

## Supporting Information

### **Hydrogen-Bridged Bis(silylene) Complexes of Ruthenium and Iron: Synthesis, Structures and Multi-Centre Bonding Interactions at the M-Si-H-Si Four-Membered Ring**

Hisako Hashimoto,\* Katsuto Komura, Takatoshi Ishizaki, Yuto Odagiri and Hiromi Tobita\*

To whom correspondence should be addressed. E-mail: hhashimoto@m.tohoku.ac.jp (H.H.);  
tobita@m.tohoku.ac.jp (T.H.)

*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578,  
Japan.*

### Contents

- 1. Experimental Procedures**
- 2. X-ray Crystal Structure Analysis**
- 3. Theoretical Calculations**
- 4. References**

## 1. Experimental Procedures

### 1-1 General procedures

All manipulations were performed using either standard Schlenk techniques, vacuum line techniques, or in a drybox under an argon atmosphere. Anhydrous tetrahydrofuran (THF) and diethyl ether were purchased from Kanto Chemical Co., Inc., and used without further purification. Toluene and hexane were dried over sodium benzophenone ketyl and distilled under nitrogen atmosphere. Benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) was dried over calcium hydride and then with molecular sieves. Toluene-*d*<sub>8</sub> was dried over calcium hydride and then with a potassium mirror, and transferred into a reaction vessel under vacuum. LiAlH<sub>4</sub> was purchased from Aldrich Chemicals and used as it was received. Cp\**Ru*(CO)(py)Me,<sup>S1</sup> Cp\**Fe*(CO)(py)Me,<sup>S2</sup> Ph<sub>2</sub><sup>*t*</sup>BuSiCl<sup>S3</sup> and <sup>*t*</sup>BuMe<sub>2</sub>SiCl<sup>S4</sup> were prepared by the literature procedures. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were obtained by a Bruker AVANCE-300 or a Bruker AVANCE-400 spectrometers. The <sup>1</sup>H or <sup>13</sup>C NMR chemical shifts were referenced to the residual proton (C<sub>6</sub>D<sub>5</sub>H in C<sub>6</sub>D<sub>6</sub>: δ = 7.15, C<sub>6</sub>D<sub>5</sub>CD<sub>2</sub>H in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>: δ = 2.09) and the carbon (C<sub>6</sub>D<sub>6</sub>: δ = 128.0, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>: δ = 20.4) of deuterated solvents. The <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were referenced to an external standard of tetramethylsilane (δ = 0.0). The coupling constant *J*(Si-Si) was measured using the INEPT-INADEQUATE pulse sequence<sup>S5</sup> on a Bruker AVANCE-400 spectrometer. IR spectra were recorded on a HORIBA FT-730 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer. High resolution mass spectroscopy and elemental analysis were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

### 1-2 Synthesis of H<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu

H<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu was prepared by applying the synthetic method for H<sub>3</sub>SiSiMe<sub>2</sub><sup>*t*</sup>Bu,<sup>S6</sup> namely chlorination of Ph<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu followed by reduction of the resulting Cl<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu with LiAlH<sub>4</sub> (vide infra). Although Ph<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu has already been reported in the literature,<sup>S7</sup> we synthesized it in much higher yield by the following method.

**Ph<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu.** A dark green solution of Ph<sub>2</sub><sup>*t*</sup>BuSiLi, which was prepared by the reaction of Ph<sub>2</sub><sup>*t*</sup>BuSiCl (24.3 g, 0.0886 mol) with a finely cut lithium wire (6.12 g, 0.882 mol) in THF (44 mL) for 2 h at room temperature, was added to <sup>*t*</sup>BuMe<sub>2</sub>SiCl (13.1g, 0.0872 mol) in THF (45 mL) at room temperature. The resulting mixture was stirred overnight at room temperature and was hydrolyzed with water. To the mixture was added diethyl ether, and the organic layer was separated. The aqueous layer was extracted with diethyl ether. All diethyl ether solutions were combined and the combined solution was washed with saturated NH<sub>4</sub>Cl aq, water, and then saturated NaCl aq. The organic layer was dried over anhydrous MgSO<sub>4</sub>, and filtered. Evaporation of the filtrate in vacuo gave Ph<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu as colorless crystals in 88% yield (27.3 g, 0.0768 mol). For elemental analysis, the product was purified by recrystallization from hexane at -30 °C to give colorless crystals. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.29 (s, 6H, Me), 0.79 (s, 9H, SiMe<sub>2</sub><sup>*t*</sup>Bu), 1.15 (s, 9H, Ph<sub>2</sub><sup>*t*</sup>BuSi), 7.15–7.21 (m, 6H, *m*-, *p*-Ph), 7.70–7.75 (m, 4H, *o*-Ph); <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, DEPT, C<sub>6</sub>D<sub>6</sub>): δ -11.2 (Ph<sub>2</sub><sup>*t*</sup>BuSi), -9.0 (SiMe<sub>2</sub><sup>*t*</sup>Bu); Mass (EI, 70 eV): *m/z* 354 (M<sup>+</sup>, 7), 297 (M<sup>+</sup>-<sup>*t*</sup>Bu, 45), 241 (M<sup>+</sup>-2<sup>*t*</sup>Bu, 12), 197 (M<sup>+</sup>-SiMe<sub>2</sub><sup>*t*</sup>Bu, 48), 135 (PhSiSi<sup>+</sup>, 100), 73 (SiMe<sub>3</sub><sup>+</sup>, 33). Anal. Calcd. for C<sub>22</sub>H<sub>34</sub>Si<sub>2</sub>: C, 74.50; H, 9.66. Found: C, 74.65; H, 9.68%.

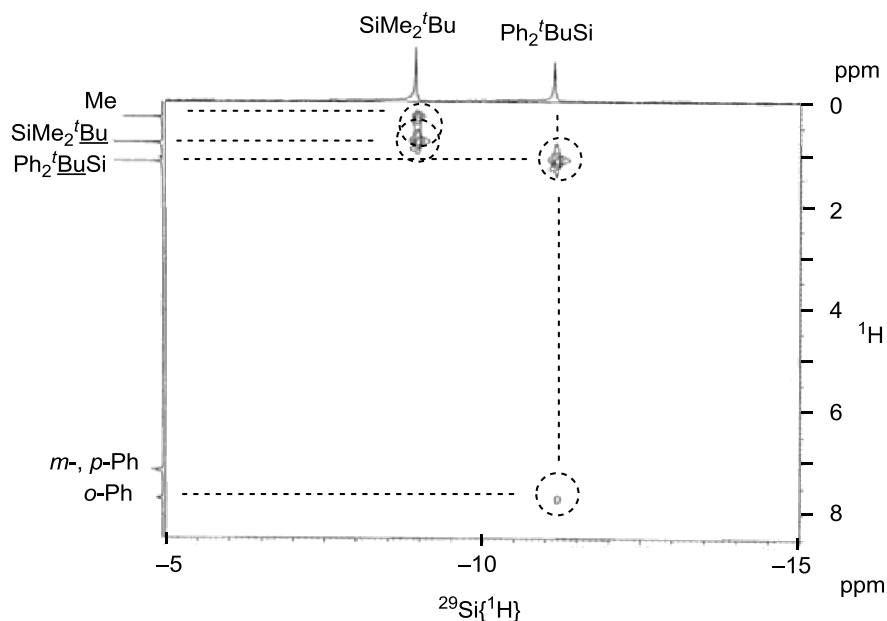
**Cl<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu.** Dry HCl gas generated by addition of concentrated sulfuric acid to sodium chloride, was injected into a solution of Ph<sub>2</sub><sup>*t*</sup>BuSiSiMe<sub>2</sub><sup>*t*</sup>Bu (20.1 g, 0.0568 mol) in toluene (98 mL) containing a catalytic amount of freshly sublimed AlCl<sub>3</sub>. The reaction was monitored by gas chromatography. After 1

h, the reaction mixture was quenched with a drop of dry acetone, and then the solvent was removed in vacuo. By molecular distillation (65 °C / 0.3 mmHg) of the residue, Cl<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu was obtained in 83% yield (12.7 g, 0.0469 mol) as a colorless liquid. This sample was used for the next reaction without further purification. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.15 (s, 6H, Me), 0.98 (s, 9H, SiMe<sub>2</sub><sup>t</sup>Bu), 1.03 (s, 9H, Cl<sub>2</sub><sup>t</sup>BuSi); <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ -3.4 (SiMe<sub>2</sub><sup>t</sup>Bu), 36.5 (Cl<sub>2</sub><sup>t</sup>BuSi).

