

Kinetic Study on the Interconversion between (Silylacetylene)- and (β -Silylvinylidene)rhodium(I) Complexes

Hiroyuki Katayama, Kiyotaka Onitsuka,[†] and Fumiyuki Ozawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received May 13, 1996[⊗]

Summary: Kinetic studies on the interconversion between *trans*-RhCl(FcC≡CSiMe₃)(PPrⁱ)₂ (**2a**) and *trans*-RhCl{=C=C(Fc)(SiMe₃)}(PPrⁱ)₂ (**3a**) (Fc = ferrocenyl group) provided the following activation parameters for the forward and the backward reactions: $\Delta H^\ddagger = 19.8 \pm 0.2$ kcal mol⁻¹ and $\Delta S^\ddagger = -4.8 \pm 0.7$ eu for **2a** to **3a** and $\Delta H^\ddagger = 22.7 \pm 0.1$ kcal mol⁻¹ and $\Delta S^\ddagger = -8.6 \pm 0.4$ eu for **3a** to **2a**. The values are consistent with the isomerization mechanism via a sigmatropic 1,2-migration of the SiMe₃ group.

Introduction

Recently, we have reported the cyclocarbonylation of 1,1'-bis(trimethylsilyl)ethynylferrocene catalyzed by Ru₃(CO)₁₂.¹ The structure of the reaction product strongly suggested a catalytic process involving a (β -silylvinylidene)ruthenium intermediate which is generated from a silylferrocenylacetylene group bound to ruthenium. In connection with this novel catalytic reaction, we have been interested in the mechanism of interconversion of silylacetylenes to the corresponding vinylidene complexes.

There have been numerous reports concerning the isomerization of terminal acetylenes to vinylidene complexes.² On the other hand, the studies of formation of vinylidene complexes from silylacetylenes are still limited.³ With regard to the reaction mechanism, Werner et al. suggested a concerted process involving a 1,2-SiMe₃ group migration of silylacetylenes (RC≡CSiMe₃) coordinated to RhCl(PPrⁱ)₂, while no direct evidence was presented.^{3a} Connelly et al. carried out kinetic studies on the redox-induced interconversion between Cr(CO)₂(Me₃SiC≡CSiMe₃)(C₆Me₆) and Cr(CO)₂{=C=C-(SiMe₃)₂}(C₆Me₆) and proposed a similar reaction process involving a sigmatropic 1,2-shift of the SiMe₃ group.^{3b}

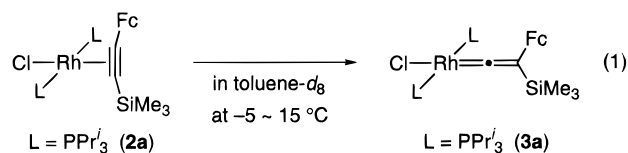
In this paper we examined the mechanism of interconversion of ((trimethylsilyl)ethynyl)ferrocene (FcC≡CSiMe₃; **1a**) to a (trimethylsilyl)ferrocenylvinylidene species. This study was initially undertaken with ruthenium systems related to the catalytic cyclocarbonylation. However, no appropriate systems for mechanistic investigations have been found. Therefore, we

employed the Werner system using RhCl(PPrⁱ)₂. The combination of **1a** and the Werner complex provided a convenient system to perform kinetic studies on the interconversion.

Results and Discussion

Isomerization of *trans*-RhCl(FcC≡CSiMe₃)(PPrⁱ)₂ (2a**) to *trans*-RhCl{=C=C(Fc)(SiMe₃)}(PPrⁱ)₂ (**3a**).** Treatment of RhCl(PPrⁱ)₂ with an equimolar amount of **1a** in toluene-*d*₈ at -20 °C instantly gave the acetylene complex *trans*-RhCl(FcC≡CSiMe₃)(PPrⁱ)₂ (**2a**) in quantitative yield, as confirmed by ¹H, ¹³C, and ³¹P NMR analysis of the reaction solution. Since complex **2a** was highly liable to isomerize to the corresponding vinylidene complex *trans*-RhCl{=C=C(Fc)(SiMe₃)}(PPrⁱ)₂ (**3a**), further investigations were carried out without isolation of **2a**.

