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Review

Structure and chemical properties of mononuclear and dinuclear silylrhodium complexes. Activation of the Si–C bond and formation of Si–Cl and Si–SR bonds promoted by Rh complexes

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Abstract

Recent studies of the structures and chemical properties of organosilylrhodium complexes are surveyed. Oxidative addition of secondary and tertiary silanes to chlororhodium(I) complexes with PMe_3 and with $P(i\text{-}Pr)_3$ ligands leads to the formation of chloro(hydrido)silylrhodium(III) complexes. The resulting Rh(III) complexes are often in equilibrium with Rh(I) complexes via a reversible reductive elimination of the organosilane and its reoxidative addition in solution. Irreversible coupling of chloro and silyl ligands of the complexes with an octahedral or a square-pyramidal Rh(III) center occurs at room temperature when the two ligands are at *cis* coordination sites. Complexes with chloro and organosilyl ligands at *trans* positions are thermally stable and release chlorosilanes upon heating above 80°C. Hydridorhodium(I) complexes formed in the above reaction mixture readily undergo oxidative addition of organosilane to give dihydrido(silyl)rhodium(III) complexes. Dinuclear silylrhodium(III) complexes, $L(H)(Ar_3Si)Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh(SiAr_3)(H)L$ (Ar = Ph, C_6H_4F; L = $P(i\text{-}Pr)_3$), prepared from the reaction of triarylsilane with $RhClI_2$, cause thermally induced Si–C bond cleavage of a triarylsilyl ligand to afford $L(H)Rh(\mu\text{-}Cl)(\mu\text{-}SiAr_3)(\mu\text{-}SiAr_2)Rh(H)L$, accompanied by the evolution of arene. The produced complexes contain a bridging triarylsilyl ligand coordinated symmetrically to the two Rh centers. $RhH(SAr)(SiHAr'_2)(PMe)_3$-type complexes with thiolato and diarylsilyl ligands at *trans* positions undergo clean thermal rearrangement to give complexes with the $Si(SAr)Ar'_2$ ligand. The Rh complex that promoted the Si–S bond forming reaction is extended to the synthesis of a new disilarhodacyclopentane and to the $RhCl(PPh_3)_3$-catalyzed polycondensation of diarylsilane with dithiols to form new Si-containing polymers.

Keywords: Rhodium; Organosilane; Silyl complexe; Bridging ligand; Reductive elimination

1. Introduction

There have been a number of studies on Rh complex catalyzed reactions of organosilicon compounds such as the hydrosilylation of ketones, alkenes, and alkynes, the silylformylation of alkynes, the dehydrogenative coupling of organosilane with alcohols and amines, and polymer synthesis based on these bond-forming reactions [1,2]. Most of the reactions are believed to involve intermediate silylrhodium complexes whose chemical properties are relevant to the mechanism involved in the above synthetic organic reactions. Although many mononuclear and dinuclear silyrhodium complexes containing phosphine or cyclopentadienyl auxiliary ligands were prepared before 1996 [3–17], reports of studies on the reactions of silylrhodium complexes are much fewer than those of their preparation and structural studies. Recently, several research groups have investigated in detail the fundamental reactions of silylrhodium complexes and discussed their relationship to the mechanism involved in the catalytic reactions. This manuscript focuses on our studies of bond-activating and bond-forming reactions promoted by rhodium complexes with auxiliary phosphine ligands.

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2. Si–Cl bond formation of silylrhodium complexes

The conversion of Si–H to Si–Cl bond of organosilicon compounds is often observed in their reaction with chloro transition metal complexes. The hydrosilylation of alkenes using H_2PtCl_6 as a catalyst is actually promoted by colloidal Pt(0) or Pt(II) species generated from the reduction of the catalyst. Although alcohols frequently used as the hydrosilylation solvent would reduce the Pt(IV) catalyst, the reaction of hydrosilane with Pt–Cl complexes would also afford low-valent Pt species and chlorosilanes, as shown in Eq. (1) [18].

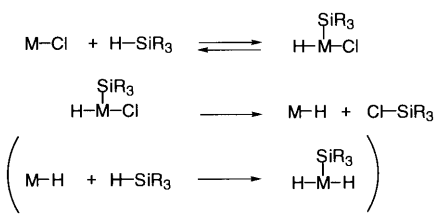
$$H_2PtCl_6 + 6\ R_2SiH_2 \longrightarrow \text{"Pt(0)"} + 6\ R_2SiHCl + 4\ H_2 \quad (1)$$

Clear examples of the reduction of chloro transition metals by triorganosilane have been presented in the reactions of triorganosilanes with $PtCl_2(PR_3)_2$ and with $IrCl(CO)(PR_3)_2$ to give hydrido complexes of these transition metals accompanied by the formation of chlorotriorganosilanes (Eq. (2)) [19].

