Notes

Formation of Substituted Vinylsilanes from the Ruthenium-Catalyzed Dehydrosilylation of Terminal Alkenes

Chae S. Yi,* Zhengjie He, and Do W. Lee

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Arnold L. Rheingold and Kin-Chung Lam

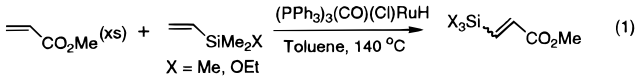
Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received February 10, 2000

Summary: *The ruthenium complexes* ***1a*** *and* ***2a*** *were found to be effective catalysts for the dehydrogenative silylation of terminal alkenes. The ruthenium complexes were prepared by following literature methods, and the molecular structure of* ***2b*** *was determined by X-ray crystallography. Both catalysts displayed high selectivity toward the formation of trans-vinylsilane products* ***3****. For alkenes with a* α*-*CH_2 *group, mixtures of* ***3*** *and* ***4*** *were formed, and* ***1a*** *was found to be more effective than* ***2a*** *in these cases. These results are consistent with the mechanism involving a silyl migration, as previously proposed by other groups.*

Introduction

Considerable efforts have been directed for developing new catalytic methods of forming vinylsilanes because vinylsilanes are known to be a versatile intermediate in organic synthesis.[1] The hydrosilylation of alkynes by the metal catalysts such as H_2PtCl_6/Pr^{i}OH and $(PPh_3)_3$RhCl has been commonly used for forming vinylsilanes,[2] but this method is known to produce other regio- and stereoisomeric byproducts. Recently, catalytic dehydrogenative silylation of alkenes has emerged as a viable alternative method for forming vinylsilanes.[3−8] For example, Wakatsuki and co-workers reported the ruthenium-catalyzed dehydrosilylation of alkenes using CH_2=$CHSiMe_2X$ (X = Me, OMe) as a silylating agent (eq 1).[3] The mechanism of this reaction has been



(1)

explained via a silyl migration, since the vinylsilane formation could not be readily explained by the classical Chalk−Harrod mechanism. Wrighton suggested a similar silyl migration mechanism in a cobalt-catalyzed photochemical hydrosilylation reaction.[4] Brookhart recently reported a detailed study on the relationship between the hydrosilylation and dehydrogenative silylation reactions of alkenes using cationic cobalt and palladium complexes and proposed a similar mechanism involving a silyl group migration.[7]

While studying the metal-catalyzed coupling reactions of alkynes and alkenes,[9] we recently found that the ruthenium hydride complex $(PCy_3)_2$(CO)(Cl)RuH (**1a**) is an effective catalyst for the hydrogenation of alkenes.[10] We also reported an effective hydrovinylation of alkynes using the cationic ruthenium complex $[(PCy_3)_2$(CO)(Cl)Ru=CHCH=$C(CH_3)_2]^+BF_4^-$ (**2a**) as a catalyst.[11] Since many of the metal catalysts were found to be effective for both hydrogenation and hydrosilylation reactions, we have begun to explore the catalytic activity of these ruthenium complexes toward the hydrosilylation reactions.

Results and Discussion

The ruthenium complexes **1** and **2** were prepared by following literature procedures. We recently developed an effective synthesis of **1a**,[11] and the cationic alkylidene complexes **2a** and **2b** were subsequently prepared from

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(2) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 25. (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: 1991; Vol 8. (c) Marciniec, B. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 1. (d) Reichl, J.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 197−265.

(3) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703−704.

(4) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289−291.

(5) (a) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748−4750. (b) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1993**, *456*, 45−47. (c) Furukawa, N.; Kourogi, N.; Seki, Y.; Kakiuchi, F.; Murai, S. *Organometallics* **1999**, *18*, 3764−3767. (d) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Organometallics* **1999**, *18*, 2033−2036, and the references therein.

(6) Tanaka, M.; Uchimara, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1−12.

(7) (a) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906−917. (b) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151−2156.

(8) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421−1429.

