# Electronic Supplementary Information

# Silyl–pyridine–amine pincer-ligated iridium complexes for catalytic silane deuteration via room temperature C–D bond activation of benzene-*d*<sub>6</sub>

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#### 1. Experimental procedures and characterisation data

**General procedures.** All manipulations except purification of  $DSi(n-Pr)_3$  were carried out under dry argon in a glovebox or using a high-vacuum line and standard Schlenk techniques. Isolation of  $DSi(n-Pr)_3$  in a preparative-scale experiment was performed in air.

**Materials.** Benzene, benzene- $d_6$  (99.6%D), diethylether, hexane, toluene and dichloromethane- $d_2$  were dried over CaH<sub>2</sub> and vacuum transferred, and then stored under argon over 4 Å molecular sieves in a glovebox. Toluene- $d_8$  was dried over potassium mirror and vacuum transferred prior to use. Hydrosilanes (HSiMe<sub>2</sub>Et, HSiMe<sub>2</sub>(*t*-Bu), HSiEt<sub>3</sub>, HSi(*n*-Pr)<sub>3</sub>, HSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, HSiMe<sub>2</sub>(*i*-Pr), HSiMe<sub>2</sub>Ph and H<sub>2</sub>SiEt<sub>2</sub>) were dried over CaH<sub>2</sub> (for the former five silanes), degassed and then vacuum-transferred, which were stored over 4 Å molecular sieves in a glovebox at -35 °C. 2-Diethylaminomethyl-6-methylpyridine,<sup>S1</sup> HSi(*n*-Pr)<sub>3</sub><sup>S2</sup> and [IrCl(coe)<sub>2</sub>]<sub>2</sub><sup>S3</sup> were prepared according to the literature methods.

**Spectroscopic measurements.** <sup>1</sup>H, <sup>2</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE III 400 Fourier transform spectrometer. Chemical shifts are reported in parts per million, and coupling constants (*J*) and line widths at half-height  $(\Delta v_{1/2})$  are given in Hz. <sup>29</sup>Si{<sup>1</sup>H} NMR measurements were performed using the DEPT pulse sequence or using an inverse gate decoupling (IG) pulse sequence. The residual proton (C<sub>6</sub>D<sub>5</sub>H, 7.15 ppm; C<sub>6</sub>D<sub>5</sub>CD<sub>2</sub>H, 2.09 ppm; CDHCl<sub>2</sub>, 5.32 ppm; CHCl<sub>3</sub>, 7.24 ppm) and the carbon resonances (C<sub>6</sub>D<sub>6</sub>, 128.0 ppm; CDCl<sub>3</sub>, 77.0 ppm) of deuterated solvents were used as internal references for <sup>1</sup>H and <sup>13</sup>C resonances, respectively. Aromatic proton or carbon and pyridyl proton or carbon are abbreviated as ArH or ArC and as pyH or pyC, respectively. <sup>29</sup>Si{<sup>1</sup>H} NMR chemical shifts were referenced to SiMe<sub>4</sub> (0 ppm) as an internal standard. <sup>2</sup>H NMR chemical shifts were referenced to C<sub>6</sub>D<sub>6</sub> (7.15 ppm) as an internal standard. The NMR data were collected at room temperature unless otherwise indicated. 2D exchange spectroscopy (EXSY) measurement of complex **1** at 260 K was carried out using a standard pulse sequence for phase-sensitive <sup>1</sup>H–<sup>1</sup>H NOESY spectra.

Infrared spectra were measured for solid samples included in KBr pellets, or for neat samples placed between KBr plates using a Horiba FT-720 spectrometer. UV–visible absorption spectra of **1** and **2** were acquired on a SHIMADZU MultiSpec-1500 spectrometer at room temperature. High-resolution mass spectra (HRMS) and mass spectra were recorded on a Bruker Daltonics solariX 9.4T spectrometer operating in the electrospray ionization (ESI) mode or atmospheric pressure chemical ionization (APCI) mode, a JEOL JMS-T100GCV spectrometer operating in the field desorption (FD) mode or on a SHIMADZU GC-MS QP-2010 SE spectrometer operating in the electron impact (EI) mode. Elemental analyses were carried out using a J-Science Lab JM11 microanalyzer. Measurement of elemental analysis and some mass spectra were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

# **1.1.** Synthesis of a ligand precursor 2-(di*-tert*-butylsilyl)methyl-6-[(diethylamino)methyl]pyridine (HLut<sup>SiNN</sup>).



To a solution of 2-diethylaminomethyl-6-methylpyridine (12.5 g, 70.1 mmol) in Et<sub>2</sub>O (200 mL) was added dropwise *n*-BuLi (1.57 M hexane solution, 45 mL, 71 mmol) at 0 °C for 25 min. The mixture was stirred for 45 min at 0 °C. The resulting reddish brown mixture was cooled to -80 °C using a MeOH isothermal bath. Di-*tert*-butylchlorosilane (13.7 g, 76.6 mmol) was added dropwise by a syringe to the solution at -80 °C for 25 min. The brown mixture was stirred at -80 °C for 3 days, and then the mixture was allowed to warm to room temperature and was further stirred for 1 day. The pale brown reaction mixture was filtered through Celite. The deep brown filtrate was evaporated under vacuum

to give a deep brown oil (24.3 g). After distillation of the oil under reduced pressure, two fractions containing the title compound HLut<sup>SiNN</sup> (at 160 °C, 0.13 mmHg and at 168 °C, 0.12 mmHg) was collected as a pale yellow liquid (14.9 g, 46.5 mmol) in 66% yield. This liquid contained a minor amount (ca. 6%) of a side product **B** but was used the following experiment (synthesis of iridium complexes **1** and **2**) without further purification. We deduced that the product **B** is 2-di-*tert*-butylsilylmethyl-2-diethylaminomethylpyridine, an isomer of HLut<sup>SiNN</sup>, on the basis of NMR spectroscopic data (see below).

**Data for HLut**<sup>SiNN</sup>: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.97 [t, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz, N(CH<sub>2</sub>C*H*<sub>3</sub>)<sub>2</sub>], 1.05 (s, 18H, *t*-Bu), 2.49 [q, 4H, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz, N(C*H*<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 2.52 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 3.2 Hz, py-CH<sub>2</sub>-Si), 3.78 (s, 2H, py-CH<sub>2</sub>-N), 3.83 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 3.2 Hz, Si–H), 6.78 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 3-pyH), 7.17 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 4-pyH), 7.28 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 5-pyH).<sup>†</sup> <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  12.5 [N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 19.4 [Si*C*(CH<sub>3</sub>)<sub>3</sub>], 22.6 (py-CH<sub>2</sub>-Si), 29.1 [SiC(*C*H<sub>3</sub>)<sub>3</sub>], 47.8 [N(*C*H<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 60.2 (py-CH<sub>2</sub>-N), 118.5 (5-pyC), 120.8 (3-pyC), 136.1 (4-pyC), 160.9 (6-pyC), 161.0 (2-pyC).<sup>† 29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, DEPT, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 14.4. IR (neat, cm<sup>-1</sup>): 3059 (vw, *v*<sub>CH</sub>), 2966 (s, *v*<sub>CH</sub>), 2931 (s, *v*<sub>CH</sub>), 2891 (s, *v*<sub>CH</sub>), 2856 (s, *v*<sub>CH</sub>), 2806 (m, *v*<sub>CH</sub>), 2092 (m, *v*<sub>SiH</sub>), 1587 (m), 1574 (m), 1469 (m), 1450 (s), 1387 (w), 1365 (w), 1163 (w), 1076 (w), 1012 (w), 825 (s), 704 (w). MS (FD): *m*/*z* 320 (M<sup>+</sup>, 100), 263 (M<sup>+</sup> – *t*-Bu, 24). HRMS (FD): *m*/*z* calcd for [<sup>12</sup>C<sub>19</sub><sup>1</sup>H<sub>36</sub><sup>14</sup>N<sub>2</sub><sup>28</sup>Si]<sup>+</sup> ([M]<sup>+</sup>) 320.2642, found 320.2650. Anal. Calcd for C<sub>19</sub>H<sub>36</sub>N<sub>2</sub>Si: C, 71.18; H, 11.32; N, 8.74. Found: C, 71.23; H, 11.32; N, 8.80.

<sup>†</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals of HLut<sup>SiNN</sup> were assigned on the basis of <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC spectra.



NMR data for a minor product B in a mixture with HLut<sup>SiNN</sup>: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.95 (s, 9H, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 2.37 (s, 3H, py-Me), 2.71 [dq, 2H, <sup>2</sup>J<sub>HH</sub> = 13.1 Hz, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, N(CH<sub>A</sub>H<sub>B</sub>CH<sub>3</sub>)<sub>2</sub>], 2.93 [dq, 2H, <sup>2</sup>J<sub>HH</sub> = 13.1 Hz, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, N(CH<sub>A</sub>H<sub>B</sub>CH<sub>3</sub>)<sub>2</sub>], 4.05 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, Si–H), 4.32 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, py-CH-Si), 6.57 (br d, 1H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, pyH), 7.06–7.15 (m, 2H, pyH). A CH<sub>3</sub> signal of the NEt<sub>2</sub> group was not assigned due to the overlap with the *t*-Bu signal of HLut<sup>SiNN</sup> at 1.05 ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  14.1 [N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 20.2 [SiC(CH<sub>3</sub>)<sub>3</sub>], 20.3 [SiC(CH<sub>3</sub>)<sub>3</sub>], 24.3 (py-CH<sub>3</sub>), 30.25 [SiC(CH<sub>3</sub>)<sub>3</sub>], 30.33 [SiC(CH<sub>3</sub>)<sub>3</sub>], 46.7 [N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 59.0 (py-CH-Si), 119.7 (pyC), 119.9 (pyC), 135.8 (pyC), 157.2 (pyC), 163.0 (pyC). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, DEPT, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.8.

