

# ORGANOMETALLICS

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## SUPPLEMENTAL MATERIAL

Diverse Mechanistic Pathways and Selectivities in Organo-f-Element-Catalyzed  
Hydroamination. Intermolecular Organolanthanide-Catalyzed Alkyne and Alkene  
Hydroamination

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**Materials and Methods**

All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum ( $10^{-6}$  Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (1-2 ppm of  $O_2$ ). Argon (Matheson, prepurified) was purified by passage through a MnO oxygen-removal column<sup>1</sup> and a Davison 4 A molecular sieve column. Before use, all solvents were distilled under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl, metal hydrides or Na/K alloy except for chlorinated solvents). Deuterium oxide and chloroform-d were purchased from Cambridge Isotopes. Benzene-d<sub>6</sub> and Toluene-d<sub>8</sub> (Cambridge Isotope Laboratories, all 99+ atom% D) used for NMR reactions and kinetic measurements were stored in *vacuo* over Na/K alloy in resealable bulbs and vacuum-transferred immediately prior to use. All organic starting materials were purchased from Aldrich Chemical Co., Farchan Laboratories Inc., or Lancaster Synthesis Inc., and when appropriate, were distilled prior to use. Alkynes were dried by stirring over BaO or CaH<sub>2</sub> overnight, then by repeated transfer onto and from freshly activated Davison 4 A molecular sieves, and degassed by freeze-pump-thaw methods, and finally stored in vacuum-tight containers. The butadiene was dried by passing through a MnO oxygen-removal column and a Davison 4 A molecular sieve column. Alkylamines and other alkenes were dried by stirring over Na/K alloy, then vacuum transferred into a storage tube. The organolanthanide precatalysts

$\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  (Ln = Sm;  $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$ ),<sup>2a</sup>  $\text{Me}_2\text{SiCp}''_2\text{LnCH}(\text{SiMe}_3)_2$  (Ln = Nd, Sm, Lu;  $\text{Cp}'' = \eta^5\text{-Me}_4\text{C}_5$ )<sup>2b</sup> were prepared by published procedures.

### **Physical and Analytical Measurements**

NMR spectra were recorded on either Varian VXRS 300 (FT, 300 MHz,  $^1\text{H}$ ; 75 MHz,  $^{13}\text{C}$ ), or UNITYplus 400 (FT, 400 MHz,  $^1\text{H}$ ; 100 MHz,  $^{13}\text{C}$ ) instruments. Chemical shifts ( $\delta$ ) for  $^1\text{H}$ ,  $^{13}\text{C}$  are referenced to internal solvent resonances and reported relative to  $\text{SiMe}_4$ . NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed tubes (J. Young). Analytical gas chromatography was performed on Varian Model 3700 gas chromatograph with FID detection and a Hewlett-Packard 3390A digital recorder/integrator using a 0.125 in. i.d. column with 3.8% w/w SE-30 liquid phase on Chromosorb W support. GC/MS studies were conducted on a VG 70-250 SE instrument with 70eV electron impact ionization.

### **Kinetic Study of Intermolecular Hydroamination**

In a typical experiment, an NMR sample was prepared as described in the typical NMR-scale catalytic reactions section but maintained at  $-78\text{ }^\circ\text{C}$  until kinetic measurements were initiated. Before the measurements, the NMR probe was equilibrated to the appropriate temperature ( $T \pm 0.2\text{ }^\circ\text{C}$ , checked with a methanol or ethylene glycol temperature standard), the NMR tube was quickly warmed up with shaking for  $\sim 8$  s, and inserted into the probe. Data were acquired using four or eight scans per time interval with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product imine resonances over 3 or more half-lives. The substrate concentration ( $C$ ) was measured from the area ( $A_S$ ) of the  $^1\text{H}$ -normalized  $\text{CH}_2$  signal, standardized to the area ( $A_1$ ) of free  $\text{CH}_2(\text{SiMe}_3)_2$  in the solution (this product is rapidly and quantitatively generated by protonolytic reaction of the precatalysts with amines; Scheme I). All the data collected could be convincingly fit ( $R > 0.98$ ) by least-squares to eq. 1, where  $C_0$  ( $C_0 = A_{S0}/A_1$ ) is the initial concentration of substrate (relative to precatalyst),  $C$  ( $A_S/A_1$ ) is the substrate concentration at time,  $t$ .

