

Unusual Reactivities of Linear Disilanes with *o*-Carboranyl Unit

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The linear disilanes 1,2-bis(1'-R-*o*-carboranyl)-1,1,2,2-tetramethyl-1,2-disilane (R = H (**2a**), Me (**2b**), Ph (**2c**)) were prepared by reacting the lithium salt of 1-R-*o*-carborane (**1**) with 1,2-dichlorotetramethyldisilane. These linear disilanes (**2**) were found to be useful precursors for the synthesis of a variety of cyclic compounds. For instance, reaction of the linear dilithiodisilane **2a** with 1,2-dichlorotetramethyldisilane afforded the four-membered cyclic compound 3,4-*o*-carboranylene-1,1,2,2-tetramethyl-1,2-disilacyclobutane (**3**). Further, whereas the reaction of linear disilane (**2a**) with Pt(PET₃)₃ was found to yield the cyclic bis(silyl)-platinum complex **4**, the reaction of the methyl-*o*-carboranyl-substituted disilane **2b** with Pt(PET₃)₃ under the same conditions yielded the decomposed bis(silyl)platinum complex **5**, formed via oxidative addition of a Si–Si bond at the platinum atom. The reaction of the cyclic disilane **3** using a catalytic amount of lithium metal afforded a five-membered cyclic trisilyl compound (**6**). The reaction of **6** with phenylacetylene in the presence of a catalytic amount of Pd(CNBU)₂ was found to yield the seven-membered trisilyl ring compound 6,7-*o*-carboranylene-1,1,4,4,5,5-hexamethyl-2-phenyl-1,4,5-trisilacyclohept-2-ene (**7**). The structures of compounds **2a,b**, **4–6**, and **7** were determined using single-crystal X-ray crystallography.

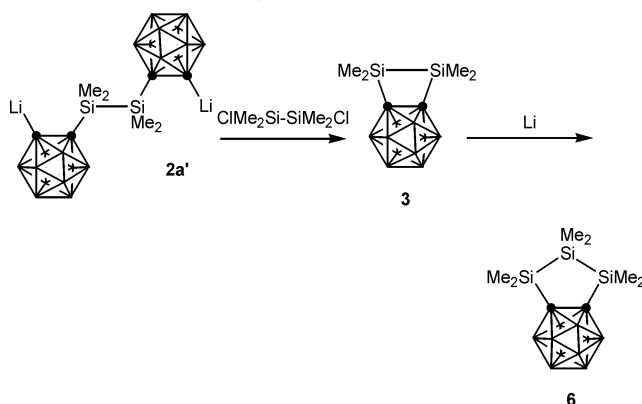
Introduction

The synthesis and study of organometallic complexes possessing an ancillary silyl-*o*-carboranyl ligand have continued to receive attention.¹ In particular, our interest in the reactivity of silyl-*o*-carborane has led us to explore the use of silyl-*o*-carboranyl ligands in the formation of unusual ring complexes. In this respect, we have started investigating the reactivity of linear disilanes bearing a bulky *o*-carboranyl unit, which might confer some additional reactivity on the silicon–silicon bond. Using suitable linear disilanes (**2**), it has been possible for us to show that the bulkiness of the *o*-carboranyl group in these disilyl compounds plays an important role in Si–Si activation, producing di- and trisilane (**3**, **6**) (Scheme 1).

Results and Discussion

Preparation of the Linear Disilanes 1,2-Bis(1'-R-*o*-carboranyl)-1,1,2,2-tetramethyl-1,2-disilane (R = H (2a**), Me (**2b**), Ph (**2c**)).** The bis(*o*-carboranyl)disilanes **2** were readily prepared from dichlorodisilane with 2 equiv of the monolithiated *o*-carboranes **1**. The monolithiated *o*-carboranes 2-Li-1-R-C₂B₁₀H₁₁ (R = H (**1a**), Me (**1b**), Ph (**1c**)), generated by the reaction

Scheme 1. Sequential Transformation of Linear Disilane **2a to the Cyclic Di- and Trisilanes **3** and **6****



of *n*-BuLi with 1-R-C₂B₁₀H₁₂, were reacted with (SiMe₂Cl)₂ to give **2** in 91–96% yield (Scheme 2).

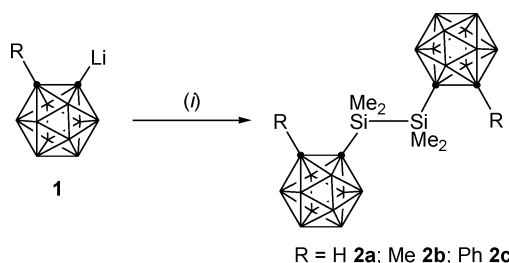
The colorless products **2** were crystalline solids that were relatively stable in air and during brief heating to 110–120 °C. Compounds **2** were readily soluble in hexane, toluene, and THF. The structures of **2a,b** were unambiguously established using single-crystal X-ray analysis and are shown in Figures 1 and 2. The four C(1), C(1)*, Si(1), and Si(1)* atoms comprising the central skeleton of the molecule are nearly coplanar. The C(1)–Si(1) bond lengths (1.933(2)–1.943(3) Å) are slightly longer than the typical values for carbon–silicon bonds (1.88–1.91 Å) and are comparable to those of the cyclic 1,2-bis(*o*-carboranyl)-1,1,2,2-tetramethyl-1,2-disi-

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(1) Review: (a) Kang, S. O.; Ko, J. *Adv. Organomet. Chem.* **2001**, 47, 66. (b) Kang, S. O.; Lee, J.; Ko, J. *Coord. Chem. Rev.* **2002**, 231, 47.

Scheme 2. Synthesis of Linear Disilanes 2^a

^a Conditions: (i) $\frac{1}{2}$ (SiMe₂Cl)₂, THF, -78 °C.

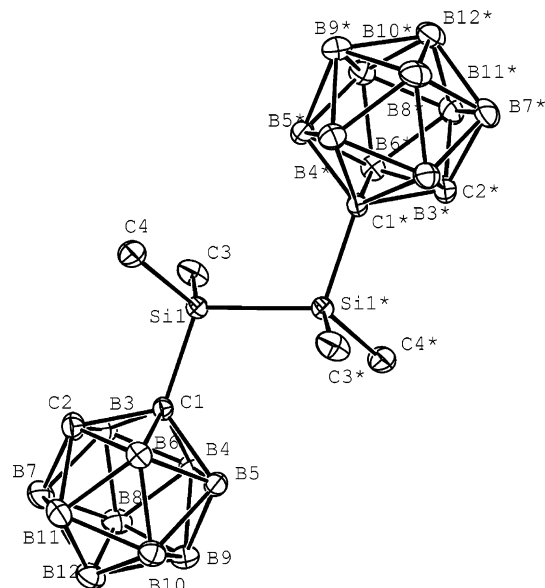


Figure 1. Molecular structure of **2a** with thermal ellipsoids drawn at the 30% level.

