of excess ethylene, **2** will catalytically convert 1,2,5,6-tetraethyl-1,3-cyclohexadiene into 1,2,3,5,6-pentaethyl-1,3-cyclohexadiene. Reaction of **1** with propene or 1-butene yields the substituted titanacyclopentane compounds **3** and **4**, respectively.[9] In the room-temperature 200-MHz ^{1}H NMR spectrum of **2**, the methylene protons of the metallacycle ring appear as two broad, equal-intensity signals at δ 1.60 and 1.98 ppm. Selective irradiation of either of these peaks results in almost complete loss of intensity for the other signal. Furthermore, spin magnetization transfer is found to occur at room temperature not only between the α- and β-methylene protons but also between the metallacycle ring protons and free ethylene in solution. A variable-temperature ^{1}H NMR study of toluene-d_8 solutions of **2** in the presence of ethylene shows that coalescence of the two methylene signals occurs at 55 °C. At temperatures above 40 °C, broadening of the signal due to the free ethylene protons is also observed. These observations can be rationalized in terms of rapid fragmentation of the titanacyclopentane ring to generate a bis(ethylene) complex. Rotation of the ethylene units followed by coupling back to **2** accounts for exchange of methylene units in the titanacyclopentane ring, while a somewhat slower dissociation of the bound ethylene ligands accounts for exchange with free C_2H_4.[10] The rate of exchange of methylene groups at 55 °C is calculated to be 187 s^{-1}, yielding an estimate of $\Delta G^\ddagger$ for the exchange process of 15.9 (5) kcal mol^{-1}. This exchange rate is considerably faster than a value of 6.5 (2) × 10^{-3} min^{-1} at 50 °C reported by Negishi et al. for the isomerization of a hafnacyclopentane ring.[5c] In the ^{13}C NMR spectrum of **2**, the two triplets at δ 89.7 ppm ($^1J(^{13}C-^1H) = 127.7$ Hz) and δ 31.1 ppm ($^1J(^{13}C-^1H) = 127.7$ Hz) confirm a titanacyclopentane structure in solution. In the solid state,

2 crystallizes with two independent molecules in the unit cell (Figure 1).[11] The [(Ar''O)$_2$Ti] unit in pseudotetrahedral **2** is unexceptional, while the titanacyclopentane ring is puckered in a manner observed for other metallacyclopentane compounds.

The solution NMR spectra of the substituted titanacyclopentane compounds **3** and **4** indicate the presence of more than one isomer. In both cases the major isomer (80%) is the trans-2,3-disubstituted species.[9]

Hydrocarbon solutions of **2** in the absence of added C_2H_4 undergo decomposition over hours at 25 °C to produce the new organometallic product **5** along with detectable amounts of ethane (Scheme I). In the presence of added ethylene (1-5 equiv), **2** is more stable in solution. However, over days decomposition to **5** takes place along with the formation of ethane and 1-butene. The identification of **5** as the titanacyclohept-3-ene species [(Ar''O)$_2$Ti-(CH$_2$CH=CHCH$_2$CH$_2$CH$_2$)] is based upon its NMR spectra.[12] The formation of **5** via a titanacyclopent-3-ene (1,3-butadiene) complex is strongly indicated by the fact that addition of 1,3-butadiene to **2** rapidly produces **5** in quantitative yield.[13]

Supplementary Material Available: Variable-temperature ^{1}H NMR spectra of **2**, a 2D NMR spectrum of **5**, and tables of fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for **2** (28 pages); a table of observed and calculated structure factors for **2** (46 pages). Ordering information is given on any current masthead page.

(9) Anal. Calcd for TiC$_{42}$H$_{38}$O$_2$ (**3**): C, 81.02; H, 6.15. Found: C, 81.21; H, 6.56. ^{1}H NMR (C$_6$D$_6$, 30 °C): trans isomer δ 6.88-7.48 (m, aromatics), 2.04 (m, CHMe), 1.88 (t), 1.24 (dd, TiCH_2), 0.93 (d, CHMe). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C): trans isomer δ 160.1 (Ti-O-C) 98.0 ($^1J(^{13}C-^1H) =$ 129.2 Hz, TiCH_2), 44.8 ($^1J(^{13}C-^1H) = 126.2$ Hz, CHMe), 23.3 (CHMe). Anal. Calcd for TiC$_{44}$H$_{42}$O$_2$ (**4**): C, 81.22; H, 6.51. Found: C, 81.54; H, 6.91. ^{1}H NMR (C$_6$D$_6$, 30 °C): trans isomer δ 6.88-7.48 (m, aromatics), 2.03 (m, CHEt), 1.85 (t), 1.22 (m, TiCH_2), 1.22 (m, CH$_2$CH$_3$), 0.60 (t, CH$_2$CH$_3$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C): trans isomer δ 160.2 (Ti-O-C) 95.0 ($^1J(^{13}C-^1H) = 126.5$ Hz, TiCH_2), 48.7 $^(1J(^{13}C-^1H) = 126.8$ Hz, CHEt) 28.9 (CH$_2$CH$_3$), 18.1 (CH$_2$CH$_3$).

