

Supplementary Material

N-Heterocyclic Silylene (NHSi) Rhodium and Iridium Complexes: Synthesis, Structure, Reactivity and Catalytic Ability

Miriam Stoelzel,^A Carsten Präsang,^{A,#} Burgert Blom,^A and Matthias Driess^{A,B}

^A Department of Chemistry: Metalorganics and Inorganic Materials

Technische Universität Berlin

Strasse des 17. Juni 135, Sekr. C2 D-10623 Berlin, Germany.

Fax: (+49) 30 314 29734

^B Corresponding author. E-mail: matthias.driess@tu-berlin.de

A. Additional Synthetic Information involving Li[HBET₃]

L(Cl)Si:→Rh(Cl)cod **10a** + 2 eq. Li[HBET₃]: [(L(H)Si:→Rh(H)cod] (**13b**)

A solution of Li[HBET₃] in THF (0.33 mL, 1.0 M, 0.33mmol, 2 eq.) was added to a solution of 120 mg L(Cl)Si:→Rh(Cl)cod **10a** (0.16 mmol) in 15 mL toluene at -40°C. The reaction mixture was warmed up to room temperature. (see: ¹H NMR of reaction mixture). All volatiles were removed *in vacuo* and the solid dissolved in *n*-hexane and cooling to -30°C afforded brown crystals.

¹H NMR of reaction mixture after warmed up to room temperature (200 MHz, C₆D₆, 25°C): δ= -6.94 (d, 1H, Rh-*H*), 1.11 – 1.18 (m, 12H, CH(CH₃)), 1.46 – 1.58 (m, 12H, CH(CH₃)), 1.58 (s, 6H, CH₃), 2.23 (br, 2H, cod-CH), 3.14 (sept, 2H, CH(CH₃)), 3.53 (sept, ³J(H,H) = 6.8 Hz, 2H, CH(CH₃)), 3.98 (br, 2H, cod-CH), 5.00 (s, 1H, γ-*H*; **13b**), 5.07 (s, 1H, γ-*H*; **13a**), 5.48 (br, 2H, cod-CH₂), 6.29 (d, 1H, Si-*H*), 7.02 – 7.20 (m, 6H, CH_{Ar}).

¹H NMR of reaction mixture after 12 h at room temperature inside nmr tube (200 MHz, C₆D₆, 25°C): 1.11, 1.15 (each d, 6H, CH(CH₃)), 1.44 (br, 4H, coe-CH₂), 1.48 (s, 6H, CH₃), 1.51, 1.53 (d, ³J(H,H) = 6.8 Hz, 6H, CH(CH₃)), 2.05 (br, 2H, coe-CH₂), 3.09, 3.53 (each sept, ³J(H,H) = 6.8 Hz, 2H, CH(CH₃)), 5.00 (s, 1H, γ-*H*; **13b**), 5.64 (m, 1H, coe-CH), 7.03 – 7.20 (m, 6H, CH_{Ar}).

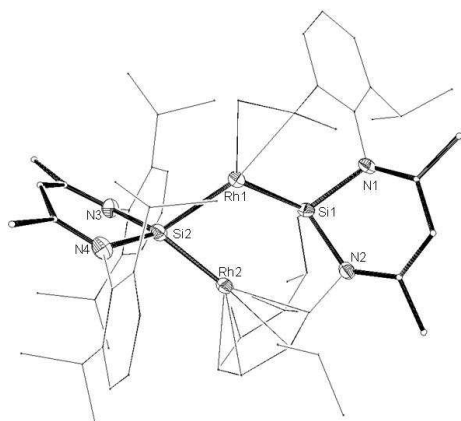


Figure S1. Molecular structure of **13b**.

brown needles

chemistry, Campus Dudweiler, Saarland University, Am Markt Zeile

triclinic, P-1

R(int) = 9.14 %

R1 = 7.62 %

wR₂ = 14.60 %

L(Cl)Si:→Rh(Cl)cod **10a** + 2 eq. Li[HBEt₃] (in CO atmosphere) (**13c**)

A solution of Li[HBEt₃] in THF (0.33 mL, 1.0 M, 0.33mmol, 2 eq.) was added to a solution of 120 mg L(Cl)Si:→Rh(Cl)cod **10a** (0.16 mmol) in 15 mL toluene at -70°C. The reaction mixture was stirred at -70°C while the reaction mixture was degassed. Subsequent the reaction vessel was charged with CO to normal pressure and was stirred at room temperature for 3 h. All volatiles were removed *in vacuo* and the solid washed with *n*-hexane and subsequent dissolved in toluene. Cooling to -30°C for several weeks afforded a few dark red crystals from the product mixture.

