Si–H and Si–C Bond Activation of a Triorganosilane Promoted by $[RhCl\{P(i\text{-}Pr)_3\}_2]$. Synthesis and Structure of a Dinuclear Rh(IV) Complex with μ-Silylene Ligands

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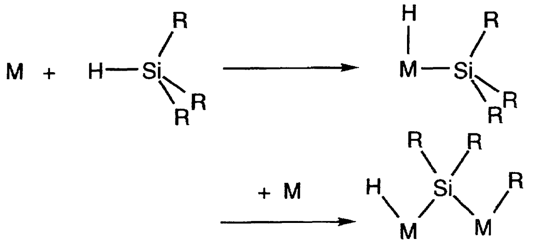
$[RhClL_2]$ ($L = P(i\text{-}Pr)_3$) reacts with tris(2-phenylethyl)silane in pentane to give a dinuclear Rh(IV) complex, $[LRh(H)_2\{\mu\text{-}Si(CH_2CH_2Ph)_2\}_2Rh(H)_2L]$ (**1**), and several organic products including ethylbenzene, chloro{tris(2-phenylethyl)}silane, and tetrakis(2-phenylethyl)silane. Results of X-ray crystallography and NMR study of **1** indicate a symmetrical molecular structure containing two Rh(IV) centers which are bonded to each other through two bridging silylene ligands. [**1**, triclinic, space group $P\bar{1}$ with $a = 12.886(4)$, $b = 13.217(3)$, $c = 10.388(3)$ Å, $\alpha = 104.78(2)$, $\beta = 106.50(2)$, $\gamma = 61.70(2)°$, $V = 1478$ Å^3, $Z = 1$, $R = 0.073$, $R_w = 0.081$ for 3930 reflections with $I > 3\sigma(I)$ and 289 variables]. The initial reaction products contain mononuclear Rh(III) complexes, $[RhCl(H)_2L_2]$ (**2**) and $[RhCl(H)\{Si(CH_2CH_2Ph)_3\}L_2]$ (**3**), the latter of which is turned into **1** on further stirring. Reactions of tribenzylsilane and of tris(p-methylbenzyl)silane with $[RhClL_2]$ cause immediate separation of $[RhL(R_3Si)H(\mu\text{-}Cl)_2RhH(SiR_3)L]$ (**4**: $R = CH_2Ph$, **5**: $R = CH_2C_6H_4Me\text{-}p$). X-Ray crystallography of **4** has revealed the structure containing two Rh(III) centers with distorted trigonal bipyramidal coordination [**4**, monoclinic, space group $P2_1/n$ with $a = 11.513(3)$, $b = 28.227(9)$, $c = 20.883(5)$ Å, $\beta = 94.14(2)°$, $V = 6769$ Å^3, $Z = 4$, $R = 0.071$, $R_w = 0.066$ for 4249 reflections with $I > 3\sigma(I)$ and 637 variables]. A prolonged reaction of tribenzylsilane leads to formation of chlorotribenzylsilane.

Transition metal complex-promoted activation of Si–C bond of organosilanes[1—7] is of significant interest relevant to the mechanisms of metal complex-catalyzed synthetic organic reactions involving transfer of an organic group bonded to an Si atom.[8—14] Oxidative addition of Si–C bond to low valent transition metals seems to be more facile than that of C–C bond, owing to smaller dissociation energy of Si–C bond than of C–C bond, and also to thermodynamically more stable M–Si bond than M–C bond.[15,16] Some dinuclear Pt and Ru complexes with organosilyl ligands undergo oxidative addition of an Si–C bond of the ligand to another metal center to give a bridging silylene ligand.[1,7] These reported results suggest to us a possible reaction of metal complex and $HSiR_3$ to result in formation of silylene bridged dinuclear complexes through initial formation of a triorganosilyl metal complex, followed by oxidative addition of an Si–C bond to the metal center of another complex, as shown in Scheme 1. Such a reaction would provide an alternative preparation method of μ–silylene complexes that have been commonly prepared from oxidative addition of two Si–H bonds of H_2SiR_2 or an Si–Si and an Si–H bond of HR_2SiSiR_2H to two transition metal centers.[17—25]

