

A New Series of Mono- and Dinuclear Hydridosilylrhodium(III) Complexes, $\text{RhCl(H)(SiAr}_3\text{)}_2$ and $\text{RhL(SiAr}_3\text{)H}(\mu\text{-Cl})(\mu\text{-H)RhH(SiAr}_3\text{)L}$ ($\text{L} = \text{P}(i\text{-Pr}_3)$). Preparation by Oxidative Addition of HSiAr_3 and Molecular Structures of the Complexes

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Reactions of triarylsilanes such as HSiPh_3 , $\text{HSi(C}_6\text{H}_4\text{Me-}p\text{)}_3$, $\text{HSi(C}_6\text{H}_4\text{OMe-}p\text{)}_3$, $\text{HSi(C}_6\text{H}_4\text{-Cl-}p\text{)}_3$, $\text{HSi(C}_6\text{H}_4\text{F-}p\text{)}_3$, and $\text{HSi(C}_6\text{H}_4\text{CF}_3\text{-}p\text{)}_3$ with RhClL_2 ($\text{L} = \text{P}(i\text{-Pr}_3)$) give a series of hydrido(triarylsilyl)rhodium(III) complexes, $\text{RhCl(H)(SiAr}_3\text{)}_2$ (**1**, $\text{Ar} = \text{Ph}$; **2**, $\text{Ar} = \text{C}_6\text{H}_4\text{-Me-}p$; **3**, $\text{Ar} = \text{C}_6\text{H}_4\text{OMe-}p$; **4**, $\text{Ar} = \text{C}_6\text{H}_4\text{Cl-}p$; **5**, $\text{Ar} = \text{C}_6\text{H}_4\text{F-}p$; **6**, $\text{Ar} = \text{C}_6\text{H}_4\text{CF}_3\text{-}p$). Tris-(phenylethynyl)silane also reacts with the Rh(I) complex to give another oxidative-addition product, $\text{RhCl(H)[Si(C}\equiv\text{CPh)}_3\text{]}_2$ (**7**). X-ray analyses of **1** and **7** show a distorted-square-pyramidal coordination around the Rh center with the silyl ligand at the apical position. Prolonged reactions of HSiPh_3 and of $\text{HSi(C}_6\text{H}_4\text{OCF}_3\text{-}p\text{)}_3$ with RhClL_2 give dinuclear complexes, $\text{RhL(SiAr}_3\text{)H}(\mu\text{-Cl})(\mu\text{-H)RhH(SiAr}_3\text{)L}$ (**8**, $\text{Ar} = \text{Ph}$; **9**, $\text{Ar} = \text{C}_6\text{H}_4\text{OCF}_3\text{-}p$). X-ray crystallography of **9** shows a molecular structure containing two Rh centers bridged with hydrido and chloro ligands. 1,1,3,3-Tetraisopropylidisiloxane undergoes oxidative addition of the Si–H bonds to RhClL_2 to give a symmetric dinuclear Rh(III) complex with bridging hydrido, chloro, and disiloxanyl ligands, $\text{RhL(H)}(\mu\text{-H})(\mu\text{-Cl})[\mu\text{-}(i\text{-Pr)}_2\text{Si-O-Si}(i\text{-Pr)}_2]\text{Rh(H)L}$ (**10**).

Introduction

Silylrhodium complexes^{1–15} have attracted increasing attention as possible intermediates of Rh-complex-

catalyzed synthetic reactions,^{16–19} including hydrosilylation of unsaturated molecules¹⁶ and silylformylation of alkenes and alkynes.¹⁷ Recently, a pentacoordinated hydridosilylrhodium complex, $\text{RhCl(H)(SiR}_3\text{)(DAD)}$ ($\text{DAD} =$ a Salen type diimine ligand), was reported to play an important role as the intermediate in hydrosilylation of alkenes catalyzed by RhCl(CO)(DAD) .⁵ Although hydrosilylation catalyzed by Rh–phosphine complexes seems to involve similar pentacoordinated silylrhodium(III) complexes as the intermediates, there have been

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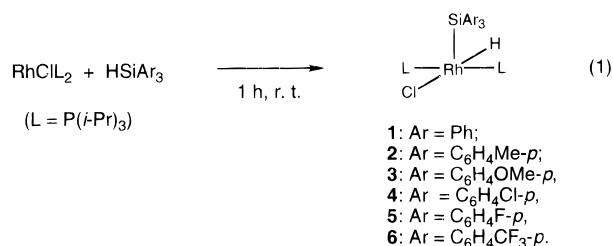
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only a few reports on such pentacoordinated silylrhodium complexes with phosphine ligands. RhCl(H)(SiCl₃)(PPh₃)₂ with five monodentate ligands around the Rh center actually has a distorted-octahedral coordination, whose sixth coordination site is occupied by an *ortho* hydrogen of the PPh₃ ligand.³ Silylrhodium(I) complexes with a trigonal-bipyramidal structure have been obtained by use of a polydentate phosphine ligand that coordinates to the Rh center in a cage-like fashion.^{7,8} In the case of silylplatinum and -iridium phosphine complexes, however, their role in hydrosilylation and bis-silylation has been well-clarified.^{20,21}