$$mt = (C_0 - C) \quad (1)$$

The ratio of catalyst to substrate was accurately measured from the ratio of  $A_{SO}$  to  $A_{I0}$ , or from the area of the product to  $A_I$ . Accurate calibration of catalyst and substrate concentrations was achieved with an internal  $\text{FeCp}_2$ . Turnover frequencies ( $N_T$ ,  $\text{h}^{-1}$ ) were calculated from least-squares determined slopes ( $m$ ) of the resulting plots. Standard Eyring and Arrhenius kinetic analyses afford the following activation parameters:  $\Delta H^\ddagger = 17.2$  (1.1)  $\text{kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -25.9$  (9.7) eu, and  $E_a = 17.8$  (1.8)  $\text{kcal mol}^{-1}$ . Typical initial amine concentrations were in the range 0.017-2.6 M, initial olefin or alkyne concentrations were in the 0.96-4.75 M, and typical catalyst concentrations were in the range 5.5-97.0 mM.

#### **Synthesis of N-trimethylsilyl-N-(1-methylethyl-1-enyl)propylamine (1)**

The title amine derivative was catalytically synthesized using the following procedure. In the glove box, the  $\text{Me}_2\text{Cp}''\text{NdCH}(\text{SiMe}_3)_2$  precatalyst (2.0 mg, 3.3  $\mu\text{mol}$ ) was loaded into an NMR tube equipped with a Teflon valve. On the high vacuum line, the NMR tube was evacuated and backfilled with argon three times. Benzene (~0.5 mL) and 1-trimethylsilyl-1-propyne (75.8 mg, 675.0  $\mu\text{mol}$ , 205-fold molar excess) were vacuum-transferred into the tube, and then *n*-propylamine (9.3 mg, 157.0  $\mu\text{mol}$ , 48-fold molar excess) was vacuum-transferred in. The NMR tube was backfilled with argon and finally sealed. The reaction mixture was heated at 60 °C and periodically monitored by  $^1\text{H}$  NMR spectroscopy. The intermediate imine concentrations of the *E*- and *Z*-N-(1-methyl-2-trimethylsilylethylidene)propylamine were determined by integration against a ferrocene internal standard.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) of the major isomer (ca. 70% yield by  $^1\text{H}$  NMR):  $\delta$  3.05 (t,  $J = 6.74$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.75 (s, 2H,  $\text{CH}_2\text{Si}$ ), 1.67 (m, 2H,  $\text{CH}_2$ ), 1.49 (s, 3H,  $=\text{CMe}$ ), 0.95 (t,  $J = 7.41$  Hz, 3H,  $\text{CH}_3$ ), -0.07 (s, 9H,  $\text{SiMe}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) of the minor isomer (ca. 30% yield by  $^1\text{H}$  NMR):  $\delta$  3.02 (t,  $J = 6.74$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.84 (s, 2H,  $\text{CH}_2\text{Si}$ ), 1.70-1.61 (m, 2H,  $\text{CH}_2$ ), 1.66 (s, 3H,  $\text{CH}_3$ ), 0.98 (t,  $J = 7.35$  Hz, 3H,  $\text{CH}_3$ ), -0.06 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $^1\text{H}$ -decoupled,  $\text{C}_6\text{D}_6$ ):  $\delta$  165.8, 164.9, 53.8, 53.4, 34.1, 34.1, 29.7, 25.1, 25.0, 19.3, 12.5,

12.4, -0.41, -0.92.  $^{13}\text{C}$  NMR (75 MHz,  $^1\text{H}$ -coupled,  $\text{C}_6\text{D}_6$ ):  $\delta$  165.9 (s), 164.9 (s), 53.7 (t,  $J_{\text{CH}} = 129.0$  Hz), 53.5 (t,  $J_{\text{CH}} = 129.7$  Hz), 34.1 (t,  $J = 119.1$  Hz), 34.1 (t,  $J = 119.1$  Hz), 29.7 (q,  $J_{\text{CH}} = 125.0$  Hz), 25.1 (t,  $J_{\text{CH}} = 116.6$  Hz), 25.0 (t,  $J_{\text{CH}} = 128.9$ ), 19.3 (q,  $J_{\text{CH}} = 125.2$  Hz), 12.5 (q,  $J_{\text{CH}} = 124.0$  Hz), 12.4 (q,  $J_{\text{CH}} = 122.0$  Hz), -0.41 (q,  $J_{\text{CH}} = 118.7$  Hz), -0.92 (q,  $J_{\text{CH}} = 118.7$  Hz).