(9) Yi, C. S.; Liu, N. *Synlett* **1999**, 281−287.

(10) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152−5126.

(11) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045.

10.1021/om000128p CCC: $19.00
Publication on Web 04/19/2000

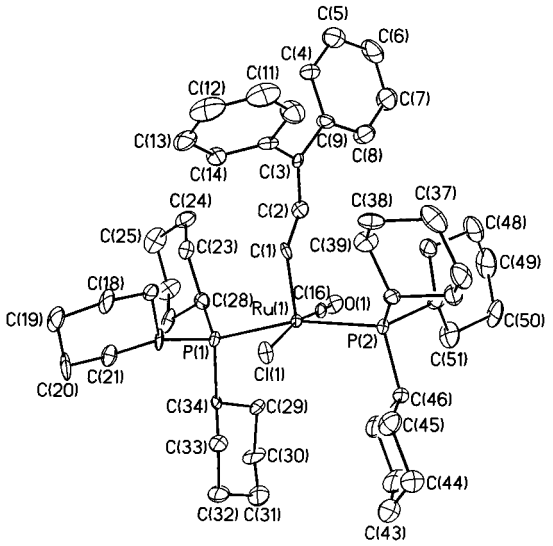
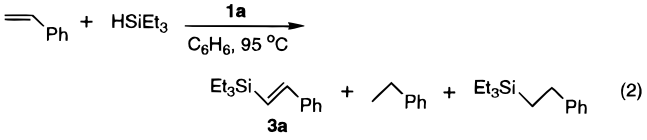


Figure 1. Molecular structure of $[(PCy_3)_2(CO)(Cl)Ru{=}CHCH{=}CPh_2]^+BAr'_4^-$ (**2b**) drawn with 50% thermal ellipsoids. The anion and hydrogen atoms were omitted for clarity.

1a by following Esteruelas's procedure.[12] These ruthenium complexes have been completely characterized by spectroscopic methods, and in particular, the solid-state structure of **2b** with BAr'_4 ion (Ar′ = 3,5-$C_6H_3(CF_3)_2$) was determined by X-ray crystallography (Figure 1). The molecular structure of **2b** showed a distorted square pyramidal geometry with an axial alkylidene ligand on the ruthenium center (Ru−C(1) = 1.885 Å), which was very similar to the previously reported PPr^i_3 analogue of the ruthenium−alkylidene complex.[13] The X-ray crystal structure **1b** has recently been reported.[14]

Initially, both ruthenium hydride complexes **1a** and **1b** were found to be active catalysts for the dehydrogenative silylation reaction of alkenes. For example, the heating of a benzene solution containing styrene (52 mg, 0.5 mmol) and 1.5 equiv of $HSiEt_3$ in the presence of **1a** (3.6 mg, 1.0 mol %) at 95 °C led to the dehydrosilylation product **3a** along with ethylbenzene (**3a**:ethylbenzene = 2.8:1, 95% conversion after 15 h) (eq 2).[15] Only a trace amount of the hydrosilylation product



(2)

(<3%) was detected by GC. Following Wakatsuki's procedure,[3] vinylsilane was employed as a silylating agent to reduce the formation of the hydrogenation product. Thus, the treatment of styrene with $CH_2{=}CHSiMe_3$ in the presence of 1.0 mol % of **1a** at 95 °C cleanly produced the silylation product **3b** in >98% yield after 4 h. In this case, virtually no other silylation product was detected by GC, but a small amount of the homocoupling product $Me_3SiCH{=}CHSiMe_3$ (<5%), which could be readily removed during the solvent evaporation, was detected in the crude product mixture.