# 1.2. Synthesis of Ir(Lut<sup>SiNN</sup>)(H)Cl (1).



[IrCl(coe)<sub>2</sub>]<sub>2</sub> (0.120 g, 0.134 mmol) and HLut<sup>SiNN</sup> (0.110 g, 0.343 mmol) were suspended in toluene (3 mL), and the suspension was transferred to a reaction tube with a Teflon valve. The orange suspension was stirred at 70 °C using an oil bath for 3 days. After the resulting deep red solution was evaporated under vacuum, the oily residue was extracted with Et<sub>2</sub>O (ca. 3 mL), and the extract was filtered into a test tube with a ground joint to remove a trace amount of insoluble solid. The filtrate was concentrated under vacuum, leading to the precipitation of crystalline solid. The solution was evaporated with hexane (< 1 mL) and evaporated to remove remaining solvents completely under vacuum, the first crop of Ir(Lut<sup>SiNN</sup>)(H)Cl (1) was obtained as reddish orange crystals (0.084 g, 0.15 mmol) in 57% yield based on Ir. The mother liquor and the hexane washing were combined

and evaporated under vacuum, and then the residue was recrystallized from  $Et_2O$  at -30 °C. After workup similar to that for the first crop, the second crop of **1** was obtained as an orange solid (0.026 g, 0.047 mmol) in 18% yield. Total yield of **1**: 75% based on Ir (0.110 g, 0.201 mmol).

<sup>1</sup>H NMR (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$ -25.58 (br s,  $\Delta v_{1/2} = 4$  Hz, 1H, Ir–H), 1.11 (t, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, NCH<sub>2</sub>C*H*<sub>3</sub>), 1.36 (br,  $\Delta v_{1/2} = 23$  Hz, 18H, *t*-Bu), 2.57 (br,  $\Delta v_{1/2} = 31$  Hz, 2H, NC*H*<sub>2</sub>CH<sub>3</sub>), 3.06 (br,  $\Delta v_{1/2} = ca$ . 290 Hz, 2H, py-CH<sub>2</sub>-N), 6.10 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, pyH), 6.44 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, pyH), 6.92 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, pyH).<sup>†</sup> Some signals for py-CH<sub>2</sub>-Si and NC*H*<sub>2</sub>CH<sub>3</sub> were not able to be assigned due to broadening of these signals. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$  10.7 (br s,  $\Delta v_{1/2} = 16$  Hz, NCH<sub>2</sub>CH<sub>3</sub>), 22.6 [Si*C*(CH<sub>3</sub>)<sub>3</sub>], 30.5 [br s,  $\Delta v_{1/2} = 16$  Hz, SiC(CH<sub>3</sub>)<sub>3</sub>], 33.7 (py-CH<sub>2</sub>-Si), 50.2 (br,  $\Delta v_{1/2} = ca$ . 70 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 64.6 (py-CH<sub>2</sub>-N), 118.4 (pyC), 122.0 (pyC), 131.3 (pyC), 160.0 (pyC), 170.0 (pyC). <sup>29</sup>Si<sup>1</sup>H} NMR (79.5 Hz, IG, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.2. IR (KBr pellet, cm<sup>-1</sup>): 2972 (s,  $v_{CH}$ ), 2925 (s,  $v_{CH}$ ), 2879 (s,  $v_{CH}$ ), 2848 (s,  $v_{CH}$ ), 2310 (w,  $v_{IrH}$ ), 1556 (w), 1468 (s), 1442 (m), 1417 (w), 1390 (m), 1362 (m), 1271 (w), 1122 (m), 1009 (w), 816 (s), 796 (m), 773 (m), 712 (w), 617 (m), 573 (m), 474 (m), 447 (w). HRMS (APCI): *m*/*z* calcd for [<sup>12</sup>C<sub>19</sub><sup>1</sup>H<sub>36</sub><sup>14</sup>N<sub>2</sub><sup>28</sup>Si<sup>35</sup>Cl<sup>193</sup>Ir]<sup>+</sup> ([M + H]<sup>+</sup>) 549.2038, found 549.2039. UV–vis ( $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>), THF): 375 (7 × 10<sup>3</sup>), 468 (5 × 10<sup>3</sup>). Anal. Calcd for C<sub>19</sub>H<sub>36</sub>N<sub>2</sub>SiClIr: C, 41.62; H, 6.62; N, 5.11. Found: C, 41.90; H, 6.70; N, 5.11.

<sup>†</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals of **1** were assigned on the basis of <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC spectra.

# 1.3. Synthesis of Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2).



In a round-bottomed flask with a Teflon valve, a mixture of HLut<sup>SiNN</sup> (1.137 g, 3.547 mmol) and [IrCl(coe)<sub>2</sub>]<sub>2</sub> (1.308 g, 1.460 mmol) were suspended in toluene (36 mL). The orange suspension was stirred at 60 °C for 24 h, and the resulting red solution was evaporated under vacuum. To the residue, which involved complex **1**, unidentified complex **A**, and unreacted HLut<sup>SiNN</sup> in ca. 1 : 0.7 : 0.8 molar ratio, was added DMAP (0.400 g, 3.27 mmol), and the mixture was dissolved in toluene (30 mL). The resulting orange solution was stirred at room temperature for 10 min, and the reaction mixture was evaporated under vacuum. The residue was washed with hexane (1 mL × 3) and then with Et<sub>2</sub>O (6 mL × 3) to give a yellow solid. Recrystallization of the solid from toluene at -35 °C gave Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl•0.5toluene (**2**•0.5toluene) (containing 0.5 mole of toluene, determined by <sup>1</sup>H NMR and elemental analysis) as orange crystals (1.287 g, 1.796 mmol) in 62% yield based on Ir. NMR data for unidentified complex **A** are also listed below.

<sup>1</sup>H NMR (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$ -21.21 (br s,  $\Delta v_{1/2} = 12$  Hz, 1H, Ir–H), 0.55 (br,  $\Delta v_{1/2} = 87$  Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), ca. 1.1–1.6 (br, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.30 (br s,  $\Delta v_{1/2} = 7$  Hz, 9H, *t*-Bu), 1.53 (br s,  $\Delta v_{1/2} = 7$  Hz, 9H, *t*-Bu), 2.03 (br s,  $\Delta v_{1/2} = 6$  Hz, 6H, NMe<sub>2</sub>), 2.10 (br s, 2H, py-CH<sub>2</sub>-Si), 2.5–3.4 (br, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 3.13, 3.30 (br AB quartet, 2H, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, py-CH<sub>2</sub>-N), 5.52 [br,  $\Delta v_{1/2} = 38$  Hz, 1H, pyH(DMAP)], 5.96 [br,  $\Delta v_{1/2} = ca.$  40 Hz, 1H, pyH(DMAP)], 6.24 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 5-pyH), 6.79–6.93 (m, 2H, 3,4-pyH), ca. 6.9–7.2 [br, 1H, pyH(DMAP)], 10.01 [br,  $\Delta v_{1/2} = 41$  Hz, 1H, pyH(DMAP)].<sup>†</sup> Accurate chemical shifts for a pyH singal of DMAP ( $\delta$  ca. 6.9–7.2) and a CH<sub>3</sub> signal of the NEt<sub>2</sub> group ( $\delta$  ca.

1.1–1.6) were not determined due to overlap with the C<sub>6</sub>D<sub>5</sub>H signal and a *t*-Bu signal, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.0 (br, NCH<sub>2</sub>CH<sub>3</sub>), 10.9 (br, NCH<sub>2</sub>CH<sub>3</sub>), 21.1 [SiC(CH<sub>3</sub>)<sub>3</sub>], 24.2 [SiC(CH<sub>3</sub>)<sub>3</sub>], 30.2 [SiC(CH<sub>3</sub>)<sub>3</sub>], 30.9 [SiC(CH<sub>3</sub>)<sub>3</sub>], 33.3 (py-CH<sub>2</sub>-Si), 38.1 (NMe<sub>2</sub>), 45.9 (br, NCH<sub>2</sub>CH<sub>3</sub>), 51.7 (br, NCH<sub>2</sub>CH<sub>3</sub>), 65.5 (py-CH<sub>2</sub>-N), 106.7 [br, *m*-pyC(DMAP)], 107.2 [br, *m*-pyC(DMAP)], 118.4 (5-pyC), 122.2 (3-pyC), 130.9 (4-pyC), 147.1 [br, *o*-pyC(DMAP)], 150.3 [br, *o*-pyC(DMAP)], 153.5 [*p*-pyC(DMAP)], 161.6 (6-pyC), 173.9 (2-pyC).<sup>† 29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.4 (br s,  $\Delta v_{1/2} = 15$  Hz). IR (KBr pellet, cm<sup>-1</sup>): 3053 (vw,  $v_{CH}$ ), 2968 (m,  $v_{CH}$ ), 2935 (m,  $v_{CH}$ ), 2922 (m,  $v_{CH}$ ), 2877 (m,  $v_{CH}$ ), 2843 (s,  $v_{CH}$ ), 2225 (w,  $v_{IrH}$ ), 1616 (s), 1525 (m), 1460 (m), 1442 (m), 1379 (m), 1358 (w), 1232 (m), 1115 (w), 1011 (m), 810 (m), 771 (w), 702 (w), 615 (w), 577 (w), 530 (w), 480 (w). HRMS (ESI): m/z calcd for [<sup>12</sup>C<sub>26</sub><sup>1</sup>H<sub>46</sub><sup>14</sup>N<sub>4</sub><sup>28</sup>Si<sup>35</sup>Cl<sup>193</sup>Ir]<sup>+</sup> ([M]<sup>+</sup>) 670.2804, found 670.2807. UV–vis ( $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>), THF): 368 (2 × 10<sup>4</sup>), 463 (5 × 10<sup>3</sup>). Anal. Calcd for C<sub>29.5</sub>H<sub>50</sub>N<sub>4</sub>SiCHr: C, 49.45; H, 7.03; N, 7.82. Found: C, 49.67; H, 7.26; N, 7.86.