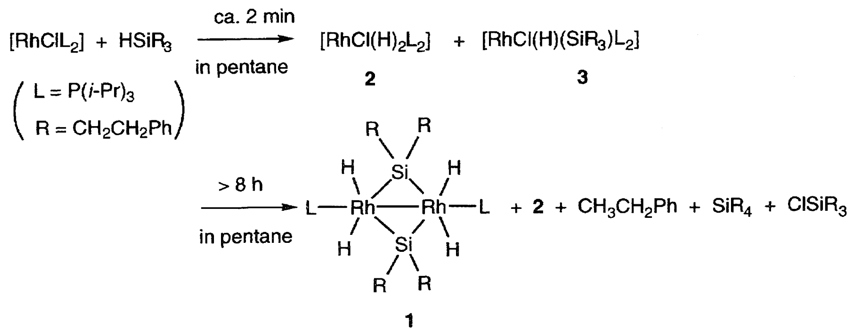
Here we report the reaction of tris(2-phenylethyl)silane with $[RhClL_2]$ ($L = P(i\text{-}Pr)_3$) to afford a novel dinuclear Rh(IV) complex with bridging silylene ligands through Si–H and Si–C bond cleavage. Reactions of tribenzylsilane and of tris(p-methylbenzyl)silane with the Rh(I) complex are also described.



Scheme 1. Schematic drawing for possible formation of bimetallic transition metal complexes with μ-silylene ligands through Si–H and ensuing Si–C bond cleavage.

Results and Discussion

Reaction of $HSi(CH_2CH_2Ph)_3$ with $[RhClL_2]$ and Structure of $[RhL(H)_2\{\mu\text{-}Si(CH_2CH_2Ph)_2\}_2Rh(H)_2L]$ (1). Scheme 2 summarizes results of 2 : 1 reaction of $HSi(CH_2CH_2Ph)_3$ with $RhClL_2$ to give a dinuclear Rh(IV) complex, $[RhL(H)_2\{\mu\text{-}Si(CH_2CH_2Ph)_2\}_2 Rh(H)_2L]$ (**1**), in 22% isolated yield after 8 h. ^{1}H NMR analysis of the reaction mixture shows the presence of $[RhCl(H)_2(L)_2]$ (**2**), ethylbenzene (26%), chloro{tris(2-phenylethyl)}silane (79% based on Rh), tetrakis(2-phenylethyl)silane (53% based on Rh) and the phosphine ligand also. The initial reaction products contain mononuclear Rh(III) complexes **2** and $[RhCl(H)\{Si(CH_2CH_2Ph)_3\}L_2]$ (**3**), as shown below. The ^{1}H NMR



Scheme 2. Products in reaction of tris(2-phenylethyl)silane with [RhCl{P(i-Pr)$_3$}$_2$] in pentane.

spectrum of a yellow solid product separated out from the reaction mixture after initial (2 min) stirring shows hydrido signals at −22.76 ppm and at −16.63 ppm. The former signal agrees with that of **2** prepared separately.[26] The latter hydrido signal (triplet of doublet with J(HRh) = 22 Hz, J(HP) = 13 Hz) and the ^{31}P{^{1}H} NMR peaks (doublet at 41.8 ppm with J(PRh) = 121 Hz) is assigned to **3** by similarity of the peak positions and coupling constants with [RhCl(H)(SiAr$_3$)L$_2$] (Ar = Ph, C$_6$H$_4$F-p) that have been fully characterized.[27] The ratio of **2** and **3** obtained is 23 : 77.

There have been only a few reports on organorhodium(IV) complexes[28] and no reports on silylene bridged dinuclear Rh(IV) complexes. Figure 1 shows molecular structure of **1** determined by X-ray crystallography. The molecule has a crystallographic C_2 symmetry around the center of a Rh$_2$Si$_2$ four-membered ring. Tables 1 and 2 summarize crystallographic data and selected bond distances and angles of the complex, respectively. Already reported Rh(IV) complexes with bridging CH$_2$ ligands, ([Rh(Cp*)$_2$Me(μ-CH$_2$)$_2$RhMe(Cp*)$_2$] (2.620 Å) and [Rh(Cp*)$_2$(CO)(μ-CH$_2$)$_2$Rh(CO)(Cp*)$_2$](BF$_4$)$_2$ (2.659 Å)),[28b,28d] have shorter Rh–Rh distances than **1**. On the other hand, several dinuclear Rh(I) ([Rh$_2$(SiHPh)$_2$(CO)$_2$(dppm)$_2$] (2.810 Å)[20a] and [Rh$_2$(SiHEt)$_2$(CO)$_2$(dppm)$_2$] (2.814 Å)[20b]) and Rh(II) complexes ([Rh$_2$H(CO)$_2$(dppm)(Ph$_2$PCH$_2$PPhSiEt)] (2.889 Å))[20b] have comparable Rh–Rh bonding distances to **1**. Rh–Si bond distances of **1** (2.365 and 2.367 Å) are similar to the Rh–Si single bond already reported.[20,29—34] Although positions of hydrogen atoms around Rh or Si atoms of **1** are not located unambiguously by crystallography, the above Rh–Si distances are sufficiently short to exclude a possible η^2-coordination of an Si–H bond to Rh center by three center two-electron bonding.[35—37] Sums of the bond angles around the Rh centers (360°) as well as of inner bond angles of Rh$_2$Si$_2$ four-membered ring (360°) indicate that all the Rh, P, and Si atoms are included in a plane.

