$P_2C_2S_3$ Norbornanes

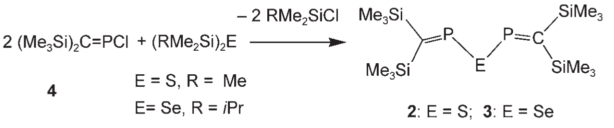
DOI: 10.1002/anie.200703000

From 2,4-Diphospha-3-Thia- and -3-Selenapentadienes $[(Me_3Si)_2C{=}P]_2E$ to Heteronorbornane Cage Compounds**

Wolf-W. du Mont, Thorsten Gust, Jens Mahnke, Roxana M. Birzoi, Lisa Barra, Delia Bugnariu, Frank Ruthe, Cathleen Wismach, Peter G. Jones, Konstantin Karaghiosoff, László Nyulászi, and Zoltán Benkõ*

Highly unsaturated organophosphorus compounds are rich in energy, and tend to rearrange to more stable rings, cages, and polymers. Niecke's 2,3,4-triphosphapentadienide anion $[\{(Me_3Si)_2C{=}P\}_2P]^-$ (**1**),[1] the only π-donor heteroatom-bridged bisphosphaalkene anion that allows electronic communication between the neighboring P$=$C bonds, is known to undergo thermal elimination/re-addition reactions to furnish anionic P_3C_2 heterocyles,[1] but its synthetic potential remains unexplored. The uncharged isoelectronic sulfide $[(Me_3Si)_2C{=}P]_2S$ (**2**), however, might be a promising synthetic precursor. We began our studies with **2** and the related selenide **3** to evaluate if and how π communication through the heteroatoms sulfur and selenium might influence the reactivity of bifunctional phosphaalkenes.

2,4-Diphospha-3-thia- and 2,4-diphospha-3-selenapentadienes **2** and **3** are formed in the reaction of $(Me_3Si)_2C{=}PCl$ (**4**)[2] with bis(trialkylsilyl)chalcogenides [Eq. (1)]. Red-brown **3** crystallizes as a monomer. The W-shaped CPSePC moiety of **3** (Figure 1) shows a close analogy to that of Niecke's anion **1**.[1] The central angle PSeP of **3** is 90.7°, whereas in the isoelectronic arsenide ion $[\{(Me_3Si)_2C{=}P\}_2As]^-$ (**5**), the angle PAsP shrinks to 85.8°.[3] The P$=$C bonds in **3** (1.664 and 1.668 Å) are slightly shorter than in **1** (1.687 Å), and the P$-$Se bonds appear to be normal single bonds.



4

2: E = S; **3**: E = Se

(1)

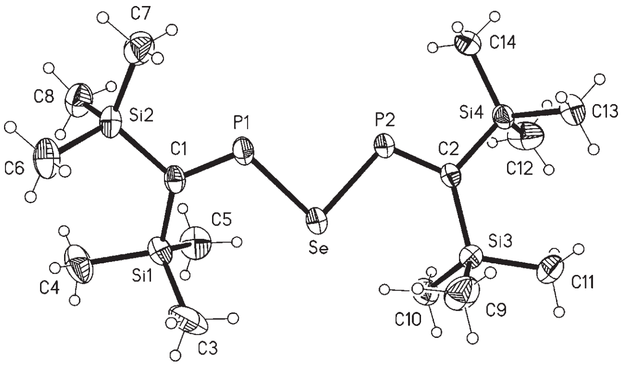


Figure 1. Molecular structure of **3**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å]: P1-C1 1.664(3), P2-C2 1.668(3), Se-P1 2.2842(10), Se-P2 2.2704(9). Selected angles [°]: P1-Se-P2 90.71(3), C1-P1-Se 109.75(11), C2-P2-Se 109.64(10).

Energies of isodesmic reactions of the model compound $[(H_3Si)_2C{=}P]_2S$ with H_2S calculated at the B3LYP/6-31+G* level (leading to $2\,(H_3Si)_2C{=}PSH$; $+0.1\ \mathrm{kcal\,mol^{-1}}$) and with PH_3 (leading to $(H_3Si)_2C{=}PH$ and $(H_2P)_2S$; $+17.6\ \mathrm{kcal\,mol^{-1}}$)[4] suggest that in the C$=$P-S unit there is π stabilization (ca. 9 $\mathrm{kcal\,mol^{-1}}$ for each P$=$C moiety), but there is no further energy gain when the second P$=$C unit is attached to sulfur.