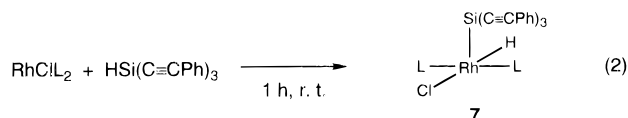
On this basis, we have sought a way to prepare a series of pentacoordinated hydridosilylrhodium(III) complexes to reveal their molecular structure and chemical properties and found that the reaction of RhClL₂ (L = P(*i*-Pr)₃) with HSiAr₃ provides such a way. RhClL₂ has been proven to serve as a convenient starting material of various organorhodium complexes owing to its 14-electron metal center that undergoes facile oxidative-addition reactions.²² The sterically bulky P(*i*-Pr)₃ ligand stabilizes the pentacoordinate hydridosilylrhodium(III) complexes, while a less bulky PMe₃ ligand is known to give hexacoordinate RhX(H)(SiAr₃)(PMe₃)₃ (X = Cl, SAr).¹² This paper will present results of reaction of triarylsilanes with RhClL₂ to give pentacoordinated hydridosilylrhodium(III) complexes, RhCl(H)(SiAr₃)L₂. Their transformation into RhL(Ar₃Si)H(*μ*-Cl)(*μ*-H)RhH(SiAr₃)L as well as oxidative addition of (*i*-Pr)₂HSiOSiH(*i*-Pr)₂ to RhClL₂ will also be reported.

Results and Discussion

Mononuclear Hydridosilylrhodium(III) Complexes. Triarylsilanes such as HSiPh₃, HSi(C₆H₄Me-*p*)₃, HSi(C₆H₄OMe-*p*)₃, HSi(C₆H₄Cl-*p*)₃, HSi(C₆H₄F-*p*)₃, and HSi(C₆H₄CF₃-*p*)₃ react smoothly with RhClL₂ to give hydridosilylrhodium(III) complexes **1–6**, as shown in eq 1.



Tris(phenylethynyl)silane gives an analogous product, RhCl(H)[Si(C≡CPh)₃]L₂ (**7**).



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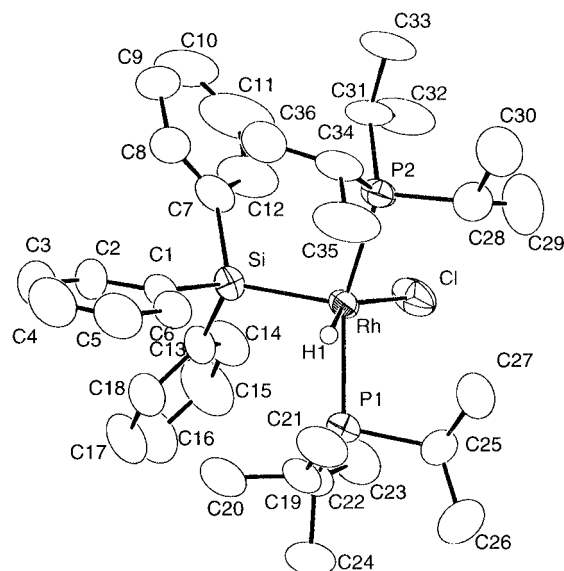


Figure 1. ORTEP drawing of **1** with 30% thermal ellipsoids. Hydrogen atoms other than hydrides are omitted for simplicity.

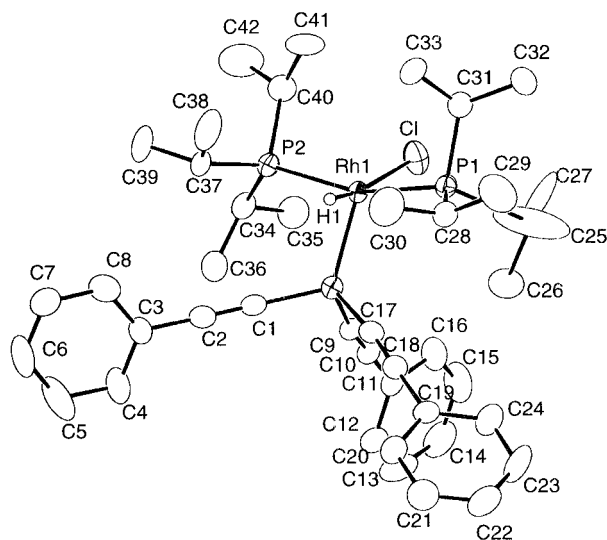


Figure 2. ORTEP drawing of **7** with 30% thermal ellipsoids. Hydrogen atoms other than hydrides are omitted for simplicity.

NMR (¹H, ³¹P, and ¹³C) data of the complexes are consistent with the pentacoordinated structure. ¹H NMR signals of the hydrido ligands at δ –15.95 to –16.50 ppm show splitting due to the presence of two magnetically equivalent P nuclei. Figures 1 and 2 respectively show the molecular structures of **1** and **7** determined by X-ray crystallography. Table 1 summarizes selected bond distances and angles of the complexes. Both complexes have a distorted-square-pyramidal coordination around the metal center with the triorganosilyl ligand at the apical position. This silyl ligand position and mutually trans position of the hydrido and chloro ligands suggest a larger trans effect of the silyl ligand than the hydrido ligand.^{20h,23} An analogous square-pyramidal hydridosilyliridium(III) complex, IrCl(H)(SiMeCl₂)L₂ (L = P(*i*-Pr)₃), with a Cl–Ir–

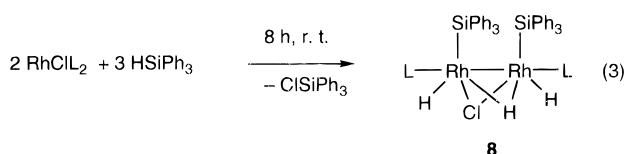
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Table 1. Selected Bond Distances (Å) and Angles (deg) of 1 and 7