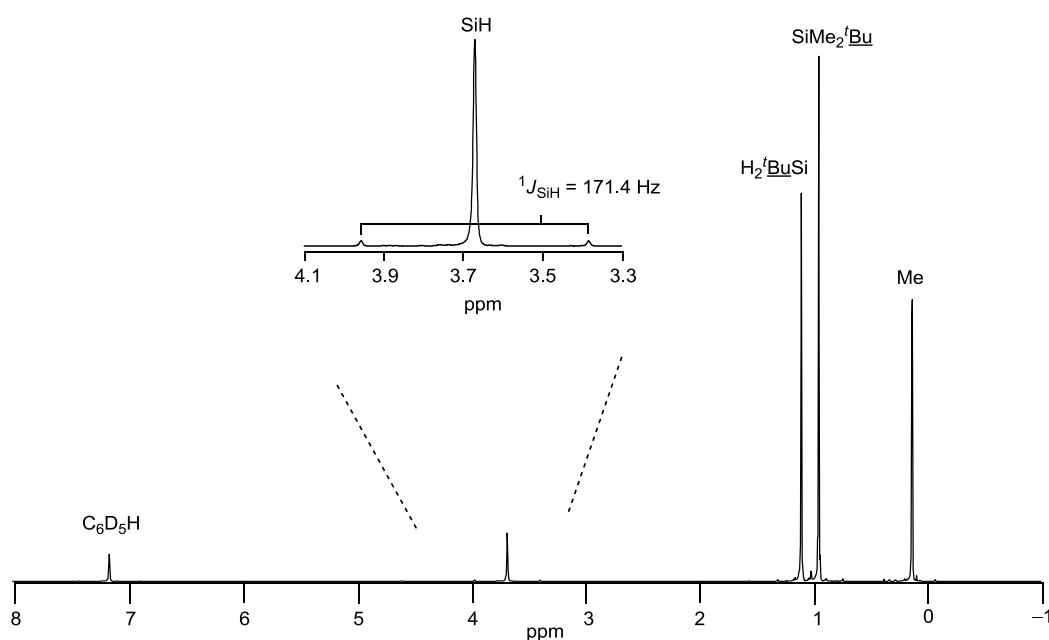
**H<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu.** A solution of Cl<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu (11.3 g, 0.0416 mol) in diethyl ether (25 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (3.18 g, 0.0838 mol) in diethyl ether (60 mL) at room temperature. The reaction mixture was refluxed for 6 h and then hydrolyzed with 0.5 M sulfuric acid at 0 °C. The mixture was moved into a separatory funnel, diethyl ether was added to it, and the organic layer was separated. The aqueous layer was extracted with diethyl ether. All diethyl ether solutions were combined and the combined one was washed with saturated NaHCO<sub>3</sub> aq, water, and saturated NaCl aq. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed from the filtrate by continuous distillation, and then the residue was distilled under reduced pressure (101 °C/28 mmHg). H<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu was obtained in 77% yield (6.51 g, 0.0321 mol) as a colorless liquid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.13 (s, 6H, Me), 0.95 (s, 9H, SiMe<sub>2</sub><sup>t</sup>Bu), 1.10 (s, 9H, SiH<sub>2</sub><sup>t</sup>Bu), 3.69 (s, <sup>1</sup>J<sub>SiH</sub> = 171.4 Hz, 2H, SiH); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.1 (Me), 16.9 (SiH<sub>2</sub>CMe<sub>3</sub>), 17.4 (SiMe<sub>2</sub>CMe<sub>3</sub>), 27.1 (SiMe<sub>2</sub>CMe<sub>3</sub>), 30.4 (H<sub>2</sub>(CMe<sub>3</sub>)Si); <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ -41.9 (SiH<sub>2</sub><sup>t</sup>Bu), -6.0 (SiMe<sub>2</sub><sup>t</sup>Bu); Mass (EI, 70 eV): *m/z* 202 (M<sup>+</sup>), 115 (M<sup>+</sup>-SiH<sub>2</sub><sup>t</sup>Bu), 85 (M<sup>+</sup>-SiMe<sub>2</sub><sup>t</sup>Bu - 2H); Exact mass for C<sub>10</sub>H<sub>26</sub>Si<sub>2</sub>: 202.1573. Found: 202.1570.

**1-3 Synthesis of Cp\*Ru(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (2).** To a solution of Cp\*Ru(CO)(py)Me (544 mg, 1.52 mmol) in toluene (12 mL) in a 50 mL Schlenk tube was added H<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu (323 mg, 1.60 mmol) and then BPh<sub>3</sub> (350 mg, 1.45 mmol). The mixture was stirred for 2 h at room temperature. During that time, a white precipitate of py·BPh<sub>3</sub> was formed. After filtration of py·BPh<sub>3</sub>, all volatiles were evaporated from the filtrate and the residue was recrystallised from hexane at -30 °C to give yellow crystals of **2** (472 mg, 1.01 mmol, 67% yield) as a mixture of *cis*- and *trans*-isomers. The ratio of *cis*- and *trans*-isomers was determined to be *cis* : *trans* = 3 : 1 by <sup>1</sup>H NMR. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K, δ) *cis*-**2**: 0.46 (d, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, 6H, SiMe), 1.20 (s, 18H, SitBu), 1.89 (s, 15H, Cp\*), 3.34 (sept, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz), 1H, Si··H··Si); *trans*-**2**: 0.56 (d, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 3H, SiMe), 0.88 (d, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 3H, SiMe), 1.08 (s, 9H, Si<sup>t</sup>Bu), 1.13 (s, 9H, Si<sup>t</sup>Bu), 1.91 (s, 15H, Cp\*), 3.42 (sept, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 1H, Si··H··Si); <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>, 300 K, δ); *cis*-**2**: 0.46 (d, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, 6H, SiMe), 1.17 (s, 18H, SitBu), 1.90 (s, 15H, Cp\*), 3.35 (sept, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, *J*<sub>SiH</sub> = 21.6 Hz (determined by <sup>1</sup>H homodecoupling), 1H, Si··H··Si); *trans*-**2**: 0.55 (d, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, 3H, SiMe), 0.88 (d, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 3H, SiMe), 1.08 (s, 9H, Si<sup>t</sup>Bu), 1.13 (s, 9H, Si<sup>t</sup>Bu), 1.91 (s, 15H, Cp\*), 3.42 (sept, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 1H, Si··H··Si); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 300K, δ) *cis*-**2**: -2.4 (SiMe), 11.6 (C<sub>5</sub>Me<sub>5</sub>), 24.2 (CMe<sub>3</sub>), 29.2 (CMe<sub>3</sub>), 96.2 (C<sub>5</sub>Me<sub>5</sub>), 210.7 (CO); *trans*-**2**: -2.6 (SiMe), 3.0 (SiMe), 11.9 (C<sub>5</sub>Me<sub>5</sub>), 24.3 (CMe<sub>3</sub>), 25.3 (CMe<sub>3</sub>), 29.1 (CMe<sub>3</sub>), 96.3 (C<sub>5</sub>Me<sub>5</sub>), 210.4 (CO); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>, DEPT, 300 K, δ) *cis*-**2**: 91.4 (SiMe<sup>t</sup>Bu); *trans*-**2**: 55.4 (SiMe<sup>t</sup>Bu), 113.8 (SiMe<sup>t</sup>Bu); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, toluene-*d*<sub>8</sub>, DEPT, 300 K, δ) *cis*-**2**: 91.3 (SiMe<sup>t</sup>Bu); *trans*-**2**: 55.8 (SiMe<sup>t</sup>Bu, *J*<sub>SiSi</sub> was not obtained because of low intensity for this signal), 113.7 (SiMe<sup>t</sup>Bu, *J*<sub>SiSi</sub> = 33.7 Hz (determined by INEPT-INADEQUATE measurement); IR (hexane, a mixture of *cis*-/*trans*-isomers, cm<sup>-1</sup>): 1911 (ν<sub>CO</sub>, s); Mass (EI, 70 eV, a mixture of *cis*-/*trans*-isomers): *m/z* 466 (M<sup>+</sup>, 48), 409 (M<sup>+</sup> - <sup>t</sup>Bu, 100); Anal. Calcd. for C<sub>21</sub>H<sub>40</sub>OSi<sub>2</sub>Ru: C: 54.15, H: 8.66, Found: C: 54.06, H: 8.64%.