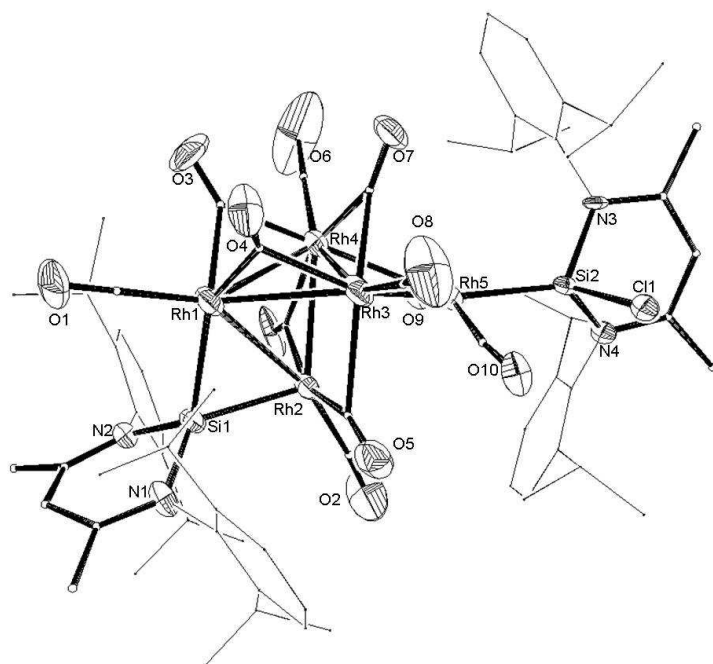


Figure S2. Molecular structure of **13c**.

dark red blocks

triclinic, P-1

R(int) = 11.2 %

R1 = 10.2 %

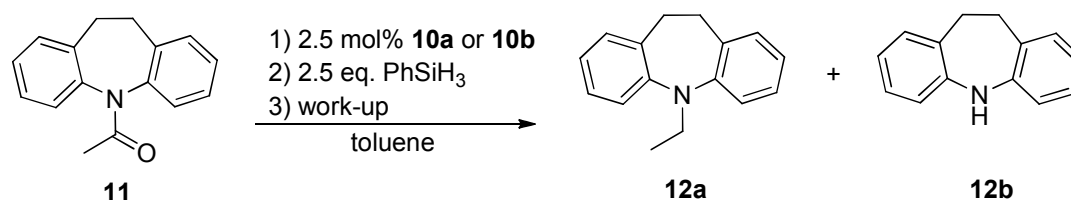
wR₂ = 29.1 %

B. Catalytic Details

General procedure for the reduction of amides:

A stock solution of phenylsilane in toluene (1.8 mL, 0.36 mmol, 0.2 mol/L, 2.5 eq.) was added to a stirring solution containing a stock solution of the pre-catalyst **10a** or **10b** (4.0 mmol/L, 0.0036 mmol, 2.5 mol%) and a

stock solution of the substrate **11** (0.9 mL, 0.16 mol/L, 0.14 mmol, 1 eq.) in toluene (1 mL). The solution was stirred at room temperature for 24 h, while the reaction progress was followed by GC-MS. After 1 h, 2 h, 4 h, 6 h and 24 h a small amount of the reaction mixture was passed through a short column with alumina to remove the catalyst from the sample, followed by elution with ethylacetate. The reaction was treated with aqueous HCl and the organic layer was dried by MgSO₄. Subsequently, the C-O and C-N cleavage products as well as the residual starting material were quantified by GC-MS.



Scheme S1. Reduction of the organic amide **11** with complexes **10a** and **10b** as precatalysts.

Catalytic activity of 10a:

Table S1. Catalytic activity of 2.5 mol% of pre-catalyst **10a** (retarded by Li[HBET₃]) and Rh(cod)Cl.

time [h]	% yield ^[a]		
	10a	10a + Li[HBET ₃]	Rh(cod)Cl
1	30,0	10,9	39,3
2	38,7	14,0	43,1
4	46,5	18,7	46,2
6	48,7	23,2	47,1
24	60,8	39,9	53,3