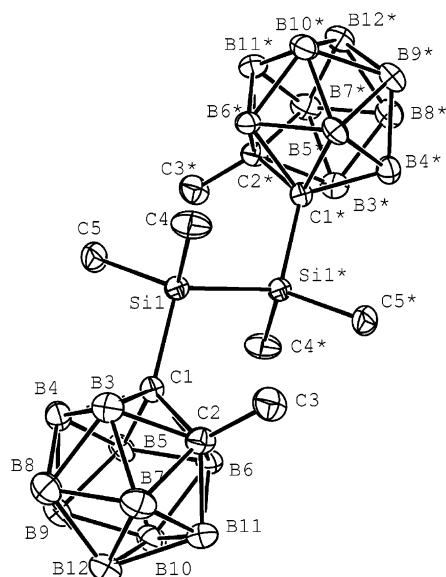
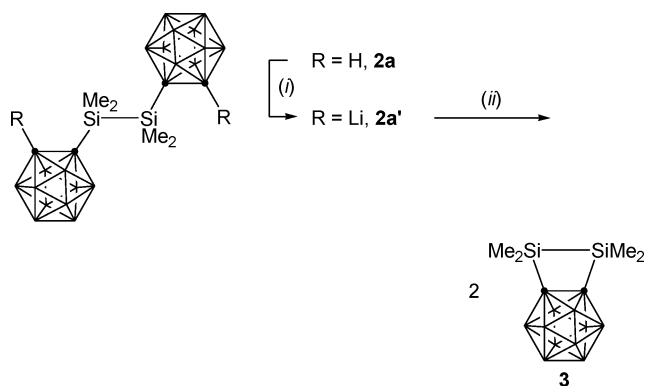


Figure 2. Molecular structure of **2b** with thermal ellipsoids drawn at the 30% level.

lanes.² The Si(1)–Si(1)* bond lengths (2.365(1)–2.386(1) Å) are within the range of values of Si–Si bond lengths found in analogous complexes.³ The ¹H, ¹³C, and ²⁹Si NMR spectra and mass spectra of **2** were found to

Scheme 3. Formation of Cyclic Disilanes 3^a

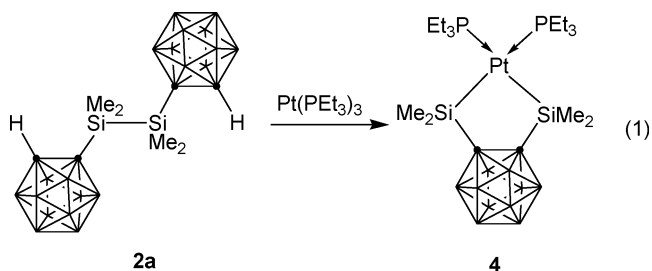
^a Conditions: (i) 2 *n*-BuLi, THF, -78 °C; (ii) (SiMe₂Cl)₂, THF, -78 °C.

be consistent with the structures determined using X-ray crystallography.

Reaction of 2a with 1,2-Dichlorotetramethyl-disilane. When the dilithium salt of **2a** was reacted with dichlorodisilane, the cyclic disilane **3** was produced in 78% yield (Scheme 3).

Initially, we attempted to promote the substitution reaction of dichlorodisilane with linear dilithiodisilane **2a** in order to generate the eight-membered tetrasilane, but no such reaction occurred, probably due to the steric bulkiness of the *o*-carboranyl substituent. After many attempts, we found that the linear disilane **2a** can be used in a reaction with an Si–Cl bond of dichlorodisilane to form the cyclic disilane **3**, without any cleavage of the Si–C(*o*-carborane) bond. Compound **3** was purified by low-temperature recrystallization from toluene as colorless crystals. The ¹H, ¹³C, and ²⁹Si NMR spectra of **3** were found to be identical with those of an authentic sample.²

Reaction of the Linear Bis(*o*-carboranyl)disilane 2a with Pt(PET₃)₃. Linear disilanes with bulky ancillary *o*-carboranyl units have also been used in chemical transformations, such as Si–Si bond activations with transition metals. Initially, we attempted the double-silylation reaction of linear bis(*o*-carboranyl)disilane **2a** and acetylenes in the presence of a catalytic amount of Pt(PET₃)₃ at 60–80 °C. However, after careful workup, the product was found to be a cyclic bis(silyl)platinum complex rather than a double-silylated product; when a mixture of Pt(PET₃)₃ (0.05 mmol) and bis(*o*-carboranyl)disilane **2a** (0.07 mmol) was heated in a sealed NMR tube (80 °C, 6 h), the solution changed slowly from orange to yellow (eq 1).



(2) De Rege, F. M.; Kassebaum, J. D.; Scott, B. L.; Abney, K. D.; Balaich, G. J. *Inorg. Chem.* **1999**, *38*, 486.

(3) (a) Söldner, M.; Šandor, M.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1671. (b) Söldner, M.; Schier, A.; Schmidbaur, H. *J. Organomet. Chem.* **1996**, *521*, 259.

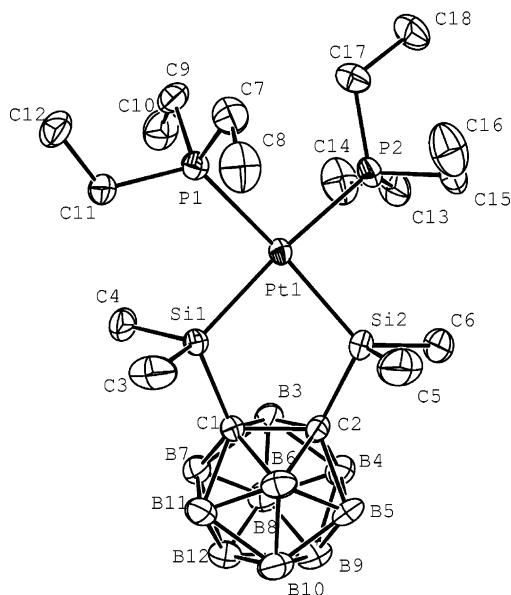


Figure 3. Molecular structure of **4** with thermal ellipsoids drawn at the 30% level.

An initial indication of the formulation of **4** was obtained from the observation of a parent ion in the mass spectrum at m/z 691. The ^{31}P NMR signal was shifted from -42.0 ppm for $\text{Pt}(\text{PET}_3)_3$ to 18.4 ppm. The structure of **4** was unambiguously established using single-crystal X-ray analysis and is shown in Figure 3. Complex **4** has a slightly distorted square-planar geometry. The five Si, P, and Pt atoms comprising the central skeleton of the molecule are all nearly coplanar, with a dihedral angle of $18.02(7)^\circ$ between the two planes defined by Si(1), Pt(1), Si(2) and P(1), Pt(1), P(2). The observed Pt–Si bond lengths ($2.354(2)$, $2.362(2)$ Å) are within the range of values of Pt–Si bond lengths found in analogous complexes.⁴

The formation of the cyclic bis(silyl)platinum complex (**4**) is unexpected and may involve the initial formation of **3** followed by the oxidative addition of a strained Si–Si bond. In an attempt to extend our understanding of this oxidative addition process, we attempted to carry out the analogous reactions of $\text{Pt}(\text{PET}_3)_3$ with linear disilanes such as methyl- (**2b**) and phenyl-*o*-carboranyl (**2c**) derivatives, but these disilanes did not react under the same experimental conditions. However, a trace amount of decomposed product **5** was observed in the case of **2b** (eq 2) on extended heating in a refluxing

