

(Electronic supplementary information)

**Thermal reaction of a ruthenium bis(silyl) complex having a lutidine-based Si,N,Si ligand: formation of a  $\mu$ -silyl( $\mu$ -silylene) diruthenium complex involving a 3c-2e Ru–Si–C interaction**

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**General procedures.** All manipulations were carried out under dry nitrogen in a glovebox or using Schlenk techniques. Benzene- $d_6$  was dried and vacuum-transferred from  $\text{CaH}_2$ , and then stored under nitrogen over 4 Å molecular sieves. Hexane, pentane and toluene were dried over sodium/benzophenone and distilled before use. 2,6-Lutidine (2,6-dimethylpyridine) and TMEDA (*N,N,N',N'*-tetramethylethylenediamine) were dried over  $\text{CaH}_2$  and distilled.  $\text{Me}_2\text{HSiCl}$  was distilled before use. Flash chromatography<sup>1</sup> was performed under nitrogen or argon using silica gel 60N (Kanto Chemical Co., Inc., 40-50  $\mu\text{m}$ , spherical, neutral).

**Physical measurements.**  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker ARX-300, Bruker AVANCE-300 or JEOL ECA-600 Fourier transform spectrometer, and chemical shifts were reported in parts per million.  $^{29}\text{Si}\{^1\text{H}\}$  NMR experiments were performed using the DEPT pulse sequence. The residual proton (7.15 ppm) and the carbon (128.0 ppm) resonances of the deuterated solvent  $\text{C}_6\text{D}_6$  were used as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts, respectively. Aromatic proton or carbon is abbreviated to ArH or ArC.  $^{29}\text{Si}\{^1\text{H}\}$  NMR chemical shifts were referenced to TMS (tetramethylsilane) as an external standard. The NMR spectra were measured at room temperature. Infrared spectra were recorded with a neat oil placed between KBr plates or with a KBr pellet using a HORIBA FT-730 spectrometer. Mass spectra were collected on a Shimadzu QP5050 mass spectrometer operating in the

electron impact (EI) mode. Elemental analysis was carried out using a Yanaco MT-6 microanalyzer. Measurement of some NMR spectra and elemental analysis were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

**Synthesis of 2,6-bis[(dimethylsilyl)methyl]pyridine.** To a solution of 2,6-lutidine (1.6 mL, 14 mmol) and TMEDA (4.4 mL, 29 mmol) in Et<sub>2</sub>O (35 mL) was added dropwise *n*-BuLi (19 mL of a 1.55 M solution in hexane, 29 mmol) with cooling in an ice bath. After allowed to warm to room temperature, the red mixture was stirred for 5 h. The resulting brown solution was added dropwise via a syringe to a cold (ca. –90 °C) solution of Me<sub>2</sub>SiHCl (3.2 mL, 29 mmol) in Et<sub>2</sub>O (35 mL) in a MeOH/liq. N<sub>2</sub> bath. The mixture was allowed to warm slowly to room temperature. After stirring for 18 h, the mixture was filtered through a Celite pad. The filtrate was evaporated under vacuum. Distillation of the residue under reduced pressure (0.3 mmHg) gave the title compound as colourless oil (2.42 g, 10.8 mmol, 77%).