^[a]Indicated yields of **12a** according to GC-MS

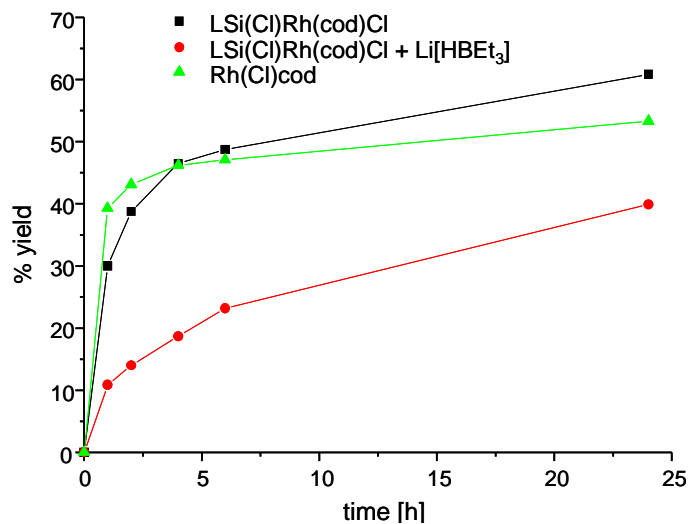


Figure S3. Catalytic activity of Rh(Cl)cod and **10a** (retarded by Li[HBEt₃]).

Catalytic activity of 10b:

Table S2. Catalytic activity of 2.5 mol% pre-catalyst **10b** and Ir(cod)Cl;

time [h]	% yield ^[a]			
	total	12a	12b	Ir(cod)Cl ^[b]
1	26,7	23,4	3,2	15,5
2	32,3	28,6	3,6	20,9
4	49,4	44,3	5,2	25,6
6	59,8	53,6	6,2	27,8

^[a]Indicated yields according to GC-MS; ^[b]exclusively **12b** as product

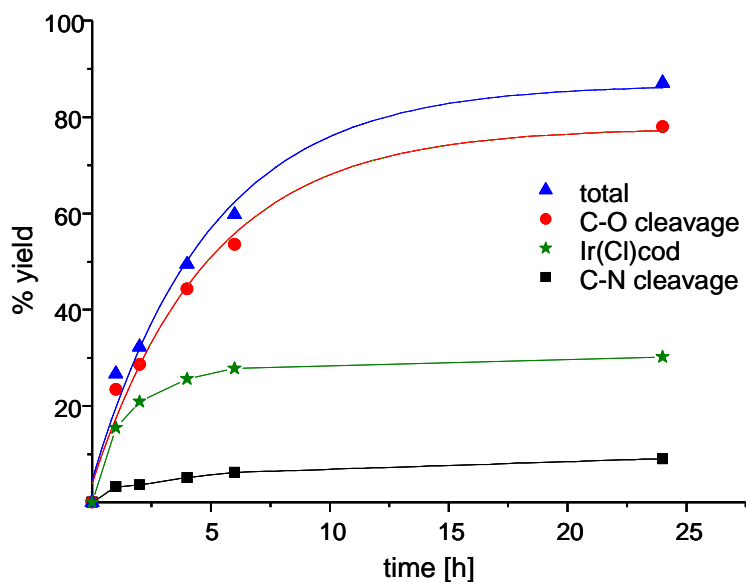


Figure S4. Catalytic activity of Ir(Cl)cod and [LSi(Cl)Ir(cod)Cl] **10b**.

C. Crystal data

Table S3. Crystal data and structure refinement for **10a**

Empirical formula	C ₃₇ H ₅₃ C ₁₂ N ₂ RhSi	
Formula weight	727.71	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.8788(3) Å	α = 90°.
	b = 21.0810(6) Å	β = 104.916(3)°.
	c = 18.0480(5) Å	γ = 90°.
Volume	3631.94(18) Å ³	
Z	4	
Density (calculated)	1.331 Mg/m ³	
Absorption coefficient	0.678 mm ⁻¹	
F(000)	1528	
Crystal size	0.17 x 0.11 x 0.08 mm ³	
Theta range for data collection	3.31 to 25.00°.	
Index ranges	-11 ≤ h ≤ 6, -24 ≤ k ≤ 13, -15 ≤ l ≤ 21	
Reflections collected	13243	
Independent reflections	6292 [R(int) = 0.0453]	
Completeness to theta = 25.00°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9478 and 0.8935	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6292 / 12 / 398	
Goodness-of-fit on F ²	0.852	
Final R indices [I > 2σ(I)]	R1 = 0.0404, wR2 = 0.0622	
R indices (all data)	R1 = 0.0777, wR2 = 0.0677	
Largest diff. peak and hole	0.495 and -0.515 e.Å ⁻³	