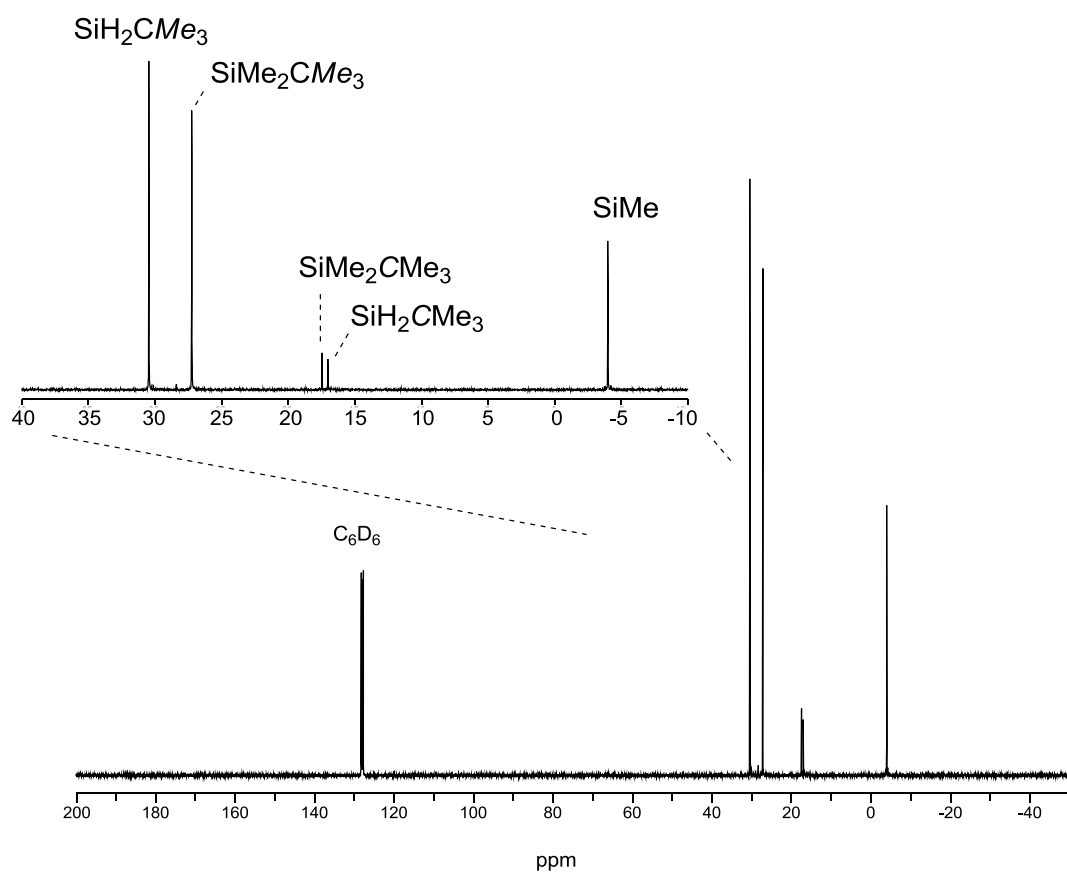
**1-4 Synthesis of Cp\*Fe(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (3).** In a manner similar to that described in 1-3, Cp\*Fe(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (3) was prepared in 87% yield (987 mg, 2.37 mmol) using Cp\*Fe(CO)(py)Me (804 mg, 3.05 mmol), H<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu (624 mg, 3.08 mmol) and BPh<sub>3</sub> (658 mg, 2.72 mmol). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K,  $\delta$ ) 0.47 (d, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, 6H, SiMe), 1.20 (s, 18H, Si<sup>t</sup>Bu), 1.75 (s, 15H, Cp\*), 3.65 (sept, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, J<sub>SiH</sub> = 19.2 Hz (determined by <sup>1</sup>H homodecoupling), 1H, Si···H···Si); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>, DEPT, 300 K,  $\delta$ ) 102.7 (SiMe<sup>t</sup>Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K,  $\delta$ ) -2.4 (SiMe), 11.4 (C<sub>5</sub>Me<sub>5</sub>), 25.1 (CMe<sub>3</sub>), 30.0 (CMe<sub>3</sub>), 90.9 (C<sub>5</sub>Me<sub>5</sub>), 223.0 (CO); IR (hexane, cm<sup>-1</sup>) 1895 ( $\nu_{\text{CO}}$ , vs); MS (EI, 70 eV) *m/z* 420 (M<sup>+</sup>, 100), 363 (M<sup>+</sup>-<sup>t</sup>Bu, 56); Calcd. for C<sub>21</sub>H<sub>40</sub>OSi<sub>2</sub>Fe : C: 59.97, H: 9.59, Found: C: 59.90, H: 9.52.



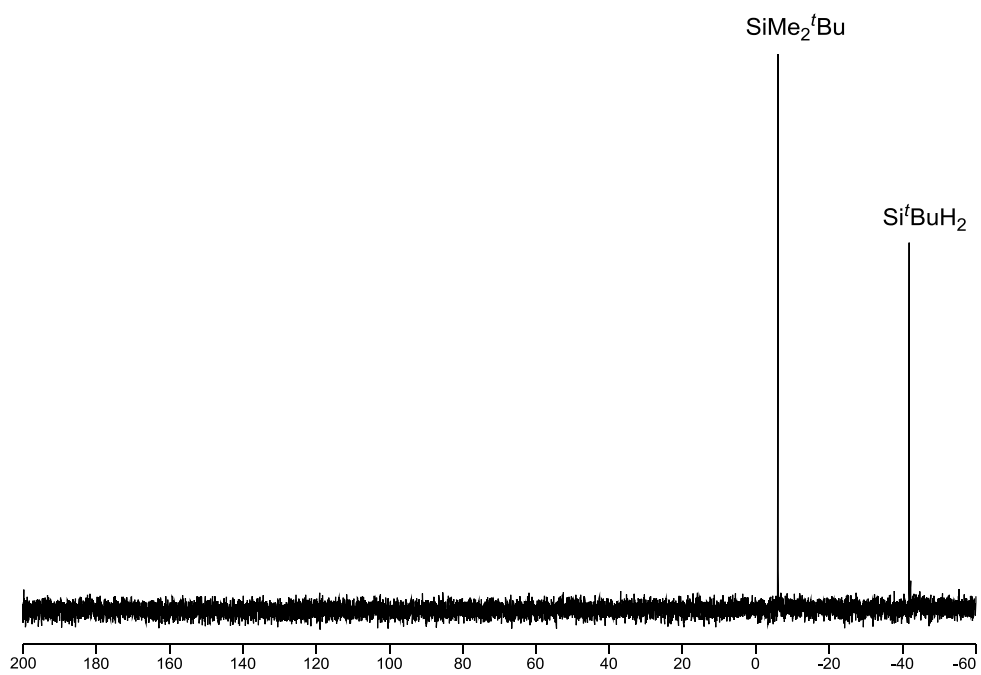
**Fig. S1** <sup>1</sup>H-<sup>29</sup>Si{<sup>1</sup>H} COSY NMR spectrum of Ph<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu (300, 59.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K).



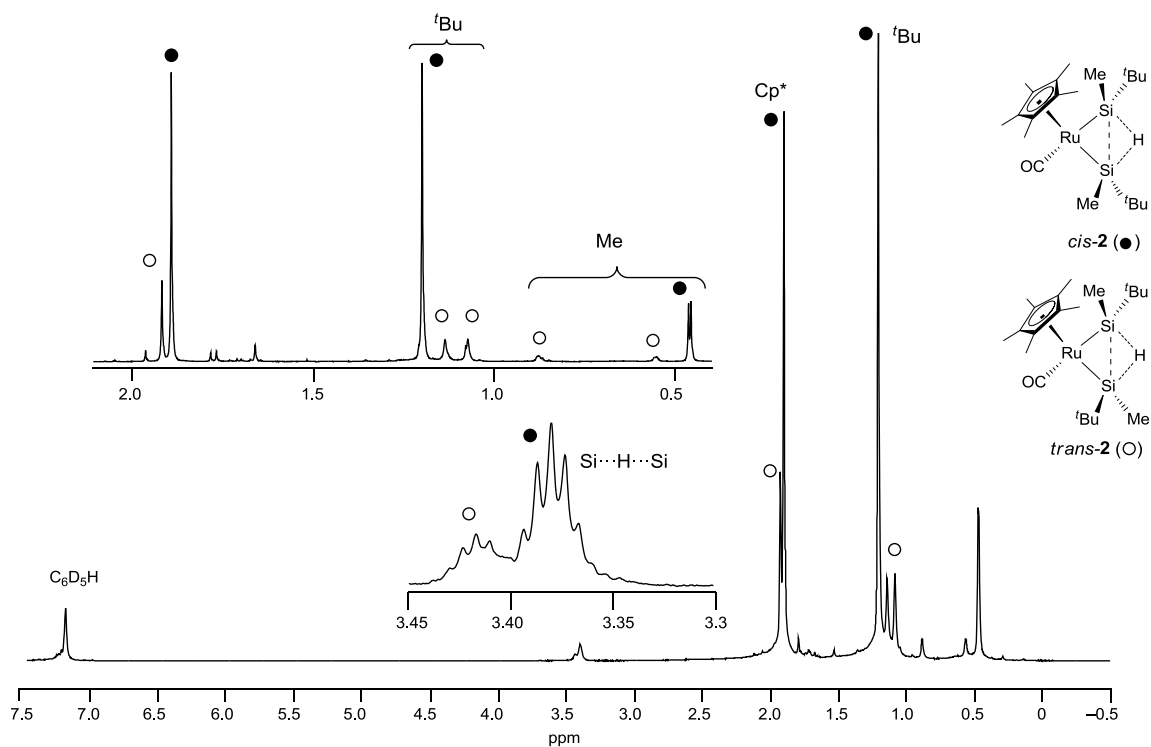
**Fig. S2** <sup>1</sup>H NMR spectrum of H<sub>2</sub><sup>t</sup>BuSiSiMe<sub>2</sub><sup>t</sup>Bu (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K).



