lution and exist in equilibrium with their monomers.[10] In the second mode, a lithium atom is η^5-bonded to a Cp ring and to two THF molecules. These two modes combined lead to an inverse sandwich in which two lithium atoms are π-bonded to opposite sides of one Cp ring. Examples of inverse sandwich structures with two lithium atoms coordinating to opposite sides of the same π-system have been reported.[11] One interesting feature of this compound is that the lithium atoms, two Cp rings, and the THF molecules are in a quasi-linear coordination, forming a Cp–Li–Cp–Li–2THF "*supersandwich*" system. Figure 2 shows a pictorial summary of selected bonding parameters. The Cp(centroid)–Li–Cp(centroid) angle is 163°. The distances between the internal lithium atom and the centroids of the two Cp rings are 2.051 and 2.094 Å, and that of the external lithium atom and the Cp ring is 2.038 Å. The Li(2)–Li(2a) distance is 4.499 Å, and the average Li–O distance is 1.916 Å. The Li–C distances vary from 2.272 to 2.518 Å with an average value of 2.397 Å. The distance between the two Cp centroids in the organic ligand is 3.899 Å. These values are comparable to experimental[12] and theoretical[3b,13] parameters of similar systems, including those of 2·2TMEDA. The trimethylsilyl groups are slightly bent out of the planes of the substituted Cp rings pointing away from the internal lithium atoms. Similar out-of-plane bending involving CH bonds in CpLi have been examined theoretically and interpreted as due to simple Coulombic effects.[3c,14] We are currently performing detailed NMR studies of 4 and synthesizing dinuclear main-group and transition-metal complexes from 4.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data and data collection details, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances and angles, and hydrogen atom coordinates for 4 (9 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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First Isolation of Six-Membered Cyclic Acetylene: Synthesis and Reaction of Tetrasilacyclohexynes

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Received November 4, 1991

Summary: Six-membered cyclic acetylenes, namely 1,1,2,2,3,3,4,4-octaalkyl-1,2,3,4-tetrasilacyclohexynes (**1**), have been synthesized directly by the reaction of 1,4-dichlorooctaalkyltetrasilanes with acetylene di-Grignard reagent followed by GC purification. It is found that the tetrasilacyclohexyne **1a** is thermally stable: $t_{1/2}$ = 8 h (decane, 174 °C). Reactions of **1a** with dicobalt octacarbonyl, 2,3-dimethyl-1,3-butadiene, phenyl azide, and diphenyldiazomethane give the corresponding cycloadducts, respectively.

In recent years, there have been a surge of activities in constructing strained cyclic silicon compounds. Two types of compounds, *trans*-cycloalkenes[1] and cycloalkynes,[1a,2] are subjects of considerable interest. We recently reported the first isolation of a seven-membered *trans*-cycloalkene which was stabilized by the long bond distance of Si–Si bonds.[3] On the other hand, many medium-ring cycloalkynes have been generated as reactive intermediates and theoretical studies were carried out.[4] Some silicon-containing cycloalkynes have been reported so far.[5] Previously, we described the synthesis of hexasilacyclooctyne 2 and pentasilacycloheptyne 3.[6] We now report the first

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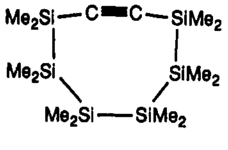
Table I. NMR and UV Spectra of Polysilacycloalkynes

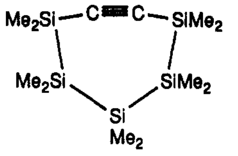
compd	NMR (C_6H_{12}), ppm ^1H	^{13}C	^{29}Si	UV (C_6H_{12}) λ_{max}, nm (ϵ)
1a	0.16 (s, 12 H)	–6.3 (q)	–30.8	237 (8700)
	0.19 (s, 12 H)	–2.9 (q)	–19.2	
		135.6 (s)		
1b	0.80–1.07[a] (m, 16 H)	4.2 (t)[a]	–17.7[a]	236 (7870)
		5.5 (t)	–8.3	258 (3520, sh)
	1.08 (t, 12 H, J = 7.5 Hz)	8.6 (q)		
		10.5 (q)		
	1.11 (t, 12 H, J = 7.5 Hz)	136.4 (s)		
3	0.16 (s, 12 H)	–5.74 (q)	–38.5	229 (10 200)
	0.18 (s, 12 H)	–5.66 (q)	–34.6	
	0.19 (s, 6 H)	–3.0 (q)	–33.8	
		123.1 (s)		
2	0.16 (s, 12 H)	–5.8 (q)	–39.6	235 (9720)
	0.17 (s, 12 H)	–4.6 (q)	–38.9	
	0.20 (s, 12 H)	–2.7 (q)	–35.8	
		117.7 (s)		

