**

R = Me: **2a**
R = *i*Pr: **2b**
R = Ph: **2c**

R = Me: **3a**
R = *i*Pr: **3b**
R = Ph: **3c**

(1)

ing exocylic P=C bonds [5], (ii) with two equivalents of cyclopentadiene and of tetrachloro-*o*-benzoquinone in double [2+4] cycloaddition reactions [5], and (iii) with elemental sulfur and selenium in a surprising fashion, different from the behaviour of comparable monofunctional phosphaalkenes [3], furnishing P_2Se_5-related heteronorbornane structures [6]. The latter reactions – in agreement with results obtained from density functional computations [6] – suggest a certain degree of electronic communication between the π systems of the two neighbouring phosphaalkene P=C bonds *via* the chalcogen element.

Such delocalisation is known from Niecke's *2,3,4*-triphosphapentadienide anion $\{[(Me_3Si)_2C{=}P]_2P\}^-$ [7] (II), which is a precursor to P_3C_2 heterocycles including bicyclic systems. Its heavier *3*-arsa congener $\{[(Me_3Si)_2C{=}P]_2As\}^-$ [7] was also characterised, but the lighter *2,4*-diphospha-*3*-azapentadienyl anion $[(Me_3Si)_2C{=}P]_2N^-$ (III) and the isoelectronic *2,4*-diphospha-*3*-oxapentadiene $[(Me_3Si)_2C{=}P]_2O$ (IV) are unknown. When studying reactions with *P*-halogenophosphaalkenes $(Me_3Si)_2C{=}PX$ (X = F, Cl, I) [8] for a number of synthetic purposes, we tentatively assigned a minor ^{31}P NMR signal at about +352 (±1) ppm in the reaction mixtures to $[(Me_3Si)_2C{=}P]_2O$ ("POP") [9] as a possible hydrolysis product. In the context of current work on related PNP ligands $[(RMe_2Si)_2C{=}P]_2NR$ (R = Me, *i*Pr, Ph; R′ = *t*Bu, Me_3Si) [9] that exhibit, as does "POP", ^{31}P NMR resonances in the range of +350 to +360 ppm, it became necessary to undertake a synthetic study of the as yet unexplored unsaturated POP system (*2,4*-diphospha-*3*-oxapentadienes = oxabisphosphaalkenes), in order to enable the unambiguous ^{31}P NMR spectroscopic discrimination of transient PNP compounds from POP hydrolysis products.

Results and Discussion

Hydrolytic approach

To suppress the formation of HCl, which would add to the P=C bond, compounds **1a** [8] or **1b** [10a] in THF were mixed with an excess of triethylamine before a THF solution of $Na_2SO_4 \cdot 10\ H_2O$ was added at 0 °C. Removal of all volatiles followed by treatment of the residue with pentane furnished brown oils. ^{31}P NMR data revealed the presence of **2a** or **2b**, accompanied by about 10 – 15 % of the phosphinic acids **3a** or **3b** (Eq. 1). The hydrolysis of $(PhMe_2Si)_2C{=}PCl$ (**1c**) proceeds less selectively [10b] (see Experimental Section).

The mixture **2a** / **3a** (approx. 9 : 1) was subsequently used for cycloaddition reactions [11]. To avoid the formation of phosphinic acids, aprotic reaction conditions are necessary.

The hydrolysis reaction of *P*-chlorophosphaalkenes **1** was also investigated by B3LYP/6-31+G* density functional calculations. All the calculations were performed on the model compound $(H_3Si)_2C{=}PCl$ (**1′**). As the hydrolysis usually starts with the substitution of the halogen by the OH group, we assumed the formation of $(H_3Si)_2C{=}POH$ (disilylmethylene phosphinous acid) in the first step. The activation barrier of this substitution reaction involving a single water molecule (Fig. 1) is quite large. It is clearly seen in the transition structure that the direct transfer of the proton from the O to the Cl atom is energetically demanding because of the formation of the strained four-membered ring. It is known, however, that the barrier of hydrolysis reactions is lowered in the presence of three or four water molecules, which enable the proton transfer *via* a hydrogen bonded network in the transition structure [12]. Whereas this reaction step is somewhat endothermic, the presence of the base (which then reacts with HCl) drives the formation of the product.

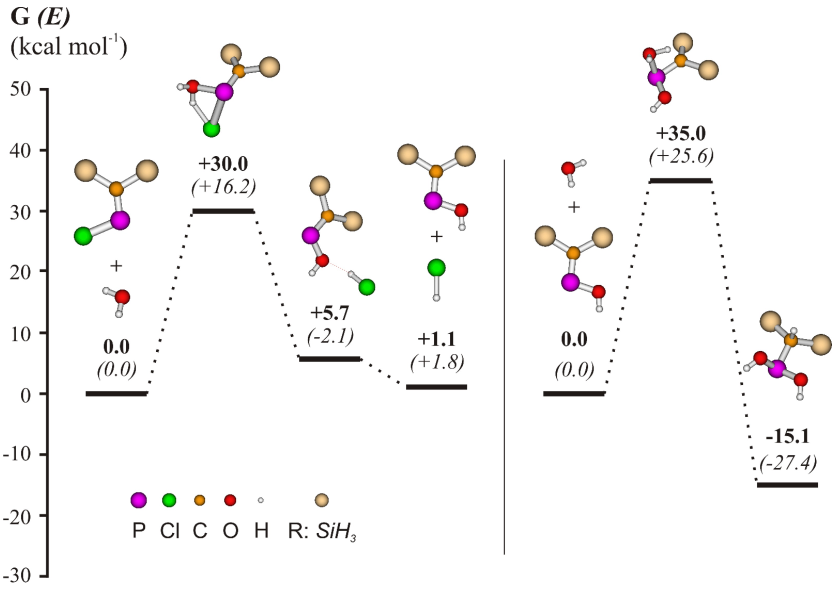
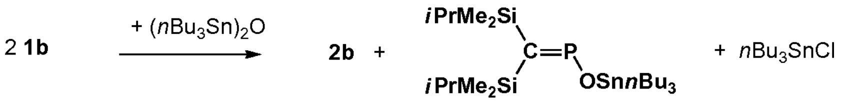