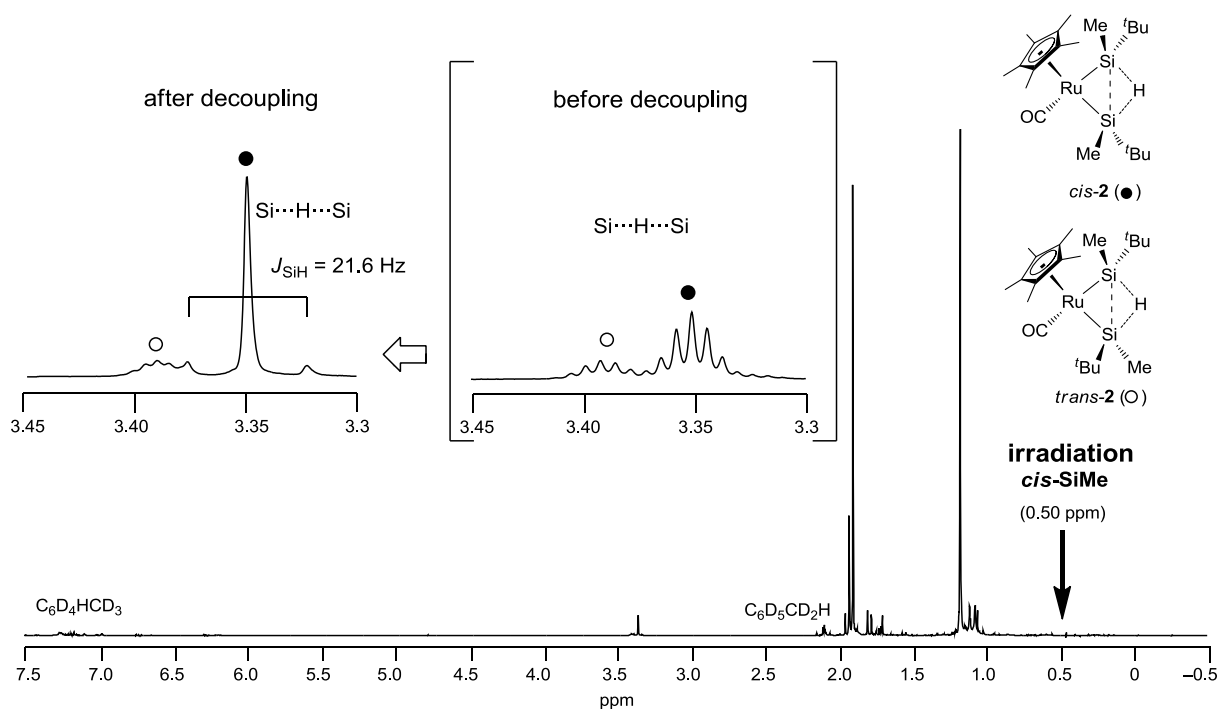
**Fig. S3**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{H}_2^i\text{BuSiSiMe}_2^t\text{Bu}$  (100.6 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



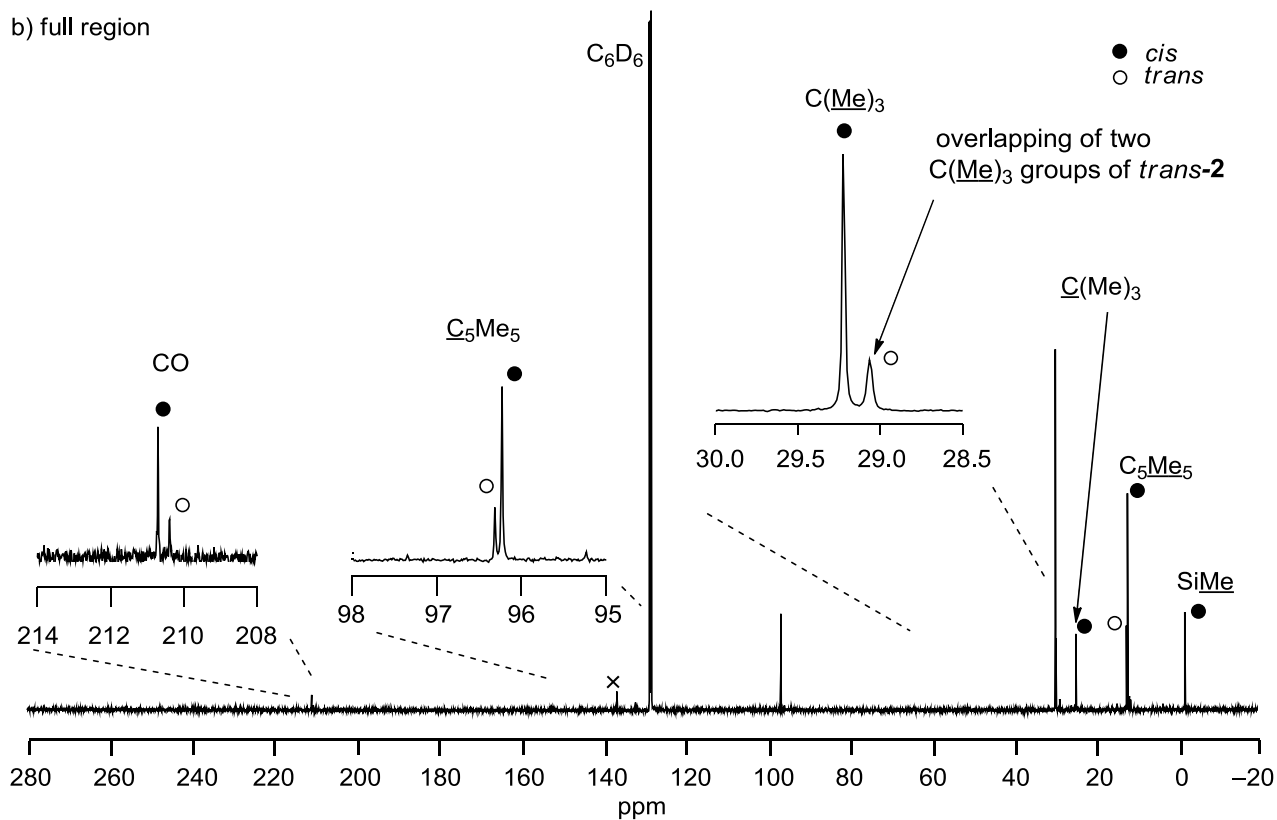
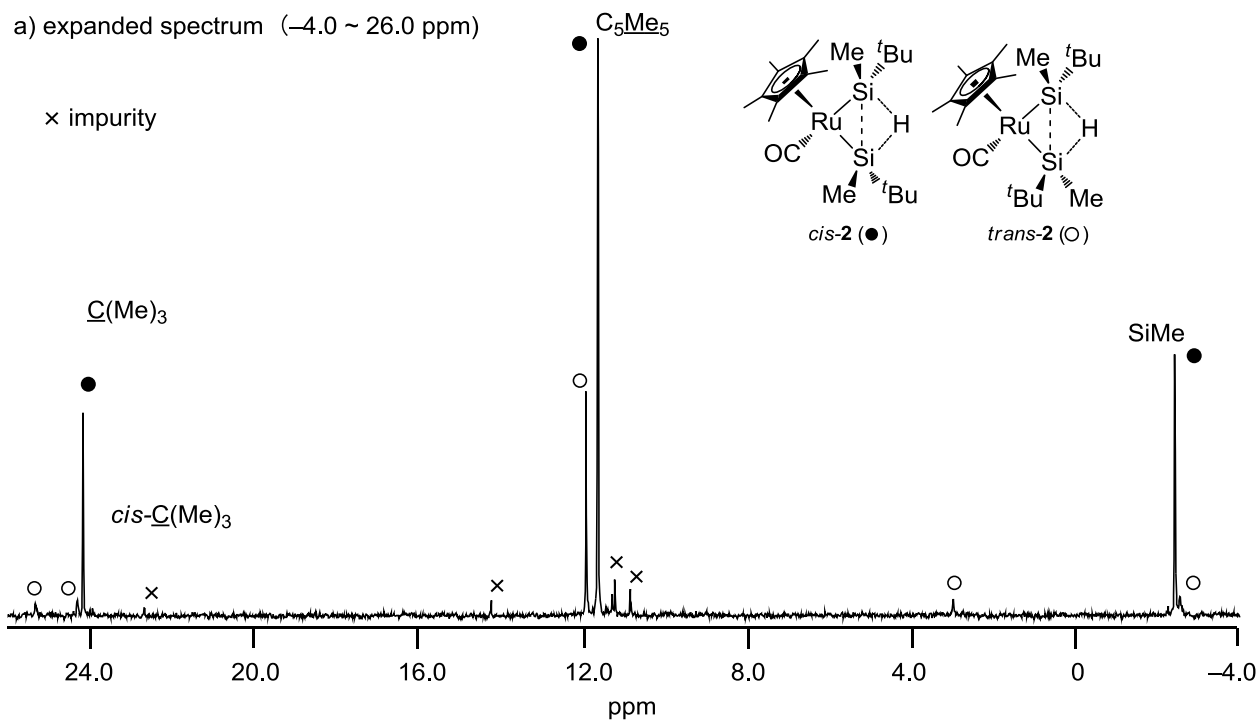
**Fig. S4**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $\text{H}_2^i\text{BuSiSiMe}_2^t\text{Bu}$  (79.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



