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

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Summary: Kinetic studies on the interconversion between trans-$RhCl(FcC{\equiv}CSiMe_3)(PPr^i_3)_2$ *(**2a**) and trans-*$RhCl\{{=}C{=}C(Fc)(SiMe_3)\}(PPr^i_3)_2$ *(**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* $SiMe_3$ *group.*

Introduction

Recently, we have reported the cyclocarbonylation of 1,1′-bis((trimethylsilyl)ethynyl)ferrocene catalyzed by $Ru_3(CO)_{12}$.[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.

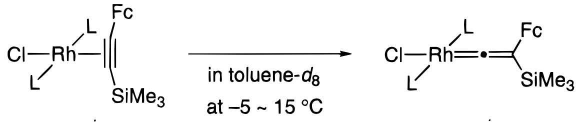
There have been numerous reports concerning the isomerization of terminal acetylenes to vinylidene complexes.[2] On the other hand, the studies of formation of vinylidene complexes from silylacetylenes are still limited.[3] With regard to the reaction mechanism, Werner et al. suggested a concerted process involving a 1,2-$SiMe_3$ group migration of silylacetylenes ($RC{\equiv}CSiMe_3$) coordinated to $RhCl(PPr^i_3)_2$, while no direct evidence was presented.[3a] Connelly et al. carried out kinetic studies on the redox-induced interconversion between $Cr(CO)_2(Me_3SiC{\equiv}CSiMe_3)(C_6Me_6)$ and $Cr(CO)_2\{{=}C{=}C(SiMe_3)_2\}(C_6Me_6)$ and proposed a similar reaction process involving a sigmatropic 1,2-shift of the $SiMe_3$ group.[3b]

In this paper we examined the mechanism of interconversion of ((trimethylsilyl)ethynyl)ferrocene ($FcC{\equiv}CSiMe_3$; **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 $RhCl(PPr^i_3)_2$. 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*-$RhCl(FcC{\equiv}CSiMe_3)(PPr^i_3)_2$ (2a) to *trans*-$RhCl\{{=}C{=}C(Fc)(SiMe_3)\}(PPr^i_3)_2$ (3a). Treatment of $RhCl(PPr^i_3)_2$ with an equimolar amount of **1a** in toluene-d_8 at −20 °C instantly gave the acetylene complex *trans*-$RhCl(FcC{\equiv}CSiMe_3)(PPr^i_3)_2$ (**2a**) in quantitative yield, as confirmed by ^1H, ^{13}C, and ^{31}P NMR analysis of the reaction solution. Since complex **2a** was highly liable to isomerize to the corresponding vinylidene complex *trans*-$RhCl\{{=}C{=}C(Fc)(SiMe_3)\}(PPr^i_3)_2$ (**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.



L = PPr^i_3 (**2a**) L = PPr^i_3 (**3a**) (1)

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 ($RC{\equiv}CSiMe_3$).[3a] For example, $Me_3SiC{\equiv}CSiMe_3$ (**1b**) forms no detectable amount of rhodium acetylene complex with $RhCl(PPr^i_3)_2$, while the formation of the corresponding vinylidene complex *trans*-$RhCl\{{=}C{=}C(SiMe_3)_2\}(PPr^i_3)_2$ (**3b**) proceeds readily even at low temperature. On the other hand, *trans*-$RhCl(PhC{\equiv}CSiMe_3)(PPr^i_3)_2$ (**2c**) is stable enough to be isolated at room temperature and its conversion to *trans*-$RhCl\{{=}C{=}C(Ph)(SiMe_3)\}(PPr^i_3)_2$

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(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.

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

entry no.	temp (°C)	10^4k_{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 $FcC{\equiv}CSiMe_3$ (**1a**).

(**3c**) requires heating.[4] Silylferrocenylacetylene (**1a**) examined in this study possesses properties intermediate between those of $Me_3SiC{\equiv}CSiMe_3$ (**1b**) and $PhC{\equiv}CSiMe_3$ (**1c**).