The mixture of imine isomers described above in 0.6 mL of  $\text{C}_7\text{D}_8$  was heated in a sealed NMR tube for 8 h at 120  $^\circ\text{C}$  to afford the rearrangement product N-trimethylsilyl-N-(1-methylethyl-1-enyl)propylamine (**1**), as a colorless liquid. The product was identified by  $^1\text{H}$ ,  $^{13}\text{C}$ , 2D NMR, and GC/MS. The yield (>90%) was estimated by the  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  4.10 (d,  $J = 3.90$  Hz, 2H,  $\text{CH}_2=$ ), 2.90 (t,  $J = 7.50$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.77 (s, 3H, =C-Me), 1.41 (m, 2H,  $\text{CH}_2$ ), 0.77 (t,  $J = 7.50$  Hz, 3H,  $\text{CH}_3$ ), 0.15 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  148.5 (N-C=), 93.2 (=CH<sub>2</sub>), 48.4 (NCH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 22.7 (=C-CH<sub>3</sub>), 11.6 (CH<sub>3</sub>), 1.79 ( $\text{SiMe}_3$ ). MS (rel. abundance):  $\text{M}^+$ (54),  $\text{M}^+-1$ (3),  $\text{M}^++1$ (13), 156.1(88), 142.1 (37), 128.1 (15), 114.1 (65), 98.1 (17), 73.1 (100), 59.0 (20), 45.0 (18). High resolution mass spectrum: Calcd for  $\text{C}_9\text{H}_{21}\text{NSi}$ : 171.1443. Found 171.1431.

### **Synthesis of N-trimethylsilyl-N-(1-methylethyl-1-enyl)butylamine (2)**

The title compound was synthesized in both NMR and preparative scale reactions. Following the procedure above, the  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  precatalyst (2.0 mg, 3.3  $\mu\text{mol}$ ), 1-trimethylsilyl-1-propyne (123.5 mg, 1100.0  $\mu\text{mol}$ ), and *n*-butylamine (2.3 mg, 31.0  $\mu\text{mol}$ ) in 0.6 mL of  $\text{C}_7\text{D}_8$  gave the intermediate imine compound N-(1-methyl-2-trimethylsilyl-ethylidene)butylamine, as a colorless liquid in the NMR-scale reaction.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  3.10 (t,  $J = 6.60$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.74 (s, 2H,  $\text{CH}_2\text{Si}$ ), 1.61 (m, 2H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 1.51 (s, 3H,  $\text{CH}_3$ ), 1.44 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 0.92 (t,  $J = 7.35$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  166, 51.3, 34.1, 33.9, 25.1, 21.1, 14.3, -0.99.

The imine compound above in 0.60 mL of  $\text{C}_7\text{D}_8$  was heated at 120  $^\circ\text{C}$  for 8 h to afford the title compound **2**. The yield (>90%) was estimated from the  $^1\text{H}$  NMR spectrum and GC/MS after vacuum transfer of volatile products. The scale-up catalytic reaction was carried out using

the following procedure. In the glovebox, 20.0 mg (33.2  $\mu\text{mol}$ ) of  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  was loaded into a storage tube (25.0 mL) equipped with a magnetic bar. Next,  $\text{C}_6\text{H}_6$  (5.0 mL), 1-trimethylsilyl-1-propyne (295.2 mg, 2630.0  $\mu\text{mol}$ ) and *n*-butylamine (182.9 mg, 2500.0  $\mu\text{mol}$ ) were successively vacuum-transferred onto the precatalyst. The mixture was then freeze-pump-thaw degassed and warmed to room temperature. The resulting solution was stirred with heating at 60  $^\circ\text{C}$  for 3 days. Distillation of  $\text{C}_6\text{H}_6$  and excess 1-trimethylsilyl-1-propyne followed by vacuum transfer afforded a mixture of *N*-(1-methyl-2-trimethylsilylethylidene)butylamine and the title compound **2**. After the mixture was heated at 120  $^\circ\text{C}$  for 72 h, the *N*-(1-methyl-2-trimethylsilylethylidene)butylamine underwent isomerization to *N*-trimethylsilyl-*N*-(1-methylethyl-1-enyl)butylamine (**2**). The *N*-trimethylsilyl-*N*-(1-methylethyl-1-enyl)butylamine (**2**), 0.29 g (62% isolated yield), was obtained as a colorless oil. It was >95% pure by  $^1\text{H}$  NMR and GC/M.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  4.18 (s, 2H,  $\text{CH}_2\text{Si}$ ), 2.98 (t, 2H,  $J = 7.50$  Hz,  $\text{CH}_2\text{N}$ ), 1.81 (s, 3H,  $\text{CH}_3\text{-C=N}$ ), 1.45 (m, 2H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 1.20 (m, 2H,  $\text{CH}_2\text{Me}$ ), 0.84 (t,  $J = 7.20$  Hz, 3H,  $\text{CH}_3\text{CH}_2$ ), 0.19 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $^1\text{H}$ -decoupled  $\text{C}_6\text{D}_6$ ):  $\delta$  148.9, 92.9, 46.6, 32.8, 23.1, 20.9, 14.4, 2.1.  $^{13}\text{C}$  NMR (75 MHz,  $^1\text{H}$ -coupled,  $\text{C}_6\text{D}_6$ ):  $\delta$  148.9 (s), 92.7 (t,  $J_{\text{CH}} = 157.0$  Hz), 46.6 (t,  $J_{\text{CH}} = 132.5$  Hz), 32.8 (t,  $J_{\text{CH}} = 123.5$  Hz), 23.1 (q,  $J_{\text{CH}} = 120.0$  Hz), 20.9 (t,  $J_{\text{CH}} = 121.5$  Hz), 14.5 (q,  $J_{\text{CH}} = 123.5$  Hz), 2.1 (q,  $J_{\text{CH}} = 106.6$  Hz). MS (rel. abundance):  $\text{M}^+(11)$ ,  $\text{M}^+-1(2)$ ,  $\text{M}^++1(2)$ , 170.2 (66), 156.3 (4), 142.1 (48), 128.1 (18), 114.1 (82), 100.1 (6), 73.0 (100), 59.1 (16), 45.0 (17). High resolution mass spectrum: Calcd for  $\text{C}_{10}\text{H}_{23}\text{NSi}$  ( $\text{M}^+$ ): 185.1600. Found: 185.1602.