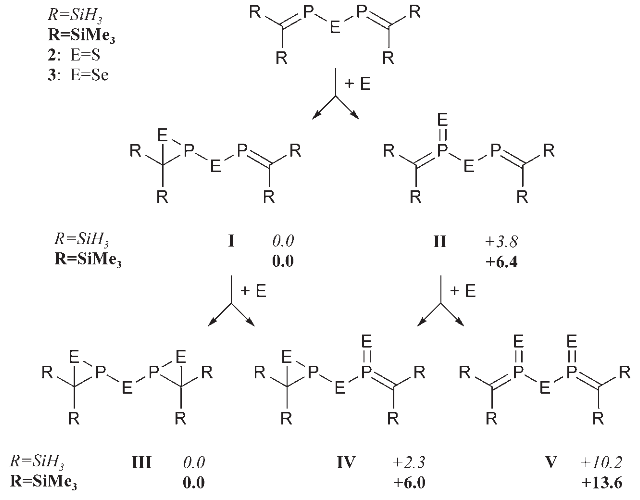
Two equivalents of elemental sulfur or selenium add to compounds **2** and **3**, respectively, in a surprising fashion:[5] norbornane-type P_2Se_5-related[6] $[(Me_3Si)_2CP]_2E_3$ cages (E $=$ S, Se) are formed. Bisphosphiranes (Scheme 1, type **III**), or thermodynamically somewhat less stable bis-σ^3,λ^5-phosphoranes (**V**), are not observed.

^{31}P NMR spectra of the reaction mixture of **2** with sulfur (see Experimental Section) exhibit a weak AX pattern at early stages of the reaction ($\delta(^{31}P) = +353.3, -25.0$ ppm; $J = 276.3$ Hz); this AX pattern is assigned to a *P*-(phosphaalkenylthio)thiaphosphirane (**6**, type **I**, see Scheme 1).[7] The main product is the C_2-symmetric compound $[(Me_3Si)_2C]_2P_2S_3$ (**7**; P^{III},P^{III}) [Eq. (2)], accompanied by partially oxidized $[(Me_3Si)_2C]_2P_2S_4$ (**8**; P^{III},P^{V}), which has an AB pattern ($J_{^{31}P^{31}P} = \pm 17.0$ Hz) in the ^{31}P NMR spectrum, and C_2-symmetric $[(Me_3Si)_2C]_2P_2S_5$ (**9**, P^{V},P^{V}). Compound **9** was isolated as a few single crystals. In a similar way, compound **3** reacts smoothly with two equivalents of selenium to give $[(Me_3Si)_2C]_2P_2Se_3$ (**10**, P^{III}, P^{III}) in high yield [Eq. (3)] which is however not further oxidized by selenium. Crude **10** is

---

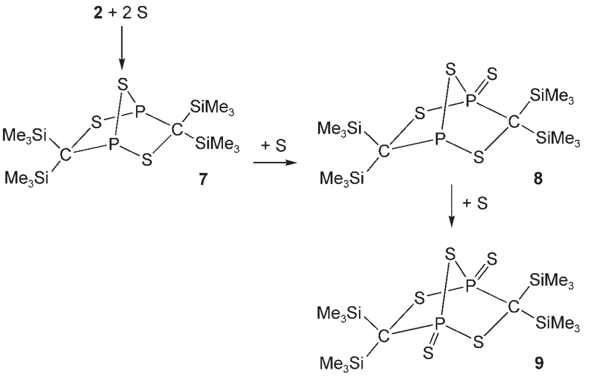
[*] Prof. Dr. W.-W. du Mont, Dr. T. Gust, Dr. J. Mahnke, R. M. Birzoi, L. Barra, D. Bugnariu, Dr. F. Ruthe, Dr. C. Wismach, Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
Fax: (+49) 531-391-5387
E-mail: w.du-mont@tu-bs.de
Prof. Dr. L. Nyulászi, Z. Benkõ
Department of Inorganic and Analytical Chemistry
Budapest University of Technology and Economics
Szt Gellért tér 4, 1521 Budapest (Hungary)
Prof. Dr. K. Karaghiosoff
Department Chemie und Biochemie
Ludwig-Maximilians-Universität München
80333 München (Germany)

[**] We thank D. Döring and Dr. U. Papke for aquisition of mass spectra. Financial support from OTKA T049258 for L.N. and Z.B. is gratefully acknowledged. E $=$ S,Se.

