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Isomers of Chloro(triarylsilyl)hydridorhodium(III) Complexes, *mer*-RhCl(H)(SiAr$_3$)(PMe$_3$)$_3$. Relevance of Their Structures to Reductive Elimination of ClSiAr$_3$

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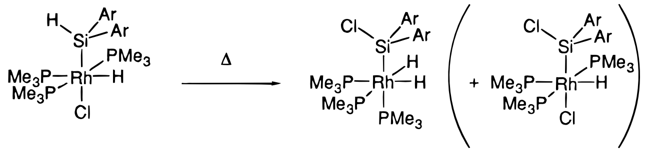
RhCl(PMe$_3$)$_3$ reacts with HSiPh$_3$ to give *mer*-RhCl(H)(SiPh$_3$)(PMe$_3$)$_3$ (**1**), whose X-ray structure shows octahedral coordination around the Rh(III) center with trans chloro and triphenylsilyl ligands. Reaction of HSi(C$_6$H$_4$CF$_3$-*p*)$_3$ with RhCl(PMe$_3$)$_3$ gives a mixture of Rh(III) complexes *mer*-RhCl(H){Si(C$_6$H$_4$CF$_3$-*p*)$_3$}(PMe$_3$)$_3$ (**2**), *fac*-RhH$_2${Si(C$_6$H$_4$CF$_3$-*p*)$_3$}(PMe$_3$)$_3$ (**3**), and *cis,mer*-RhCl$_2$(H)(PMe$_3$)$_3$ (**4**) with relative amounts that depend on the specific reaction conditions. X-ray crystallography of **2** shows that the Si(C$_6$H$_4$CF$_3$-*p*)$_3$ ligand is cis to both the H and Cl ligands. The differing chemical reactivity of **2** and **1** indicates the importance of the cis-configuration for reductive elimination of HSiAr$_3$ and ClSiAr$_3$ from the complexes.

Introduction

Reductive elimination of chloroalkane or chloroarene from the RhCl(H)(R)(PR′$_3$)$_n$-type complexes[1] is regarded as a crucial step in Rh complex catalyzed decarbonylation of acyl chloride to give alkyl or aryl chloride.[2] The reaction is much less common than the C−C bond-forming reaction from dialkyl transition-metal complexes and is often observed under the high-temperature conditions. On the other hand, Ir(III) and Pt(IV) complexes containing the chloro and organosilyl ligands have been reported to undergo smooth reductive elimination of chloroorganosilanes at room temperature.[3] The intramolecular coupling of the ligands seems to be significantly influenced by the coordination geometry. Recently, we have observed facile formation of chlorotriorganosilane from RhCl(H)(SiR$_3$)[P(*i*-Pr)$_3$]$_2$ containing a labile pentacoordinated metal center at room temperature.[4] On the other hand, *mer*-RhCl(H)(SiHAr$_2$)(PMe$_3$)$_3$, whose chloro and diarylsilyl ligands are at mutually trans positions of the rigid octahedral coordination, gives *fac*-RhH$_2$(SiClAr$_2$)(PMe$_3$)$_3$ as a product of the thermal reaction, as shown in Scheme 1.[5]

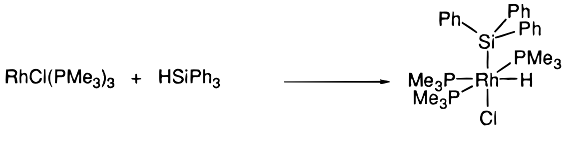
Scheme 1



Initial formation of ClSiHAr$_2$ and ensuing oxidative addition of its Si−H bond to the resulting RhH(PMe$_3$)$_3$ would account for generation of the (chlorodiaryl)silylrhodium(III) complex. In this paper, we report the preparation and structure of the chloro(triarylsilyl)rhodium(III) complexes containing the Cl and SiAr$_3$ ligands at cis or trans coordination sites and their different reactivity toward reductive-elimination reactions.