Fig. 1. B3LYP/6-31+G* energy (E, kcal mol^{-1}, in italics) and Gibbs free energy (G, kcal mol^{-1}, in bold) of the hydrolysis products of $(H_3Si)_2C{=}PCl$ along the reaction coordinate. Left: formation of $(H_3Si)_2C{=}POH$; right: formation of $(H_3Si)_2CH–P(OH)_2$.

$$2\ \mathbf{1a} + (n\mathrm{Bu_3Sn})_2\mathrm{O} \longrightarrow \mathbf{2a} + 2\ n\mathrm{Bu_3SnCl} \qquad (2)$$



(3)

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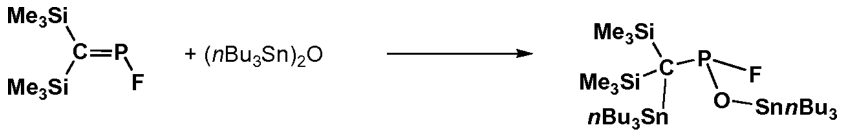
The addition of the second molecule of water at the double bond of $(H_3Si)_2C{=}POH$ produces the disilylmethylphosphonous acid $(H_3Si)_2CH–P(OH)_2$, which is a tautomer of the disilylmethylphosphinic acid **3′**. The reaction is exothermic, and the activation energy of this step (26 kcal mol^{-1}) is larger than that of the first step (16 kcal mol^{-1}). The experimental finding that **3** is formed only in small amounts besides **2**, is in good accordance with the substantial activation barrier of this reaction step. The formation of the bis(phosphavinyl)ether **2′** in a condensation reaction is a well known reaction that needs no further evaluation.

Germoxane and stannoxane method

Hexamethyldisiloxane is unreactive towards **1a**–**1c**. After mixing dissolved **1a** with the germoxane $(Me_2GeO)_4$ the ^{31}P NMR spectrum showed signals at $\delta = 344$ ppm (**1a**, still about 70 %), at $\delta = 352.7$ ppm (about 20 %, **2a**, or a closely related species) and at $\delta = 25.4$ ppm (about 10 %). Separation by distillation was not successful [13].

Hexamethyldistannoxane reacts with **1a** in toluene within 1 h furnishing **2a** in *ca.* 20 % yield in a selective fashion, but subsequently several ^{31}P NMR signals in the chemical shift range of tri-coordinated phosphorus appear with increasing intensity. Satellite doublets indicate the existence of P–Sn bonds and of P–O–Sn and / or of P–C–Sn units. After complete consumption of **1a**, **2a** cannot be separated from the other products [11].

Liquid hexa-*n*-butyldistannoxane reacts in a straightforward fashion with **1a** giving **2a** and $n\mathrm{Bu_3SnCl}$ (Eq. 2). This allowed measurement of the NMR data of **2a** undisturbed by other phosphorus species. Separation of **2a** from $n\mathrm{Bu_3SnCl}$ however was not achieved since attempted distillation of **2a** led to its decomposition. The related reaction of hexa-*n*-butyldistannoxane with **1b** remained incomplete. ^{31}P and ^{119}Sn NMR spectra reveal that **1b**, **2b** and $n\mathrm{Bu_3SnCl}$ are accompanied by $(i\mathrm{PrMe_2Si})_2\mathrm{C{=}POSn}(n\mathrm{Bu})_3$ [**4**; $\delta^{31}\mathrm{P} = 382.2$; $\delta^{119}\mathrm{Sn} = 98.2$; $^{2}J(\mathrm{SnP}) = 30.4$ Hz] (Eq. 3) [10a].



