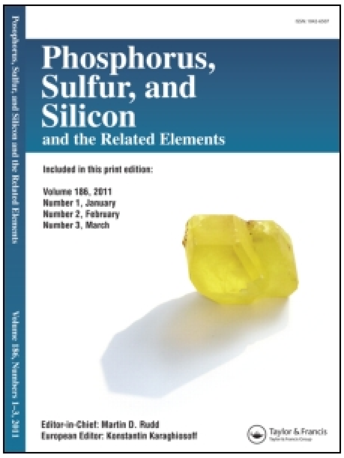


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Diastereoselective Reactions of Sulfur- and Selenium-Bridged Bisphosphaalkenes with Tetrachloro-*o*-benzoquinone

Thorsten Gust[a]; Wolf-W. du Mont[a]; Reinhard Schmutzler[a]; Cristian G. Hrib[a]; Cathleen Wismach[a]; Peter G. Jones[a]
[a] Institut fuer Anorganische und Analytische Chemie, Technische Universitaet Braunschweig, Braunschweig, Germany

To cite this Article Gust, Thorsten , du Mont, Wolf-W. , Schmutzler, Reinhard , Hrib, Cristian G. , Wismach, Cathleen and Jones, Peter G.(2009) 'Diastereoselective Reactions of Sulfur- and Selenium-Bridged Bisphosphaalkenes with Tetrachloro-*o*-benzoquinone', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 6, 1599 — 1611

To link to this Article: DOI: 10.1080/10426500902947948

URL: http://dx.doi.org/10.1080/10426500902947948

Phosphorus, Sulfur, and Silicon, 184:1599–1611, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902947948

Diastereoselective Reactions of Sulfur- and Selenium-Bridged Bisphosphaalkenes with Tetrachloro-*o*-benzoquinone

Thorsten Gust, Wolf-W. du Mont, Reinhard Schmutzler, Cristian G. Hrib, Cathleen Wismach, and Peter G. Jones
Institut fuer Anorganische und Analytische Chemie, Technische Universitaet Braunschweig, Braunschweig, Germany

*2,4-Diphospha-3-thia- and 3-selenapentadienes $[(Me_3Si)_2C{=}P]_2E$ (**1a**: E = S; **1b**: Se) react as bifunctional phosphaalkenes with two equivalents of cyclopentadiene and of tetrachloro-o-benzoquinone (TOB), furnishing **2a** and **2b** from double [2+4] cycloaddition reactions of the diene and **3a** and **3b** from the reactions of TOB with the P=C double bonds. The phosphanorbornane-related chalcogenophosphinous anhydrides **2a** and **2b** are obtained as pairs of isomers, whereas the reactions with TOB proceed diastereoselectively. X-ray crystallographic data confirm that bis-dioxaphospholene-related **3b** consists of a mixture of (RR) and (SS) enantiomers. A third equivalent of TOB can be added oxidatively to one phosphorus atom of **3a** and **3b**, furnishing the spirocyclic compounds **6a** and **6b** with $P(\sigma^3\lambda^3)$-E-$P(\sigma^5\lambda^5)$ connectivity. **3a** and **6a** are configurationally stable at room temperature, whereas the selenium derivatives **3b** and **6b** undergo slow isomerisation in solution.*

Keywords Bisphosphaalkenes; chalcogenophosphoranes; cycloaddition; oxidative addition; selenobisphosphanes; thiobisphosphanes

INTRODUCTION

4-Diphospha-3-thia- and 3-selenapentadienes $[(Me_3Si)_2C{=}P]_2E$ (**1a**: E = S; **1b**: Se) are π-donor heteroatom-bridged bis-phosphaalkenes, in which electronic communication between the π-systems (P=C bonds) of two neighbouring phosphaalkene moieties may be possible.[1–2] **1a** and

Received 30 January 2008; accepted 12 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

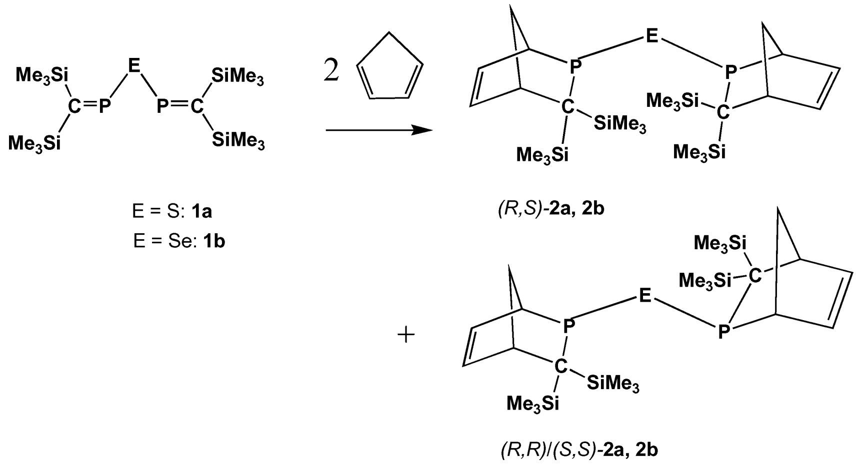
We thank Mrs. D. Döring and Dr. U. Papke (mass spectrometry) and Mrs. D. Deuse and Professor L. Ernst (NMR spectroscopy) for support.