Results and Discussion

RhCl(PMe$_3$)$_3$ reacts with HSiPh$_3$ to give the oxidative-addition product *mer*-RhCl(H)(SiPh$_3$)(PMe$_3$)$_3$ (**1**) in 21% yield[6] after recrystallization from a toluene−pentane mixture, as shown in eq 1. X-ray crystallography of **1**



(1)

1

established the structure shown in Figure 1. The molecule has a slightly distorted octahedral coordination around the Rh center that is bonded to three meridional PMe$_3$ ligands and to chloro and triphenylsilyl ligands at mutually trans positions. Table 1 summarizes selected bond distances and angles of the molecule. The Rh−Si bond distance (2.346(2) Å) is shorter than that found in the structurally analogous complexes *mer*-Rh(SAr)H(SiPh$_3$)(PMe$_3$)$_3$ (2.38 Å),[7] indicating a smaller trans influence of the chloro ligand.

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(1) (a) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508. (b) Stille, J. K.; Fries, R. W. *Ibid.* **1974**, *96*, 1514. (c) Stille, J. K.; Huang, F.; Regan, M. T. *Ibid.* **1974**, *96*, 1518. (d) Lau, K. S. Y.; Huang, B. F.; Baenziger, N.; Stille, J. K. *Ibid.* **1977**, *99*, 5664. (e) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B. Jr. *Ibid.* **1981**, *103*, 1847.

(2) (a) Tsuji, J. *Organic Synthesis via Metal Carbonyls*; John Wiley: New York, 1977; Vol. 2, p 633. (b) Doughty, D. H.; Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1982; p 343.

(3) (a) Chalk A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Chalk, A. J. *J. Chem. Soc., Chem. Commun.* **1969**, 1207.

(4) (a) Osakada, K.; Koizumi, T.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 189. (b) Osakada, K.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 2063.

(5) Osakada, K.; Sarai, S.; Koizumi, T.; Yamamoto, T. *Organometallics* **1997**, *16*, 3973.

(6) The low isolated yield of **1** is due to a rapid and reversible equilibrium between the complex and Rh(I) complexes resulting from reductive elimination of HSiPh$_3$ from **1** in the solution. See, ref 9 also.

(7) Osakada, K.; Hataya, K.; Yamamoto, T. *Inorg. Chim. Acta* **1997**, *259*, 203.

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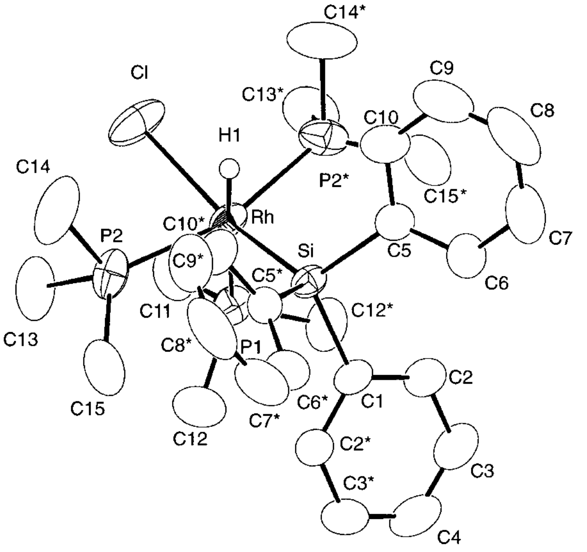


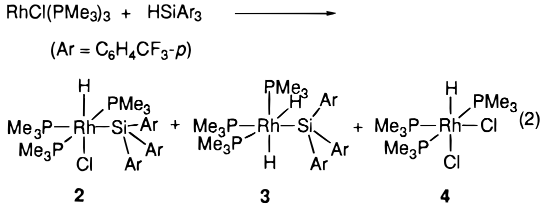
Figure 1. ORTEP drawing of *mer*-$RhCl(H)(SiPh_3)(PMe_3)_3$ (**1**) at the 30% ellipsoidal level. The crystal contains solvated toluene molecules. The molecule has a crystallographic mirror plane containing the Rh, Cl, and Si atoms as well as the P atom at a trans position to the hydrido. Atoms with asterisks are crystallographically equivalent to those with the same number without an asterisk. The hydrogen atoms, except for the hydrido and atoms in the solvent molecule, are omitted for simplicity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1, 2, and 3