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(4)

To overcome separation problems, precipitation of the insoluble nBu$_3$SnF was attempted. For that purpose, $(Me_3Si)_2C{=}PF$ was used as starting material for the intended exchange reaction with hexa-*n*-butyldistannoxane (Eq. 4) [11]. This reaction led, however, selectively and without P–F cleavage to a fluorophosphane **5** [δ^{31}P = 226.8, ^1J(PF) = 1075 Hz, ^2J(SnP) = 83.3 Hz] that can be considered as the product of the 1,2-addition of a stannoxane Sn–O bond to the P=C double bond. **5** is accompanied by about 5 % of a second unidentified fluorophosphane species [**6**; δ^{31}P = 225.4, ^1J(PF) = 1059 Hz]. The ^{119}Sn NMR spectrum of **5** exhibits two resonances, δ^{119}Sn = 8.5 (s) and −9.5 (d,d). The d,d pattern of the upfield ^{119}Sn resonance is due to ^2J(SnP) = ±83.3 Hz and to ^3J(SnF) = ±97.7 Hz. The occurence of *two* tin atoms in the main product **5** is also supported by the EI mass spectrum, which exhibits typical isotopic patterns for the ions *m/z* = 691 $[M-2\ C_4H_9]^+$ and 673 $[M-C_4H_9,\ -\ C_4H_8,\ -\ F]^+$. The presence of an isomer with geminal Sn and F substituents at P can be excluded on chemical and spectroscopic grounds, but a reliable assignment of the two ^{119}Sn signals of **5** ("coupling" / "non-coupling", Sn–O *vs*. Sn–C) is not possible [11].

Silver oxide method

Stirring a suspension of two equivalents **1b** with Ag_2O in pentane for an extended period leads to the formation of oxabisphosphaalkene **2b**. The necessary reaction time (from 1 d to several months) clearly depends greatly on the source of commercial Ag_2O. Better results were obtained with the related *P*-iodophosphaalkene $(i\text{PrMe}_2\text{Si})_2C{=}PI$ (Eq. 5). After separation of the precipitate and subsequent removal of all volatiles from the solution, a brown oily residue remained that consisted – according to NMR and elemental analysis – predominantly of **2b**. Reactions of **1a**–**1c** with Li_2O and with ZnO did not lead to satisfactory results [11].

$$2\ (i\text{PrMe}_2\text{Si})_2\text{C}{=}\text{PI} + \text{Ag}_2\text{O} \rightarrow \mathbf{2b} + 2\ \text{AgI} \qquad (5)$$

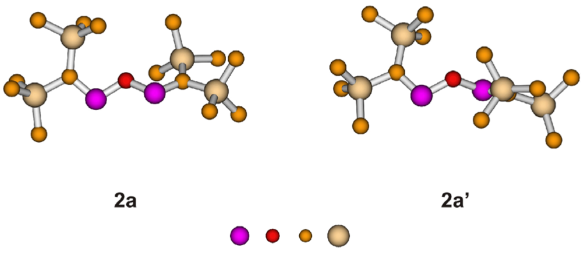


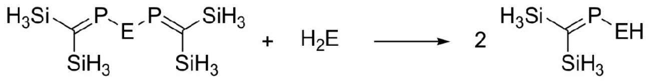
Fig. 2. Calculated structures of conformers of $[(Me_3Si)_2C{=}P]_2O$ (**2a**). Bond lengths and bond angles: **2a**: P–O 1.697, P–C 1.665; P–O–P 120.5, C–P–O 107.5; **2a′**: P–O 1.691, P–C 1.666; P–O–P 127.9, C–P–O 107.4.

Structure and bonding

Among the B3LYP/6-31+G* optimised **2a** and **2a′** structures (Fig. 2) the **2a** isomer is more stable by 1.2 kcal · mol^{-1}. In both structures the C=P–O–P=C linkage forms a W-shape with C_2 symmetry. While the corresponding structure with SiH_3 groups is planar, the trimethylsilyl substituted **2a** is nearly planar, and in **2a′** the deviation from planarity is substantial, presumably for a better steric accommodation of the bulky trimethylsilyl groups. The bond lengths and bond angles are in the usual range.

The stabilising effect of the conjugation for the SiH_3 substituted model compounds was estimated by the isodesmic reactions below (see ref. [6] for the S analogue).

The computed stabilisation energies are collected in Table 1. Reaction (6) is nearly thermoneutral for each chalcogen, showing that the stabilisation energy in the two C=P–OH fragments is nearly equal to that in the C=P–O–P=C moiety. Data for reaction (7) estimate the interaction between the C=P and chalcogen fragments, which is 30.2 kcal mol^{-1} for oxygen, *i. e.* a remarkably high 15.1 kcal mol^{-1} for each of the C=P–O units. In the case of **2a** the isodesmic reaction energy is somewhat reduced to 27.0 kcal mol^{-1} (13.5 kcal mol^{-1} for each C=P–O unit). The slight decrease can be attributed to the non-planarity of the molecule, resulting in a weaker interaction between the



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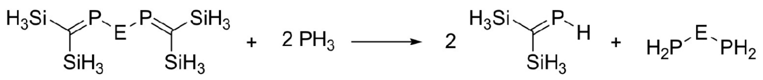


(7)

Table 1. Stabilisation energies of the reactions (6) and (7): E = O, S, Se (kcal · mol^{-1}).