(10) The fragmentation and isomerization of metallacyclopentane rings has been well documented.[5]

(11) Crystal data for TiC$_{40}$H$_{34}$O$_2$ (**2**) at -61 °C: a = 10.047 (1) Å, b = 14.625 (2) Å, c = 22.415 (2) Å, V = 3088 (1) Å^3, Z = 4, ρ_{calcd} = 1.211 g cm^{-3} in space group P$\bar{1}$. A total of 8046 unique intensities were collected with use of Mo Kα radiation ($4 \leq 2\theta \leq 45°$), of which 6555 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.033 and R_W = 0.049.

(12) Anal. Calcd for TiC$_{42}$H$_{36}$O$_2$ (**5**): C, 81.28; H, 5.85. Found: C, 81.27; H, 5.92. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 6.8-7.5 (m, aromatics), 4.41 (td, TiCH$_2$CH), 3.21 (broad td, TiCH$_2$CHCH), 2.27 (m, TiCH$_2$CH_2), 1.94 (dd), 0.86 (dd, TiCH$_2$CH), 1.7 (m, TiCH$_2$CH$_2$CH_2), 1.7 (m), -0.18 (m, TiCH_2CH$_2$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 160.4, 160.3 (Ti-O-C), 136.3, 135.6 (TiCH$_2$CHCH), 77.7, 77.2 (Ti-CH$_2$), 45.3, 35.8 (TiCH$_2$CH$_2$-CH$_2$).

(13) The formation of 1,3-butadiene from a titanacyclopentane compound has precedence.[5b]

Platinum-Complex-Catalyzed Dehydrogenative Double Silylation of Acetylenes, Dienes, and Olefins with Bis(hydrosilane) Compounds

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Summary: Acetylenes, dienes, and olefins underwent dehydrogenative double silylation with bis(hydrosilane) species in the presence of platinum complex catalysts to give disilacyclic compounds in good yields.

The synthesis of silicon compounds is a rapidly growing field relevant to silicon-based functional polymers, selective organic synthesis, and biological activity.[1] Of particular

importance among complex-catalyzed syntheses of silicon compounds is the double silylation of unsaturated hy-

(1) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Adv. Chem. Ser. 224; American Chemical Society: Washington, DC, 1990. *Silicon Chemistry*; Corey, J. Y., Corey, E. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988. *Organosilicon and Bio-organosilicon Chemistry*; Sakurai, H., Ed., Ellis Horwood: Chichester, U.K., 1985. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983.

drocarbons with disilanes.[2] Previously we could successfully demonstrate the first examples of double and/or dehydrogenative single silylation of simple olefinic compounds that proceeded in the presence of platinum complex catalysts.[3,4] Further studies aimed at extension of the scope of double silylation have revealed that various unsaturated hydrocarbons readily undergo dehydrogenative double silylation with bis(hydrosilane) species to give disilacyclic compounds in high yields.[5]

A benzene solution (2 mL) of an acetylene (1, 0.25 mmol) was added at room temperature to a mixture of o-bis(dimethylsilyl)benzene (2, 0.25 mmol) and (ethylene)bis(triphenylphosphine)platinum (0.005 mmol) dissolved in benzene (2 mL). Immediate GC analysis ("0" reaction time) revealed that dehydrogenative double silylation had already taken place to a considerable extent to give the corresponding disilacyclohexadiene derivative (3).[6] The yield increased while the solution was kept at 30 °C for 19 h (eq 1).

$$R^1C{\equiv}CR^2 \ + \ \text{(o-bis(dimethylsilyl)benzene)} \longrightarrow \text{(disilacyclohexadiene 3)} \qquad (1)$$