The isomerization of **2a** to **3a** obeyed a first-order rate law in the concentration of **2a** over 3 half-lives, giving a quantitative yield of **3a**, which was isolated as a violet crystalline solid after recrystallization from a toluene/hexane solution (67%) and characterized by NMR spectroscopy and elemental analysis (eq 1). First-order



rate constants measured at four different temperatures are listed in Table 1. The reaction rate was independent of the initial concentration of **2a** (entries 4 and 5) and was little affected by addition of free **1a** to the system (entries 4 and 6), indicating an intramolecular process for the isomerization. The Eyring plot of the data in entries 1–4 was linear and led to the following activation parameters: $\Delta H^\ddagger = 19.8 \pm 0.2$ kcal mol⁻¹, $\Delta S^\ddagger = -4.8 \pm 0.7$ eu.

It has been shown that the stability of acetylene complexes and the ease of formation of vinylidene complexes are dependent mainly upon the electronic properties of the R groups of silylacetylenes (RC≡CSiMe₃).^{3a} For example, Me₃SiC≡CSiMe₃ (**1b**) forms no detectable amount of rhodium acetylene complex with RhCl(PPrⁱ)₂, while the formation of the corresponding vinylidene complex *trans*-RhCl{=C=C(SiMe₃)₂}(PPrⁱ)₂ (**3b**) proceeds readily even at low temperature. On the other hand, *trans*-RhCl(PhC≡CSiMe₃)(PPrⁱ)₂ (**2c**) is stable enough to be isolated at room temperature and its conversion to *trans*-RhCl{=C=C(Ph)(SiMe₃)}(PPrⁱ)₂

[†] Present address: The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1996.

(1) Onitsuka, K.; Katayama, H.; Sonogashira, K.; Ozawa, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2267.

(2) Bruce, M. I. *Chem. Rev.* **1991**, 91, 197.

(3) (a) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, 13, 1089. (b) Connelly, N. G.; Geiger, W. E.; Lagunas, M. C.; Metz, B.; Rieger, A. L.; Rieger, P. H.; Shaw, M. J. *J. Am. Chem. Soc.* **1995**, 117, 12202. (c) Sakurai, H.; Fujii, T.; Sakamoto, K. *Chem. Lett.* **1992**, 339. (d) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, 499, 35.

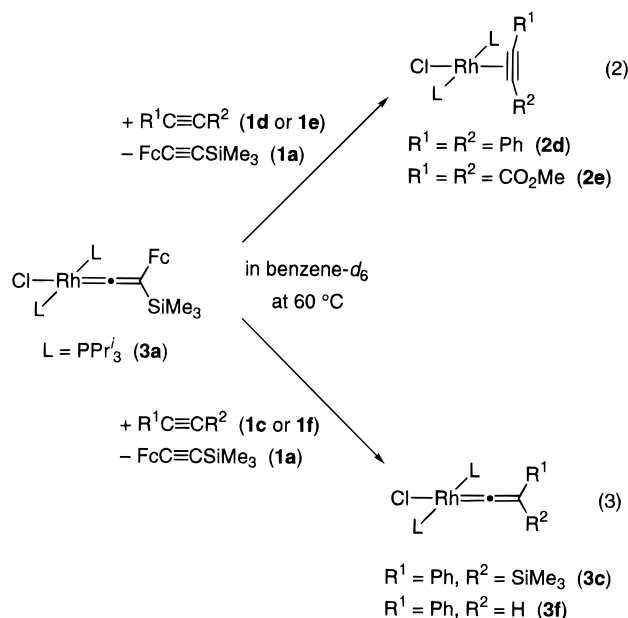
Table 1. Rates for the Isomerization of 2a to 3a^a

entry no.	temp (°C)	10 ⁴ k _{obsd} (s ⁻¹)	r ^b
1	-5.0	0.368	1.000
2	5.0	1.26	0.999
3	10.0	2.34	0.999
4	15.0	5.55	0.999
5 ^c	15.0	5.55	0.999
6 ^d	15.0	5.17	0.998

^a All reactions were carried out in toluene. The initial concentration of **2a** was 0.016 M, unless otherwise noted. ^b Correlation coefficient for the first-order plot. ^c The initial concentration of **2a** was 0.032 M. ^d The reaction was examined in the presence of 0.048 M of free FcC≡CSiMe₃ (**1a**).

(**3c**) requires heating.⁴ Silylferrocenylacetylene (**1a**) examined in this study possesses properties intermediate between those of Me₃SiC≡CSiMe₃ (**1b**) and PhC≡CSiMe₃ (**1c**).