Table 1. Dehydrogenative Silylation of Styrene by $CH_2{=}CHSiMe_3$[a]

entry	catalyst	yield (%)
1	$(PCy_3)_2(CO)(Cl)RuH$ (**1a**)	83
2	$(PPr^i_3)_2(CO)(Cl)RuH$ (**1b**)	88
3	$[(PCy_3)_2(CO)(Cl)Ru{=}CHCH{=}C(CH_3)_2]^+BF_4^-$ (**2a**)	92
3	$[(PCy_3)_2(CO)(Cl)Ru{=}CHCH{=}CPh_2]^+BF_4^-$ (**2b**)	89
4	$(PPh_3)_3(CO)(Cl)RuH$	8
5	$(PPh_3)_3RuCl_2$	trace
6	$RuCl_3{\cdot}xH_2O$	trace

[a] Reaction conditions: 3.3 mmol of styrene; 5.0 mmol of $CH_2{=}CHSiMe_3$; 0.3 mol % of the catalyst; 95 °C; 4 h; 3 mL of CH_2Cl_2.

We next compared the catalyst activity of the selected ruthenium catalysts by using styrene and $CH_2{=}CHSiMe_3$ as reagents (Table 1). We found that both ruthenium complexes **1** and **2** were found to exhibit similar catalytic activity, but the complexes $(PPh_3)_3(CO)(Cl)RuH$, $(PPh_3)_3RuCl_2$, and $RuCl_3{\cdot}xH_2O$ gave little product under similar reaction conditions. Previously, the catalyst $(PPh_3)_3(CO)(Cl)RuH$ was reported to give 66% yield of an *E*/*Z* mixture of **3a**, but at a considerably higher temperature (140 °C) and by using an excess amount of alkenes.[3] In a related reaction, the complex **1b** was also reported to be an effective catalyst for the hydrosilylation of terminal alkynes.[16]

We surveyed the scope of the silylation reaction by using **1a** and **2a** as the catalysts.[17] The catalyst activity of **1a** and **2a** was found to be comparable in most cases, and both catalysts led to the *trans*-vinylsilane products **3** exclusively (Table 2, entries 1−4). The cis/trans isomerization of vinylsilane was found to be very slow under the reaction conditions; for example, only a small amount of the cis product *cis*-**3d** was formed for the allylsilane after 15 h of reaction time at 75 °C (entry 4). For alkenes with an α-CH_2 group, a mixture of **3** and **4** was produced, and **1a** was found to be a more effective catalyst than **2a**, in part because **2a** was found to promote more alkene isomerization products (entries 5−7). In these cases, the silylation reactions were found to be relatively slow, which allowed more alkene isomerization reactions and led to lower yields of **3** and **4**. The ratio of products **3** and **4** was found to remain constant even after a prolonged reaction time. In most cases, CH_2Cl_2 was found to be the most suitable solvent, especially for the reactions catalyzed by the cationic complex **2a**.

These results are consistent with the mechanism involving a silyl migration as previously proposed by Wakatsuki and Brookhart.[3,7] The following preliminary results also support the silyl migration mechanism. First, the formation of ethylene was detected in the

(12) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748−5755, and the references therein.

(13) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258−4265.

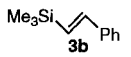
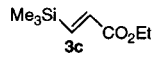
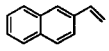
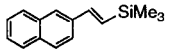
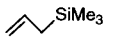
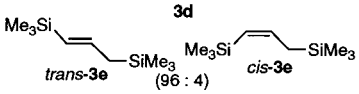
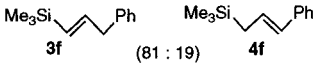
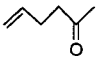
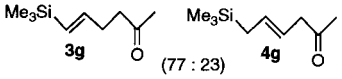
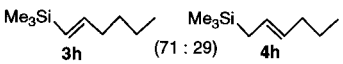
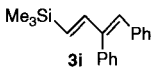
(14) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087−8097.

(15) As a referee pointed out, the reaction proceeded in the presence of excess hydrosilane. A possible explanation for this observation may be due to the relatively high coordinating ability of alkenes by the ruthenium catalyst. In support of this hypothesis, we previously observed that complex **1a** readily reacted with alkenes at low temperatures.[10] A similar result was also reported by Brookhart and coworkers, where the coordination of alkenes to the cationic Pd complexes was found to occur rapidly at −78 °C.[7a]

(16) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379.