Bp: 37–41 °C/0.3 mmHg. Found: C, 58.74; H, 9.22; N, 6.31. Calc. for C<sub>11</sub>H<sub>21</sub>NSi<sub>2</sub>: C, 59.12; H, 9.47; N, 6.27. IR (neat): 3059 (w, ν<sub>CH</sub>), 2958 (m, ν<sub>CH</sub>), 2900 (m, ν<sub>CH</sub>), 2117 (s, ν<sub>SiH</sub>), 1583 (s), 1572 (s), 1448 (s), 1404 (w), 1250 (s, δ<sub>SiC</sub>), 1225 (m), 1149 (s), 1072 (m), 989 (w), 945 (m), 887 (vs, δ<sub>SiH</sub>), 841 (s, ν<sub>SiC</sub>), 823 (s, ν<sub>SiC</sub>), 779 (w), 762 (m), 739 (m), 712 (m), 625 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.03 (t, 1H, *J* = 7.7 Hz, *p*-ArH), 6.49 (d, 2H, *J* = 7.7 Hz, *m*-ArH), 4.27 (m, 2H, SiH), 2.31 (d, 4H, *J* = 3.1 Hz, SiCH<sub>2</sub>), 0.08 (d, 12H, *J* = 3.6 Hz, SiMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 160.5 (*o*-ArC), 136.0 (*p*-ArC), 118.1 (*m*-ArC), 27.4 (<sup>1</sup>*J*<sub>SiC</sub> = 45.8 Hz, CH<sub>2</sub>Si), –4.2 (<sup>1</sup>*J*<sub>SiC</sub> = 51.7 Hz, SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ –12.0. MS (EI): *m/z* 223 (M<sup>+</sup>, 34), 222 (M<sup>+</sup> – H, 33), 208 (M<sup>+</sup> – Me, 100), 164 (M<sup>+</sup> – HSiMe<sub>2</sub>, 67), 150 (M<sup>+</sup> – HSiMe<sub>2</sub> – CH<sub>2</sub>, 85).

**Synthesis of Ru{κ<sup>3</sup>Si,Si,N-(Me<sub>2</sub>SiCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}(CO)<sub>3</sub> (1).** Ru<sub>3</sub>(CO)<sub>12</sub> (0.087 g, 0.14 mmol) and 2,6-bis(dimethylsilyl)pyridine (0.100 g, 0.448 mmol) were mixed in hexane (20 mL). The suspension was exposed to ultrasonic waves for few minutes, and the mixture was refluxed for 15 h. After removal of volatiles, the residue was extracted

with pentane (5 mL × 2). The pentane extracts were centrifuged, and the combined supernatant liquid was evaporated. The residue was purified by flash chromatography on silica gel (eluent: hexane). The first lemon-yellow band was collected, and the solvent was removed under vacuum to give analytically pure **1** as lemon-yellow crystals (0.106 g, 0.261 mmol, 64%).