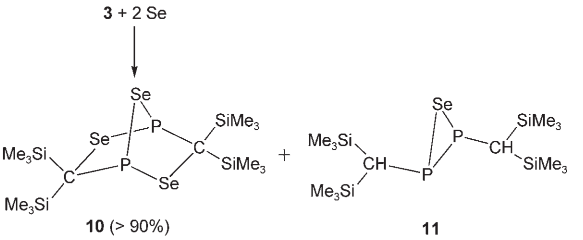


Scheme 1. Potential modes of sulfur and selenium addition to **2** and **3**. Relative energies (kcal mol^{-1}) calculated at the B3LYP/6-31+G* level for E = S.

accompanied by very small amounts of the known selenadiphosphirane **11**.[8]



(2)



(3)

The structure of **9** consists of C_2-symmetric molecules with distinctly different P–S bond lengths (endocyclic: 2.120, 2.130 Å; exocyclic: 1.904 Å). The distorted norbornane-like structures of **9** and **10** are closely related (Figures 2 and 3). Compound **10** crystallizes without imposed symmetry as two independent molecules that are both *RR* (or *SS*) configured. P–Se bond lengths in **10** (2.263–2.280 Å) are slightly longer than those in P_2Se_5 (2.234 and 2.254 Å)[6] and the central angle P1-Se3-P2 (91.6/91.9°) is narrower than in P_2Se_5 (97.6°).

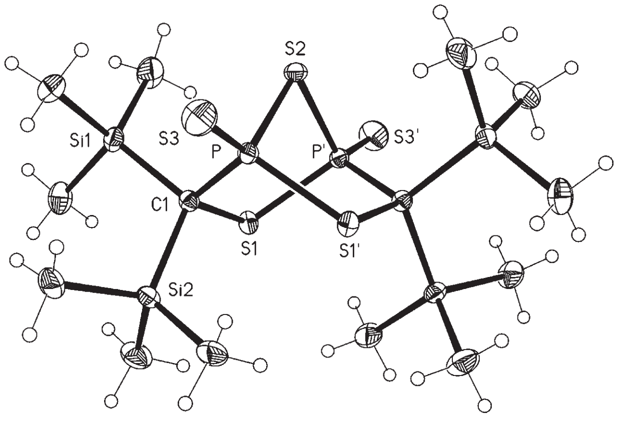


Figure 2. Molecular structure of **9**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å]: P–S1′ 2.1296(9), P–S2 2.1197(9), P–S3 1.9043(10), P–C1 1.822(3), S1–C1 1.848(2). Selected angles [°]: P-S2-P′ 88.66(5), S2-P-S3 118.06(4), C1-P-S3 117.44(9), S2-P-S1′ 98.78(3), P-C1-S1 106.44(13), C1-S1-P′ 104.32(8).

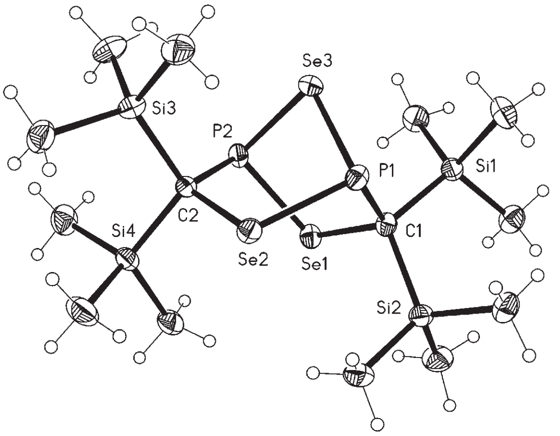


Figure 3. Structure of one of the two independent molecules of **10**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å]: P1–Se3 2.2662(9), 2.2632(8) (second molecule); P2–Se3 2.2803(9), 2.2638(8); P1–Se2 2.2751(9), 2.2752(8); P2–Se1 2.2694(9), 2.2739(9). Selected angles [°]: P1-Se3-P2 91.63(3), 91.89(3); Se2-P1-Se3 97.21(3), 96.51(3).