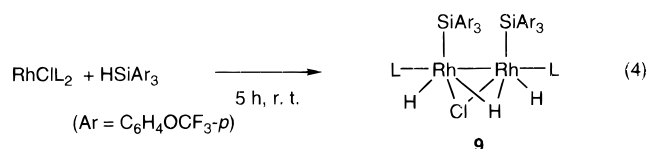
	1	7
Rh–Si	2.299(2)	2.229(3)
Rh–Cl	2.427(3)	2.403(3)
Rh–P1	2.383(2)	2.357(3)
Rh–P2	2.389(2)	2.382(3)
Rh–H	1.12	1.22
Si–Rh–Cl	111.09(8)	126.4(1)
Si–Rh–P1	99.54(7)	98.6(1)
Si–Rh–P2	100.56(7)	97.0(1)
P1–Rh–Cl	91.66(8)	89.2(1)
P2–Rh–Cl	95.06(8)	89.4(1)
P1–Rh–P2	154.84(7)	161.5(1)
Si–Rh–H	82.5	65.2
P1–Rh–H	112.1	87.2
P2–Rh–H	56.3	90.5
Cl–Rh–H	150.8	168.4

Si angle (106.7°) smaller than the Cl–Rh–Si angles of **1** and **7**, has been reported, although the hydrido position has not been clarified by the X-ray structural study.²⁴ On the other hand, a hydrido(boryl)iridium(III) complex, IrCl(H)(BO₂C₆H₄)L₂, reportedly has a distorted-trigonal-bipyramidal structure with a large B–Ir–Cl angle (137.5°) around the metal center.²⁵

Conversion of the Hydrosilylrhodium(III) Complexes into Dinuclear Complexes. Although the reaction of HSiPh₃ with RhClL₂ in a 2:1 molar ratio gives **1** as the sole product for the initial 1 h, a prolonged reaction for 7 h at room temperature gives a dinuclear complex, RhL(Ph₃Si)H(*μ*-Cl)(*μ*-H)RhH(SiPh₃)L (**8**), in 35% isolated yield.

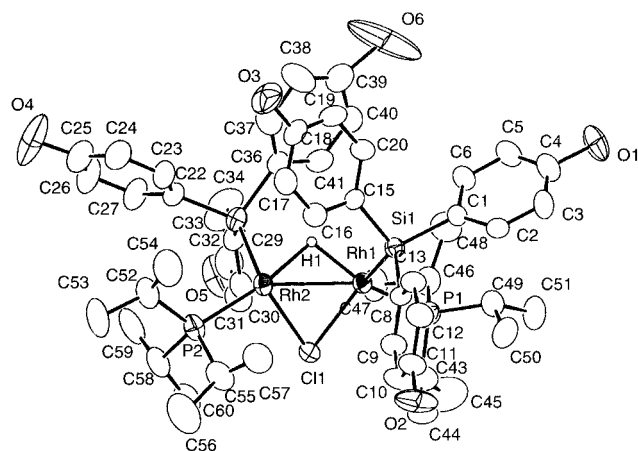


The NMR (¹H, ³¹P{¹H}, and ²⁹Si{¹H}) analyses of the reaction mixture revealed concomitant formation of RhCl(H)₂L₂ (23%) and ClSiPh₃ (58% based on RhClL₂). Since a similar reaction in a 1:1 ratio for 8 h at room temperature gives **8** in a much lower yield, formation of **8** in eq 3 results from reaction of excess HSiPh₃ with **1**. A similar reaction of HSi(C₆H₄OCF₃-*p*)₃ with RhClL₂ also gives RhL[(C₆H₄OCF₃-*p*)₃Si]H(*μ*-Cl)(*μ*-H)-RhH[Si(C₆H₄OCF₃-*p*)₃]L (**9**).



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**Figure 3.** ORTEP drawing of **9** with 30% thermal ellipsoids. Hydrogen atoms and CF₃ groups are omitted for simplicity.**Table 2. Selected Bond Distances and Angles (deg) of 9 and 10**

	9	10
Rh1–Rh2	2.797(1)	2.777(1)
Rh1–P1	2.320(3)	2.283(3)
Rh2–P2	2.322(3)	2.296(3)
Rh1–H1	1.84	1.64
Rh2–H1	1.77	1.67
Rh1–H2		1.26
Rh2–H3		1.17
Rh1–Cl	2.399(2)	2.439(3)
Rh2–Cl	2.403(3)	2.439(3)
Rh1–Si1	2.279(3)	2.286(3)
Rh2–Si2	2.273(3)	2.295(3)
Rh2–Rh1–Si1	100.79(8)	95.78(9)
Rh1–Rh2–Si2	100.19(8)	91.70(8)
Rh2–Rh1–P1	151.08(7)	152.15(9)
Rh1–Rh2–P2	149.77(8)	153.35(9)
Cl–Rh1–P1	98.77(9)	99.9(1)
Cl–Rh2–P2	97.67(10)	101.5(1)
Cl–Rh1–Si1	128.78(10)	114.8(1)
Cl–Rh2–Si2	125.8(1)	115.0(1)
P1–Rh1–H1	159	166
P2–Rh2–H1	166	166
P1–Rh1–H2		105
P2–Rh2–H3		98

Figure 3 shows the molecular structure of **9** determined by X-ray crystallography. The molecule has a symmetrical structure with two Rh centers. Each metal center is bonded to chloro, silyl, and phosphine ligands as well as to a bridging hydrido ligand. The final *D* map shows the presence of a bridging hydrido ligand, H1, unambiguously. Although precise positions of other hydrido ligands have not been clarified by X-ray crystallography, the ¹H NMR data (*vide infra*) indicate the presence of the two magnetically equivalent nonbridging hydrido ligands shown in eq 4. Bond distances and angles of the complex are summarized in Table 2. P1–Rh1–H1 and P2–Rh2–H1 (159 and 166°) as well as Si1–Rh1–Cl and Si2–Rh2–Cl bond angles (128.8 and 125.8°) indicate a distorted-trigonal-bipyramidal coordination around the Rh center.