(17) Both **1a** and **1b** were found to exhibit similar activity toward the catalytic reactions. We have chosen to use **1a** primarily because of lower cost for preparing **1a** than **1b** and due to its relative ease of preparation.

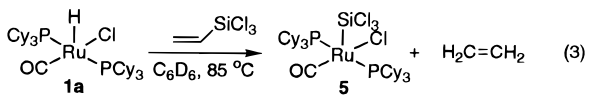
Table 2. Dehydrogenative Silylation of Alkenes Catalyzed by 1a and 2a[a]

entry	alkene	catalyst (mol%)	product (ratio)	time (h)	temp (°C)	% yield[b]
1		**1a** (1.0)	 **3b**	4	95	>98 (8)
2		**1a** (0.3) **2a** (0.3)	 **3c**	7 7	75 75	95 (trace) 97 (trace)
3		**1a** (1.0)	 **3d**	3	95	>98 (6)
4		**1a** (1.0)	 *trans*-**3e** (96 : 4) *cis*-**3e**	15	75	97 (25)
5		**1a** (1.0)	 **3f** (81 : 19) **4f**	2	95	88 (13)[c]
6		**1a** (0.3) **2a** (0.3)	 **3g** (77 : 23) **4g**	2 2	95 95	90 (<5)[c] 79 (8)[c]
7		**1a** (0.3)	 **3h** (71 : 29) **4h**	2	95	78 (6)[c]
8		**1a** (1.0)	 **3i**	15	85	95 (24)

[a] Reaction conditions: 3.3 mmol of alkene; 5.0 mmol of CH_2=$CHSiMe_3$; 10 μmol of the catalyst; 3 mL of CH_2Cl_2. [b] The numbers in parentheses represent % yield of the homocoupling product Me_3SiCH=$CHSiMe_3$ in the crude product mixture. [c] Significant amount of the isomerization products was also formed in these cases.

crude reaction mixture by both GC and NMR. For activated alkenes, similar results were achieved by running the reaction under refluxing conditions at a considerably lower temperature (50 °C oil bath temperature for styrene and ethyl acrylate). In this case, the reaction appeared to be further driven by the removal of ethylene from the solution, and this procedure could be useful for a large-scale reaction.

Wakatsuki previously reported that the metal−silyl complex $(PPh_3)_3(CO)(Cl)RuSiMe_3$, isolated from the reaction of $(PPh_3)_3(CO)(Cl)RuH$ and CH_2=$CHSiMe_3$, was an active species for the silylation reaction.[3] The analogous reaction of **1a** with CH_2=$CHSiMe_3$ did not result in any detectable intermediate species in the temperature range from +40 to −80 °C. The reaction of **2a** with a more activated vinylsilane CH_2=$CHSiCl_3$ initially formed the new silyl species **5**, the structure of which was tentatively assigned on the basis of the spectroscopic data (eq 3). Unfortunately, the complex **5**



(3)

was found to be inactive for the silylation reaction, possibly due to a strong bonding of the silyl group to the metal center; the complex instead turned into an insoluble and unidentified solid upon removal of the solvent. In addition, the formation of allylsilane products **4** can be explained by invoking a competitive β-H elimination from a secondary metal−alkyl intermediate.

In summary, an effective catalytic method of forming substituted vinylsilanes has been developed from the dehydrogenative silylation of terminal alkenes by using well-defined ruthenium complexes **1a** and **2a**. Further studies are currently underway to extend the scope and synthetic utility of this reaction.

Experimental Section

General Information. All reactions were carried out in an inert-atmosphere glovebox or by using standard high-vacuum and Schlenk line techniques unless otherwise noted. Benzene, hexanes, and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. CH_2Cl_2 was distilled from CaH_2. The NMR solvents were dried from activated molecular sieves (4 Å). All organic alkene substrates were vacuum distilled from molecular sieves or sodium prior to use. The ruthenium complexes **1** and **2** were prepared according to the reported procedures.[11,12] The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5890 GC/MS spectrometer. Gas chromatographs were recorded from a Hewlett-Packard HP 6890 GC spectrometer.