<sup>†</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals of **2** were assigned on the basis of <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC spectra.

Data for unidentified iridium complex A: <sup>1</sup>H NMR (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$  –26.86 (s with satellites, 1H,  $J_{SiH}$  = 41 Hz, Ir–H), 1.04 (t, 3H, <sup>3</sup> $J_{HH}$  = 7.1 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.14 (t, 3H, <sup>3</sup> $J_{HH}$  = 7.1 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.52 (s, 9H, *t*-Bu), 1.56 (s, 9H, *t*-Bu), 1.72 (d, 1H, <sup>2</sup> $J_{HH}$  = 16.4 Hz, py-CH<sub>2</sub>-Si), 2.35 (d, 1H, <sup>2</sup> $J_{HH}$  = 16.4 Hz, py-CH<sub>2</sub>-Si), 3.33 (d, 1H, <sup>2</sup> $J_{HH}$  = 14.4 Hz, py-CH<sub>2</sub>-N), 3.85 (dq, <sup>2</sup> $J_{HH}$  = 14.5 Hz, <sup>3</sup> $J_{HH}$  = 7.1 Hz, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 4.17–4.30 (m, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 4.24 (d, 1H, <sup>2</sup> $J_{HH}$  = 14.4 Hz, py-CH<sub>2</sub>-N), 6.06 (br d, 1H, <sup>3</sup> $J_{HH}$  = 7.6 Hz, pyH), 6.58 (br d, 1H, <sup>3</sup> $J_{HH}$  = 7.6 Hz, pyH), 6.63 (t, 1H,  $J_{HH}$  = 7.6 Hz, pyH). Some <sup>1</sup>H signals assignable to cyclooctene ligand(s) were also observed in the range of ca. 1.1–2.6 ppm. Due to overlap with other signals, some <sup>1</sup>H signals of NCH<sub>2</sub>CH<sub>3</sub> were not able to be assigned. <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, r.t., C<sub>6</sub>D<sub>6</sub>): *δ*12.0.

# 1.4. NMR monitoring of a reaction of Ir(Lut<sup>SiNN</sup>)(H)Cl (1) with DMAP.

An NMR tube (5 mm o.d.) with a J. Young Teflon valve was charged with 1 (4 mg, 7  $\mu$ mol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (< 1 mg, an internal standard), and then they were dissolved in C<sub>6</sub>D<sub>6</sub> (0.5 mL). A <sup>1</sup>H NMR spectrum of the solution was measured to determine the intensity ratio of the signals of 1 and Si(SiMe<sub>3</sub>)<sub>4</sub>. To the solution was added a C<sub>6</sub>D<sub>6</sub> solution of DMAP (0.14 M, 0.06 mL, 8  $\mu$ mol). Within 5 min at room temperature, the <sup>1</sup>H NMR spectrum of the reaction mixture showed that Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2) was formed quantitatively (ca. 100% NMR yield). The product 2 was identified by comparing the <sup>1</sup>H NMR spectrum with that of the authentic sample synthesized by the aforementioned procedure.

# 1.5. NMR monitoring of a reaction of Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2) with BPh<sub>3</sub>.

In an NMR tube (5 mm o.d.) with a J. Young Teflon valve, **2**•0.5toluene (5 mg, 7  $\mu$ mol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (< 1 mg, an internal standard) were dissolved in C<sub>6</sub>D<sub>6</sub> (0.6 mL). A <sup>1</sup>H NMR spectrum of the solution was measured to determine the intensity ratio of the signals of **2** and Si(SiMe<sub>3</sub>)<sub>4</sub>. To the solution was added BPh<sub>3</sub> (2 mg, 8  $\mu$ mol). The <sup>1</sup>H NMR spectrum of the reaction mixture showed that Ir(Lut<sup>SiNN</sup>)(H)Cl (**1**) was formed quantitatively (ca. 100% NMR yield) within 5 min at room temperature. The <sup>1</sup>H NMR signals of DMAP·BPh<sub>3</sub> were also observed. Complex **1** was identified by comparing the <sup>1</sup>H NMR spectrum with that of the authentic sample synthesized by the aforementioned procedure.

# 1.6. Measurement of variable-temperature <sup>1</sup>H NMR spectra of Ir(Lut<sup>SiNN</sup>)(H)Cl (1).

A Pyrex NMR tube (5 mm o.d.) with a ground joint was charged with **1** (5 mg, 9  $\mu$ mol) and toluene- $d_8$  (ca. 0.5 mL). This tube was then connected to a vacuum line, the solution was degassed by a freeze-pump-thaw cycle, and the tube was flame-sealed under vacuum. Variable-temperature <sup>1</sup>H NMR spectra of the sample were measured at 300, 290, 280, 270, 260, 250, 240 and 230 K. The spectra at 300 and 230 K are depicted in Fig. S1, and their data are described below.

<sup>1</sup>H NMR (400 MHz, 300 K, toluene-*d*<sub>8</sub>):  $\delta$ -25.71 (s, 1H, Ir–H), 1.11 (t, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.30 (br,  $\Delta v_{1/2} = 27$  Hz, 18H, *t*-Bu), 2.58 (br,  $\Delta v_{1/2} = 30$  Hz, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 3.11 (br,  $\Delta v_{1/2} = ca. 210$  Hz, 2H, py-CH<sub>2</sub>-N), 6.16 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, pyH), 6.46 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, pyH), 6.97 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, pyH). Some py-CH<sub>2</sub>-Si and NCH<sub>2</sub>CH<sub>3</sub> signals were not able to be assigned due to broadening of these signals.

<sup>1</sup>H NMR (400 MHz, 230 K, toluene-*d*<sub>8</sub>):  $\delta$ -25.15 (s, 1H, Ir–H), 1.09 (t, 3H, <sup>3</sup>*J*<sub>HH</sub> = ca. 7 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.13 (t, 3H, <sup>3</sup>*J*<sub>HH</sub> = ca. 7 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.24 (s, 9H, *t*-Bu), 1.25 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 16.4 Hz, py-CH<sub>2</sub>-Si), 1.55 (s, 9H, *t*-Bu), 1.80 (dq, 1H, <sup>2</sup>*J*<sub>HH</sub> = 12.9 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 2.21 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 16.4 Hz, py-CH<sub>2</sub>-Si), 2.29–2.42 (m, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 2.47 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 14.7 Hz, py-CH<sub>2</sub>-N), 2.53–2.66 (m, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 3.28 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 14.7 Hz, py-CH<sub>2</sub>-N), 3.42 (dq, 1H, <sup>2</sup>*J*<sub>HH</sub> = 12.9 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 6.09 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 17.6 Hz, pyH), 6.35 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, pyH), 6.91 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, pyH).



**Fig. S1** Variable temperature <sup>1</sup>H NMR spectra of  $Ir(Lut^{SiNN})(H)Cl(1)$  in the range of 0.5–3.5 ppm (400 MHz, toluene-*d*<sub>8</sub>).

# **1.7.** Measurement of variable-temperature <sup>1</sup>H NMR spectra and a 2D EXSY NMR spectrum of Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2).

By a procedure analogous to that described in the above section 1.6, a sealed Pyrex NMR tube containing a toluene- $d_8$  (ca. 0.4 mL) solution of **2** (5 mg, 7 µmol) was prepared using a vacuum line. Variable-temperature <sup>1</sup>H NMR spectra of the sample were measured at 300, 270 and 260 K. The spectra at 300 and 260 K are depicted in Fig. S2, and their data are also shown below. A 2D EXSY NMR spectrum of complex **2** was measured at 260 K (Fig. S3), showing that EXSY cross peaks between two methyl(NEt) signals and between methylene(NEt) signals (Fig. S3(a)). A possible mechanism for the dynamic behaviour of **2** involving exchange of ethyl groups on the amine nitrogen is illustrated in Scheme S1.

*Note:* The broad <sup>1</sup>H NMR signals of the pyridyl hydrogens of DMAP at 300 K became sharper at 260 K (Fig. S2(b)). Moreover, the 2D EXSY NMR spectrum at 260 K (Fig. S3(b)) shows cross peaks between the pyH(DMAP) signals at 5.39 and 5.90 ppm and between those at ca. 7.03 and 9.94 ppm. These observations indicate that another dynamic behaviour of **2** via exchange of the DMAP hydrogens also occurs in this temperature range. This behaviour is possibly caused by rotation of the DMAP ligand around the Ir–N(DMAP) axis.

<sup>1</sup>H NMR (400 MHz, 300 K, toluene-*d*<sub>8</sub>):  $\delta$ -21.30 (br s, 1H, Ir–H), 0.59 (br,  $\Delta v_{1/2} = 92$  Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), ca. 1.1–1.6 (br, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.21 (br s, 9H, *t*-Bu), 1.44 (br s, 9H, *t*-Bu), 2.05 (br s, 2H,  $\Delta v_{1/2} = 7$  Hz, py-CH<sub>2</sub>-Si), 2.10 [br s, 6H, NMe<sub>2</sub>(DMAP)], 2.6–3.4 (br, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 3.15 (br d, 1H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, py-CH<sub>2</sub>-N), 3.34 (br d, 1H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, py-CH<sub>2</sub>-N), 5.54 [br,  $\Delta v_{1/2} = 38$  Hz, 1H, pyH(DMAP)], 5.97 [br,  $\Delta v_{1/2} = 40$  Hz, 1H, pyH(DMAP)], 6.28 (br t, 1H, J<sub>HH</sub> = 4.5 Hz, pyH), 6.84–6.91 (m, 2H, pyH), ca. 6.9–7.2 [br, 1H, pyH(DMAP)], 9.91 [br,  $\Delta v_{1/2} = 37$  Hz, 1H, pyH(DMAP)]. Accurate chemical shifts of a CH<sub>3</sub>(NEt) signal and a pyH(DMAP) signal were not able to be determined due to the overlap with two *t*-Bu signals and with residual aromatic proton signals of toluene-*d*<sub>8</sub>,

respectively. A CH<sub>2</sub>(NEt) signal was not able to be assigned due to the overlap with other <sup>1</sup>H signals and significant broadening.

