Synthesis of the first stable 1,2-silathietane

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Organometallics, **1990**, 9 (8), 2205-2206• DOI: 10.1021/om00158a014 • Publication Date (Web): 01 May 2002

is shown as an ORTEP plot in Figure 1.[10] The platinum atom is surrounded by a bromine, two phosphorus, and one carbon atom in a slightly distorted square planar geometry. The phosphorus atoms occupy mutual trans positions. The carbon fragment can be identified as a substituted 2(3*H*)-furanone, bearing an iso-C_3 fragment at the 4-position and a platinum substituent at the 5-position. A rationalization of the reaction sequence for the formation of **3** is shown in Scheme II.

The first step in the formation of **3** is CO insertion into the metal–carbon bond of **1**, which results in the acyl complex **2**. Compound **2b** has indeed been isolated from reaction of **1b** with CO (1.5 bar during 14 h). The acylplatinum compound **2b** has been fully characterized[15] and was shown in a separate experiment to react further with CO to give **3b**. The existence of acylpalladium compound **2a** has been confirmed by low-temperature ^{1}H NMR and IR experiments. Under an atmosphere of CO at temperatures higher than 0 °C this complex reacts further to give **3a**.

The next step in the reaction sequence is a 1,3-metal shift resulting in the vinylketene intermediate **4**, followed by a second CO insertion into the new metal–carbon bond to give the metallo-α-acylketene compound **5** (not observed). The occurrence of the ketene intermediate **4** is indicated by the observation of a strong absorption at 2092 cm^{-1} in the IR spectrum during the conversion of **1** or **2** into **3**.[16] The last step may consist of ring closure concomitant with a 1,4-H shift, or alternatively a metal-promoted enolization via **6** may occur. Intermediate **6** has been neither observed nor isolated, but an α-acylketene is known to give a butenolide after enolization and cyclization.[17] The latter process would in our case involve a 1,5-hydrogen shift of a hydrogen atom from either of the two methyl groups to the oxygen atom of the metalloacyl group to give **6**, followed by normal addition of the enolic OH function to the ketene moiety.

Currently, investigations on the reactivity of the metallofuranone complexes toward small molecules and organometallic reagents with the aim of catalytic synthesis of derivatized butenolides are in progress.

Acknowledgment. We thank Prof. K. Vrieze for his interest.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal data and data collection and refinement parameters, atomic coordinates, thermal parameters, and bond distances and angles (12 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for compound **3b**: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.613$ (1) Å, $b = 34.694$ (4) Å, $c = 11.007$ (2) Å, $\beta = 104.07$ (1)°, $V = 4031.7$ Å^3, μ(Mo Kα) = 43.19 cm^{-1}, $d_{calc} = 1.43$ g cm^{-3}. Crystal dimensions were 0.25 × 0.50 × 0.50 mm. A total of 7673 intensities were measured on a Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation ($1.1 \leq \theta \leq 25°$; h −13 to 13, k 0–41, l 0–13). Of these, 2486 were below the 2.5$\sigma(I)$ level and were treated as unobserved. The structure was solved by means of the heavy-atom method. Refinement was carried out by means of anisotropic block-diagonal least-squares calculations. The hydrogen atoms were introduced at their calculated positions and not refined. An empirical absorption correction (DIFABS) has been applied.[11] The weighting scheme $w = 1/(50 + F_o)$ has been employed, and the anomalous dispersions of Pt, Br, and P have been taken into account. The final R value was 0.053 ($R_w = 0.089$). The calculations were carried out with XTAL 2.4.[12] The scattering factors and the dispersion correction factors were taken from the literature.[13,14]

(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(12) *XTAL User's Manual, Version 2.4*; Hall, S. R., Stewart, J. M., Eds.; University of Western Australia: Nedlands, Western Australia, and University of Maryland: College Park, MD, 1988.

(13) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(15) Selected data for **2b**: ^{1}H NMR (C_6D_6, 100 MHz) δ 1.56 (d, ^5J(H,H) = 2.8 Hz, 6 H, 2 CH_3), 5.23 (m, ^3J(Pt,H) = 37 Hz, 1 H, $=C=CH-$), 7.00 (m, 18 H, meta and para Ph), 7.90 (m, 12 H, ortho Ph); ^{31}P NMR (C_6D_6, 100 MHz) δ 19.51 (s, J(Pt,P) = 3071 Hz); IR (KBr, cm^{-1}) ν(C=O) 1620 (vs), ν(C=C=C) 1940 (w); FD-mass found $m/z = 895$, calcd $M^{\bullet +}$ 895.