General Procedure of the Catalytic Reaction. In a glovebox, 2.2 mL of a freshly prepared CH_2Cl_2 solution of **1a** (4.5 mM, 10 μmol) was charged with CH_2=$CHSiMe_3$ (5.0 mmol) and an alkene (3.3 mmol) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a stirring bar. Enough CH_2Cl_2 (~1 mL) was added to bring the total volume of the solution to 3 mL. The reaction tube was brought out of the box and was heated in an oil bath under the conditions specified in Table 2. After the reaction tube was allowed to cool to room temperature, the crude reaction mixture was analyzed by GC. The organic product was isolated after filtering the solution through a short silica column (hexanes:Et_2O = 3:1), and the solvent was evaporated by a rotary evaporator.

For **3a**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.29 (m, Ph), 6.96 (d, J = 19.2 Hz, =CHPh), 6.33 (d, J = 19.2 Hz, =C*H*$SiEt_3$), 1.06 (t, J = 7.8 Hz, $SiCH_2CH_3$), 0.73 (q, $SiCH_2CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 144.8 (=*C*HPh), 138.5 (=*C*H$SiEt_3$), 128.4, 127.9, 126.3 and 125.8 (Ph carbons), 7.4 ($Si(CH_2CH_3)_3$), 3.5 ($Si(CH_2CH_3)_3$); GC−MS ($M^+ - C_2H_5$ = 189).

For **3b**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58−7.38 (m, Ph), 7.02 (d, J = 19.2 Hz, =C*H*Ph), 6.62 (d, J = 19.2 Hz, =C*H*$SiMe_3$), 0.31 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 143.6 (=*C*HPh), 138.3 (=*C*H$SiMe_3$), 129.4, 128.5, 127.9 and 126.3 (Ph carbons), −1.3 ($Si(CH_3)_3$); GC−MS (M^+ = 176).

For **3c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23 (d, J = 19.2 Hz, =C*H*CO_2Et), 6.21 (d, J = 19.2 Hz, =C*H*$SiMe_3$), 4.18 (q, J = 7.2 Hz, $CO_2CH_2CH_3$), 1.28 (t, J = 7.2 Hz, $CO_2CH_2CH_3$), 0.12 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 165.9 (*C*O_2Et), 149.5 (=*C*HCO$_2$Et), 134.1 (=*C*HSiMe$_3$), 60.5 (CO_2CH_2CH$_3$), 14.3 ($CO_2CH_2CH_3$), −1.8 ($Si(CH_3)_3$); GC−MS (M^+ = 172).

For **3d**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84−7.45 (m, Ar), 7.05 (d, J = 19.1 Hz, =C*H*Ar), 6.62 (d, J = 19.1 Hz, =C*H*SiMe$_3$), 0.20 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 143.7 (=*C*HAr), 137.0 (=*C*HSiMe$_3$), 135.9, 133.6, 133.3, 130.1, 128.2, 127.7, 126.5, 126.2, 125.8 and 123.4 (Ar carbons), −1.2 ($Si(CH_3)_3$); GC−MS (M^+ = 226).

For *trans*-**3e**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.02 (dt, J = 18.3, 7.8 Hz, =C*H*CH$_2$), 5.43 (dt, J = 18.3, 1.2 Hz, =C*H*SiMe$_3$), 1.63 (dd, J = 7.8, 1.2 Hz, =CHC*H*$_2$), 0.12 and 0.06 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 143.9 (=*C*HCH$_2$), 128.3 (=*C*HSiMe$_3$), 28.6 (=CH*C*H$_2$), −0.8 and −1.8 ($Si(CH_3)_3$); GC−MS (M^+ = 186).