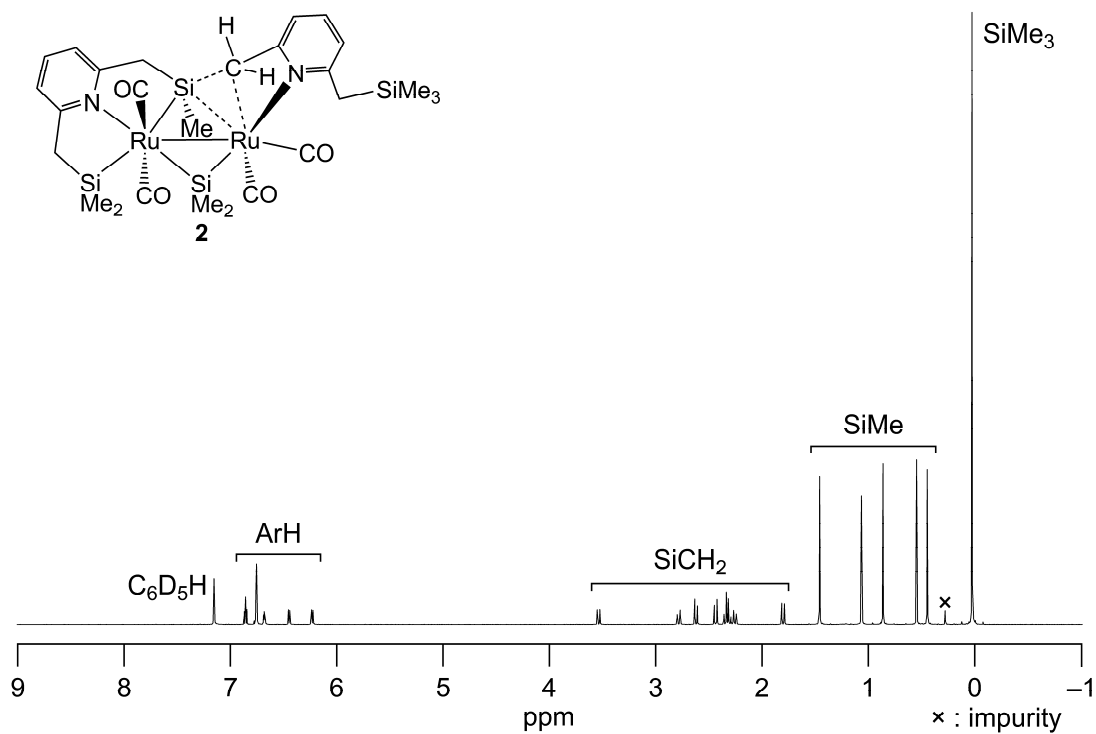
Found: C, 41.32; H, 4.46; N, 3.46. Calc. for C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub>Si<sub>2</sub>Ru: C, 41.36; H, 4.71; N, 3.45. IR (KBr-pellet): 2945 (w, ν<sub>CH</sub>), 2906 (w, ν<sub>CH</sub>), 2891 (w, ν<sub>CH</sub>), 2050 (m, ν<sub>CO</sub>), 1977 (s, ν<sub>CO</sub>), 1603 (w), 1589 (w), 1560 (w), 1450 (w), 1396 (w), 1254 (w, δ<sub>SiC</sub>), 1242 (w), 953 (w), 829 (w, ν<sub>SiC</sub>), 814 (m), 796 (w), 768 (w), 744 (w), 677 (w), 602 (m), 418 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.54–6.63 (multiplet, 1H, *p*-ArH), 6.47–6.54 (multiplet, 2H, *m*-ArH), 2.51 (s, 4H, SiCH<sub>2</sub>), 0.67 [s, 12H, <sup>2</sup>J<sub>SiH</sub>(satellite) = 6.4 Hz, SiMe<sub>2</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 211.6 (CO), 205.8 (CO), 169.9 (*o*-ArC), 136.9 (*p*-ArC), 121.0 (*m*-ArC), 42.1 (SiCH<sub>2</sub>), 4.8 (SiMe<sub>2</sub>, <sup>1</sup>J<sub>SiC</sub> = 40 Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.6 MHz, C<sub>6</sub>D<sub>6</sub>): 34.5. MS (EI): *m/z* 407 (M<sup>+</sup>, 27), 379 (M<sup>+</sup> – CO, 9), 351 (M<sup>+</sup> – 2CO, 100).

**Synthesis of Ru<sub>2</sub>(μ-SiMe<sub>2</sub>)[(Me<sub>2</sub>SiCH<sub>2</sub>)C<sub>5</sub>H<sub>3</sub>N{CH<sub>2</sub>Si(Me)CH<sub>2</sub>}C<sub>5</sub>H<sub>3</sub>N(CH<sub>2</sub>SiMe<sub>3</sub>)](CO)<sub>4</sub> (**2**).** A solution of **1** (0.299 g, 0.735 mmol) in toluene (9 mL) was refluxed for 66 h. The lemon-yellow colour of the solution turned to dark brown, and TLC of the reaction mixture showed that most of **1** has been consumed. After removal of volatiles, the residue was extracted with hexane (20 mL × 3), and then the extracts were centrifuged. The combined supernatant liquid was evaporated, and the reddish-brown residue was purified by flash chromatography on silica gel (eluent: toluene:hexane = 1 : 5). An orange band containing **2** was collected, and the solvent was removed under vacuum. Recrystallization of the residue with hexane at –30 °C gave **2** as red plates (47 mg, 0.062 mmol, 17%).

