# Dehydrogenative Coupling of Monohydrosilanes Mediated by (2-Phosphinoethyl)silylrhodium(I) Complex

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Treatment of $HSiMe_2Ph$ with a square-planar rhodium(I) complex $Rh[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$ gave rise to selective dehydrogenative coupling of hydrosilanes to afford $(SiMe_2Ph)_2$ and $RhH_2[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$.

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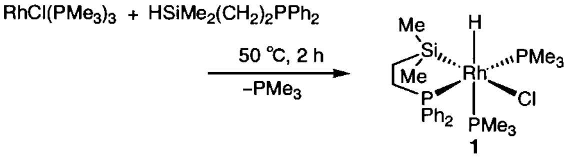
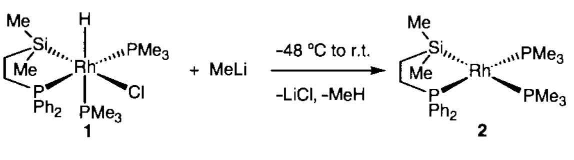
The empirical *trans*-influencing ability of silyl ligands has been estimated to exceed both hydrido and alkyl ligands.[1] Considering the strong σ-donor and the high *trans*-influencing ability of silyl ligands, the silyl ligands are expected to exhibit exceptionally strong *trans*-effect. Therefore, silyl ancillary ligands would greatly accelerate the generation of the reactive unsaturated metal center. Nevertheless, to our knowledge, little has been known about the influence of silyl ancillary ligands on the reactivity of transition-metal complexes.[2] This comes mainly from the facile cleavage of the metal–silicon bonds via reductive elimination, nucleophilic attack at the silyl silicon atom, insertion, and σ-bond metathesis.[3] To suppress the elimination of silyl ligands, five-membered (2-phosphinoethyl)silyl chelate ligands have been employed.[4,5] In this communication, we report the synthesis, structure, and reactivity of $Rh[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$.

Reaction of $RhCl(PMe_3)_3$ with $HMe_2SiCH_2CH_2PPh_2$ in toluene at 50 °C gave $RhCl(H)[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2]\text{-}(PMe_3)_2$ (**1**)[6] in 65% yield (eq 1). The $^1H$, $^{29}Si$, and $^{31}P$ NMR data support the octahedral *mer*-geometry of complex **1**. The iridium analogue $IrCl(H)[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$ has been synthesized by the thermal reaction of $[Ir(CO)(PMe_3)_4]Cl$ with $HMe_2SiCH_2CH_2PPh_2$.[5c]



(1)

Treatment of **1** with 1 equiv of MeLi at room temperature led to the almost quantitative formation of a coordinatively unsaturated silylrhodium(I) complex $Rh[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2\text{-}\ CH_2PPh_2]\text{-}(PMe_3)_2$ (**2**)[7] (eq 2). Workup of the resulting solution and recrystallization from toluene at –75 °C gave orange crystals of **2** in 35% isolated yield. The molecular structure and selected bond lengths and angles of **2** are shown in Figure 1.[8] Complex **2** is among few silyl rhodium(I) complexes[9] and adopts a slightly distorted square planar geometry. The angles P1–Rh–P2 and P3–Rh–Si are 167.65(3) Å and 176.58(2) Å, respectively. The Rh–Si bond length is 2.3937(8) Å that is relatively longer than those of the previously reported silylrhodium(I) complexes $(Ph_3Si)Rh(PMe_3)_3$ [2.317(1) Å][9a] and $(PhMe_2Si)Rh(PMe_3)_3$ [2.3804(10) Å].[9c] The change of the Rh–Si bond lengths is attributable to the degree of the M(dπ)–SiX(σ*) interaction.[10] When more electron-withdrawing groups are bonded to silicon, this interaction becomes stronger and, as a result, the Rh–Si bond becomes shorter.[3] The silyl ligand in **2** bears three electron-donating alkyl groups on the silicon atom which makes the Rh–Si bond of **2** the longest among them. In agreement with the strong *trans*-influence of the silyl ligand, the length of the Rh–P3 bond is longer by 0.05 Å than that of the Rh–P2 bond.