For *cis*-**3e**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.40 (dt, J = 14.2, 7.8 Hz, =C*H*CH$_2$), 5.38 (d, J = 14.2 Hz, =C*H*SiMe$_3$), 1.78 (d, J = 7.8 Hz, =CHC*H*$_2$), 0.18 and 0.05 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 139.5 (=*C*HCH$_2$), 125.6 (=*C*HSiMe$_3$), 17.6 (=CH*C*H$_2$), −0.3 and −1.5 ($Si(CH_3)_3$); GC−MS (M^+ = 186).

For **3f**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.15 (m, Ph), 6.18 (dt, J = 18.3, 6.3 Hz, =C*H*CH$_2$), 5.72 (dt, J = 18.3, 1.8 Hz, =C*H*SiMe$_3$), 3.47 (d, J = 6.3 Hz, =CHC*H*$_2$), 0.08 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 145.3 (=*C*HCH$_2$), 140.2 (=*C*HSiMe$_3$), 131.7, 128.9, 128.6 and 126.2 (Ph carbons), 43.4 (=CH*C*H$_2$), −1.0 ($Si(CH_3)_3$); GC−MS (M^+ = 190).

For **3g**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.97 (dt, J = 18.6, 5.9 Hz, =C*H*CH$_2$), 5.61 (dt, J = 18.6, 1.5 Hz, =C*H*SiMe$_3$), 2.51 (t, J = 7.2 Hz, =CHCH$_2$C*H*$_2$), 2.33 (qt, J = 6.5, 1.5 Hz, =CHC*H*$_2$), 2.11 (s, $COCH_3$), −0.01 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 208.3 (*C*OCH_3), 144.9 (=*C*HCH$_2$), 131.7 (=*C*HSiMe$_3$), 42.6 (=CH*C*H$_2$), 30.6 (=CHCH$_2$*C*H$_2$), 23.2 (CO*C*H$_3$), −1.1 ($Si(CH_3)_3$); GC−MS (M^+ = 170).

For **3h**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.07 (dt, J = 18.3, 6.3 Hz, =C*H*CH$_2$), 5.63 (dt, J = 18.3, 1.5 Hz, =C*H*SiMe$_3$), 2.11 (m, =CHC*H*$_2$), 1.44−1.24 (m, =CHCH$_2$(C*H*$_2$)$_2$CH$_3$), 0.91 (t, J = 7.2 Hz, =CH(CH$_2$)$_3$C*H*$_3$), 0.06 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 147.9 (=*C*HCH$_2$), 125.9 (=*C*HSiMe$_3$), 29.8 (=CH*C*H$_2$), 23.6 and 18.9 (=CHCH$_2$(*C*H$_2$)$_2$CH$_3$), 14.3 (=CHCH$_2$-(CH$_2$)$_2$*C*H$_3$), −1.5 ($Si(CH_3)_3$); GC−MS (M^+ = 156).

For **3i**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45−6.88 (m, Ph), 6.91 (d, J = 18.6 Hz, Me$_3$SiCH=C*H*), 6.66 (s, =CHPh), 5.56 (d, J = 18.6 Hz, =C*H*SiMe$_3$), 0.09 (s, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 148.4 (d, J = 153.8 Hz, Me$_3$SiCH=*C*H), 142.9 and 138.2 (s, Ph$_{ipso}$), 136.8 (s, Ph*C*=CHPh), 132.4 (d, J = 133.7 Hz, =*C*HPh), 132.2, 129.7, 129.5, 128.7, 127.9 and 127.2 (Ph carbons), 126.9 (d, J = 161.6 Hz, Me$_3$Si*C*H=), −1.2 (q, J = 117.8 Hz, $Si(CH_3)_3$); GC−MS (M^+ = 278).

For **4f**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.15 (m, Ph), 6.43 (dt, J = 15.6, 1.2 Hz, =C*H*Ph), 6.26 (dt, J = 15.6, 6.0 Hz, =C*H*CH$_2$), 1.69 (m, =CHC*H*$_2$), 0.08 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 146.8 (=*C*HPh), 139.7 (=*C*HCH$_2$), 130.4, 128.5, 128.0 and 126.4 (Ph carbons), 39.8 (=CH*C*H$_2$), 0.5 ($Si(CH_3)_3$); GC−MS (M^+ = 190).