<sup>1</sup>H NMR (400 MHz, 260 K, toluene-*d*<sub>8</sub>):  $\delta$ -21.11 (s, 1H, Ir–H), 0.53 (t, 3H, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz, NCH<sub>2</sub>C*H*<sub>3</sub>), 1.28 (s, 9H, *t*-Bu), 1.41 (t, 3H, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, NCH<sub>2</sub>C*H*<sub>3</sub>), 1.53 (s, 9H, *t*-Bu), 2.01 [s, 6H, NMe<sub>2</sub>(DMAP)], 2.07 (br s, 2H, py-CH<sub>2</sub>-Si), ca. 2.0–2.2 (m, 1H, NC*H*<sub>2</sub>CH<sub>3</sub>), 2.70 (dq, 1H, <sup>2</sup>*J*<sub>HH</sub> = 12.2 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, NC*H*<sub>2</sub>CH<sub>3</sub>), 3.02 (dq, 1H, <sup>2</sup>*J*<sub>HH</sub> = 12.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz, NC*H*<sub>2</sub>CH<sub>3</sub>), 3.11 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 14.4 Hz, py-CH<sub>2</sub>-N), 3.21 (dq, 1H, <sup>2</sup>*J*<sub>HH</sub> = 14.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, NC*H*<sub>2</sub>CH<sub>3</sub>), 3.26 (d, 1H, <sup>2</sup>*J*<sub>HH</sub> = 14.4 Hz, py-CH<sub>2</sub>-N), 5.39 [dd, 1H, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.1 Hz, pyH(DMAP)], 5.90 [dd, 1H, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.1 Hz, pyH(DMAP)], 6.25 (dd, 1H, <sup>3</sup>*J*<sub>HH</sub> = 5.9 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.0 Hz, pyH), 6.82–6.89 (m, 2H, pyH), ca. 7.03 [d, 1H, *J*<sub>HH</sub> = ca. 7 Hz, pyH(DMAP)], 9.94 [d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, pyH(DMAP)]. Accurate chemical shifts of a CH<sub>2</sub>(NEt) signal and a pyH(DMAP) signal were not able to be determined due to the overlap with residual proton signals of toluene-*d*<sub>8</sub>.



**Fig. S2** Variable temperature <sup>1</sup>H NMR spectra of Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2) in the ranges of (a)  $0 \sim 3.5$  and  $-22.0 \sim -20.5$  ppm and (b)  $5.0 \sim 10.5$  ppm (400 MHz, toluene- $d_8$ ).



Fig. S3 2D EXSY NMR spectrum of 2 in the ranges of (a)  $0 \sim 3.5$  ppm and (b)  $5.0 \sim 10.25$  ppm (400 MHz, 260 K, toluene- $d_8$ ).



Scheme S1 A possible mechanism for dynamic behaviour of 2 via exchange of the NEt groups in solution.

1.8. Thermal isomerisation of DMAP complex 2: synthesis of 2'.



In a 30 mL reaction tube with a Teflon valve, complex 2 (60 mg, 0.084 mmol) was dissolved in toluene (6 mL). The orange solution was heated using an oil bath at 60 °C for 3 days. The resulting yellow solution was concentrated under vacuum to give a yellow oil (60 mg). After the oil was washed with hexane (1 mL  $\times$  3) and dried under vacuum, complex 2' was obtained as a yellow powder (54 mg, 0.081 mmol, 96%). Complex 2' was characterised by NMR, IR and mass spectroscopy (see below data) and X-ray crystallography (see section 2).

<sup>1</sup>H NMR (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>):  $\delta$ -22.40 (s with satellites, 1H,  $J_{SiH}$  = ca. 8 Hz, Ir–H), 0.73 (br, 3H,  $\Delta v_{1/2}$  = 30 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 0.95 (br, 3H,  $\Delta v_{1/2}$  = 29 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 1.29 (s, 9H, *t*-Bu), 1.60 (s, 9H, *t*-Bu), 2.01 (s, 6H, NMe<sub>2</sub>), 2.13 (d, 1H, <sup>2</sup> $J_{HH}$  = 15.8 Hz, py-CH<sub>2</sub>-Si), 2.63 (br, 2H,  $\Delta v_{1/2}$  = 31 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 2.77 (d, 1H, <sup>2</sup> $J_{HH}$  = 15.8 Hz, py-CH<sub>2</sub>-Si), 3.08 (br, 1H,  $\Delta v_{1/2}$  = 39 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 3.35 (d, 1H, <sup>2</sup> $J_{HH}$  = 13.9 Hz, py-CH<sub>2</sub>-N), 3.61 (br, 1H,  $\Delta v_{1/2}$  = 38 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 5.20 (d, 1H, <sup>2</sup> $J_{HH}$  = 13.9 Hz, py-CH<sub>2</sub>-N), 5.67–5.73 [m, 2H,

pyH(DMAP)], 6.24–6.30 (m, 1H, 5-pyH), 6.75–6.81 (m, 2H, 3,4-pyH), 9.41 [br d, 2H,  ${}^{3}J_{HH}$ = 6.0 Hz, pyH(DMAP)].<sup>† 13</sup>C{<sup>1</sup>H} NMR (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>): δ 8.2 (br,  $\Delta v_{1/2}$  = ca. 24 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 10.6 (br,  $\Delta v_{1/2}$  = ca. 28 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 21.8 [SiC(CH<sub>3</sub>)<sub>3</sub>], 23.4 [SiC(CH<sub>3</sub>)<sub>3</sub>], 31.2 [SiC(CH<sub>3</sub>)<sub>3</sub> × 2], 34.6 (py-CH<sub>2</sub>-Si), 38.1 (NMe<sub>2</sub>), 45.5 (br,  $\Delta v_{1/2}$  = ca. 36 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 50.8 (br,  $\Delta v_{1/2}$  = ca. 33 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 64.7 (py-CH<sub>2</sub>-N), 107.2 [*m*pyC(DMAP)], 117.5 (5-pyC), 121.1 (3-pyC), 133.0 (4-pyC), 152.2 [*p*-pyC(DMAP)], 157.9 [*o*-pyC(DMAP)], 162.3 (6-pyC), 173.1 (2-pyC).<sup>† 29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, r.t., C<sub>6</sub>D<sub>6</sub>): δ 9.3. IR (KBr pellet, cm<sup>-1</sup>): 3091 (w, *v*<sub>CH</sub>), 3060 (w, *v*<sub>CH</sub>), 2974 (m, *v*<sub>CH</sub>), 2922 (s, *v*<sub>CH</sub>), 2877 (s, *v*<sub>CH</sub>), 2841 (s, *v*<sub>CH</sub>), 2233 (m, *v*<sub>IrH</sub>), 1626 (vs), 1529 (s), 1464 (s), 1439 (m), 1381 (s), 1358 (m), 1269 (w), 1227 (s), 1184 (w), 1117 (w), 1036 (m), 1024 (m), 1009 (w), 964 (w), 949 (w). 814 (s), 798 (m), 769 (m), 704 (m), 683 (w), 615 (m), 580 (w), 530 (w), 480 (w), 449 (w). HRMS (FD): *m*/*z* calcd for [ ${}^{12}C_{26}{}{}^{11}H_{46}{}^{14}N_{4}{}^{28}Si^{35}Cl^{193}Ir$ ]<sup>+</sup> ([M]<sup>+</sup>) 670.2804, found 670.2807. Anal. Calcd for C<sub>26</sub>H<sub>46</sub>N<sub>4</sub>SiCIIr: C, 46.58; H, 6.92; N, 8.36. Found: C, 46.62; H, 7.09; N, 8.26.

<sup>†</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals of **2**' were assigned on the basis of <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC spectra.

#### 1.9. NMR monitoring of Ir-H deuteration reactions of complexes 1 and 2 in C<sub>6</sub>D<sub>6</sub>.

In an NMR tube with a J. Young Teflon valve, complex 1 (4 mg, 7  $\mu$ mol) or 2•0.5toluene (5 mg, 7  $\mu$ mol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (internal standard, less than 1 mg) were dissolved in C<sub>6</sub>D<sub>6</sub> (0.6 mL,  $d = 0.950 \text{ g} \cdot \text{mL}^{-1}$ , 6.8 mmol;  $1 \times 10^3$  equiv). The tube was allowed to stand at room temperature, and the reaction was monitored by NMR spectroscopy. After 1 h (for 1) or 18 h (for 2) at room temperature, the product of Ir–H deuteration, 1-*d* or 2-*d*, was formed quantitatively in 97%D incorporation in each case. The products were identified by comparison of the <sup>1</sup>H NMR spectra with those of 1 and 2 and by confirming the agreement of the chemical shift of the <sup>2</sup>H NMR signal of Ir–D with that of the <sup>1</sup>H NMR signal of Ir–H.

<sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>) data for 1-*d*:  $\delta$ -25.2 (br s,  $\Delta v_{1/2}$  = ca. 3 Hz, Ir–D); for 2-*d*:  $\delta$ -21.0 (br,  $\Delta v_{1/2}$  = ca. 16 Hz, Ir–D).