Isomerization of trans-RhCl{=C=C(Fc)(SiMe₃)}-(PPrⁱ)₂ (3a**) to trans-RhCl(FcC≡CSiMe₃)(PPrⁱ)₂ (**2a**).** Complex **3a** was found to release the vinylidene ligand as the original acetylene **1a**. This reaction occurred instantly in benzene-*d*₆ at room temperature under a CO atmosphere.⁵ On the other hand, in the presence of free acetylenes, the reaction proceeded at elevated temperatures (eqs 2 and 3). The reactions of



3a with 10 equiv of internal acetylenes (PhC≡CPh (**1d**) and MeO₂CC≡CCO₂Me (**1e**)) in benzene-*d*₆ at 60 °C provided **1a** and the corresponding acetylene complexes (**2d** and **2e**, respectively) in quantitative yields (eq 2). The quantitative formation of **1a** was also observed when complex **3a** was treated with 10 equiv of silyl and terminal acetylenes (PhC≡CSiMe₃ (**1c**) and PhC≡CH (**1f**)) at 60 °C (eq 3). These reactions afforded the vinylidene complexes *trans*-RhCl{=C=C(Ph)(SiMe₃)}-(PPrⁱ)₂ (**3c**) and *trans*-RhCl{=C=C(H)(Ph)}(PPrⁱ)₂ (**3f**), respectively.

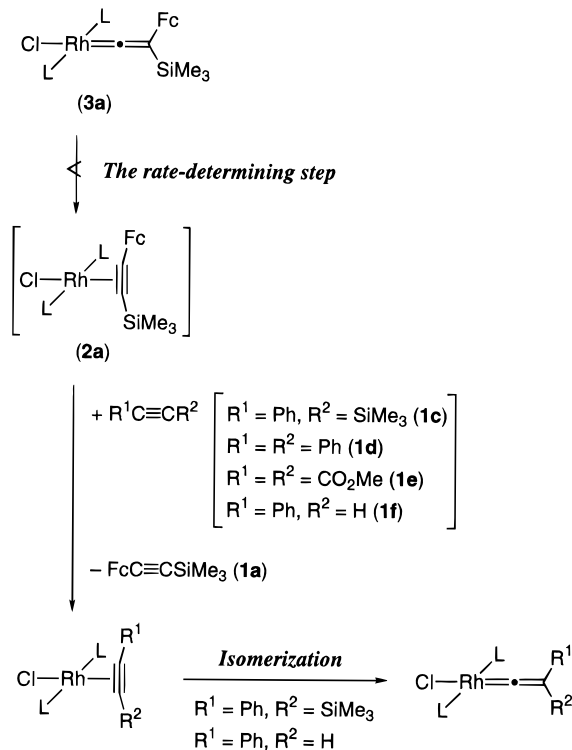
(4) We confirmed the first-order rate constant for the conversion of **2c** to **3c** to be 3.13 × 10⁻⁴ s⁻¹ (Δ*G*[‡] = 24.9 kcal mol⁻¹) at 60 °C in toluene.

(5) The CO-induced formation of acetylene from the corresponding vinylidene complex has been reported: (a) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49. (b) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156.

Table 2. Rates for the Reactions of 3a with Acetylenes^a

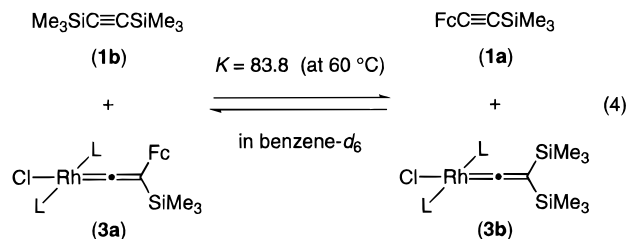
entry no.	acetylene [amt (equiv)]	temp (°C)	10 ⁴ k _{obsd} (s ⁻¹)	r ^b
1	PhC≡CPh (1d) [10]	60.0	1.27	0.997
2	PhC≡CPh (1d) [20]	60.0	1.26	0.999
3	MeO ₂ CC≡CCO ₂ Me (1e) [10]	60.0	1.86	1.000
4	PhC≡CH (1f) [10]	60.0	1.27	0.998
5	PhC≡CSiMe ₃ (1c) [10]	60.0	1.08	0.998
6	PhC≡CPh (1d) [10]	55.0	0.660	0.999
7	PhC≡CPh (1d) [10]	65.0	2.08	0.999
8	PhC≡CPh (1d) [10]	70.0	3.18	0.998

^a All reactions were carried out in benzene-*d*₆. The initial concentration of **3a** was 0.016 M. ^b Correlation coefficient for the first-order plot.

