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.

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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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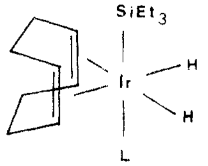
olefin)iridium complexes. Treatment of acetone solutions of $[Ir(OMe)(cod)]_2$ and L (L = PPh_3 or $AsPh_3$), in a 1:1 ratio of Ir:L, with $HSiEt_3$ at room temperature leads to the formation of $MeOSiEt_3$ (detected by GC) and $IrH_2(SiEt_3)(cod)L$, according to eq 1. The complexes were

$$^1/_2[Ir(OMe)(cod)]_2 + L + 2HSiEt_3 \rightarrow IrH_2(SiEt_3)(cod)L + MeOSiEt_3 \quad (1)$$

obtained, in 60–70% yield, as white, air-stable powders after the solution was concentrated and methanol was subsequently added. Formulation of these complexes as indicated is supported by microanalytical data as well as by IR and NMR measurements.[4] The observed reaction presumably involves the intermediate IrH(cod)L, formed by an initial oxidative addition of $HSiEt_3$ to methoxyiridium(I) species and subsequent reductive elimination of $MeOSiEt_3$. It is interesting to note that iridium–phosphine or –arsine complexes have been reported previously[5] as catalysts in the reaction between $HSiR_3$ and alcohols.

The ^1H NMR spectra of the $IrH_2(SiEt_3)(cod)L$ complexes are consistent with a structure containing equivalent hydrides. On the other hand, the strong IR absorptions above 2000 cm^{-1}, attributable to ν(IrH), are in concordance with a cis dihydride,[6] as shown in structure 1.



1a, L = PPh_3
b, L = $AsPh_3$

Since hydrides and silyl groups have mutually cis positions, competitive elimination of H_2 or $HSiEt_3$ from the complexes could be potentially possible; however, the H_2 reductive elimination is expected to be less favored relative to $HSiEt_3$ elimination. This may be due to the trans disposition of the chelating cod relative to the hydrogen atoms. Thus, the reaction with PPh_3, in dichloromethane at room temperature, leads to the rapid formation of $IrH(cod)(PPh_3)_2$[7] and $HSiEt_3$ (eq 2).

$$IrH_2(SiEt_3)(cod)L \xrightarrow{PPh_3} IrH(cod)(PPh_3)_2 + HSiEt_3 \quad (2)$$

$$L = PPh_3 \text{ or } AsPh_3$$

This result is also in agreement with the stability toward H_2 loss of dihydrido(silyl)iridium complexes, such as those derived from $IrH(CO)(PPh_3)_3$.[8]

A more interesting reaction occurs between these complexes and ethylene. When a solution of $IrH_2(SiEt_3)(cod)L$ (0.1 mmol) in $CDCl_3$ (1 mL) was allowed to react with ethylene (1 atm, room temperature) for 4 h, the presence of $CH_3CH_2SiEt_3$ and $CH_2{=}CHSiEt_3$, detected by ^1H NMR and GC in the relative amounts shown in eq 3, was observed.

$$H_2C{=}CH_2 \xrightarrow[\substack{\mathbf{1a},\ L = PPh_3 \\ \mathbf{1b},\ L = AsPh_3}]{IrH_2(SiEt_3)(cod)L} \begin{array}{ccc} CH_2{=}CHSiEt_3 & + & CH_3CH_2SiEt_3 \\ 45\% & & 55\% \\ 80\% & & 20\% \end{array} \quad (3)$$

Thus, the stoichiometric reaction gives rise to the normal hydrosilylation product along with the unexpected unsaturated product (dehydrogenative silylation[9]). The ^1H NMR spectrum of the resulting orange solutions did not show the presence of hydridic protons, and on adding $HSiEt_3$ the starting complex was not recovered.

As expected $IrH_2(SiEt_3)(cod)L$ complexes were found to be active catalysts for this type of unusual silylation, using 1-hexene as starting olefin. The reactions were carried out by mixing the complex (0.04 mmol) with $HSiEt_3$ (2 mmol) and 1-hexene (6 mmol) in 1,2-dichloroethane (8 mL) at 60 °C. After 1 h of reaction, completion (based on $HSiEt_3$, determined by GC) is 50% and 95% for complex **1a** and **1b**, respectively. ^1H NMR and GC–MS of the solutions showed the formation of hexyltriethylsilane and hexenyltriethylsilanes as the silylated products,[10] in the relative amounts quoted in eq 4. Hexane is also

$$C_6H_{12} + HSiEt_3 \xrightarrow[\substack{\mathbf{1a},\ L = PPh_3 \\ \mathbf{1b},\ L = AsPh_3}]{IrH_2(SiEt_3)(cod)L} \begin{array}{ccccc} C_6H_{14} & + & C_6H_{11}SiEt_3 & + & C_6H_{13}SiEt_3 \\ 41\% & & 41\% & & 18\% \\ 46\% & & 46\% & & 8\% \end{array} \quad (4)$$

formed in a similar amount to the unsaturated silanes $C_6H_{11}SiEt_3$. It is noteworthy that in both reactions (eq 3 and 4) complex **1b** gives a higher yield of alkenyltriethylsilane than complex **1a**. The catalytic reactions showed a small induction period. This can be attributed to the fact that the initial 18-electron complexes $IrH_2(SiEt_3)(cod)L$ should form unsaturated intermediates, presumably without the cod ligand, which is probably removed from the iridium center by hydrogenation and/or isomerization of the coordinated 1,5-cyclooctadiene. In fact, we have observed that if 1,5-cyclooctadiene (0.5 mmol) is added to a mixture of the arsine complex and $HSiEt_3$, under conditions similar to those used in the catalytic reaction, the diene is isomerized to 1,3-cyclooctadiene in 0.5 h. After this time, addition of 1-hexene caused hydrogenation of 1,3-cyclooctadiene along with silylation of 1-hexene. Further work in this area is in progress.

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(4) Anal. Calcd for $IrH_2(SiEt_3)(cod)(PPh_3)$: C, 56.53; H, 6.52. Found: C, 56.38; H, 6.49. Calcd for $IrH_2(SiEt_3)(cod)(AsPh_3)$: C, 53.11; H, 5.37. Found: C, 53.18; H, 5.38. IR spectra (Nujol, ν(Ir H)): **1a**, 2105, 2090 cm^{-1}; **1b**, 2078 cm^{-1}. $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$): **1a**, δ 7.22. ^1H NMR (220 MHz, $CDCl_3$, olefinic and hydride protons): **1a**, δ 3.89 (br, 2 H), 3.11 (br, 2 H), −12.85 (d, 2 H, *J*(PH) = 21.4 Hz); **1b**, δ 3.98 (br, 2 H), 3.44 (br, 2 H), −12.60 (s, 2 H).

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(10) Hexyltriethylsilane (GC–MS, *m/e* 171 ($C_6H_{13}SiEt_2^+$)) and three different hexenyltriethylsilanes (GC–MS, *m/e* 198 or 169 ($C_6H_{11}SiEt_3^+$ or $C_6H_{11}SiEt_2^+$)) were detected by GC, but separation of the silicon products by preparative GC was not achieved. ^1H NMR spectra of the mixtures showed signals characteristic of olefinic protons at 5.1–5.4 ppm, confirming the formation of hexenyltriethylsilanes.