(16) Alternatively, a σ- to π-allyl conversion followed by carbonylation of the (π-allyl)palladium species may be involved. The intermediate π-allylic ligand would be intriguing because of the unsaturation at both terminal allyl carbon atoms. We thank one of the reviewers for drawing our attention to this point.

(17) Deshong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575.

Synthesis of the First Stable 1,2-Silathietane

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Received April 13, 1990

Summary: Sulfur reacts with 1,1-di-*tert*-butyl-2,3-dimethylsilirane (**1**) to produce the first isolable silthietane, 1,1-di-*tert*-butyl-3,4-dimethyl-1,2-silathietane (**2**), and 1,1-di-*tert*-butyl-3,4-dimethyl-1-sila-2,3-dithiacyclopentane (**3**) in 60% and 19% yields, respectively. Pyrolysis (200 °C) of **2** generates 1,1,3,3-tetra-*tert*-butyl-2,4-dithiadisilacyclobutane (**4**) and 1,1,3,3-tetra-*tert*-butyl-5,6-dimethyl-2,4-dithia-1,3-disilacyclohexane (**5**). **4** is formally the dimer of the reactive intermediate di-*tert*-butylsilathione, t-$Bu_2Si=S$, and **5** is the product of insertion of the silathione fragment into **2**. When **1** is heated in the presence of hexamethylcyclotrisiloxane, 1,1-di-*tert*-butyl-3,3,5,5,7,7-hexamethyl-2,4,6-trioxa-1,3,5,7-tetrasila-8-thiacyclooctane (**6**) is formed. Sulfur insertion into **1** to produce **2** is stepwise, as is the cleavage of **2**.

1,2-Silathietanes have been postulated as reactive intermediates in the reaction of thio ketones with silenes at high temperatures en route to silathiones.[1] However, characterization of any member of this ring system has, until now, proven elusive. Insertion of sulfur into cyclic carbosilanes is a well-known and useful method of preparing unusual sulfur-containing heterocycles.[2] However, in the case of siliranes with small substituents on silicon, the reaction with sulfur cannot be limited to single-atom insertion and thus is not a viable route to stable 1,2-silathietanes.[3] We have found that by placing *tert*-butyl

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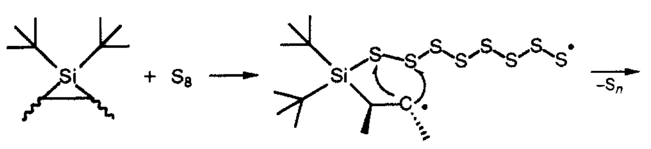
(1) Sommer, L. H.; McLick, J. *J. Organomet. Chem.* **1975**, *101*, 171.

(2) (a) Weidenbruch, M.; Schäfer, A. *J. Organomet. Chem.* **1984**, *269*, 231. (b) West, R.; Carlson, C. W. *Organometallics* **1983**, *2*, 1798. (c) Dubac, J.; Mazerolles, P. *C.R. Seances Acad. Sci., Ser. C* **1968**, *267*, 411.

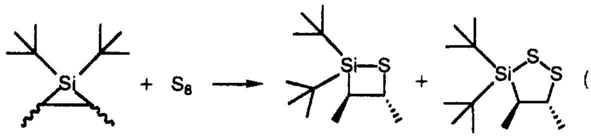
Scheme I



2 + 3

groups on the silicon atom of a silirane, sulfur insertion can be stopped after one atom is placed in the ring, leading to the formation of stable 1,2-silathietanes in good yield.

When 1.00 g (5.05 mmol) of *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane (1)[4] was stirred in 5.0 mL of degassed hexane with 0.170 g (5.30 mmol) of sulfur for 3–6 h at room temperature, most of the sulfur slowly dissolved to produce a colorless solution. 1,1-Di-*tert*-butyl-1,2-silathietane (2) and 1,1-di-*tert*-butyl-1-sila-2,3-dithiacyclopentane (3) were