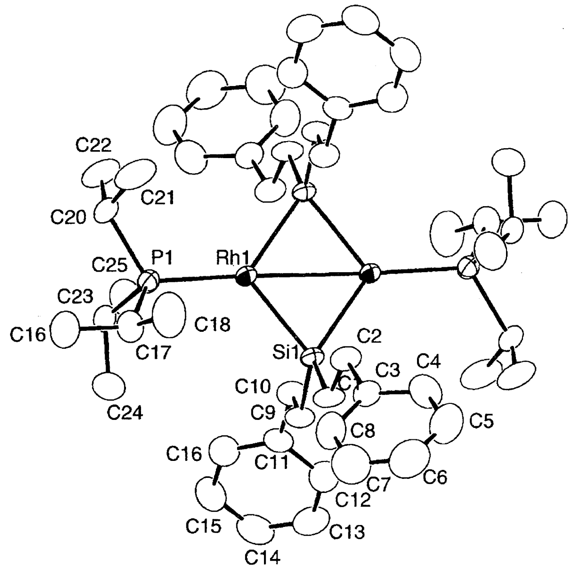


Fig. 1. ORTEP drawing of [Rh(H)$_2$(i- Pr$_3$P){μ- Si(CH$_2$CH$_2$Ph)$_2$}Rh(H)$_2$(i-Pr$_3$P)] (**1**) showing thermal ellipsoids at 30% probability. The molecule has crystallographic C_2 symmetry around the midpoint of Rh–Rh bond. Hydrogen atoms bonded to Rh are not located. The other hydrogen atoms determined by calculation as well as solvated toluene molecule are omitted.

The ^{1}H NMR spectrum of **1** shows a signal due to four hydrogen atoms bonded to Rh centers at −7.09 ppm as a doublet of doublets (J = 24 and 4 Hz). The signal is assigned to non-bridging hydrido ligands since it is split by coupling with one Rh and one P nuclei. The peak shape does not change in the range, −40 °C to 25 °C, indicating that mutual exchange of the hydrido ligands does not occur on the NMR time scale. T_1 value of the hydrido ligand is obtained as 890 ms at 25 °C with 400 MHz instrument, and is sufficiently large to exclude coordination of the ligands as a molecular hydrogen.[38] Figure 2 shows the ^{31}P{^{1}H} NMR spectrum of **1** showing an AA′XX′ spin system. Coupling constants are determined from the simulated spectrum as J(PP) = 11 Hz, J(RhP) = 142 and 2 Hz, and J(RhRh) = 32 Hz, respectively. These NMR results in the solution as well as symmetrical Rh$_2$Si$_2$ framework revealed by crystallography suggest that each of the two Rh centers has two hydrido ligands which are coordinated at mutually trans positions of the metal center.

Reactions of HSi(CH$_2$Ph)$_3$ and of HSi(CH$_2$C$_6$H$_4$Me-p)$_3$. Reactions of tribenzylsilane and of tris(p-methylbenzyl)silane with [RhClL$_2$] in pentane lead to formation of [Rh L(R$_3$Si)H(μ-Cl)$_2$RhH(SiR$_3$)L] (**4**: R = CH$_2$Ph, **5**: R = CH$_2$C$_6$H$_4$Me-p), which are separated as yellow brown solids from the reaction mixtures after 10 min stirring.

Formation of **4** seems to be attributed to oxidative addition of HSi(CH$_2$Ph)$_3$ to [RhClL$_2$] to give [RhCl(H){Si-

Table 1. Crystal Data and Details of Structure Refinement of Complexes **1** and **4**