Further monitoring of the reaction of complex **1** in benzene- $d_6$  revealed that parts of C– H hydrogens in the Lut<sup>SiNN</sup> ligand were also deuterated slowly. After 4 days at room temperature and then 12 days under heating at 70 °C, the <sup>1</sup>H NMR spectrum of the reaction mixture showed decrease of intensities of the signals of Lut<sup>SiNN</sup>, in particular the signals of the pyridiyl and methyl(NEt) hydrogens almost disappeared. In the <sup>2</sup>H NMR spectrum, signals assignable to deuterium atoms in methyl(NEt), *t*-butyl and methylene(NEt) groups of Lut<sup>SiNN</sup> were observed at 1.0, ca. 1.2–1.5 (br) and ca. 2.3–2.8 (br) ppm, respectively. <sup>2</sup>H NMR signals for deuterium atoms in the pyridine ring were not observed probably because these signals were obscured by the strong <sup>2</sup>H signal of C<sub>6</sub>D<sub>6</sub>.

# 1.10. Synthesis of Ir(Lut<sup>SiNN</sup>)(D)(DMAP)Cl (2-d).

A C<sub>6</sub>D<sub>6</sub> (6 mL,  $d = 0.950 \text{ g} \cdot \text{mL}^{-1}$ , 0.07 mol;  $0.9 \times 10^3$  equiv) solution of **2**•0.5toluene (52 mg, 0.073 mmol) in a round-bottomed flask with a Teflon valve was warmed at 28 °C using an oil bath for 18 h. After the reaction mixture was evaporated under vacuum, the residue was washed with hexane and then dried under vacuum. The title compound (50 mg, 0.074 mmol, 98%D) was obtained as a yellow powder in ca. 100% yield. The product was identified by comparison of the <sup>1</sup>H and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra with those of **2** and by confirming the agreement of the chemical shift ( $\delta$  –21.0) of the <sup>2</sup>H NMR signal of Ir–D with that of the <sup>1</sup>H NMR signal of Ir–H.

#### 1.11. Stoichiometric reaction of complex 1 or 2 with HSiEt<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>.

To an NMR tube with a J. Young Teflon valve was introduced a 0.013 M  $C_6D_6$  solution of HSiEt<sub>3</sub> (0.55 mL, 7.2 µmol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (internal standard, less than 1 mg). The <sup>1</sup>H NMR spectrum of the solution was measured to determine the intensity ration between hydrosilane and internal standard. Complex **1** (4 mg, 7 µmol) or **2**•0.5toluene (5 mg, 7

µmol) was weighed in a vial and was added to the tube. The washing of the vial with  $C_6D_6$ (0.05 mL) was also added to the same tube (total of  $C_6D_6$ : 0.60 mL,  $d = 0.950 \text{ g} \cdot \text{mL}^{-1}$ , 6.8 mmol;  $0.97 \times 10^3$  equiv). The mixture was allowed to stand at room temperature, and the reaction was monitored by NMR spectroscopy. After 1 h (for 1) or 12 h (for 2) at room temperature, a mixture of the Ir–H deuteration product 1-*d* or 2-*d* (97%D each) and DSiEt<sub>3</sub> (97%D or 95%D, respectively) was obtained. Further monitoring of the reaction indicated that the ratio of the species in the reaction mixture did not change.

1.12. NMR monitoring of the deuteration reactions of trialkylsilanes with  $C_6D_6$  catalysed by complex 1 or 2 (general procedure).

$$H-SiR_{3} + D \xrightarrow{D_{5}} D_{5}$$

$$(23 \text{ equiv})$$

$$Cat. 1 \text{ or } 2$$

$$(1 \text{ mol}\%)$$

$$D-SiR_{3} + H \xrightarrow{D_{5}} D_{5}$$

These reactions were all carried out by the same procedures, and a general procedure for them is as follows. In an NMR tube with a J. Young Teflon valve, trialkylsilane HSiR<sub>3</sub> (R<sub>3</sub> = Me<sub>2</sub>Et, Me<sub>2</sub>(*i*-Pr), Me<sub>2</sub>(*t*-Bu), Et<sub>3</sub> or (*n*-Pr)<sub>3</sub>) (0.29–0.30 mmol) and Si(SiMe<sub>3</sub>)<sub>4</sub> (internal standard, less than 1 mg) were dissolved in benzene- $d_6$  (0.45 mL (for 1) or 0.55 mL (for 2)). The intensity ratio between HSiR<sub>3</sub> and Si(SiMe<sub>3</sub>)<sub>4</sub> was determined by <sup>1</sup>H NMR spectroscopy. To the solution was added a 0.02 M solution of 1 in C<sub>6</sub>D<sub>6</sub> (0.15 mL, 3 µmol) or a solid of 2•0.5toluene (2 mg, 3 µmol) weighed in a vial. For the latter complex, the washing of the vial with C<sub>6</sub>D<sub>6</sub> (0.05 mL) was also transferred into this tube. The orange solution in C<sub>6</sub>D<sub>6</sub> (total 0.60 mL, d = 0.950 g·mL<sup>-1</sup>, 6.8 mmol; 23 equiv to HSiR<sub>3</sub>) was allowed to stand at room temperature, and the reaction was monitored by the decay of the <sup>1</sup>H NMR signal of Si–H of HSiR<sub>3</sub>. Intensities of the <sup>1</sup>H signals of HSiR<sub>3</sub> except for the Si– H signal did not decrease during the reaction. As the deuteration reaction progressed, the intensity of the residual <sup>1</sup>H signal of C<sub>6</sub>D<sub>5</sub>H increased. After the deuteration was almost completed, the deuterium incorporation (%D) of the product DSiR<sub>3</sub> (see Table 1 in the manuscript) was determined by comparison of the intensity ratio of the <sup>1</sup>H NMR signals of Si–H and selected C–Hs of other substituents R with the corresponding intensity ratio of the original hydrosilane HSiR<sub>3</sub>. The product DSiR<sub>3</sub> was identified by comparison of the <sup>1</sup>H, <sup>2</sup>H and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra (chemical shifts) with those of the corresponding hydrosilane. NMR spectroscopic data for the deuterated silanes except DSi(*n*-Pr)<sub>3</sub> (vide infra) are listed below.

#### NMR spectroscopic data for deuterated trialkylsilanes

**DSiMe<sub>2</sub>Et:** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ -0.01 (s, 6H, SiMe), 0.48 (q, 2H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.93 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.1 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 27 Hz, Si-D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, DEPT, C<sub>6</sub>D<sub>6</sub>):  $\delta$ -11.2 (t, <sup>1</sup>J<sub>SiD</sub> = 27 Hz).

**DSiMe**<sub>2</sub>(*i*-**Pr**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.03 (s, 6H, SiMe), 0.72 [sept, 1H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 0.96 [d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>]. <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.0 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 27 Hz, Si–D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –6.4 (t, <sup>1</sup>J<sub>SiD</sub> = 27 Hz).

**DSiMe**<sub>2</sub>(*t*-**Bu**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.03 (s, 6H, SiMe), 0.90 (s, 9H, *t*-Bu). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.9 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 28 Hz, Si–D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –1.6 (t, <sup>1</sup>J<sub>SiD</sub> = 28 Hz).

**DSiEt<sub>3</sub>:** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.53 (q, 6H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.97 (t, 9H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, SiCH<sub>2</sub>CH<sub>3</sub>). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.9 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 27 Hz, Si–D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, C<sub>6</sub>D<sub>6</sub>):  $\delta$ –0.1 (t, <sup>1</sup>J<sub>SiD</sub> = 27 Hz).

#### **1.13.** Synthesis of DSi(*n*-Pr)<sub>3</sub> by a preparative-scale catalytic deuteration reaction.

In a 30 mL round-bottomed flask, complex 2•0.5toluene (5 mg, 7 µmol; ca. 0.1 mol%) and  $HSi(n-Pr)_3$  (1.00 g, 6.27 mmol) were dissolved in C<sub>6</sub>D<sub>6</sub> (13.6 mL, d = 0.95 g·mL<sup>-1</sup>, 154

mmol; 25 equiv to HSi(*n*-Pr)<sub>3</sub>). A part of the solution (ca. 0.6 mL) was transferred to an NMR tube with a J. Young Teflon valve. Both of the solution in the flask and the NMR tube were warmed at 28 °C for 19 h using an oil bath where the former solution was stirred. The <sup>1</sup>H NMR spectrum of the resulting mixture showed the formation of DSi(*n*-Pr)<sub>3</sub> with 98%D content. The solution in the NMR tube was transferred into the flask and the washings of the previous tube with hexane (0.1 mL × 3) were also transferred into the same flask. Most of C<sub>6</sub>D<sub>6</sub> and hexane were evaporated from the mixture under a reduced pressure (16 mmHg) using a diaphragm pump. To remove the catalyst **2**-*d* in the mixture, the residue was chromatographed on silica gel (15 g) with hexane as an eluent. Volatiles of the eluate were completely removed under a reduced pressure (9 mmHg) to give DSi(*n*-Pr)<sub>3</sub> (98%D) as a colourless liquid in 76% yield (0.757 g, 4.8 mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.53–0.61 (m, 6H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.95 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 9H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.37 (sext, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>H<sub>6</sub>):  $\delta$  4.1 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 27 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$ 14.0 (s with satellites, <sup>1</sup>J<sub>SiC</sub> = 51 Hz, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.0 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.2 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, CDCl<sub>3</sub>):  $\delta$ –8.0 (t, <sup>1</sup>J<sub>SiD</sub> = 27 Hz). IR (neat, cm<sup>-1</sup>): 2956 (s, *v*<sub>CH</sub>), 2925 (s, *v*<sub>CH</sub>), 2870 (s, *v*<sub>CH</sub>), 2798 (m, *v*<sub>CH</sub>), 1529 (s, *v*<sub>SiD</sub>), 1456 (s), 1412 (m), 1375 (m), 1333 (s), 1215 (m), 1200 (m), 1066 (s), 1030 (w), 1005 (s), 893 (m), 814 (s), 756 (s), 742 (s), 708 (s), 544 (s). MS (EI, 70 eV): *m*/*z* 159 (M<sup>+</sup>, 7), 156 (M<sup>+</sup> – H – D, 91), 116 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>, 91), 74 (100). Anal. Calcd for C<sub>9</sub>H<sub>21.02</sub>D<sub>0.98</sub>Si (based on the deuteration ratio 98%D): C, 67.83; H/D, 13.92. Found: C, 67.93; H/D, 14.14.