### **Synthesis of *N*-trimethylsilyl-*N*-(1-methylethyl-1-enyl)isobutylamine (3)**

A procedure analogous to that for *N*-trimethylsilyl-*N*-(1-methylethyl-1-enyl)butylamine (**2**) was used in the synthesis of the title compound with  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  (2.0 mg, 3.3  $\mu\text{mol}$ ), 1-trimethylsilyl-1-propyne (75.8 mg, 675.0  $\mu\text{mol}$ ), and isobutylamine (9.0 mg, 123.0  $\mu\text{mol}$ ) in 0.60 mL of  $\text{C}_6\text{D}_6$ . The yield (>90%) was estimated by the  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

The intermediate imine was characterized by  $^1\text{H}$  NMR (300 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  2.88 (d,  $J$  = 5.97 Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.94 (m, 1H, CH), 1.74 (s, 2H,  $\text{CH}_2\text{Si}$ ), 1.50 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 0.99 (d,  $J$  = 6.69 Hz, 6H, 2 $\text{CH}_3$ ), 0.04 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $^1\text{H}$ -coupled,  $\text{C}_7\text{D}_8$ ):  $\delta$  165.9 (s,  $\text{C}=\text{N}$ ), 59.7 (t,  $J_{\text{CH}}$  = 128.7 Hz,  $\text{CH}_2\text{N}$ ), 34.0 (t,  $J_{\text{CH}}$  = 119.1 Hz,  $\text{CH}_2\text{Si}$ ), 30.5 (d,  $J_{\text{CH}}$  = 126.2 Hz, CH), 29.6 (q,  $J_{\text{CH}}$  = 125.0 Hz,  $\text{CH}_3$ ), 21.1 (q,  $J_{\text{CH}}$  = 128.2 Hz, 2 $\text{CH}_3$ ), -0.92 (q,  $J_{\text{CH}}$  = 117.5 Hz,  $\text{SiMe}_3$ ).

The imine was heated at 120  $^\circ\text{C}$  for 8 h to afford the title compound as colorless liquid.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  4.21 (d,  $J$  = 5.10 Hz, 2H,  $\text{CH}_2=$ ), 2.72 (d,  $J$  = 7.20 Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.74 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 1.51 (m, 1H, CH), 0.80 (d,  $J$  = 6.60 Hz, 6H, 2 $\text{CH}_3$ ), 0.15 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  148.7, 96.7, 53.8, 28.3, 22.0, 20.6, 1.63. MS (rel. abundance):  $\text{M}^+$ (33),  $\text{M}^+-1$ (2),  $\text{M}^++1$ (9), 170.1 (52), 142.1 (70), 128.1 (15), 114.1 (40), 98.1 (9), 73.0 (100), 57.1 (22), 41.0 (21). High resolution mass spectrum: Calcd for  $\text{C}_{10}\text{H}_{23}\text{NSi}$  ( $\text{M}^+$ ): 185.1600. Found: 185.1581.