(2)

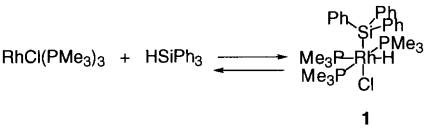
One of the possible pathways of the reaction (Scheme 1) involves the oxidative addition of organosilane to give complexes with chloro, hydrido, and silyl ligands and the subsequent reductive elimination of chloroorganosilanes.

The facile oxidative addition of organosilane containing an Si–H bond to low-valent late transition metals reported so far is consistent with the pathway, while the concerted reductive elimination of chlorosilane from transition metal complexes containing chloro and silyl ligands is not generally accepted and not always employed to account for the chlorination of organosilicon compounds promoted by transition metal complexes. In addition, organotransition metal complexes containing chloro and alkyl (or aryl) ligands at *cis* positions hardly undergo intramolecular reductive elimination of chloroalkanes. Thus, it is of interest to determine whether the formation of chlorosilane from organosilyl transition metal complexes occurs via the concerted reductive elimination or an alternative intermolecular mechanism. Our recent study on the structure and chemical properties of silylrhodium complexes has provided some information on the above issue.



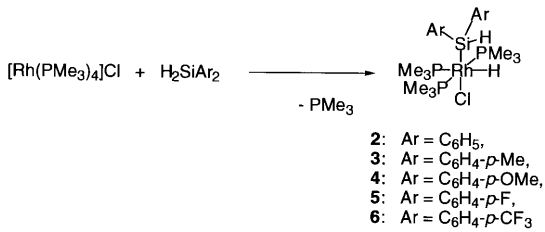
Scheme 1.

The reaction of $HSiPh_3$ with $RhCl(PMe_3)_3$ proceeds smoothly to give the oxidative addition product, *mer*-$RhCl(H)(SiPh_3)(PMe_3)_3$ (**1**), which has Cl and $SiPh_3$ ligands at *trans* positions (Eq. (3)) [20].



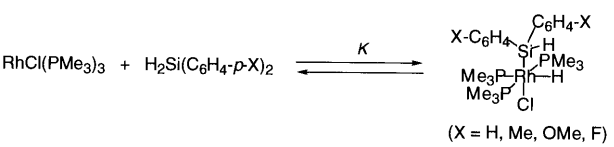
(3)

The NMR spectra of **1** show the presence of equilibrium between **1** and a mixture of $HSiPh_3$ with $RhCl(PMe_3)_3$ via the reversible reductive elimination of $HSiPh_3$ and its reoxidative addition in the solution. Other Rh(III) complexes are not observed in the NMR spectra of the mixture, indicating that complex **1** is thermodynamically much more stable than other isomeric complexes. Highly electron releasing hydrido and silyl ligands [21] tend to occupy mutual *cis* positions of the octahedral coordination. A similar reaction of diarylsilanes with $[Rh(PMe_3)_4]Cl$ gives the oxidative addition product, *mer*-$RhCl(H)(SiHAr_2)(PMe_3)_3$ (**2**–**6**), as shown in Eq. (4).



(4)

The diarylsilylrhodium(III) complexes exist as equilibrated mixtures with $RhCl(PMe_3)_3$ in solution; the thermodynamic parameters of reaction (5) are as follows: $\Delta H^\circ = 4.16$ kJ mol^{-1} and $\Delta S^\circ = 8.2$ J mol^{-1} K^{-1} for X = Me, $\Delta H^\circ = 6.51$ kJ mol^{-1} and $\Delta S^\circ = 11.7$ J mol^{-1} K^{-1} for X = OMe, and $\Delta H^\circ = -2.33$ kJ mol^{-1} and $\Delta S^\circ = -5.3$ J mol^{-1} K^{-1} for X = F, at 298 K.



(5)

The large negative ρ value of the Hammett plot of the reaction enthalpy versus σ_p (Fig. 1) suggests that electron-withdrawing para substituents in the aryl groups render the oxidative addition product more stable. Since the substituents influence Si–H bond energies to a small extent, the stability of the Rh–$SiHAr_2$ bond increases in the presence of electron-withdrawing substituents such as F.

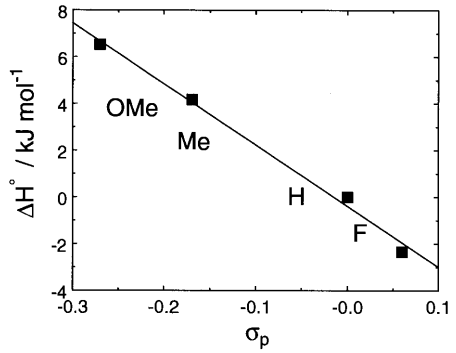
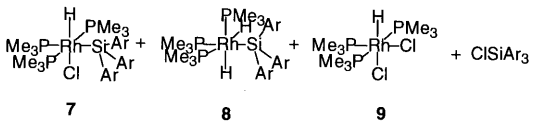


Fig. 1. Hammett plots of the equilibrium constants of reaction (5).