Scheme 1

The rates of the formation of **1a** in the presence of a variety of acetylenes are summarized in Table 2. Good first-order kinetics was observed for all the reactions examined. The reaction rate was little dependent upon the concentration and the sort of acetylenes (entries 1–5), indicating the reaction process initiated by the rate-determining isomerization of **3a** to **2a**, followed by a rapid ligand displacement of the resulting **2a** with added acetylenes (Scheme 1). The Eyring plot of the rate constants for the reactions with PhC≡CPh (Table 2, entries 1 and 6–8) provided the following activation parameters for the interconversion of **3a** to **2a**: Δ*F*[‡] = 22.7 ± 0.1 kcal mol⁻¹, Δ*S*[‡] = -8.6 ± 0.4 eu.

Relative stability of the three (β-silylvinylidene)-rhodium complexes (**3a–c**) was examined by crossover reactions of these complexes with the parent silylacetylenes (**1a–c**). Complex **3a** (0.0113 mmol) and acetylene **1b** (0.0154 mmol) were heated in benzene-*d*₆ at 60 °C for 1 day. ¹H NMR analysis of the reaction solution revealed the presence of **3a**, **3b**, **1a**, and **1b** in the ratio 0.10/3.48/3.71/1.54: *K*(**3b/3a**) = [**3b**][**1a**]/[**3a**][**1b**] = 83.8 (Δ*G*[‡]₃₃₃ = -2.9 kcal mol⁻¹) (eq 4). Almost the same equilibrium constant was obtained by starting from **3b** and **1a** in place of **3a** and **1b**, respectively. Similar sets



of experiments were performed between **3a** and **3c**, and between **3b** and **3c**, and the following equilibrium constants were estimated: $K(\mathbf{3a}/\mathbf{3c}) = 2.1$ ($\Delta G^\circ_{333} = -0.49$ kcal mol⁻¹), $K(\mathbf{3b}/\mathbf{3c}) = 142$ ($\Delta G^\circ_{333} = -3.3$ kcal mol⁻¹). Clearly, the thermodynamic stability of vinylidene complexes increases in the order **3c** < **3a** < **3b**.

Isomerization Mechanism. We could measure the activation parameters for both the forward and backward reactions between silylacetylene and β -silylvinylidene complexes (**2a** and **3a**, respectively). Scheme 2 illustrates the reaction coordinate. The simple kinetic features and the magnitude of activation entropies (-4.8 and -8.6 eu) observed in this study are in good accord with an isomerization mechanism with least motion; namely, the 1,2-SiMe₃ group shifts in a concerted fashion.⁶ This type of mechanism has been proposed independently by Werner and Connelly^{3a,b} and also predicted by Hoffmann using the EHMO calculations.⁷

It has been noted that the stability of (β -silylvinylidene)rhodium(I) complexes, *trans*-RhCl{ η^1 -C=C(R)-SiMe₃}₂(PPR'₃)₂, increases as the R substituent becomes more electron-donating (R = SiMe₃ > Fc > Ph). Since it is generally assumed that the transition metal-vinylidene bond is stabilized by π -back-donation from the filled d orbital to the empty p orbital on the α -vinylidene carbon,^{2,7} the stability order observed in this study is the reverse of the general assumption. Although we do not have an exact explanation for this unexpected observation, the particularly high stability of the bis(trimethylsilyl)vinylidene complex **3b** may be attributed in part to the great stabilization effect of the SiMe₃ groups via (σ -p) π -hyperconjugation.⁸

Experimental Section

General Procedure and Materials. All manipulations were carried out under an argon atmosphere using conventional Schlenk techniques. Argon gas was dried by passage through P₂O₅ (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-A400 spectrometer (¹H NMR, 399.65 MHz; ¹³C NMR, 100.40 MHz; ³¹P NMR, 161.70 MHz). Chemical shifts are reported in δ (ppm) referenced to an internal SiMe₄ standard for ¹H and ¹³C NMR and to an external 85% H₃PO₄ standard for ³¹P NMR.