(2)

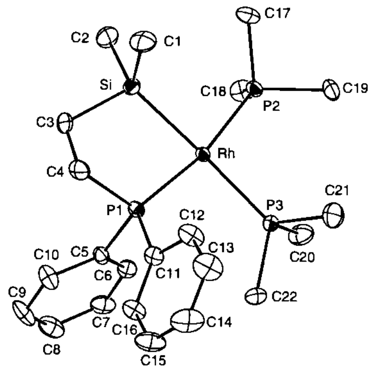
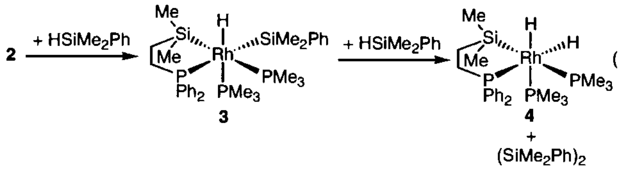


**Figure 1**. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Rh-P1 2.2672(7), Rh-P2 2.2823(7), Rh-P3 2.3339(7), Rh-Si 2.3937(8), P1-Rh-P2 167.65(3), P1-Rh-P3 95.96(3), P1-Rh-Si 81.24(3), P2-Rh-P3, 95.13(3), P2-Rh-Si 87.85(3), P3-Rh-Si 176.58(2).

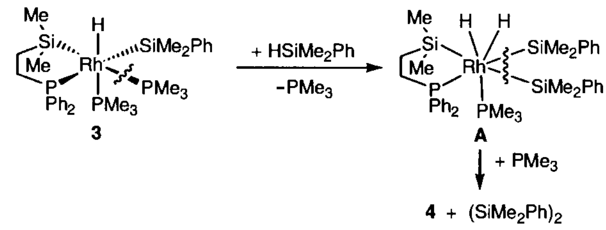
The reaction 2 may proceed via formation of $RhH(Me)[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$, but it was not detected spectroscopically in the course of the reaction. We previously reported the synthesis of $IrH(Me)[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$ by the reaction of $IrCl(H)[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$ with MeLi.[5c] Thermolysis of the hydrido(methyl)iridium complex in toluene at 55 °C led to the elimination of methane to give the unidentified product(s) with an Ir–H bond. No formation of the iridium analogue of **2** $Ir[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)_2$ was observed. This striking difference of the thermal stability between Rh and Ir is consistent with the general trend: The iridium complexes with high oxidation state are more stable than the corresponding rhodium complexes.[11] Complex **2** represents the first example of a coordinatively unsaturated trialkylsilylrhodium(I) complex. Due to the strongly electron-releasing character of the trialkylsilyl moiety, **2** may be highly reactive toward various small molecules.

In fact, the reaction of **2** with 6 equiv of $HSiMe_2Ph$ proceeded spontaneously at room temperature to give the hydrido(silyl)rhodium(III) complex **3**[12] quantitatively. After 20 h at room temperature, the mixture of **3** and $HSiMe_2Ph$ was converted to dihydrido complex **4**[13] and $(SiMe_2Ph)_2$ in 91% yield each. The $^{31}P\{^1H\}$ NMR data established the *fac*-geometry of **3**. The RhH signal in the $^1H$ NMR spectrum appears at –10.30 ppm as pseudo double quartets



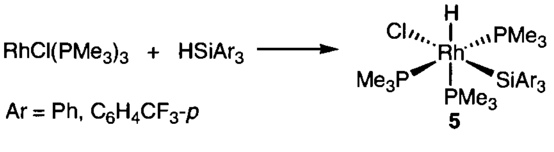
(3)

