tives undergo symmetrization with formation of R_2Hg.[10b]

Treating $(CO)_3Co(HgI)_3$ with 3 equiv of silver *p*-toluenesulfonate in THF resulted in the formation of monomeric, $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$ and quantitative precipitation of AgI (eq 3).[11] As far as we know, this type

$$2 + 3Ag[p\text{-}CH_3C_6H_4SO_3] \rightarrow (p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3 + 3AgI \quad (3)$$

of metathesis reaction has not been previously reported for HgX derivatives of transition-metal carbonyls. The product serves as a synthetic intermediate for preparation of other $(CO)_3Co(HgY)_3$ derivatives.[12]

A most intriguing observation was that $Hg_9Co_6(CO)_{18}$ reformed in high yield when $(CO)_3Co(HgCl)_3$ was treated with triphenylphosphine (eq 4.)[13]

$$6(CO)_3Co(HgCl)_3 + 18PPh_3 \rightarrow 1 + 9(PPh_3)_2HgCl_2 \quad (4)$$

It is particularly significant that this reaction proceeds to completion *nearly quantitatively*, forming *only one cluster* out of a large number of possible oligomers or polymers. The reformation of 1 in this way is formally the reverse of the reaction shown in eq 1 with Ph_3P removing the mercuric halide formed. Symmetrization of simple $XHgM(L)_n$ compounds, effected by Ph_3P, has been described.[2]

The reassembly of 1, to the exclusion of other possible oligomers of $(CO)_3CoHg_{1.5}$, places stringent demands on the spatial orientation of each of the six *fac*-$(XHg)_3Co$ moieties during cluster reconstruction. We suggest that the departing HgX_2 may exert the necessary stereochemical influence by coordinating to several Co–HgX units simultaneously.

Acknowledgment. We thank Ace Glass Inc. for partial support of this work.

Registry No. 1, 100851-89-6; 2, 102651-39-8; 3 (X = Cl), 102651-40-1; 3 (X = O_2CCF_3), 102651-41-2; 3 (X = Ph), 102651-42-3; 3 (X = $O_3SC_6H_4\text{-}p\text{-}CH_3$), 102651-43-4; $(CO)_3Co(HgI)_3I^-Bu_4N^+$, 102651-45-6; Co, 7440-48-4; Hg, 7439-97-6.

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[11] A solution of 2 in THF, prepared in situ from 1 and HgI_2, was stirred with slightly more than 3 equiv of $p\text{-}CH_3C_6H_4SO_3Ag$ and then filtered to remove AgI. Removal of the solvent and recrystallization from CH_2Cl_2 gave $(p\text{-}CH_3C_6H_4SO_3Hg)_3Co(CO)_3$ as a yellow powder. Found (calcd): Hg, 48.1 (47.8); Co, 4.57, (4.68); M_r 1295 (1258).[8]

[12] Burlitch, J. M.; Ragosta, J. M., to be submitted for publication.

[13] A suspension of yellow $(CO)_3Co(HgCl)_3$ in THF (prepared in situ) was stirred with a solution of the stoichiometric amount of triphenylphosphine in THF for 3 h. This gave a dark red solution with a gray-white precipitate identified as $(PPh_3)_2HgCl_2$ by mixed melting point with an authentic sample; the yield was 92%. The filtrate contained 1, as identified by its IR spectrum; the yield of recrystallized product was 82%. 2 also reacted with triphenylphosphine to form 1 and $(PPh_3)_2HgI_2$, but the reaction required several days for completion and some decomposition of 2 occurred during this time.

Silicon–Carbon Unsaturated Compounds. 21. Isomerization of a 1-Silapropadiene in the Presence of Tetrakis(triethylphosphine)nickel(0)

