Supporting information

Addition of (η^5-C_5Me_5)IrH_4 to a Zwitterionic Silylene: Stepwise Formation of Iridium(V)-Silyl and Iridium(III)-Silylene Complexes

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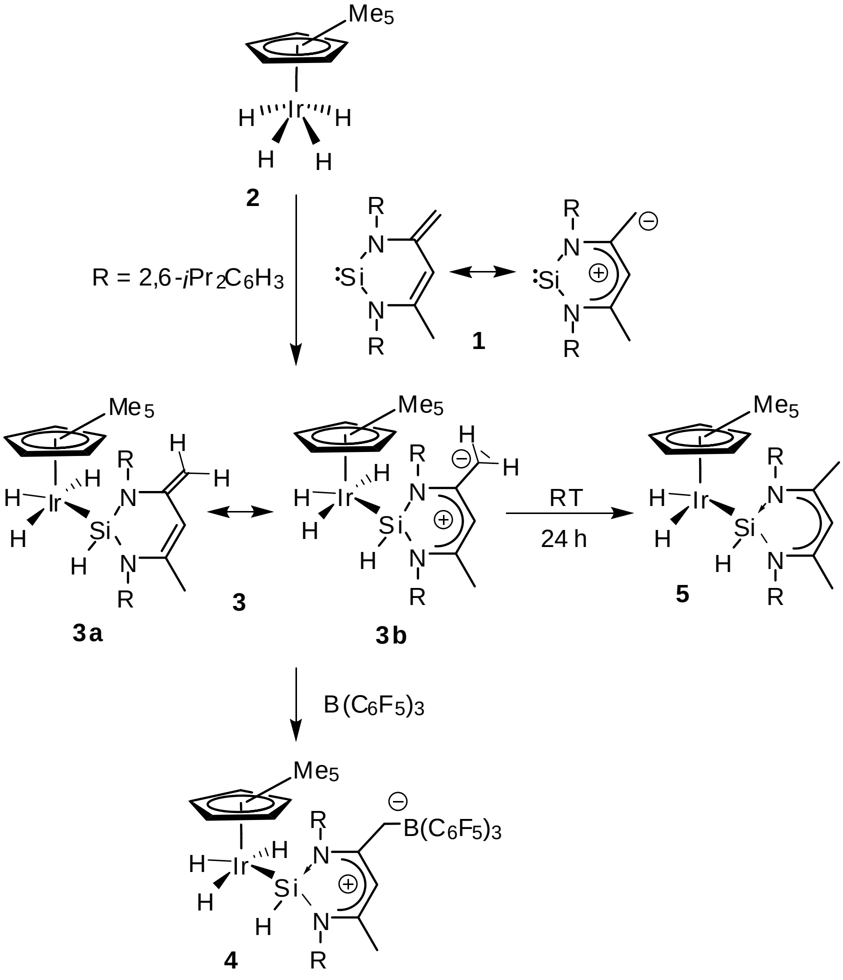
Experimental Details

The synthetic work was carried out on Schlenk line or an argon-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and destilled under argon before use. The Silyene **1**[1] and Cp*IrH$_4$[2] **2** were prepared according to the literature.

The NMR spectra were recorded at 298 K on a Bruker DPX 300 or Bruker AV 400 spectrometer. The ^{1}H-NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15 or [D$_7$]Toluene at δ 2.15. The ^{19}F-NMR spectra were referenced externally to C_6F_6 at δ −162.9. The ^{11}B-NMR spectrum was referenced to $BF_3 \cdot OEt_2$ at δ 0.0. The ^{13}C{^{1}H}-NMR spectra were referenced to Si(Me$_3$)$_4$ at δ 0.0. Infrared spectra were recorded on a Bruker Vector 22 spectrometer which was equipped with an ATR unit (ZnSe or diamond).



Synthesis of 3: The Silylene **1** (34 mg, 0.077 mmol) was added to a solution of Cp^*IrH_4 **2** (25 mg, 0.077 mmol) in 0.5 ml toluene. The yellow reaction mixture was then stored at -30 °C to obtain **3** as yellow crystals. Yield 55 mg (93%).