Address correspondence to Wolf-W. Du Mont, Institut fuer Anorganische und Analytische Chemie, Technische Universitaet Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. E-mail: w.du-mont@tu-bs.de

2b are expected to be interesting starting materials—reactions at one of the P=C bonds may influence the reactivity of the other P=C-moiety because of electronic and/or steric "communication" between the two P=C functions. Recently it was observed that **1a** and **1b** add elemental sulfur and selenium in a surprising way, different from the behavior of comparable monofunctional phosphaalkenes.[2] In the following, we report our first experiments on reactions of **1a** and **1b** with cyclopentadiene and with tetrachloro-*o*-benzoquinone (TOB), both of which are typical reagents for [2+4] cycloadditions to phosphaalkenes.[3–5] TOB also adds oxidatively to other shortlived or persistent compounds of low-coordinated phosphorus,[6–8] and—in a [4+1] fashion—to P($\sigma^3\lambda^3$)-compounds,[6,9–12] furnishing benzo-1,3,2-dioxaphospholane structures and spirophosphoranes.[13]

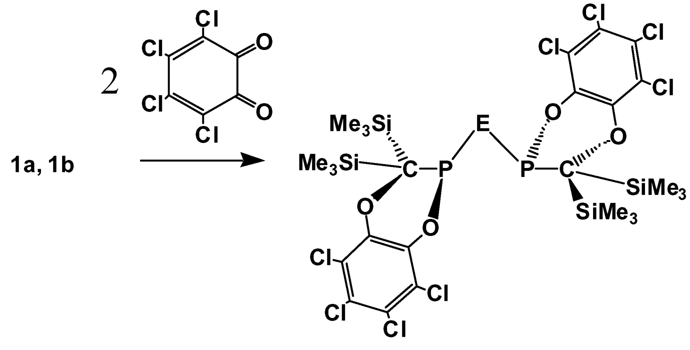
REACTIONS

1a and **1b** react with two equivalents of cyclopentadiene in dichloromethane at room temperature within 24 h to form bis-[2+4] cycloadducts **2a** and **2b** (Scheme 1).



SCHEME 1

{^{1}H} ^{31}P NMR spectra of **2a** and of **2b** each exhibit two singlet signals, indicating the presence of the new "selenophosphinous anhydrides" either as pairs of *endo, endo* and *exo, exo* isomers of diastereochemically pure *RS*/*SR* or *RR*/*SS*–configurated products, or as pairs of *RS*/*SR* and *RR*/*SS*–configurated products, existing either as *endo,endo* or as



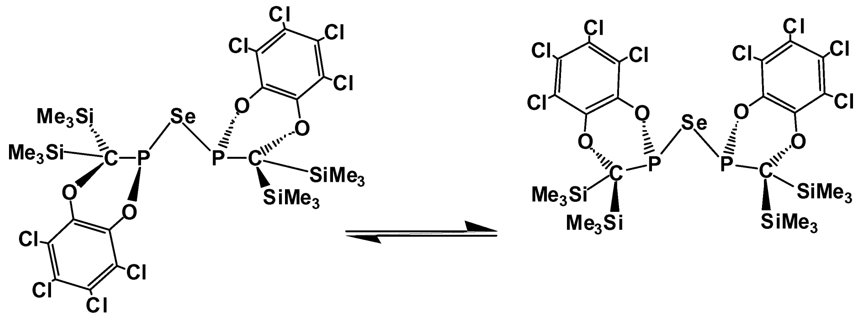
(R,R)/*(S,S)*-**3a, 3b**

SCHEME 2

exo,exo-isomers. In [2+4] cycloadditions of related thio- and selenophosphaalkenes $(Me_3Si)_2C{=}P\text{-}E\text{-}PR_2$ (R = *t*Bu, *i*Pr) with cyclopentadiene, the initially formed *endo*-isomers usually rearranged to the more stable *exo*-isomers within 24 h[4]; we therefore assume that both diastereomers of **2a** and **2b** were isolated as the *exo,exo*-isomers, as depicted in Scheme 1.

The formation of the 1:2 adducts **3a** and **3b** from the reactions of **1a** and **1b** with two equivalents of TOB proceeds diastereoselectively (Scheme 2). The stereochemistry of the seleno-bridged bis-1-phospha-2,5-dioxa-3,4-benzophospholene derivative **3b** was determined by X-ray crystallography (Figure 1), which revealed the presence of a racemic mixture of *(RR)* and *(SS)* enantiomers of approximately (r.m.s. deviation 0.2 Å) C_2-symmetric **3b**. As in the parent bisphosphaalkene **1b**,[2] the C-P-Se-P-C moiety exhibits a distorted W-shaped arrangement (torsion angles C2-P2-Se1-P1 −170, P2-Se1-P1-C1 −159°). From this central backbone, the benzophospholene-related heterocycles extend in opposite directions, allowing the phosphorus atoms to minimize their lone-pair interactions in a "gauche"-type fashion. Over several days, solutions of **3b** develop a second set of NMR signals, indicating the presence of increasing amounts of the achiral (C_s-symmetric) *(RS)* isomer. The formation of *(RR)*/*(SS)*-**3b** is apparently kinetically controlled, and in solution slow isomerisation occurs (Scheme 3), probably by phosphorus inversion.