	O	S	Se
(6)	−1.8	0.1 (ref. [6])	−1.5
(7)	30.2	17.6 (ref. [6])	20.7

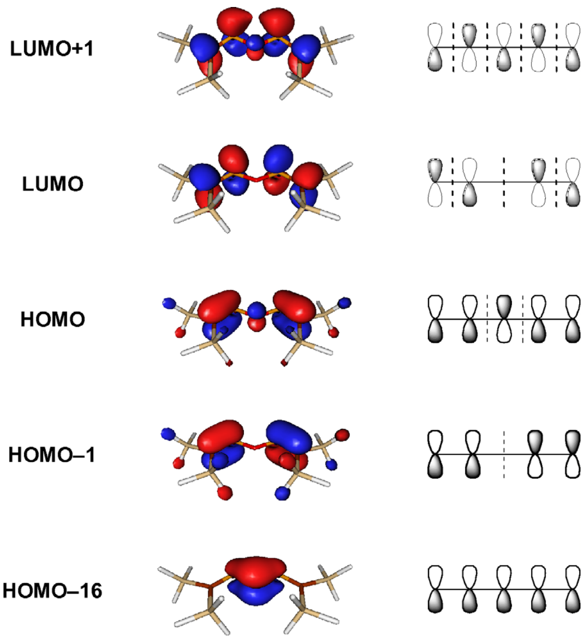


Fig. 3. Canonic molecular orbitals of an oxabisphosphaalkene (HF/6-31G*//B3LYP/6-31+G*).

lone pair of the oxygen and the π^*(C=P) orbitals. According to the second order perturbational analysis of the Fock matrix in the NBO basis (which estimates the energy of donor-acceptor interactions between natural orbitals) a value of 9.4 kcal mol^{-1} was obtained for the interaction between the oxygen lone pair and each antibonding π^*(C=P) orbital, which is comparable to that obtained using reaction (7) for **2a** – see above. (It is worth noting that no other significant stabilising interaction within the CPOPC moiety was observed in this analysis). The conjugation effect can also be illustrated by the molecular orbitals of $[(H_3Si)_2C{=}P]_2O$ (Fig. 3), which clearly show the characteristic nodal properties of five-membered conjugated systems. The energies of the isodesmic reactions (6) and (7) give similar results for the sulfur and selenium analogues, but the stabilisation for the oxygen analogue is higher than for the heavier chalcogens.

Cycloaddition reactions

2a reacts with two equivalents of cyclopentadiene in dichloromethane at r. t. within 24 h to form the bis-[2+4] cycloadduct **7**, accompanied by the phosphinous acid **3a** because of impurities in the starting material (Eq. 8). **7** is identified by two singlet signals in the $^{31}P\{^1H\}$ NMR spectrum indicating the presence of new oxygen-bridged bis(2-phospha-norbornene) derivatives as pairs, either (i) *endo,endo* and *exo,exo* isomers of diastereochemically pure *RS/SR or RR/SS* or (ii) as *RS/SR* and *RR/SS* configurated products, existing either as *endo,endo* or as *exo,exo*-isomers [5]. Since in the case of [2+4] cycloadditions of related

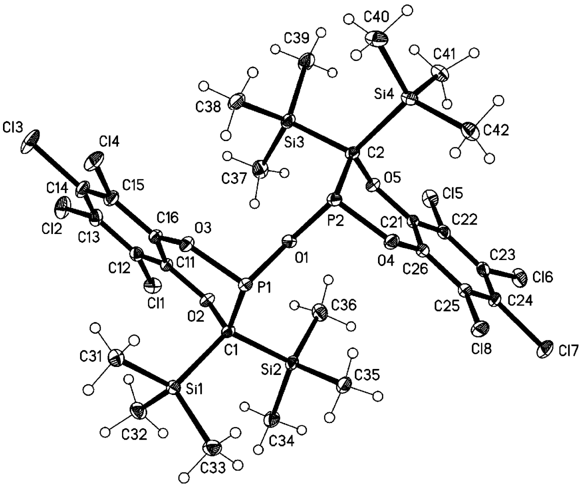
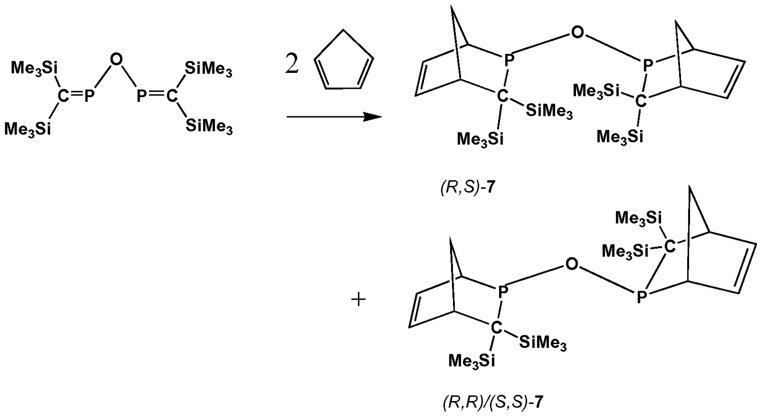


Fig. 4. The structure of compound **8** in the crystal. Ellipsoids represent 30 % probability levels. Selected bond lengths (Å), angles and torsion angles (deg): P1–O3 1.6586(10), P1–O1 1.6644(10), P1–C1 1.8271(14), P2–O4 1.6544(11), P2–O1 1.6636(10), P2–C2 1.8271(15); O3–P1–O1 99.40(5), O3–P1–C1 99.05(6), O1–P1–C1 99.77(6), O4–P2–O1 99.44(5), O4–P2–C2 99.51(6), O1–P2–C2 99.52(6), P2–O1–P1 118.81(6); C1–P1–O1–P2 −161.73(7), C2–P2–O1–P1 −164.93(7).