Analytical data for **3**: ^{1}H NMR (400 MHz, $[\text{D}_8]$toluene): δ 7.20-6.97 (m, 7 H, $2,6\text{-}i\text{Pr}_2\text{C}_6H_3$ and SiH), 5.37 (s, 1 H, ring-CH), 3.84 (s, 1 H, NCCH_2), 3.58 (sept, J_{HH} = 6.8 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 3.44 (sept, J_{HH} = 6.8 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 3.22 (s, 1 H, NCCH_2), 1.99 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 1.34 (s, 3 H, NCCH_3), 1.31 (d, J_{HH} = 7.3 Hz, 6 H, $\text{CH}(\text{C}H_3)_2$), 1.30 (d, J_{HH} = 7.0 Hz, 6 H, $\text{CH}(\text{C}H_3)_2$), 1.26 (d, J_{HH} = 7.0 Hz, 6 H $\text{CH}(\text{C}H_3)_2$), 1.16 (d, J_{HH} = 6.9 Hz, 6 H, $\text{CH}(\text{C}H_3)_2$), −15.58 (s, 3 H, IrH; at 198 K: δ −15.11 (s, br), −15.96 (s, br), −17.40 (s, br); ^{1}H,^{29}Si HMBC NMR (400/79.49 MHz, $[\text{D}_8]$toluene): δ(^{29}Si) −7.7 (J_{HSi} = 215 Hz); ^{13}C NMR (75.47 MHz, C_6D_6): δ 150.87, 150.44 (NC), 149.73, 149.41, 149.16, 143.78, 143.28, 142.60 (aromatic C), 127.76, 127.49, 125.90, 124.82, 124.57, 124.18 (aromatic CH), 104.44 (ring-CH), 98.30 ($C_5(\text{CH}_3)_5$), 85.26 ($\text{NC}C\text{H}_2$), 30.15, 29.85, 29.14, 28.97 ($C\text{H}(\text{CH}_3)_2$), 27.74, 26.68, 27.17, 26.30, 25.77, 24.93, 24.54, 24.51, 24.08 ($\text{CH}(C\text{H}_3)_2$ and $\text{NC}C\text{H}_3$), 10.45 ($\text{C}_5(C\text{H}_3)_5$). IR(ATR, cm^{-1}): 2173, 2016 (IrH, SiH). Elemental analysis (%) cald for $\text{C}_{39}\text{H}_{59}\text{N}_2\text{IrSi}$: C 60.35; H 7.66; N 3.61, found: C 60.21, H 7.41; N 3.26.

Synthesis of 4: $\text{B}(\text{C}_6\text{F}_5)_3$ (25 mg, 0.049 mmol) was added to a yellow solution of **3** (38 mg, 0.049 mmol). The mixture was stirred at room temperature and turned orange within 2 h. After 4 h the volatiles were removed to give an orange oil. Yield: 72 % (45 mg).

Analytical data for **4**:

^{1}H NMR (400 MHz, $[\text{D}_8]$toluene): δ 7.23-6.94 (m, 6 H, $2,6\text{-}i\text{Pr}_2\text{C}_6H_3$), 6.53 and 6.52 (both s, 2 H, SiH, ring-CH), 3.26 (sept, J_{HH} = 6.8 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 3.12 (d, br, J_{HH} = 20 Hz, 1 H, CH_2), 2.98 (sept, J_{HH} = 6.8 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 2.84 (sept, J_{HH} = 6.8 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 2.57 (sept, J_{HH} = 6.7 Hz, 1 H, $\text{C}H(\text{CH}_3)_2$), 2.41 (d, br, J_{HH} = 20 Hz, 1 H, CH_2), 1.72 (d, J_{HH} = 6.7 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 1.62 (s, 6 H, NCCH_3), 1.45 (s, 15 H, $\text{C}_5(\text{C}H_3)_5$), 1.42 (d, J_{HH} = 6.8 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 1.38 (d, J_{HH} = 6.9 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 1.25 (d, J_{HH} = 6.8 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 1.22 (d, J_{HH} = 6.9 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 1.04 (d, J_{HH} = 6.6 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 0.96 (d, J_{HH} = 6.9 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), 0.92 (d, J_{HH} = 6.8 Hz, 3 H, $\text{CH}(\text{C}H_3)_2$), −15.65 (s, 3 H, IrH); ^{11}B NMR (128.37 MHz, $[\text{D}_8]$toluene): δ −15.5; ^{1}H,^{29}Si-NMR (400/79.49 MHz, $[\text{D}_8]$toluene): δ(^{29}Si) 12.7 (J_{HSi} = 224 Hz); ^{13}C-NMR (75.47 MHz, C_6D_6): δ 171.39, 186.73(NC), 147.53, 147.06, 144.70, 144.58, 139.93, 138.97 (aromatic C), 129.76, 129.68, 126.56, 126.01, 125.64, 125.44, (aromatic CH), 105.08 (ring-CH), 101.18 (CH_2B), 100.62($C_5(\text{CH}_3)_5$), 30.56, 30.48, 29.29, 29.19, ($C\text{H}(\text{CH}_3)_2$), 27.82, 25.92, 25.62, 24.78, 24.72, 24.57, 24.25, 24.20, 23.37, (CH(*C*H_3)$_2$) und NC*C*H_3), 10.24 (C_5(*C*H_3)$_5$); IR(ATR, cm^{-1}): 2187, 2071 (IrH, SiH). Elemental analysis (%) cald for $C_{57}H_{59}BF_{15}N_2IrSi$: C 53.15; H 4.62; N 2.17, found: C 52.80, H 4.38; N 1.83.

Synthesis of 5: A solution of **3** (53 mg, 0.068 mmol) in 0.5 ml toluene was stirred at room temperature for 24 h. At 243 K orange crystals formed which consisted of **5**. Yield: 95 % (50 mg).

Analytical data for **5**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.22-7.10 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 6.45 (s, 1 H, SiH), 4.95 (s, 1 H, ring-CH), 3.57 (sept, J_{HH} = 6.9 Hz, 2 H, C*H*(CH_3)$_2$), 3.01 (sept, J_{HH} = 6.9 Hz, 2 H, C*H*(CH_3)$_2$), 1.93 (s, 15 H, $C_5(CH_3)_5$), 1.62 (d, J_{HH} = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.49 (d, J_{HH} = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.48 (s, 6 H, NCCH_3), 1.17 (d, J_{HH} = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.07 (d, J_{HH} = 7.2 Hz, 6 H, CH(C*H*$_3$)$_2$), −19.24 (s, 2 H, IrH); ^{1}H,^{29}Si HMBC NMR (400/79.49 MHz, [D$_8$]toluene): δ(^{29}Si) 13.6 (J_{HSi} = 170 Hz); ^{13}C-NMR (75.47 MHz, C_6D_6): δ 170.41(NC), 145.96, 144.69, 142.75 (aromatic C), 128.25, 124.80, 124.75 (aromatic CH), 100.8 (ring-CH), 91.67 (*C*$_5$(CH_3)$_5$), 29.41, 30.61 (*C*H(CH_3)$_2$), 25.31, 26.26, 25.13, 24.64, 24.34 (CH(*C*H_3)$_2$) and NC*C*H_3), 12.35 (C_5(*C*H_3)$_5$); IR(ATR, cm^{-1}): 2164, 1968 (SiH, IrH); Elemental analysis (%) cald for $C_{39}H_{59}N_2IrSi$: C 60.35; H 7.66; N 3.61 found: C 60.33, H 7.60; N 3.30.

Crystal Structure Determination of Complexes 3 and 5

Colourless crystals of **3** and red crystals of **5** were obtained from a solution in toluene at 243 K. The diffraction data for **3** and **5** were collected on a STOE IPDS 2T diffractometer at 100 K. Crystallographic data and some experimental details are summarized in Tables 1 to 4. The structures were solved by direct methods and refined with the full matrix least square methods on F^2 (SHELXL97).[3] The disordered CH_3 group (C14) in **5** was refined on two positions (57:43), the corresponding methyl groups were restrained with “sadi” instructions and were refined anisotropically. The hydrogen atoms coordinated at the Si and Ir centres in **3** could not be localized in the difference Fourier map. The Ir bound hydrogen atoms in **5** could not be localised in the difference Fourier map; the position of H(1) at Si could be refined. All other hydrogens atoms were placed at calculated positions and refined using a riding model.