Compound	**1** (toluene solvated)	**4** (benzene solvated)
Formula	$C_{57}H_{86}P_2Rh_2Si_2$	$C_{66}H_{92}Cl_2P_2Rh_2Si_2$
Molecular weight	1095.27	1280.33
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	12.866(4)	11.513(3)
b/Å	13.217(3)	28.227(9)
c/Å	10.388(3)	20.883(5)
α/deg	104.78(2)	—
β/deg	106.50(2)	94.14(2)
γ/deg	61.70(2)	—
V/Å^3	1478	6769
Z	1	4
μ/cm^{-1}	6.74	6.75
F(000)	576	2680
d_{calcd}/g cm^{-1}	1.231	1.257
Crystal size (mm × mm × mm)	0.3 × 0.4 × 0.4	0.4 × 0.5 × 0.5
2θ range/deg	5.0—50.0	5.0—50.0
Unique reflections	5205	12198
Used reflections ($I > 3\sigma(I)$)	3930	4249
No. of variables	289	637
R	0.073	0.071
R_w	0.081	0.066
Weighting scheme	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$

$(CH_2Ph)_3\}L_2]$ which undergoes dimerization, accompanied by loss of the phosphine ligands to give chloro ligand-bridged bimetallic complexes. Figure 3 shows molecular structure of **4** determined by X-ray crystallography. The Rh–Si bonds (2.313 and 2.301 Å) are shorter than bond between Rh and bridging Si atom of **1**. The bond angles, Cl1–Rh1–P1, Cl1–Rh2–P2, Cl2–Rh1–Si1, and Cl2–Rh2–Si2 are 167.0°, 165.0°, 135.6°, and 111.9°, respectively, while the other angles between coordination bonds are in the range 81.7°—105.0°. Each of the Rh centers are bonded to the two bridging chloro, a phosphine, a silyl, and a hydrido ligands to form distorted trigonal bipyramidal coordination with Cl1 and with P1 or P2 at the apical positions, although positions of the hydrido ligands are not determined by X-ray crystallography. The presence of two hydrido ligands in the molecule is confirmed by the ^{1}H NMR spectrum showing a peak at −19.17 ppm as a doublet of doublets due to Rh–H and P–H coupling. The distance between the two Rh(III) centers bridged by the chloro ligands is out of the range of Rh–Rh bonding. The absence of Rh–Rh interaction is consistent with the $^{31}P\{^1H\}$ NMR spectrum showing a simple doublet at 70.2 ppm with $^1J(\mathrm{RhP}) = 168$ Hz.

Further stirring the reaction mixture without isolation of **4** causes its gradual dissolution, followed by separation of chlorotribenzylsilane, as shown in Scheme 3. It is characterized by elemental analysis and X-ray crystallography.[39] The NMR spectra of a prolonged reaction mixture do not show signals that can be assigned to a dinuclear Rh(IV) complex with bridging silylene ligands.

Reaction Pathway for Formation of 1. The reaction of $[RhClL_2]$ and tris(2-phenylethyl)silane resulting in formation of **1** involves several crucial steps such as elimination of chloro ligand from the complex, oxidative addition of Si–C bonds to a Rh center, and formation of ethylbenzene and tetrakis(2-phenylethyl)silane. The chloro ligand in an initial product, **3**, may be eliminated as chlorosilane, similarly to the reaction of tribenzylsilane with $[RhClL_2]$. Conversion of triorganosilane into chlorotriorganosilane promoted by chloroplatinum and -iridium complexes has been previously reported.[40] Si–C bond cleavage of a tris(2-phenylethyl)silyl ligand promoted by Rh centers leaves a 2-phenylethyl ligand that would undergo β-hydrogen elimination of styrene or coupling with a hydrido ligand to give ethylbenzene. Formation of ethylbenzene can be attributed also to hydrogenation of styrene, as is often observed in Rh complex-catalyzed hydrosilylation reaction of styrene and 1-alkenes.[41—45] Scheme 4 shows possible pathways for formation of **1**. Mononuclear bis(2-phenylethyl)silylenerhodium complex formed by Si–C bond cleavage of mononuclear tris(2-phenylethyl)silyl rhodium complex, followed by elimination of styrene, would cause dimerization to give a more stable bimetallic μ-silylene complex **1** (Scheme 4 path (i)). Mononuclear transition metal complexes with silylene ligands have been often regarded as intermediates of transformations of organosilicon compounds promoted by metal complexes.[11,14,46—48] An alternative pathway involving initial formation of chlorobridged silyl rhodium complexes, followed by repetition of Si–C bond cleavage of tris(2-phenylethyl)silyl ligands by Rh centers, also accounts for formation of **1** (Scheme 4 path (ii)).