[a] Measured in C_6D_6.

isolation and some reactions of tetrasilacyclohexynes as the smallest stable polysilacycloalkyne.[7]

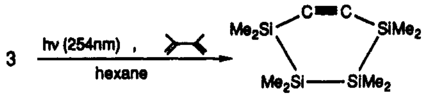


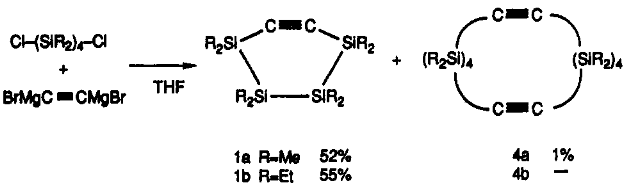
2



3

Irradiation of a hexane solution (33 mL) of decamethylpentasilacycloheptyne (**3**; 104 mg, 0.33 mmol) with a low-pressure mercury lamp (254 nm) through a quartz tube in the presence of 2,3-dimethyl-1,3-butadiene (in 20-fold excess of **3**) formed ring-contracted octamethyltetrasilacyclohexyne (**1a**), though in only 20% yield.[7] Increased yields of **1a** have been achieved by direct synthesis via the reaction of 1,4-dichlorooctamethyltetrasilane with the acetylene di-Grignard reagent. A 1.50-g (4.9-mmol) amount of 1,4-dichlorooctamethyltetrasilane was added to 300 mL of a THF suspension of acetylene di-Grignard reagent prepared from ethylmagnesium bromide (13 mmol) and acetylene. The mixture was stirred for 12 h. Tetrasilacyclohexyne **1a**, a colorless liquid, was isolated and purified from the reaction mixture by gas chromatography (10% SF96, column temperature 100 °C). Dimeric compound **4a** also was obtained as a side product in 1% yield.[8] The structure of **1a** was determined by the spectroscopic analyses.[9] In particular, the ^{13}C NMR signal of the acetylenic sp carbons of **1a** (in cyclohexane) is observed at 135.6 ppm, which is lower than those of the corresponding cycloheptyne **3** (123.1 ppm) and cyclooctyne **2** (117.7 ppm).[6] The ^{29}Si NMR signal of the acetylene-bonded silicon of **1a** appears at –19.2 ppm, which also is lower than those of the corresponding silicon atoms of **3** and **2**. Octaethyl-substituted tetrasilacyclohexyne **1b** was also obtained in 55% yield.[10] Characteristic spectral data for **1a** and **1b** are summarized in Table I, along with those for the eight- and seven-membered cycloalkynes **2** and **3**.