# 1.14. NMR monitoring of reactions of siloxy- or aryl-substituted tertiary silanes $(HSiMe(OSiMe_3)_2 \text{ and } HSiMe_2Ph)$ and diethylsilane with $C_6D_6$ in the presence of complex 1 or 2.

NMR monitoring of the title deuteration reactions was performed by a procedure similar to that described in 1.10. for the deuteration reactions of trialkylsilanes, using HSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, HSiMe<sub>2</sub>Ph and H<sub>2</sub>SiEt<sub>2</sub> (0.28–0.29 mmol) in the presence of **1** or **2** (3 µmol, 1 mol%). The reaction times and D incorporation of the silanes are summarised in Table S1. In the case of the reaction with HSiMe<sub>2</sub>Ph, scrambling of the silane substituents also proceeded competitively, and NMR signals for H/DSiMe<sub>3</sub>, H/DSiMePh<sub>2</sub> and HSiPh<sub>3</sub> (only for the reaction using **1**) were observed. Silanes DSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, DSiMe<sub>2</sub>Ph, H/DSiMePh<sub>2</sub> and HSiPh<sub>3</sub> were identified by comparison of the <sup>1</sup>H, <sup>2</sup>H and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra (chemical shifts) with those of the corresponding hydrosilanes (for the deuterated silanes) or with those reported in the literature (for HSiMe<sub>3</sub>, <sup>S4</sup> HSiMePh<sub>2</sub><sup>S5</sup> and HSiPh<sub>3</sub><sup>S6</sup>). NMR spectroscopic data for DSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, DSiMe<sub>2</sub>Ph, DSiMe<sub>3</sub> and DSiMePh<sub>2</sub> formed by the reactions are also listed below.

**Table S1** Deuteration of siloxy- or aryl-substituted tertiary silanes (HSiMe(OSiMe<sub>3</sub>)<sub>2</sub> and HSiMe<sub>2</sub>Ph) and diethylsilane with  $C_6D_6$  in the presence of 1 mol% of **1** or **2** 

H−SiR <sub>3</sub> +	D	cat. 1 or 2 (1 mol%) → D—Sil room temp.	R <sub>3</sub> + H-∕_∑_D <sub>5</sub>
hydrosilane	cat.	Time (h)	D incorporation $(\%D)^a$
HSiMe(OSiMe <sub>3</sub> ) <sub>2</sub>	1	9	12
HSiMe(OSiMe <sub>3</sub> ) <sub>2</sub>	2	47	20
HSiMe <sub>2</sub> Ph	1	173	81 (50% NMR yield) <sup><math>b</math></sup>
HSiMe <sub>2</sub> Ph	2	22	3 (97% NMR yield) <sup>c</sup>
$H_2SiEt_2$	1	1	$\sim 0^d$
$H_2SiEt_2$	2	6	~0

<sup>*a*</sup>Deuterium incorporation (%D) of deuterated silane DSiR<sub>3</sub> was determined by comparison of the intensity ratio of the <sup>1</sup>H NMR signals of Si–H and selected C–Hs of other substituents R with the corresponding intensity ratio for the original hydrosilane HSiR<sub>3</sub>.

<sup>b</sup>Scrambling products H/DSiMe<sub>3</sub> (ca. 74%D, 34% NMR yield), H/DSiMePh<sub>2</sub> (88%D, 15% NMR yield) and H/DSiPh<sub>3</sub> (ca. 1% NMR yield) were also formed. Deuterium incorporation of H/DSiMePh<sub>2</sub> was determined in a manner identical to that described in the above footnote<sup>*a*</sup> using the data for the authentic sample of HSiMePh<sub>2</sub> for comparison. On the other hand, that of HSiMe<sub>3</sub> was estimated by comparison of the intensities of the SiMe signals for HSiMe<sub>3</sub>/DSiMe<sub>3</sub> in a <sup>1</sup>H NMR spectrum of the reaction mixture. That of HSiPh<sub>3</sub> was not determined due to the low intensity of its <sup>1</sup>H NMR signals.

<sup>c</sup>Trace amounts of scrambling products HSiMe<sub>3</sub> (ca. 1% NMR yield) and HSiMePh<sub>2</sub> (ca. 2% NMR yield) were also formed. Deuterium incorporations of these products were not determined due to low intensity of their <sup>1</sup>H NMR signals.

<sup>*d*</sup>The <sup>1</sup>H NMR spectrum of the resulting reaction mixture showed very weak signals assignable to a scrambling product HSiEt<sub>3</sub>. The NMR yield of HSiEt<sub>3</sub> could not be determined due to the overlap of their <sup>1</sup>H NMR signals with those of  $H_2SiEt_2$ .

NMR spectroscopic data for deuterated silanes (DSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, DSiMe<sub>2</sub>Ph, DSiMe<sub>3</sub> and DSiMePh<sub>2</sub>):

**DSiMe**(**OSiMe**<sub>3</sub>)<sub>2</sub>: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.14 (s, 21H, SiMe + OSiMe<sub>3</sub>). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.0 (s with satellites, <sup>1</sup>J<sub>SiD</sub> = 36 Hz, Si–D).

**DSiMe<sub>2</sub>Ph:** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.20 (s, 6H, SiMe), 7.16–7.20 (m, 3H, Ph), 7.42–7.47 (m, 2H, Ph). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.6 (s, Si–D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, C<sub>6</sub>D<sub>6</sub>):  $\delta$ –17.2 (t, <sup>1</sup>J<sub>SiD</sub> = 29 Hz).

**DSiMe<sub>3</sub>:** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.00 (s, 9H, SiMe). <sup>2</sup>H NMR (61.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.2 (s, Si–D). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, IG, C<sub>6</sub>D<sub>6</sub>):  $\delta$ –16.5 (t, <sup>1</sup>J<sub>SiD</sub> = 28 Hz).

**DSiMePh<sub>2</sub>:** <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta 0.45$  (s, 3H, SiMe), 7.11–7.16 (m, 6H, Ph), 7.47–7.52 (m, 4H, Ph). <sup>2</sup>H NMR (61.4 MHz,  $C_6D_6$ ):  $\delta 5.1$  (s, Si–D).



Scheme S2 A tentatively proposed mechanism for Si–H deuteration of hydrosilanes with  $C_6D_6$  catalysed by Ir–Lut<sup>SiNN</sup> complexes 1 and 2. The catalytic cycle was simplified by omitting the arrows indicating reverse reactions. This mechanism involves activation of a C–D or Si–H bond by its oxidative addition accompanied by dissociation of the amine coordinating moiety of Lut<sup>SiNN</sup>.

#### 2. X-ray crystal structure determination of complexes 1, 2 and 2'

X-ray quality single crystals of **1** and **2**•1.5toluene were obtained from Et<sub>2</sub>O as red block crystals (for 1) and from toluene as orange block crystals (for  $2 \cdot 1.5$  toluene) at -35 °C in a freezer. Single crystals of 2' were obtained from a toluene solution of 2' layered by hexane at -35 °C as yellow plate crystals. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo Ka radiation ( $\lambda = 0.71069$  Å) under a cold nitrogen stream (T = 150 K). A numerical absorption correction was applied to the data. The structures were solved by the Patterson method using the DIRDIF-2008 program<sup>S7</sup> refined by full matrix least-squares techniques on all  $F^2$  data with SHELXL-2016/6.<sup>88</sup> Anisotropic refinement was applied to all nonhydrogen atoms. The metal-hydrido hydrogens in 1, 2 and 2' were found on the difference Fourier map and refined isotropically. Other hydrogen atoms were put at calculated positions. The asymmetric unit of the single crystal of **1** contains two crystallographically independent molecules, namely, molecules 1-A and 1-B. In the crystal structure of 2.1.5 toluene, positions of a methyl group and an aromatic hydrogen atom of a toluene molecule are disordered over two sites related by an inversion centre. Some reflections, i.e.  $(h \ k \ l) = (1 \ 0 \ 1), (0 \ 1 \ 1), (-1 \ 0 \ 1) \text{ and } (0 \ 2 \ 0) \text{ for } \mathbf{1}, (h \ k \ l) = (1 \ 0 \ 0), (1 \ 1 \ 0), (0 \ 0 \ 2) \text{ and } (0 \ 1 \ 1 \ 0)$ 2) for 2•1.5 toluene and  $(h \ k \ l) = (-1 \ 0 \ 1)$  for 2', were omitted from the final refinement because their intensities were significantly affected by the beam stop. All calculations were carried out using Yadokari-XG.<sup>\$9</sup> Selected crystallographic data for 1, 2•1.5toluene and 2' are listed in Table S2. Crystal structures of 1, 2 and 2' are depicted in Figs. S4, S5 and S6, respectively. CCDC reference numbers: 1590105 (for 1), 1590106 (for 2) and 1879207 (for 2'). Crystallographic data are available as a CIF file.