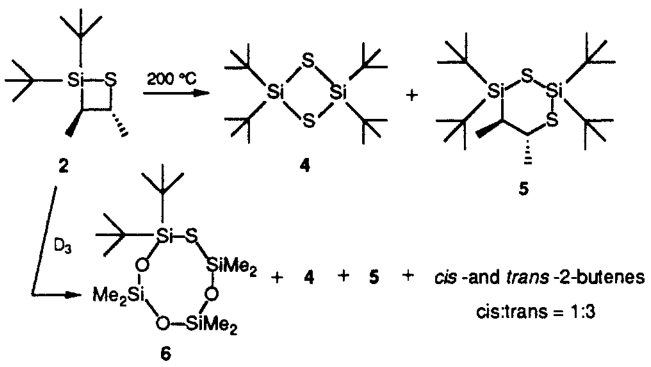


(1)

1 2 3

isolated by preparative gas chromatography. The structures were assigned on the basis of elemental analyses and MS and NMR data.[5] Yields of 2 and 3 were estimated as 60% and 19%, respectively, by GLC. GC–MS analysis detected a minor product (<2%) of slightly longer retention time than 3 with the same molecular weight. Presumably this is the cis isomer of 3. Identical results were obtained when the cis isomer of 1 was used. Our assignments of trans configurations to 2 and 3 are based on the observation that only one isomer of each was detected from the insertion reactions of both the cis and trans siliranes. Treating 2 with sulfur does not produce the siladithiacyclopentane 3, implying that two atoms of sulfur are transferred directly from S_8 to the silirane 1. The conversion of the cis silirane to exclusively trans 2 and trans 3 leads us to speculate that a stepwise radical mechanism may be important (Scheme I).

Scheme II



Pyrolysis of 1,1-di-*tert*-butyl-1,2-silathietane in benzene at 200 °C yields two compounds, 1,1,3,3-tetra-*tert*-butyl-1,3-disilacyclobutane (4) and 1,1,3,3-tetra-*tert*-butyl-1,3-disila-2,4-dithiacyclohexane (5) in 33% and 30% yields, respectively, and a mixture of *cis*- and *trans*-2-butenes (Scheme II). Cyclobutane 4 is formally the dimer of di-*tert*-butylsilathione, $t\text{-Bu}_2\text{Si}{=}\text{S}$, and cyclohexane 5 is formally the result of insertion of the di-*tert*-butylsilathione fragment into the 1,2-silathietane 2. When a mixture of 2, hexane, and hexamethylcyclotrisiloxane (D_3) is pyrolyzed (200 °C, 4 h), 6, which is formally the result of the insertion of di-*tert*-butylsilathione into one of the Si–O bonds of D_3, is obtained in 27% yield in addition to 4 (24%) and 5 (40%) and *cis*- and *trans*-2-butenes. Increasing the temperature to 340 °C for 6 h leads to an increase in 6 at the expense of 5 with essentially no change in the amount of 4. When 5 is heated to 350 °C, a complex mixture results but the silathione dimer 4 is not detected. On the other hand, when 5 is pyrolyzed in the presence of D_3, 6 is produced. These results suggest that both 2 and 5 deliver the $t\text{-Bu}_2\text{Si}{-}\text{S}$ fragment to D_3 in a bimolecular reaction but may not actually generate $t\text{-Bu}_2\text{Si}{=}\text{S}$.[6] This reaction is under further study.

These results are noteworthy for several reasons: they supply further support[4] for the concept that the reactivity of siliranes is more controlled by steric bulk on silicon than on carbon, they challenge the implication of a silathione intermediate in the reaction of silenes with thio ketones,[1] and they provide a sharp contrast with the reaction of silacyclobutanes with sulfur, which leads to ring fragmentation.[7]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Grant No. 88-0060. The assistance of Steve Bahr and Steve Castellino in obtaining ^{29}Si NMR spectra is gratefully acknowledged.

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(3) Seyferth, D.; Duncan, D. P.; Hass, C. K. *J. Organomet. Chem.* **1979**, *164*, 305.

(4) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27* 1355.

