Supporting Information

Synthesis of 1,2-Diheteroatom-Substituted Alkenes Via Rhodium Catalyzed Intramolecular Hydrogen Transfer

M. Mar Diaz-Requejo, Darren DiSalvo and Maurice Brookhart.*

*Department of Chemistry, University of North Carolina at Chapel Hill, CB # 3290 Venable Hall,
Chapel Hill, North Carolina 27599-3290.*

I- Characterization of $\text{Cp}^*\text{Rh}[\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{O}]$ (**7**)

Tabla1. NMR Data for **7**: (400 MHz, 20 °C, CD_3COCD_3)

^1H	^{13}C
2.44 (dd, 12 Hz, 3 Hz, 2H)	96.9 (C_5Me_5)
1.69 (s, 15H)	50.7 (d, 14Hz, $\text{H}_2\text{C}=\text{}$)
1.62 (dd, 15 Hz, 3Hz, 2H)	41.3 (d, 14Hz, $=\text{HCSi}$)
0.95 (td, 15Hz, 3 Hz, 2H)	8.9 (C_5Me_5)
0.143 (s, 6H)	2.4 ($-\text{SiMe}$)
-0.59 (s, 6H)	1.8 ($-\text{SiMe}$)

- Elemental analysis for $\text{C}_{18}\text{H}_{33}\text{OSi}_2\text{Rh}$, **7**:

Calculated: %C= 50.92; %H= 7.84

Found: %C= 51.16; %H= 7.82

II- Spectroscopic data for 5a-f.

Tabla2. NMR Data for **5a-f**: (300 MHz, 20 °C, CDCl₃)

Substrate	¹ HNMR	¹³ CNMR
<p>5a</p>	6.05, 5.85, 5.75 (dd, 3H) 3.70 (t, 2H) 3.55 (m, 1H) 3.45 (t, 2H) 1.10 (d, 6H) 0.17 (s, 6H)	137.4 (H ₂ C=) 133.0 (=HCSi) 71.7 (O-CH) 69.2 (CH ₂ -O) 65.5 (O-CH ₂) 22.0 (2CH ₃) -2.1 (Si-Me ₂)
<p>5b</p>	6.05, 5.82, 5.75 (dd, 3H) 3.70 (t, 2H) 3.45 (t, 2H) 3.30 (s, 3H) 0.15 (s, 6H)	137.3 (H ₂ C=) 133.0 (=HCSi) 73.8 (O-CH ₂) 62.0 (CH ₂ -O) 58.7 (O-CH ₃) -2.3 (Si-Me ₂)
<p>5c</p>	7.2 ,6.7 (t, m, 2:3 Har) 5.85, 5.75, 5.60 (dd, 3H) 3.82 (t, 2H) 3.70 (t, 2H) 0.05 (s, 6H)	158.8, 129.4, 120.7, 114.5 (<i>Ph</i>) 137.2 (H ₂ C=) 133.4 (=HCSi) 68.9 (CH ₂ -O) 61.6 (O-CH ₂) -2.0 (Si-Me ₂)
<p>5d</p>	7.4, 7.35 (t, m, 2:3 Har) 6.28, 5.95, 5.90 (dd, 3H) 4.43 (s, 2H) 3.80 (t, 2H) 3.5 (t, 2H) 0.28 (s, 6H)	139.1, 128.5, 127.6, 127.4 (<i>Ph</i>) 138.0 (H ₂ C=) 133.1 (=HCSi) 73.2 (CH ₂ -O) 71.7 (O-CH ₂) 62.6 (CH ₂ -O) -1.9 (Si-Me ₂)

Substrate	¹ HNMR	¹³ CNMR
<p>5e</p>	6.01, 5.85, 5.75 (dd, 3H) 3.65 (t, 2H) 2.40 (t, 2H) 2.20 (s, 6H) 0.15 (s, 6H)	137.2 (H ₂ C=) 133.1 (=HCSi) 61.35 (O-CH ₂) 60.89 (CH ₂ -N) 46.1 (N(CH ₃) ₂) -2.23 (Si-Me ₂)
<p>5f</p>	7.2, 6.55 (t, m, 2:3 Har) 5.85 (m, 2H) 5.65 (dd, 1H) 3.60 (t, 2H) 3.30 (t, 2H) 2.81 (s, 3H) 0.10 (s, 6H)	148, 129, 116.5, 112 (<i>Ph</i>) 137.5 (H ₂ C=) 134.2 (=HCSi) 60.0 (O-CH ₂) 54.1 (CH ₂ -N) 38.5 (N-CH ₃) -2.50 (Si-Me ₂)