#### **Synthesis of N-(1-Methyl-2-phenylethylidene)propylamine (4)**

A procedure analogous to that for **1** was used in synthesis of the title imine with  $\text{Me}_2\text{Cp}''_2\text{NdCH}(\text{SiMe}_3)_2$  (3.0 mg, 5.0  $\mu\text{mol}$ ), 1-phenyl-1-propyne (78.4 mg, 675.0  $\mu\text{mol}$ ), and *n*-propylamine (15.5 mg, 262.0  $\mu\text{mol}$ ) in 0.60 mL of  $\text{C}_6\text{D}_6$ . The yield (>85%) was estimated by  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.16 – 7.09 (m, 5H, Ph), 3.44 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.03 (t,  $J$  = 6.75 Hz, 2H,  $\text{CH}_2\text{N}$ ), 1.70 (m, 2H,  $\text{CH}_2$ ), 1.32 (s, 3H,  $=\text{CMe}$ ), 0.95 (t,  $J$  = 7.35 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  166.6, 129.4, 128.7, 126.6, 123.4, 53.4, 49.8, 24.6, 16.1, 12.4. MS (rel. abundance):  $\text{M}^+$ (4), 146.2 (5), 115.2 (5), 105.2 (5), 91.1 (23), 84.2 (65), 65.1 (8), 42.1 (100). High resolution mass spectrum: Calcd for  $\text{C}_{12}\text{H}_{17}\text{N}$  ( $\text{M}^+$ ): 175.1361. Found: 175.1359.

#### **Synthesis of N-(2-butylidene)propylamine (5)**

A procedure analogous to that for **1** was used in synthesis of the title imine with  $\text{Me}_2\text{Cp}''_2\text{NdCH}(\text{SiMe}_3)_2$  (3.0 mg, 5.0  $\mu\text{mol}$ ), 2-butyne (36.5 mg, 675.0  $\mu\text{mol}$ ), and *n*-propylamine

(9.3 mg, 158.0  $\mu\text{mol}$ ) in 0.60 mL of  $\text{C}_6\text{D}_6$ . The yield (91%) was estimated by  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.09 (t,  $J = 6.40$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 2.09 (q,  $J = 7.40$  Hz, 2H,  $\text{MeCH}_2\text{C}=\text{N}$ ), 1.75 (m, 2H,  $\text{CH}_2$ ), 1.36 (s, 3H,  $\text{CH}_3\text{-C}=\text{N}$ ), 1.09 (t,  $J = 7.35$  Hz, 3H,  $\text{CH}_3\text{-CH}_2\text{C}=\text{N}$ ), 1.00 (t,  $J = 7.35$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  167.9, 53.2, 35.3, 24.7, 12.4, 10.7, 1.4. MS (rel. abundance):  $\text{M}^+$ (23),  $\text{M}^+ + 1$  (2),  $\text{M}^+ - 1$  (2), 98.1 (7), 84.1 (100), 56.1 (40), 42.1 (65). High resolution mass spectrum: Calcd for  $\text{C}_7\text{H}_{15}\text{N}$  ( $\text{M}^+$ ): 113.1204. Found: 113.1186.

### **Synthesis of N-(2-trimethylsilylethyl)N-*n*-propyl-1-amine (6)**

An NMR tube with a Teflon valve was charged with  $\text{Me}_2\text{SiCp}''_2\text{SmCH}(\text{SiMe}_3)_2$  precatalyst (10.0 mg, 16.4  $\mu\text{mol}$ ), and a mixture of trimethylsilylethylene (57.5 mg, 574.0  $\mu\text{mol}$ ), and *n*-propylamine (4.8 mg, 82.0  $\mu\text{mol}$ ) in 0.60 mL of  $\text{C}_6\text{D}_6$ . The reaction mixture was heated at 60  $^\circ\text{C}$  and monitored by  $^1\text{H}$  NMR spectrometry. Only the title compound<sup>4</sup> was detected as a product. The yield (93%) was estimated by  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  2.57 (m, 2H,  $\text{CH}_2\text{N}$ ), 2.45 (m, 2H,  $\text{CH}_2\text{N}$ ), 1.41 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 0.89 (t,  $J = 7.41$  Hz, 3H,  $\text{CH}_3$ ), 0.68 (t,  $J = 8.00$  Hz, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 0.31 (br, 1H, NH), 0.03 (s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  52.1, 46.1, 23.8, 18.5, 12.2, 1.2. MS (rel. abundance):  $\text{M}^+$ (14),  $\text{M}^+ - 1$ (3),  $\text{M}^+ + 1$ (3), 145.1(4), 130.1 (39), 116.1 (43), 102.1 (35), 84.1 (21), 73.0 (100), 59.0 (21), 45.0 (13). High resolution mass spectrum: Calcd for  $\text{C}_8\text{H}_{21}\text{NSi}$  ( $\text{M}^+$ ): 159.1443. Found: 159.1432.