Isomerization of *trans*-RhCl{=C=C(Fc)(SiMe$_3$)}(PPr$^i_3$)$_2$ (3a) to *trans*-RhCl(FcC≡CSiMe$_3$)(PPr$^i_3$)$_2$ (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 ($PhC{\equiv}CPh$ (**1d**) and $MeO_2CC{\equiv}CCO_2Me$ (**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 ($PhC{\equiv}CSiMe_3$ (**1c**) and $PhC{\equiv}CH$ (**1f**)) at 60 °C (eq 3). These reactions afforded the vinylidene complexes *trans*-RhCl{=C=C(Ph)(SiMe$_3$)}(PPr$^i_3$)$_2$ (**3c**) and *trans*-RhCl{=C=C(H)(Ph)}(PPr$^i_3$)$_2$ (**3f**), respectively.

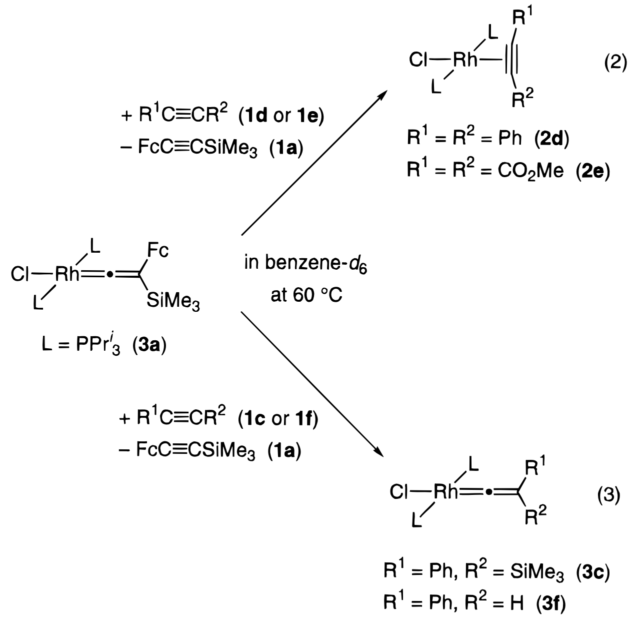
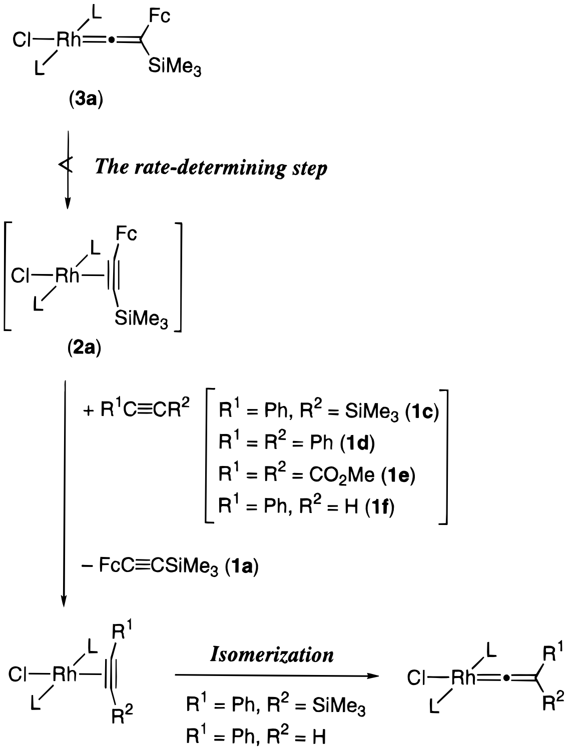


Table 2. Rates for the Reactions of 3a with Acetylenes[a]