Table 1. Crystal data and structure refinement for **3**

Identification code	complex **3**
Empirical formula	C39 H59 Ir N2 Si
Formula weight	776.17
Temperature	100(2) K
Wavelenght	0.71073 Å
Crystal system	*orthorhombic*
Space group	*P na*2_1
Unit cell dimensions	a = 18.1058(4)Å b = 11.9735(3) Å c = 11.9735(3) Å
Volume	3636.87(16)A^3
Z	4
Density (calculated)	1.418 Mg/m^3
Absorption coefficient	3.732 mm^{-1}
F(000)	1592
Crystal size	0.20 x 0.08 x 0.08 mm
Theta range for data collection	2.37 to 30.55°
R(int)	0.0583
Reflections collected	42435
Reflections unique	11005
Completeness to theta = 30.55	98.9 %
Absorption correction	Numerical
Max. and min. transmission	0.7545 and 0.5223
Refinement method	Full-matrix least-squares on F^2
Data/ restraints / parameters	11005 / 37 / 402
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0586
R indices (all data)	R1 = 0.0508, wR2 = 0.0609
Largest diff. peak and hole	2.150 and -2.310 e.A^{-3}

Table 2: Selected bond lengths (Å) and angles (°) in **3** with estimated standard deviations in parentheses.

Ir(1)-Si(1)	2.3293(11)	C(32)-Ir(1)	2.238(4)
N(1)-Si(1)	1.785(4)	C(33)-Ir(1)	2.276(5)
N(2)-Si(1)	1.771(4)	C(34)-Ir(1)	2.282(4)
C(1)-N(1)	1.406(5)	C(30)-C(31)	1.429(6)
C(6)-N(1)	1.444(5)	C(31)-C(32)	1.430(7)
C(3)-N(2)	1.399(6)	C(32)-C(33)	1.426(7)
C(18)-N(2)	1.427(5)	C(33)-C(34)	1.441(8)
C(1)-C(2)	1.436(6)	C(30)-C(34)	1.422(7)
C(1)-C(4)	1.373(6)	C(30)-C(35)	1.509(6)
C(2)-C(3)	1.364(7)	C(31)-C(36)	1.505(6)
C(3)-C(5)	1.486(7)	C(32)-C(37)	1.507(6)
C(30)-Ir(1)	2.256(4)	C(33)-C(38)	1.507(7)
C(31)-Ir(1)	2.243(4)	C(34)-C(39)	1.497(6)
N(1)-Si(1)-Ir(1)	119.75(13)	C(33)-Ir(1)-Si(1)	165.97(14)
N(2)-Si(1)-Ir(1)	115.27(12)	C(34)-Ir(1)-Si(1)	129.65(15)
N(2)-Si(1)-N(1)	100.27(18)	C(30)-C(31)-C(32)	107.4(4)
C(1)-N(1)-Si(1)	120.4(3)	C(33)-C(32)-C(31)	108.6(4)
C(3)-N(2)-Si(1)	118.3(3)	C(32)-C(33)-C(34)	107.5(4)
N(1)-C(1)-C(2)	118.6(4)	C(30)-C(34)-C(33)	107.8(4)
C(4)-C(1)-N(1)	122.4(4)	C(34)-C(30)-C(31)	108.7(4)
C(3)-C(2)-C(1)	127.9(4)	C(30)-C(31)-Ir(1)	72.0(2)
C(2)-C(3)-N(2)	121.6(4)	C(31)-C(32)-Ir(1)	71.6(3)
N(2)-C(3)-C(5)	118.7(4)	C(32)-C(33)-Ir(1)	70.1(3)
C(30)-Ir(1)-Si(1)	105.24(11)	C(33)-C(34)-Ir(1)	71.3(3)
C(31)-Ir(1)-Si(1)	110.81(11)	C(34)-C(30)-Ir(1)	72.7(3)
C(32)-Ir(1)-Si(1)	143.00(14)		