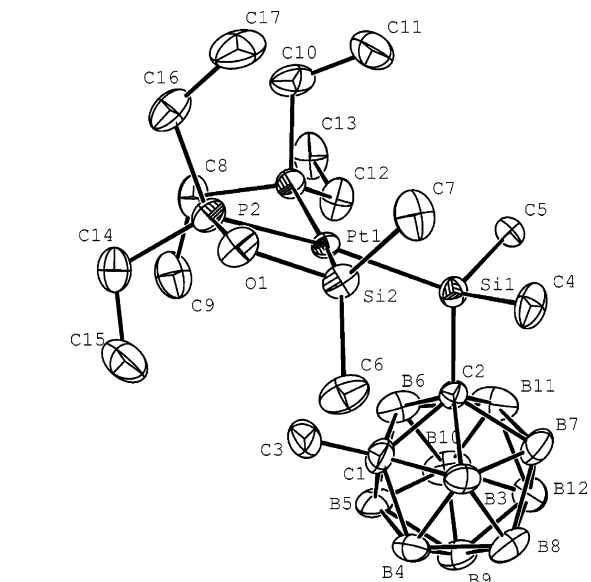
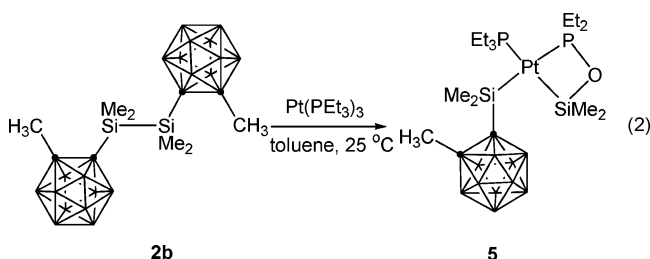
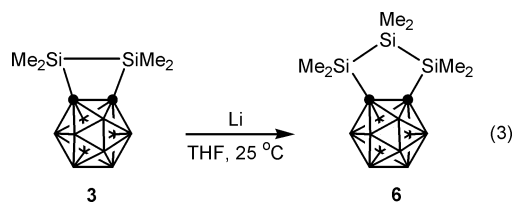


Figure 4. Molecular structure of **5** with thermal ellipsoids drawn at the 30% level.

involving the ethyl moiety of the phosphine group and the *o*-carboranyl unit of the dimethylsilyl group.

Synthesis of 4,5-*o*-Carboranylene-1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclopentane (6). Of particular interest is the reaction of disilacyclobutane with lithium reagents in a polar solvent (eq 3), since a reactive silyllithium species might be involved in the transformation of trisilacyclopentane. Indeed, when lithium was



used as the reagent, treatment of the reaction mixture with **3** produced the trisilane **6** (46%). The reaction of lithium with the disilacyclobutane did not stop after the Si–Si cleavage; an intermolecular addition of the silyllithium species to the *o*-carboranysilyl group followed. The addition of metal silyl reagents to disilane systems is a known reaction;⁵ therefore, this closure to a five-membered ring is not surprising.

The colorless product **6** is a crystalline solid that is relatively stable in air and during brief heating to 110 – 120 °C. The structure of **6** was unambiguously estab-

toluene solution (Figure 4). The formation of **5** is probably due to traces of oxygen in the reacting system. However, another experiment showed that **5** is probably not formed from the disilane **2b**. A possible explanation for the formation of **5** is the oxidation of the phosphorus and silicon atoms, followed by an elimination reaction

(4) Recent articles on silylplatinum complexes: (a) Ozawa, F.; Hikida, T. *Organometallics* **1996**, *15*, 4501. (b) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894. (c) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108. (d) Levy, C. J.; Puddephatt, R. J.; Vittal, J. J. *Organometallics* **1994**, *13*, 1559. (e) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844. (f) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1993**, *12*, 988. (g) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373. (h) Braunstein, P.; Knorr, M.; Hirle, B.; Reinhard, G.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1583. (i) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1. (j) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (k) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (l) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333. (m) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.

(5) (a) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *J. Organomet. Chem.* **2000**, *611*, 420. (b) Naka, A.; Hayashi, M.; Okazaki, S.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994.

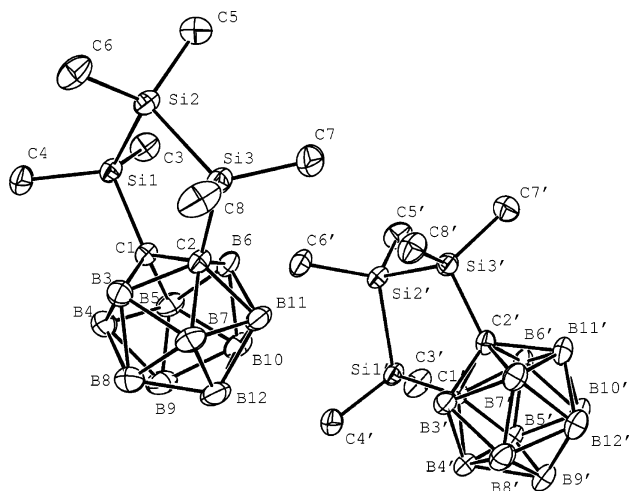


Figure 5. Molecular structure of **6** with thermal ellipsoids drawn at the 30% level.

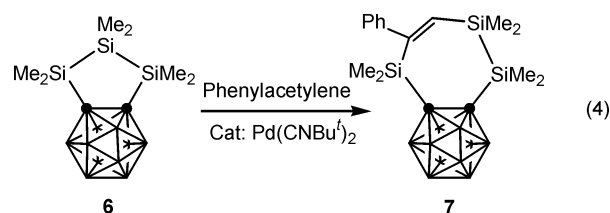
lished using single-crystal X-ray analysis and is shown in Figure 5. The five C(1), C(2), Si(1), Si(2), and Si(3) atoms comprising the central skeleton of the molecule are nearly coplanar. The C(1)–Si(1) and C(2)–Si(3) bond lengths (1.917(4)–1.930(4) Å) are slightly longer than the typical values for the carbon–silicon bonds (1.88–1.91 Å)⁶ and are comparable to those in **3** (R = Me (**a**),² Et (**b**)⁷). The Si(1)–Si(2) and Si(2)–Si(3) bond lengths (2.336(2)–2.341(2) Å) are within the range of values of Si–Si bond lengths found in analogous compounds.⁸ The ¹H, ¹³C, and ²⁹Si NMR spectra and the elemental analysis of **6** were found to be consistent with the structure determined using X-ray crystallography. Similar results were observed in the thermolysis of the four-membered phenylene disilacycle,^{5b} digermacycle,⁹ and distannacycle.¹⁰

Although the cyclic disilane analogue **3'** has been used extensively in double-silylation reactions,¹¹ many variants of this compound remain virtually unexplored. Variants from the series of cyclic trisilanes 4,5-benzo-1,1,2,2,3,3-hexaalkyl-1,2,3-trisilacyclopent-4-ene (**6'**) have only been identified by Ishikawa (alkyl = Et)^{5b} and Tanaka (alkyl = Me).¹² However, the yields obtained in their thermolysis reactions are too low. To advance the understanding of such compounds, a methodology is needed for synthesizing cyclic trisilane precursors with high efficiency and under mild conditions. We feel that the *o*-carboranyl substituent is very useful for the promotion of the formation of cyclic five-membered trisilyl species.