compound	1	2•1.5toluene	2
formula	C <sub>19</sub> H <sub>36</sub> N <sub>2</sub> SiClIr	C <sub>36.5</sub> H <sub>58</sub> N <sub>4</sub> SiClIr	C <sub>26</sub> H <sub>46</sub> N <sub>4</sub> SiClIr
formula weight	548.24	808.61	670.41
crystal system	monoclinic	monoclinic	monoclinic
crystal size/mm <sup>3</sup>	$0.17 \times 0.11 \times 0.07$	$0.19 \times 0.18 \times 0.07$	$0.17 \times 0.11 \times 0.09$
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	14.6082(5)	14.4572(4)	12.3393(12)
<i>b</i> /Å	18.4684(6)	10.2996(3)	12.1936(5)
c/Å	17.6685(5)	25.5865(9)	19.8566(7)
$lpha/^{\circ}$	90	90	90
$\beta^{\prime}$	112.3885(4)	98.7314(11)	107.3131(11)
$\gamma^{\prime \circ}$	90	90	90
V/Å <sup>3</sup>	4407.5(2)	3765.8(2)	2852.3(3)
Ζ	8	4	4
$D_{ m calcd}/ m g\cdot  m cm^{-3}$	1.652	1.426	1.561
<i>F</i> (000)	2176	1652	1352
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	6.238	3.678	4.837
reflections collected	52087	42766	40777
unique reflections $(R_{int})$	10066 (0.0700)	8619 (0.0799)	6514 (0.0845)
refined parameters	457	413	312
R1, $wR2$ (all data) <sup><math>a,b</math></sup>	0.0433, 0.0731	0.0465, 0.0877	0.0558, 0.0813
$R1, wR2 \left[I > 2 \sigma(I)\right]^{a,b}$	0.0348, 0.0703	0.0404, 0.0858	0.0450, 0.0779
GOF	1.127	1.246	1.141
largest residual peak, hole/ $e \cdot \text{\AA}^{-3}$	1.905, -1.246	1.694, -1.303	1.509, -1.494

**Table S2** Crystallographic data for  $Ir(Lut^{SiNN})(H)Cl$  (1) and  $Ir(Lut^{SiNN})(H)(DMAP)Cl$  (2 and 2')

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, {}^{b}wR2 = \{\Sigma [w (F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w (F_{o}^{2})^{2}]\}^{1/2}$ 



**Fig. S4** Crystal structure of **1** (two crystallographically independent molecules **1**-A and **1**-B). Selected interatomic distances (Å) and angles (deg) for molecule **1**-A: Ir1–Si1 2.2991(12), Ir1–Cl1 2.3352(11), Ir1–N1 2.005(4), Ir1–N2 2.225(4), Ir1–H1 1.41(7), Si1…H1 2.14(7); Si1–Ir1–Cl1 99.89(4), Si1–Ir1–N1 84.14(11), Si1–Ir1–N2 143.22(10), Cl1–Ir1–N1 175.09(11), Cl1–Ir1–N2 95.08(10), N1–Ir1–N2 80.01(14), Si1–Ir1–H1 66(3), N2–Ir1–H1 146(3), Ir1–H1–Si1 78(3); molecule **1**-B: Ir2–Si2 2.3001(13), Ir2–Cl2 2.3303(11), Ir2–N3 1.998(4), Ir2–N4 2.259(4), Ir2–H37 1.41(4), Si2…H37 1.89(4); Si2–Ir2–Cl2 99.52(4), Si2–Ir2–N3 84.64(12), Si2–Ir2–N4 144.60(10), Cl2–Ir2–N3 175.54(12), Cl2–Ir2–N4 96.08(10), N3–Ir2–N4 79.54(15), Si2–Ir2–H37 55.0(18), N4–Ir2–H37 156.0(18), Ir2–H37–Si2 87(2).



**Fig. S5** Crystal structure of **2.** Selected bond distances (Å) and angles (deg) for **2**: Ir–Si 2.2938(11), Ir–Cl 2.3724(11), Ir–N1 2.019(4), Ir–N2 2.386(4), Ir–N3 2.212(4), Ir–H1 1.66(5); Si–Ir–Cl 96.89(4), Si–Ir–N1 85.87(10), Si–Ir–N2 161.45(10), Si–Ir–N3 103.81(10), Cl–Ir–N1 176.82(10), N1–Ir–N2 80.21(14), Si–Ir–H1 79.8(16), N3–Ir–H1 175.5(16).



**Fig. S6** Crystal structure of **2**<sup>'</sup>. Selected bond distances (Å) and angles (deg) for **2**<sup>'</sup>: Ir–Si 2.3030(15), Ir–Cl 2.5363(13), Ir–N1 2.025(4), Ir–N2 2.357(4), Ir–N3 2.095(4), Ir–H1 1.39(5); Si–Ir–Cl 101.39(13), Si–Ir–N1 85.16(12), Si–Ir–N2 160.54(12), Si–Ir–N3 100.32(12), Cl–Ir–N1 89.23(12), Cl–Ir–N2 85.47(11), N1–Ir–N2 77.69(16), N1–Ir–N3 174.23(16), N2–Ir–N3 96.61(16), Cl–Ir–H1 176(2).

#### 3. DFT calculation of an optimized structure of complex 1

To estimate a probable location of the hydrido hydrogens in Ir(Lut<sup>SiNN</sup>)(H)Cl (1), the geometry of **1** was optimized by the DFT method using the B3PW91 hybrid functional.<sup>S10,S11</sup> The LanL2DZ basis set was employed for the iridium atom in which the core electrons were replaced with the effective core potentials (ECPs).<sup>S12</sup> The 6-31G(d,p) basis sets<sup>S13</sup> were employed for the other atoms (H, C, N, Si and Cl). Frequency calculation was performed to confirm that the optimized structure had no imaginary frequencies. All calculations were carried out using the Gaussian09 program package.<sup>S14</sup> The optimized structure of **1** is depicted in Fig. S7. Cartesian coordinates of all atoms in **1** and selected distances and angles of the optimized structure with those for the crystal structure are listed in Tables S3 and S4, respectively.



**Fig. S7** Optimized structure of Ir(Lut<sup>SiNN</sup>)(H)Cl (1). Hydrogen atoms except the hydrido hydrogen were omitted for clarity.

Atomic Type	Coordinates (Å)		
	<i>x</i>	<i>y</i>	2
Ir	0.006479	0.036308	-0.014561
Н	0.099515	-0.087417	1.527105
Cl	2.368386	0.076764	-0.134440
Si	-0.328610	2.002924	1.187075
Ν	-2.000297	-0.047000	-0.098750
Ν	-0.296031	-1.025216	-2.050861
С	-0.341740	3.569393	0.016432
С	-1.391678	3.340049	-1.082924
Н	-2.402106	3.212840	-0.678007
Н	-1.155698	2.454600	-1.680907
Н	-1.419674	4.203839	-1.762864
С	1.023799	3.773972	-0.658847
Н	0.958126	4.577535	-1.407069
Н	1.367402	2.865744	-1.162176
Н	1.801225	4.056841	0.055465
С	-0.725471	4.853783	0.769630
Н	-0.819554	5.688060	0.058989
Н	0.029503	5.145257	1.505704
Н	-1.686991	4.763582	1.288930
С	0.626842	2.309568	2.864056
С	-0.209451	3.187440	3.815516
Н	0.345355	3.353226	4.750017
Н	-1.158465	2.712143	4.088805
Н	-0.438600	4.171893	3.398664
С	1.988849	2.982073	2.623468
Н	1.886354	4.002691	2.241090
Н	2.601889	2.411047	1.918718
Н	2.544045	3.050082	3.570157
С	0.890865	0.972242	3.577138
Н	1.568523	0.334617	3.001431
Н	-0.030066	0.405504	3.765238

**Table S3** Cartesian coordinates for the optimized structure of  $Ir(Lut^{SiNN})(H)Cl$  (1) (TotalEnergy = -1709.42014175 a.u.)

Н	1.355999	1.160406	4.555487
С	-2.160951	1.597663	1.690996
Н	-2.054216	1.000646	2.609586
Н	-2.798678	2.450079	1.945996
С	-2.816503	0.743749	0.660662
С	-4.195957	0.727440	0.444801
Н	-4.823253	1.363037	1.061007
С	-4.753050	-0.080567	-0.537518
Н	-5.825091	-0.086516	-0.708306
С	-3.907155	-0.883368	-1.299555
Н	-4.294033	-1.530843	-2.079724
С	-2.544227	-0.852830	-1.051050
С	-1.561369	-1.738749	-1.761693
Н	-1.326427	-2.573915	-1.095092
Н	-2.004580	-2.154995	-2.679436
С	0.798861	-1.965399	-2.410583
Н	1.701253	-1.356839	-2.488564
Н	0.583356	-2.396090	-3.402715
С	1.058706	-3.069299	-1.397080
Н	1.160676	-2.653891	-0.389699
Н	2.007080	-3.553420	-1.647656
Н	0.289767	-3.847973	-1.394833
С	-0.535127	-0.071709	-3.166823
Н	-1.354403	0.582072	-2.852453
Н	-0.897173	-0.642362	-4.039566
С	0.674795	0.762218	-3.555481
Н	1.151875	1.196114	-2.672874
Η	0.353008	1.575333	-4.212776
Н	1.424946	0.179749	-4.096096

	Optimized structure (DFT)	Crystal structure
Ir–Si	2.329	2.2991(12), 2.3001(13)
Ir–Cl	2.365	2.3352(11), 2.3303(11)
Ir–N1	2.010	2.005(4), 1.998(4)
Ir-N2	2.316	2.225(4), 2.259(4)
Ir–H1	1.549	1.41(7), 1.41(4)
Si–H1	2.161	2.14(7), 1.89(4)
Si–Ir–Cl	98.94	99.89(4), 99.52(4)
Si–Ir–N1	85.01	84.14(11), 84.64(12)
Si-Ir-N2	145.27	143.22(10), 144.60(10)
Cl-Ir-N1	174.51	175.09(11), 175.54(12)
Cl-Ir-N2	95.38	95.08(10), 96.08(10)
N1–Ir–N2	79.27	80.01(14), 79.54(15)
Si–Ir–H1	64.07	66(3), 55.0(18)
N2–Ir–H1	147.78	146(3), 156.0(18)
Ir-H1-Si	75.78	78(3), 87(2)

**Table S4** Selected bond distances (Å) and angles (°) for the optimized structure of $Ir(Lut^{SiNN})(H)Cl(1)$  and for its crystal structure (two independent molecules)