	1	2	3
Rh−Cl	2.543(2)	2.463(7)	
Rh−P1	2.394(2)	2.387(8)	2.325(4)
Rh−P2	2.333(2)	2.327(4)	2.326(4)
Rh−P3			2.346(4)
Rh−Si	2.346(2)	2.377(8)	2.338(4)
Cl−Rh−P1	94.72(7)	94.4(3)	
Cl−Rh−P2	82.52(4)	83.4(1)	
P1−Rh−P2	93.00(4)	92.4(1)	100.2(1)
P2−Rh−P2*	164.29(7)	166.3(3)	
P1−Rh−P3			96.4(1)
P2−Rh−P3			99.8(1)
Si−Rh−Cl	161.19(7)	109.8(2)	
Si−Rh−P1	104.09(7)	155.7(3)	103.2(1)
Si−Rh−P2	96.30(4)	90.5(2)	145.6(1)
Si−Rh−P3			102.2(1)

The ^1H NMR spectrum of **1** in benzene-d_6 shows not only the peaks of **1** but those of the SiH and phenyl hydrogens of $HSiPh_3$ that are liberated from **1** through reductive elimination in solution. The ^1H NMR signal of the hydrido ligand at δ −9.49 has a large coupling constant (161 Hz) between the H and *trans*-P nuclei. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet of doublets and a doublet of triplets in ca. 2:1 peak area ratio similar to *mer*-$RhCl(H)(SiHAr_2)(PMe_3)_3$ and *mer*-$Rh(SAr)(H)(SiAr_3)(PMe_3)_3$.[7,8] The ^1H NMR spectrum of **1** at 25 °C in toluene-d_8 shows a SiH hydrogen peak (δ 5.70) whose relative intensity decreases on cooling the solution and is almost negligible at −70 °C. The temperature-dependent NMR spectra suggest that complex **1** is in a reversible equilibrium with a mixture of $HSiPh_3$ and Rh(I) complexes formed through reductive elimination of $HSiPh_3$. The data indicate that complex **1** is favored at lower temperatures.[9] Preferential formation of **1** among several possible isomers with the formula $RhCl(H)(SiPh_3)(PMe_3)_3$, despite the apparently facile reductive elimination of $HSiPh_3$ and its reoxidative addition, indicates that **1** has a greater thermodynamic stability. The oxidative-addition reactions of oxirane, HCl, and thiol to $RhCl(PMe_3)_3$ formed complexes containing the hydrido trans to PMe_3 as the thermodynamic products.[10] A theoretical study of the oxidative addition of $HSiR_3$ to $RhCl(PH_3)_2$ also suggests a higher stability of the product containing Cl and silyl ligands at trans sites.[11]

$HSi(C_6H_4CF_3\text{-}p)_3$ reacts with $RhCl(PMe_3)_3$ to produce Rh(III) complexes with different structures from **1**. The product contains a mixture of Rh(III) complexes, *mer*-$RhCl(H)\{Si(C_6H_4CF_3\text{-}p)_3\}(PMe_3)_3$ (**2**), *fac*-$RhH_2\{Si(C_6H_4CF_3\text{-}p)_3\}(PMe_3)_3$ (**3**), and *cis,mer*-$RhCl_2(H)(PMe_3)_3$ (**4**), as shown in eq 2. Concomitant formation of $ClSi(C_6H_4CF_3\text{-}p)_3$ and several uncharacterized Rh complexes in small amounts is also noted.[12]



The product ratio, obtained from relative ^1H NMR peak area ratios, depends on the initial molar ratio of $HSi(C_6H_4CF_3\text{-}p)_3$ and $RhCl(PMe_3)_3$. An equimolar reaction of $HSi(C_6H_4CF_3\text{-}p)_3$ and $RhCl(PMe_3)_3$ for 8 h gives **2** (20%) and **3** (33%) accompanied by recovery of $RhCl(PMe_3)_3$ (>25%). The reaction in a 2:1 molar ratio for a short period (15 min) results in formation of **2** (20%), **3** (24%), and **4** (8%). Increasing the ratio of $HSi(C_6H_4CF_3\text{-}p)_3$ and $RhCl(PMe_3)_3$ to 3:1 changes the yields of complexes **2**, **3**, and **4** to 11%, 78%, and 12%, respectively. The three Rh(III) products were isolated by fractional crystallization and characterized by means of X-ray crystallography as well as NMR spectroscopy.