For **4g**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.50 (dtt, J = 15.0, 7.8, 1.2 Hz, Me$_3$SiCH$_2$CH=C*H*), 5.30 (dtt, J = 15.0, 7.8, 1.2 Hz, Me$_3$SiCH$_2$C*H*=CH), 3.05 (d, J = 7.8 Hz, =CHC*H*$_2$CO), 1.45 (dd, J = 7.8, 1.2 Hz, Me$_3$SiC*H*$_2$CH=), 2.10 (s, $COCH_3$), −0.04 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 207.9 (*C*OCH_3), 130.8 (=*C*HCH$_2$CO), 120.1 (Me$_3$SiCH$_2$*C*H=), 48.1 (=CH*C*H$_2$-CO), 30.0 (CO*C*H$_3$), 19.1 (Me$_3$Si*C*H$_2$CH=), −1.8 ($Si(CH_3)_3$); GC−MS (M^+ = 170).

For **4h**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.50−5.20 (m, Me$_3$Si-CH$_2$C*H*=C*H*), 1.96 (m, =CHC*H*$_2$), 1.48 (d, J = 6.3 Hz, Me$_3$-SiC*H*$_2$CH=), 1.42 (m, C*H*$_2$CH$_3$), 0.89 (t, J = 7.2 Hz, =CH-(CH$_2$)$_3$C*H*$_3$), 0.00 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 129.5 and 126.7 (Me$_3$SiCH$_2$*C*H=*C*H), 35.6 (=CH*C*H$_2$CH$_2$), 23.8 and 23.1 (*C*H$_2$CH$_3$ and *C*H$_2$SiMe$_3$), 14.1 (CH$_2$*C*H$_3$), −1.6 ($Si(CH_3)_3$); GC−MS (M^+ = 156).

Spectroscopic Observation of 5. In a J-Young NMR tube, **1a** (7.3 mg, 0.01 mmol) and 2 equiv of trichlorosilane were dissolved in C_6D_6. The tube was heated in an oil bath at 85 °C for 15 h, while the sample was periodically analyzed by NMR. The signals due to **5** and ethylene (δ 5.25 in ^{1}H NMR) began to appear after 1 h of heating. The complex **5** decomposed into an insoluble white solid upon removal of the solvent.

Selected spectroscopic data of **5**: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.6 MHz) δ 200.3 (t, J_{PC} = 10.5 Hz, CO), 35.8 (pseudo t, J_{PC} = 10.5 Hz, C_{ipso} of P(C_6H_{11})$_3$), 31.5 (d, J_{PC} = 176 Hz, C_{ortho} of P(C_6H_{11})$_3$), 28.3 (m, C_{meta} of P(C_6H_{11})$_3$), 27.0 (s, C_{para} of P(C_6H_{11})$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 125 MHz) δ 35.2 (s, PCy_3).

Crystallographic Structural Determination of 2b. Orange single crystals of **2b** suitable for X-ray crystallographic analysis were grown from CH_2Cl_2/hexanes solutions. The data collections were performed on a Siemens P4/CCD diffractometer. The crystallographic data are summarized in the Supporting Information. The space group $P\bar{1}$ yielded chemically reasonable and computationally stable results of the refinement. The structure was solved by using the direct method, completed by subsequent difference Fourier synthesis, and refined with full-matrix, least-squares procedures. The F(81)−F(86) of the anion were positionally disordered in a 50:50 distribution about F(1) and were refined isotropically. All non-hydrogen atoms were refined with anisotropic displacement parameters and were treated as idealized contributions. The relatively high R factor may be due to a high thermal activity associated with both the borate anion and the cyclohexyl groups and from the disorder of anion. All software and sources of the scattering factors are contained in the SHELXTL (version 5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. Financial support from the National Institutes of Health (R15 GM55987) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data of **5** (PDF). This material is available free of charge via the Internet at http//:pubs.acs.org.

OM000128P