($J(HP_{trans})$ = 123.0 Hz, $J$(HRh) = $J(HP_{cis})$ = 16.0 Hz). Other NMR data also support the structure of **3**. The dihydrido complex **4** was independently synthesized by treatment of **1** with $LiAlH_4$ in THF and characterized based on the results of elemental analysis and spectroscopic data. Scheme 1 shows a plausible mechanism for the formation of **4** and $(SiMe_2Ph)_2$. The first step is the dissociation of $PMe_3$ from **3** and then oxidative addition of $HSiMe_2Ph$ takes place to give a silylrhodium(V) intermediate $RhH_2(SiMe_2Ph)_2[(\kappa^2\text{-}Si,P)\text{-}Me_2SiCH_2CH_2PPh_2](PMe_3)$ (**A**). A similar silylrhodium(V) complex to **A** has been reported by Nagashima et al.[14] Complex **A** undergoes reductive elimination of disilane and subsequent ligation of $PMe_3$ to Rh gives **4**.



**Scheme 1.** Formation mechanism of **4** and disilane.

Osakada et al. reported the reaction of $RhCl(PMe_3)_3$ with $HSiAr_3$.[15] The reaction proceeded at room temperature to give *mer*-$[RhCl(H)(SiAr_3)(PMe_3)_3]$ (**5**) (eq 4). In the reaction, the Si–Si reductive elimination products such as $RhCl(H)_2(PMe_3)_3$ and $(SiAr_3)_2$ were not observed.[16] The dramatic difference of reactivity between **3** and **5** is of great interest. The difference is attributable to the exceptionally strong *trans*-effect of the silyl ligand in **3**. Further reaction of **3** and **5** requires the dissociation of the phosphine ligand, which allows it to form bis(silyl)rhodium(V) intermediate. In complex **3**, the silyl moiety of (2-phosphinoethyl)silyl chelate ligand would accelerate the dissociation of the *trans*-$PMe_3$ ligand, while such an effect is not operative in complex **5**.



(4)

It has been known that the dehydrogenative coupling of monohydrosilanes requires the considerably severe conditions and is accompanied by the scrambling of substituents on the silicon atoms.[17] It should be noted that the reaction 3 proceeds at room temperature to give the silicon–silicon coupling product exclusively.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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6 Data for **1**: $^1H$ NMR (300 Hz, $C_6D_6$) δ –9.32 (pseudo dq, $^2J(HP_{trans})$ = 158.1 Hz, $^2J(HP_{cis})$ = $^1J$(HRh) = 15.3 Hz, 1H, RhH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$) δ –25.1 (broad m, $PMe_3$ (*trans* to RhH)), –7.6 (ddd, $^2J(PP_{trans})$ = 364.3 Hz, $^1J$(PRh) = 107.5 Hz, $^2J(PP_{cis})$ = 31.5 Hz, $PMe_3$ (*trans* to $PPh_2$)), 55.5 (ddd, $^2J(PP_{trans})$ = 364.3 Hz, $^1J$(PRh) = 109.7 Hz, $^2J(PP_{cis})$ = 26.2 Hz, $PPh_2$). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $C_6D_6$) δ 40.4 (dddd, $^1J$(SiRh) = 26.1 Hz, $^2J(SiP_{cis})$ = 10.5, 8.2, 6.9 Hz). Anal. Calcd for $C_{22}H_{39}SiP_3ClRh$: C 46.94, H 6.98%. Found: C 47.21, H 6.99%.