### **Synthesis of N-*trans*-2-buten-N-*n*-propyl-1-amine (7)**

The  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  precatalyst (35.0 mg, 58.0  $\mu\text{mol}$ ) was weighed into an NMR tube with a Teflon valve in the glove box, then 1.0 mL of  $\text{C}_6\text{D}_6$ , 1, 3-butadiene (154.2 mg, 2850.0  $\mu\text{mol}$ , 49-fold molar excess) and *n*-propylamine (92.8 mg, 1570.0  $\mu\text{mol}$ , 27-fold) were vacuum-transferred into the tube on the high-vacuum line. Only the *trans*-1,4-addition product<sup>3</sup>

was detected in the  $^1\text{H}$  NMR spectrum (ca. 90% yield) by comparison with an authentic sample prepared from the reaction of *n*-propylamine with *trans*-1-chloro-2-butene.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.65 – 5.45 (m, 2H, 2CH=), 3.04 (d,  $J = 6.00$  Hz, 2H, =C-CH<sub>2</sub>-N), 2.40 (t,  $J = 7.50$  Hz, 2H, CH<sub>2</sub>N), 1.58 (d,  $J = 4.80$  Hz, 3H, CH<sub>3</sub>-C=), 1.48 (m, 2H, CH<sub>2</sub>), 0.88 (t,  $J = 7.80$  Hz, 3H, CH<sub>3</sub>), 0.57 (b.r., 1H, NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  129.6, 126.7, 51.6, 51.2, 23.1, 17.5, 11.6. MS (rel. abundance):  $\text{M}^+(7)$ ,  $\text{M}^+-1(11)$ ,  $\text{M}^++1(7)$ , 98.2 (13), 84.1 (100), 66.1 (23), 55.1 (100), 43.1 (19). High resolution mass spectrum: Calcd for  $\text{C}_7\text{H}_{15}\text{N}$  ( $\text{M}^+$ ): 113.1204. Found: 113.1201.

### **Synthesis of N-*n*-propyl-1-methyl-*n*-butyl-1-amine (8)**

An NMR tube with a Teflon valve was charged with  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  precatalyst (3.0 mg, 5.0  $\mu\text{mol}$ ), and a mixture of 1-pentene (124.8 mg, 1780.0  $\mu\text{mol}$ , 356-fold molar excess), and *n*-propylamine (1.5 mg, 25.0  $\mu\text{mol}$ , 5-fold molar excess) in 0.60 mL of  $\text{C}_6\text{D}_6$ . The reaction mixture was heated at 60  $^\circ\text{C}$  while monitoring by  $^1\text{H}$  NMR spectroscopy. Only the Markovnikov addition product was detected in the  $^1\text{H}$  NMR spectrum by comparison with an authentic sample prepared from the reaction of *n*-propylamine with 2-bromopentane. The yield (90%) was estimated by  $^1\text{H}$  NMR and GC/MS after vacuum transfer of the volatile products.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  2.54-2.36 (m, 3H), 1.42-1.33 (m, 2H), 1.31-1.17 (m, 4H), 0.95 (d,  $J = 6.30$  Hz, 3H), 0.87 (t,  $J = 7.20$  Hz, 6H), 0.61 (br, 1H, NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  53.2, 49.5, 40.1, 24.2, 20.8, 19.5, 14.6, 12.1. MS (rel. abundance):  $\text{M}^+(3)$ ,  $\text{M}^+-1(3)$ ,  $\text{M}^++1(1)$ , 114.2(15), 100.2(12), 86.1(100), 70.1(5), 58.1 (8), 44.1(36). High resolution mass spectrum: Calcd for  $\text{C}_8\text{H}_{19}\text{N}$  ( $\text{M}^+$ ): 129.1517. Found: 129.1514.