To investigate the mechanism leading to heteronorbornanes **7** and **10**, reactions of the mixed systems (**2** with Se, and **3** with S) were carried out and monitored by ^{31}P NMR spectroscopy. Initially, this leads to reversible chalcogen exchange ($\mathbf{2}+\mathrm{Se}\rightleftharpoons\mathbf{3}+\mathrm{S}$). According to B3LYP/6-31+G* calculations,[4] among the mixed type-**II** intermediates that are possible by chalcogen exchange (see Scheme 1, with $R = SiMe_3$)[9] the selenium-bridged isomer is more stable than the sulfur-bridged isomer by 5.4 kcal mol^{-1}. Compound **10** and C_2-symmetric $[(Me_3Si)_2C]_2P_2SSe_2$ (**12**) subsequently form (**12**: $\delta\ ^{31}P = 136.1$(s), $\delta^{77}Se = 506.6$, X part of an AA′X pattern).[10] Formation of the $C_2P_2E_3$ heteronorbornane cages **7**, **10**, and **12** is unexpected, because related thia- and selenaphosphiranes, which are the known products of sulfur or selenium additions to P=C double bonds, do not dimerize under comparable conditions.[5,11–14] Assuming the presence of the type **III** (see Scheme 1) compound **A** (Figure 4) or type **IV** (**B**) intermedi-

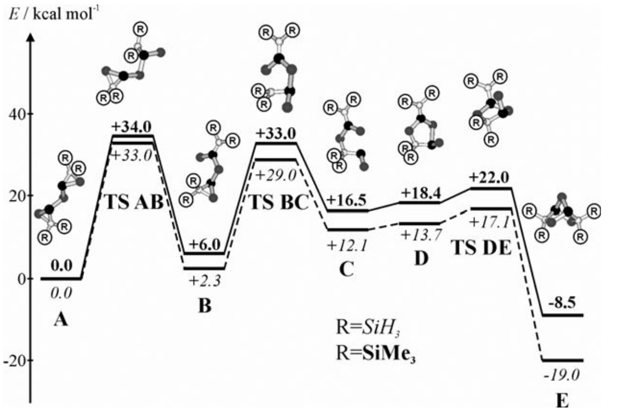


Figure 4. Calculated pathway for the isomerization of a bis(thiaphosphiranyl)sulfide **A** (see Scheme 1, type **III**) to the heteronorbornane **E**. E = S, R = SiH_3 (italics) and R = $SiMe_3$ (bold) Black P, dark gray S, light gray C.

ates obtainable by sulfur addition to intermediate **I**, density-functional theory (DFT) calculations at the B3LYP/6-31 + G* level were carried out on model systems (with SiH_3 substituents) and on the real compounds.[4]

Molecule **B** (which is most likely obtained directly from the reaction of the $P{=}C$ double bond with sulfur) is related to the more stable bisthiaphosphirane **A** by the open-shell state **AB**.[15] The activation barrier (**TS AB**) is comparable to that computed for the monosulfurated type **I** intermediate. However, opening of the second phosphirane ring followed by P–S to C–S bond shift and subsequent cyclization by P–S bond formation leading to intermediates **C**/**D** (two minima) requires somewhat less activation energy (see **TS BC**). Transition state **DE** is followed by the final cyclization through C–S bond formation providing bicyclic **E**. From the energy profile shown in Figure 4, it is understandable that the formation of the norbornane analogue **E** is controlled both thermodynamically and kinetically. As in the mixed system leading to **12**, the central sulfur atom of the starting material is in the central position of the heteronorbornane.

These considerations set an experimental challenge to characterize yet unknown type **III** bisthiaphosphiranes and type **IV** thiaphosphiranylthiothiophosphoranes.