III- Characterization of 1a-f

Tabla3. NMR Data for 1a-f: (300 MHz, 20 °C, CDCl₃)

Product	E isomer		Z isomer	
	¹ HNMR	¹³ CNMR	¹ HNMR	¹³ CNMR
1a	6.35 (d, 14 Hz, 1H) 6.15 (d, 14 Hz, 1H) 3.75 (m, 1H) 1.16 (d, 6H) 0.94 (t, 3H) 0.61 (q, 2H) 0.11 (s, 6H)	140.0 (O-CH=) 132.1 (=HC-O) 71.98 (O-CH) 22.09 (2CH ₃) 10.05 (CH ₂ -CH ₃) 6.77 (CH ₂ -CH ₃) -0.23 (Si-Me ₂)	5.42 (d, 4.5 Hz, 1H) 5.34 (d, 4.5 Hz, 1H) 3.80 (m, 1H) 1.21 (d, 6H) 0.96 (t, 3H) 0.63 (q, 2H) 0.13 (s, 6H)	139.8 (O-CH=) 131.2.0 (=HC-O) 71.98 (O-CH) 25.35 (2CH ₃) 10.01 (CH ₂ -CH ₃) 6.74 (CH ₂ -CH ₃) -0.42 (Si-Me ₂)
1b	6.34 (d, 14 Hz, 1H) 6.25 (d, 14 Hz, 1H) 3.46 (s, 3H) 0.95 (t, 3H) 0.60 (q, 2H) 0.10 (s, 6H)	139.1 (O-CH=) 126.5 (=HC-O) 58.2 (O-CH ₃) 9.4 (CH ₂ -CH ₃) 6.4 (CH ₂ -CH ₃) -3.0 (Si-Me ₂)	5.43 (d, 4.5 Hz, 1H) 5.28 (d, 4.5 Hz, 1H) 3.54 (s, 3H) 1.02 (t, 3H) 0.61 (q, 2H) 0.14 (s, 6H)	138.5 (O-CH=) 126.0 (=HC-O) 58.2 (O-CH ₃) 9.5 (CH ₂ -CH ₃) 6.6 (CH ₂ -CH ₃) -2.8 (Si-Me ₂)
1c	7.1, 6.75 (t, m, 2:3 Har) 6.50 (d, 14 Hz, H) 6.32 (d, 14 Hz, 1H) 0.75 (t, 3H) 0.5 (q, 2H) 0.01 (s, 6H)	160.5, 129.5, 120.8, 115 (Ph) 134.5 (O-CH=) 131.5 (=HC-O) 9.38 (CH ₂ -CH ₃) 6.57 (CH ₂ -CH ₃) -0.91 (Si-Me ₂)
1d	7.15, 7.32 (t, m, 2:3 Har) 6.60 (q, 10.6 Hz, 2H) 4.49 (s, 2H) 1.0 (t, 3H) 0.62 (q, 2H) 0.15 (s, 6H)	128.6, 127.4, 127.0 (Ph) 140.8 (O-CH=) 139.8 (=HC-O) 64.8 (CH ₂ -O) 14.1 (CH ₂ -CH ₃) 10.5 (CH ₂ -CH ₃) 1.2 (Si-Me ₂)	7.15, 7.32 (t, m, 2:3 Har) 5.58 (d, 3.6 Hz, 1H) 5.40 (d, 3.6 Hz, 1H) 4.60 (s, 2H) 1.05 (t, 3H) 0.72 (q, 2H) 0.21 (s, 6H)	137.2, 128.6, 127.4, 127.0 (Ph) 138.5 (O-CH=) 136.5 (=HC-O) 64.1 (CH ₂ -O) 12.2 (CH ₂ -CH ₃) 9.5 (CH ₂ -CH ₃) 1.0 (Si-Me ₂)