To study the reaction paths leading to **3b** under kinetic control, and to diastereomeric mixtures of **2b**, 1:1 reactions of **1b** with cyclopentadiene and with TOB were carried out. 1:1 adducts were not formed selectively, but ^{31}P NMR spectra of the reaction mixtures revealed the



(R,R)/(S,S)-**3b**

(R,S)-**3b**

SCHEME 3

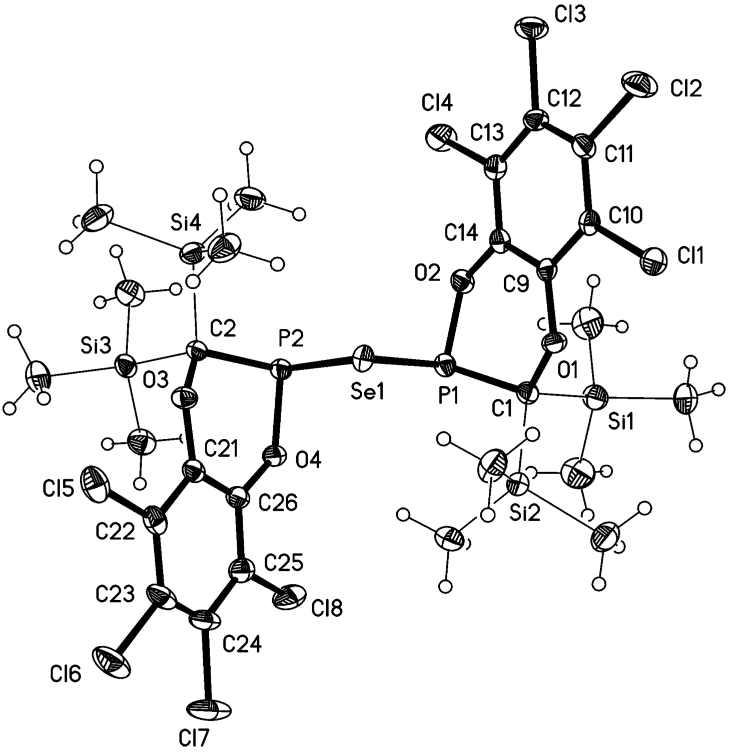
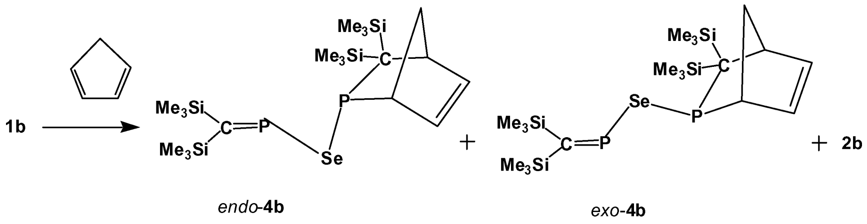


FIGURE 1 The structure of **3b** in the crystal. Ellipsoids represent 50% probabililty levels. Selected bond lengths (Å) and angles (°): Se1-P1 2.2746(8), Se1-P2 2.2828(8), P1-O2 1.668(2), P1-C1 1.833(3), P2-O4 1.673(2), P2-C2 1.825(3); P1-Se1-P2 87.86(3), O2-P1-C1 99.32(11), O2-P1-Se1 100.06(8), C1-P1-Se1 104.32(9), O4-P2-C2 98.76(11), O4-P2-Se1 100.06(7), C2-P2-Se1 102.63(9).



SCHEME 4

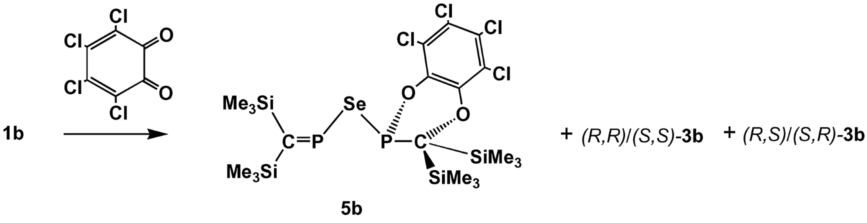
presence of starting material, **1b**, of 1:1 products, **4b** [with cyclopentadiene (Scheme 4)] or **5b** [with TOB (Scheme 5)], and of the isomeric mixtures **2b** or **3b**.

In the case of the reaction with cyclopentadiene, a mixture of *endo*/*exo* isomers of **4b** is observed by ^{31}P NMR (*exo/endo* = 100:40, from ^{13}C and ^{31}P NMR intensities).

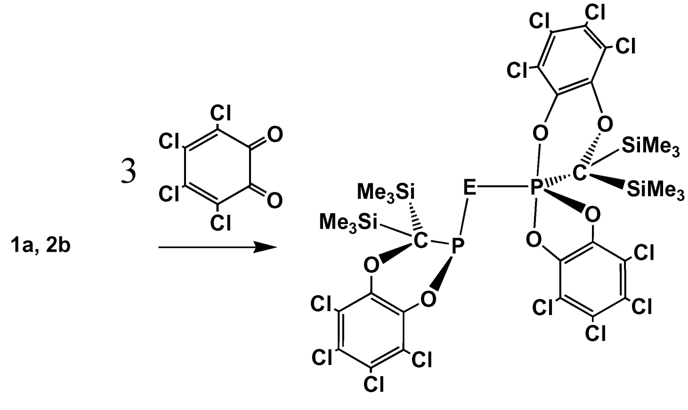
Following an attempt to synthesize the 1:1 product **5b**, the AX-type ^{31}P NMR pattern of **5b** was found to be accompanied by the singlet due to the starting material **2b**, and two singlets, apparently associated with the disasteromeric mixture of *(RR/SS)-* and *(RS/SR)-***3b**. The rate of the second step of the cycloaddition to the P=C bonds of **1b**, leading from the 1:1 products **4b** or **5b** to **2b** or **3b**, is apparently not significantly affected by the adjacent three-coordinate P$^{\mathrm{III}}$ atom. When a small amount of TOB is added to **5b**, the second cycloaddition step proceeds much less diasteroselectively than in the case of the straightforward 1:2 reaction.