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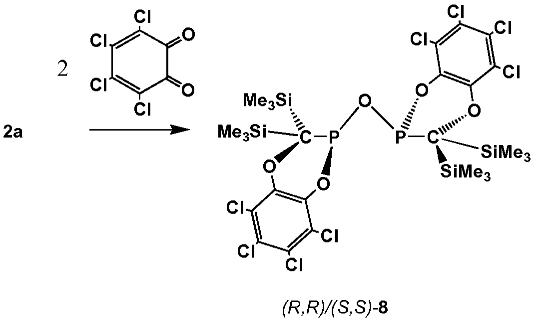

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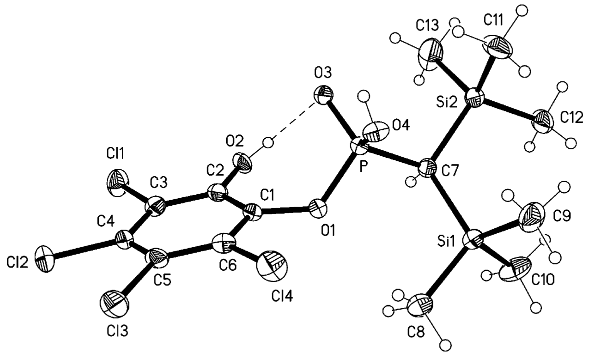

Fig. 5. The structure of the asymmetric unit of compound **9** in the crystal. Ellipsoids represent 50 % probability levels. Selected bond lengths (Å) and angles (deg): P–O3 1.5017(15), P–O4 1.5455(16), P–O1 1.6020(15), P–C7 1.763(2); O3–P–O4 113.08(8), O3–P–O1 108.40(8), O4–P–O1 106.16(8), O3–P–C7 115.49(9), O4–P–C7 109.48(9), O1–P–C7 103.36(9), C1–O1–P 126.23(13).

thio- and selenophosphaalkenes (Me$_3$Si)$_2$C=P–E–PR$_2$ (R = *t*Bu, *i*Pr) with cyclopentadiene, rearrangements of the *endo*-isomers, as initially formed, into more stable *exo*-isomers occurred within 24 h [14], we assume that both diastereomers of the phosphinous anhydride **7** exist as the *exo,exo*-isomers [5], as depicted in Eq. 8.

The formation of the 1 : 2 adduct **8** from the reaction of **2a** with two equivalents of tetrachloro-*o*-benzoquinone (TOB) [5, 15] proceeds diastereoselectively (Eq. 9). In the recrystallisation of **8** the phosphinic acid **3a** (from the impure starting material) is removed.

The proposed identity and stereochemistry of the oxo-bridged bis(2-phospha-2,5-dioxa-3,4-benzophospholene) derivative **8** were confirmed by X-ray crystallography. Compound **8** (Fig. 4) crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ as a racemic mixture of *(RR)* and *(SS)* enantiomers with approximate C_2 symmetry (r. m. s. devation 0.07 Å).

The C1–P1–O1–P2–C2 moiety of **8** exhibits a distorted W-shaped arrangement, whereby the five atoms are approximately coplanar (mean deviation 0.14 Å). From this central backbone the benzophospholene-related heterocycles extend in opposite directions, allowing the phosphorus atoms to minimise their lone pair interactions in a "*gauche*"-type fashion. Central and endocyclic P–O distances are close to 1.66 Å, and all angles around the phosphorus atoms lie between 99 and 100°. The angle P–O–P of 118.81(6)° is significantly larger than in the analogous selenium-bridged compound [87.86(3)°] [5]. The two molecules are otherwise very similar, but the structures are not isotypic; the selenium derivative crystallizes as a chloroform solvate [5].

The packing in the crystal involves one borderline C–H···Cl contact and four Cl···Cl contacts between 3.33 and 3.61 Å, leading to a three-dimensional connectivity. The intramolecular contacts H36A···O1 and H37B···O1, although of narrow angle (129°), may be structurally significant.

From the attempted reaction of **2a** with three equivalents of TOB, a bis(silyl)methylphosphonic acid

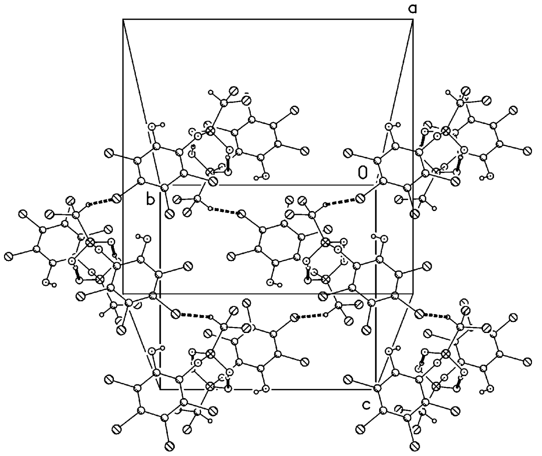

Fig. 6. Packing diagram of the dimers of compound **9**. Methyl groups are omitted for clarity. Hydrogen bonds are indicated by thicker lines (dashed for H···Cl). View direction perpendicular to (100); region $x \approx 1/4$.

