1082 *Organometallics* **1995,** *14,* 1082−1084

# Highly Selective Dehydrogenative Silylation of Ethylene Using the Bis(dihydrogen) Complex $RuH_2(H_2)_2(PCy_3)_2$ as Catalyst Precursor

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*Received December 19, 1994*[®]

*Summary: The complex $RuH[(\eta^3\text{-}C_6H_8)P(C_6H_{11})_2](C_2H_4)(PCy_3)$ (**4**), resulting from the dehydrogenation of a cyclohexyl ring of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with $C_2H_4$, is a highly efficient catalyst for the selective dehydrogenative silylation of ethylene into the vinylsilane $CH_2{=}CHSiEt_3$ (**2**). Total conversion of 1000 equiv of $HSiEt_3$ under 20 bar of $C_2H_4$ is achieved, in less than 15 min at 17 °C, leading to **2** in 93% selectivity.*

Although the reactivity of molecular dihydrogen complexes is a very active area, relatively few studies concerning their activity in catalysis have been carried out.[1] Thus, dihydrogen derivatives represent likely catalytic intermediates but more evidence is needed to demonstrate their activity.

As part of our current studies on the properties of the thermally stable bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**),[2] we recently reported the stoichiometric reactions of **1** with $HER_3$ (E = Si, Ge). Dihydrogen substitution leads to the novel compounds $RuH_2(H_2)(HER_3)(PCy_3)_2$ in which the $HER_3$ ligand is weakly coordinated.[2e] We now demonstrate the catalytic activity of **1** toward ethylene and triethylsilane.

The hydrosilylation of olefins catalyzed by transition-metal complexes (eq 1) has been extensively studied,[3] but the competitive reaction of dehydrogenative silylation of olefins has been much less documented (eq 2).[4] This alternative reaction has synthetic value because the vinylsilanes are versatile synthetic intermediates.[5]

**Table 1. Reaction of Ethylene with $HSiEt_3$ Catalyzed by the Ruthenium Complexes 1, 4, and 5**

| entry no. | catalyst M | $HSiEt_3$:M | *T* (°C) | *P* (bar) | time (min) | product ratio[a] **2**:**3** |
|---|---|---|---|---|---|---|
| 1 | **1** | 100 | 21 | 1 | 105 | 78:22 |
| 2 | **1** | 100 | 22 | 2 | 30 | 80:20 |
| 3 | **1** | 100 | 60 | 2 | 10 | 79:21 |
| 4 | **1** | 1000 | 13 | 20 | 30 | 76:24 |
| 5[b] | **1** | 100 | 22 | 1 | 150 | 97:3 |
|  |  | +100[c] | 22 | 1 | 290 | 98:2 |
|  |  | +100[c] | 22 | 1 | 410 | 98:2 |
| 6 | **4** | 100 | 17 | 1 | 80 | 99:1 |
| 7 | **4** | 1000 | 17 | 20 | 15 | 93:7 |
| 8 | **5** | 100 | 18 | 1 | 90 | 98:2 |

[a] Determined by GC; in all cases, $HSiEt_3$ was totally consumed. [b] $C_2H_4$ was first bubbled into **1** in pentane before addition of $HSiEt_3$. [c] 100 additional equiv of $HSiEt_3$ added.

$$CH_2{=}CH_2 + HSiR_3 \rightarrow CH_3CH_2SiR_3 \qquad (1)$$

$$2CH_2{=}CH_2 + HSiR_3 \rightarrow CH_2{=}CHSiR_3 + C_2H_6 \qquad (2)$$

We describe herein an effective system for the dehydrogenative silylation of ethylene.