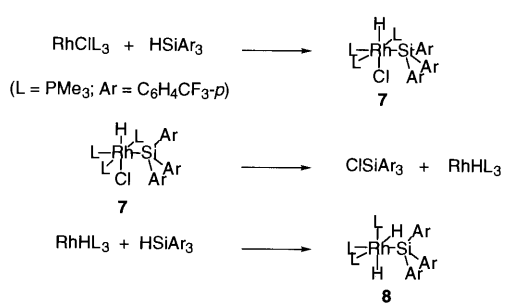
The reaction of $HSi(C_6H_4CF_3\text{-}p)_3$ with the Rh(I)–PMe_3 complex provided results that are quite different from those of the above reactions [22]. The reaction for 15 min at room temperature gives a mixture of Rh(III) complexes **7**, **8**, and **9** in 20%, 24%, and 4% yields, respectively (Eq. (6)). The concomitant formation of $ClSi(C_6H_4CF_3\text{-}p)_3$ is observed from the $^{29}Si\{^1H\}$-NMR spectrum of the reaction mixture.



(6)

The complexes were isolated from the fractional crystallization of the products and characterized by X-ray crystallography and NMR spectroscopy. The oxidative addition product of the reaction, **7**, has chloro and triarylsilyl ligands at *cis* positions, and is different from those of reactions (3) and (4). Complexes **8** and **9** are the secondary products from the initially formed **7** because prolonged reaction leads to an increase in the yields of these two complexes. Scheme 2 depicts a plausible pathway for the reaction which involves the initial oxidative addition of $HSi(C_6H_4CF_3\text{-}p)_3$ to give **7**.

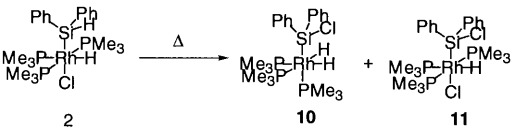
The reductive elimination of $ClSi(C_6H_4CF_3\text{-}p)_3$ from **7** that has Cl and silyl ligands at *cis* sites probably occurs in a concerted manner to generate $RhH(PMe_3)_3$. Further reaction of $HSi(C_6H_4CF_3\text{-}p)_3$ with $RhH(PMe_3)_3$ leads to the formation of **8**, while the pathway



Scheme 2. A plausible pathway for reaction (6).

to **9** is not clear at present. 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 at room temperature. The formation of a dihydridosilyliridium complex in reaction (2) can also be attributed to the reductive elimination of chlorosilane from the initially formed $IrCl(H)(SiR_3)(CO)(PPh_3)_2$, leaving $IrH(CO)(PPh_3)_2$, which further reacts with $HSiR_3$ in the reaction mixture.

The diphenylsilylrhodium complex **2** does not give $ClSiHPh_2$ at room temperature, but heating of its solution above 80°C led to the formation of two Rh(III) complexes, as shown in Eq. (7).



(7)

The formation of **10** can be accounted for by assuming the reductive elimination of $HSiClPh_2$ from **2** and its subsequent reactions with the formed $RhH(PMe_3)_3$. Although the direct reductive elimination of $HSiClPh_2$ from **2** with *trans* Cl and $SiHPh_2$ ligands is not plausible, the thermodynamically less favored isomer of **2** with the two ligands at *cis* positions may be formed in a small amount via a repeated reductive elimination of H_2SiPh_2 from **2** and its rapid reoxidative addition to $RhCl(PMe_3)_3$. The reaction of $HSiClPh_2$ with $RhCl(PMe_3)_3$ gives **11** quantitatively, suggesting that reaction (7) involves the oxidative addition of $HSiClPh_2$ liberated from the thermal reaction of **2** to $RhCl(PMe_3)_3$ which is equilibrated with **2** in solution. The involvement of alternative intermolecular pathways could not be excluded for the reaction which gives **10** and **11** in different ratios depending on the reaction conditions.

$RhCl[P(i\text{-}Pr)_3]_2$ with a 14-electron Rh(I) center is highly coordinatively unsaturated and undergoes facile oxidative addition of various molecules to afford penta-coordinated Rh(III) complexes [23]. Silylrhodium(III) complexes with a penta-coordinated structure would be more labile and reactive than the octahedral Rh(III) complexes with compact PMe_3 ligands. The reactions of triarylsilane with $RhCl[P(i\text{-}Pr)_3]_2$ in 1 h gave the Rh(III) complexes **12**–**17** which were separated from the hexane solution and obtained quantitatively (Eq. (8)) [24].

12: Ar = Ph;
13: Ar = $C_6H_4Me\text{-}p$,
14: Ar = $C_6H_4OMe\text{-}p$,
15: Ar = $C_6H_4Cl\text{-}p$,
16: Ar = $C_6H_4F\text{-}p$,
17: Ar = $C_6H_4CF_3\text{-}p$.