Understanding the diastereoselective course of the 1:2 addition of TOB to **1b** via **5b**, with TOB additions to P=C bonds (formally [2+4]) generally regarded as non-concerted processes, will require a quantum chemical treatment. In contrast to **3b**, the sulfur compound **3a** is configurationally stable in solution at room temperature.

The molecular structure of the 1:3 adduct **6a** (derived from **1a**), involving three equivalents of TOB, implies that *(RR)/(SS)-***3a** is the



SCHEME 5



6a, 6b

SCHEME 6

precursor, which undergoes [1+4] cycloaddition with the third equivalent of TOB, leading to the P^{III}-S-P^{V} compound **6a** (Scheme 6). Despite poor crystal quality, the structure of **6a** could be established, at least qualitatively, by X-ray structure analysis (Figure 2). The bridging sulfur atom connects a spirophosphorane and a cyclic phosphonite moiety, each including a 1-phospha-2,5-dioxa-3,4-benzophospholene heterocycle. The P^{V} atom P2 exhibits trigonal pyramidal grometry to a good approximation, with O3 and O5 axial, C20, S1 and O6 equatorial. Excess TOB does not further attack the P^{III} atoms of the mixed valence products **6a** and **6b**.

The ^{31}P NMR spectra of the predominant isomer of **6b** from the 1:3 addition of TOB to **1b** do not confirm that this compound exists in the same configuration as **6a**. The course of the reaction (straightforward 1:3 reaction with TOB, whereas isomerization of **3b** is a slow process, see above), however, supports the assumption that **6a** and the primary product of **6b** will exist in the same configuration. Like **3a**, **6a** is configurationally stable, whereas **6b** is selectively formed as one isomer, which undergoes subsequent isomerisation leading to a second species. ^{31}P NMR spectra do not allow us to decide whether this isomerization occurs at P^{III} or at P^{V}. From a comparison with the behavior of **3b**, it would appear likely that P^{III} inversion in **6b** may be the reason for isomerization. Van der Knaap and Bickelhaupt had explained the formation of a mixture of stereoisomers of a related phosphorane after addition of two equivalents of TOB to a monofunctional phosphaalkene [1-(2,6-dimethylphenyl)-2,2-diphenylmethylenephosphosphane] by a

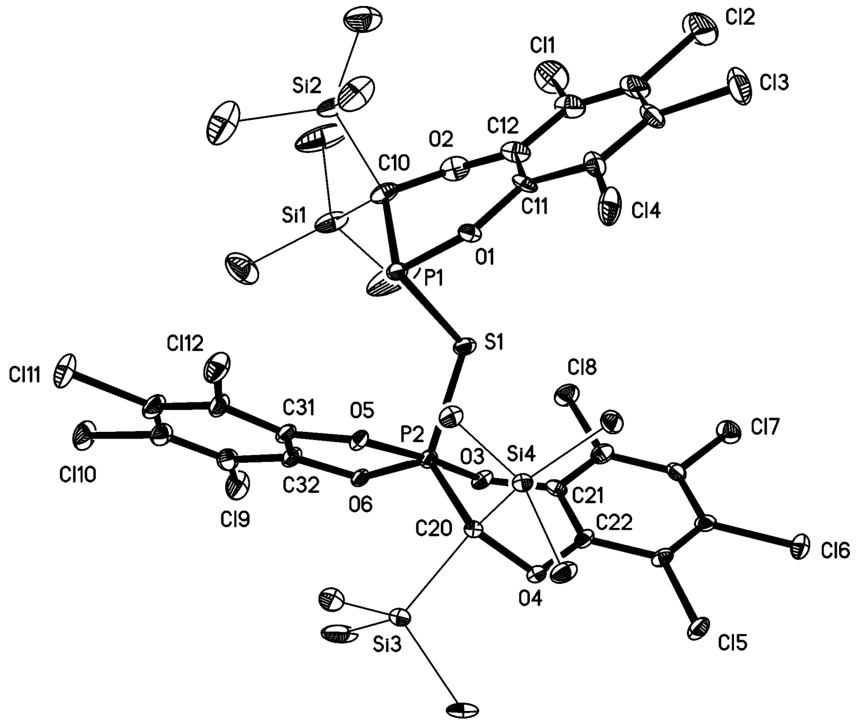


FIGURE 2 The structure of **6a** in the crystal. Ellipsoids represent 30% probabililty levels. Hydrogen atoms are omitted for clarity.

dissociative polar type of pseudorotation, leading to diequatorial orientation of the phospha-2,5-dioxa-3,4-benzophospholene ring.[4,5] Without further studies, it remains uncertain if the P^{III} inversion pathway will be lower in activation energy than a pseudorotative rearrangement at the pentacoordinate P^{V} atom.