7 Data for **2**: $^1H$ NMR (300 MHz, toluene-$d_8$, –40 °C) δ 0.80 (d, $^2J$(HP) = 4.7 Hz, 9H, $PMe_3$), 0.86 (s, 6H, $SiMe_2$), 1.32 (d, $^2J$(HP) = 5.7 Hz, 9H, $PMe_3$), 2.43 (m, 2H, $PCH_2$), 6.95–7.07, 7.95 (m, 10H, $PPh_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$, –40 °C) δ –21.1 (pseudo dt, $^1J$(PRh) = 112.9 Hz, $^2J(PP_{cis}) \cong$ 35.9 Hz, $PMe_3$ (*trans* to $SiMe_2$)), –9.0 (ddd, $^2J(PP_{trans})$ = 296.0 Hz, $^1J$(PRh) = 148.0 Hz, $^2J(PP_{cis})$ = 36.6 Hz, $PMe_3$ (*trans* to $PPh_2$)), 70.5 (ddd, $^2J(PP_{trans})$ = 296.0 Hz, $^1J$(PRh) = 157.2 Hz, $^2J(PP_{cis})$ = 35.1 Hz, $PPh_2$). Anal. Calcd for $C_{22}H_{38}SiP_3Rh$: C 50.19, H 7.28%. Found: C 49.77, H 7.15%.

8 Crystallographic data for **2**: $C_{22}H_{38}SiP_3Rh$, $M_r$ = 526.45, *triclinic*, space group $P\bar{1}$ (variant No.2), $a$ = 11.4349(6) Å, $b$ = 12.9113(9) Å, $c$ = 9.5714 Å, $\alpha$ = 100.379(5)°, $\beta$ = 104.093(2)°, $\gamma$ = 106.562(3)°, $V$ = 1265.5(1) Å$^3$, $T$ = –123.0 °C, $Z$ = 2, $D_c$ = 1.38 g cm$^{-3}$, $\mu$(Mo Kα) = 9.61 cm$^{-1}$, $R$ = 0.068, $Rw$ = 0.189 for 5596 unique reflections.

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12 Isolation of **3** was unsuccessful due to its thermal instability. Data for **3**: $^1H$ NMR (300 MHz, toluene-$d_8$, –20 °C) δ –10.30 (pseudo dq $^1J(HP_{trans})$ = 123.0 Hz, $^1J$(HRh) = $^2J(HP_{cis})$ = 16.0 Hz, 1H, Rh*H*). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$, –20 °C) δ –28.3 (ddd, $^1J$(PRh) = 80.0 Hz, $^2J(PP_{cis})$ = 32.0 Hz, $^2J(PP_{cis})$ = 28.6 Hz, $PMe_3$), –18.2 (ddd, $^1J$(PRh) = 103.0 Hz, $^2J(PP_{cis})$ = 28.6 Hz, $^2J(PP_{cis})$ = 24.8 Hz, $PMe_3$), 60.1 (ddd, $^1J$(PRh) = 82.0 Hz, $^2J(PP_{cis})$ = 32.0 Hz, $^2J(PP_{cis})$ = 24.8 Hz, $PPh_2$).

13 Data for **4**: $^1H$ NMR (300 MHz, toluene-$d_8$) δ –10.57 (pseudo dq, $^2J(HP_{trans})$ = 135.0 Hz, $^2J(HP_{cis})$ = $^1J$(HRh) = 18.0 Hz, 1H, RhH), –9.27 (pseudo dq, $^2J(HP_{trans})$ = 135.0 Hz, $^2J(HP_{cis})$ = $^1J$(HRh) = 21.0 Hz, 1H, RhH), 0.61, 0.83 (s, 3H, SiMe). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$) δ –20.0 (ddd, $^1J$(PRh) = 87.7 Hz, $^2J$(PP) = 28.6 Hz, $^2J$(PP) = 19.1 Hz, $PMe_3$), –11.3 (dt, $^1J$(PRh) = 101.1 Hz, $^2J$(PP) = 26.7 Hz, $PMe_3$), 68.2 (dt, $^1J$(PRh) = 101.1 Hz, $^2J$(PP) = 21.9 Hz, $PPh_2$). Anal. Calcd for $C_{22}H_{40}SiP_3Rh$: C 50.00, H 7.63%. Found: C 49.29, H 7.44%.

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16 The reaction of $RhCl(PMe_3)_3$ with $HSiMe_2Ph$ gave the Si–H oxidative addition product quantitatively. Even at 70 °C, no formation of $(SiMe_2Ph)_2$ was observed.

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