(8)

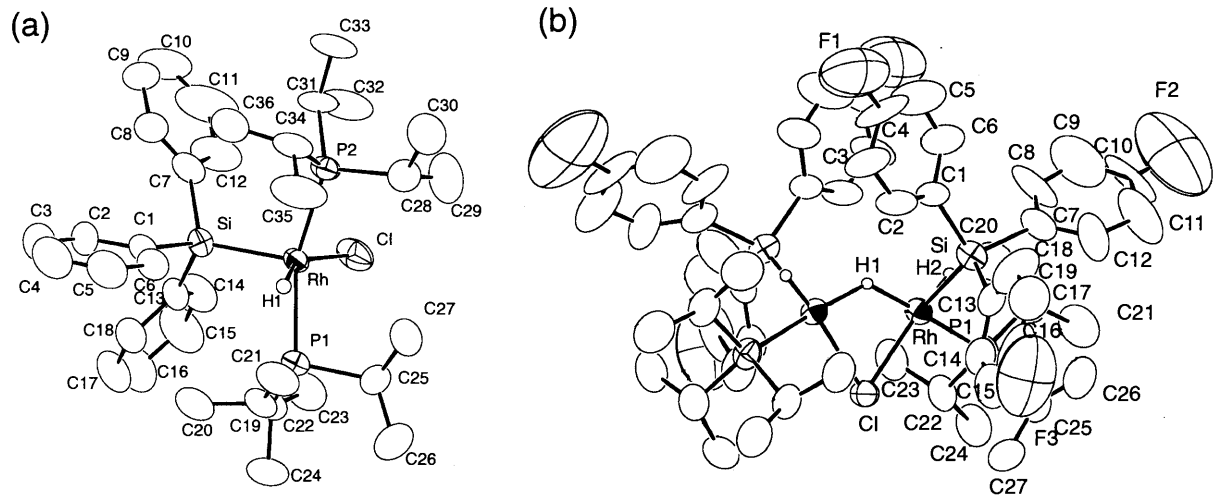
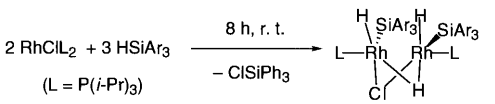


Fig. 2. Molecular structures of (a) **12** and (b) **18**.

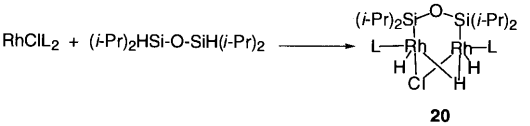
X-ray crystallography of **12** (Fig. 2a) revealed the square-pyramidal coordination with Cl and H ligands at *trans* positions. The *trans* position of the triarylsilyl ligand is vacant, probably due to a large *trans* effect of the silyl ligand which excludes the ligand at *trans* site and prefers the square-pyramidal structure rather than the trigonal-bipyramidal one.

Complex **12** does not undergo reductive elimination of $HSiPh_3$ at room temperature but is gradually converted to a mixture of several Rh complexes including the dinuclear L(H)(Ph_3Si)Rh(μ-H)(μ-Cl)Rh($SiPh_3$)(H)L (**18**). The reaction of $HSiPh_3$ with **12** and the reaction of $HSiPh_3$ with $RhCl[P(i\text{-}Pr)_3]_2$ for over 12 h in toluene also gave **18** (Eq. (9)).



18: Ar = Ph;
19: Ar = $C_6H_4OCF_3$-*p*. (9)

Crystallographic study revealed the structure (Fig. 2b) with a Rh–Rh bond distance (2.815(1) Å) that is slightly longer than the usual Rh–Rh bond distance. Since the presence of a metal–metal bond between d^6 transition metal centers is not plausible, the complex with two Rh(III) centers probably does not contain Rh–Rh bonds. Each Rh center is bonded to non-bridging hydrido, $SiPh_3$, and $P(i\text{-}Pr)_3$ ligands, as well as bridging chloro and hydrido ligands. The H1–Rh–P and H2–Rh–Cl angles (168° and 165°) suggest a distorted square-pyramidal coordination with the $SiPh_3$ ligand at the apical site rather than trigonal-bipyramidal coordination. Complex **20** with a bridging disiloxane ligand is obtained from a similar reaction of tetrakisisopropyldisiloxane, as shown in Eq. (10).

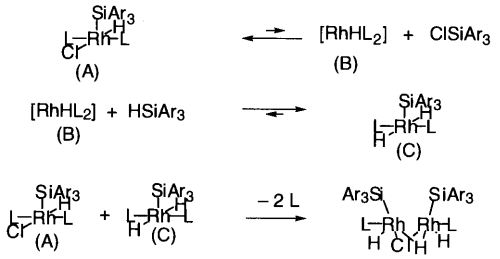


20 (10)

The bridging coordinated disiloxanyl ligand forms a stable dinuclear framework and renders the Rh–Rh bond distance (2.777(1) Å) shorter than that of **18** (2.815(1) Å).

A plausible pathway for the reaction of $HSiPh_3$ with the Rh(I) complex to form **18** is shown in Scheme 3. The reductive elimination of chlorotriarylsilane generates the 14-electron $RhH[P(i\text{-}Pr)_3]_2$ that reacts readily with $HSiAr_3$ in the mixture to give the dihydridosilylrhodium complex (C). The coupling of two Rh(III) complexes (A) and (C) accounts for the formation of the obtained dinuclear complex. Other conceivable reaction pathways include the initial coupling of two molecules of (A), followed by the conversion of the Rh–Cl bond into the Rh–H bond upon reaction with $HSiAr_3$.