To obtain a better understanding of the results of the present experiments, computational analyses of benzo-

(disilacyclobutane) (**3'**) and benzo(trisilacyclopentane) (**6'**) and their *o*-carboranyl analogues (**3** and **6**) were carried out using the DFT method.^{13,14} These di- and trisilacycloalkanes are nearly planar molecules (Figure 6). In these structures, the observed Si–Si distances of 2.381–2.405 Å and Si–C distances of 1.951 Å are as expected, because the atomic radii (r_{cov}) of Si and C are 1.18 and 0.77 Å, respectively.¹⁵ Our computational results are consistent with the results from X-ray structural studies of **3** and **6**. As shown in Figure 6, the trisilacyclopentanes **6'** and **6** are lower in energy than their disilacyclobutane counterparts **3'** and **3**. In addition, the *o*-carboranyl trisilacyclopentane **6** appears to have the lower energy state; thus, the *o*-carboranyl disilacyclobutane **3** is expected to be easily converted into the corresponding cyclic trisilane **6**. This computational result is qualitatively consistent with the experimental observation that the *o*-carboranyl trisilacyclopentane **6** is readily prepared.

Reaction of 6 with Phenylacetylene. Because of the stability of the 1,2,3-trisilacyclopentane ring, the structure of **6** might have a damping effect on the usual reactivity of the Si₃C₂ ring. Nevertheless, we hoped that, as in the cases of 1,2-disilacyclobutanes **3'** and **3**, the cyclic trisilane **6** would be a very reactive system. Accordingly, we embarked upon a study of the reactivity of **6**. One of the interesting reactions of the Si–Si bond of the more reactive disilanes is the transition-metal-catalyzed insertion of unsaturated hydrocarbons. Equation 4 suggests that such a reaction occurs for **6** with



phenylacetylene in the presence of a catalytic amount of Pd(CNBU)₂. The palladium-catalyzed reaction of **6** with phenylacetylene afforded 6,7-*o*-carboranyl-ene-1,1,4,4,5,5-hexamethyl-2-phenyl-1,4,5-trisilacyclohept-2-ene (**7**) in 80% yield as the sole product.

To obtain structural information for the newly prepared compound, a single-crystal X-ray diffraction study of the phenylacetylene insertion product **7** was undertaken (Figure 7). The X-ray crystal structure of **7** confirmed the presence of a seven-membered ring comprised of *o*-carborane, three silicon atoms, and an unsaturated hydrocarbon fragment containing a C=C bond. The C=C bond length (1.342(3) Å) is slightly longer than the typical value for the carbon–carbon double bond (1.317 Å)¹⁶ and is comparable to that of the six-membered-ring product formed in the reaction between phenylacetylene and **3** (1.355(4) Å).⁶

In summary, we have prepared a series of linear disilanes (**2**). These linear disilanes readily undergo a Si–Si activation reaction with suitable metals to afford

(6) Song, K. H.; Jung, I.; Lee, S. S.; Park, K.-M.; Ishikawa, M.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 5537.

(7) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401.

(8) (a) Sita, L. R.; Lyon, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 10374.

(b) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566.

(9) Komoriya, H.; Kako, M.; Nakadaira, Y. *Organometallics* **1996**, *15*, 2014.

(10) Lee, C.; Lee, J.; Lee, S. W.; Kang, S. O.; Ko, J. *Inorg. Chem.* **2002**, *41*, 3084.

(11) (a) Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101. (b) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35. (c) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawachi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114.

(12) Uchimara, Y.; Tanaka, M. *J. Organomet. Chem.* **1996**, *521*, 335.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(15) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; HarperCollins College: New York, 1993.

(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, 51.

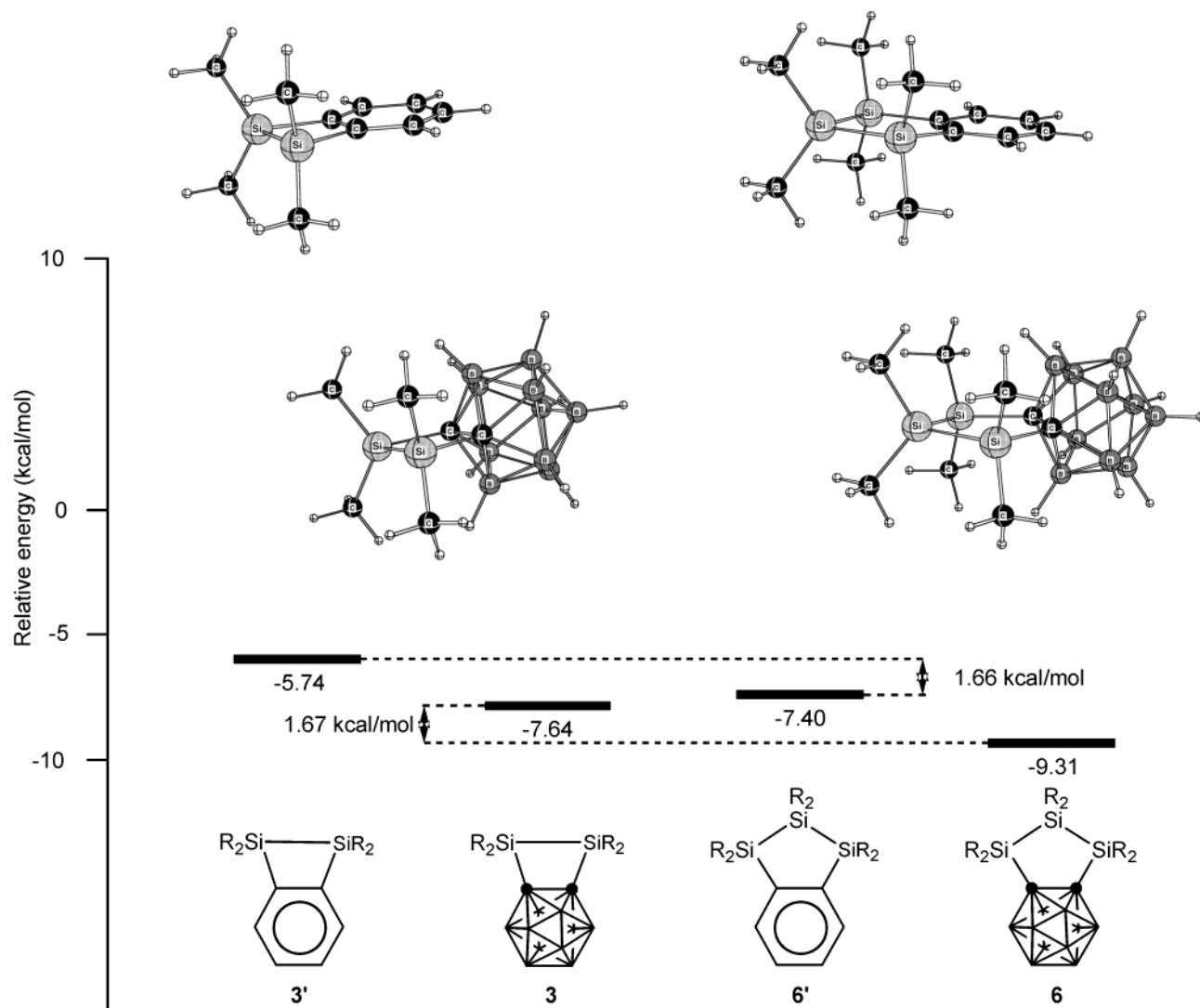


Figure 6. Energy profiles of **3'**, **3**, **6'**, and **6**.