Experimental Section

2: $(Me_3Si)_2C{=}PCl$[2] (2.0 g, 9.0 mmol) was added to $(Me_3Si)_2S$ (0.8 g, 4.5 mmol) in toluene (5 mL). After stirring the mixture for 12 h at 60 °C, all volatiles were removed at room temperature under vacuum (about 0.1 mbar), giving **2** as a yellow oil (1.74 g, 95 %). ^{31}P NMR: (81.0 MHz, C_6H_6): $\delta = 359.9$ ppm (s). Elemental analysis (%) calcd for $C_{14}H_{36}P_2SSi_4$ ($M = 410.8$ g mol^{-1}): C 40.93, H 8.83, S 7.81; found: C 39.89, H 8.52, S 8.93.

3: In an analogous fashion to **2**, $(Me_3Si)_2C{=}PCl$ (0.86 g, 3.8 mmol) was added to $(i\mathrm{PrMe_2Si})_2Se$[16] (0.54 g, 1.9 mmol) in toluene (10 mL). After heating the mixture for 12 h at 60 °C, work-up led to **3** as a red-brown oil (0.80 g, 92 %) that crystallized on storing. ^{31}P NMR: (81.0 MHz, C_6H_6): $\delta = 382.8$ ppm (s) $^1J_{SeP}$ 281.6 Hz. Elemental analysis (%) calcd for $C_{14}H_{36}P_2SeSi_4$ ($M = 457.7$ g mol^{-1}): C 36.74, H 7.93; found: C 36.69, H 7.99.

9: A mixture of **2** (0.51 g, 1.25 mmol) and sulfur (0.08 g, 2.5 mmol) in toluene (20 mL) was stirred for 3 days at 60 °C. ^{31}P NMR spectrum of the solution: $\delta = 353.5$ and -25.0 (AX pattern, $J = 276.3$ Hz), **6** (ca. 25 %); 129.9 (s), **7** (ca. 43 %); 145.1 and 90.7 (AX pattern $J = 17.0$ Hz), **8** (ca. 17 %); 97.3 (s), **9** (ca. 12 %); -85.8 ppm (s, traces of the thiadiphosphirane analogue of **11**). Crystallization from pentane at +4 °C led to a few crystals of pure **9** that were suitable for X-ray diffraction.[17] ^1H NMR: (400 MHz, C_6D_6): $\delta = 0.15$ (s, $SiMe_3$); 0.21 ppm (s, $SiMe_3$). ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 97.3$ ppm (s). MS (EI, 70 eV: m/z(%) 474(5) $[M{-}2S]^+$; 147(100) $[PPCSiMe_3]^+$; 73(40) $[SiMe_3]^+$. Elemental analysis (%) calcd for $C_{14}H_{36}P_2S_5Si_4$ ($M = 539.05$ g mol^{-1}), C 31.19, H 6.73; found: C 32.89, H 6.86.

10: A mixture of **3** (0.55 g, 1.2 mmol) with powdered gray selenium (0.18 g, 2.4 mmol) in toluene (10 mL) was heated for 2 days at 60 °C. The solution contained **10** and traces of **11** (δ $^{31}P = -70.5$ ppm (s); $J_{SeP} = 114$ Hz).[8] Crystallization from pentane gave **10** (0.68 g, 93 %) as a yellow solid, m.p. 106 °C. ^{31}P NMR: (81.0 MHz, C_6D_6): $\delta = 129.0$ (s); $^2J_{PP}$ 58.7 ppm (calcd from simulated ^{77}Se satellite pattern, X part of AA′X). ^{77}Se NMR (38.0 MHz, C_6D_6): $\delta = 494.2$ (t), $^1J_{SeP} = -229.9$ Hz, $^2J_{SeSe} = 24.6$ Hz, SeP_2; 543.6 ppm (AA′X,), $^1J_{SeP} = -298.0$ Hz, $^2J_{SeP} = -10.2$ Hz, CSeP. Elemental analysis (%) calcd for $C_{14}H_{36}P_2Se_3Si_4$ ($M = 615.6$ g mol^{-1}): C 27.31, H 5.89; found: C 27.93, H 6.14.

X-Ray structure determinations: Data collection and reduction: Crystals were mounted in an inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**10**: Siemens P4; others, Bruker SMART 1000 CCD). Measurements were performed with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.70173$ Å). Absorption corrections for the area detector were performed with the program SADABS. Structure solution and refinement: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). H atoms were included with a riding model or as rigid methyl groups. Special features of refinement: Compound **10** has two large peaks (3–4 e Å^{-3}) in the residual electron density, presumably corresponding to an unidentified disorder or twinning phenomenon.