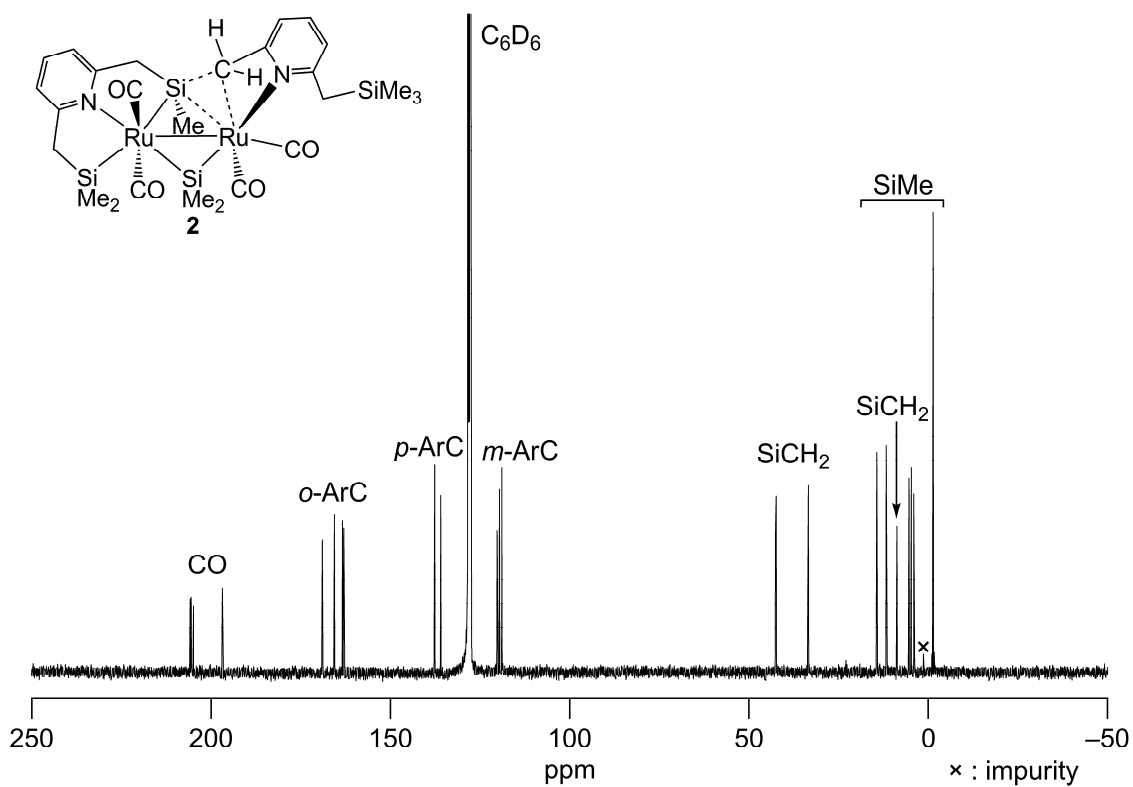
Found: C, 41.66; H, 5.28; N, 3.72. Calc. for C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>4</sub>Ru<sub>2</sub>: C, 41.25; H, 5.06; N, 3.70. IR (KBr-pellet): 2951 (w, ν<sub>CH</sub>), 2885 (w, ν<sub>CH</sub>), 2011 (m, ν<sub>CO</sub>), 1981 (s, ν<sub>CO</sub>), 1925 (s, ν<sub>CO</sub>), 1905 (s, ν<sub>CO</sub>), 1599 (w), 1562 (w), 1454 (m), 1396 (w), 1250 (m, δ<sub>SiC</sub>), 1157 (w), 960 (w), 951 (w), 849 (m, ν<sub>SiC</sub>), 816 (m), 768 (m), 756 (w), 690 (w), 671 (w), 663