Toluene, benzene, and hexane were dried over sodium benzophenone ketyl and distilled just before using. Benzene-*d*₆ and toluene-*d*₈ were dried over LiAlH₄, vacuum-transferred, and stored under an argon atmosphere. Triisopropylphosphine,⁹ [RhCl(PPR'₃)₂]₂,¹⁰ FcC≡CSiMe₃ (**1a**),¹¹ and *trans*-RhCl-

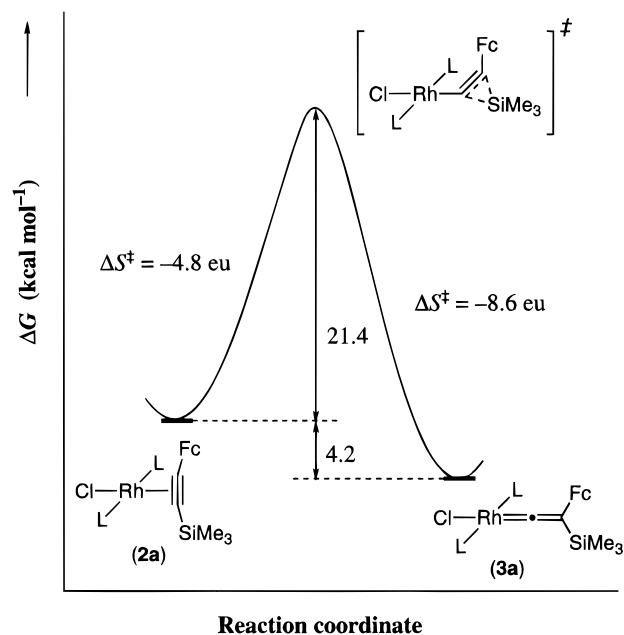
(6) The values of activation entropy are in the typical range for 1,2-sigmatropic shifts of silyl groups in pure organic systems ($\Delta S^\ddagger = -9.2$ to -3.8 eu): Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

(7) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(8) There is a possibility that σ -donation from the vinylidene ligand to the rhodium center predominates over the π -back-donation in the present 16-electron complexes. In this case, the vinylidene complex becomes more stable as the donating ability of the R substituent increases, consistent with the experimental observations. We thank a reviewer for bringing this possibility to our attention.

(9) Cowley, A. H.; Mills, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 2915.

Scheme 2



{ η^1 -C=C(R)(SiMe₃)₂}₂(PPR'₃)₂ (R = SiMe₃ (**3b**), Ph (**3c**))^{3a} were prepared according to the literature. All other compounds used in this study were obtained from commercial sources and used without further purification.

Preparation of *trans*-RhCl{FcC≡CSiMe₃}₂(PPR'₃)₂ (**2a**).

To a solution of [RhCl(PPR'₃)₂]₂ (30 mg, 33 mmol) in toluene-*d*₈ (1 mL) was added FcC≡CSiMe₃ (**1a**; 19 mg, 67 mmol) at -40 °C. A part of the solution (ca. 0.6 mL) was transferred into an NMR sample tube by means of a cannula at the same temperature. NMR analysis of the solution at -20 °C revealed the quantitative formation of **2a**. ¹H NMR (C₆D₅CD₃, -20 °C): δ 4.40 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C₅H₄), 3.98 (s, 5H, C₅H₅), 3.78 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C₅H₄), 2.38 (m, 6H, PCHCH₃), 1.28 (doublet of virtual triplets, $^3J_{\text{HH}} = 6.6$ Hz, $J = 6.8$ Hz, 12H, PCHCH₃), 1.20 (doublet of virtual triplets, $^3J_{\text{HH}} = 6.6$ Hz, $J = 6.5$ Hz, 12H, PCHCH₃), 0.41 (s, 9H, SiCH₃). ¹³C{¹H} NMR (C₆D₅CD₃, -20 °C): δ 105.1 (dt, $^1J_{\text{RhC}} = 18$ Hz, $^2J_{\text{PC}} = 3$ Hz, Me₃SiC≡C), 76.1 (d, $^1J_{\text{RhC}} = 14$ Hz, FcC≡C), 72.0 and 70.7 (both s, C₅H₄), 69.8 (s, C₅H₅), 68.2 (s, ipso C of C₅H₄), 22.2 (virtual triplet, $J = 9$ Hz, 12 PCHCH₃), 21.0 (s, PCHCH₃), 19.5 (s, PCHCH₃), 2.5 (s, SiCH₃). ³¹P{¹H} NMR (C₆D₅CD₃, -20 °C): δ 31.6 (d, $^1J_{\text{RhP}} = 119$ Hz).