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[8] Osakada, K.; Hataya, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1995**, 2315.

[9] The results of the temperature-dependent NMR measurement of **1** are as follows. The ^1H and $^{31}P\{^1H\}$ NMR spectra of a toluene-d_8 solution of the complex at −70 °C show the signals of **1** only. The $^{31}P\{^1H\}$ NMR spectrum at −30 °C shows a decrease in the amount of **1**, which is accompanied by the generation of a multitude of signals inclucing those due to $RhCl(PMe_3)_3$ (δ −1.13 and −12.47). At 25 °C, the $^{31}P\{^1H\}$ NMR spectrum shows the peaks due to **1** (δ −13.04 and −28.35) and a broad signal ($\nu_{1/2}$ = ca. 200 Hz) at δ −10. The latter signal is assigned to the Rh(I) complexes which undergo structural change on the NMR time scale, because Rh(III) complexes with PMe_3 ligands do not undergo such fluxional behavior in the NMR spectra at room temperature. The ^1H NMR spectrum at 25 °C shows a single broad peak at δ 1.19 assigned to the PMe_3 hydrogens of the Rh(I) complexes in addition to signals due to **1** and $HSiPh_3$. The fluxional behavior among the Rh(I) complexes may be attributed to reversible coordination of the SiH group of $HSiPh_3$ and its liberation.

[10] (a) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221 and references therein. (b) Sacco, A.; Ugo, R.; Moles, A. *J. Chem. Soc. A* **1966**, 1670. (c) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2067. (d) Osakada, K.; Hataya, K.; Yamamoto, T. *Inorg. Chem.* **1993**, *32*, 2360. (e) Osakada, K.; Hataya, K.; Yamamoto, T. *Organometallics* **1993**, *12*, 3358.

[11] Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 6883. See also: Jiménez-Catano, R.; Hall, M. B. *Organometallics* **1996**, *15*, 1889.

[12] Formation of $ClSi(C_6H_4CF_3\text{-}p)_3$ was confirmed by comparison of the $^{29}Si\{^1H\}$ NMR spectrum of the reaction mixture with that of the authentic sample. The presence of an isomer of *mer*-$RhCl(H)[Si(C_6H_4CF_3\text{-}p)_3](PMe_3)_3$, having the Cl and $Si(C_6H_4CF_3\text{-}p)_3$ ligands at mutually trans positions similar to **1**, in the reaction product cannot be excluded because the ^1H NMR spectrum of the crude product shows hydrido peaks due to several uncharacterized Rh(III) complexes also. Isolation and further characterization of these minor products were unsuccessful.

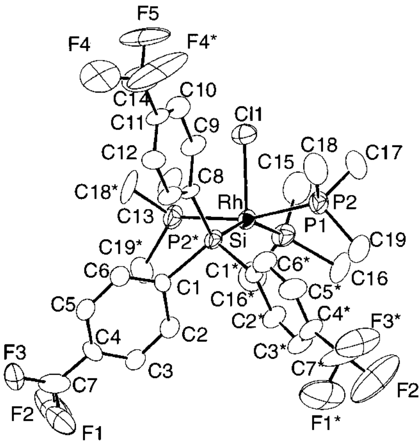


Figure 2. ORTEP drawing of *mer*-RhCl(H){Si($C_6H_4CF_3$-*p*)$_3$}(PMe_3)$_3$ (**2**) at the 50% ellipsoidal level. The crystal contains solvated hexane molecules. Atoms with asterisks are crystallographically equivalent to those with the same number without an asterisk. The hydrogen atoms and atoms in the solvent molecule are omitted for simplicity.