The main results are summarized in Table 1. When ethylene is bubbled at room temperature into a mixture of **1** and $HSiEt_3$ in a 1:100 ratio in pentane solution, total conversion of $HSiEt_3$ is observed within 2 h, producing the vinylsilane $CH_2{=}CHSiEt_3$ (**2**) in 78% yield together with the hydrosilylated product $SiEt_4$ (**3**) in 22% yield (entry 1). According to GC analysis, **3** is formed in the early stage of the catalysis (Figure 1). Ethane was detected by GC as well as by $^1H$ NMR monitoring. The reaction can be run at higher pressure and temperature (entries 2−4) without modification of the selectivity, but this lead to an increase in the reaction rate. High turnover numbers (entry 4) were obtained, and clearly much higher total turnovers can be achieved. Higher selectivity can be simply achieved by bubbling ethylene into a pentane solution of **1** before the addition of $HSiEt_3$ (entry 5): the vinylsilane **2** is thus obtained in 97% yield. The system is stable since successive additions of $HSiEt_3$ can be done (entry 5) without any decomposition of the catalyst (even after

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[®] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

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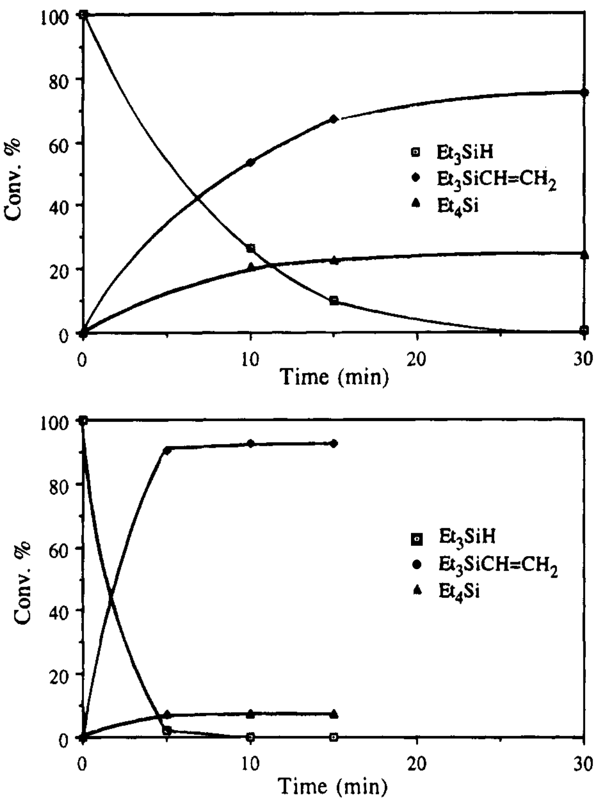
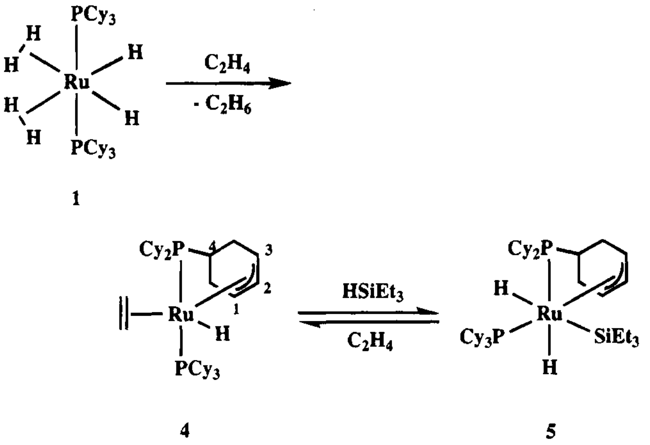


**Figure 1.** Variation in relative amounts of HSiEt$_3$, CH$_2$=CHSiEt$_3$, and SiEt$_4$ *vs* time: (top) **1** (0.025 mmol), HSiEt$_3$ (25 mmol), 20 bar of C$_2$H$_4$, 13 °C; (bottom) **4** (0.025 mmol), HSiEt$_3$ (25 mmol), 20 bar of C$_2$H$_4$, 17 °C.

the mixture is kept overnight in the absence of ethylene and silane). Finally, when H$_2$ is bubbled into the reaction mixture at the end of a run (for example such as in entry 2), hydrogenation of the vinylsilane is rapidly achieved and the saturated silane **3** is obtained in 100% yield. We must notice that under the same conditions as entry 1 or 5, less than 5% conversion of HSiEt$_3$ was obtained using Ru$_3$(CO)$_{12}$ or Ru(COD)(COT) instead of **1** as catalysts.