Preparation of *trans*-RhCl{ η^1 -C=C(Fc)(SiMe₃)₂}₂(PPR'₃)₂ (**3a**).

The complex [RhCl(PPR'₃)₂]₂ (328 mg, 367 mmol) was placed in a Schlenk tube and dissolved in toluene (20 mL) at room temperature. FcC≡CSiMe₃ (**1a**; 214 mg, 758 mmol) was added at -20 °C, and the solution was stirred at room temperature for 2 h and then concentrated to dryness under reduced pressure. The resulting solid was dissolved in toluene (ca. 5 mL) at room temperature; this solution was diluted with hexane (ca. 7 mL) and allowed to stand at -70 °C overnight to give violet crystals of **3a** (381 mg, 67%). ¹H NMR (C₆D₆, room temp): δ 4.12 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C₅H₄), 4.04 (s, 5H, C₅H₅), 3.97 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C₅H₄), 2.79-2.71 (m, 6H, PCHCH₃), 1.36 (doublet of virtual triplets, $^3J_{\text{HH}} = 6.6$ Hz, $J = 7.1$ Hz, 12H, PCHCH₃), 1.34 (doublet of virtual triplets, $^3J_{\text{HH}} = 6.6$ Hz, $J = 7.1$ Hz, 12H, PCHCH₃), 0.44 (s, 9H, SiCH₃). ¹³C{¹H} NMR (C₆D₆, room temp): δ 284.5 (dt, $^1J_{\text{RhC}} = 61$ Hz, $^2J_{\text{PC}} = 15$ Hz,

(10) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395.

(11) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113.

(12) Apparent coupling constant for the virtual triplet signal.

C_o), 98.2 (dt, $^2J_{\text{RhC}} = 15$ Hz, $^3J_{\text{PC}} = 6$ Hz, C _{β}), 70.4 and 69.2 (both s, C₅H₄), 66.6 (s, C₅H₅), 66.1 (s, ipso C of C₅H₄), 24.5 (virtual triplet, $J = 9$ Hz, $^{12}\text{PCHCH}_3$), 21.1 and 20.9 (both s, PCHCH₃), 1.8 (s, SiCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, room temp): δ 42.4 (d, $^1J_{\text{RhP}} = 136$ Hz). Anal. Calcd for C₃₃H₆₀ClFeP₂-RhSi: C, 53.48; H, 8.16. Found: C, 53.56; H, 8.02.

Kinetic Studies on the Isomerization of 2a to 3a. A solution of **2a** (ca. 0.6 mL), which was prepared from [RhCl-(PPr^{*i*})₃]₂ (30 mg, 33 μmol) and FcC \equiv CSiMe₃ (**1a**; 19 mg, 67 μmol) in toluene (1 mL) at -40 °C, was placed in an NMR sample tube. The sample was placed in an NMR sample probe controlled to 15.0 \pm 0.1 °C and examined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The time course of the reaction was followed by measuring the relative peak integration of the signals of **2a** (δ 31.6) and **3a** (δ 42.4).

Kinetic Studies on the Reactions of 3a with Acetylenes. A typical procedure is as follows. Complex **3a** (11.7 mg, 16 μmol), PhC \equiv CPh (28.5 mg, 0.16 mmol), and MeSiPh₃ (8.3 mg, 30 μmol) were placed in a Schlenk tube and dissolved in benzene-*d*₆ (1 mL) at room temperature. A part of the solution (ca. 0.6 mL) was transferred into an NMR sample

tube, which was sealed under vacuum. The sample was placed in an NMR sample probe controlled to 60.0 \pm 0.1 °C and examined by ^1H NMR spectroscopy. The amount of FcC \equiv CSiMe₃ (**1a**) produced with time was determined by measuring the relative peak integration of the methyl signals of **1a** (δ 0.24) and MeSiPh₃ (δ 0.73). After completion of the reaction the sample solution was analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, showing the selective formation of *trans*-RhCl(PhC \equiv CPh)-(PPr^{*i*})₃ (δ 32.7; d, $^1J_{\text{RhP}} = 116$ Hz).¹³

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics (No. 07216261) from the Ministry of Education, Science, Sports and Culture of Japan. Partial financial support from Asahi Glass Foundation is gratefully acknowledged.

OM9603575

(13) Wang, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 4010.