accord with a rotating η^4-butadiene ligand[6] and an AX_4 pattern for the fluxional allyl unit.

Possible mechanisms to account for the formation of the observed product are shown in Scheme II. The intermediate allyl–butadiene **3** can undergo a formal electrocyclic rearrangement to generate an olefin allylic C_7 fragment; a 1,3-shift of the hafnium to the more substituted end of the allylic moiety allows for a β-elimination and subsequent hydride addition across the terminal olefin functionality to generate the observed species. Another plausible route is the direct insertion of one end of the butadiene ligand into the hafnium–carbon bond of the allyl moiety followed by β-elimination and hydride addition. The fact that the intermediate allyl–butadiene complex **3b** with the more hindered isopropyl substituents is only transiently observed suggests that the acceleration in product formation is due to relief of steric strain in the intermediate by coupling of the two hydrocarbon units.

This coupling of an allyl unit with a 1,3-butadiene fragment appears to be unique.[8] The analogous cyclopentadienylzirconium complex (η^5-C_5H_5)Zr(allyl)(butadiene) is apparently stable and not subject to this coupling reaction.[9] Interestingly, the use of the bulkier pentamethylcyclopentadienyl ancillary ligand also allows for the isolation of similar complexes of the formula (η^5-C_5Me_5)M(1-Me-allyl)(butadiene) (M = Zr and Hf), with no reported[10] evidence for carbon–carbon bond formation. These observations clearly show that the choice of the ancillary ligands is crucial for observing this reaction sequence; in addition, fine-tuning the rate of this coupling/rearrangement is also possible by modifying the steric demands of the amido–phosphine donors.

Further investigations of this unusual coupling/rearrangement reaction are underway. We are particularly interested in the diastereoselectivity of the transformation when the reaction involves substituted allyl and diene ligands.

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Registry No. **1a**, 94481-25-1; **1b**, 113773-38-9; **2a**, 113686-58-1; **2b**, 113686-59-2; **3a**, 113686-60-5; **3b**, 113725-86-3; **4a**, 113703-95-0; **4b**, 113703-96-1; Mg·C_4H_6·2THF, 60300-64-3.

Supplementary Material Available: Preparative experimental details, microanalytical, ^1H, ^{13}C, and ^{31}P NMR data for all new compounds, stereoview of **4b**, and tables of final positional and isotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, final anisotropic thermal parameters, bond lengths, bond angles, and intraannular torsion angles (15 pages); a listing of measured and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[8] Coupling of an allyl and butadiene substrate is the proposed first step in the polymerization of 1,3-butadiene by π-allyl complexes of nickel and palladium; see: Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: Toronto, 1980; p 54–56 and references therein.

[9] (a) Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 455. (b) Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 625.

[10] Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

A New Route to 1,4-Disilabenzenes and 1,4-Disilabarrelenes

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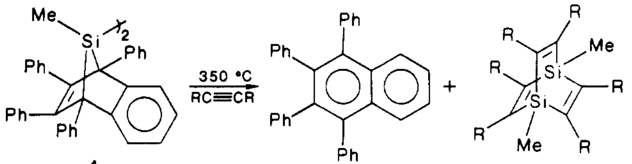
Summary: Heating bi(7-silanorboranadien-7-yl) **4** with diphenylacetylene at 350 °C produces 1,4-disilabarrelene **6a**. The X-ray crystal structure of **6a** is reported. Thermolysis of **4** in the presence of 3-hexyne also produces small amounts of the corresponding 1,4-disilabarrelene. Mechanisms for the formation of these products are proposed; the probable immediate precursor is a 1,4-disilabenzene.

Earlier papers from these laboratories[2,3] have described the isolation of trapped products believed to arise from hexamethyl-1,4-disilabenzene,[4] including several 1,4-disilabarrelenes. Photolysis or thermolysis of the 9,10-bridged anthracene compound **1** or thermolysis of the *cis*-1,4-disilacyclohexadiene **2** in the presence of acetylenes led to disilabarrelenes **3a–c** (Scheme I).

We now report synthesis of disilabarrelenes by another route, starting from the bi(7-silanorborandien-7-yl) compound **4** previously described as a synthon for dimethyldisilyne, MeSi≡SiMe.[5] Thermolysis of **4** (1.82 mmol) with diphenylacetylene (18.4 mmol) and ca. 1 g of benzene in a sealed tube at 350 °C for 2 h gave a mixture that was chromatographed on silica gel (hexane/benzene, 3:1), affording 1,2,3,4-tetraphenylnaphthalene (**5**) (1.21 g, 77%) and disilabarrelene **6a** (136 mg, 12%) as the sole silicon-containing product.[6] Similar thermolysis of **4** with 3-hexyne also led to the formation of the corresponding disilabarrelene **6b** (ca. 2%) along with **5**.[7] The structure of **6a**, determined by X-ray crystallography, is shown in Figure 1.[8]



4

5

6a, R = Ph, 12%
b, R = Et, 2%

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[1] Present address: Department of Chemistry, Tohoku University, Sendai 980, Japan.