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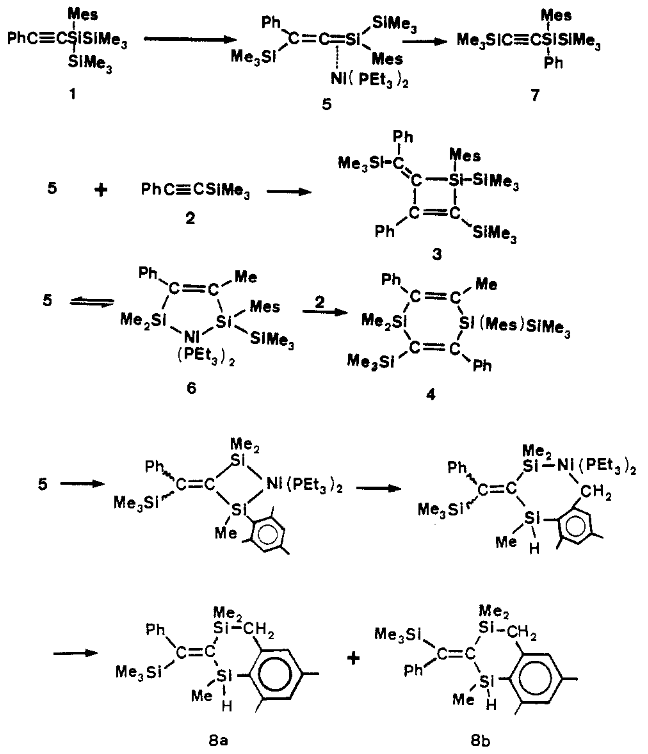
Summary: The nickel-catalyzed reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**1**) with phenyl(trimethylsilyl)acetylene (**2**) gave two products arising from the isomerization of **1**, followed by addition to **2**. In the absence of **2**, products derived from the isomerization of a 1-silapropadiene generated from **1**, 5,6-benzo-1,3-disilacyclohexene derivatives, were obtained in high yields.

Scheme I



Recently, we have found that the nickel-catalyzed reaction of phenylethynylpolysilanes and silacyclopropenes with phenyl(trimethylsilyl)acetylene affords products which can be best explained by assuming the formation of 1-silapropadiene–nickel complexes.[1] In this communication we report the novel isomerization of the 1-silapropadiene intermediate generated from 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (1) in the presence of a nickel(0) catalyst.

When 1 was heated with a small excess of phenyl(trimethylsilyl)acetylene (2) in the presence of a catalytic amount of $Ni(PEt_3)_4$ in a sealed glass tube at 195 °C for 20 h, two products, 1-mesityl-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene (3) and 2,5-diphenyl-1-mesityl-4,4,6-trimethyl-1,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (4), were obtained in 77 and 11% yields, respectively. Compound 3 could readily be separated from 4 by fractional recrystallization from ethanol. The structures of 3 and 4 were verified by mass and ^1H and ^{13}C NMR spectroscopic analysis.[2,3]

The formation of 3 can be best explained in terms of the reaction of the 1-silapropadiene–nickel complex 5 with acetylene 2. It seems likely that product 4 would be formed by the reaction of the nickeladisilacyclopentene

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[1] Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

[2] For compound 3: mp 165–166 °C; 100-MHz ^1H NMR δ (CCl_4) −0.32 (9 H, s, Me_3Si), −0.15 (9 H, s, Me_3Si), 0.40 (9 H, s, Me_3Si), 2.36 (3 H, s, *p*-Me), 2.70 (6 H, s, *o*-Me), 6.64–7.04 (12 H, m, phenyl and mesityl ring protons); ^{13}C NMR δ ($CDCl_3$) −1.0 (Me_3Si), 0.0 (Me_3Si), 1.1 (Me_3Si), 21.1 (*o*- and *p*-Me), 124.5, 125.3, 126.5, 126.8, 127.0, 128.1, 128.9 (two carbons), 131.4, 139.2, 142.2, 142.3 (ring carbons), 144.9, 155.8, 162.6, 174.1 (olefinic carbons); MS, *m/e* 568 (M^+). Anal. Calcd for $C_{34}H_{48}Si_4$: C, 71.76; H, 8.50. Found: C, 71.75; H, 8.64.

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intermediate **6** produced from the isomerization of **5**, with acetylene **2** (Scheme I). Although evidence for the production of the intermediate **6** from **5** has not yet been obtained, similar behavior of the 1-silapropadiene derivative has been observed in a different system.[1]

Interestingly, heating **1** in the absence of **2** under the same conditions afforded 1-mesityl-1-phenyl-1-(trimethylsilylethynyl)trimethyldisilane (**7**), whose spectral data were identical with those of an authentic sample prepared by an independent route,[4] and two isomers of 5,6-benzo-1,3-disilacyclohexane derivative (**8a** and **8b**) in 36, 36, and 22% yields, respectively. Product **7** could be readily separated from the mixture of **8a** and **8b** by preparative TLC. Pure **8a** and **8b** could be isolated by preparative GLC. The structures of **8a** and **8b** were confirmed by spectroscopic analysis[5,6] and, particularly, by a NOE–FID difference experiment at 400 MHz. Thus, saturation of the resonances of the trimethylsilyl protons of **8a** produced a positive Overhauser effect (NOE) of the hydrogen (H–Si(Me)) and methyl protons (CH_3–Si(H)) and also the phenyl ring protons and one of two methyl protons on an aromatic ring. Irradiation of the trimethylsilyl protons of **8b**, however, caused a positive NOE of the dimethylsilyl protons in a disilacyclohexene ring and the phenyl ring protons.