(w), 606 (w), 588 (m), 420 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (594 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.85 (t, 1H,  $J = 7.7$  Hz,  $p$ -ArH), 6.73–6.78 (m, 2H,  $m$ -ArH), 6.65–6.70 (m, 1H,  $p$ -ArH), 6.45 (d, 1H,  $J = 7.7$  Hz,  $m$ -ArH), 6.23 (d, 1H,  $J = 7.7$  Hz,  $m$ -ArH), 3.54 (d, 1H,  $^2J_{\text{HH}} = 14.8$  Hz,  $\text{SiCH}_a\text{H}_b$ ), 2.79, 2.63 (AB quartet, 2H,  $^2J_{\text{HH}} = 15.7$  Hz,  $\text{SiCH}_2$ ), 2.44, 2.26 (AB quartet, 2H,  $^2J_{\text{HH}} = 15.5$  Hz,  $\text{SiCH}_2$ ), 2.35, 2.31 (AB quartet, 2H,  $^2J_{\text{HH}} = 13.6$  Hz,  $\text{SiCH}_2$ ), 1.81 (d, 1H,  $^2J_{\text{HH}} = 14.8$  Hz,  $\text{SiCH}_a\text{H}_b$ ), 1.47 (s, 3H, SiMe), 1.07 (s, 3H, SiMe), 0.87 (s, 3H, SiMe), 0.55 (s, 3H, SiMe), 0.45 (s, 3H, SiMe), 0.03 (s, 9H,  $^2J_{\text{SiH}} = 6.5$  Hz,  $\text{SiMe}_3$ ).<sup>†</sup>  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  205.9 (CO), 205.5 (CO), 204.9 (CO), 196.9 (CO), 168.9 ( $o$ -ArC), 165.6 ( $o$ -ArC), 163.4 ( $o$ -ArC), 163.0 ( $o$ -ArC), 137.6 ( $p$ -ArC), 136.0 ( $p$ -ArC), 120.2 ( $m$ -ArC), 119.6 ( $m$ -ArC), 118.9 ( $m$ -ArC), 118.7 ( $m$ -ArC), 42.6 ( $\text{SiCH}_2$ ), 42.5 ( $\text{SiCH}_2$ ), 33.5 ( $\text{SiCH}_2$ ), 14.4 (SiMe), 11.8 (SiMe), 8.8 ( $\text{SiCH}_2$ ), 5.4 (SiMe), 4.8 (SiMe), 4.1 (SiMe), –1.3 ( $\text{SiMe}_3$ ,  $^1J_{\text{SiC}} = 52$  Hz).<sup>†</sup>  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ ): 165.0 [ $\mu$ - $\text{SiMe}_2$ (silylene)], 62.9 [ $\mu$ -SiMe(silyl)], 31.9 ( $\text{SiMe}_2$ ), 3.6 ( $\text{SiMe}_3$ ).<sup>†</sup> MS (EI):  $m/z$  758 ( $\text{M}^+$ , 8), 700 ( $\text{M}^+ - \text{SiMe}_2$ , 100). The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of **2** are depicted in Figs S1, S2 and S3, respectively.