In summary, the reaction of $[RhClL_2]$ with tris(2-phenylethyl)silane gives a novel Rh(IV) complex with a bridging silylene ligand, **1**, through activation of Si–H and Si–C bonds of the substrate, although a similar reaction with tribenzylsilane does not give products from Si–C bond activation. Facile

Table 2. Selected Bond Distances and Angles of Complexes **1** and **4**

	1		
	Distances (Å)		
Rh1–Rh1′	2.879(2)	Rh1–P1	2.265(2)
Rh1–Si1	2.365(3)	Rh1–Si1′	2.367(3)
P1–C17	1.84(1)	P1–C20	1.87(1)
P1–C23	1.85(1)	Si1–C1	1.878(9)
Si1–C9	1.887(9)		
	Angles (deg)		
Rh1′–Rh1–P1	177.76(8)	Rh1–Si1–Rh1′	74.95(8)
Rh1′–Rh1–Si1	52.55(6)	Rh1–Rh1′–Si1	52.50(7)
P1–Rh1–Si1	125.55(9)	P1–Rh1–Si1′	129.4(1)
Si1–Rh1–Si1′	105.08(8)	C1–Si1–C9	105.8(4)
Rh1–Si1–C1	119.5(3)	Rh1–Si1′–C1′	119.1(3)
Rh1–Si1–C9	117.4(3)	Rh1–Si1′–C9′	118.3(3)
Rh1–P1–C17	114.0(3)	Rh1–P1–C20	118.9(3)
Rh1–P1–C23	113.4(3)	C17–P1–C20	102.9(5)
C17–P1–C23	103.1(5)	C20–P21–C23	102.7(5)
	4		
	Distances (Å)		
Rh1–P1	2.227(5)	Rh2–P2	2.236(5)
Rh1–Cl1	2.451(4)	Rh1–Cl2	2.485(4)
Rh2–Cl1	2.435(4)	Rh2–Cl2	2.520(4)
Rh1–Si1	2.315(5)	Rh1–Si2	2.301(5)
P1–C1	1.83(2)	P1–C4	1.86(2)
P1–C7	1.87(2)	P2–C31	1.84(2)
P2–C34	1.86(2)	P2–C37	1.79(2)
Si1–C10	1.83(2)	Si1–C17	1.92(1)
Si1–C24	1.94(1)	C10–C11	1.52(2)
C17–C18	1.55(2)	C24–C25	1.48(2)
Si2–C40	1.95(2)	Si2–C47	1.92(1)
Si2–C54	1.84(1)	C40–C41	1.48(2)
C47–C48	1.51(2)	C54–C55	1.49(2)
	Angles (deg)		
Cl1–Rh1–Cl2	81.7(1)	Cl1–Rh1–P1	167.0(2)
Cl1–Rh1–Si1	85.4(2)	Cl2–Rh1–P1	95.0(2)
Cl2–Rh1–Si1	135.6(2)	P1–Rh1–Si1	105.4(2)
Cl1–Rh1–Cl2	81.3(1)	Cl1–Rh2–P2	165.0(2)
Cl1–Rh2–Si2	87.3(2)	Cl2–Rh2–P2	100.3(2)
Cl2–Rh2–Si2	111.9(2)	P2–Rh2–Si2	105.6(2)
Rh1–Cl1–Rh2	99.4(1)	Rh1–Cl2–Rh2	96.2(1)
Rh1–P1–C1	119.2(6)	Rh1–P1–C4	104.1(6)
Rh1–P1–C7	118.5(7)	C1–P1–C4	100.9(9)
C1–P1–C7	104.4(9)	C4–P1–C7	107.9(9)
Rh2–P2–C31	104.6(6)	Rh2–P2–C34	119.7(7)
Rh2–P2–C37	119.3(6)	C31–P2–C34	106(1)
C31–P2–C37	101.7(9)	C34–P2–C37	103.3(9)
Rh1–Si1–C10	114.2(5)	Rh1–Si1–C17	120.5(5)
Rh1–Si1–C24	103.1(5)	C10–Si1–C17	104.2(7)
C10–Si1–C24	106.1(7)	C17–Si1–C24	107.9(7)
Rh2–Si2–C40	104.2(5)	Rh2–Si2–C47	119.5(5)
Rh2–Si2–C54	113.0(5)	C40–Si2–C47	106.0(7)
C40–Si2–C54	106.9(7)	C47–Si2–C54	106.4(7)

Si–C bond cleavage in the bimetallic system would provide a clue to solve the mechanistic problem of the organorhodium complex-catalyzed reaction of organosilanes to cause transfer of the organic group bonded to Si atom.