Thus, chlororhodium(I) complexes with phosphine ligands convert the Si–H group of the organosilane into the Si–Cl group under mild conditions. This is accompanied by the generation of a highly reactive Rh(I) species containing a hydrido ligand and a coordi-

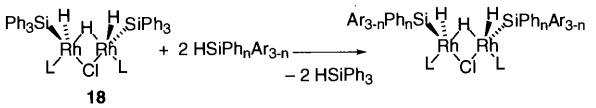


Scheme 3. A plausible pathway for the formation of dinuclear Rh complexes.

natively unsaturated metal center. The formation of chloroorganosilane from the Rh complex with chloro and silyl ligands at *cis* positions is reasonably interpreted as the result of intramolecular reductive elimination from the complex with these ligands.

3. Si–C bond cleavage of dinuclear silylrhodium complex

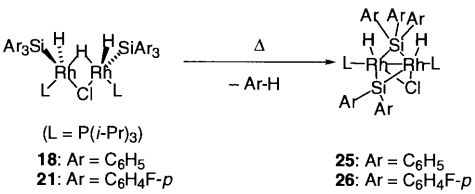
The dinuclear Rh(III) complex **18** with $SiPh_3$ ligands reacts with excess amounts of $HSi(C_6H_4F\text{-}p)_3$, $HSiPh_2(C_6H_4F\text{-}p)$, $HSiPh(C_6H_4F\text{-}p)_2$ and $HSiPh(C_6H_4CF_3\text{-}p)_2$ to give complexes with fluorinated triarylsilyl ligands **21**–**24**, respectively (Eq. (11)). Since the NMR spectra of the reaction mixture show no signals due to mononuclear Rh complexes throughout the reaction, the exchange of silyl ligands is thought to occur in the dinuclear form of the complexes. An attempt to prepare **21** and **24** from the direct reaction of $HSi(C_6H_4F\text{-}p)_3$ and $HSiPh(C_6H_4CF_3\text{-}p)_2$ with $RhCl[P(i\text{-}Pr)_3]_2$ gave mononuclear oxidative addition products, **16** and **17**, which were not converted into the expected dinuclear complexes.



(11)

The reactions of $HSi(C_6H_4\text{-}p\text{-}Me)_3$ and of $HSi(C_6H_4\text{-}p\text{-}OMe)_3$ with **18** gave mixtures of **18** and dinuclear rhodium complexes with one and two tri(4-methylphenyl)silyl or tri(4-methoxyphenyl)silyl ligands even when a large excess of triarylsilane was allowed to react. As demonstrated in reaction (5), $Rh\text{–}SiHAr_2$ bonds in $RhCl(H)(SiHAr_2)(PMe_3)_3$ tend to be stabilized to a larger extent by a more electron-withdrawing substituent on the aryl group. The smooth conversion of **18** to **21**–**24** is partly due to the higher thermodynamic stability of $Rh\text{–}Si(C_6H_4F\text{-}p)_3$ and $Rh\text{–}Si(C_6H_4CF_3\text{-}p)_3$ bonds than $Rh\text{–}SiPh_3$ bonds in the dinuclear Rh complexes. The exchange of the organosilyl ligand was also reported to occur in several other mononuclear and dinuclear transition metal complexes containing the M–Si bond and to be used as a synthetic tool for transition metal silyl complexes which could not be obtained otherwise. Examples of smooth silyl ligand exchange of dinuclear metal complexes were presented in the reaction of triorganosilane with Fe and Ru complexes having a non-bridging triorganosilyl ligand which is replaced easily upon addition of triorganosilane [25].

Heating of hydrocarbon solutions of **18** and **21** causes thermally induced C–Si bond cleavage to give dinuclear Rh complexes with bridging diarylsilylene and triarylsilyl ligands and quantitative amounts of arene (Eq. (12)) [26].



(12)

The $^{31}P\{^1H\}$-NMR spectra measured during the reaction of **18** showed signals of **18** and **25** exclusively, indicating the quantitative conversion of the starting complex to the product and the absence of side reactions. The results of X-ray crystallographic study of **26** (Fig. 3) reveal the presence of several unique structural features. The Rh–Si bond distances between Rh centers and the Si atom of the triarylsilyl ligand are similar (2.444(4) and 2.487(3) Å), and are significantly longer than the bond distances between Si of the silylene