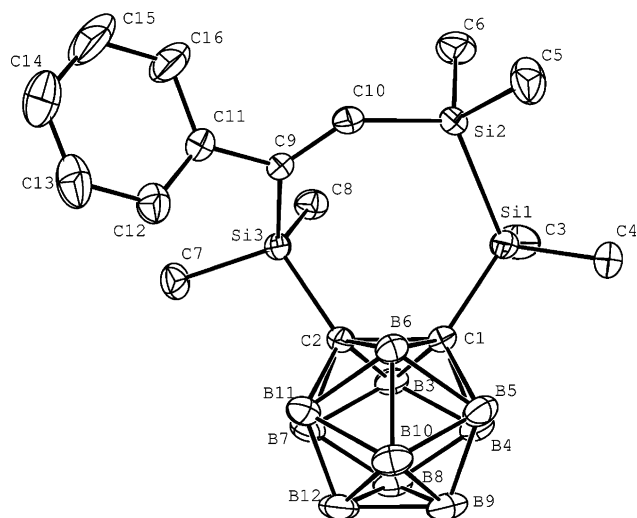


Figure 7. Molecular structure of **7** with thermal ellipsoids drawn at the 30% level.

new classes of cyclic di- and trisilanes (**3**–**7**). We have shown that the *o*-carboranyl unit is an excellent substituent, because this unit stabilizes reactive intermediates and is stable enough to be handled without any

special precautions. We have further exploited this potential in a series of novel chemical transformations. We now describe (i) the synthesis of the series of linear disilanes **2**, (ii) the facile conversion of the linear disilane **2a** to the cyclic disilane **3**, (iii) the isolation of the bis-(disilyl)platinum complex **4** by the oxidative addition reaction of linear disilane **2a**, (iv) the efficient synthesis of the cyclic trisilane **6** from cyclic disilane **3**, and (v) the double-silylation reaction of **6** with phenylacetylene in the presence of palladium catalyst.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. Diethyl ether, toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH_2 . Benzene- d_6 was distilled under nitrogen from sodium and stored in a Schlenk storage flask until needed. CDCl_3 was predried under CaH_2 and vacuum-transferred. *n*-BuLi (1.6 M in hexanes) and 1,2-dichlorotetramethyldisilane were used as received from Aldrich. *o*-Carborane was purchased from KATCHEM Ltd. and used without purification. $\text{Pt}(\text{PET}_3)_3$ ¹⁷ and $\text{Pt}(\text{CNBu})_2$ ¹⁸ were prepared according to the literature procedures. All ^1H (300.1

Table 1. NMR Spectroscopic Data for Compounds 2, 4, 6, and 7

compd	NMR (δ)		
	^1H	^{13}C	^{29}Si
2a ^a	0.46 (s, 12H, SiMe ₂) 3.38 (s, 1H, C _{cab} H)	-1.35 (SiMe ₂) 60.16, 65.11 (C(cab))	-3.29
2b ^a	0.61 (s, 12H, SiMe ₂) 2.01 (s, 6H, C(cab)CH ₃)	0.76 (SiMe ₂) 26.14 (C(cab)CH ₃) 71.40 (C(cab))	-9.63
2c ^a	-0.06 (s, 12H, SiMe ₂) 7.30-7.62 (10H, C(cab)Ph)	-1.79 (SiMe ₂) 86.42 (C(cab)) 128.56, 129.26, 131.24, 132.84 (C(cab)Ph)	-6.84
4 ^a	0.33 (s, 12H, SiMe ₂ , $^3J_{\text{Pt-H}} = 18$ Hz) 1.04 (q, 18H, PCH ₂ Me) 1.90 (q, 12H, PCH ₂ Me)	-0.01 (SiMe ₂) 8.62 (d, PCH ₂ Me, $^2J_{\text{Pt-C}} = 105$ Hz) 19.46 (PCH ₂ Me)	38.40 (dd, $^2J_{\text{Pt-Si}} = 1285$ Hz, $^2J_{\text{P-Si(trans)}} = 132$ Hz, $^2J_{\text{P-Si(cis)}} = 10$ Hz)
6 ^b	-0.11 (s, 6H, Si(cent)Me ₂) 0.05 (s, 12H, Si(cab)Me ₂)	-7.52 (Si(cent)Me ₂) -2.65 (Si(cab)Me ₂)	-42.22 (Si(cent)Me ₂) -0.70 (Si(cab)Me ₂)
7 ^a	0.28, 0.34, 0.43 (s, 18H, SiMe ₂) 6.72 (s, 1H, C=C _H) 7.05-7.33 (5H, C=C _{Ph})	-0.86, 1.66, 2.89 (SiMe ₂) 126.53, 126.75, 128.32, 151.35 (C=C _{Ph}) 147.73, 159.85 (C=C)	-25.88, -4.75, 0.36 (SiMe ₂)

^a CDCl₃ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent. ^b C₆D₆ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent.

Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 2a,b and 4-7

	2a	2b	4	5	6	7
formula	B ₁₀ C ₄ H ₁₇ Si	B ₁₀ C ₅ H ₁₉ Si	B ₁₀ C ₁₈ H ₅₂ Si ₂ P ₂ Pt	B ₁₀ C ₁₇ H ₅₀ OSi ₂ P ₂ Pt	B ₂₀ C ₁₆ H ₅₆ Si ₆	B ₁₀ C ₁₆ H ₃₄ Si ₃
fw	201.37	215.39	689.91	691.88	633.35	418.80
cryst class	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P2</i> ₁ / <i>c</i>
<i>Z</i>	4	4	4	4	2	4
cell constants						
<i>a</i> , Å	7.0029(6)	8.1440(6)	16.052(2)	8.7323(2)	9.452(2)	10.5643(6)
<i>b</i> , Å	15.1842(9)	12.5958(6)	12.059(9)	19.005(4)	13.841(8)	12.8852(7)
<i>c</i> , Å	11.5040(8)	13.4148(9)	16.648 (1)	19.217(4)	16.754(1)	19.510(1)
α , deg					100.523(5)	
β , deg	91.296(6)	106.940(6)	90.512(8)	94.23(3)	105.372(9)	105.056(1)
γ , deg					106.040(8)	
<i>V</i> , Å ³	1223.0(2)	1316.4(2)	3222.5(5)	3180.6(1)	1952.1(4)	2564.6(2)
μ , mm ⁻¹	0.094	0.135	4.536	4.599	0.227	0.187
cryst size, mm	0.3 × 0.35 × 0.4	0.4 × 0.4 × 0.4	0.35 × 0.35 × 0.40	0.3 × 0.3 × 0.4	0.4 × 0.4 × 0.5	0.2 × 0.2 × 0.25
<i>d</i> _{calcd} , g/cm ³	1.094	1.087	1.422	1.445	1.077	1.085
<i>F</i> (000)	420	452	1384	1384	672	888
radiation			Mo K α ($\lambda = 0.7107$)			
θ range, deg	2.22-24.97	2.27-25.97	1.27-25.97	1.51-25.97	1.31-25.97	1.91-28.32
<i>h</i> , <i>k</i> , <i>l</i> collected	+8, +18, ± 13	+10, +15, ± 16	+19, +14, ± 20	+10, +23, ± 23	+11, +17, ± 20	± 14 , ± 17 , ± 25
no. of rflns measd	2328	2768	6586	6701	8178	18 488
no. of unique rflns	2145	2583	6318	6240	7649	6349
no. of rflns used in refinement	1570	1618	4306	3770	5002	3615
(<i>I</i> > 2 σ (<i>I</i>))						
no. of params	149	158	318	318	411	278
R1 ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0453	0.0518	0.0358	0.0464	0.0746	0.0491
wR2 ^a (all data)	0.1300	0.1447	0.0777	0.1129	0.2000	0.1539
GOF	1.032	1.006	1.037	0.889	1.177	1.000

^a R1 = $\sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma(F_o^2)$). ^b wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma(F_o^2)$).