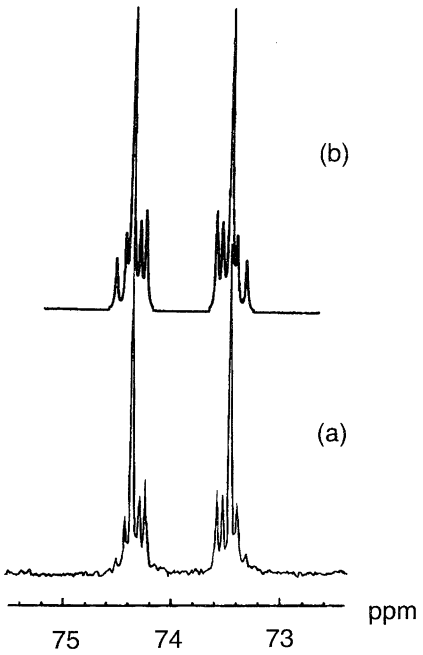


Fig. 2. (a) Observed and (b) simulated $^{31}P\{^{1}H\}$ NMR spectra of **1** (at 160 MHz in C_6D_6).

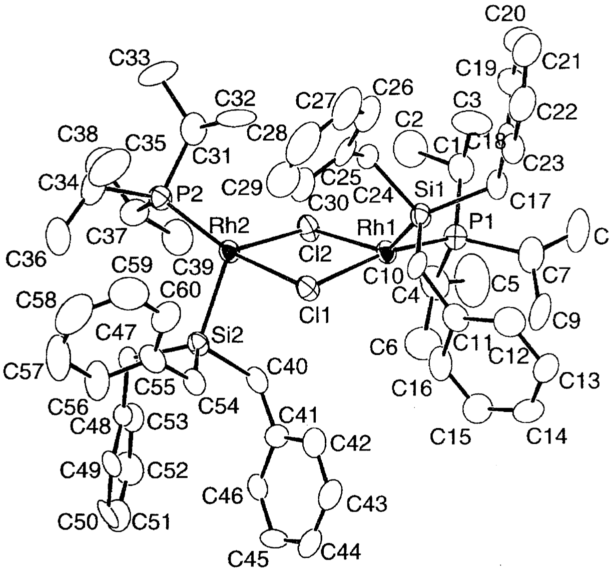
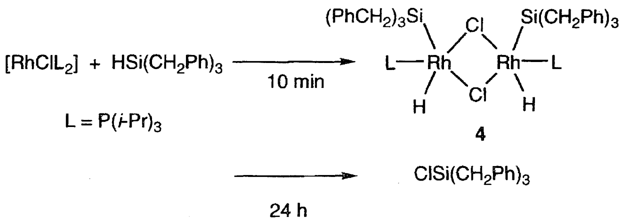


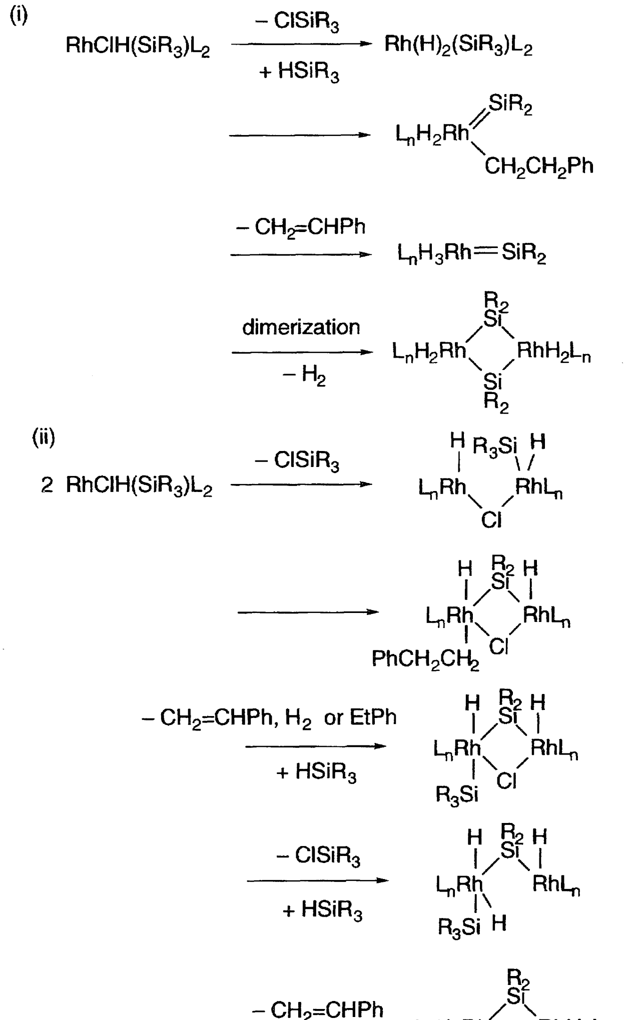
Fig. 3. ORTEP drawing of $[\{RhH[(PhCH_2)_3Si](i\text{-}Pr_3P)\}(\mu\text{-}Cl)_2\{RhH[(PhCH_2)_3Si](i\text{-}Pr_3P)\}]$ (**4**) showing thermal ellipsoids at 50% probability. Hydrogen atoms bonded to Rh are not located. The other hydrogen atoms determined by calculation as well as carbon atoms of solvated benzene are omitted.