entry no.	acetylene [amt (equiv)]	temp (°C)	10^4k_{obsd} (s^{-1})	r^b
1	$PhC{\equiv}CPh$ (**1d**) [10]	60.0	1.27	0.997
2	$PhC{\equiv}CPh$ (**1d**) [20]	60.0	1.26	0.999
3	$MeO_2CC{\equiv}CCO_2Me$ (**1e**) [10]	60.0	1.86	1.000
4	$PhC{\equiv}CH$ (**1f**) [10]	60.0	1.27	0.998
5	$PhC{\equiv}CSiMe_3$ (**1c**) [10]	60.0	1.08	0.998
6	$PhC{\equiv}CPh$ (**1d**) [10]	55.0	0.660	0.999
7	$PhC{\equiv}CPh$ (**1d**) [10]	65.0	2.08	0.999
8	$PhC{\equiv}CPh$ (**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 $PhC{\equiv}CPh$ (Table 2, entries 1 and 6−8) provided the following activation parameters for the interconversion of **3a** to **2a**: $\Delta H^{\ddagger} = 22.7 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8.6 \pm 0.4$ 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. ^{1}H 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: $K(\mathbf{3b}/\mathbf{3a}) = [\mathbf{3b}][\mathbf{1a}]/[\mathbf{3a}][\mathbf{1b}] = 83.8$ ($\Delta G^{\circ}_{333} = -2.9$ 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

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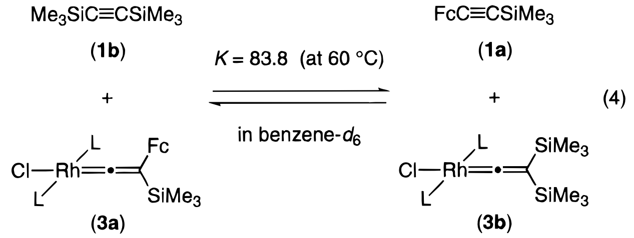
(4) We confirmed the first-order rate constant for the conversion of **2c** to **3c** to be 3.13×10^{-4} s^{-1} ($\Delta G^{\ddagger} = 24.9$ kcal mol^{-1}) at 60 °C in toluene.

(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.



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-$SiMe_3$ 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]

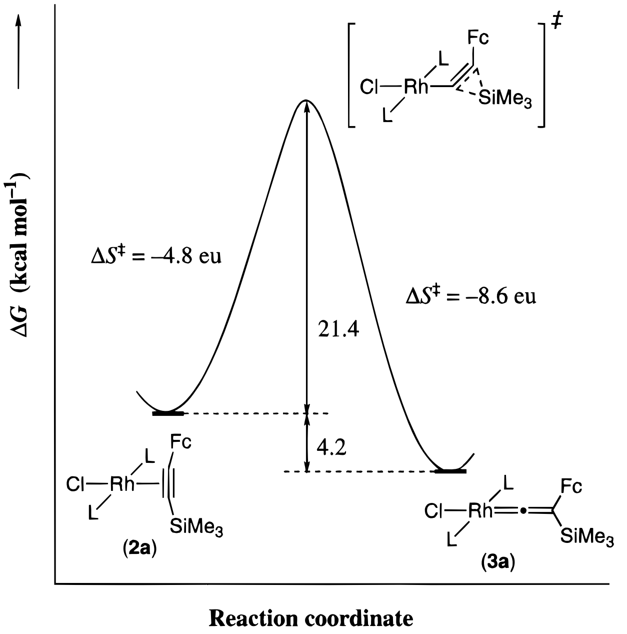
It has been noted that the stability of (β-silylvinylidene)rhodium(I) complexes, *trans*-RhCl{=C=C(R)($SiMe_3$)}$(PPr^{i}_{3})_2$, increases as the R substituent becomes more electron-donating (R = $SiMe_3$ > Fc > Ph). Since it is generally assumed that the transition metal–vinylidene bond is stabilized 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 $SiMe_3$ 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 P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^{1}H NMR, 399.65 MHz; ^{13}C NMR, 100.40 MHz; ^{31}P NMR, 161.70 MHz). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H and ^{13}C NMR and to an external 85% H_3PO_4 standard for ^{31}P 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 $LiAlH_4$, vacuum-transferred, and stored under an argon atmosphere. Triisopropylphosphine,[9] $[RhCl(PPr^{i}_{3})_2]_2$,[10] FcC≡C$SiMe_3$ (**1a**),[11] and *trans*-RhCl{=C=C(R)($SiMe_3$)}$(PPr^{i}_{3})_2$ (R = $SiMe_3$ (**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.