The NMR spectra of **8** and **9** are consistent with the dinuclear structures. Two sets of signals due to the hydrido ligands are observed in a 1:2 area ratio. The

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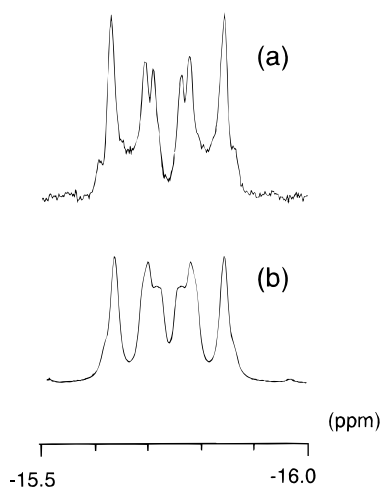


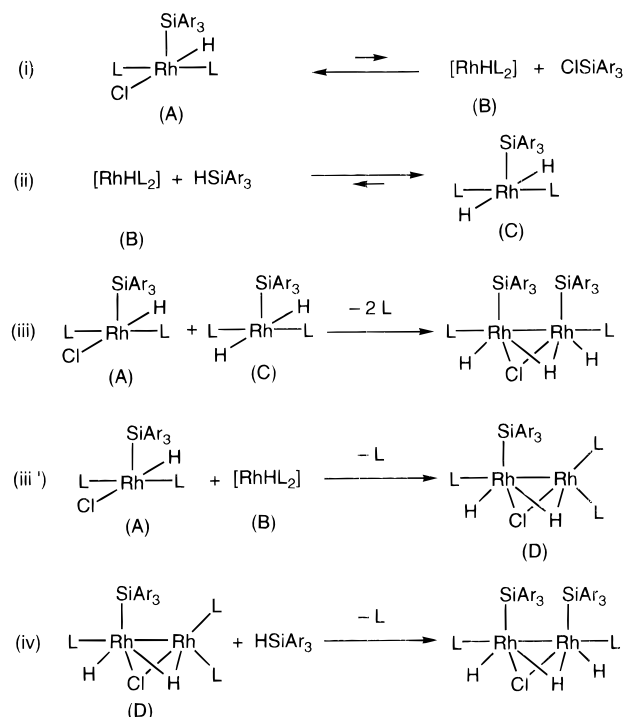
Figure 4. (a) Observed and (b) simulated ^1H NMR signals due to nonbridging hydrides of **8**. Coupling constants were determined as follows by comparison of the spectra: $^1J(\text{HRh}) = 29$ Hz, $^2J(\text{HP}) = 14$ Hz, $^2J(\text{HRh}) = 1$ Hz, $^3J(\text{HP}) = -1$ Hz, $^4J(\text{HH}) = 1$ Hz.

smaller signal appears as a triplet of triplets (**8**, -15.78 ppm; **9**, -16.12 ppm) and is assigned to the bridging hydrido ligand. The larger signal due to the nonbridging hydrido ligands shows a more complicated pattern (**8**, -12.16 ppm; **9**, -12.62 ppm). Figure 4 shows the signal due to the nonbridging hydrido signal of **8** as well as that obtained from simulation based on the assumption of an AA' part of the $\text{AA}'\text{MM}'\text{XX}'$ spin system. The appearance of nonbridging and bridging hydride signals with splitting due to reasonable coupling indicates that the complex has the same solution structure as that by crystallography and that the hydrido ligands do not show any fluxional behavior on the NMR time scale.

Deuterium labeling experiments for the reaction expressed by eq 3 reveal scrambling of hydrogens among the hydrido ligands, the phosphine ligands, and organosilanes. Reaction of DSiPh_3 with RhClL_2 gives a mixture of partially deuterated **1** and **8**. The hydrido ligand of **1** is 15% deuterated, while both the bridging and nonbridging hydrido ligands of **8** show the same 20% content of deuterium. The phosphine ligands are also deuterated, as observed in the ^1H and ^2H NMR spectra. A reaction of HSiPh_3 with RhClL_2 in hexane- d_{14} does not introduce deuterium into the products. Similar H–D exchange between trialkylphosphine and hydrido ligands has been reported in the photoreaction of hydridoruthenium complexes.²⁶ An equimolar reaction of **1** and DSiPh_3 gives HSiPh_3 and **8**, the latter of which contains 32% deuterated bridging and nonbridging hydrido ligands. The equal deuterium content in the bridging and nonbridging hydrido ligands is attributed to rapid exchange of the hydrogen between **1** and HSiPh_3 (or DSiPh_3) prior to formation of **8** or to the exchange between bridging and nonbridging hydrido ligands in **8**.

Process for the Formation of the Dinuclear Complex. Scheme 1 depicts possible reaction pathways for formation of the dinuclear complexes.

Scheme 1. Possible Pathways for Formation of Dinuclear Silylrhodium Complexes



In the first step (i), the mononuclear complex (A) undergoes reductive elimination of ClSiAr_3 to generate RhHL_2 (B). A new complex (C) may be formed by the reaction expressed in (ii) and the bimetallic complex by coupling of A and C as shown in (iii). An alternative route involves a direct coupling of A and B accompanied by phosphine liberation (iii'). The intermediate unsymmetrical dinuclear complex D in this pathway further undergoes oxidative addition of HSiAr_3 to give the dinuclear complex (cf. iv). In relation to the reaction expressed in (i), reductive elimination of chloroorganosilanes from transition-metal complexes with chloro and triorganosilyl ligands has been reported with a $\text{Pt}(\text{II})$ complex.²⁷

Reactions of $\text{HSi}(\text{C}_6\text{H}_4\text{Cl-}p)_3$, $\text{HSi}(\text{C}_6\text{H}_4\text{F-}p)_3$, and $\text{HSi}(\text{C}_6\text{H}_4\text{CF}_3-p)_3$ with RhClL_2 in a 2:1 ratio for several hours at room temperature give the corresponding mononuclear complexes **4**–**7**. They are converted into the dinuclear complexes to only a small extent even in the prolonged reactions. The difference in the reactivity of the mononuclear complexes depending on the kind of HSiAr_3 is accounted for by high stability of the Rh–Si bond, with the Ar groups having electron-withdrawing ability, which prevent the previously discussed reductive elimination of ClSiAr_3 under the conditions.