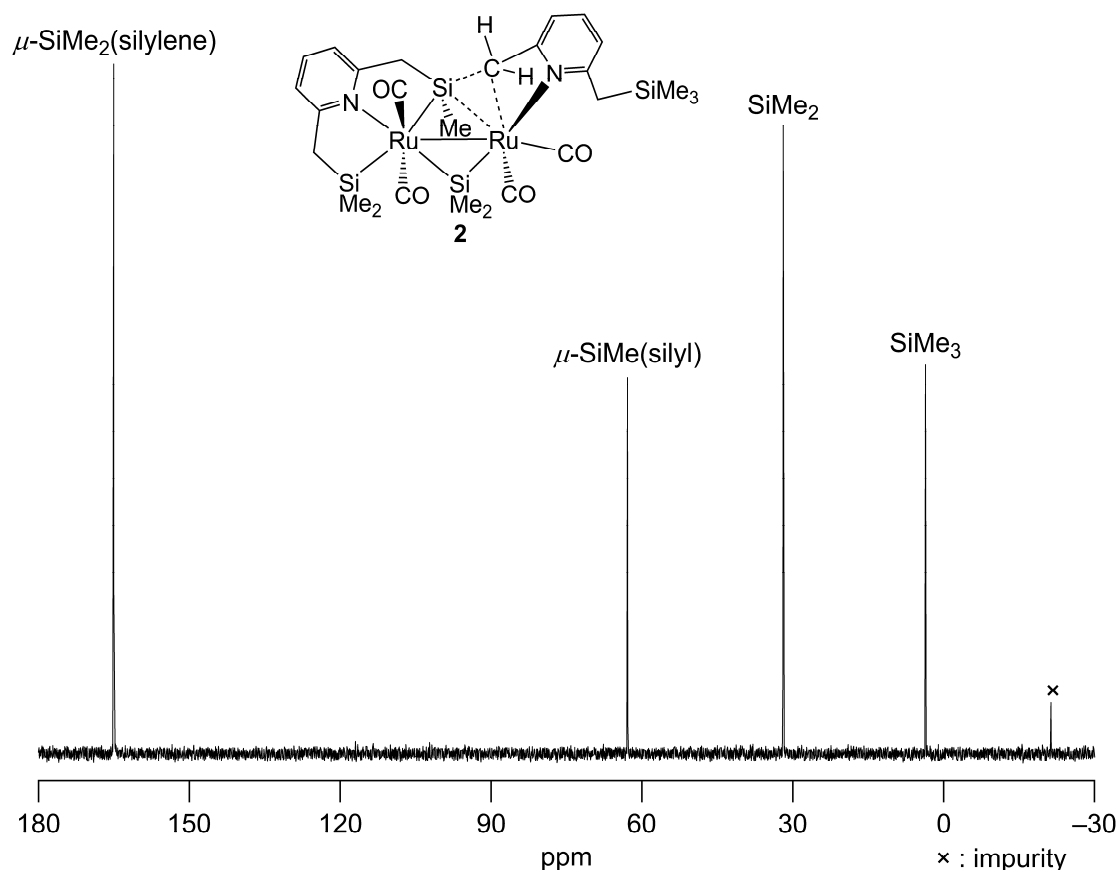
<sup>†</sup> Assignment of signals in the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of **2** was confirmed by  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HMQC,  $^1\text{H}$ - $^{13}\text{C}$  HMBC,  $^{13}\text{C}$  DEPT-135 and  $^1\text{H}$ - $^{29}\text{Si}$  HMBC NMR spectra. In the  $^{13}\text{C}$  DEPT-135 NMR spectrum of **2**, four  $^{13}\text{C}$  signals at  $\delta$  42.6, 42.5, 33.5 and 8.8 are inverted. In the  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectrum of **2**, the  $^{13}\text{C}$  signal at  $\delta$  8.8 shows two cross-peaks with two methylene proton resonances ( $\delta$  3.54, 1.81). These data indicate that the  $^{13}\text{C}$  resonance at  $\delta$  8.8 is assignable to a  $\text{SiCH}_2$  carbon. In the  $^1\text{H}$ - $^{29}\text{Si}$  HMBC NMR spectrum of **2**, only one cross-peak is observed between the  $^{29}\text{Si}$  signal assignable to a silyl ligand at  $\delta$  62.9 and a SiMe proton resonance ( $\delta$  0.55), whereas two cross-peaks are observed between the  $^{29}\text{Si}$  signal assignable to the other silyl ligand at  $\delta$  31.9 and two SiMe proton resonances ( $\delta$  0.87, 0.45). This observation confirms the assignment of the former  $^{29}\text{Si}$  resonance ( $\delta$  62.9) to the silicon of the bridging silyl ligand in **2**.