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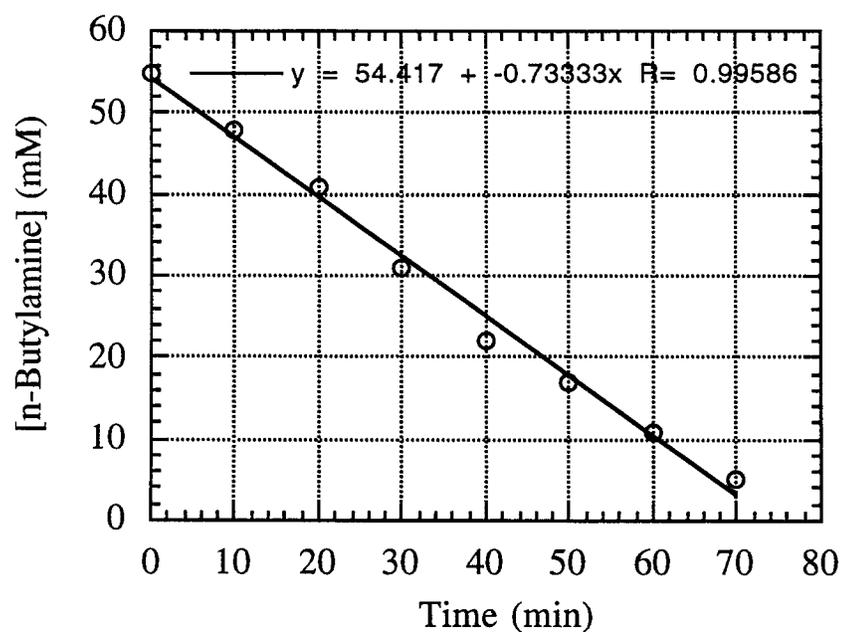


Figure 1. Plot of amine concentration vs. time for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_8$ . The line represents the least-squares fit to the data points.

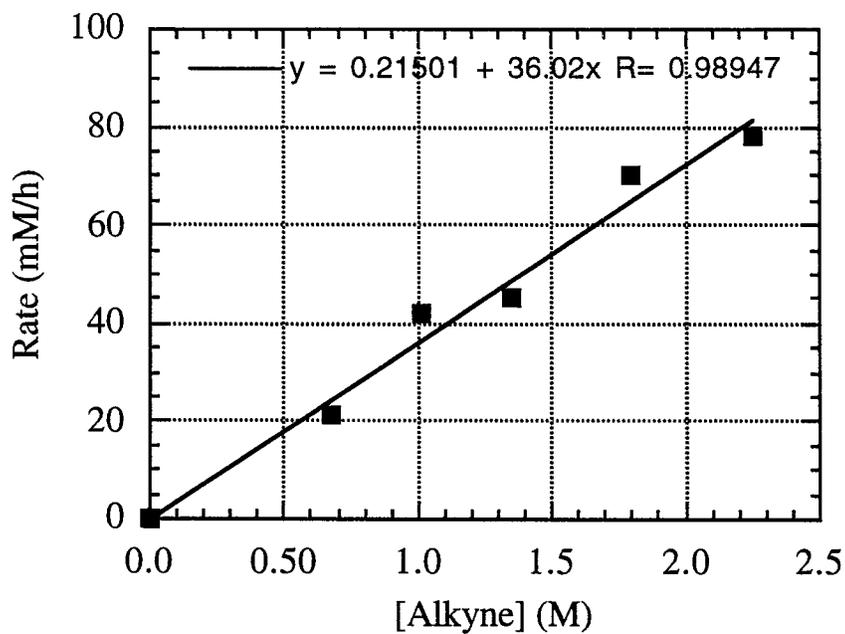


Figure 2. Plot of observed reaction rate vs. alkyne concentration for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_8$ . The line represents the least-squares fit to the data points.

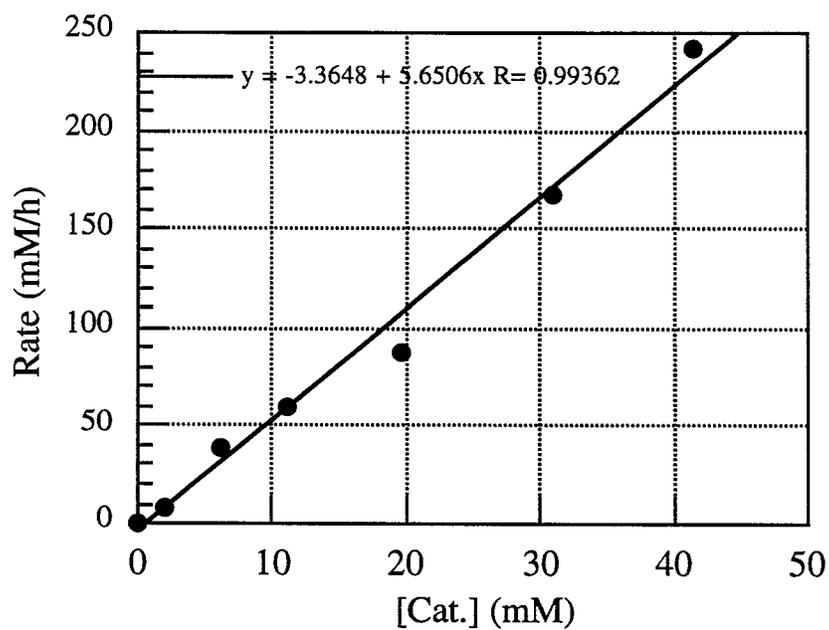


Figure 3. Plot of observed reaction rate vs. catalyst concentration for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_8$ . The line represents the least-squares fit to the data points.