Having established that **1** is a powerful catalyst, we sought mechanistic information. Bubbling ethylene into a pentane solution of **1** results in the formation of RuH[($\eta^3$-C$_6$H$_8$)P(C$_6$H$_{11}$)$_2$](C$_2$H$_4$)(PCy$_3$) (**4**).[6] At 223 K, the hydride signal for **4** is observed as a doublet of doublets at $\delta$ −7.1, $J_{P-H}$ = 18.9 and 26.2 Hz, and as a singlet upon $^{31}$P decoupling. The $^{31}$P{$^1$H} NMR spectrum displays an AB pattern ($\delta$ 82.2 and 42.2, $J_{P-P}$ = 283 Hz). Particularly diagnostic for the allyl ligand are the $^{13}$C NMR spectra (JMOD and $^{13}$C{$^{31}$P}). The doublets at $\delta$ 77.9 ($J_{C-H}$ = 161 Hz), $\delta$ 67.0 ($J_{C-H}$ = 150 Hz), and $\delta$ 45.8 ($J_{C-H}$ = 156 Hz) are assigned to the three allylic carbons (see Scheme 1).

## Scheme 1



Addition of HSiEt$_3$ to **4** leads to the new complex Ru(H)$_2$(SiEt$_3$)[($\eta^3$-C$_6$H$_8$)P(C$_6$H$_{11}$)$_2$](PCy$_3$) (**5**), a formally Ru(IV) complex resulting from oxidative addition (see Scheme 1).[7] The two hydride ligands for **5** give a broad triplet ($\delta$ −9.54, $J_{P-H}$ = 17 Hz) and a doublet of doublets of doublets ($\delta$ −12.63, $J_{P-H}$ = 57 Hz, $J_{P-H}$ = 25 Hz, $J_{H-H}$ = 5 Hz), whereas an AB pattern ($\delta$ 79.9 and 65.4, $J_{P-P}$ = 18 Hz) is observed in the $^{31}$P{$^1$H} spectrum. The low $J_{P-P}$ value is in agreement with a formally heptacoordinated structure in which the two phosphines are not in a trans position any more. Finally, upon exposure of **5** to C$_2$H$_4$, we successfully regenerate **4**.

$^1$H and $^{31}$P NMR monitoring of the catalytic reaction at different temperatures revealed that **1** is converted into the complex RuH[($\eta^3$-C$_6$H$_8$)P(C$_6$H$_{11}$)$_2$](C$_2$H$_4$)(PCy$_3$) (**4**).[8] **4** is observed during all of the catalysis and is the only detected complex after total conversion of HSiEt$_3$. Realizing that the catalytic cycle is entered by reaction of **1** with C$_2$H$_4$ to produce **4**, we generated a long-lived catalyst system by simply starting with isolated complex **4** (entries 6 and 7); it is noteworthy that there is no reaction between **4** and **2**, which favors the catalytic formation of **2**. When the reaction was carried out under 20 bar of C$_2$H$_4$ at 17 °C with the HSiEt$_3$:**4** ratio equal to 1000:1, total conversion of HSiEt$_3$ was observed in less than 15 min and **2** and **3** were obtained in a 93:7 ratio (eq 3).[9] Finally, **5** was also found to be an effective catalyst precursor (entry 8), therefore suggesting its participation in the catalytic cycle.

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(6) The reaction of **1** with C$_2$H$_4$ was previously described as producing a bis(ethylene) complex.[2a] Additional data, particularly from $^{13}$C NMR spectra, lead us to reformulate the complex as RuH[($\eta^3$-C$_6$H$_8$)P(C$_6$H$_{11}$)$_2$](C$_2$H$_4$)(PCy$_3$) (**4**). Complex **4**: A suspension of **1** (500 mg; 0.75 mmol) in pentane (30 mL) was placed in a Fischer–Porter bottle, which was pressurized to 3 bar of ethylene. After immediate dissolution, a white solid precipitated (yield 87%). When ethylene was bubbled, the precipitation was slower. Anal. Calcd for RuC$_{38}$H$_{68}$P$_2$: C, 66.3; H, 10.0. Found: C, 66.4; H, 10.4. $^1$H NMR (250 MHz, 223 K, C$_7$D$_8$): $\delta$ −7.1 (dd, $J_{P-H}$ = 18.9 and 26.2 Hz, Ru–H), 3.24, 3.39, 3.74, 4.26, 5.19, 5.32, 5.54 (all br, 1H each; allylic and ethylenic protons). $^{31}$P{$^1$H} NMR (81.015 MHz, C$_6$D$_6$): $\delta$ 82.2, 42.2 ($J_{P-P}$ = 283 Hz). $^{13}$C NMR (50.32 MHz, C$_6$D$_6$): $\delta$ 77.9 (d, $J_{C-H}$ = 161 Hz, C$_2$), 67.0 (d, $J_{C-H}$ = 150 Hz, C$_1$), 45.8 (d, $J_{C-H}$ = 156 Hz, C$_3$), 42.3 (dd, $J_{C-H}$ = 130 Hz, $J_{C-P}$ = 19 Hz, C$_4$); the ethylenic carbons are presumably hidden by the multiplets of the cyclohexyl carbons between $\delta$ 27 and 33.