tetrachlorocatechol monoester **9** $(Me_3Si)_2CH–P(=O)-(OH)–o-OC_6Cl_4OH$ was isolated as colourless crystals. **9** is formally related to phosphinic acid **3a** by 1,4-addition of the P–H function to the quinone system [16]. Compound **9** (Fig. 5) crystallizes in the monoclinic space group *C*2/*c* with *Z* = 8. The largest angles at phosphorus involve the formal double bond P=O3. An intramolecular hydrogen bond O2–H02···O3 is observed; the other OH function causes the molecules to associate in inversion-symmetric hydrogen-bonded dimers *via* bonds O4–H···O3 / O4′–H···O3. The extended packing involves three C–H···X contacts (X = Cl, O) and three Cl···Cl contacts between 3.46 and 3.61 Å. A section of the packing at $x \approx 1/4$, showing the dimers and the effect of the contact H7···Cl2, is shown in Fig. 6.

NMR spectra

Di(1-phosphavinyl) ethers **2a**–**2c** give singlet signals in their ^{1}H-decoupled ^{31}P NMR spectra in a narrow chemical shift range from +352 to +358 ppm. In the ^{13}C and ^{29}Si NMR spectra they exhibit characteristic X parts of AA′X patterns (see Experimental Section). *cis*- and *trans*-Silyl groups give separate sets of signals.

Experimental Section

The experiments were carried out in an atmosphere of dry nitrogen gas. NMR spectra were recorded using Bruker spectrometers AC 200 and Avance 400 with $SiMe_4$ and 85 % H_3PO_4 as internal or external standards, respectively.

*2,4-Diphospha-3-oxa-1,1,5,5-tetrakis(trimethylsilyl)-pentadiene (**2a**)*

*(a) Hydrolysis of **1a***: To a mixture of 1.5 g (6.6 mmol) of **1a** and 3.0 g (30 mmol) of triethylamine in THF (10 mL) was added dropwise a solution of 0.108 g (3.3 mmol) of $Na_2SO_4 \cdot 10\ H_2O$ in THF (10 mL). Subsequently all volatiles were removed under reduced pressure, the residue was treated with pentane, and solid $MgSO_4$ was added as a drying agent. After filtration and removal of pentane under reduced pressure a brown oil was left. A proton-coupled ^{31}P NMR spectrum shows **2a** (δ^{31}P = 353.4; I = 12), accompanied by less than 10 % **3a**, δ^{31}P = 25.4 (d, d), ^1J(PH) = 531.3 Hz, ^2J(PH) 19.2 Hz; I = 0.8.

2a: $C_{14}H_{36}P_2OSi_2$, M = 394.2 g · mol^{-1}. – Analysis: calcd. C 42.61, H 9.19; found C 41.06, H 9.05.

*(b) Reaction of **1a** with $(nBu_3Sn)_2O$:* To 1.56 g (1.32 mmol) $(n\text{Bu}_3\text{Sn})_2\text{O}$ was added 0.59 g (2.64 mmol) **1a**. The mixture turned brown immediately. Attempted separation of **2a** from nBu$_3$SnCl by distillation led to decomposition of **2a**. – ^{1}H NMR (400 MHz, [D$_8$]toluene): δ = 0.09 (s, Me$_3$Si), 0.06 (s, Me$_3$Si). – ^{13}C NMR (101 MHz, [D$_8$]toluene): δ = 1.9 (pseudo-t, X part of AA′X, N = 7.1 Hz *C*H$_3$Si), 2.6 (s, *C*H$_3$Si), 171.5 (four lines, X part of an AA′X system, N = 31.9 Hz; distance of outer lines N = 76.8 Hz, *C*=P). – ^{29}Si NMR (38.8 MHz, [D$_8$]toluene): δ = −0.8 (pseudo-t, X part of AA′X, N = 3.5 Hz, CH$_3$*Si*), −6.1 (pseudo-t, X part of an AA′X system, N = 20.7 Hz, CH$_3$*Si*). – ^{31}P{^{1}H} NMR (81.0 MHz, [D$_8$]toluene): δ = 352.7 (s).

*2,4-Diphospha-3-oxa-1,1,5,5-tetrakis(i-propyldimethylsilyl)pentadiene (**2b**)*

*(a) Hydrolysis of **1b**:* To a mixture of 1.6 g (6 mmol) **1b** and 2.52 g (25 mmol) of triethylamine in THF (10 mL) was added dropwise a solution of 0.99 g (3 mmol) of $Na_2SO_4 \cdot 10\ H_2O$ in THF (10 mL). After 12 h stirring at r. t. all volatiles were removed under reduced pressure, and the residue was treated with pentane. After filtration and removal of pentane under reduced pressure a brown oil was left. A proton-coupled ^{31}P NMR spectrum shows that **2a** (δ ^{31}P = 352.43) was accompanied by bis(*iso*propyldimethylsilyl)-methylphosphinic acid **3b** (*i*PrMe$_2$Si)$_2$CHPH(=O)(OH) (δ ^{31}P = 31.3).