#### 4. References

- S1 J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, J. Am. Chem. Soc., 2005, 127, 10840.
- S2 F. P. Price, J. Am. Chem. Soc., 1947, 69, 2600.
- S3 J. L. Herde, J. C. Lambert and C. V. Senoff, Inorg. Synth., 1974, 15, 18.
- S4 K. Yan, G. Schoendorff, B. M. Upton, A. Ellern, T. L. Windus and A. D. Sadow, Organometallics, 2013, 32, 1300; Y. Nishibayashi, I. Takei and M. Hidai, Angew. Chem., Int. Ed., 1999, 38, 3047.
- S. Schwieger, R. Herzog, C. Wagner and D. Steinborn, J. Organomet. Chem., 2009, 694, 3548.
- S6 V. Leich, T. P. Spaniol, L. Maron and J. Okuda, *Chem. Commun.*, 2014, **50**, 2311.
- S7 P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould and J. M.
   M. Smits, *The DIRDIF2008 program system*, Crystallography Laboratory, University of Nijmegen, The Netherlands, 2008.
- S8 G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3; G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2008, 64, 112.
- S9 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. Crystallogr. Soc. Jpn. 2009, 51, 218.
- S10 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- S11 J. P. Perdew, in *Electronic Structure of Solids '91*, ed. P. Ziesche and H. Eschrig, Akademie Verlag, Berlin, 1991, p 11; J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533.
- S12 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 299.
- S13 W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972, 56, 2257; P. C. Hariharan and J. A. Pople, Theor. Chim. Acta, 1973, 28, 213; M. M. Francl, W. J.

Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, J. Chem. Phys., 1982, 77, 3654.

S14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian Inc., Wallingford, CT, 2013.

# 5. NMR spectra of a ligand precursor HLut<sup>SiNN</sup> and complexes 1, 2 and 2<sup>′</sup>



**Fig. S8** <sup>1</sup>H NMR spectrum of 2-diethylaminomethyl-6-di-*tert*-butylsilylmethylpyridine (HLut<sup>SiNN</sup>) (400 MHz, r.t.,  $C_6D_6$ ).



Fig. S9  ${}^{13}C{}^{1}H$  NMR spectrum of HLut<sup>SiNN</sup> (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_37_Figure_0.jpeg)

Fig. S10 <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of HLut<sup>SiNN</sup> (79.5 MHz, DEPT, r.t.,  $C_6D_6$ ).

![](_page_37_Figure_2.jpeg)

**Fig. S11** <sup>1</sup>H NMR spectrum of Ir(Lut<sup>SiNN</sup>)(H)Cl (1) (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_38_Figure_0.jpeg)

**Fig. S12**  ${}^{13}C{}^{1}H$  NMR spectrum of **1** (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_39_Figure_0.jpeg)

**Fig. S13**<sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **1** (79.5 MHz, IG, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_39_Figure_2.jpeg)

**Fig. S14** <sup>1</sup>H NMR spectrum of  $Ir(Lut^{SiNN})(H)(DMAP)Cl \cdot 0.5$ toluene (2 · 0.5 toluene) (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_40_Figure_0.jpeg)

Fig. S15  ${}^{13}C{}^{1}H$  NMR spectrum of 2.0.5toluene (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_41_Figure_0.jpeg)

Fig. S16 <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of 2•0.5toluene (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

![](_page_42_Figure_0.jpeg)

**Fig. S17** <sup>1</sup>H NMR spectrum of Ir(Lut<sup>SiNN</sup>)(H)(DMAP)Cl (2') (400 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_43_Figure_0.jpeg)

**Fig. S18**  ${}^{13}C{}^{1}H$  NMR spectrum of **2**' (101 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_44_Figure_0.jpeg)

**Fig. S19**<sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **2** $(79.5 \text{ MHz}, \text{ IG}, \text{ r.t.}, C_6D_6)$ .

### 6. NMR spectra of reaction mixtures of catalytic deuteration of trialkylsilanes

![](_page_45_Figure_1.jpeg)

**Fig. S20** <sup>1</sup>H NMR spectrum of a reaction mixture of HSiMe<sub>2</sub>Et with  $C_6D_6$  catalysed by **2** (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_45_Figure_3.jpeg)

**Fig. S21** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2Et$  with  $C_6D_6$  catalysed by **2** (61.4 MHz, r.t.,  $C_6D_6$ ).

![](_page_46_Figure_0.jpeg)

**Fig. S22** <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of HSiMe<sub>2</sub>Et with C<sub>6</sub>D<sub>6</sub> catalysed by **2** (79.5 MHz, DEPT, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_47_Figure_0.jpeg)

**Fig. S23** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2(i-Pr)$  with  $C_6D_6$  catalysed by **2** (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_47_Figure_2.jpeg)

**Fig. S24** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2(i-Pr)$  with  $C_6D_6$  catalysed by **2** (61.4 MHz, r.t.,  $C_6D_6$ ).

![](_page_48_Figure_0.jpeg)

**Fig. S25** <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of  $HSiMe_2(i-Pr)$  with  $C_6D_6$  catalysed by **2** (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

![](_page_48_Figure_2.jpeg)

**Fig. S26** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2(t-Bu)$  with  $C_6D_6$  catalysed by **2** (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_49_Figure_0.jpeg)

**Fig. S27** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2(t-Bu)$  with C<sub>6</sub>D<sub>6</sub> catalysed by **1** (61.4 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_49_Figure_2.jpeg)

**Fig. S28** <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of  $HSiMe_2(t-Bu)$  with  $C_6D_6$  catalysed by **1** (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

![](_page_50_Figure_0.jpeg)

**Fig. S29** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSiEt_3$  with  $C_6D_6$  catalysed by 2 (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_50_Figure_2.jpeg)

**Fig. S30** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiEt_3$  with  $C_6D_6$  catalysed by 2 (61.4 MHz, r.t.,  $C_6D_6$ ).

![](_page_51_Figure_0.jpeg)

**Fig. S31**<sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of HSiEt<sub>3</sub> with  $C_6D_6$  catalysed by 1 (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

![](_page_52_Figure_0.jpeg)

**Fig. S32** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSi(n-Pr)_3$  with  $C_6D_6$  catalysed by **2** (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_52_Figure_2.jpeg)

**Fig. S33** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSi(n-Pr)_3$  with C<sub>6</sub>D<sub>6</sub> catalysed by **2** (61.4 MHz, r.t., C<sub>6</sub>D<sub>6</sub>).

![](_page_53_Figure_0.jpeg)

**Fig. S34** <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of  $HSi(n-Pr)_3$  with  $C_6D_6$  catalysed by **2** (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

# 7. NMR spectra of DSi(*n*-Pr)<sub>3</sub>

![](_page_54_Figure_1.jpeg)

**Fig. S35** <sup>1</sup>H NMR spectrum of DSi(*n*-Pr)<sub>3</sub> (98%D) (400 MHz, r.t., CDCl<sub>3</sub>).

![](_page_55_Figure_0.jpeg)

**Fig. S36** <sup>2</sup>H NMR spectrum of DSi(*n*-Pr)<sub>3</sub> (98%D) (61.4 MHz, r.t., C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>H<sub>6</sub>).

![](_page_56_Figure_0.jpeg)

**Fig. S37** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of DSi(*n*-Pr)<sub>3</sub> (98%D) (101 MHz, r.t., CDCl<sub>3</sub>).

![](_page_57_Figure_0.jpeg)

**Fig. S38**<sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of DSi(*n*-Pr)<sub>3</sub> (98%D) (79.5 MHz, IG, r.t., CDCl<sub>3</sub>).

8. NMR spectra of reaction mixtures of HSiMe(OSiMe<sub>3</sub>)<sub>2</sub>, HSiMe<sub>2</sub>Ph and H<sub>2</sub>SiEt<sub>2</sub> with

C<sub>6</sub>D<sub>6</sub> in the presence of complex 1 or 2

![](_page_58_Figure_2.jpeg)

**Fig. S39** <sup>1</sup>H NMR spectrum of a mixture of  $HSiMe(OSiMe_3)_2$  and  $C_6D_6$  in the presence of **1** (1 mol%) (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_58_Figure_4.jpeg)

**Fig. S40** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSiMe(OSiMe_3)_2$  with  $C_6D_6$  in the presence of **2** (1 mol%) (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_59_Figure_0.jpeg)

**Fig. S41** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiMe(OSiMe_3)_2$  with  $C_6D_6$  in the presence of **2** (1 mol%) (61.4 MHz, r.t.,  $C_6D_6$ ).

![](_page_60_Figure_0.jpeg)

**Fig. S42** <sup>1</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2Ph$  with  $C_6D_6$  in the presence of **1** (1 mol%) (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_61_Figure_0.jpeg)

**Fig. S43** <sup>2</sup>H NMR spectrum of a reaction mixture of  $HSiMe_2Ph$  with  $C_6D_6$  in the presence of **1** (1 mol%) (61.4 MHz, r.t.,  $C_6D_6$ ).

![](_page_61_Figure_2.jpeg)

**Fig. S44** <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of a reaction mixture of HSiMe<sub>2</sub>Ph with  $C_6D_6$  in the presence of **1** (1 mol%) (79.5 MHz, IG, r.t.,  $C_6D_6$ ).

![](_page_62_Figure_0.jpeg)

**Fig. S45** <sup>1</sup>H NMR spectrum of a mixture of  $H_2SiEt_2$  and  $C_6D_6$  in the presence of **1** (1 mol%) (400 MHz, r.t.,  $C_6D_6$ ).

![](_page_62_Figure_2.jpeg)

**Fig. S46** <sup>1</sup>H NMR spectrum of a mixture of  $H_2SiEt_2$  and  $C_6D_6$  in the presence of **2** (1 mol%) (400 MHz, r.t.,  $C_6D_6$ ).