1   **2**   **3**

a: $R^1 = R^2 = Ph$ **a** (0 h: 74%, 19 h: 98%)
b: $R^1 = R^2 = {}^nPr$ **b** (0 h: 31%, 19 h: 100%)
c: $R^1 = Ph$, $R^2 = H$ **c** (0 h: 41%, 19 h: 76%)
d: $R^1 = {}^nHex$, $R^2 = H$ **d** (0 h: 67%, 19 h: 86%)
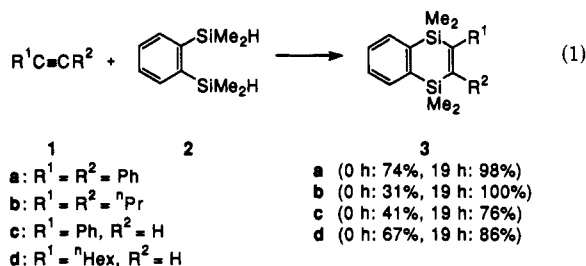
Internal acetylenes **1a,b** very selectively reacted to give **3a,b**, respectively, in nearly quantitative yield. However, the selectivity in the reactions of terminal acetylenes **1c,d** was somewhat low, and **4c,d** were also formed in 10 and

4c: $R^1 = Ph$
d: $R^1 = {}^nHex$

12% yield, respectively, at 19 h reaction time.

The performance of various complexes (0.005 mmol) was examined for the reaction of **1c** with **2** at 80 °C for 7 h. The results were as follows: $Pt(CH_2{=}CH_2)(PPh_3)_2$ (yield of **3c** 50%), $PtCl_2(PPh_3)_2$ (23%), $Ru_3(CO)_{12}$ (20%), Pd-(dba)$_2$·2PPh$_3$ (8%), $RhCl(PPh_3)_3$ (3%), $PdCl_2(PPh_3)_2$ (3%), and $Pd(PPh_3)_4$ (1%). Thus, $Pt(CH_2{=}CH_2)(PPh_3)_2$ proved to be the best catalyst for the present reaction.

Besides **2**, other bis(hydrosilane) compounds also reacted with **1b** at 80 °C. However, the selectivity very much depended on the framework between the two silicon atoms (eq 2). Only 1,2-bis(dimethylsilyl)ethane (**5f**) gave a fairly

Scheme I

$$E{<}^{SiMe_2H}_{SiMe_2H} \ + \ {}^nPrC{\equiv}C{}^nPr \longrightarrow \qquad (2)$$

5   **1b**

e: E = O, **f**: E = $(CH_2)_2$,
g: E = $(CH_2)_3$, **h**: E = $(CH_2)_4$

6   **7**   **8**

e (8%)   **e** (79%)   **e** (6%)
f (55%)   **f** (13%)   **f** (16%)
g (12%)   **g** (34%)   **g** (23%)
h (0%)   **h** (46%)   **h** (26%)
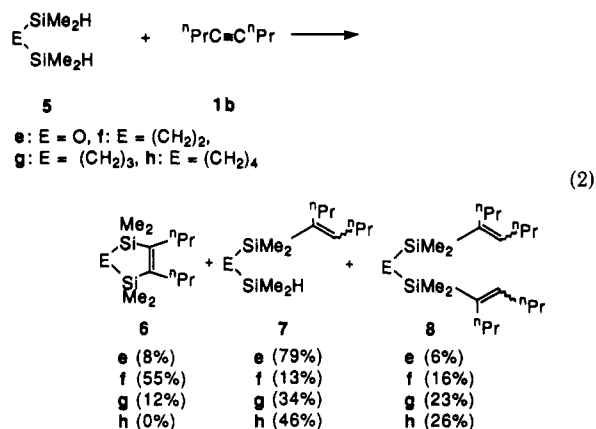
good yield of the cyclic compound (**6f**), and the others ended up with formation of large amounts of simple hydrosilylation byproducts (**7**, **8**).[6,7]

With regard to the reaction mechanism, Eaborn et al.[8] reported that the reaction of **2** with the platinum complex formed the cyclic bis(silyl)platinum complex **9**. We could confirm the result (eq 3). On the other hand, we have

$$\text{(o-bis(dimethylsilyl)benzene, 2)} \ + \ Pt(CH_2{=}CH_2)(PPh_3)_2 \longrightarrow$$

$$\text{(9)} \ + \ H_2 \ + \ CH_2{=}CH_2 \qquad (3)$$

9 (95%)