Product	E isomer		Z isomer	
	¹ HNMR	¹³ CNMR	¹ HNMR	¹³ CNMR
<p>1e</p>	5.86 (d, 13 Hz, 1H) 5.67 (d, 13 Hz, 1H) 2.4 (s, 6H) 0.95 (t, 3H) 0.55 (q, 2H) 0.10 (s, 6H)	130.5 (O-CH=) 122.3 (=HC-N) 42.24 (N(CH ₃) ₂) 8.83 (CH ₂ -CH ₃) 6.69 (CH ₂ -CH ₃) -2.76 (Si-Me ₂)	5.34 (d, 4 Hz, 1H) 4.65 (d, 4 Hz, 1H) 2.61 (s, 6H) 0.96 (t, 3H) 0.59 (q, 2H) 0.13 (s, 6H)	124.1 (O-CH=) 109.8 (=HC-N) 50.9 (N(CH ₃) ₂) 7.87 (CH ₂ -CH ₃) 6.59 (CH ₂ -CH ₃) -2.84 (Si-Me ₂)
<p>1f</p>	7.05, 6.65, 6.60 (t, t d 2:1:2 Har) 6.25 (d, 14 Hz, 1H) 6.05 (d, 14 Hz, 1H) 2.85 (s, 3H) 0.85 (t, 3H) 0.50 (q, 2H)	148.5, 129.5, 122.2, 117.2 (<i>Ph</i>) 162.3 (O-CH=) 131.5 (=HC-N) 39.92 (N-CH ₃) 9.91 (CH ₂ -CH ₃) 6.64 (CH ₂ -CH ₃) -0.35 (Si-Me ₂)	7.01, 6.6 (t, m, 2:3 Har) 5.57 (d, 4.5 Hz, 1H) 5.13 (d, 4.5 Hz, 1H) 3.05 (s, 3H) 0.90 (t, 3H) 0.55 (q, 2H)	149.1, 129.1, 126.3, 112.3 (<i>Ph</i>) 153 (O-CH=) 131.3 (=HC-N) 30.59 (N-CH ₃) 9.78 (CH ₂ -CH ₃) 6.62 (CH ₂ -CH ₃) -0.51 (Si-Me ₂)

*Mass Spectrometry data for 1a-f:***(1a):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHO}-i\text{Pr})$ (EI method)HRMS m/s: 188 $[\text{M}^+]$, 173 $[\text{M}-\text{CH}_3^+]$, 143, 131, 129, 116.HRMS m/s $[\text{M}-\text{CH}_3^+]$ calcd for $\text{C}_8\text{H}_{17}\text{O}_2\text{Si}$: 173.210. Found: 173.199.**(1b):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHO}-\text{CH}_3)$ (EI method)HRMS m/s: 173 $[\text{M}-\text{CH}_3^+]$, 131, 115, 101.HRMS m/s $[\text{M}-\text{CH}_3^+]$ calcd for $\text{C}_6\text{H}_{13}\text{O}_2\text{Si}$: 145.150. Found: 145.068**(1c):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHO}-\text{Ph})$ (EI method)HRMS m/s: 222 $[\text{M}^+]$, 207 $[\text{M}-\text{CH}_3^+]$, 193, 163, 129.HRMS m/s $[\text{M}^+]$ calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Si}$: 222.190. Found: 222.109.**(1d):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHO}-\text{CH}_2\text{Ph})$ (EI method)HRMS m/s: 236 $[\text{M}^+]$, 221 $[\text{M}-\text{CH}_3^+]$, 207, 191, 91.HRMS m/s $[\text{M}^+]$ calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$: 236.220. Found: 236.124.**(1e):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHN}(\text{CH}_3)_2)$ (EI method)HRMS m/s: 173 $[\text{M}^+]$, 178 $[\text{M}-\text{CH}_3^+]$, 144.HRMS m/s $[\text{M}^+]$ calcd for $\text{C}_8\text{H}_{19}\text{ONSi}$: 173.230. Found: 173.124.**(1f):** $\text{CH}_3\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OCH}=\text{CHNPh}(\text{CH}_3))$ (CI method)HRMS m/s: 236 $[\text{MH}^+]$, 253 $[\text{M}+\text{NH}_4^+]$, 220, 136.HRMS m/s $[\text{M}^+]$ calcd for $\text{C}_{13}\text{H}_{21}\text{ONSi}$: 235.390. Found: 235.245.

Tabla 4. *Elemental analysis for 1a-f*.

Molecular formula	Calculated		Found	
	% H	% C	% H	% C
C ₉ H ₂₀ O ₂ Si (1a)	10.70	57.39	10.64	55.27
C ₇ H ₁₆ O ₂ Si (1b)	10.06	52.45	10.00	50.52
C ₁₂ H ₁₈ O ₂ Si (1c)	8.16	64.81	8.11	64.20
C ₁₃ H ₂₀ O ₂ Si (1d)	8.53	66.05	8.47	65.76
C ₈ H ₁₉ ONSi (1e)	11.04	55.43	11.22	55.05
C ₁₃ H ₂₁ ONSi (1f)	8.99	66.33	9.00	66.08

S8

Figure 1 ^1H NMR (**1a**)

Figure 2 ^1H NMR (**1b**)

S10

Figure 3 ^1H NMR (**1c**)

Figure 4 ^1H NMR (**1d**)

Figure 5 ^1H NMR (**1e**)

Figure 6 ^1H NMR (**1f**)