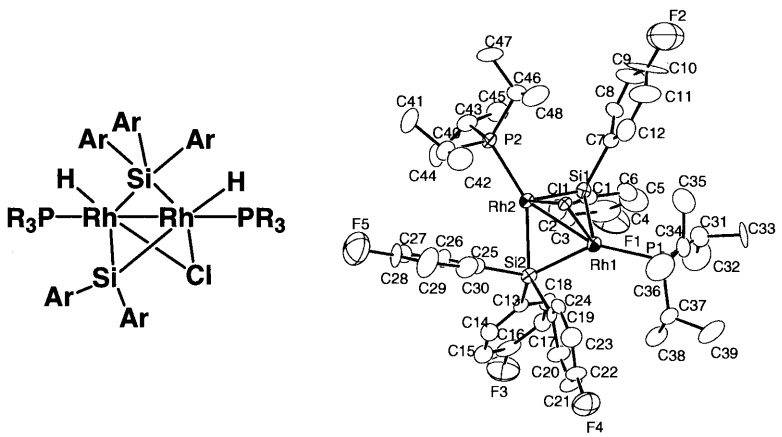
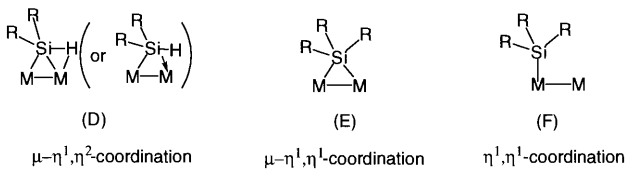


Fig. 3. Molecular structure of **26**.

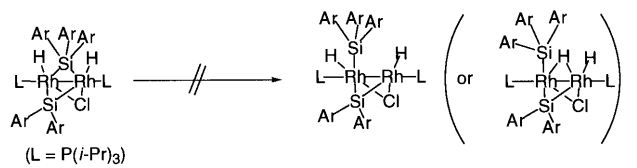
ligand and Rh centers (2.290(3) and 2.250(3) Å) as well as than the Rh–Si σ-bond distances already reported (2.203–2.379 Å). They are comparable even to the Rh–Si bond distance involved in a Rh–H–Si three-center two-electron bond. Although the crystallography of **26** did not reveal the positions of the hydrido ligands, the ^{1}H-NMR spectra of **25** and **26** show the presence of two magnetically equivalent hydrido ligands. The Rh–H bonds are stable and do not undergo fluxional behavior on the NMR time scale. Heating up to 90°C or addition of diarylsilane or alkynes to a solution does not cause any changes in the NMR signals of the complex, indicating the high stability of the complex despite the long Rh–Si σ-bond.

Dinuclear and multinuclear metal complexes with bridging coordinated organosilyl ligands mostly contain $SiHR_2$ or SiH_2R ligands which are bonded to one metal center in a σ fashion and to another via an Si–H–M three-center two-electron bond. Such a μ-η^1,η^2-coordination of the ligand (Scheme 4 (D)) renders the distances between the two M–Si bonds different [27].

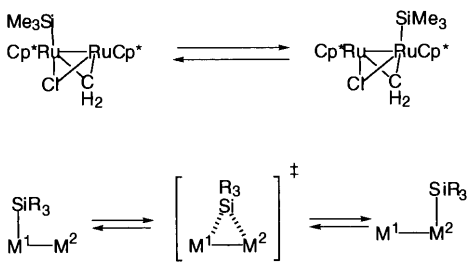
The μ-η^1,η^1-bridging coordination of silyl ligand (Scheme 4 (E)) is much less common, probably because it includes the Si center with a larger coordination number and a weaker coordination bond to metal than the non-bridging coordination of the ligand to a single metal center (Scheme 4 (F)). In most cases, the μ-η^1,η^1-bridging coordination would be less stable than the other coordination forms shown in Scheme 4. Thus, there have been a limited number of studies on non-transition metal complexes with symmetrically bridging triorganosilyl ligands and only a few reports on the transition metal version. The bridging coordination of a triorganosilyl group to Na, Al, and B to form the M–Si–M bond is reported as an analog of the M–H–M or M–CH_3–M three-center two-electron bond of non-transition metals [28]. A dinuclear platinum complex with a bridging $SiMeCl_2$ ligand was reported although no clear structural information was provided by X-ray crystallography [29]. Dinuclear or tetranuclear copper complexes with a sterically demanding $Si(SiMe_3)_3$ group as the bridging ligands were characterized structurally [30]. A diplatinum complex with symmetrically bridging triorganophosphine that is isolobal to a triorganosilyl anion suggests the possibility of the stable coordination of a triorganosilyl group to two transition metal centers [31].



Scheme 4.



Scheme 5.



Scheme 6.

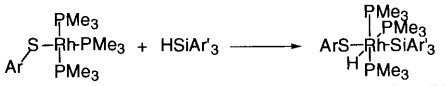
The markedly high thermal stability of the symmetrically bridging coordination of the trisubstituted silyl ligand of **25** and **26** seems to have electronic and steric reasons. The molecular structure with a Rh–Rh bond between two 16-electron Rh(II) centers is maintained by the symmetrical coordination of the silyl ligand. The sterically demanding P(*i*-Pr)$_3$ ligands probably increase the kinetic stability of the Rh–Si–Rh linkage. The conversion of the μ-η^1,η^2-coordination of the silyl ligand of the complex into a non-bridging coordination appears to be a facile reaction process, as shown in Scheme 5, but does not occur even under heating due to the steric repulsion among P(*i*-Pr)$_3$, $SiAr_3$, and $SiAr_2$ ligands. Thus, the isolation of stable dinuclear Rh complexes with a bridging triarylsilyl ligand was realized by choosing a bulky phosphine as the auxiliary ligand.