NMR SPECTROSCOPIC STUDIES

^{31}P and ^{77}Se NMR data of compounds **2–6** are assembled in Table I. For comparison, data of the cyclopentadiene cycloaddition products of related thio- and selenophosphaalkenes $(Me_3Si)_2C{=}P\text{-}Se\text{-}P(t\mathrm{Bu})i\mathrm{Pr}$ should be considered.[4] In these examples, *endo*-compounds show ^{31}P NMR signals by 5–7 ppm to higher field, exhibiting $^{2}J(^{31}P,^{31}P)$ couplings 30 Hz larger than those of the *exo*-isomers. Concerning the pair of ^{31}P NMR signals from **2a** and **2b**, the differences in δ (^{31}P) are about 5 ppm, and the difference in $^{1}J(^{77}Se,^{31}P)$ is about 12 Hz. From the

TABLE I ^{31}P and ^{77}Se NMR Data of Cyclopentadiene and Tetrachloro-*o*-benzoquinone Addition Products from S- and Se-Bridged Bisphosphaalkenes

	δ ^{31}P [ppm]	$|J(PP)|$ [Hz]	δ ^{77}Se [ppm]	$|J(SeP)|$ [Hz]
1a	359.9			
1b	382.8		779.9	*281.6*
2a (**1a** + 2 Cp)	68.5			
	63.9			
2b (**1b** + 2 Cp)	72.8		165.2	*196.4*
	67.7		167.5	*184.8*
4b (**1b** + 1 Cp)	398.3, 80.3	*256.7*		*264.0, 191.4*
	394.9, 73.8	*232.0*		*225.8, **
3a (**1a** + 2 TOB)	133.6			
3b (**1b** + 2 TOB)	142.0		412.8	*261.4*
	140.3		393.5	255.3
5b (**1b** + 1 TOB)	371.0, 140.4	*206.1*		*254.4, 274.3*
6a (**1a** + 2 TOB)	135.5, 4.5	*41.8*		
6b (**1b** + 2 TOB)	144.6, −7.8	*46.3*	523.2	*239.8, 563.7*
	148.4, −2.1	*37.4*	**	*279.4, 572.1*

Coupling constants in italics.

*^{77}Se satellites not resolved due to overlap from signals of **2b**.

**The mixture of isomers was not analyzed by ^{77}Se NMR.

exo,exo/*endo,endo* pair of the 1:1 adducts **4b**, the more deshielded ^{31}P NMR signals (+398.3/+80.3 ppm vs. +394.9/+73.8 ppm) exhibit the larger $^{2}J(^{31}P,^{31}P)$ coupling (by magnitude; ± 256.7 vs. ± 232.0 Hz). In the case of the diastereomeric pair of **3b**, ^{31}P NMR shifts differ by less than 2 ppm. In the 1:1 adduct **5b**, $^{1}J(^{77}Se,^{31}P)$ of $P(\sigma^3\lambda^3)$ is larger than that of $P(\sigma^2\lambda^3)$.

The P^{III}-E-P^{V} compounds **6a** and **6b** exhibit significantly smaller $^{2}J(^{31}P,^{31}P)$ couplings than the P^{III}-E-P^{III} compounds, and the magnitude of $^{1}J(^{77}Se,^{31}P)$ of P^{V} is significantly larger than for P^{III}. Oxidation of one of the phosphorus atoms to $P(\sigma^5\lambda^5)$ correlates with about 100 ppm deshielding in the ^{77}Se NMR.

CONCLUSION

[4+2] Cycloaddition reactions of the bifunctional phosphaalkenes **1a** and **1b** with cyclopentadiene proceed in a manner comparable to those of related monofunctional phosphaalkenes; the formation of diastereomeric mixtures of S- and Se-bridged diphosphanes **2a** and **2b** is expected. The unanticipated stereoselective course of the TOB additions to **1a** and **1b**, furnishing the bisphosphonite ligands **3a** and **3b**, is apparently kinetically controlled. Further studies are required to establish how the chiral selenophosphonite moiety in the intermediate ("1:1 product") **5b** controls the stereochemistry of TOB addition to the remaining P=C function, under the aspect that TOB additions to phosphaalkenes are believed to proceed in a non-concerted fashion.[4,5] One of the two P^{III} atoms in **3a** and **3b** can be oxidized selectively with TOB, yielding a phosphorane function in each of the racemic P^{III}-S-P^{V} and P^{III}-Se-P^{V} compounds **6a** and **6b**.

EXPERIMENTAL

All procedures were carried out using standard inert gas techniques.

NMR: Bruker AC 200: ^1H 200, ^{13}C 50.3, ^{31}P 81.0 and ^{77}Se 38.2 MHz; Bruker AC 400: ^1H 400, ^{13}C 100.6, ^{31}P 162.0 MHz. Chemical shifts δ(ppm); references: TMS for ^1H and ^{13}C, ext. 85% H_3PO_4 for ^{31}P, Me_2Se for ^{77}Se.

MS: Finnigan MAT 8400, 8530 and 90X, EI (70 eV) and CI; in isotope patterns m/z was assigned to the highest peak.