Complex **2** was obtained in a hexane-solvated form by repeated recrystallization of the product of the equimolar reaction. The coordination geometry around the Rh center of the complex shown in Figure 2 can be rationalized as a distorted octahedron having the triarylsilyl and chloro ligands at mutually cis positions and three PMe_3 ligands at meridional coordination sites; the hydrido ligand that should occupy the remaining site trans to the chloro ligand was not located in the final difference-Fourier map. Significantly distorted coordination with P1−Rh−Si (155.7(3)°) and Si−Rh−Cl (109.8(2)°) bond angles suggests severe steric congestion between triarylsilyl and PMe_3 or Cl ligands. The difference of the Rh−Si bond distances of **1** (2.346(2) Å) and **2** (2.377(8) Å) can be attributed to a smaller trans influence of the Cl than the PMe_3 ligand.[13] Dissolution of analytically pure crystals of **2** in benzene-d_6 produces a mixture containing **2**, **3**, **4**, and uncharacterized complexes. The ^{1}H NMR signal at δ −12.96 due to the hydrido ligand of **2** does not contain a P−H coupling constant larger than 100 Hz, indicating a structure with the three PMe_3 ligands all cis to the hydrido ligand.

Recrystallization of the product in the 3:1 reaction of HSi($C_6H_4CF_3$-*p*)$_3$ and RhCl(PMe_3)$_3$ led to preferential crystallization of **4**. Complex **3** is obtained from recrystallization of the product after removal of **4** and characterized by X-ray crystallography, as shown in Figure 3. The PMe_3 ligands occupy three facial coordination sites of a highly distorted octahedron. The presence of two equivalent hydrido ligands was indicated by the ^{1}H NMR spectrum, which shows the hydrido peak at δ −10.47 with a similar coupling pattern to *fac*-RhH_2($SiClPh_2$)(PMe_3)$_3$.[5] X-ray crystallography and NMR data of **4** show a structure having two chloro ligands at mutually cis positions and three PMe_3 ligands at meridional coordination sites (Supporting Information).

Scheme 2 depicts a plausible pathway of the reaction of HSi($C_6H_4CF_3$-*p*)$_3$ and RhCl(PMe_3)$_3$ to give **2** and **3**. Initial oxidative addition of HSi($C_6H_4CF_3$-*p*)$_3$ to the Rh-

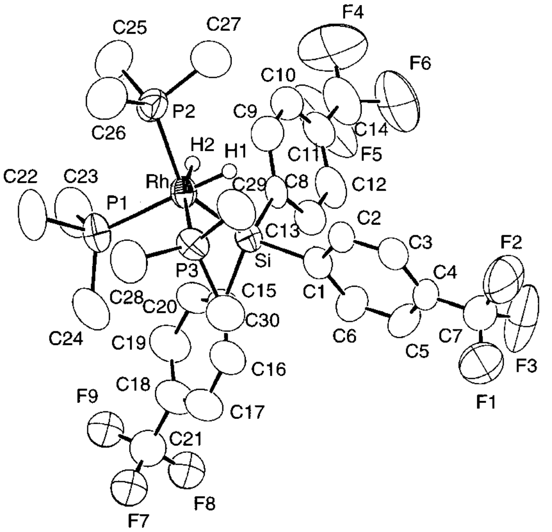


Figure 3. ORTEP drawing of *fac*-Rh(H)$_2${Si($C_6H_4CF_3$-*p*)$_3$}(PMe_3)$_3$ (**3**) at the 30% ellipsoidal level. The crystal contains solvated hexane molecules. The hydrogen atoms, except for hydrido ligands and atoms in the solvent molecule, are omitted for simplicity. One of the two disordered positions of F7−F9 are shown.

Scheme 2

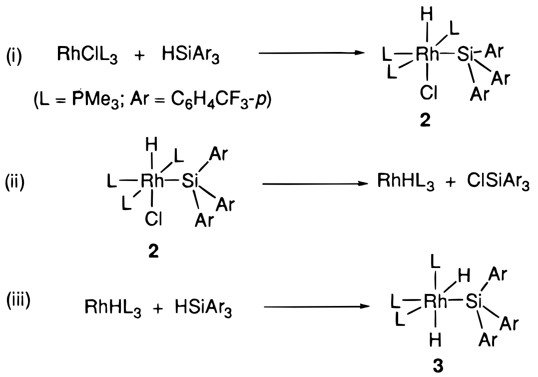
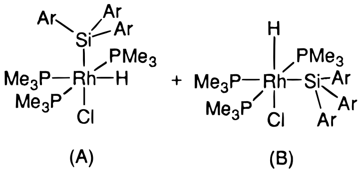