Although the above complexes exhibit negligible reactivity under various conditions, their structures and formation pathway are intriguing in terms of the mechanism of ligand migration reactions of dinuclear transition metal complexes. A dinuclear Rh complex with an alkyl ligand bonded to one of the metal centers undergoes smooth alkyl group transfer between the two metal centers [32]. The reaction is of significant interest, but the small number of examples of similar ligand transfer has prevented elucidation of the reaction in detail. Recently, analogous organosilyl ligand migration was presented by several research groups. The Fe–Pt or Fe–Pd heterobimetallic complexes stabilized by a bridging diphosphine ligand undergo dissociation of a carbonyl ligand followed by facile transfer of the silyl ligand bonded to Fe to give the product with a newly formed Pt–Si bond [33]. Homonuclear metal complexes also undergo rapid silyl ligand transfer beween metal centers [34,35]. The unsymmetrical diruthenium complex with a non-bridging $SiMe_3$ ligand exhibits a flux-

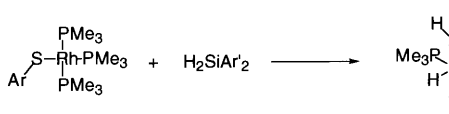
ional NMR spectrum that is ascribed to the rapid and reversible silyl group migration (Scheme 6). The reaction probably involves a dinuclear complex with a symmetrically bridging $SiMe_3$ ligand as an intermediate with similarly high energy to the transition state.

4. Stoichiometric and catalytic Si–S bond forming reactions

The thiolato group is more nucleophilic than Cl and seems to have a higher affinity with Si. The Rh–phosphine complex that promoted the Si–S bond forming reaction was examined by using PMe_3 ligands and compared with analogous Si–Cl bond formation shown in Section 2. The oxidative addition of triarylsilanes and diarylsilanes to $Rh(SAr)(PMe_3)_3$ [36] afforded silylrhodium complexes with hexacoordinated structures, as shown in Eqs. (13) and (14), similarly to reactions (3) and (4) [37]. The silyl and thiolato ligands are at *trans* positions of the octahedral coordination, similarly to **1**–**6**.

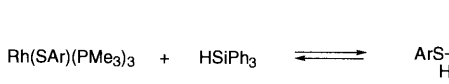


27: Ar = Ph, Ar' = Ph,
28: Ar = C_6H_4-p-Me, Ar' = Ph,
29: Ar = C_6H_4-p-OMe, Ar' = Ph
30: Ar = Ph, Ar' = C_6H_4-m-Me
31: Ar = C_6H_4-p-OMe, Ar' = C_6H_4-m-Me
32: Ar = Ph, Ar' = Ar' = C_6H_4-p-Me
33: Ar = C_6H_4-p-Me, Ar' = C_6H_4-p-F (13)



34: Ar = C_6H_5, Ar' = C_6H_5;
35: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
36: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
37: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
38: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
39: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
40: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
41: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
42: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p* (14)

Complexes **43** and **44** with triarylsilyl ligands are isolated from the mixture containing excess silane but are in equilibrium with $Rh(SAr)(PMe_3)_3$ in solution via repeated rapid reductive elimination and reoxidative addition, as shown in Eq. (15).



43: Ar = Ph,
44: Ar = C_6H_4-p-Me (15)

Thermodynamic parameters of the reaction for Ar = C_6H_4-*p*-Me are determined as $\Delta H^\circ = -61.7 \pm 0.7$ kJ mol^{-1}, $\Delta S^\circ = -227 \pm 15$ J mol^{-1} K^{-1}, and $\Delta G^\circ = 5.9$ kJ mol^{-1} at 298 K, based on the temperature-dependent NMR spectra. The equilibrium in Eq. (15) is favored to the right to a larger extent than that in Eq. (3), probably because the thiolato ligand is more basic than the chloro ligand and tends to stabilize the oxidative addition product more significantly.

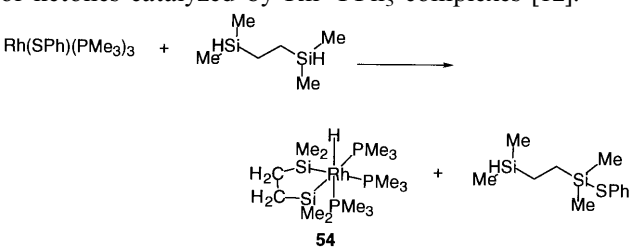
Analogous Rh(III) complexes with diarylsilyl and thiolato ligands at *trans* positions are thermodynamically stable and do not undergo an apparent reductive elimination of diarylsilane at room temperature, but are converted to new Rh(III) complexes with two hydrido ligands and a thiolatosilyl ligand quantitatively upon heating (Eq. (16)) [38].