X-Ray Crystal Structures: Data were recorded at –140°C on a Bruker SMART 1000 CCD diffractometer using Mo-$K\alpha$ radiation. Absorption corrections were applied using the multi-scan method (program SADABS). Refinement was performed on F^2 with the program SHELXL-97.[14] Hydrogen atoms were included using rigid methyl groups for **3b**, otherwise riding. Compound **3b** ·$2CHCl_3$: $C_{28}H_{38}Cl_{14}O_4P_2SeSi_4$, M_r = 1188.14, triclinic, $P\bar{1}$, a = 11.7929(10), b = 12.9220(10), c = 18.8345(16) Å, α = 72.408(3), β = 85.774(3), γ = 63.349(3)°, U = 2438.8(3) Å^3, Z = 2. Crystal habit: colorless tablet, 0.4 × 0.1 × 0.05 mm. Final $wR2$ 0.106, $R1$ 0.040 for 12048 unique reflections ($2\theta_{max}$ 56.6°) and 490 parameters; S = 1.01, max. $\Delta\rho$ 1.8 e Å^{-3}. Compound **6a** CH_2Cl_2: $C_{33}H_{38}Cl_{14}O_6P_2SSi_4$, M_r = 1233.29, monoclinic, $P2_1/n$, a = 11.9013(18), b = 24.583(4), c = 17.991(3)(16) Å, β = 101.652(8)°, U = 5155.0(14) Å^3, Z = 4. Crystal habit: colorless prism, 0.20 × 0.15 × 0.13 mm. Final $wR2$ 0.36, $R1$ 0.148 for 10532 unique reflections ($2\theta_{max}$ 52.7°), 541 parameters and 238 restraints; S = 1.13, max. $\Delta\rho$ 3.0 e Å^{-3}. Neither structure determination was entirely satisfactory; the largest peak for **3b** was ca. 1.8 Å from P2 and might indicate a small admixture of a partially oxidised product. The crystal for **6a** was of very moderate quality and deteriorated further during the data collection; in view of the poor R values, we do not discuss the structure quantitatively, but it serves to establish the chemical nature of **6a**. Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-673337 (**3b**), 673338 (**6a**). Copies may be requested free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Reaction of 1a with Two Equivalents of Cyclopentadiene

To a solution of 0.83 g (2 mmol) **1a** in 10 mL of dichloromethane, 0.27 g (4 mmol) of cyclopentadiene were added. When consumption of **1a** was confirmed by ^{31}P NMR (about 1 day), the solvent was stripped off, and the residue was recrystallized from pentane. At –60°C, 0.94 g (87%) colorless solid **2a** precipitated as a mixture of isomers.

^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.11$ (s, $SiMe_3$), 0.34 (s, $SiMe_3$), 1.75 (m, H_2C-), 2.90 (m, HC), 3.51 (m, HC), 5.62 (m, HC), 6.01 (m, HC).

^{31}P NMR (81.0 MHz, C_6D_6): $\delta =$ 68.9 (s); 68.5(s) (about equal intensity).

MS (EI, 70 eV): m/z (%) = 542(5) $[M]^+$; 476 (3) $[M - C_5H_6]^+$; 403 (5) $[M - C_5H_6, - SiMe_3]^+$; 147 (90) $[PPCSiMe_3]^+$; 73 (70) $[SiMe_3]^+$; 66 (100) $[C_5H_6]^+$.

$C_{24}H_{48}P_2SSi_4$ (542.99): calc. C 53.09, H 8.91, S 5.90; found C 52.89, H 8.36, S 5.85.

Reaction of 1b with Two Equivalents of Cyclopentadiene

As described for **2a**, 0.55 g (92%) of a colorless solid **2b** were precipitated from pentane as a mixture of isomers, upon reaction of 0.46 g (1 mmol) of **1b** with 0.13 g (2 mmol) of cyclopentadiene in dichloromethane.

^{1}H NMR (200 MHz, C_6D_6): $\delta =$ 0.23 (s, $SiMe_3$), 0.34 (s, $SiMe_3$), 1.75(m, H_2C-), 2.85 (m, HC), 3.59 (m, HC), 5.71 (m, HC), 6.02 (m, HC).

^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 72.8$ (s) [^{1}J(SeP) 196.4 Hz]; $\delta = 67.7$ (s) [^{1}J(SeP) 184.8 Hz] (about equal intensity).

^{77}Se NMR (38.0 MHz, C_6D_6): $\delta =$ 165.2 (t) [^{1}J(SeP) 196.4 Hz]; $\delta =$ 167.5 (t) [^{1}J(SeP) 184.8 Hz].

MS (EI, 70 eV): m/z (%) = 590(3) $[M]^+$; 524 (3) $[M - C_5H_6]^+$; 452 (10) $[M - C_5H_6, - SiMe_3]^+$; 147 (50) $[PPCSiMe_3]^+$; 73 (70) $[SiMe_3]^+$; 66 (100) $[C_5H_6]^+$.

$C_{24}H_{48}P_2SeSi_4$ (589.89): calc. C 48.87, H 8.20; found C 48.15, H 8.26.

Reaction of 1b with One Equivalent of Cyclopentadiene

Under similar conditions as described for the synthesis of **2b**, cyclopentadiene and **1b** were mixed in a 1:1 ratio. ^{31}P NMR spectra of the reaction mixture showed the signals of unchanged **1b**, of the 1:2 products **2b** (two singlets), and of the 1:1 products **4b** (two AX patterns).

2b, isomer **I**: $\delta^{31}P$ = 72.8 (s [J(SeP) 196.4 Hz]); $\delta^{77}Se$ = 165.2 (t [J(SeP) 196.4 Hz]); **2b**, isomer **II**: $\delta^{31}P$ = 67.7 (s [J(SeP) 184.8 Hz]); $\delta^{77}Se$ = 167.5 (t [J(SeP) 184.8 Hz]).