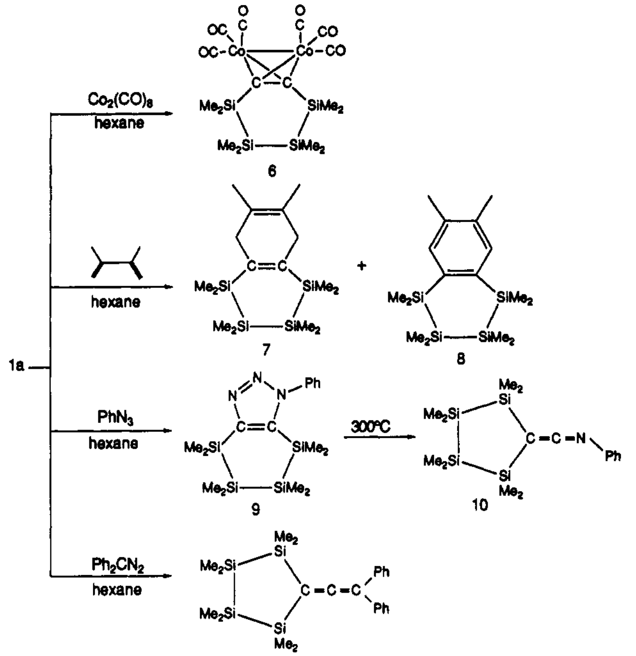




It was found that tetrasilacyclohexyne **1a** is thermally stable in boiling toluene even after 1 day. However, **1a** slowly decomposed in boiling decane (174 °C; $t_{1/2}$ = 8 h) and gave bicyclic compound **5** in 2.5% yield as a volatile material.[11] The bicyclo olefin **5** may be considered to be formed by oxidation of disilacyclobutene **5x**.[12] The mechanism of its formation is now under investigation.

The reactivity of the carbon–carbon triple bond of **1a** was examined. When a hexane solution of tetrasilacyclohexyne **1a** was treated with $Co_2(CO)_8$, the cobalt car-

Scheme I. Reactions of Tetrasilacyclohexyne



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[7] (a) The photochemical generation of tetrasilacyclohexyne **1a** has been reported: Ando, W. IXth International Symposium on Organosilicon Chemistry; Edinburgh, July 1990, Abstract I.17. Ando, W.; Kabe, Y. In *Frontiers of Organosilicon Chemistry* (Proceedings); Bassindale, A. R., Gaspar, P. P., Eds.; The Royal Society of Chemistry: London, 1991; pp 170–181. (b) Isolation and reactivities of **1a** have been reported: Hojo, F.; Shimizu, T.; Ando, W. 38th Symposium on Organometallic Chemistry; Kyoto, Japan, Oct 1991, Abstract PA203. Ando, W.; Shimizu, K.; Hojo, F.; Sekigawa, S.; Shimizu, T. IVth Kyushu International Symposium on Physical Organic Chemistry; Kyushu, Japan, Oct 3, 1991; p 60. Ando, W. In *Reviews on Heteroatom Chemistry*; Oae, S. Ed.; Myu: Tokyo, 1991; Vol. 5, p 180.

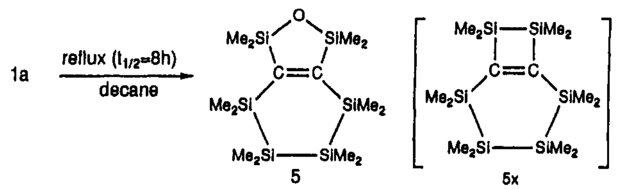
[8] Spectroscopic data are as follows for **4a**: ^1H NMR ($CDCl_3$, 500 MHz) δ 0.17 (s, 24 H), 0.24 (s, 24 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –6.0 (q), –1.7 (q), 115.6 (s); ^{29}Si NMR ($CDCl_3$, 17.6 MHz) δ –44.0, –36.5; MS (EI, 70 eV) *m/e* 497 (M^+ – Me); IR (neat) ν 2122 cm^{-1} (C≡C).

[9] NMR and UV spectra for **1a** are mentioned in Table I: IR (neat, ν) 2082 cm^{-1} (C≡C); LRMS (EI, 70 eV) *m/e* 256 (M^+), 241 (base), 183, 73; HRMS (EI, 20 eV) *m/e* calcd for $C_{10}H_{24}Si_4$ 256.0921, found 256.0938.

[10] NMR and UV spectra for **1b** are mentioned in Table I: IR (neat) 2076 cm^{-1} (C≡C); LRMS (EI, 70 eV) *m/e* 368 (M^+), 339 (base), 311, 283; HRMS (EI, 20 eV) *m/e* calcd for $C_{18}H_{40}Si_4$ 368.2207, found 368.2210.

[11] Data are as follows for **5**: mp 48–49 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{14}H_{36}Si_6O$ 388.1382, found 388.1416; LRMS (EI, 70 eV) *m/e* 388 (M^+), 373 (M^+ – Me), 315 (M^+ – $SiMe_3$); ^1H NMR (C_6D_6, 90 MHz) δ 0.24 (s, 12 H), 0.34 (s, 12 H), 0.37 (s, 12 H); ^{13}C NMR (C_6D_6, 125 MHz) δ –6.4 (q), –0.18 (q), 2.5 (q), 189.8 (s); ^{29}Si NMR ($CDCl_3$, 17.6 MHz) δ –53.8, –32.0, 17.8; IR (hexane) ν 1060 cm^{-1} (Si—O—Si); UV (hexane) λ_{max} (ε) 226 (8160), 272 (360), 338 nm (450). See the supplementary material for the X-ray structural determination of **5**.