Table 3. Crystal data and structure refinement for **5**

Identification code	complex **5**	
Empirical formula	C39 H59 Ir N2 Si	
Formula weight	776.17	
Temperature	100(2) K	
Wavelenght	0.71073 Å	
Crystal system	*monoclinic*	
Space group	*C* 2/*c*	
Unit cell dimensions	a = 30.6330(10) Å	
	b = 16.3992(4) Å	β = 118.185(3)°
	c = 16.7702(6) Å	
Volume	7425.7(4) A^3	
Z	8	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	3.656 mm^{-1}	
F(000)	3184	
Crystal size	0.30 x 0.20 x 0.20 mm	
Theta range for data collection	2.37 to 29.20 °	
R(int)	0.0509	
Reflections collected	34592	
Reflections unique	10001	
Completeness to theta = 29.20	99.3 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5284 and 0.4068	
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints / parameters	10001 / 7 / 417	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0795	
R indices (all data)	R1 = 0.0470, wR2 = 0.0825	
Largest diff. peak and hole	5.648 and -4.648 $e.A^{-3}$	

Table 4: Selected bond lengths (Å) and angles (°) in **5** with estimated standard deviations in parentheses.

Ir(1)-Si(1)	2.2328(9)	C(32)-Ir(1)	2.267(4)
Si(1)-H(1)	1.45(5)	C(33)-Ir(1)	2.249(4)
N(1)-Si(1)	1.850(3)	C(34)-Ir(1)	2.233(4)
N(2)-Si(1)	1.855(3)	C(30)-C(31)	1.411(6)
C(1)-N(1)	1.336(4)	C(31)-C(32)	1.428(6)
C(6)-N(1)	1.450(4)	C(32)-C(33)	1.440(6)
C(3)-N(2)	1.337(5)	C(33)-C(34)	1.404(6)
C(18)-N(2)	1.451(5)	C(30)-C(34)	1.444(6)
C(1)-C(2)	1.403(5)	C(30)-C(35)	1.497(6)
C(1)-C(4)	1.495(5)	C(31)-C(36)	1.516(6)
C(2)-C(3)	1.393(5)	C(32)-C(37)	1.521(7)
C(3)-C(5)	1.504(5)	C(33)-C(38)	1.505(6)
C(30)-Ir(1)	2.235(4)	C(34)-C(39)	1.499(6)
C(31)-Ir(1)	2.245(4)		
Ir(1)-Si(1)-H(1)	123.7(19)	Si(1)-Ir(1)-C(31)	151.45(12)
N(1)-Si(1)-Ir(1)	116.93(10)	Si(1)-Ir(1)-C(32)	121.04(12)
N(2)-Si(1)-Ir(1)	120.01(10)	Si(1)-Ir(1)-C(33)	112.95(10)
N(1)-Si(1)-N(2)	94.46(13)	Si(1)-Ir(1)-C(34)	132.64(11)
N(1)-Si(1)-H(1)	101(2)	C(30)-C(31)-C(32)	108.7(4)
N(2)-Si(1)-H(1)	95.0(19)	C(31)-C(32)-C(33)	107.5(4)
C(1)-N(1)-Si(1)	121.3(2)	C(34)-C(33)-C(32)	107.8(4)
C(3)-N(2)-Si(1)	121.6(2)	C(33)-C(34)-C(30)	108.7(4)
N(1)-C(1)-C(2)	122.1(3)	C(31)-C(30)-C(34)	107.3(4)
N(1)-C(1)-C(4)	119.9(3)	C(30)-C(31)-Ir(1)	71.3(2)
C(3)-C(2)-C(1)	124.9(3)	C(31)-C(32)-Ir(1)	70.7(2)
N(2)-C(3)-C(2)	122.1(3)	C(32)-C(33)-Ir(1)	72.1(2)
N(2)-C(3)-C(5)	119.6(3)	C(33)-C(34)-Ir(1)	72.4(2)
Si(1)-Ir(1)-C(30)	169.27(12)	C(34)-C(30)-Ir(1)	71.1(2)

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