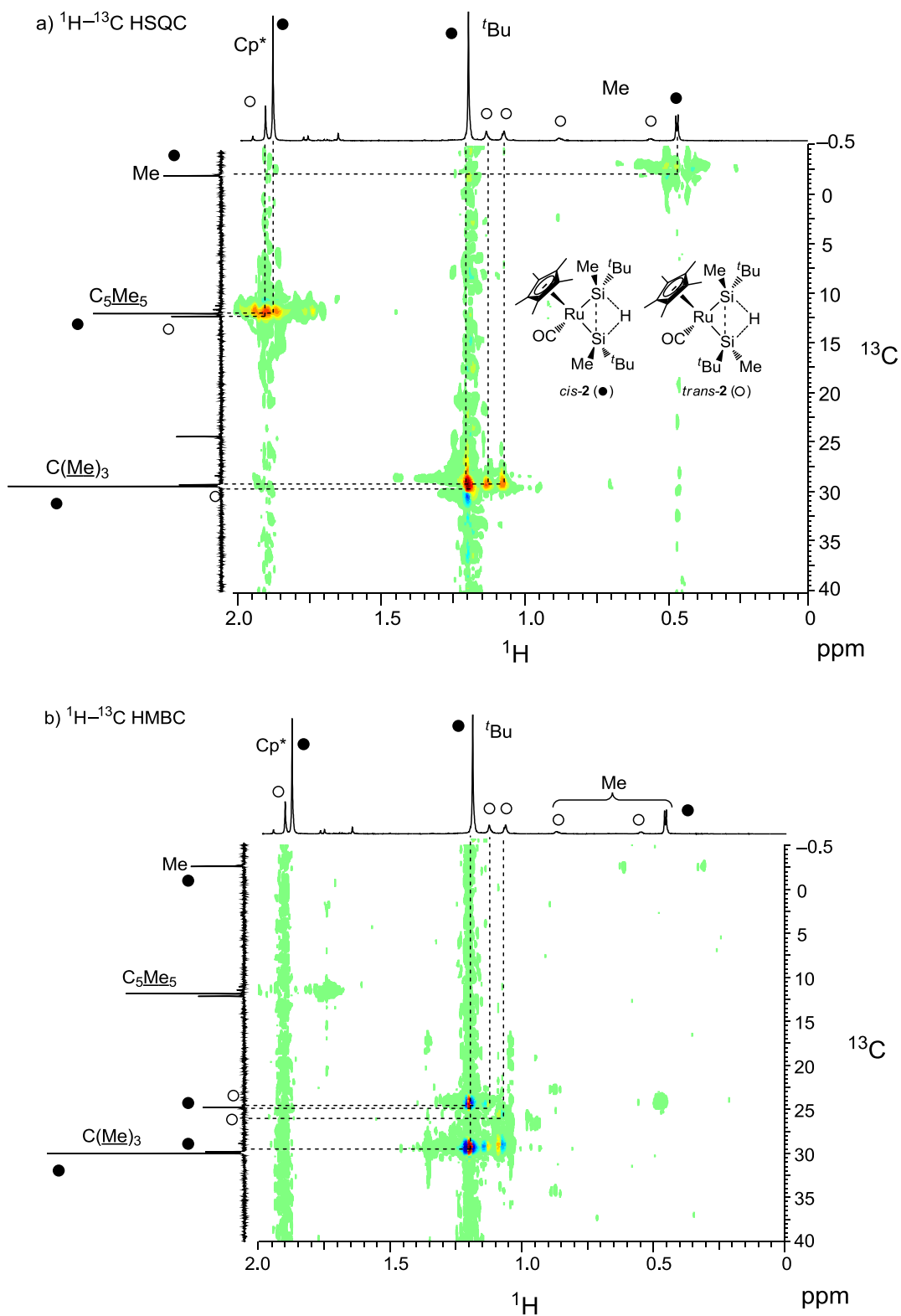
**Fig. S5**  $^1\text{H}$  NMR spectrum of  $\text{Cp}^*\text{Ru}(\text{CO})\{(\text{'Bu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{'Bu})\}$  (**2**) (400 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



**Fig. S6**  $^1\text{H}$  homo-decoupling NMR spectrum of **2** (400 MHz, toluene- $d_8$ , 300 K).



**Fig. S7**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{Cp}^*\text{Ru}(\text{CO})\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  (**2**)  
(100.6 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



**Fig. S8**  $^1\text{H}$ - $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{Cp}^*\text{Ru}(\text{CO})\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  (**2**)  
 (a) HSQC and (b) HMBC methods (400, 100.6 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



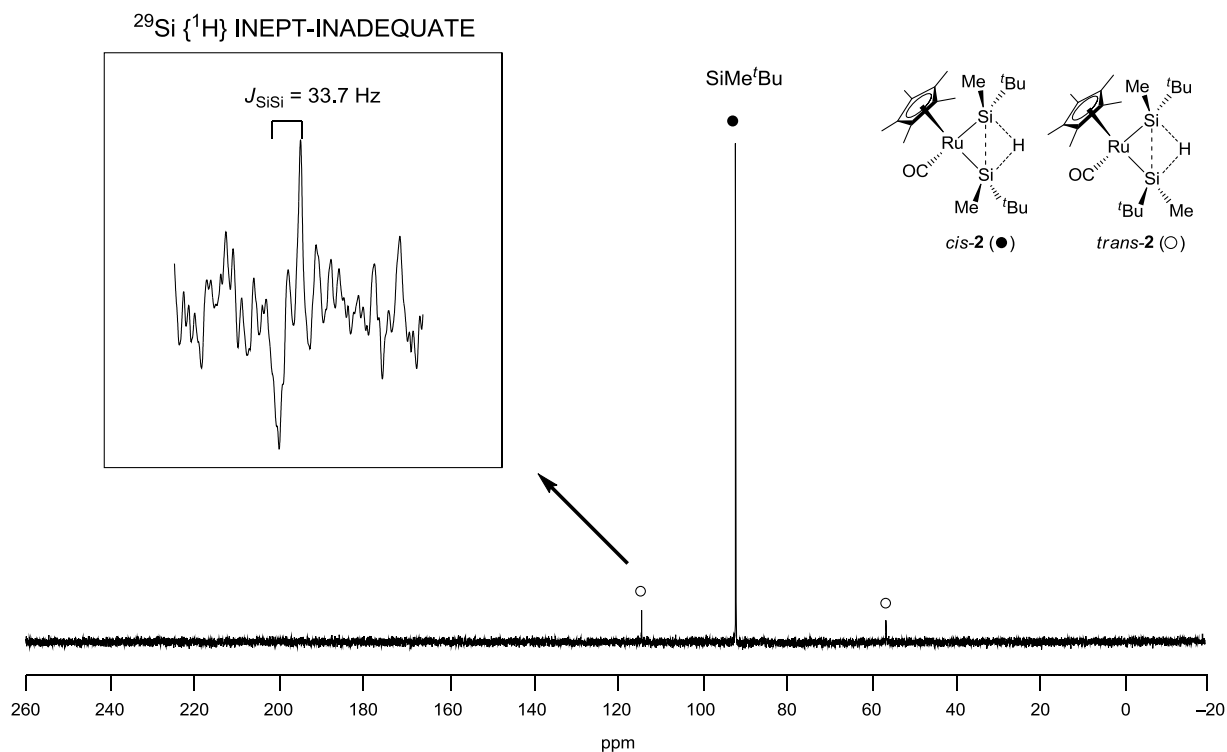
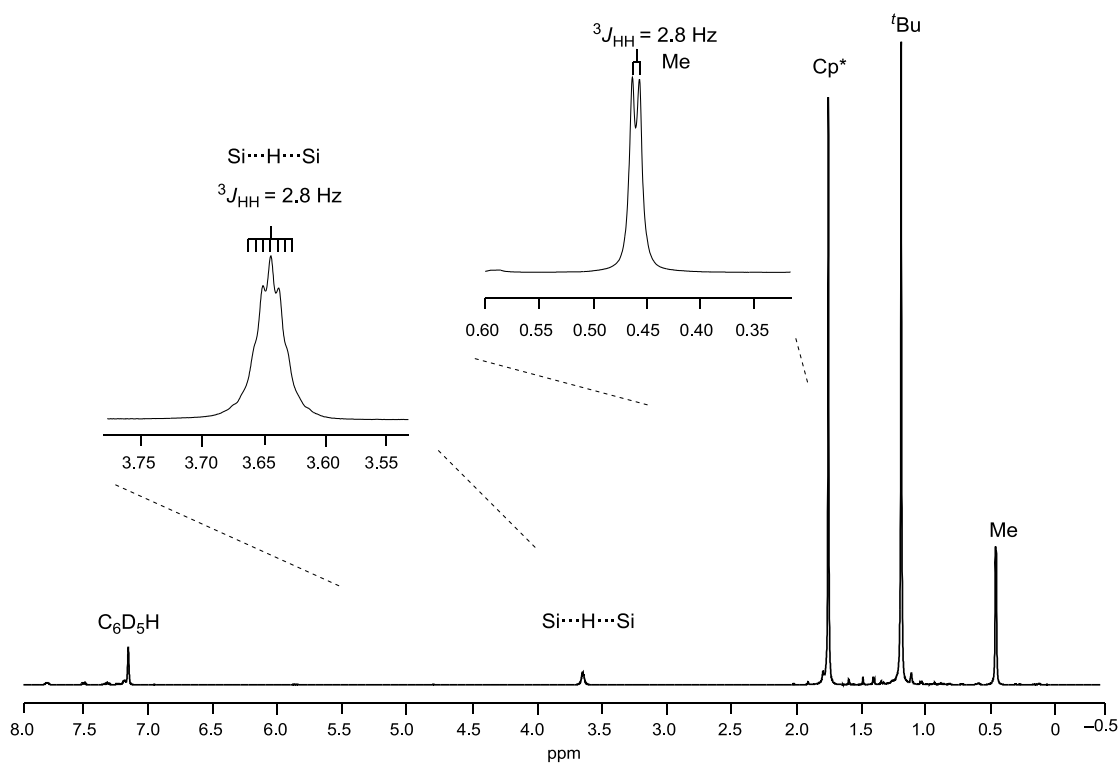
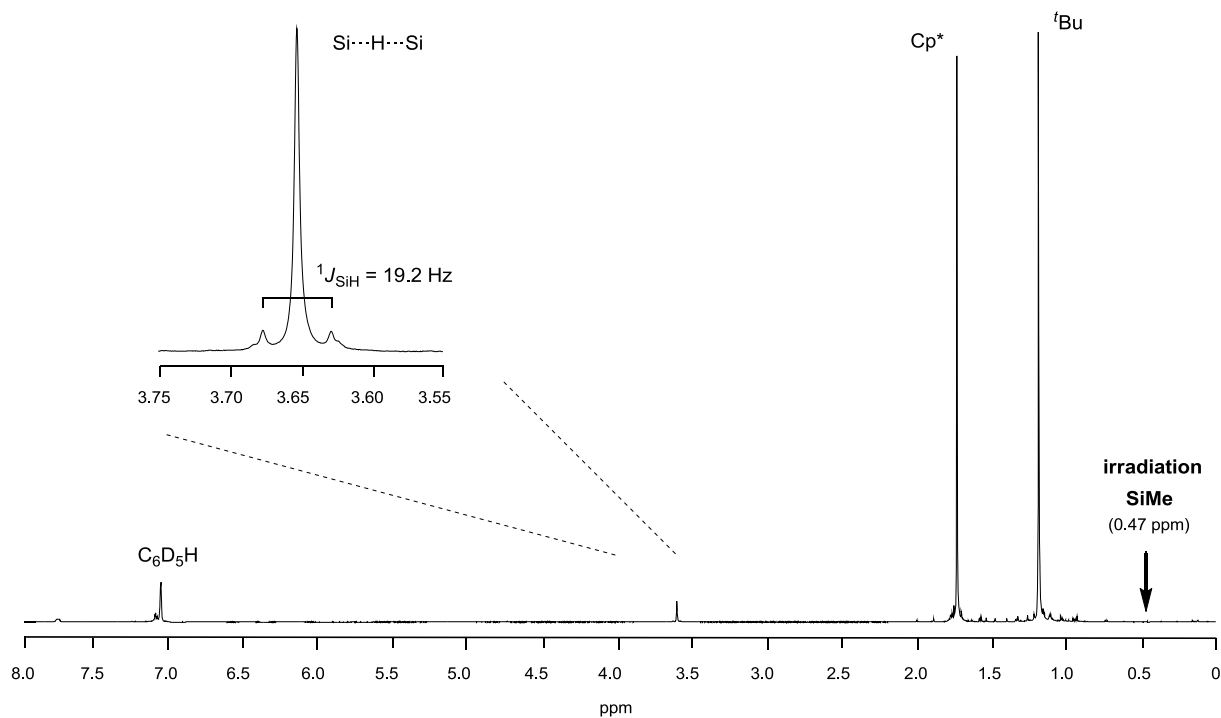