A Dinuclear Rh Complex with a Bridging Disiloxanyl Ligand. It is reported that 1,1,3,3-tetramethyldisiloxane, $\text{Me}_2\text{HSiOSiHMe}_2$, oxidatively adds to $\text{Pt}(\text{0})$ and $\text{Ir}(\text{I})$ PPh_3 complexes to give the respective $\text{Pt}(\text{II})$ and $\text{Ir}(\text{III})$ complexes with a chelating disiloxanyl ligand (Chart 1a).^{28,29} Contact of $\text{Pt}(\text{SiMe}_2=\text{SiMe}_2)(\text{dppe})$ ($\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane), having an η^2 -

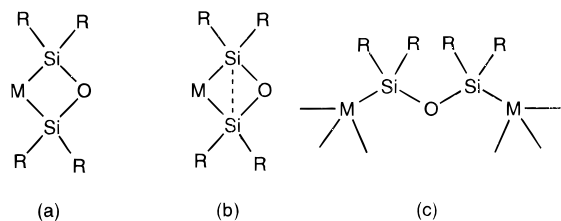
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Chart 1. Possible Coordination Modes of the Disiloxanyl Ligand



disilene ligand, with oxygen results in formation of $\text{Pt}(\text{SiMe}_2\text{OSiMe}_2)(\text{dppe})$, whose crystallographic study disclosed a short contact between two Si atoms as shown in Chart 1b.³⁰ A bimetallic complex, $\{\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2\}_2\text{O}$, with a bridging disiloxanyl ligand (Chart 1c) was prepared by hydrolysis of Si–Cl bonds of $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$.³¹ This versatility in coordination of the $-\text{SiX}_2-\text{O}-\text{SiX}_2-$ group is partially due to the flexibility of the Si–O–Si bond angle.

1,1,3,3-Tetraisopropylidisiloxane reacts with RhClL_2 in a 2:1 ratio to give a mixture of $\text{RhL}(\text{H})(\mu\text{-H})[\mu\text{-}(i\text{-Pr})_2\text{Si-O-Si}(i\text{-Pr})_2]\text{Rh}(\text{H})\text{L}$ (**10**) and RhClH_2L_2 in a 60:40 molar ratio. Complex **10** is isolated by fractional crystallization of the products.

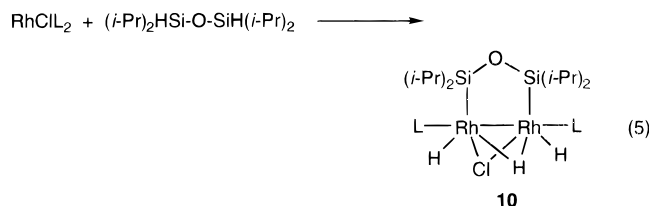


Figure 5 shows a molecular structure of **10** determined by X-ray crystallography. The molecule contains bridging chloro, hydrido, and disiloxanyl ligands. Non-bridging hydrido ligands occupy syn positions of the $\text{Rh}_2\text{Si}_2\text{O}$ five-membered ring, while complex **9** has two silyl ligands at mutually anti positions with respect to the plane, including two Rh and bridging chloro and hydrido atoms. The distance between the Si atoms (3.08 Å) is large enough to exclude a direct Si–Si interaction suggested by the structural study of a Pt complex, $\text{Pt}(\text{SiMe}_2\text{OSiMe}_2)(\text{dppe})$ (Si–Si = 2.54 Å).³⁰ The Si–O–Si bond angle of **10** (138.9°) is within the range of the angle of linear and cyclic siloxanes ($130\text{--}180^\circ$).³²

Coordination of the disiloxanyl ligand of **10** forms an $\text{Rh}_2\text{Si}_2\text{O}$ five-membered-ring system stabilized by bridging coordination of hydrido and chloro ligands. It differs from that of a bimetallic complex, $\{\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2\}_2\text{O}$, whose two Os centers are apart from each other due to an anti orientation of Os(1) and Si(2) (and Os(2) and Si(1)) in the Os(1)–Si(1)–O–Si(2)–Os(2) bonding. This new type of coordination of the disiloxanyl group containing a thermally stable Si–O bond

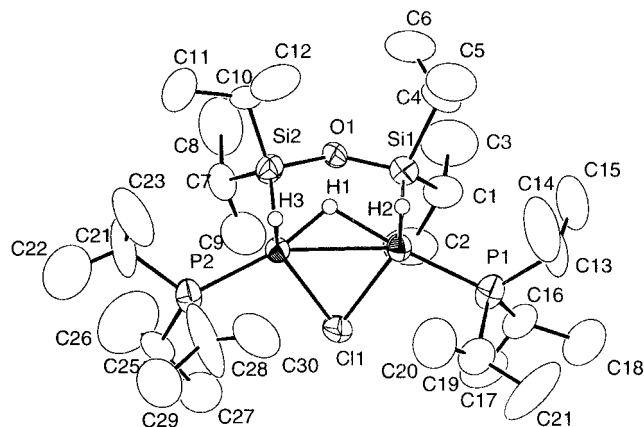


Figure 5. ORTEP drawing of **10** with 30% thermal ellipsoids. Hydrogen atoms other than hydrides are omitted for simplicity.

suggests a potential utility as the Si-containing supporting ligand for dinuclear complexes.