[12] Atwell, W. H.; Uhlmann, J. G. *J. Organomet. Chem.* **1973**, *52*, C21.



bonyl complex 6 was formed in 21% yield.[13] Reaction of 1a with 2,3-dimethyl-1,3-butadiene in hexane smoothly proceeded via a Diels–Alder reaction to give the cycloadduct 7[14] and its oxidized compound 8[15] in 29% and 19% yields, respectively. Compound 8 must have been formed by air oxidation of 7 during the purification (silica gel chromatography) of the products, since the isolated 7 was slowly converted to 8 in benzene-d_6 solution in the presence of air. However, no reaction with 1,3-diphenylisobenzofuran occurred even in refluxing hexane, probably because of steric repulsion of the phenyl groups of the isobenzofuran and the methyl substituents of **1a**. Tetrasilacyclohexyne **1a** also reacted smoothly with phenyl azide and diphenyldiazomethane at room temperature and afforded the triazole derivative **9**[16] and tetrasilacyclopentylallene derivative **11**[17] in quantitative yields, respectively. These addition reactions are uniquely characteristic of tetrasilacyclohexyne **1a**, since pentasilacycloheptyne **3** did not react with phenyl azide under the same conditions. Finally, the triazole derivative **9** was easily converted to ketenimine **10**[18] by heating and was obtained in quantitative yield.

While this work was in the process of submission, a paper on the synthesis of tetrasilacyclohexyne by the group of T. Barton was accepted for publication in *J. Am. Chem. Soc.*

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Area of Molecular Design by Heteroatom (No. 03214101) and for General Scientific Research (No. 1430006) from the Ministry of Education, Science, and Culture of Japan. We thank Shin-Etsu Chemical Co. Ltd. for a gift of organosilicon reagents.

Registry No. **1a**, 138542-16-2; **2**, 129415-87-8; **3**, 129415-88-9; **4a**, 138542-17-3; **5**, 138542-18-4; **6**, 138542-22-0; **7**, 138542-19-5; 8, 138542-20-8; **9**, 138542-21-9; **10**, 138570-96-4; **11**, 138570-97-5; Cl(SiMe$_2$)Cl, 754-75-6; Cl(SiEt$_2$)Cl, 87434-43-3; BrMgC≡CMgBr, 4301-15-9; Co$_2$(CO)$_8$, 10210-68-1; 2,3-dimethyl-1,3-butadiene, 513-81-5; phenyl azide, 622-37-7; diphenyldiazomethane, 883-40-9; 1,3-diphenylisobenzofuran, 5471-63-6.

Supplementary Material Available: Text giving details of the data collection and structure solution and refinement, tables of bond lengths and angles, crystallographic data, and thermal and positional parameters by X-ray analysis, and figures showing the structure of 5 (17 pages); a listing of *h*, *k*, *l*, F_o, F_c, and $d(F_o)$ (11 pages). Ordering information is given on any current masthead page.

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(13) Data are as follows for 6: decomposition at 114–116 °C; red-black crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{24}O_6Si_4Co_2$ 541.9314, found 541.9355; LRMS (EI, 70 eV) *m/e* 542 (M^+), 514 ($M^+ - CO$), 486 ($M^+ - 2CO$), 458 ($M^+ - 3CO$), 430 ($M^+ - 4CO$), 402 ($M^+ - 5CO$), 374 ($M^+ - 6CO$); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.20 (s, 12 H), 0.35 (s, 12 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ –6.5 (q), –0.02 (q), 94.8 (s), 200.9 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –44.5, –11.3; IR (KBr) ν 2086, 2046, 2020 cm^{-1} (CO); UV (hexane) λ_{max} (ϵ) 260 (sh) (11 500), 359 (1750), 425 (sh) (100), 450 (sh) nm (90).