The production of **7** and **8** may be understood in terms of the isomerization of the 1-silapropadiene–nickel complex **5**.[7] The thermal isomerization of the silicon-unsaturated compounds involving a mesityl or 2,6-dimethylphenyl group on an sp^2 silicon atoms to the cyclic system has recently been found by two research groups.[8-10]

Product **7** is stable under the conditions used. No change was observed when **7** was heated at 200 °C for 20 h in the presence of a catalytic amount of $Ni(PEt_3)_4$. The reaction of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene[11] produced photochemically from **1** with a catalytic amount of $Ni(PEt_3)_4$ at 135 °C afforded only **8a** and **8b** in 45 and 27% yields, respectively. No ethynylpolysilanes such as compound **7** were detected by GLC or spectroscopic analysis. We are continuing to explore this and related systems.

Acknowledgment. We express our appreciation to Shin-etsu Chemical Co., Ltd., and Toshiba Silicone Co., Ltd., for a gift of organochlorosilanes.

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[3] For compound **4**: mp 191–191.5 °C; 400-MHz ^1H NMR δ ($CDCl_3$) −0.36 (9 H, s, Me_3Si), −0.12 (9 H, s, Me_3Si), 0.56 (3 H, s, MeSi), 0.57 (3 H, s, MeSi), 1.85 (3 H, s, MeC), 2.32 (3 H, s, Me(mesityl)), 2.43 (3 H, s, Me(mesityl)), 2.60 (3 H, s, Me(mesityl)), 6.58–7.08 (12 H, m, phenyl and mesityl ring protons); ^{13}C NMR δ ($CDCl_3$) 0.6 (Me_3Si), 1.5 (MeSi), 2.0 (Me_3Si), 2.6 (MeSi), 21.1, 25.1, 25.6 (Me(mesityl)), 28.5 (MeC), 125.6, 126.9, 127.0, 127.2, 127.3, 127.7, 128.4, 128.8, 135.4, 138.4, 139.1, 143.7, 144.7, 147.2 (ring carbons), 148.1, 160.0, 162.5, 179.3 (olefinic carbons). Exact Mass. Calcd for $C_{34}H_{48}Si_4$: 568.2833. Found: 568.2817.

[4] Compound **7** was prepared by the reaction of 1,1-dichloro-1-phenyltrimethyldisilane with 1 equiv of mesityllithium, followed by treatment of the resulting solution with ((trimethylsilyl)ethynyl)lithium: 100-MHz ^1H NMR δ (CCl_1) 0.20 (18 H, s, Me_3Si), 2.26 (3 H, s, *p*-Me), 2.41 (6 H, s, *o*-Me), 6.82 (2 H, b s, mesityl ring protons), 7.20–7.61 (5 H, m, phenyl ring protons); MS, *m/e* 394 (M^+). Anal. Calcd for $C_{23}H_{34}Si_3$: C, 69.98; H, 8.68. Found: 70.24; H, 8.77.

[5] Compound **8a**: mp 96 °C; 400-MHz ^1H NMR δ ($CDCl_3$) −0.34 (3 H, s, MeSi(Me)), −0.20 (9 H, s, Me_3Si), 0.09 (3 H, s, MeSi(Me)), 0.60 (3 H, d, MeSi(H), J= 4.2 Hz), 2.00 (1 H, d, HC(H), J = 4.5 Hz), 2.26 (3 H, s, Me aryl)), 2.51 (3 H, s, Me(aryl)), 3.04 (1 H, d, HC(H), J = 4.5 Hz), 5.11 (1 H, q, HSi(Me), J = 4.2 Hz), 6.68–7.25 (7 H, m, phenyl and aryl ring protons); ^{13}C NMR δ ($CDCl_3$) −3.9 (MeSi), −1.3 (MeSi), −1.1 (MeSi), 1.2 (MeSi), 21.2 (Me(aryl)), 24.4 (Me(aryl)), 27.4 (Me(aryl)), 125.7, 126.7, 127.3, 127.4, 127.5, 127.7, 127.8, 131.1, 139.3, 143.9, 146.9, 147.3 (phenyl and aryl ring carbons), 158.2, 175.3 (olefinic carbons). Exact Mass. Calcd: 394.1968. Found: 394.1952. Anal. Calcd for $C_{23}H_{34}Si_3$ (1:1 mixture of **8a** and **8b**): C, 69.98; H, 8.68. Found: C, 69.96; H, 8.86.