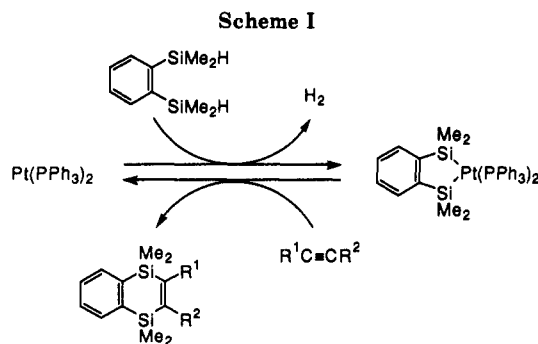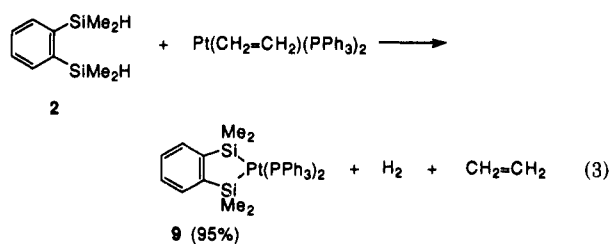provided evidence which supports that cis-bis(silyl)plati-

(2) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185. Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149. Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 617. Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inoue, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *255*, 343. Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801. Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229. Seyferth, D.; Gordman, E. W., Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337. Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 1807.

(3) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

(4) We previously reported dehydrogenative single silylation of terminal olefins, with a disilane, at the terminal carbon to give vinylsilanes and a hydrosilane. See: Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563.

(5) Kumada et al. have briefly reported nickel-catalyzed double silylation of internal acetylenes with hydrosilanes. See: Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603.

(6) All new compounds gave satisfactory analytical and spectral data. Spectral and analytical data for the compounds **3a–d**, **4c,d**, **6f**, **7f–h**, **8g,h**, **11**, and **12** are available as supplementary material.

(7) Itoh et al. very recently reported fast and selective mono hydrosilylation of acetylenes, olefins, and ketones with these bis(hydrosilane) compounds in the presence of $RhCl(PPh_3)_3$. See: Nagashima, H.; Tatebe, K.; Ishibashi, T.; Sakakibara, J.; Itoh, K. *Organometallics* **1989**, *8*, 2495. Nagashima, H.; Tatebe, K.; Itoh, K. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1707.

(8) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

Scheme II

num species are the key intermediates involved in platinum-catalyzed double silylation with noncyclic disilanes.[9] When 1c (0.125 mmol) was added at 30 °C to a toluene-d_8 (1 mL) solution of the complex 9 (0.055 mmol) in an NMR tube, 3c was immediately formed quantitatively (eq 4).

Thus, the reactivity of 9 is exactly the same as that of noncyclic bis(silyl)platinum complexes. On the basis of these observations, it seems reasonable to propose the mechanism depicted in Scheme I. The foregoing effect of the structure of the linear bis(hydrosilane) compounds 5f–h on the reaction course is presumably associated with the ease of formation of the cyclic bis(silyl)platinum intermediate. The compound 5f reacts with the platinum catalyst to relatively easily form a five-membered-ring intermediate. On the other hand, 5e,g,h are reluctant to form the sterically less favorable four-, six-, and seven-membered rings, respectively. Accordingly, after the oxidative addition of one of the Si–H bonds, octyne comes into the platinum center to undergo hydrosilylation.

Olefins also reacted with 2 in the presence of Pt-$(CH_2=CH_2)(PPh_3)_2$. Different from the reactions of acetylenes, the major reaction pathway was not 1,2- but 1,1-double silylation (eq 5).[6] The formation of a 1,1-adduct can be explained by intramolecular insertion of the C=C bond into the Pt–H or Pt–Si bond of the complex 14

(9) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* 1989, 467. Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* 1990, 1447.

(Scheme II), which is formed via either path A, olefin insertion into one of the two Si–Pt bonds of the complex 9 and subsequent β-elimination of the resulting complex,[4] or path B, dehydrogenative silylation of an olefin with one of the two Si–H bonds of 2.[10]

Dienes also reacted with 2. In the double silylation of conjugated dienes with disilanes, 1,4-addition is normally the major pathway. However, the present reaction of isoprene proceeded to give 1,2-addition to the less substituted double bond (eq 6).[6] Penta-1,2-diene also underwent 1,2-addition to the less hindered double bond (eq 7).[6]

To summarize, this paper offers another useful variation of double silylation that provides interesting intermediates with synthetic applications. Mechanistic studies and extension to other substrates will be reported shortly.

(10) We could neither confirm nor exclude path A from the results below. NMR analysis revealed that the cyclic bis(silyl)platinum complex 9 did not react with styrene even at 120 °C. In the presence of an equimolar amount of the bis(hydrosilane) 2, however, the 1,1-adduct 4 was formed and the complex 9 was re-produced immediately at 40 °C. On the other hand, styrene underwent neither dehydrogenative silylation (a reaction similar to path B) nor hydrosilylation with phenyldimethylsilane under conditions similar to those of the catalytic reaction of the bis(hydrosilane) 2.