(5) **2**: ^{1}H NMR (benzene-d_6, δ) 3.29 (1 H, SCH), 1.88 (m, 1 H, SiCH), 1.46 (d, J = 7.33 Hz, 3 H, $\mathrm{C}H_3$), 1.31 (s, 9 H, *t*-Bu), 1.18 (s, 9 H, *t*-Bu), 1.10 (d, J = 7.52, 3 H, $\mathrm{CHC}H_3$); ^{13}C NMR (benzene-d_6, δ) 44.43 (S*C*), 35.51, 26.29 (C–$\mathrm{CH_3}$), 28.34, 28.15 ($\mathrm{C}(C\mathrm{H_3})_3$), 23.08, 21.42 ($C(\mathrm{CH_3})_3$), 15.37 (Si–*C*); ^{29}Si (benzene-d_6, δ): 26.43; MS *m/e* 230 (M^+, 5%), 173 (M^+ − 57, 33%), 57 (100%). Anal. Calcd: C, 62.53; H, 11.37. Found: C, 62.77; H, 11.64. **3**: ^{1}H NMR (benzene-d_6, δ) 3.06 (m, 1 H, SCH), 1.29 (m, 1 H, SiCH), 1.26 (s, 9 H, *t*-Bu), 1.19 (d, J = 6.35 Hz, 3 H, $\mathrm{C}H_3$), 1.18 (s, 9 H, *t*-Bu), 1.10 (d, J = 7.5 Hz, 3 H, $\mathrm{C}H_3$); ^{13}C NMR (benzene-d_6, δ) 53.99 (S*C*), 17.13, 34.79 ($C\mathrm{H_3}$), 28.83, 28.34 ($\mathrm{C}(C\mathrm{H_3})_3$), 22.59 ($C(\mathrm{CH_3})_3$), 13.23 (Si*C*); ^{29} Si NMR (benzene-d_6, δ) 48.18; MS *m/e* 262 (M^+, 50%) 205 (M^+ − 57, 72%), 163 (M^+ − 57–56, 80%), 57 (100%). Anal. Calcd: C, 54.89; H, 9.98. Found: C, 55.02; H, 10.06. **4**: mp 128 °C; ^{1}H NMR (benzene-d_6, δ) 1.38 (*t*-Bu); ^{13}C NMR (benzene-d_6, δ) 29.14 ($\mathrm{C}(C\mathrm{H_3})_3$), 25.7 ($C(\mathrm{CH_3})$); ^{29}Si NMR (benzene-$d_6$, δ) 29.72; MS *m/e* 291 (M^+ − 57, 31%), 249 (M^+ − 57 −42, 64%), 75 (100%). Anal. Calcd: C, 55.10; H, 10.40. Found: C, 55.51; H, 10.38. **5**: mp 121–123 °C; ^{1}H NMR (benzene-d_6, δ) 3.45 (m, 1 H, SCH), 1.63 (m, 1 H, SiCH), 1.29 (d, J = 6.98, 3 H, $\mathrm{C}H_3$), 1.26, 1.23, 1.22, 1.18 (singlets, *t*-Bu, 9 H each), 1.02 (d, J = 7.29, $\mathrm{C}H_3$); ^{13}C NMR (benzene-d_6, δ) 38.58 (S*C*), 30.19, 30.03, 29.34, 28.77 ($\mathrm{C}(C\mathrm{H_3})_3$), 28.50, 27.48, 25.41, 24.52 ($C(\mathrm{CH_3})_3$), 23.36, 15.55 ($C\mathrm{H_3}$), 14.34 (Si*C*); ^{29}Si NMR (benzene-d_6, δ) 30.59, 25.92; MS *m/e* 347 (M^+ − 57, 23%), 291 (M^+ − 57 − 56, 32%), 249 (M^+ − 57 − 56 − 42, 100%). Anal. Calcd: C, 59.33; H, 10.95. Found: C, 59.08; H, 11.17. **6**: ^{1}H NMR (benzene-d_6, δ) 1.30 (s, 18 H, *t*-Bu), 0.60, 0.33, 0.26 (singlets, 6 H each, $\mathrm{SiCH_3}$); ^{13}C NMR (benzene–d_6, δ) 27.95 ($\mathrm{C}(C\mathrm{H_3})_3$), 23.37 ($C(\mathrm{CH_3})_3$), 6.62, 1.42, 0.94 ($\mathrm{Si}C\mathrm{H_3}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, δ) 9.74, 4.57, −17.50, −19.93; MS *m/e* 339 (M^+ − 57, 100%), 240 (M^+ − 57 − 42, 99%). Anal. Calcd: C, 42.37; H, 9.14. Found: C, 42.36; H, 9.38.

(6) It is relevant to note that a convincing case against the intermediacy of silanones in the thermolysis of siloxetanes and in support of a bimolecular mechanism to explain the products of "$R_2\mathrm{Si}{=}\mathrm{O}$ insertion" has been made: Barton, T. J.; Hussman, G. P. *Organometallics* **1983**, *2*, 692.

(7) Weidenbruch, M.; Schäfer, A.; Rankers, R. *J. Organomet. Chem.* 1980, *195*, 171.