[2] Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884.

[3] Welsh, K. M.; Rich, J. D.; Michl, J.; West, R. *Organometallics* in press.

[4] The parent compould 1,4-disilabenzene has been isolated in argon matrix. See: Maier, G.; Schottler, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4078.

[5] Sekiguchi, A.; Zigler, S. S.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 4241.

[6] **6a**: mp > 300 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.13 (s, 6 H, SiMe), 6.78–6.95 (m) and 6.95–7.21 (m) (total of 30 aromatic protons in the ratio 2:3); ^{13}C NMR ($CDCl_3$) δ −8.36 (SiMe), 125.35 (aromatic C), 127.79 (aromatic C), 127.82 (aromatic C), 141.90 (aromatic C) and 160.05 (olefinic C); ^{29}Si NMR ($CDCl_3$) 16.9 ppm; high resolution mass, *m/e* 620.2335, calcd for $C_{44}H_{36}Si_2$, *m/e* 620.2355.

[7] Compound **6b** was isolated by preparative GLC: mp 71–72 °C; NMR ($CDCl_3$, δ) 0.59 (s, 6 H, SiMe), 0.86 (t, 18 H, CCH_3) and 2.29 (q, 11 H, $C{=}CCH_2$); high-resolution mass, *m/e* 332.2365, calcd for $C_{20}H_{36}Si_2$, *m/e* 332.2355.

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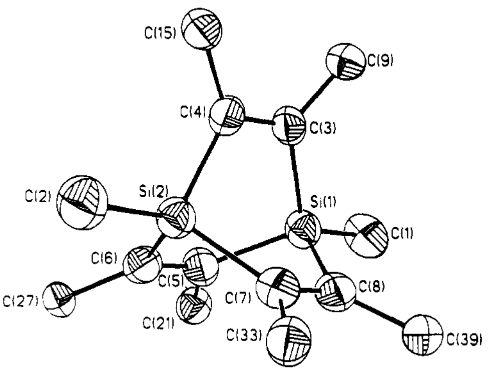
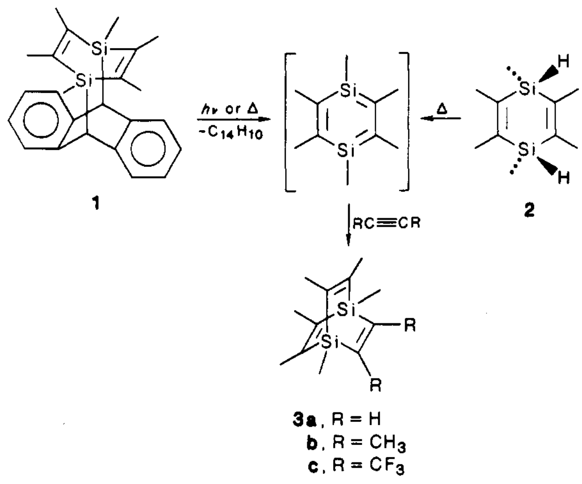


Figure 1. Crystal structure of **6a**. All atoms of the phenyl rings except the ipso carbon atoms and all hydrogen atoms have been omitted for clarity. Bond lengths (pm): 185.5 [Si(1)–C(1)], 184.9 [Si(2)–C(2)], 188.6 [Si(1)–C(3)], 188.7 [Si(2)–C(4)], 190.4 [Si(1)–C(5)], 189.7 [Si(2)–C(6)], 188.6 [Si(1)–C(8)], 190.5 [Si(2)–C(7)], 136.7 [C(3)–C(4)], 133.4 [C(5)–C(6)], 135.3 [C(7)–C(8)]. The silicon–silicon nonbonded distance is 293 pm.