**Fig. S1** <sup>1</sup>H NMR spectrum of **2** (594 MHz, C<sub>6</sub>D<sub>6</sub>).



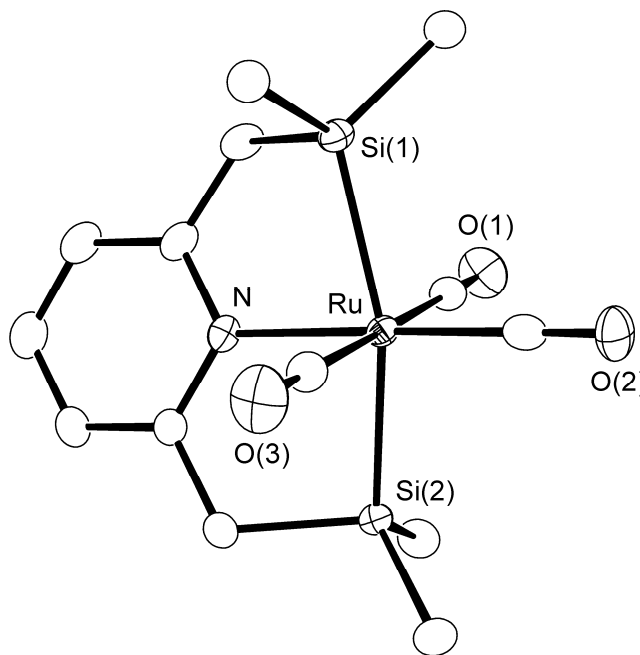
**Fig. S2** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** (75.5 MHz, C<sub>6</sub>D<sub>6</sub>).



**Fig. S3**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **2** (59.6 MHz,  $\text{C}_6\text{D}_6$ ).

**X-Ray crystal structure determination of 1 and 2.** X-ray quality single crystals of **1** and **2** were obtained from hexane at  $-30\text{ }^\circ\text{C}$  as lemon-yellow plates for **1** and at room temperature as red plates for **2**. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069\text{ \AA}$ ) under a cold nitrogen stream ( $T = 150\text{ K}$ ). Both structures were solved by the Patterson method using the DIRDIF-99<sup>2</sup> program and refined by full matrix least-squares techniques on all  $F^2$  data with SHELXL-97.<sup>3</sup> Anisotropic refinement was applied to all non-hydrogen atoms. All of the hydrogen atoms in **1** were put at calculated positions. In the case of **2**, two hydrogen atoms on the methylene carbon C(13) that participates in the 3c-2e Ru-Si-C interaction were found on the difference Fourier map and refined isotropically, and other hydrogen atoms were put at calculated positions. CCDC reference numbers: 742957 (**1**) and 742958 (**2**). Crystallographic data are available as a CIF file.

**Crystallographic data for 1.**  $C_{14}H_{19}NO_3Si_2Ru$ ,  $M = 406.55$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 7.1593(4)$ ,  $b = 20.572(2)$ ,  $c = 12.361(1)$  Å,  $\beta = 104.361(5)^\circ$ ,  $V = 1763.7(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150$  K,  $\mu(\text{Mo-K}\alpha) = 1.03$  mm<sup>-1</sup>, 13609 reflections measured, 3918 unique ( $R_{\text{int}} = 0.048$ ),  $R1 = 0.043$  and  $wR2 = 0.075$  (all data). The crystal structure of **1** is depicted on Fig. S4.



**Fig. S4** Crystal structure of **1**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–Si(1) 2.4477(8), Ru–Si(2) 2.4432(8), Ru–N 2.206(2), Si(1)–Ru–Si(2) 161.39(3), Si(1)–Ru–N 81.18(6), Si(2)–Ru–N 80.52(6).

## References

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2. P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, *The DIRDIF-99 program system*, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
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