[6] Compound **8b**: mp 83.5 °C; 400-MHz ^1H NMR δ ($CDCl_3$) −0.23 (9 H, s, Me_3Si), −0.05 (3 H, s, MeSi(Me)), 0.28 (3 H, d, MeSi(H), J = 4.3 Hz), 0.33 (3 H, s, MeSi(Me)), 2.01 (1 H, d, HC(H), J = 4.4 Hz), 2.27 (3 H, s, Me (aryl)), 2.41 (3 H, s, Me(aryl)), 2.87 (1 H, d, HC(H), J = 4.4 Hz), 4.82 (1 H, q, HSi(Me), J = 4.3 Hz), 6.68–7.31 (7 H, m, phenyl and aryl ring protons); ^{13}C NMR δ ($CDCl_3$), −4.7 (MeSi), −1.5 (MeSi), 1.6 (MeSi), 2.5 (Me_3Si), 21.3 (Me(aryl)), 23.6 (Me(aryl)), 29.5 (CH_2(aryl)), 126.1, 126.6, 127.1, 127.5, 127.6, 128.2, 129.0, 129.2, 139.7, 144.2, 147.6, 149.1 (phenyl and aryl ring carbons), 160.9, 174.8 (olefinic carbons). Calcd for $C_{23}H_{34}Si_3$: 394.1968. Found: 394.1981.

[7] One reviewer suggested an alternative mechanism involving a free diradical intermediate such as $Me_3Si(Ph)C{=}C(\dot{S}iMe_2)\dot{S}i(Me)Mes$ in order to explain the production of **8a** and **8b**. At present, however, no evidence for a key intermediate has been obtained.

[8] Fink, M. J.; Deyoung, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

[9] Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776.

[10] The thermal production of a cyclic compound from the silicon–carbon unsaturated compound containing a mesityl group on an sp^2 carbon also has been reported. See: Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

[11] 1-Mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene: 100-MHz ^1H NMR δ (CCl_4) 0.15 (9 H, s, Me_3Si), 0.29 (9 H, s, Me_3Si), 2.20 (3 H, s, *p*-Me), 2.55 (6 H, s, *o*-Me), 6.65 (2 H, broad s, mesityl ring protons), 7.05–7.52 (5 H, m, phenyl ring protons). Exact Mass. Calcd for $C_{23}H_{34}Si_3$: 394.1968. Found: 394.1991.

Synthesis and Reactions of Dihydrido(triethylsilyl)(1,5-cyclooctadiene)iridium(III) Complexes: Catalysts for Dehydrogenative Silylation of Alkenes

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Summary: $IrH_2(SiEt_3)(cod)L$ (L = PPh_3 or $AsPh_3$, cod = 1,5-cyclooctadiene) complexes have been obtained by reaction of $[Ir(OMe)(cod)]_2$ with L and $HSiEt_3$. These complexes react with PPh_3 to give $IrH(cod)(PPh_3)_2$ and $HSiEt_3$. They are active catalyst precursor for the dehydrogenative silylation of alkenes. $IrH_2(SiEt_3)(cod)L$ complexes react with ethylene to give $CH_2{=}CHSiEt_3$ and $CH_3CH_2SiEt_3$ in different proportions depending on the ancillary L ligand.

Although M(H)(silyl)(olefin) species have been postulated as intermediates in the catalytic hydrosilylation of olefins,[1] they have rarely, if ever, been isolated. Only just recently $Rh(C_5Me_5)H(SiEt_3)(CH_2{=}CH_2)$[2a] and $Rh(C_5H_5)H(SiEt_3)(CH_2{=}CH_2)$[2b] have been detected in solution. We wish to report here the preparation and reactivity of $IrH_2(SiEt_3)(cod)L$ (cod = 1,5-cyclooctadiene; L = PPh_3 or $AsPh_3$), which, as far as we know, represent the first isolated complexes of the type mentioned above.

Most of the silyl complexes of iridium(III) previously reported have been obtained by oxidative addition of $HSiR_3$ to iridium(I) compounds.[3] We have now developed an easy route to prepare isolable dihydrido(silyl)(di-

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[1] (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407–447. (b) Green, M.; Spencer, J. L.; Stone, F. G.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519–1525.

[2] (a) Bentz, P. O.; Ruiz, J.; Mann, B. E.; Spencer, C. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1374–1375. (b) Haddleton, D. M.; Perutz, R. N. *Ibid.* **1985**, 1372–1374.

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