Scheme 2



Preparation of *trans*-RhCl(FcC≡CSiMe$_3$)(PPr$^i_3$)$_2$ (2a). To a solution of $[RhCl(PPr^{i}_{3})_2]_2$ (30 mg, 33 mmol) in toluene-d_8 (1 mL) was added FcC≡C$SiMe_3$ (**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**. ^{1}H NMR ($C_6D_5CD_3$, -20 °C): δ 4.40 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C_5H_4), 3.98 (s, 5H, C_5H_5), 3.78 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C_5H_4), 2.38 (m, 6H, PCHCH$_3$), 1.28 (doublet of virtual triplets, $^3J_{HH} = 6.6$ Hz, $J = 6.8$ Hz,[12] 18H, PCHCH_3), 1.20 (doublet of virtual triplets, $^3J_{HH} = 6.6$ Hz, $J = 6.5$ Hz,[12] 18H, PCHCH_3), 0.41 (s, 9H, SiCH_3). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, -20 °C): δ 105.1 (dt, $^1J_{RhC} = 18$ Hz, $^2J_{PC} = 3$ Hz, Me_3Si*C*≡C), 76.1 (d, $^1J_{RhC} = 14$ Hz, Fc*C*≡C), 72.0 and 70.7 (both s, C_5H_4), 69.8 (s, C_5H_5), 68.2 (s, ipso C of C_5H_4), 22.2 (virtual triplet, $J = 9$ Hz,[12] P*C*HCH$_3$), 21.0 (s, PCH*C*H$_3$), 19.5 (s, PCH*C*H$_3$), 2.5 (s, SiCH_3). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, -20 °C): δ 31.6 (d, $^1J_{RhP} = 119$ Hz).

Preparation of *trans*-RhCl{=C=C(Fc)(SiMe$_3$)}(PPr$^i_3$)$_2$ (3a). The complex $[RhCl(PPr^{i}_{3})_2]_2$ (328 mg, 367 mmol) was placed in a Schlenk tube and dissolved in toluene (20 mL) at room temperature. FcC≡C$SiMe_3$ (**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%). ^{1}H NMR (C_6D_6, room temp): δ 4.12 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C_5H_4), 4.04 (s, 5H, C_5H_5), 3.97 (apparent triplet, $J = 2.0$ Hz, 2H, two H of C_5H_4), 2.79–2.71 (m, 6H, PCHCH$_3$), 1.36 (doublet of virtual triplets, $^3J_{HH} = 6.6$ Hz, $J = 7.1$ Hz,[12] 18H, PCHCH_3), 1.34 (doublet of virtual triplets, $^3J_{HH} = 6.6$ Hz, $J = 7.1$ Hz,[12] 18H, PCHCH_3), 0.44 (s, 9H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6, room temp): δ 284.5 (dt, $^1J_{RhC} = 61$ Hz, $^2J_{PC} = 15$ Hz,

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[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.

[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_α), 98.2 (dt, $^2J_{RhC} = 15$ Hz, $^3J_{PC} = 6$ Hz, C_β), 70.4 and 69.2 (both s, C_5H_4), 66.6 (s, C_5H_5), 66.1 (s, ipso C of C_5H_4), 24.5 (virtual triplet, $J = 9$ Hz,[12] P*C*HCH$_3$), 21.1 and 20.9 (both s, PCH*C*H$_3$), 1.8 (s, SiCH$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, room temp): δ 42.4 (d, $^1J_{RhP} = 136$ Hz). Anal. Calcd for $C_{33}H_{60}ClFeP_2RhSi$: 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 $[RhCl(PPr^i_3)_2]_2$ (30 mg, 33 μmol) and FcC≡CSiMe$_3$ (**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 ± 0.1 °C and examined by $^{31}P\{^1H\}$ 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≡CPh (28.5 mg, 0.16 mmol), and MeSiPh$_3$ (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 ± 0.1 °C and examined by ^1H NMR spectroscopy. The amount of FcC≡CSiMe$_3$ (**1a**) produced with time was determined by measuring the relative peak integration of the methyl signals of **1a** (δ 0.24) and MeSiPh$_3$ (δ 0.73). After completion of the reaction the sample solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, showing the selective formation of *trans*-RhCl(PhC≡CPh)(PPr$^i_3$)$_2$ (δ 32.7; d, $^1J_{RhP} = 116$ Hz).[13]

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