Chart 1



(I) complex gives **2**, which undergoes coupling of the chloro and triarylsilyl ligands to afford RhH(PMe_3)$_3$. The resulting hydridorhodium(I) complex reacts with the HSi($C_6H_4CF_3$-*p*)$_3$ contained in the reaction mixture to afford **3**. The above mechanism is consistent with the results that complex **1**, having trans Cl and $SiPh_3$ ligands, is not converted into other Rh(III) complexes in the solution containing $HSiPh_3$ at room temperature.

As described above, the Rh(III) complexes formulated as RhCl(H)($SiAr_3$)(PMe_3)$_3$ undergo reductive elimination of $HSiAr_3$ and/or $ClSiAr_3$ depending on the coordination geometry. Oxidative addition of triarylsilane to RhCl(PMe_3)$_3$ could provide two isomeric Rh(III) complexes **A** and **B** having three meridional PMe_3 ligands, as shown in Chart 1.

The complex with structure **A** undergoes reductive elimination of $HSiAr_3$ followed by its rapid reoxidative

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[13] Elongation of Rh−Si bond is not due to the presence of the CF_3 group on the phenyl group because the substituent on the aryl group, X, of RhCl(H){SiH(C_6H_4X-*p*)$_2$}(PMe_3)$_3$ has been reported to influence the Rh−Si bond distance to a negligible extent. See, ref 5.

Table 2. Crystal Data and Details of the Structure Refinement of 1, 2, and 3

compound	$\mathbf{1}\cdot C_7H_8$	$\mathbf{2}\cdot C_6H_{14}$	$\mathbf{3}\cdot 0.5C_6H_{14}$
formula	$C_{34}H_{51}ClP_3RhSi$	$C_{36}H_{54}ClF_9P_3RhSi$	$C_{33}H_{48}F_9P_3RhSi$
mol wt	719.14	917.18	839.64
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pnma* (No. 62)	*Pnma* (No. 62)	$P2_1/n$ (No. 14)
a (Å)	23.746(9)	12.121(4)	13.387(7)
b (Å)	14.641(6)	20.461(7)	21.547(9)
c (Å)	10.483(2)	17.684(7)	14.162(10)
β (deg)			100.74(4)
V (Å^3)	3644	4385	4013
Z	4	4	4
μ (cm^{-1})	7.27	6.39	6.27
F(000)	1504	1888	1724
D_{calcd} (g cm^{-3})	1.311	1.390	1.390
cryst size (mm × mm × mm)	0.3 × 0.4 × 0.4	0.3 × 0.5 × 0.5	0.4 × 0.5 × 0.6
2θ range (deg)	5.0−55.0	5.0−50.0	5.0−55.0
no. of unique reflns	5354	3057	9454
no. of reflns used	2166	1459	3635
no. of variables	205	258	415
R	0.049	0.070	0.077
R_w	0.039	0.072	0.078

^{a} Weighting scheme: $[\sigma(F_o)^2]^{-1}$.

addition. Structure **B** has the Cl, H, and SiAr$_3$ ligands at the coordination sites which are suited for direct reductive elimination of both HSiAr$_3$ and ClSiAr$_3$. Liberation of ClSiAr$_3$ from **2** with structure **B** seems to occur through an intramolecular pathway, while complex **1** with structure **A** does not undergo direct coupling of the ligands at mutually trans positions. The present study shows that the structure of the product of the oxidative addition of an Si−H bond in HSiAr$_3$ depends on the substituent on the aryl group.