(b) Reaction of (iPrMe$_2$Si)$_2$C=PI with Ag$_2$O: To a solution of (*i*PrMe$_2$Si)$_2$C=PCl (1.20 g, 4.28 mmol) in THF (5 mL) was added Me$_3$SiI (0.86 g, 4.28 mmol) at r. t. After 3 h of stirring, the ^{31}P NMR spectrum of the solution showed the quantitative formation of (*i*PrMe$_2$Si)$_2$C=PI (δ = 358.2 ppm). The resulting Me$_3$SiCl and the solvent were removed *in vacuo*, and the residue was dissolved in THF (10 mL). To the solution of (*i*PrMe$_2$Si)$_2$C=PI was added Ag$_2$O (0.5 g, 2.14 mmol) at r. t. After 3 d of stirring at r. t.

AgI was removed by filtration. After the removal of the solvent, the crude product of **2b** was obtained as an yellow oil. Yield: 0.94 g (86 %). Analysis: $C_{22}H_{52}OP_2Si_4$ (506.94): calcd. C 52.12, H 10.34; found C 52.06, H 10.46.

2b: ^{1}H NMR (300.1 MHz, [D$_6$]benzene) δ = 0.00 ppm (s, broad, CH_3), 0.78 – 0.82 ppm (m, CH(CH_3)$_2$), 1.13 – 1.25 ppm (m CH(CH$_3$)$_2$). – ^{13}C NMR (75.47 MHz, [D$_6$]benzene): δ = −2.19 ppm (pseudo-t, X part of AA′X, N = 18 Hz, (CH$_3$)$_2$*i*PrSi), −1.80 ppm (pseudo-t, X part of AA′X, N = 3.08 Hz, (CH$_3$)$_2$*i*PrSi), 14.07 ppm (pseudo-t, X part of AA′X, N = 8 Hz, CH(CH$_3$)$_2$), 14.77 ppm (pseudo-t, X part of AA′X, N = 3.76 Hz, CH(CH$_3$)$_2$), 17.53 ppm (s, CH(CH$_3$)$_2$), 17.65 ppm (s, CH(CH$_3$)$_2$), 166.27 ppm (six lines, X part of AA′X, distances of outer lines N = 168.86 Hz, C=P). – ^{29}Si NMR (59.6 MHz, [D$_6$]benzene): δ = −1.54 ppm (pseudo-t, X part of AA′X, N = 6.12 Hz, *i*Pr(CH$_3$)$_2$*Si*); −0.24 (pseudo-t, X part of AA′X, N = 35.87 Hz, *i*Pr(CH$_3$)$_2$*Si*). – ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]benzene): δ = 352.8 ppm (s).

*(c) Reaction of **1b** with (nBu$_3$Sn)$_2$O:* To 2.29 g (3 mmol) of (nBu$_3$Sn)$_2$O was added 1.68 g (6 mmol) of **1b**. The mixture turned brown. Attempted separation of **2b** from nBu$_3$SnCl by distillation (75 °C / 0.2 mbar) led to its decomposition.

2b: ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]benzene): δ = 352.6 ppm (s).

4: δ ^{31}P = 382.2 (s), $^2J(^{119}\text{Sn}, ^{31}\text{P})$ = ±30.4 Hz. – δ^{119}Sn = 98.2 [d, $^2J(^{119}\text{Sn}, ^{31}\text{P})$ = ±30.4 Hz].

*Hydrolysis of **1c***

To a mixture of 2.09 g (6 mmol) (PhMe$_2$Si)$_2$C=PCl (**1c**) and 2.52 g (25 mmol) triethylamine in THF (10 mL) was added 0.99 g (3 mmol) $Na_2SO_4 \cdot 10\,H_2O$ in THF (10 mL). A ^{31}P NMR spectrum taken after 5 d at r. t. indicated that only a very small amount of *2,4*-diphospha-*3*-oxa-*1,1,5,5*-tetrakis-[(dimethyl)phenylsilyl)]pentadiene (**2c**, δ = 358.7 ppm) accompanied the starting material **1c**. Upon heating the reaction mixture, the ^{31}P NMR signals of **1c** disappeared in favour of a number of signals in the shift range of tetracoordinated phosphorus, and only a small amount of **2c** was present in the mixture. Another experiment with (nBu$_3$Sn)$_2$O led also to only small amounts of **2c** in a mixture with tetracoordinated phosphorus species. Attempted isolation of **2c** by distillation led to its decomposition.

*Reaction of **2a** with cyclopentadiene*

To 0.36 g (0.91 mmol) of **2a**, prepared by method (a), in dichloromethane was added 5 mL of cyclopentadiene (excess). Following the ensuing reaction by ^{31}P NMR spectroscopy allowed the detection of two species of 2-oxo-bis(2-phosphabicyclo[2.2.1]hept-5-ene) **7** with a 1 : 1 intensity ratio, accompanied by unconsumed **3a**. – ^{31}P NMR (81.0 MHz, [D$_6$]benzene): δ = 65.5 (s) **7** isomer #1; 62.7 (s) **7** isomer #2.