Conclusion

The triarylsilanes HSiAr_3 and $\text{HSi}(\text{C}\equiv\text{CPh})_3$ undergo oxidative addition to RhClL_2 to give a new series of pentacoordinate hydridosilylrhodium(III) complexes. The complexes with SiPh_3 and $\text{Si}(\text{C}_6\text{H}_4\text{OCF}_3\text{-}p)_3$ ligands further react to result in the formation of a new type of dinuclear silylrhodium complex. The reaction of 1,1,3,3-tetraalkylidisiloxane also successfully gives a new dinuclear Rh complex with a bridging disiloxanyl ligand. This ligand, having a stable Si–O bond and flexible Si–O–Si bond angle, seems to serve as a bridging ligand to stabilize various bimetallic frameworks of transition-metal complexes similarly to *dppm* that is suited for the bridging ligand of bimetallic Pd and Pt complexes.

Experimental Section

General Considerations, Measurements, and Materials. Manipulation of the complexes was carried out under nitrogen or argon using the standard Schlenk technique. RhClL_2 , triarylsilanes, and tris(phenylethynyl)silane were prepared according to the literature method.^{33,34} DSiPh_3 was prepared by LiAlD_4 reduction of ClSiPh_3 . 1,1,3,3-Tetraisopropylsiloxane was prepared by reaction of HSiCl_3 with *i*-PrMgBr followed by passage through a short silica gel column. NMR spectra (^1H , ^{13}C , ^{31}P , and ^{29}Si) were recorded on a JEOL EX-400 spectrometer. Simulation of the NMR spectrum of **8** was carried out by using a program system, gNMR.³⁵ Elemental analyses were carried out with a Yanagimoto type MT-2 CHN autocorder.

Preparation of 1–6. To RhClL_2 (230 mg, 0.49 mmol) dispersed in pentane (5 mL) was added HSiPh_3 (260 mg, 0.98 mmol) at room temperature. The reaction mixture soon turned from purple to yellow-orange. A yellow solid began to be separated from the solution. After it was stirred for 1 h, the reaction mixture was cooled to -30°C for 12 h to complete separation of the solid product, which was collected by filtration, washed with a minimum amount of pentane, and dried in vacuo to give **1** (200 mg, 58%). Anal. Calcd for $\text{C}_{36}\text{H}_{58}\text{ClP}_2\text{RhSi}$: C, 60.1; H, 8.1. Found: C, 59.9; H, 8.0. ^1H NMR (400

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Table 3. Crystallographic Data and Details of Refinement of 1, 7, 9, and 10

	1	7	9	10
chem formula	C ₃₆ H ₅₈ ClP ₂ SiRh	C ₄₂ H ₅₈ ClP ₂ SiRh	C ₆₅ H ₈₁ ClF ₁₈ O ₆ P ₂ Si ₂ Rh ₂	C ₃₀ H ₇₃ ClOP ₂ Si ₂ Rh ₂
fw	719.25	791.31		809.29
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
<i>a</i> , Å	11.899(5)	9.935(5)	15.208(4)	13.132(3)
<i>b</i> , Å	15.750(7)	20.84(1)	18.671(5)	23.460(8)
<i>c</i> , Å	20.48(1)	20.27(1)	13.804(5)	13.028(3)
α , deg			92.50(3)	
β , deg	93.31(4)	91.70(4)	92.78(3)	
γ , deg			103.66(2)	
<i>V</i> , Å ³	3832	4194	3798	4013
<i>Z</i>	4	4	2	4
μ , cm ⁻¹	9.14	5.93	6.32	10.47
<i>F</i> (000)	1520	1664	1692	1704
ρ_{calcd} , g cm ⁻³	1.247	1.253	1.451	1.339
cryst size, mm	0.2 × 0.2 × 0.2	0.4 × 0.6 × 0.6	0.2 × 0.4 × 0.4	0.2 × 0.4 × 0.4
2 θ range, deg	3.0–55.0	3.0–55.0	3.0–55.0	3.0–55.0
scan rate, deg min ⁻¹	8	8	8	8
<i>hkl</i>	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 17, –22 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 25, –25 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 19, –23 ≤ <i>k</i> ≤ 23, –16 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 30, 0 ≤ <i>l</i> ≤ 16
no. of unique rflns	8639	9887	17416	5124
no. of rflns used (<i>I</i> ≥ 3 σ (<i>I</i>))	3201	3641	7659	3734
no. of variables	410	424	865	343
<i>R</i> (<i>F</i> _o) ^a	0.047	0.061	0.070	0.048
<i>R</i> _w (<i>F</i> _o) ^a	0.054	0.052	0.071	0.036

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$, $R_w = [\sum w|F_o - F_c|^2 / \sum w|F_o|^2]^{1/2}$; weighting scheme $\{[\sigma(F_o)]\}^{-1}$.

MHz in C₆D₆ at 25 °C): δ –16.20 (dt, 1H, Rh–H, *J*(HRh) = 21 Hz, *J*(HP) = 13 Hz), 1.11 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.19 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.88 (m, 6H, PCH), 7.10–7.20 (m, 9H, C₆H₅ (*meta* and *para*)), 8.25 (d, 6H, C₆H₅ (*ortho*), *J* = 7 Hz). ³¹P{¹H} NMR (160 MHz in C₆D₆ at 25 °C): 37.14 ppm (d, *J*(RhP) = 114 Hz).