MHz), ^{13}C (75.4 MHz), ^{31}P (121.4 MHz), and ^{29}Si (59.60 MHz) NMR spectra were recorded on a Varian Mercury-300BB spectrometer unless otherwise stated. High-resolution mass spectra were measured at the Korea Basic Science Institute. The NMR data for complexes **2**, **4**, **6**, and **7** are given in Table 1. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer.

Synthesis of the Linear Disilane 1,2-Bis(1'-R-*o*-carboranyl)-1,1,2,2-tetramethyl-1,2-disilane (R = H (2a**), Me (**2b**), Ph (**2c**)).** A representative procedure is as follows: to a

solution of 1.44 g (10.0 mmol) of *o*-carborane in 40 mL of THF, precooled to -78 °C, was added 6.30 mL of *n*-butyllithium (1.6 M in hexanes). The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was transferred, via cannula, to a suspension of 1.0 mL (0.5 equiv) of 1,2-dichlorotetramethyldisilane in 20 mL of Et₂O that was cooled to -78 °C. The resultant yellow mixture was warmed to room temperature and stirred for 2 h. The volatiles were then removed under reduced pressure; the crude mixture was taken up in a minimal amount of Et₂O and filtered through a 1 × 5

(17) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 107.

(18) Sugimoto, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170.

Table 3. Selected Interatomic Distances (Å) for Compounds 2a,b and 4–7

Compound 2a									
Si(1)–Si(1)#1	2.365(1)	Si(1)–C(1)	1.933(2)	Si(1)–C(3)	1.857(3)	Si(1)–C(4)	1.865(3)	C(1)–C(2)	1.670(3)
Compound 2b									
Si(1)–Si(1)#1	2.386(1)	Si(1)–C(1)	1.943(3)	Si(1)–C(4)	1.860(3)	Si(1)–C(5)	1.859(3)	C(1)–C(2)	1.692(4)
C(2)–C(3)	1.512(4)								
Compound 4									
Pt(1)–P(1)	2.378(2)	Pt(1)–P(2)	2.370(2)	Pt(1)–Si(1)	2.354(2)	Pt(1)–Si(2)	2.362(2)	Si(1)–C(1)	1.950(6)
Si(2)–C(2)	1.938(6)	Si(2)–C(5)	1.890(8)	Si(2)–C(6)	1.887(7)	Si(1)–C(3)	1.893(7)	Si(1)–C(4)	1.889(7)
P(2)–C(13)	1.842(7)	P(2)–C(15)	1.820(7)	P(2)–C(17)	1.840(7)	P(1)–C(7)	1.821(7)	P(1)–C(9)	1.855(7)
P(1)–C(11)	1.844(6)	C(7)–C(8)	1.52(1)	C(9)–C(10)	1.51(1)	C(11)–C(12)	1.520(8)	C(13)–C(14)	1.49(1)
C(15)–C(16)	1.51(1)	C(17)–C(18)	1.528(9)						
Compound 5									
Pt(1)–P(1)	2.363(2)	Pt(1)–P(2)	2.324(3)	Pt(1)–Si(1)	2.380(3)	Pt(1)–Si(2)	2.351(3)	P(1)–C(8)	1.82(1)
P(1)–C(10)	1.82(1)	P(1)–C(12)	1.83(1)	P(2)–O(1)	1.605(7)	P(2)–C(14)	1.80(1)	P(2)–C(16)	1.81(1)
Si(1)–C(2)	2.00(1)	Si(1)–C(4)	1.88(1)	Si(1)–C(5)	1.87(1)	Si(2)–O(1)	1.738(7)	Si(2)–C(6)	1.86(1)
C(16)–C(17)	1.52(2)	Si(2)–C(7)	1.88(1)	C(1)–C(3)	1.51(2)	C(8)–C(9)	1.51(2)	C(10)–C(11)	1.51(2)
C(12)–C(13)	1.508(2)	C(14)–C(15)	1.51(2)						
Compound 6									
Si(1)–Si(2)	2.341(2)	Si(2)–Si(3)	2.336(2)	Si(1)–C(1)	1.930(4)	Si(3)–C(2)	1.917(4)	Si(1)–C(3)	1.859(4)
Si(1)–C(4)	1.871(4)	Si(2)–C(5)	1.877(4)	Si(2)–C(6)	1.882(4)	Si(3)–C(7)	1.856(5)	Si(3)–C(8)	1.868(5)
C(1)–C(2)	1.727(5)	Si(1')–Si(2')	2.335(2)	Si(2')–Si(3')	2.344(2)	Si(1')–C(1')	1.922(4)	Si(3')–C(2')	1.936(4)
Si(1')–C(3')	1.868(4)	Si(1')–C(4')	1.859(5)	Si(2')–C(5')	1.883(4)	Si(2')–C(6')	1.877(4)	Si(3')–C(7')	1.860(4)
Si(3')–C(8')	1.861(4)	C(1')–C(2')	1.714(5)						
Compound 7									
Si(1)–Si(2)	2.361(1)	Si(1)–C(1)	1.933(2)	C(1)–C(2)	1.685(3)	C(2)–Si(3)	1.928(2)	Si(3)–C(9)	1.885(2)
C(9)–C(10)	1.342(3)	C(10)–Si(2)	1.862(3)	Si(1)–C(3)	1.868(3)	Si(1)–C(4)	1.871(3)	Si(2)–C(5)	1.872(3)
Si(2)–C(6)	1.867(3)	Si(3)–C(7)	1.859(3)	Si(3)–C(8)	1.854(3)	C(9)–C(11)	1.488(3)	C(11)–C(12)	1.377(4)
C(12)–C(13)	1.378(4)	C(13)–C(14)	1.333(6)	C(14)–C(15)	1.360(7)	C(15)–C(16)	1.383(6)	C(16)–C(11)	1.379(4)