Experimental

General Procedure, Materials, and Measurement. All the manipulations of the complexes were carried out under nitrogen or argon using Schlenk technique. Solvents were dried in usual manners, distilled and stored under nitrogen atmosphere. $[RhCl\{P(i\text{-}Pr)_3\}_2]$, tris(2-phenylethyl)silane, and tribenzylsilane were prepared according to the literature method.[26,49,50] NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on JEOL EX-90 and EX-400 spec-



Scheme 3. Isolated products in reaction of tribenzylsilane with $[RhCl\{P(i\text{-}Pr)_3\}_2]$.



Scheme 4. Schematic drawing of possible pathways for formation of **1** involving Si–C bond activation.

trometers. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. T_1 measurement was carried out by standard inversion-recovery method. Gas chromatography and GC-MS measurement were carried out on a Shimadzu GC-8A and a Hitachi M-80 instrument equipped with a 2 m Silicone OV-1 packed column, respectively.

Reaction of Tris(2-phenylethyl)silane with $[RhClL_2]$. (i) To $[RhClL_2]$ (330 mg, 0.71 mmol) dispersed in pentane (3 cm^3) was added $HSi(CH_2CH_2Ph)_3$ (490 mg, 1.4 mmol) at room temperature. The initial purple reaction mixture is soon turned into a brown solution, from which a yellow solid was precipitated immediately. After stirring for 8 h, the resulting solid product was collected by filtration and dried in vacuo to give $[RhL(H)_2\{\mu\text{-}Si(CH_2CH_2Ph)_2\}_2Rh(H)_2L]$ (**1**) (80 mg, 22%). Recrystallization of the product from a toluene-pentane mixture gave yellow single crystals. Found: C, 59.63; H, 8.21%. Calcd for $C_{50}H_{82}P_2Ph_2Si_2$: C, 60.07; H, 8.72%. ^1H NMR (400 MHz in C_6D_6) $\delta = -7.09$ (dd, 4H, $J = 24$ and 4 Hz, H-Rh), 1.11 and 1.08 (d, 36H, $J = 7$ and 6 Hz, CH_3), 1.84—1.93 (m, 14H, CH–P and CH_2Si), 3.09 (m, 8H, CH_2Ph), 7.05 (t, 4H, $J = 7$ Hz), 7.20 (t, 8H, $J = 7$ Hz), 7.34 (d, 8H, $J = 7$ Hz). $^{31}P\{^1H\}$ NMR chemical shift (ppm from external 85% H_3PO_4 at 160 MHz in C_6D_6) 73.9 (AA′ part of AA′XX′ pattern, $J(PP) = 11$ Hz, $J(RhP) = 142$ Hz, $J(RhP) = 2$ Hz, and $J(RhRh) = 32$ Hz). The filtrate from the above reaction mixture was analyzed by ^1H NMR spectroscopy after addition of diphenylmethane as an internal standard. The analysis showed the presence of **2**, ethylbenzene (26%), chloro{tris(2-phenylethyl)}silane (79% based on $[RhClL_2]$), and tetrakis(2-phenylethyl)silane (53% based on $[RhClL_2]$). Yield of **2** was tentatively determined as 37%, although the value is not so accurate due to the small peak intensity of the hydrido peak.

(ii) To $RhClL_2$ (100 mg, 0.22 mmol) dispersed in pentane (1 cm^3) was added $HSi(CH_2CH_2Ph)_3$ (150 mg, 0.44 mmol) at room temperature. The initial purple reaction mixture was turned into a brown solution accompanied by instant formation of a yellow solid which was collected by filtration after stirring for 2 min, washed with pentane and dried in vacuo (110 mg). The ^1H NMR spectrum of the solid product shows peaks due to $[RhCl(H)_2L_2]$ (**2**) (dt, −22.76 ppm, $J(HRh) = 26$, $J(HP) = 13$ Hz) and those due to $[RhCl(H)\{Si(CH_2CH_2Ph)_3\}L_2]$ (**3**) (dt, −16.63 ppm, $J(HRh) = 22$ Hz, $J(HP) = 13$ Hz). The $^{31}P\{^1H\}$ NMR signals corresponding to **3** appear at 41.8 ppm as a doublet ($J(RhP) = 121$ Hz).