CCDC-623170 (**3**), CCDC-623172 (**9**), and CCDC-623171 (**10**) 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.

Received: July 5, 2007

Keywords: cage compounds · chalcogens · density functional calculations · phosphaalkenes · X-ray diffraction

---

[1] V. Thelen, D. Schmidt, M. Nieger, E. Niecke, W.-W. Schoeller, *Angew. Chem.* **1996**, *108*, 354–356; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 313–315.

[2] R. Appel, A. Westerhaus, *Angew. Chem.* **1980**, *92*, 578; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 556; R. Appel, A. Westerhaus, *Tetrahedron Lett.* **1981**, *22*, 4957–4960.

[3] A. A. Rozhenko, W. W. Schoeller, *Ph.D. Seminar on Phosphorus Chemistry*, Bonn (Germany), **2005**, Abstract B3.

[4] a) Computations were carried out with the Gaussian 03 program package(Gaussian 03 (Revision C.02): M. J. Frisch et al., see Supporting Information. For each of the optimized structures, the second derivative of the energy was determined to check whether the stationary point located is a minimum of the potential energy hypersurface, or a first-order saddle point. The stability of the wavefunction was also tested, and in the case of instability the UB3LYP formalism was used, and the geometries were reoptimized, resulting in more stable species than the closed-shell analogues. At the saddle points, IRC calculations were performed to locate the minima related to the saddle

points; b) for visualization of the molecules the Molden program was used: G. Schaftenaar, J. H. Nordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

[5] a) J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe, P. G. Jones, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1447–1454; b) W.-W. du Mont, G. Dobreva, W. Grahn, S. Vollbrecht, T. Gust, J. Mahnke, *Phosphorus Sulfur Silicon Relat. Elem.* **2002**, *177*, 1753–1755 (*15th Int. Conf. on Phosphorus Chemistry*, Sendai, **2001**, Abstract).

[6] R. Blachnik, P. Lönnecke, K. Boldt, *Acta Crystallogr. Sect. C* **1994**, *50*, 659–661.

[7] A related weak AX pattern ($\delta^{31}P = +358.0$, -27.4 ppm, $J = 278$ Hz) is also observed, when the bulkier precursor $[(i\text{Pr-Me}_2\text{Si})_2\text{C{=}P}]_2\text{S}$ is stirred with 1 equivalent of sulfur at room temperature for 2 weeks.

[8] The assignment of **11** was supported by comparison of its ^{77}Se NMR and ^{13}C NMR spectra with data from a reference sample prepared by addition of selenium to di-[bis(trimethylsilyl)methyl]diphosphene according to a published procedure: H. Ranaivonjatovo, J. Escudie, C. Couret, *Phosphorus Sulfur* **1987**, *31*, 81–87.

[9] Precedence for rapid 1,3-migration of σ2λ3 phosphorus between two chalcogen atoms in an iminophosphanyldiselenophosphinate: E. Niecke, M. Nieger, F. Reichert, W. W. Schoeller, *Angew. Chem.* **1988**, *100*, 1779–1780; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1713–1714.

[10] NMR spin systems of $(\text{CH}_2\text{P})_2\text{Se}_3$: K. Eckstein, M. Schuster, K. Karaghiosoff, *Main Group Chem. News* **1997**, *4*(4), 10–15.

[11] E. Niecke, D.-A. Wildbredt, *J. Chem. Soc. Chem. Commun.* **1981**, 72–73.

[12] R. Appel, C. Casser, *Tetrahedron Lett.* **1984**, *25*, 4109–4112.

[13] R. Appel, C. Casser, *Chem. Ber.* **1985**, *118*, 3419–3423.

[14] E. Niecke, E. Symalla, *Chimia* **1985**, *39*, 320–322.

[15] It should be noted that the spin contamination is quite large $S^2 = 0.50$).

[16] D. Sewing, W.-W. du Mont, S. Pohl, W. Saak, D. Lenoir, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1363–1368.

[17] From **2** with 4 equivalents of sulfur, compound **9** is formed as main product.