図3-4 Cp\*Ru(CO){(tBu)MeSi...H...SiMe(tBu)} (15)の $^{29}\text{Si}\{^1\text{H}\}$  NMRスペクトル (79.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K)

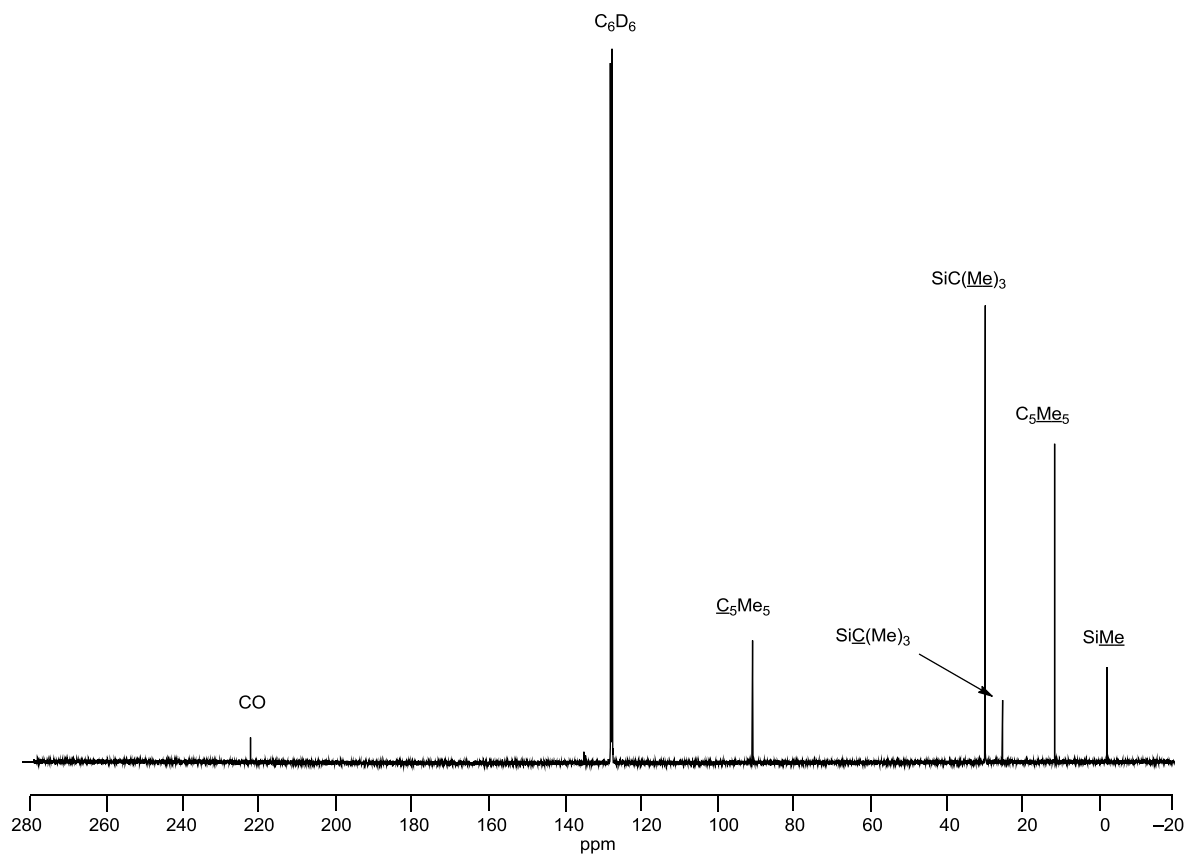
**Fig. S9**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of Cp\*Ru(CO){(tBu)MeSi...H...SiMe(tBu)} (2) (79.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K). The  $^{29}\text{Si}\{^1\text{H}\}$  INEPT-INADEQUATE signal at 113.8 ppm for *trans*-2 is inserted in the square: The corresponding signal was not clearly observed at 55.4 ppm.



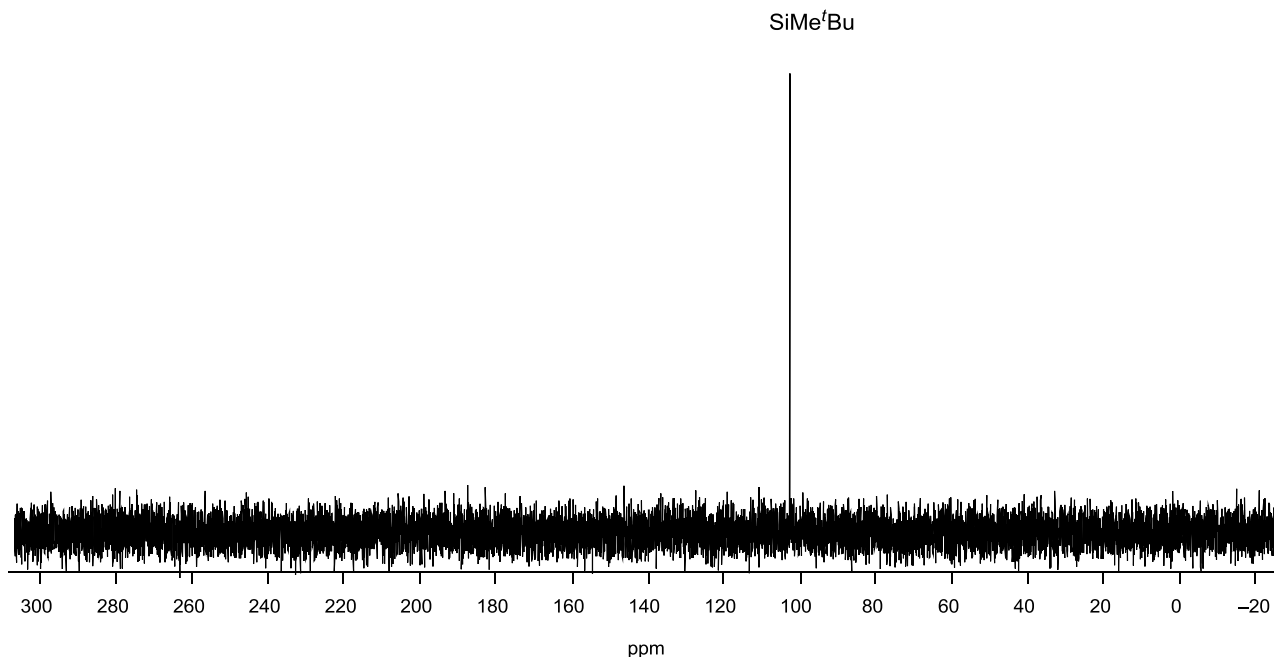
**Fig.S10**  $^1\text{H}$  NMR spectrum of Cp\*Fe(CO){(tBu)MeSi...H...SiMe(tBu)} (3) (400 MHz,  $\text{C}_6\text{D}_6$ , 300 K).