34: Ar = C_6H_5, Ar' = C_6H_5;
35: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
36: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
37: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
38: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
39: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
40: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
41: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
42: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p*

45: Ar = C_6H_5, Ar' = C_6H_5;
46: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
47: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
48: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
49: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
50: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
51: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
52: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
53: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p* (16)

The Si–S bond forming reactions occur at a lower reaction temperature (ca. 50–70°C) than the analogous reaction of thermally induced conversion of **2** with chloro and diraylsilyl ligands at *trans* positions to **10** in Eq. (7) (>80°C). The above reactions proceed very cleanly without the formation of by-products such as $RhH(SAr)[Si(SAr)Ar'_2](PMe_3)_3$.

$Rh(SPh)(PMe_3)_3$ reacts with 1,2-bis(dimethylsilyl)ethane to give disilarhodacyclopentane **54** (Eq. (17)) [39]. The chelating coordination of the ligand to Rh complexes plays an important role in the hydrosilylation of ketones catalyzed by Rh–PPh_3 complexes [12].

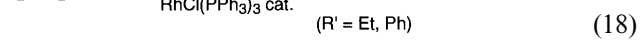


54

(17)

Loss of the thiolato ligand during the reaction can be ascribed to the elimination of the thiolatosilane via the initial oxidative addition of an Si–H group to the Rh center and the subsequent coupling of silyl and thiolato ligands of the Rh(III) intermediate.

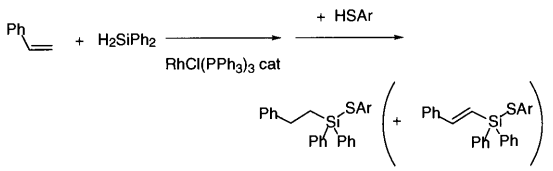
Rh–PMe_3 complexes containing both thiolato and silyl ligands and their stoichiometric Si–S bond forming reaction in Eq. (16) seem to be related to the already reported dehydrogenative coupling of diarylsilane with thiol catalyzed by $RhCl(PPh_3)_3$ (Eq. (18)) [40].



(R' = Et, Ph) (18)

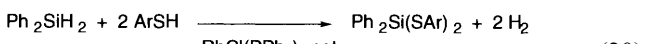
Complexes with silyl and thiolato ligands at *trans* positions of the octahedral coordination were isolated because the structure prevented facile coupling of these ligands. Since the Rh(III) complex with PPh_3 ligands has a more labile penta-coordinated structure, the complex with silyl and thiolato ligands generated in the above catalytic reaction would cause facile Si–S bond formation.

The catalytic reaction was combined with hydrosilylation to obtain the product from three starting compounds, as shown in Eq. (19) [41]. The accompanying dehydrosilylation [42] is controlled by the reaction conditions.

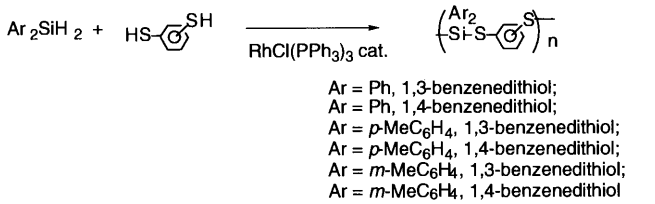


(19)

Extension of the dehydrogenative coupling to dithiol and diarylsilane is expected to give an Si–S bond containing polymers whose preparation method is quite limited [43]. Both a model reaction of H_2SiPh_2 with two times its molar amount of thiol (Eq. (20)) and the polycondensation of diarylsilanes with aromatic dithiols (Eq. (21)) proceed smoothly to give the desired products [44]. GPC analyses of the polymerization mixture showed the initial formation of oligomers which are converted to higher polymers on heating. The molecular weight of the product from bis(4-methylphenyl)-silane with 1,3-benzenedithiol was $M_n = 5400$ and $M_w = 7000$ based on polystyrene standards.



(20)



(21)

The polymers are gradually hydrolyzed in air and converted to polysiloxane which is insoluble in organic solvents and can be kept for several weeks without decomposition under Ar.

5. Conclusion

Si–Cl and Si–S bond-forming reactions are thermodynamically favored and occur more easily and more selectively by using transition metal catalysts. The stoichiometric bond-forming reactions shown above demonstrate the important roles of intermediate metal complexes with both silyl and chloro (or thiolato) ligands in these catalytic reactions. The concerted reductive elimination of chlorosilane from the complex with chloro and triarylsilyl ligands is established, whereas several other reactions included in this paper are left for future investigation for the complete elucidation of the mechanism. Si–C bond activation of a dinuclear Rh complex takes place cleanly to afford a new type of complex with a bridging trisubstituted silyl ligand. The selective activation and formation of various kinds of interelemental linkage promoted by transition metal compounds will, with continued efforts, be achieved by many research groups including ours in the near future.

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