Table S4. Crystal data and structure refinement for **10b**

Empirical formula	$C_{37}H_{53}Cl_2IrN_2Si$	
Formula weight	817.00	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	P21/c	
Space group	Monoclinic	
Unit cell dimensions	$a = 9.9110(6)$ Å	$\alpha = 90^\circ$.
	$b = 21.0914(9)$ Å	$\beta = 105.099(8)^\circ$.
	$c = 18.0257(15)$ Å	$\gamma = 90^\circ$.
Volume	$3638.0(4)$ Å ³	
Z	4	
Density (calculated)	1.492 Mg/m ³	
Absorption coefficient	3.877 mm ⁻¹	
F(000)	1656	
Crystal size	0.11 x 0.11 x 0.03 mm ³	
Theta range for data collection	3.31 to 25.00°.	
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 24, -17 ≤ l ≤ 21	
Reflections collected	26737	
Independent reflections	6382 [R(int) = 0.0313]	
Completeness to theta = 25.00°	99.7 %	
Max. and min. transmission	0.8795 and 0.6795	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6382 / 0 / 398	
Goodness-of-fit on F ²	0.978	
Final R indices [I > 2σ(I)]	R1 = 0.0217, wR2 = 0.0512	
R indices (all data)	R1 = 0.0292, wR2 = 0.0525	
Largest diff. peak and hole	0.859 and -0.498 e.Å ⁻³	

Table S5. Crystal data and structure refinement for **15**.

Empirical formula	$C_{39}H_{59}C_{10}IrN_2Si$	
Formula weight	776.17	
Temperature	173(2) K	
Wavelength	71.073 pm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	$a = 1010.45(8)$ pm	$\alpha = 90^\circ$.

	b = 1831.84(11) pm	$\beta = 90^\circ$.
	c = 1941.09(7) pm	$\gamma = 90^\circ$.
Volume	3.5929(4) nm ³	
Z	4	
Density (calculated)	1.435 Mg/m ³	
Absorption coefficient	3.778 mm ⁻¹	
F(000)	1592	
Crystal size	0.33 x 0.07 x 0.04 mm ³	
Theta range for data collection	3.34 to 25.00°.	
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 21, -23 ≤ l ≤ 23	
Reflections collected	14451	
Independent reflections	6286 [R(int) = 0.0580]	
Completeness to theta = 25.00°	99.6 %	
Max. and min. transmission	0.8666 and 0.3722	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6286 / 0 / 400	
Goodness-of-fit on F ²	0.894	
Final R indices [I > 2σ(I)]	R1 = 0.0386, wR2 = 0.0605	
R indices (all data)	R1 = 0.0448, wR2 = 0.0629	
Absolute structure parameter	-0.020(8)	
Largest diff. peak and hole	1.549 and -1.007 e.Å ⁻³	

Table S6. Crystal data and structure refinement for **13b**.

Empirical formula	C ₆₁ H ₈₇ N ₄ Rh ₂ Si ₂	
Formula weight	1138.35	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8052(6) Å	$\alpha = 92.625(4)^\circ$.
	b = 12.8126(7) Å	$\beta = 95.787(4)^\circ$.
	c = 23.6516(11) Å	$\gamma = 104.310(5)^\circ$.
Volume	2856.8(3) Å ³	
Z	2	
Density (calculated)	1.323 Mg/m ³	
Absorption coefficient	0.660 mm ⁻¹	
F(000)	1198	
Crystal size	0.29 x 0.14 x 0.03 mm ³	

Theta range for data collection	3.25 to 25.00°.
Index ranges	-11<=h<=11, -14<=k<=15, -26<=l<=28
Reflections collected	22927
Independent reflections	10043 [R(int) = 0.0914]
Completeness to theta = 25.00°	99.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10043 / 0 / 641
Goodness-of-fit on F ²	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0762, wR2 = 0.1460
R indices (all data)	R1 = 0.1162, wR2 = 0.1699
Largest diff. peak and hole	1.203 and -0.909 e.Å ⁻³

Table S7. Crystal data and structure refinement for **13c**.

Empirical formula	C ₆₉ H ₈₂ ClN ₄ O ₁₁ Rh ₅ Si ₂	
Formula weight	1749.57	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7014(6) Å	α = 78.108(3)°.
	b = 16.6523(7) Å	β = 74.266(4)°.
	c = 21.7110(8) Å	γ = 76.377(4)°.
Volume	4245.7(3) Å ³	
Z	2	
Density (calculated)	1.369 Mg/m ³	
Absorption coefficient	1.061 mm ⁻¹	
F(000)	1764	
Crystal size	0.10 x 0.13 x 0.02 mm ³	
Theta range for data collection	3.31 to 25.00°.	
Index ranges	-15<=h<=15, -19<=k<=18, -25<=l<=25	
Reflections collected	32605	
Independent reflections	14893 [R(int) = 0.1121]	
Completeness to theta = 25.00°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14893 / 0 / 849	
Goodness-of-fit on F ²	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.1017, wR2 = 0.2906	

R indices (all data)

R1 = 0.1739, wR2 = 0.3505

Largest diff. peak and hole

3.325 and -1.191 e.Å⁻³

References

[1] M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628.

[2] J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.*, *15*, 18.

[3] G. M. Sheldrick, *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.