Table 4. Selected Interatomic Angles (deg) for Compounds 2a,b and 4–7

Compound 2a							
C(1)–Si(1)–Si(1)#1	107.53(8)	C(3)–Si(1)–Si(1)#1	111.0(1)	C(4)–Si(1)–Si(1)#1	112.1(1)	C(3)–Si(1)–C(1)	107.2(1)
C(4)–Si(1)–C(1)	107.1(1)	C(2)–C(1)–Si(1)	118.0(2)	C(3)–Si(1)–C(4)	111.7(2)		
Compound 2b							
C(1)–Si(1)–Si(1)#1	110.35(8)	C(4)–Si(1)–Si(1)#1	111.7(1)	C(5)–Si(1)–Si(1)#1	111.9(1)	C(4)–Si(1)–C(1)	109.8(1)
C(5)–Si(1)–C(1)	104.1(1)	C(2)–C(1)–Si(1)	123.9(2)	C(5)–Si(1)–C(4)	108.7(2)	C(3)–C(2)–C(1)	119.6(2)
Compound 4							
P(2)–Pt(1)–P(1)	97.05(6)	Si(1)–Pt(1)–P(1)	91.52(6)	Si(2)–Pt(1)–P(1)	164.13(7)	Si(2)–Pt(1)–P(2)	90.15(7)
Si(1)–Pt(1)–P(2)	167.35(6)	Si(1)–Pt(1)–Si(2)	83.92(6)	C(13)–P(2)–Pt(1)	111.2(2)	C(15)–P(2)–Pt(1)	116.4(3)
C(17)–P(2)–Pt(1)	121.0(2)	C(7)–P(1)–Pt(1)	108.1(3)	C(9)–P(1)–Pt(1)	117.2(2)	C(11)–P(1)–Pt(1)	122.7(2)
Pt(1)–Si(1)–C(3)	119.0(3)	Pt(1)–Si(1)–C(4)	112.6(3)	Pt(1)–Si(2)–C(5)	108.3(3)	Pt(1)–Si(2)–C(6)	125.7(3)
C(13)–P(2)–C(15)	103.9(4)	C(13)–P(2)–C(17)	100.0(3)	C(15)–P(2)–C(17)	102.0(4)	C(7)–P(1)–C(9)	105.9(4)
C(7)–P(1)–C(11)	101.9(3)	C(9)–P(1)–C(11)	99.1(3)	C(5)–Si(2)–C(6)	104.2(5)	C(3)–Si(1)–C(4)	107.1(4)
Si(1)–C(1)–C(2)	112.5(4)						
Compound 5							
P(1)–Pt(1)–P(2)	98.55(9)	P(1)–Pt(1)–Si(1)	101.97(9)	P(1)–Pt(1)–Si(2)	163.02(9)	P(2)–Pt(1)–Si(1)	159.34(9)
P(2)–Pt(1)–Si(2)	67.2(1)	P(2)–O(1)–Si(2)	101.4(3)	Pt(1)–P(1)–C(8)	113.7(4)	Pt(1)–P(1)–C(10)	108.4(4)
Pt(1)–P(1)–C(12)	124.8(4)	Pt(1)–P(2)–O(1)	98.1(3)	Pt(1)–Si(2)–O(1)	93.3(2)	Si(1)–C(2)–C(1)	123.8(6)
Pt(1)–Si(1)–C(2)	114.8(3)	O(1)–P(2)–C(14)	104.2(5)	O(1)–P(2)–C(16)	104.3(5)	C(3)–C(1)–C(2)	121.2(9)
Compound 6							
Si(1)–Si(2)–Si(3)	98.12(5)	C(1)–Si(1)–Si(2)	102.4(1)	Si(1)–C(1)–C(2)	117.8(2)	C(1)–C(2)–Si(3)	118.1(2)
C(2)–Si(3)–Si(2)	102.8(1)	C(5)–Si(2)–C(6)	111.3(2)	C(7)–Si(3)–C(8)	111.5(3)	Si(1')–Si(2')–Si(3')	98.33(5)
C(1')–Si(1')–Si(2')	102.7(1)	Si(1')–C(1')–C(2')	118.5(2)	C(1')–C(2')–Si(3')	118.0(2)	C(2')–Si(3')–Si(2')	102.3(1)
C(3')–Si(1')–C(4')	111.4(2)	C(5')–Si(2')–C(6')	111.9(2)	C(7')–Si(3')–C(8')	111.1(2)		
Compound 7							
Si(1)–C(1)–C(2)	123.4(2)	C(1)–C(2)–Si(3)	123.5(2)	C(2)–Si(3)–C(9)	111.2(1)	Si(3)–C(9)–C(10)	122.7(2)
C(9)–C(10)–Si(2)	134.6(2)	Si(2)–Si(1)–C(1)	114.83(8)	Si(1)–Si(2)–C(5)	106.6(1)	Si(1)–Si(2)–C(6)	110.1(1)
C(1)–Si(1)–C(3)	108.9(1)	C(1)–Si(1)–C(4)	106.0(1)	C(2)–Si(3)–C(7)	106.9(1)	C(2)–Si(3)–C(8)	110.9(1)
Si(3)–C(9)–C(11)	118.6(2)	C(10)–C(9)–C(11)	118.5(2)	C(9)–C(11)–C(12)	122.6(2)	C(9)–C(11)–C(16)	120.3(3)

cm pad of silica gel on a glass frit. Removal of the volatiles provided the final crude product, which was further crystallized from toluene at $-5\text{ }^{\circ}\text{C}$ to provide the pure bis(*o*-carboranyl)disilane **2a** as a colorless solid. Yield: 90% (1.81 g, 4.5 mmol). Anal. Calcd for $\text{B}_{20}\text{C}_8\text{H}_{34}\text{Si}_2$: C, 23.62; H, 8.43. Found: C, 23.70; H, 8.40. Mp: 183–185 $^{\circ}\text{C}$. IR (cm^{-1}): 3069 m, 2959 m (ν_{CH}), 2654 s, 2629 s, 2567 s (ν_{BH}).

For **2b**, a procedure analogous to the preparation of **2a** was used, but starting from **1b** (1.58 g, 10.0 mmol) in benzene. Thus, **2b** was crystallized from toluene at $-5\text{ }^{\circ}\text{C}$. Yield: 96% (2.07 g, 4.8 mmol). Anal. Calcd for $\text{B}_{20}\text{C}_{10}\text{H}_{38}\text{Si}_2$: C, 27.62; H,

8.82. Found: C, 27.70; H, 8.79. Mp: 197–199 $^{\circ}\text{C}$. IR (cm^{-1}): 2953 m (ν_{CH}), 2648 w, 2577 vs (ν_{BH}).

For **2c**, a procedure analogous to the preparation of **2a** was used, but starting from **1c** (2.20 g, 10.0 mmol) in benzene. Thus, **2c** was crystallized from toluene at $-5\text{ }^{\circ}\text{C}$. Yield: 94% (2.56 g, 4.7 mmol). Anal. Calcd for $\text{B}_{20}\text{C}_{20}\text{H}_{42}\text{Si}_2$: C, 42.97; H, 7.58. Found: C, 42.84; H, 7.55. Mp: 232–234 $^{\circ}\text{C}$. IR (cm^{-1}): 3065 w, 2961 w (ν_{CH}), 2631 w, 2567 s (ν_{BH}).

Reaction of the Dilithium Salt of 2a with 1,2-Dichlorotetramethyldisilane. THF (20 mL) and 1.0 mmol of **2a** were added to the reaction flask. The solution was cooled to

–78 °C, and *n*-butyllithium (1.25 mL, 2.0 mmol, 1.6 M in hexanes) was added. The solution was warmed to room temperature, whereupon a thick suspension of white precipitate formed. After the reaction mixture had stirred for 1 h at room temperature, it was again cooled to –78 °C and 1,2-dichlorotetramethyldisilane (1.1 equiv) was added as a neat liquid. The solution was warmed to –5 °C very slowly (for over 1 h) and stirred at –5 °C for a total of 3 h. The volatiles were then removed under reduced pressure; the crude mixture was taken up in a minimal amount of Et₂O and filtered through a 1 × 5 cm pad of silica gel on a glass frit. Removal of the volatiles provided the final crude product, which was further crystallized from toluene at –5 °C to provide pure 3,4-*o*-carboranylene-1,1,2,2-tetramethyl-1,2-disilacyclobutane (**3**) as a colorless solid. Yield: 78% (0.762 g, 1.56 mmol).