*Formation of **8** by reaction of **2a** with tetrachloro-o-benzoquinone (TOB)*

To 0.93 g (2.35 mmol) of **2a**, prepared by method (a), in pentane (15 mL) was added 1.14 g (4.7 mmol) of TOB in one portion. After the addition a pale brown solid product precipitated from the mixture. After 2 h at r. t. the residue was isolated by filtration, washed with small amounts of pentane and dried *in vacuo*. Recrystallisation from dichloromethane at −20 °C gave 1.6 g (78 %) **8** as colourless crystals, m. p. 171 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.01 (s, Me$_3$Si), 0.13 (s, Me$_3$Si). – ^{13}C NMR (101 MHz, CDCl$_3$): δ = 0.17 (pseudo-t, X part of AA′X, distance of outer lines N = 5.0 Hz CH$_3$Si), −1.1 (pseudo-t, X part of AA′X, distance of outer lines N = 6.3 Hz CH$_3$Si), 2.6 (s, CH$_3$Si); the resonances of quaternary and aromatic ^{13}C nuclei of **8** were not detected because of an insufficient signal-to-noise ratio. – ^{31}P NMR (CDCl$_3$, [D$_8$]toluene): δ = 160.1 (s). – MS (CI, NH$_3$, 150 °C): m/z = 887 [(M+1)$^+$]. – Analysis $C_{26}H_{36}Cl_8O_5Si_4P_2$ (881.47): calcd. C 35.23, H 4.09, Cl 31.99; found C 33.50, H 4.18, Cl 31.56.

*Bis(trimethylsilyl)methylphosphonic acid mono-ortho-(2,3,4,5-tetrachloro-6-hydroxyphenyl) ester **9***

After addition of three equivalents of TOB to 3 mmol of impure **2a** in a procedure similar to the synthesis of **8**, a solid formed that was separated from the red pentane solution (35 mL) by filtration. The ^{31}P NMR spectrum of the solid dissolved in toluene showed a transient ^{31}P NMR signal at δ = 57 (^2J (PH) 26.7) that lost intensity in favour of the persistent signal of **9**, δ = 44.5 (^2J (PH) 28.2). Crystallisation from dichloromethane at −20 °C provided a few single crystals, m. p. 187 °C. – ^{1}H NMR (400 MHz, [D$_8$]toluene): δ = 0.19 (s, Me$_3$Si), 0.91 (d, H–C–P, ^2J (PH) 28.2), 9.9 (br., H–O). – ^{31}P{^{1}H} NMR ([D$_8$]toluene): δ = 44.5 (d, ^2J (PH) 28.2). – MS (CI, NH$_3$, 150 °C) m/z = 470 [M]$^+$. – Analysis $C_{13}H_{21}Cl_4O_4PSi_2$ (881.47): calcd. C 33.20, H 4.50, Cl 30.16; found C 34.82, H 4.48, Cl 30.34.

X-Ray structure determinations

Data were recorded using MoK_α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer. Structures were refined using the program SHELXL-97 [17]. Methyl groups were refined as idealised rigid groups allowed to rotate but not to tip; OH hydrogen atoms were refined freely but with an O–H distance restraint; other hydrogen atoms were refined using a riding model.

CCDC 707741 (**8**) and 707742 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

*Crystal data for **8***: $C_{26}H_{36}Cl_8O_5P_2Si_4$, M_r = 886.45, triclinic, space group $P\bar{1}$, a = 10.9978(10), b = 13.5384(12), c = 14.5595(14) Å, α = 106.195(3), β = 100.083(3), γ = 102.311(3)°, V = 1969.3(3) Å^3, Z = 2, ρ_{calc} = 1.495 Mg m^{-3}, $\mu(MoK_\alpha)$ = 0.81 mm^{-1}, $F(000)$ = 908 e, T = 133 K; colourless prism 0.23 × 0.16 × 0.16 mm^3. Of 32596 reflections collected to 2θ = 61°, 11939 were independent (R_{int} = 0.042). Final $R1$ = 0.0314 [$I \geq 2\sigma(I)$], $wR2$ = 0.0765 (all data) for 418 parameters; S = 0.94, max. $\Delta\rho$ = 0.53 e Å^{-3}.

*Crystal data for **9**:* $C_{13}H_{21}Cl_4O_4PSi_2$, M_r = 470.25, mono clinic, space group $C2/c$, a = 25.210(3), b = 13.3980(16), c = 12.6721(16) Å, β = 105.207(3)°, V = 4130.3(9) Å^3, Z = 8, ρ_{calc} = 1.512 mg/m^3, $\mu(MoK_\alpha)$ = 0.78 mm^{-1}, $F(000)$ = 1936 e, T = 133 K; colourless tablet 0.26 × 0.16 × 0.07 mm^3. Of 18216 reflections collected to 2θ = 52.7°, 4226 were independent (R_{int} = 0.044). Final $R1$ = 0.0308 [$I \geq 2\sigma(I)$], $wR2$ = 0.0819 (all data) for 231 parameters; S = 1.02, max. $\Delta\rho$ = 0.55 e Å^{-3}.

Computational details

All the calculations were carried out using the GAUSSIAN 03 suite of programmes [18]. The B3LYP/6-31+G* [19] level of theory was used for optimisation of the geometries. For all the optimised structures vibrational analysis was performed (at the same level) to check the nature of the stationary point (at a minimum all the eigenvalues of the Hessian matrix are positive, in the transition states there is exactly one negative eigenvalue). In the case of transition states IRC (intrinsic reaction coordinate) calculations were performed to check which minima are connected by the transition state. The molecular orbitals were calculated at the HF/6-31G*//B3LYP/6-31 G* level of theory. For the natural orbital calculations the NBO 5.0 [20] code was applied. The molecules and orbitals were visualised by the program MOLDEN [21].

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