Complexes **2**–**6** were prepared analogously. **2** (containing 0.5 mol of C₆H₁₄): yield 91%. Anal. Calcd for C₄₂H₇₁ClP₂RhSi: C, 62.7; H, 8.9. Found: C, 62.5; H, 8.4. ¹H NMR (in C₆D₆ at 25 °C): δ –16.22 (dt, 1H, Rh–H, *J*(HRh) = 22 Hz, *J*(HP) = 13 Hz), 1.15 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.24 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.96 (m, 6H, PCH), 2.10 (s, 3H, CH₃), 7.04 (d, 6H, SiC₆H₄ (*meta*), *J* = 8 Hz), 8.20 (d, 6H, SiC₆H₄ (*ortho*), *J* = 8 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 37.37 ppm (d, *J*(RhP) = 117 Hz). **3**: yield 99%. Anal. Calcd for C₃₉H₆₄ClO₃P₂RhSi: C, 57.9; H, 8.0. Found: C, 58.4; H, 7.6. ¹H NMR (in C₆D₆ at 25 °C): δ –16.17 (dt, 1H, Rh–H, *J*(HRh) = 22 Hz, *J*(HP) = 13 Hz), 1.15 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.26 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.95 (m, 6H, PCH), 3.32 (s, 3H, OCH₃), 6.84 (d, 6H, SiC₆H₄ (*meta*), *J* = 7 Hz), 8.21 (d, 6H, SiC₆H₄ (*ortho*), *J* = 7 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 37.15 ppm (d, *J*(RhP) = 117 Hz). **4**: yield 89%. Anal. Calcd for C₃₆H₅₅Cl₄P₂RhSi: C, 52.6; H, 6.7. Found: C, 52.8; H, 6.6. ¹H NMR (in C₆D₆ at 25 °C): δ –16.15 (dt, 1H, Rh–H, *J*(HRh) = 21 Hz, *J*(HP) = 13 Hz), 0.97 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.10 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.75 (m, 6H, PCH), 7.16 (d, 6H, SiC₆H₄ (*meta*), *J* = 8 Hz), 7.92 (d, 6H, SiC₆H₄Cl (*ortho*), *J* = 8 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 37.97 ppm (d, *J*(RhP) = 110 Hz). **5**: yield, 83%. Anal. Calcd for C₃₆H₅₅ClF₃P₂RhSi: C, 55.9; H, 7.2. Found: C, 56.2; H, 6.9. ¹H NMR (in C₆D₆ at 25 °C): δ –16.16 (dt, 1H, Rh–H, *J*(HRh) = 21 Hz, *J*(HP) = 13 Hz), 1.01 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.13 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.78 (m, 6H, PCH), 6.86 (dd, 6H, SiC₆H₄F (*ortho*), *J* = 9 and 1 Hz), 8.00 (dd, 6H, SiC₆H₄F (*meta*), *J* = 9 and 2 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 37.71 ppm (d, *J*(RhP) = 117 Hz). **6**: yield, 39%. Anal. Calcd for C₃₉H₅₅ClF₉P₂RhSi: C, 50.7; H, 6.0. Found: C, 49.9; H, 6.0. Insufficient agreement of elemental analysis of **6** and **7** with the calculated value is partially due to contamination of RhCl(H)₂L₂ formed during recrystallization. ¹H NMR (in C₆D₆ at 25 °C): δ –15.95 (dt, 1H, Rh–H, *J*(HRh) = 19 Hz, *J*(HP) = 13 Hz), 0.89 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.07 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.59 (m, 6H, PCH), 7.38 (d, 6H, SiC₆H₄ (*meta*), *J* = 9 Hz),

8.05 (d, 6H, SiC₆H₄ (*ortho*), *J* = 9 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 37.39 ppm (d, *J*(RhP) = 110 Hz).

Preparation of 7. To RhClL₂ (190 mg, 0.42 mmol) dispersed in pentane (3 mL) was added HSi(C≡CPh)₃ (170 mg, 0.51 mmol) at room temperature. After the mixture was stirred for 12 h at room temperature, the solvent was removed under reduced pressure to leave a brown solid which was recrystallized from toluene–pentane, giving **7** as yellow crystals (64%). Anal. Calcd for C₄₂H₅₈ClP₂RhSi·0.5C₇H₈: C, 65.6; H, 7.4. Found: C, 64.9; H, 7.1. ¹H NMR (in C₆D₆ at 25 °C): δ –16.50 (dt, 1H, Rh–H, *J*(HRh) = 21 Hz, *J*(HP) = 12 Hz), 1.40 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 1.53 (dt, 18H, CHCH₃, *J* = 7 and 6 Hz), 3.15 (m, 6H, PCH), 6.92 (m, 9H, C₆H₅ (*meta* and *para*)), 7.49 (m, 6H, C₆H₅ (*ortho*)). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 43.71 ppm (d, *J*(RhP) = 114 Hz).

Preparation of 8. To a pentane (10 mL) solution of RhClL₂ (290 mg, 0.63 mmol) was added HSiPh₃ (580 mg, 1.3 mmol) at room temperature. The purple solution was soon turned into yellow and then into brown. Stirring for 1 h caused initial separation of a yellow solid which, on further stirring, underwent dissolution accompanied by separation of a new yellow–orange solid from the solution. After it was stirred for 8 h at room temperature, the resulting solid product was collected by filtration and recrystallized from toluene–pentane to give **8** as orange crystals (35%). Anal. Calcd for C₅₄H₇₅ClP₂Rh₂Si₂: C, 59.9; H, 7.0. Found: C, 59.7; H, 6.8. ¹H NMR (in C₆D₆ at 25 °C): δ –15.78 (m, 2H, Rh–H, coupling constants obtained from simulation of the spectrum: ¹*J*(HRh) = 29 Hz, ²*J*(HP) = 14 Hz, ²*J*(HRh) = 1 Hz, ³*J*(HP) = –1 Hz, ⁴*J*(HH) = 1 Hz), –12.16 (tt, 1H, Rh–H–Rh, *J*(HRh) = 60 Hz, *J*(HP) = 24 Hz), 0.7–1.2 (br, 36H, CH₃), 1.65 (m, 6H, *J* = 7 Hz), 7.15–7.25 (m, 18H, C₆H₅ (*meta* and *para*)), 7.88 (d, 12H, C₆H₅ (*ortho*), *J* = 6 Hz). ³¹P{¹H} NMR (in C₆D₆ at 25 °C): 53.26 ppm (AA' part of an AA'XX' pattern, coupling constants obtained from simulation of the spectrum: *J*(PP) = 5 Hz, ¹*J*(RhP) = 141 Hz, ²*J*(RhP) = 5 Hz, *J*(RhRh) = 49 Hz). Formation of RhCl(H)₂L₂ (23%) and ClSiPh₃ (58% based on RhClL₂) was observed in the NMR spectrum of the reaction mixture.