Reactions of Tribenzylsilane and of Tris(*p*-methylbenzyl)silane with $[RhClL_2]$. (i) To $[RhClL_2]$ (210 mg, 0.46 mmol) dispersed in pentane (10 cm^3) was added $HSi(CH_2Ph)_3$ (210 mg, 0.70 mmol) at room temperature. The initial purple reaction mixture soon turned into a yellow and then into a brown solution. Stirring for 10 min gave a yellow brown solid of **4**, which was collected by filtration, and dried in vacuo (200 mg, 40%). Recrystallization from a benzene–pentane mixture gave yellow crystals with solvated benzene. Found: C, 61.53; H, 7.63%. Calcd for $(C_{60}H_{86}Cl_2P_2Rh_2Si_2)(C_6H_6)$: C, 61.92; H, 7.24%. ^1H NMR (400 MHz, in C_6D_6) $\delta = -19.17$ (dd, 2H, $J = 28$ and 25 Hz, H–Rh), 0.99 and 1.12 (36H, d, $J = 7$ Hz, CH_3), 1.95 (6H, m, CH–P), 2.99 (12H, s, CH_2Si), 7.12 (6H, t, $J = 7$ Hz), 7.23 (12H, t, $J = 7$ Hz), 7.35 (12H, d $J = 7$ Hz). $^{31}P\{^1H\}$ NMR chemical shift (ppm from external 85% H_3PO_4 at 160 MHz in C_6D_6) 70.2 (d, $J(RhP) = 168$ Hz).

Complex **5** was obtained as yellow crystals similarly (4%). Found: C, 61.65; H, 8.20%. Calcd for $C_{66}H_{98}Cl_2P_2Rh_2Si_2$: C, 61.63; H, 7.68%. ^1H NMR (400 MHz, in C_6D_6) $\delta = -19.11$ (dd, 2H, $J = 26$ and 22 Hz, H–Rh), 1.05 and 1.08 (36H, d, $J = 7$ and 6 Hz, CH_3), 1.26 (6H, m, CH–P), 2.14 (18H, s, $C_6H_4CH_3$), 3.00 (12H, s, CH_2Si), 7.09 (12H, d, $J = 8$ Hz), 7.32 (12H, d, $J = 8$ Hz), $^{31}P\{^1H\}$ NMR chemical shift (ppm from external 85% H_3PO_4 at 160 MHz in C_6D_6) 70.4 (d, $J(RhP) = 168$ Hz).

(ii) To $[RhClL_2]$ (210 mg, 0.46 mmol) dispersed in pentane (10 cm^3) was added $HSi(CH_2Ph)_3$ (280 mg, 0.93 mmol) at room temperature. The initially formed yellow-brown solid was dissolved on stirring the mixture. After 12 h the yellow solution containing a small amount of solid was cooled at −30 °C to give a pale yellow solid, which was collected by filtration, washed with pentane at low temperature and dried in vacuo to give chloro(tribenzyl)silane

(160 mg, 0.46 mmol). Found: C, 74.90; H, 6.30%. Calcd for $C_{21}H_{21}ClSi$: C, 74.86; H, 6.28%. Recrystallization from pentane affords single crystals for X-ray crystallography.

Crystal Structure Determination.[51] Crystals of **1**, **4**, and tribenzylchlorosilane suitable for crystallography were obtained by recrystallization from a toluene–pentane mixture, a benzene–pentane mixture, and pentane, respectively. Crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with $25 \leq 2\theta \leq 35°$. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and the ω–2θ method.

Calculations were carried out by using a program package TEXSAN on a DEC Micro VAXII computer. Atomic scattering factors were obtained from the literature.[52] A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms bonded to Rh center were not located, while the other hydrogen atoms were located from calculation by assuming the ideal geometry (d(C–H) = 0.95 Å) and included in the structure calculation without further refinement of the parameters. Empirical absorption correction (Ψ scan method) of the collected data was applied.

Crystals of **1** contain a solvated toluene molecule which possesses a center of symmetry at the center of the phenyl ring. Consequently, the methyl carbon occupies two positions at the opposite site of the benzene ring with 50% occupancy for each position. Since significant decay of the intensity of standard reflections was observed, data collection was carried out by changing the crystals when the intensity of the standard reflections was decreased down to 85%. The intensity data were corrected against the decay of the crystals.

Crystals of **4** from recrystallization from a benzene-pentane mixture contained solvated benzene molecules.

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