(14) Data are as follows for 7: mp 54–56 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{34}Si_4$ 338.1738, found 338.1740; LRMS (EI, 70 eV) *m/e* 338 (M^+), 265 ($M^+ - SiMe_3$); ^1H NMR (C_6D_6, 90 MHz) δ 0.34 (s, 24 H), 1.70 (s, 6 H), 2.87 (s, 4 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ –6.2 (q), –1.8 (q), 18.7 (t), 39.1 (q), 123.7 (s), 147.3 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –52.3, –26.2; IR (KBr) ν 2892, 1243, 806 cm^{-1}.

(15) Data are as follows for 8: mp 94–96 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{32}Si_4$ 336.1581, found 336.1575; LRMS (EI, 70 eV) *m/e* 336 (M^+), 263 ($M^+ - SiMe_3$); ^1H NMR (C_6D_6, 90 MHz) δ 0.32 (s, 12 H), 0.54 (s, 12 H), 2.18 (s, 6 H), 7.59 (s, 2 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 6.3 (q), –0.32 (q), 19.9 (q), 128.0 (s), 136.6 (s), 136.8 (d); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –53.0, –23.8; IR (KBr) ν 2950, 2892, 1243, 1131, 806 cm^{-1}.

(16) Data are as follows for 9: mp 112–114 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{29}Si_4N_3$ 375.1439, found 375.1408; LRMS (EI, 70 eV) *m/e* 375 (M^+), 347 ($M^+ - N_2$), 332 ($M^+ - N_2 - Me$); ^1H NMR (C_6D_6, 500 MHz) δ 0.09 (s, 6 H), 0.22 (s, 6 H), 0.34 (s, 6 H), 0.76 (s, 6 H), 7.0–7.1 (m, 3 H), 7.18 (d, J = 9.5 Hz, 2 H); ^{13}C NMR (C_6D_6, 125 MHz) δ –6.7 (q), –6.6 (q), –1.6 (q), –1.3 (q), 127.6 (d), 129.3 (d), 129.7 (d), 140.4 (s), 140.7 (s), 153.2 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –50.9, –48.1, –27.4, –26.8; IR (KBr) ν 2956, 2896, 1601, 1499, 1251, 816, 768 cm^{-1}.

(17) Data are as follows for **11**: mp 101–103 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{23}H_{34}Si_4$ 422.1738, found 422.1774; LRMS (EI, 70 eV) *m/e* 422 (M^+), 407 ($M^+ - Me$), 349 ($M^+ - SiMe_3$); ^1H NMR (C_6D_6, 500 MHz) δ 0.29 (s, 12 H), 0.40 (s, 12 H), 7.1–7.3 (m, 6 H), 7.61 (d, J = 8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ –7.1 (q), –2.1 (q), 92.7 (s), 96.7 (s), 125.5 (d), 127.5 (d), 128.2 (d), 138.0 (s), 206.3 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –44.9, –12.2; IR (KBr) ν 1897 cm^{-1} (C=C=C); UV (hexane) λ_{max} (ϵ) 277 (16 480), 325 nm (sh) (400).

(18) Data are as follows for **10**: colorless oil; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{29}Si_4N$ 347.1377, found 347.1372; LRMS (EI, 70 eV) *m/e* 347 (M^+), 332 ($M^+ - Me$); ^1H NMR (C_6D_6, 500 MHz) δ 0.29 (s, 12 H), 0.42 (s, 12 H), 6.9–7.1 (m, 3 H), 7.42 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (C_6D_6, 125 MHz) δ –6.7 (q), –0.50 (q), 95.8 (s), 123.8 (d), 126.1 (d), 130.1 (d), 143.6 (d), 171.6 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ –44.5, –7.4; IR (neat) ν 1997, 1968 cm^{-1} (C=C=N).

Synthesis and Structural Characterization of a Tetranuclear Organolanthanide Hydrazido Complex

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Received December 16, 1991

Summary: Reaction of Cp*$_2$Sm (Cp* = η^5-C$_5$Me$_5$) with excess hydrazine leads to the formation of a yellow crystalline material in high yield. The product was structurally characterized by a single-crystal diffraction study which shows the molecule to consist of a distorted-tetrahedron arrangement of samarium atoms with bridging hydrazido anions on each edge of the tetrahedron.

Metal complexes containing hydrazido (NHNH$_2^-$) units have been considered to play an important role in the reduction of dinitrogen to hydrazine[1] (eq 1); however, few

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