Preparation of 9. To RhClL₂ (200 mg, 0.41 mmol) dispersed in pentane (2 mL) was added HSi(C₆H₄OCF₃-*p*)₃ (410 mg, 0.83 mmol) at room temperature. The purple solution was soon turned into yellow and then into brown. Stirring the reaction mixture for 5 h at room temperature followed by cooling the system at –20 °C caused separation of orange

microcrystals, which were collected by filtration and dried in vacuo (260 mg). Recrystallization of the product from toluene–pentane gave **9**. Anal. Calcd for $C_{60}H_{69}ClF_{18}O_6P_2Si_2Rh_2$: C, 45.4; H, 4.4. Found: C, 46.1; H, 5.0. 1H NMR (in C_6D_6 at 25 °C): δ -16.12 (m, 2H, Rh–H), -12.62 (tt, 1H, Rh–H–Rh, $J(HRh) = 57$ Hz, $J(HP) = 25$ Hz), 0.60–1.00 (broad peak, 36H, P–CH–CH₃), 1.49 (m, 6H, P–CH), 7.01 (d, 12H, SiC₆H₄ (*meta*), $J = 9$ Hz), 7.53 (d, 12H, SiC₆H₄ (*ortho*), $J = 9$ Hz). $^{31}P\{^1H\}$ NMR (in C_6D_6 at 25 °C): 54.30 ppm (AA' part of an AA'XX' pattern; $J(PP) = 2$ Hz, $^1J(RhP) = 139$ Hz, $^2J(RhP) = 5$ Hz, and $J(RhRh) = 44$ Hz).

Preparation of 10. To a pentane (5 mL) dispersion of RhClL₂ (200 mg, 0.44 mmol) was added 1,1,3,3-tetraisopropylsiloxane (140 mg, 0.57 mmol) at room temperature. The purple solution soon turned yellow-brown. Stirring the reaction mixture for 12 h and removing the solvent under reduced pressure left a brown paste. The product was washed with a minimum amount of acetone and recrystallized from acetone to give **10** as yellow crystals (47 mg, 26%). Anal. Calcd for $C_{30}H_{73}ClOSi_2P_2Rh$: C, 44.5; H, 9.1. Found: C, 44.0; H, 9.4. 1H NMR (in C_6D_6 at 25 °C): δ -14.67 (m, 2H, Rh–H), -12.90 (tt, 1H, Rh–H–Rh, $J(HRh) = 56$ Hz, $J(HP) = 28$ Hz), 1.12 (dd, 18 H, P–CH–CH₃, $J(PH) = 13$ Hz, $J(HH) = 7$ Hz), 1.35 (septet, 1H, Si–CH, $J(HH) = 7$ Hz), 1.37 (septet, 1H, Si–CH, $J(HH) = 7$ Hz), 1.45 (d, 6H, Si–CH–CH₃, $J(HH) = 7$ Hz), 1.51 (d, 6H, Si–CH–CH₃, $J(HH) = 7$ Hz), 2.11 (doublet of septets, 2H, P–CH, $J(PH) = 7$ Hz, $J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz in C_6D_6 at 25 °C): δ 20.23 (P–CH–CH₃), 20.38 and 20.91 (Si–CH–CH₃), 22.4 (Si–CH), 25.84 (a filled-in doublet due to virtual coupling, P–CH). $^{31}P\{^1H\}$ NMR (in C_6D_6 at 25 °C): 57.65 ppm (AA' part of an AA'XX' pattern; $J(PP) = 1$ Hz, $^1J(RhP) = 145$ Hz, $^2J(RhP) = 3$ Hz, and $J(RhRh) = 45$ Hz). The low isolated yield of **10** in the above reaction is due to low yield in the recrystallization procedure. The 1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture before purification indicate formation of **10** and RhCl(H)₂L₂ in a 60:40 molar ratio.

(36) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.

Crystal Structure Determination. Crystals of **1**, **7**, and **9** suitable for crystallography were obtained by recrystallization from toluene–pentane mixtures, while recrystallization of **10** was carried out from acetone. 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 $25^\circ \leq 2\theta \leq 35^\circ$. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and the ω - 2θ method. Empirical absorption correction (ψ scan method) of the collected data was applied. Table 3 summarizes crystal data and details of data refinement.

Calculations were carried out by using the program package teXsan on a VAX-II computer. Atomic scattering factors were taken from the literature.³⁶ A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Positions of hydrido ligands were determined by the difference Fourier technique, while the other hydrogens were located by assuming ideal positions. Positions of nonbridging hydrido ligands of **9** were not determined unambiguously, due to insufficient convergence of the structural calculations. These hydrogens were included in the structure calculation without further refinement of the parameters.

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Supporting Information Available: Crystallographic data for complexes **1**, **7**, **9**, and **10** (43 pages). Ordering information is given on any current masthead page.

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