Experimental Section

General, Measurements, and Materials. Manipulations of the metal complexes were carried out under nitrogen or argon using standard Schlenk techniques. RhCl(PMe$_3$)$_3$ and HSi(C$_6$H$_4$CF$_3$-*p*)$_3$ were prepared according to the literature methods.[14] Other chemicals were used as received from commercial suppliers. IR and NMR spectra (^{1}H and ^{31}P) were recorded on a JASCO810 spectrophotometer and on a JEOL EX-400 spectrometer, respectively. Peak positions of the ^{31}P{^{1}H} NMR spectra were referenced to external 85% H$_3$PO$_4$. Elemental analyses were carried out on a Yanaco MT-5 CHN autocorder and on a Yanaco YS-10 by ion chromatography.

Reaction of HSiPh$_3$ with RhCl(PMe$_3$)$_3$. To a pentane (3 mL) dispersion of RhCl(PMe$_3$)$_3$ (151 mg, 0.41 mmol) was added HSiPh$_3$ (107 mg, 0.41 mmol) at room temperature to lead to dissolution of the complex. The solution changed color from orange to colorless, which was accompanied by a gradual deposition of a colorless solid. After 8 h, the separated solid product was collected by filtration and dried in vacuo. Recrystallization from a toluene−pentane mixture gave **1** as a toluene-solvated form (61 mg, 21%). Anal. Calcd for $C_{34}H_{51}ClP_3RhSi$: C, 56.79; H, 7.15; Cl, 4.93. Found: C, 56.72; H, 7.07; Cl, 4.89. IR (cm^{-1}, KBr): 1930 (ν(Rh−H)).

The ^{1}H NMR spectrum at 25 °C showed the presence of **1** and HSiPh$_3$ in a 48:52 molar ratio. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −9.49 (ddt, 1H, RhH, J(RhH) = 13 Hz, J(HP$_{trans}$) = 161 Hz, J(HP$_{cis}$) = 18 Hz), 0.96 (d, 9H, P(CH$_3$)$_3$, J(PH) = 7 Hz), 1.23 (apparent triplet due to virtual coupling, 18H, P(CH$_3$)$_3$), 7.90 (d, 6H, C$_6$H$_5$(*ortho*), J (HH) = 7 Hz, J(HSi) = 90 Hz). The signal due to the meta and para hydrogens of the phenyl group is overlapped with the signals due to HSiPh$_3$. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 160 MHz): δ −13.04 (dd, J(PP) = 31 Hz, J(PRh) = 102 Hz), −28.35 (dt, J(PP) = 31 Hz, J(PRh) = 94 Hz).

Reactions of HSi(C$_6$H$_4$CF$_3$-*p*)$_3$ with RhCl(PMe$_3$)$_3$. (a) 1:1 and 2:1 Reactions. To a pentane (3 mL) dispersion of RhCl(PMe$_3$)$_3$ (157 mg, 0.43 mmol) was added HSi(C$_6$H$_4$CF$_3$-*p*)$_3$ (198 mg, 0.43 mmol) in one portion at room temperature. The orange solid dispersed in, and the solvent gradually turned colorless upon stirring. After 8 h, the resulting pale yellow solid was collected by filtration, washed with a minimum amount of pentane, and dried in vacuo (359 mg). The^{1}H and ^{31}P{^{1}H} NMR spectra of the solid product showed the presence of **2** (20%) and **3** (33%) in addition to several uncharacterized products and unreacted RhCl(PMe$_3$)$_3$ (>25%). Recrystallization from a toluene−hexane mixture gave **2** in a hexane-solvated form as colorless crystals (12%). Anal. Calcd for $C_{36}H_{54}ClF_9P_3RhSi$: C, 47.14; H, 5.93, Cl, 3.86; F, 18.64. Found: C, 47.15; H, 5.86; Cl, 3.73; F, 18.27. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −17.29 (ddt, 1H, RhH, J(RhH) = 21 Hz, J(HP) = 18, 18, and 15 Hz), 1.13 (d, 9H, P(CH$_3$)$_3$, J(HP) = 6 Hz), 1.30 (triplet due to virtual coupling, 18H, P(CH$_3$)$_3$), 7.40 (d, 6H, C$_6$H$_4$(*meta*), J = 9 Hz), 7.69 (d, 6H, C$_6$H$_4$(*ortho*), J = 7 Hz).