4b, isomer **I**: $\delta^{31}P$ = 398.3 (d [J(PP) 256.7 Hz, J(SeP) 264.0 Hz]); 80.3 (d [J(PP) 256.7 Hz, J(SeP) 191.4 Hz]); **4b**, (isomer **II**: $\delta^{31}P$ = 394.9 (d [J(PP) 232.0 Hz, J(SeP) 225.8 Hz]); 73.8 (d [J(PP) 256.7 Hz, J(SeP) not resolved due to overlap with signals of **4b**]).

Reaction of 1a with Two Equivalents of Tetrachloro-*o*-benzoquinone (TOB)

A solution of 0.55 g (2.16 mmol) of TOB in 15 mL of dichloromethane was added to a stirred solution of 0.46 g (1.11 mmol) of **1a** in 5 mL of dichloromethane. Within 2 h, the color of the solution changed from red to yellow-brown. After removal of all volatiles, the residue was dissolved in dichloromethane. At –20°C, 0.83 g (84%) **3a** were obtained as colorless crystals, mp 165°C.

^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.05$ (s, $SiMe_3$), 0.37 (s, $SiMe_3$).

^{13}C NMR (101 MHz, $CDCl_3$): All signals appear as pseudo-triplet-like X-parts of AA'X-patterns; $\delta = 0.38$ (outer line distance N = 7.4 Hz, $SiMe_3$); 0.54 (N = 4.9 Hz, $SiMe_3$); 123.4 (N = 113.9 Hz); 125.7 (N = 136.6 Hz); 135.8 (N = 10.4 Hz); 142.3 (N = 8.4 Hz). The resonances due to quaternary carbon nuclei were not resolved because of an insufficient S/N ratio.

^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 133.6$ (s).

MS (CI, NH_3, 150°C): m/z (%) = 922 $[M+2+NH_4]^+$; 904 $[M+2]^+$.

$C_{26}H_{25}Cl_8O_4P_2SSi_4$ (891.75): calc. C 35.03, H 2.83, Cl 31.42, S 3.55; fd. C 33.31, H 4.06, Cl 32.20, S 3.17.

Reaction of 1a with Three Equivalents of TOB

In a manner similar to the 1:2 reaction, 0.46 g (1.11 mmol) **1a** were allowed to react with 0.81 g (3.33 mmol) of TOB within 2 h, yielding (at –20°C from CH_2Cl_2) 1.12 g (88 %) of **6a** as colorless crystals, mp 118°C.

^1H NMR (400 MHz, toluene-d_8): $\delta = -0.13$ (s, $SiMe_3$); –0.05, (s, $SiMe_3$); 0.11 (d [^4J(PH) 0.9 Hz] $SiMe_3$); 0.49 (s, $SiMe_3$).

^{13}C NMR (101 MHz, toluene-d_8): $\delta = -0.25$ (d [^3J(PC) 2.5 Hz, $SiMe_3$); –0.14 (d [^3J(PC) 1.9 Hz, $SiMe_3$); 0.98 (d [^3J(PC) 2.4 Hz, $SiMe_3$); 2.21 (d [^3J(PC) 3.1 Hz, $SiMe_3$); 123.4 (N = 113.9 Hz); 125.7 (N = 136.6 Hz);

135.8 ($N = 10.4$ Hz); 142.3 ($N = 8.4$ Hz). The resonances due to quaternary and aromatic carbon nuclei were not resolved because of an insufficient S/N ratio.

^{31}P NMR (81.0 MHz, toluene-d$_8$): $\delta = 135.5$ (d [^2J(PP) 42.0 Hz], P-$\sigma^3\lambda^3$); 4.5 (d [^2J(PP) 41.9 Hz], P-$\sigma^5\lambda^5$).

$C_{32}H_{36}Cl_{12}O_6P_2SSi_4$ (1148.41): calc. C 33.47, H 3.16, Cl 37.05, S 2.80; found C 34.63, H 4.14, Cl 32.47, S 2.14.

Reaction of 1b with Two Equivalents of TOB

As described for **3a**, 1.02 g (4.1 mmol) of TOB and 0.94 g (2.05 mmol) of **1b** in dichloromethane yielded 1.7 g (87%) of **3b** as colorless crystals of mp 157°C.

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.04$ (s, SiMe$_3$), 0.22 (s, SiMe$_3$).

^{13}C NMR (101 MHz, CDCl$_3$): all signals appear as pseudo-triplet-like X-parts of AA'X-patterns; $\delta = 0.1$ (outer line distance $N = 6.0$ Hz, SiMe$_3$); 0.17 ($N = 5.1$ Hz, SiMe$_3$); 123.0 ($N = 108.1$ Hz); 125.4 ($N = 130.8$ Hz); 136.0 ($N = 10.4$ Hz); 142.3 ($N = 9.6$ Hz). The resonances due to quaternary carbon nuclei were not resolved because of the insufficient S/N ratio.

^{31}P NMR (81.0 MHz, CDCl$_3$): $\delta = 142.0$ (s) [J(SeP) 261.3 Hz].

^{77}Se NMR (38.0 MHz, CDCl$_3$): $\delta = 412.8$ (t) [^1J(SeP) 261.4 Hz];

MS (CI, NH$_3$, 150°C): m/z (%) = 955 [M+2]$^+$.