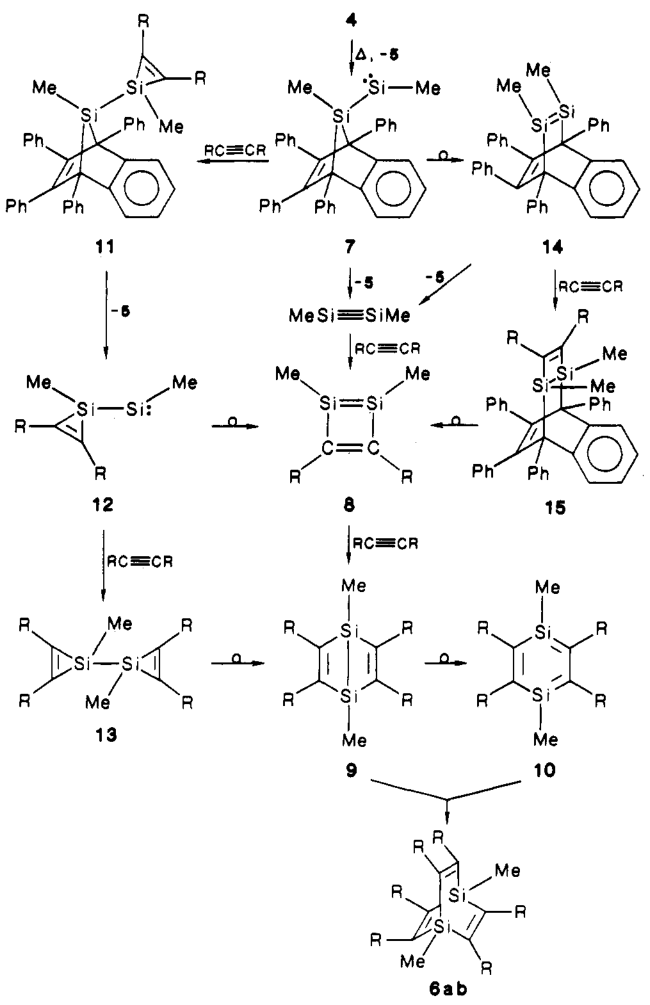
Scheme I



There are several possible mechanisms for the formation of **6ab** summarized in Scheme II, which involve intermediates of some interest. The probable initial step is loss of **5** to give silylene **7**, which might then lose a second molecule of **5** to give $\mathrm{MeSi{\equiv}SiMe}$. Dimethyldisilyne would probably react rapidly with alkynes to give disilacyclobutadiene **8** followed by Dewar benzene **9**,[9] which could add a final molecule of alkyne to give disilabarrelene either directly or after rearranging to 1,4-disilabenzene **10**. An alternative route involves trapping of **7** with alkyne to give a silacyclopropene, **11**, which could lose **5** to produce the silylene **12**; the latter could add another alkyne molecule to give **13**, which could rearrange to **9**. Rearrangement of **12** to **8** is also possible. Finally, 1,2-rearrangement of **7** to give disilene **14** is conceivable; **14** could form $\mathrm{MeSi{\equiv}SiMe}$, or, in two steps, **8**.

All of these and other plausible mechanisms converge at 1,4-disilabenzene, in either the open (**10**) or Dewar (**9**) form. We propose that one of these species is the immediate precursor to disilabarrelene, both in these reactions and in the syntheses from **1** and **2** mentioned above.

Scheme II



Registry No. 4, 102649-09-2; 5, 751-38-2; 6a, 113668-64-7; 6b, 113685-62-4; PhC≡CPh, 501-65-5; EtC≡CEt, 928-49-4.

Supplementary Material Available: Tables of crystal data, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and H-atom coordinates and isotropic thermal parameters (6 pages); a listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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(8) A crystal of $C_{44}H_{36}Si_2$ (**6a**) (M_r 620; 0.2 mm × 0.2 mm × 0.4 mm) was found to be triclinic with a = 10.849 (3) Å, b = 16.968 (6) Å, c = 9.746 (3) Å, α = 98.76 (2)°, β = 92.51 (3)°, γ = 97.20 (3), V = 1755.84 Å^3, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 1.25 cm^{-1}, D_{calcd} = 1.173 g cm^{-3}. Data were collected on a Nicolet $P\bar{1}$ diffractometer with Mo Kα X-radiation using θ–2θ scans. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to R = 0.073 for 3507 observed reflections ($|F_o| > 3\sigma|F_o|$; $2\theta \leq 45.770°$).

(9) 1,4-Cycloaddition of disilenes with alkynes is precedented: De Young, D. J.; West, R. *Chem. Lett.* **1986**, *6*, 883. De Young, D. J.; Fink, M. J.; Michl, J.; West, R. *Main Group Metal Chem.* **1987**, *1*, 19.

Mixed σ-Alkynyl–σ-Vinyl Bis(triphenylphosphine)platinum Complexes via a Labile σ-Vinyl Platinum Triflate Precursor

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Summary: Addition of a vinyl platinum(II) complex with a labile triflate ligand to a THF solution of selected acetylides, generated from the corresponding terminal acetylenes and $LiNH_2$, gives trans σ-alkynyl-σ-vinyl Pt(II) complexes in good yields. Key spectral features and a single-crystal X-ray structure determination are described.

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