(7) Complex **5**: Et$_3$SiH (89 $\mu$L; 0.56 mmol) was added to a solution of **4** (200 mg; 0.28 mmol) in pentane (200 mL). After the mixture was stirred overnight at room temperature, the yellow solution was concentrated to 20 mL, affording a gray solid on storing at −20 °C for 3 h (yield 91%). Anal. Calcd for RuC$_{42}$H$_{80}$P$_2$Si: C, 65.0; H, 10.41. Found: C, 65.4; H, 10.7. $^1$H NMR (250 MHz, C$_6$D$_6$): $\delta$ −12.63 (ddd, $J_{P-H}$ = 57 and 25 Hz, $J_{H-H}$ = 5 Hz, Ru–H), −9.54 (br t, $J_{P-H}$ = 17 Hz, Ru–H), 1.08 (q, $J_{H-H}$ = 8 Hz, SiC*H*$_2$CH$_3$), 1.48 (t, $J_{H-H}$ = 8 Hz, SiCH$_2$C*H*$_3$), 3.14 (br, 1H), 3.98 (br, 1H), 4.95 (pseudo t, 1H, *J* = 6 Hz). $^{31}$P{$^1$H} NMR (81.015 MHz, C$_6$D$_6$): $\delta$ 79.9, 65.4 ($J_{P-P}$ = 18 Hz).

(8) We have previously shown that stoichiometric reaction of HSiPh$_3$ with **1** yields within 5 min the complex RuH$_2$(H$_2$)(HSiPh$_3$)(PCy$_3$)$_2$.[2e] When HSiEt$_3$ is used, the reaction is much slower and **1** and the new complex RuH$_2$(H$_2$)(HSiEt$_3$)(PCy$_3$)$_2$ (**6**) could not be separated. Under ethylene, this mixture regenerates **4** and the organic products **2** and **3**. The competitive formation of **6** and **4** could be responsible for the different selectivity observed when HSiEt$_3$ is added to **1** prior to bubbling ethylene.

(9) Under conditions of [**4**] = 18 mg (0.025 mmol) and [HSiEt$_3$] = 4 mL (25 mmol), the initial turnover rate is *ca.* 3 s$^{-1}$ (mol of **4**)$^{-1}$. The reaction is essentially first order in HSiEt$_3$.

$$\underset{1000}{\mathrm{HSiEt_3}} \xrightarrow[17\ ^\circ\mathrm{C},\ 15\ \mathrm{min}]{20\ \mathrm{bar\ of\ C_2H_4},\ \mathbf{4}} \underset{930}{\mathrm{CH_2{=}CHSiEt_3}} + \underset{70}{\mathrm{SiEt_4}} \quad (3)$$

The present results clearly indicate that the bis(dihydrogen) complex **1** is an effective precursor for the catalytic reaction of silane with ethylene but is not involved in the catalytic cycle producing vinylsilane. Indeed, **4** is the catalyst resting state and the formation of the vinylsilane **2** is promoted by high olefin-to-silane ratios. Further exploration of the activity of **4**, the first complex presenting such a dehydrogenated cyclohexyl ligand on a cyclohexylphosphine, is currently in progress.

**Acknowledgment.** M.L.C. thanks the CONACYT (Mexico) for support.

OM940967+