**Fig. S11**  $^1\text{H}$  homodecoupling NMR spectrum of **3** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K).



**Fig. S12**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of Cp\*Fe(CO){(tBu)MeSi...H...SiMe(tBu)} (**3**) (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K).



**Fig. S13**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $\text{Cp}^*\text{Fe}(\text{CO})\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  (**3**)  
(79.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K).

## 2. X-ray Crystal Structure Analysis of *cis-2* and **3**

Single crystals suitable for X-ray diffraction measurement of *cis-2* and **3** were coated with a layer of paraffin oil and were mounted on a nylon loop, and held at a position under a cold stream of  $\text{N}_2$  on the diffractometer. Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate Diffractometer with graphite monochromated  $\text{Mo-K}\alpha$  radiation about 150 K. Numerical absorption collection were made using the program NUMBAS.<sup>S8</sup> The structures were solved by Patterson and Fourier transform methods (SHELXS-97)<sup>S9a</sup> and refined by full matrix least-square technique on  $F^2$  with SHELXL-97,<sup>S9b</sup> using Yadokari-XG 2009 software<sup>S10</sup> as a graphical user interface. The positions of the bridging hydrogen atoms for both complexes *cis-2* and **3** were found from difference Fourier electron density map and refined isotropically. All other hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically. Crystallographic data of *cis-2* and **3** are summarized in Tables S1 and S2, respectively. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre: CCDC 1530379 (*cis-2*), CCDC 1530380 (**3**).

**Table S1** Crystallographic data of Cp\*Ru(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (*cis-2*)

Empirical formula	C <sub>21</sub> H <sub>40</sub> ORuSi <sub>2</sub>	
Formula weight	465.78	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 8.3493(2) Å	<i>α</i> = 98.5709(10)°
	<i>b</i> = 9.67910(10) Å	<i>β</i> = 92.1420(9)°
	<i>c</i> = 16.9592(2) Å	<i>γ</i> = 114.1722(15)°
Volume	1229.02(4) Å <sup>3</sup>	
<i>Z</i>	2	
Density (calculated)	1.259 Mg/m <sup>3</sup>	
Absorption coefficient	0.742 mm <sup>-1</sup>	
<i>F</i> (000)	492	
Crystal size	0.31 x 0.16 x 0.14 mm <sup>3</sup>	
Theta range for data collection	1.22 to 27.48°	
Index ranges	-10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 12, -22 ≤ <i>l</i> ≤ 21	
Reflections collected	11939	
Independent reflections	5607 [ <i>R</i> (int) = 0.0446]	
Completeness to theta = 27.48°	99.4 %	
Max. and min. transmission	0.9033 and 0.8026	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	5607 / 0 / 243	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.143	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0429, <i>wR</i> 2 = 0.0872	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0539, <i>wR</i> 2 = 0.0908	
Largest diff. peak and hole	0.630 and -0.504 e.Å <sup>-3</sup>	
<i>R</i> 1 = Σ   <i>F</i> <sub>o</sub>    -   <i>F</i> <sub>c</sub>  /Σ   <i>F</i> <sub>o</sub>   , <i>wR</i> 2 = [Σ [w( <i>F</i> <sub>o</sub> <sup>2</sup> - <i>F</i> <sub>c</sub> <sup>2</sup> ) <sup>2</sup> ]/Σ [w( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>0.5</sup> , calcd. <i>w</i> = 1/[2( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0277 <i>P</i> ) <sup>2</sup> + 2.3052 <i>P</i> ] where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3.		

**Table S2** Crystallographic data of Cp\*Fe(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (**3**)

Empirical formula	C <sub>21</sub> H <sub>40</sub> FeOSi <sub>2</sub>	
Formula weight	420.56	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 8.3327(4) Å	<i>α</i> = 98.2428(15)°
	<i>b</i> = 9.4416(7) Å	<i>β</i> = 92.326(3)°
	<i>c</i> = 16.9080(12) Å	<i>γ</i> = 114.276(3)°
Volume	1192.74(14) Å <sup>3</sup>	
<i>Z</i>	2	
Density (calculated)	1.171 Mg/m <sup>3</sup>	
Absorption coefficient	0.739 mm <sup>-1</sup>	
<i>F</i> (000)	456	
Crystal size	0.27 x 0.24 x 0.08 mm <sup>3</sup>	
Theta range for data collection	1.22 to 27.48°	
Index ranges	-10 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 12, -21 ≤ <i>l</i> ≤ 21	
Reflections collected	15181	
Independent reflections	5394 [ <i>R</i> (int) = 0.0299]	
Reflections with <i>I</i> > 2.0σ( <i>I</i> )	4944	
Completeness to theta = 27.48°	98.5 %	
Max. and min. transmission	0.9432 and 0.8253	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	5394 / 0 / 243	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.081	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0324, <i>wR</i> 2 = 0.0800	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0380, <i>wR</i> 2 = 0.0824	
Largest diff. peak and hole	0.680 and -0.314 e.Å <sup>-3</sup>	
<i>R</i> 1 = Σ   <i>F</i> <sub>o</sub>    -   <i>F</i> <sub>c</sub>  /Σ   <i>F</i> <sub>o</sub>   , <i>wR</i> 2 = [Σ [w( <i>F</i> <sub>o</sub> <sup>2</sup> - <i>F</i> <sub>c</sub> <sup>2</sup> ) <sup>2</sup> ]/Σ [w( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>0.5</sup> , calcd. <i>w</i> = 1/[2( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0387 <i>P</i> ) <sup>2</sup> + 0.7419 <i>P</i> ] where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3.		

### 3. Theoretical Calculations

Geometries of model complexes  $\text{CpRu(CO)}\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  (*cis-2'*) and  $\text{CpFe(CO)}\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  (**3'**) were optimized by the DFT method with the B3LYP functional.<sup>S11</sup> For Ru and Fe, the LANL2DZ basis set was employed, where the core electrons were replaced with the effective core potentials (ECPs). The 6-31G(d) basis sets were employed for the other atoms. Geometry optimization started from structures of silyl(silylene) complexes  $\text{Cp(OC)M=SiMe}(\text{tBu})\{\text{SiMe}(\text{tBu})\text{H}\}$  (M = Ru, Fe) that has no M-Si-H-Si four-membered ring, and finally reached the structures of  $\text{CpM(CO)}\{(\text{tBu})\text{MeSi}\cdots\text{H}\cdots\text{SiMe}(\text{tBu})\}$  having a four-membered ring as the optimized structures. For the analysis of molecular orbitals, a smaller model  $\text{CpRu(CO)}(\text{H}_2\text{Si}\cdots\text{H}\cdots\text{SiH}_2)$  (**2''**) was optimized for simplicity and was used. For the analysis of the electronic structure such as NBO (Natural Bond Orbital) analysis<sup>S12</sup> and WBI (Wiberg Bond Indices) calculations,<sup>S13</sup> the 6-311G(d) basis sets were employed for Si atom and the 6-31G(d) basis sets for the other main group atoms. All calculations were carried out with Gaussian03 program package.<sup>S14</sup> Atomic coordinates for the optimized structures of **2''**, *cis-2'* and **3'** are listed in Tables S3, S4 and S5, respectively. Important Kohn-Sham orbitals of **2''** are depicted in Fig. S14.

**Table S3** Atomic coordinates of  $\text{CpRu(CO)}(\text{H}_2\text{Si}\cdots\text{H}\cdots\text{SiH}_2)$  (**2''**)

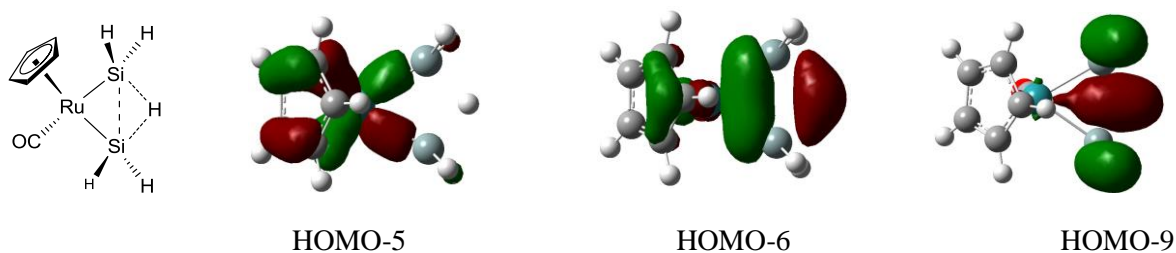
number	atom	X	Y	Z
1	Ru1	0.000000	0.000000	0.000000
2	Si1	0.000000	0.000000	2.330300
3	Si2	2.109751	0.000000	0.990512
4	C1	-0.016717	-1.877604	-0.044240
5	O1	-0.050590	-3.036914	-0.108814
6	C2	-0.401541	2.211954	-0.515758
7	C3	0.309977	1.644301	-1.621505
8	C4	-0.499494	0.625600	-2.190100
9	C5	-1.731256	0.573858	-1.450537
10	C6	-1.675885	1.561243	-0.431758
11	H1	1.676955	0.049169	2.642140
12	H2	-0.265745	1.226767	3.137753
13	H3	-0.189211	-1.166212	3.238674
14	H4	2.957881	1.223306	1.097550
15	H5	3.004569	-1.170468	1.214790
16	H6	-0.066193	3.035592	0.100064
17	H7	1.291593	1.942363	-1.964528
18	H8	-0.244989	0.011109	-3.043027
19	H9	-2.563234	-0.087819	-1.651255
20	H10	-2.459064	1.786226	0.279489