$C_{26}H_{25}Cl_8O_4P_2SeSi_4$ (938.35): calc. C 33.28, H 2.69, Cl 30.23; found C 31.97, H 3.71, Cl 30.89.

Reaction of 1b with Three Equivalents of TOB

As in the 1:2 reaction, 0.65 g (1.43 mmol) of **1b** reacted with 1.06 g (4.29 mmol) of TOB within 2 h to form, initially, **6b** accompanied by two byproducts [δ^{31}P = 131.9, ^1J(SeP) 963.9 Hz, ^2J(PH) 27.7 Hz; and δ^{31}P 55.3, ^1J(SeP) 963.9 Hz, ^1J(PH) 531 Hz], according to ^{31}P NMR. Impure solid **6b** was precipiated from dichloromethane at –20 °C; after storing the sample for 3 days at room temperature, an additional AX-pattern in the ^{31}P NMR (signals too weak to allow ^{77}Se satellites to be resolved) was observed, indicating the presence of a second isomer of **6b**.

^{31}P NMR (81.0 MHz, toluene-d$_8$): **6b**, isomer **I:** $\delta = 147.1$ (d [^2J(PP) 46.2 Hz], ^1J(SeP) 294.3 Hz, P-$\sigma^3\lambda^3$); –6.6 (d [^2J(PP) 46.2 Hz], ^1J(SeP) 563.4 Hz, P-$\sigma^5\lambda^5$). **6b**, isomer **II**: $\delta = 148.4$ (d [^2J(PP) 37.2 Hz]; –2.1 (d [^2J(PP)37.2 Hz], P-$\sigma^5\lambda^5$).

$C_{32}H_{36}Cl_{12}O_6P_2SeSi_4$ (1195.31): calc. C 32.15, H 3.04, Cl 35.59; found C 31.45, H 3.24, Cl 33.95 (solid precipitated from dichloromethane at –20°C).

Reaction of 1b with One Equivalent of TOB

As described for the synthesis of **3b**, TOB and **1b** were mixed in a 1:1 ratio. ^{31}P NMR showed product signals of **3b** and of the 1:1 adduct **5b**, in about equal intensity.

5b: $\delta^{31}P = 140.5$ [d, ^{2}J(PP) 206.1 Hz, ^{1}J(SeP) 274.3 Hz, $\underline{P}$-Se-P=C], 371.0 [d, ^{2}J(PP) 206.1 Hz, ^{1}J(SeP) 254.1 Hz, $\underline{P} = C$].

REFERENCES

[1] W.-W. du Mont, G. Dobreva, W. Grahn, S. Vollbrecht, T. Gust, and J. Mahnke, 15th Int. Conf. on Phosphorus Chemistry, Sendai, 2001; Abstract: *Phosphorus, Sulfur, Silicon*, **177,** 1753 (2002).

[2] W.-W. du Mont, T. Gust, J. Mahnke, R. M. Birzoi, L. Barra, D. Bugnariu, F. Ruthe, C. Wismach, P. G. Jones, K. Karaghiosoff, L. Nyulászi, and Z. Benkõ, *Angew. Chem. Int. Ed. Engl.*, **46,** 8682 (2007); *Angew. Chem.*, **119,** 8836 (2007).

[3] M. Regitz and O. J. Scherer (Eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Thieme, Stuttgart, 1990), pp. 163–164, and references therein.

[4] J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe, and P. G. Jones, *Z. Anorg. Allg. Chem.*, **624,** 1447 (1998).

[5] (a) T. A. van der Knaap and F. Bickelhaupt, *Phosphorus, Sulfur, Relat. Elem.*, **18**, 47 (1983); (b) T. A. van der Knaap and F. Bickelhaupt, *Tetrahedron*, **39,** 3189 (1983).

[6] F. H. Osman and F. A. El-Shamaly, *Chem. Rev.*, **102,** 629 (2002).

[7] M. Sanchez, R. Réau, H. Gornitzka, F. Dahan, M. Regitz, and G. Bertrand, *J. Am. Chem. Soc.*, **119,** 9720 (1997).

[8] M. Freytag, P. G. Jones, R. Schmutzler, and M. Yoshifuji, *Heteroatom Chem.*, **12,** 300 (2001).

[9] A. Kutyrev and V. V. Moskva, *Uspekh. Chem.*, **56,** 1798 (1987).

[10] J. Krill, I. V. Shevchenko, A. Fischer, P. G. Jones, and R. Schmutzler, *Chem. Ber.*, **130,** 1479 (1997).

[11] V. Plack, J. R. Goerlich, H. Thoenessen, P. G. Jones, and R. Schmutzler, *Heteroatom Chem.*, **10,** 277 (1999).

[12] J. Breker, R. Schmutzler, B. Dorbath, and M. Wieber, *Z. Naturforsch. B*, **45,** 1177 (1990).

[13] (a) F. Ramirez, *Acc. Chem. Res.*, **1,** 168 (1968); (b) Addition on correction [May 2009]: The reaction of TOB with an oxygen-bridged bisphosphaalkene was reported recently: R. M. Birzoi, D. Bugnariu, C. Goers, R. Guerrero Gimeno, T. Gust, A. Riecke, Z. Benko, L. Könczöl, L. Nyulaszi, C. Wismach, P. G. Jones, R. Schmutzler, R. Bartsch, and W.-W. du Mont, *Z. Naturforsch. B*, **64,** 73 (2009).

[14] G. M. Sheldrick, *Acta Cryst. A*, **64,** 112 (2008).