Reaction of Linear Bis(*o*-carboranyl)disilane **2a with Pt(PtEt₃)₃.** Benzene (15 mL) was added to a mixture of Pt(PtEt₃)₃ (0.110 g, 0.2 mmol) and **2a** (0.080 g, 0.2 mmol). The mixture was stirred for 3 h, and then the volatile compounds were removed under reduced pressure. Extraction of the residue with toluene (20 mL), followed by concentration of the extract to approximately half its volume and cooling to –5 °C, resulted in crystallization of the cyclic bis(silyl)platinum complex **4**. Yield: 75% (0.103 g, 0.15 mmol). The supernatant was decanted and further reduced, and the residue was chromatographed. Elution with hexane removed a UV-active band, from which *o*-carborane (0.020 g, 69%) was obtained as a white crystalline solid after evaporation in vacuo. ³¹P{¹H} NMR: δ 18.40 (d, ¹J_{Pt-P} = 1695 Hz). Anal. Calcd for B₁₀C₁₈H₅₂Si₂P₂Pt: C, 31.24; H, 7.58. Found: C, 31.35; H, 7.61. Mp = 173–175 °C dec. IR (cm⁻¹): 3120 s, 2913 w (ν_{CH}), 2647 w, 2597 s (ν_{BH}).

For **5**, a procedure analogous to the preparation of **4** was used, but starting from **2b** (0.086 g, 0.2 mmol) in benzene. Thus, **5** was crystallized from toluene at –5 °C. Yield: 2.5% (0.004 g, 0.005 mmol). IR (cm⁻¹): 2963 s, 2930 m, 2876 w (ν_{CH}), 2581 (ν_{BH}).

Synthesis of 4,5-*o*-Carboranylene-1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclopentane (6**).** A catalytic amount of lithium metal (0.014 g, 0.02 mmol) was added to a solution of **3** (0.488 g, 1.0 mmol) in THF (20 mL), and the mixture was stirred for 1 h at 25 °C; conversion into **6**, as monitored by ¹H NMR spectroscopy, was quantitative. The solvent was removed in vacuo and the resulting solid crystallized from toluene to give 0.146 g (0.46 mmol) of colorless microcrystals (46% yield). Anal. Calcd for B₁₀C₈H₂₈Si₃: C, 30.17; H, 8.87. Found: C, 30.06; H, 8.84. Mp: 142–144 °C. IR (cm⁻¹): 2963 w, 2897 w (ν_{CH}), 2588 vs, 2559 s (ν_{BH}).

Reaction of **6 with Phenylacetylene.** Phenylacetylene (0.12 mL, 1.1 mmol) and Pt(CNBU)₂ (0.0055 g, 20 μmol) were added to a solution of **6** (0.316 g, 1.0 mmol) in toluene (20 mL), and the mixture was heated for 1 h at 110 °C; conversion into **7**, as monitored by ¹H NMR spectroscopy, was quantitative. The solvent was removed in vacuo and the resulting solid crystallized from toluene to give 0.335 g (0.80 mmol) of colorless microcrystals (80% yield). Anal. Calcd for B₁₀C₁₆H₃₄Si₃: C, 45.68; H, 8.15. Found: C, 45.84; H, 8.18. Mp: 150–154 °C. IR (cm⁻¹): 3074 w, 3053 w, 3018 w, 2961 m, 2901 w (ν_{CH}), 2633 w, 2598 s, 2584 s, 2572 s, 2557 s (ν_{BH}), 1487 m (ν_{C=C}).

Crystal Structure Determination. Crystals of **2a, b** and **4–7** were obtained from toluene, sealed in glass capillaries under argon, and mounted on the diffractometer. Data were collected and corrected for Lorentz and polarization effects. Each structure was solved by the application of direct methods using the SHELXS-96 program^{19a} and least-squares refinement using SHELXL-97.^{19b} After anisotropic refinement of all non-H atoms several H atom positions could be located in difference Fourier maps. These were refined isotropically,

while the remaining H atoms were calculated in idealized positions and included in the refinement with fixed atomic contributions. Further detailed information is given in Table 1, and selected interatomic distances and angles are given in Tables 3 and 4, respectively.

Computational Details. Stationary points on the potential energy surface were calculated using the Amsterdam Density Functional (ADF) program, developed by Baerends et al.^{20,21} and vectorized by Ravenek.²² The numerical integration scheme applied for the calculations was developed by te Velde et al.^{23,24} The geometry optimization procedure was based on the method due to Versluis and Ziegler.²⁵ The electronic configurations of the molecular systems were described by double-ζ STO basis sets with polarization functions for the H, B, and C atoms, while triple-ζ Slater type basis sets were employed for the Si, P, and Pt atoms.^{26,27} The 1s electrons of B and C, the 1s–2p electrons of Si and P, and the 1s–4d electrons of Pt were treated as frozen cores. A set of auxiliary²⁸ s, p, d, f, and g STO functions, centered on all nuclei, was used in order to fit the molecular density and the Coulomb and exchange potentials in each SCF cycle. Energy differences were calculated by augmenting the local exchange-correlation potential by Vosko et al.²⁹ with Becke's³⁰ nonlocal exchange corrections and Perdew's³¹ nonlocal correlation corrections (BP86). Geometries were optimized by including nonlocal corrections at this level of theory. First-order Pauli scalar relativistic corrections^{32,33} were added variationally to the total energy for all systems. In view of the fact that all systems investigated in this work show a large HOMO–LUMO gap, a spin-restricted formalism was used for all calculations. No symmetry constraints were used.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures of **2a, b** and **4–7** reported in this paper and listings giving optimized geometries of the crucial structures (**3**, **3'**, **6**, and **6'**) reported (Cartesian coordinates, in Å); crystallographic data are also available in electronic form as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXL, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(20) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(21) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52.

(22) Ravenek, W. In *Algorithms and Applications on Vector and Parallel Computers*; te Riele, H. J. J., Dekker, T. J., van de Horst, H. A., Eds.; Elsevier: Amsterdam, The Netherlands, 1987.

(23) te Velde, G.; Baerends, E. J. *J. Comput. Chem.* **1992**, *99*, 84.

(24) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87.

(25) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.

(26) Snijders, J. G.; Baerends, E. J.; Vernoijis, P. *At. Nucl. Data Tables* **1982**, *26*, 483.

(27) Vernoijis, P.; Snijders, J. G.; Baerends, E. J. *Slater Type Basis Functions for the Whole Periodic System*; Internal Report (in Dutch); Department of Theoretical Chemistry, Free University: Amsterdam, The Netherlands, 1981.

(28) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS Method*; Internal Report (in Dutch); Department of Theoretical Chemistry, Free University: Amsterdam, The Netherlands, 1984.

(29) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(30) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.

(31) (a) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(32) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789.

(33) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.