**Table S4** Atomic coordinates of CpRu(CO){(<sup>t</sup>Bu)MeSi···H···SiMe(<sup>t</sup>Bu)} (*cis-2'*)

number	atom	X	Y	Z
1	Ru1	0.000000	0.000000	0.000000
2	Si1	0.000000	0.000000	2.345700
3	Si2	2.144139	0.000000	0.961123
4	C1	-0.042435	-1.852281	-0.165010
5	O1	-0.127090	-2.996866	-0.377957
6	C2	-0.412923	2.237297	0.505643
7	C3	0.269873	1.678432	-1.632013
8	C4	-0.557526	0.668218	-2.187827
9	C5	-1.770815	0.614803	-1.420717
10	C6	-1.686580	1.591339	-0.394970
11	H1	1.703207	-0.136367	2.611087
12	C7	-0.183772	1.695567	3.204016
13	C8	-0.603975	-1.343787	3.612007
14	C9	3.032673	1.684569	1.087094
15	C10	3.503836	-1.383764	0.932903
16	H2	-0.064413	3.059030	0.104865
17	H3	1.241831	1.978419	-1.999660
18	H4	-0.327290	0.058118	-3.051247
19	H5	-2.608257	-0.045052	-1.605128
20	H6	-2.452267	1.814265	0.335706
21	H7	-1.221623	2.038656	3.110287
22	H8	0.064582	1.668155	4.270539
23	H9	0.450331	2.447598	2.724813
24	C11	-0.621547	-2.767059	3.028081
25	C12	0.252353	-1.333759	4.895176
26	C13	-2.057819	-0.945511	3.968106
27	H10	3.631431	1.837744	0.179312
28	H11	2.314343	2.507610	1.141900
29	H12	3.708796	1.752658	1.945088
30	C14	2.986353	-2.743263	1.436616
31	C15	3.949262	-1.528601	-0.541802
32	C16	4.721414	-0.974681	1.788974
33	H13	0.377035	-3.112853	2.743138
34	H14	-1.010425	-3.471002	3.778425
35	H15	-1.261742	-2.839841	2.144073
36	H16	0.299174	-0.343420	5.362117
37	H17	-0.175769	-2.022683	5.638059
38	H18	1.279910	-1.660555	4.698283
39	H19	-2.703133	-0.914011	3.080682
40	H20	-2.487575	-1.688832	4.654579
41	H21	-2.115866	0.029023	4.466452
42	H22	2.127247	-3.103596	0.864426
43	H23	3.779660	-3.499941	1.349078
44	H24	2.699143	-2.698649	2.494203
45	H25	4.344236	-0.589197	-0.950604
46	H26	4.752225	-2.275733	-0.618901
47	H27	3.125171	-1.855929	-1.185115
48	H28	4.450244	-0.821477	2.840831
49	H29	5.482257	-1.768117	1.758667
50	H30	5.195816	-0.056599	1.425999

**Table S5** Atomic coordinates of CpFe(CO){('Bu)MeSi...H...SiMe('Bu)} (3')

number	atom	X	Y	Z
1	Fe1	0.000000	0.000000	0.000000
2	Si1	0.000000	0.000000	2.248286
3	Si2	2.085527	0.000000	0.843799
4	C1	-0.046546	-1.718317	-0.199207
5	O1	-0.128100	-2.856625	-0.439380
6	C2	-0.378486	2.072576	-0.363540
7	C3	0.323509	1.521658	-1.478582
8	C4	-0.471205	0.481461	-2.026723
9	C5	-1.679575	0.394539	-1.256591
10	C6	-1.623357	1.378965	-0.237028
11	H1	1.697810	-0.171046	2.502150
12	C7	-0.146051	1.683472	3.142543
13	C8	-0.611030	-1.346147	3.514482
14	C9	3.007386	1.667929	0.984970
15	C10	3.434914	-1.398425	0.749879
16	H2	-0.045271	2.894446	0.254032
17	H3	1.288238	1.844973	-1.845407
18	H4	-0.209964	-0.144613	-2.869413
19	H5	-2.483118	-0.312102	-1.415794
20	H6	-2.390561	1.575339	0.499548
21	H7	-1.168674	2.066248	3.036930
22	H8	0.076059	1.622588	4.213277
23	H9	0.525773	2.424701	2.699720
24	C11	-0.648904	-2.764643	2.919574
25	C12	0.250643	-1.359590	4.793445
26	C13	-2.058426	-0.934533	3.881980
27	H10	3.581354	1.835540	0.063766
28	H11	2.310749	2.504808	1.087652
29	H12	3.713550	1.698318	1.820574
30	C14	2.948696	-2.740103	1.327947
31	C15	3.759768	-1.587217	-0.751145
32	C16	4.719400	-0.982136	1.496275
33	H13	0.344287	-3.117784	2.624607
34	H14	-1.038713	-3.471526	3.666817
35	H15	-1.296385	-2.824187	2.039642
36	H16	0.312106	-0.374166	5.268861
37	H17	-0.180579	-2.051013	5.532477
38	H18	1.273675	-1.695052	4.587429
39	H19	-2.710771	-0.896671	2.999713
40	H20	-2.490827	-1.671966	4.573281
41	H21	-2.102957	0.041644	4.378664
42	H22	2.048919	-3.109041	0.828806
43	H23	3.729001	-3.505150	1.202190
44	H24	2.740309	-2.664989	2.402117
45	H25	4.119610	-0.660523	-1.217871
46	H26	4.552612	-2.339180	-0.874370
47	H27	2.884010	-1.929112	-1.313757
48	H28	4.532924	-0.800199	2.561902
49	H29	5.468752	-1.784120	1.426420
50	H30	5.172207	-0.077756	1.075607



**Fig. S14** Important Kohn-Sham orbitals of CpRu(CO)(H<sub>2</sub>Si···H···SiH<sub>2</sub>) (**2''**).

#### 4. References

- S1.** M. Iwata, M. Okazaki and H. Tobita, *Organometallics*, 2006, **25**, 6115.
- S2.** H. Hashimoto, A. Matsuda and H. Tobita, *Chem Lett.*, 2005, **34**, 1374.
- S3.** (a) R. Savela, W. Zawartka and R. Leino, *Organometallics*, 2012, **31**, 3199; (b) K. Hassler and M. Weidenbruch, *J. Organomet. Chem.*, 1994, **465**, 127.
- S4.** (a) P. Patschinski and H. Zipse, *Org. Lett.*, 2015, **17**, 3318; (b) P. Patschinski, C. Zhang and H. Zipse, *J. Org. Chem.*, 2014, **79**, 8348; (c) A. Bartoszewicz, M. Kalek, and J. Stawinski, *Tetrahedron*, 2008, **64**, 8843.
- S5.** (a) O. W. Sørensen, R. Freeman, T. Frenkiel, T. H. Mareci and R. Schuck, *J. Magn. Reson.*, 1982, **46**, 180; (b) H. B. Yokelson, A. J. Milleolte, B. R. Adams and R. West, *J. Am. Chem. Soc.*, 1987, **109**, 4116.
- S6.** H. Hashimoto, Y. Odagiri, Y. Yamada, N. Takagi, S. Sakaki and H. Tobita, *J. Am. Chem. Soc.*, 2015, **137**, 158.
- S7.** A. Furstner and H. Weidmann, *J. Organomet. Chem.*, 1988, **354**, 15.
- S8.** Higashi, T. *NUMBUS*, Rigaku Corporation, Tokyo, Japan.
- S9.** (a) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination; University of Göttingen; Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Determination; University of Göttingen; Göttingen, Germany, 1997.
- S10.** K. Wakita, *Yadokari-XG, Software for Crystal Structure Analyses*, (2001); C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses*, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.
- S11.** (a) A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic-behavior," *Phys. Rev. A*, 1988, **38**, 3098; (b) C. Lee, W. Yang and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B*, 1988, **37**, 785; (c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, "Results obtained with the correlation-energy density functionals of Becke and Lee, Yang, Parr," *Chem. Phys. Lett.*, 1989, **157**, 200.
- S12.** (a) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold; (b) J. E. Carpenter and F. Weinhold, *J. Mol. Struct. (Theochem)*, 1988, **169**, 41; (c) J. E. Carpenter, PhD thesis, University of Wisconsin, Madison, WI, 1987; (d) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211; (e)



A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066; (f) A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 1736; (g) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; (h) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899; (i) F. Weinhold, J. E. Carpenter, *Plenum.*, **1988**, 227.

**S13.** K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

**S14.** Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.