Although the isolated crystalline **2** gave satisfactory elemental analyses and X-ray diffraction data, dissolution of the crystals in benzene-d_6 caused an immediate change into a mixture of **2**, **3**, **4**, and other uncharacterized Rh(III) complexes. The above NMR data of **2** was obtained from the mixture. The partial conversion of **2** into other Rh complexes in solution is significantly retarded by addition of HSi(C$_6$H$_4$-CF$_3$-*p*)$_3$.

Similar reaction in a 2:1 molar ratio for 15 min at room temperature gave a mixture of **2** (20%), **3** (24%), and **4** (8%) in addition to several uncharacterized complexes.

(b) 3:1 Reaction. To a THF (3 mL) solution of RhCl(PMe$_3$)$_3$ (186 mg, 0.51 mmol) was added HSi(C$_6$H$_4$CF$_3$-*p*)$_3$ (708 mg, 1.5 mmol) at room temperature. Stirring the solution caused a color change from orange to colorless. After 8 h, the solvent was evaporated to dryness. Addition of pentane (10 mL) to the resulting viscous product caused separation of a colorless solid (357 mg). The ^{1}H NMR spectrum indicated the presence of **2** (11%), **3** (78%), and **4** (12%).

Recrystallization of the product from a THF−pentane mixture caused preferential separation of **4** as crystals (11%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −17.20 (ddt, 1H, RhH, J(HRh) = 21 Hz, J(HP) = 18 and 15 Hz), 0.95 (d, 9H, P(CH$_3$)$_3$, J(HP) = 10 Hz), 1.40 (triplet due to virtual coupling, 18H, P(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (160 MHz in C$_6$D$_6$): δ −6.75 (dd, J(PP) = 31 Hz, J(PRh) = 94 Hz), 6.57 (dt, J(PP) = 31 Hz, J(PRh) = 133 Hz).

The filtrate of the above recrystallization was evaporated to dryness. Addition of pentane to the resulting yellow paste led to the separation of **3** as a colorless solid. Anal. Calcd for $C_{30}H_{41}F_9P_3RhSi$: C, 45.24; H, 5.19. Found: C, 45.74; H, 5.80. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −10.47 (m, 2H, RhH, J(HP) = 116 Hz), 0.65 (d, 27H, P(CH$_3$)$_3$, J(HP) = 7 Hz), 7.45 (d, 6H, C$_6$H$_4$(*meta*)), 7.78 (d, 6H, C$_6$H$_4$(*ortho*)). ^{31}P{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ −19.77 (dd, J(PP) = 23 Hz, J(PRh) = 98 Hz), −25.07 (dt, J(PP) = 23 Hz, J(PRh) = 90 Hz). Further recrystallization from a toluene−hexane mixture afforded single crystals of $\mathbf{3}\cdot 0.5\,C_6H_{14}$, which was characterized by X-ray crystallography.

Crystal Structure Determination. Crystals were mounted in a glass capillary tube under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with 25° ≤ 2θ ≤ 35°. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and the $\omega-2\theta$ method. An empirical absorption correction (ψ scan method) of the collected data was applied. Crystal data

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and details of the structure refinement are summarized in Table 2. Calculations were carried out by using the teXsan program package on a VAX-II computer. Atomic scattering factors were taken from the literature.[15] A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms except for the RhH hydrogen were located by assuming ideal positions ($d = 0.95$ Å) and were included in the structure calculation without further refinement of the parameters. The positions of the RhH hydrogen of **1** and **3** were determined with the difference Fourier technique and included in the calculation with isotropic thermal factors (**1**) or without further refinement of the parameters (**3**). The RhH hydrogen of **2** was not located due to insufficient convergence of the structural calculation. A CF_3 group in a molecule of **3** has three F atoms (F7−F9) at two disordered positions with 50% probability. The corresponding C and F atoms and the C atoms of the solvent in **3** were refined isotropically.

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Supporting Information Available: Tables of positional parameters, thermal parameters, and bond distances and angles of **1**, **2**, and **3** and the results of crystallography of **4** (26 pages). Ordering information is given on any current masthead page.

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(15) *International Tables for X-ray Crystallography;* Kynoch: Birmingham, England, 1974; Vol. IV.