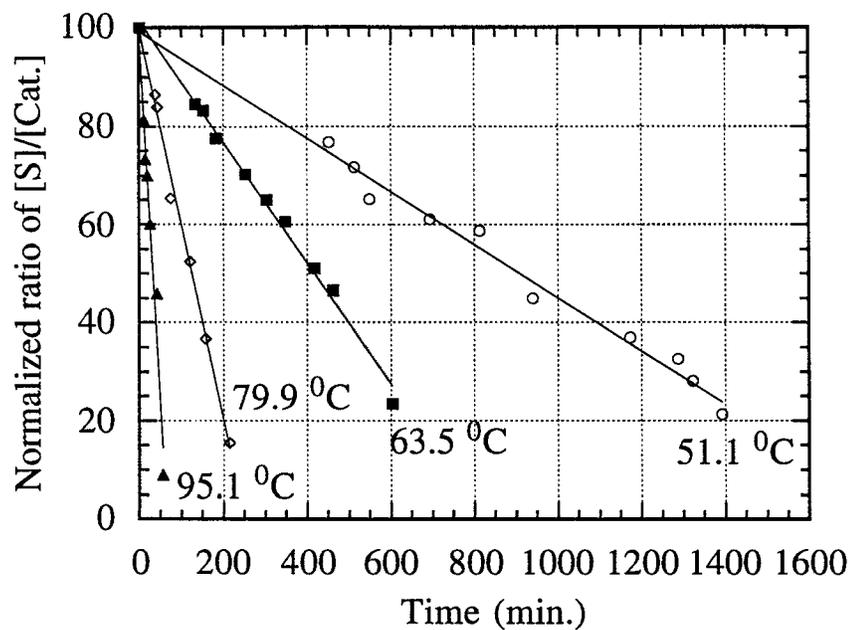


Figure 4. Normalized ratio of amine to lanthanide concentration as a function of time and temperature for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_8$ . Starting amine, alkyne, and catalyst concentrations are held constant. The line represents the least-squares fit to the data points.

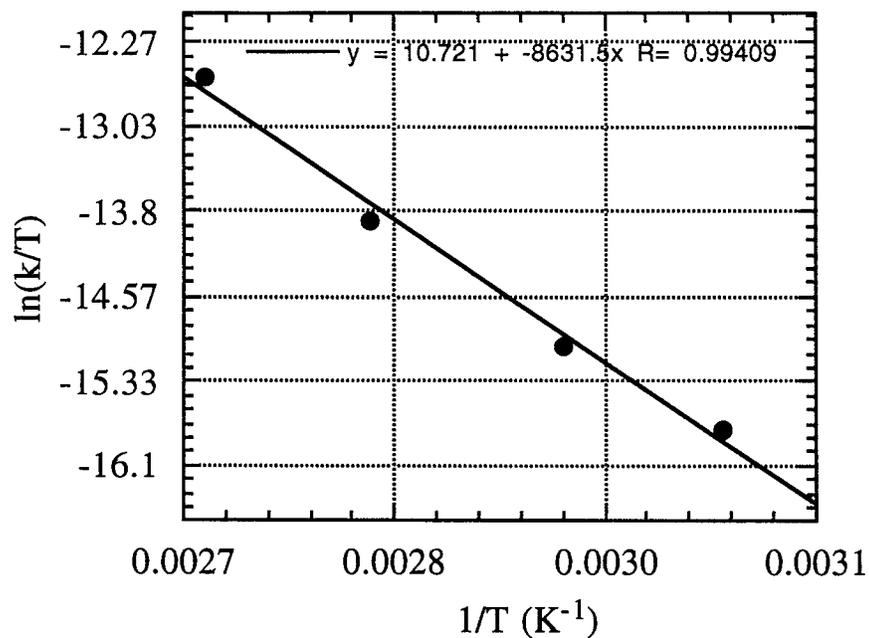


Figure 5. Eyring plot for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_6$ . The line represents the least-squares fit to the data points.

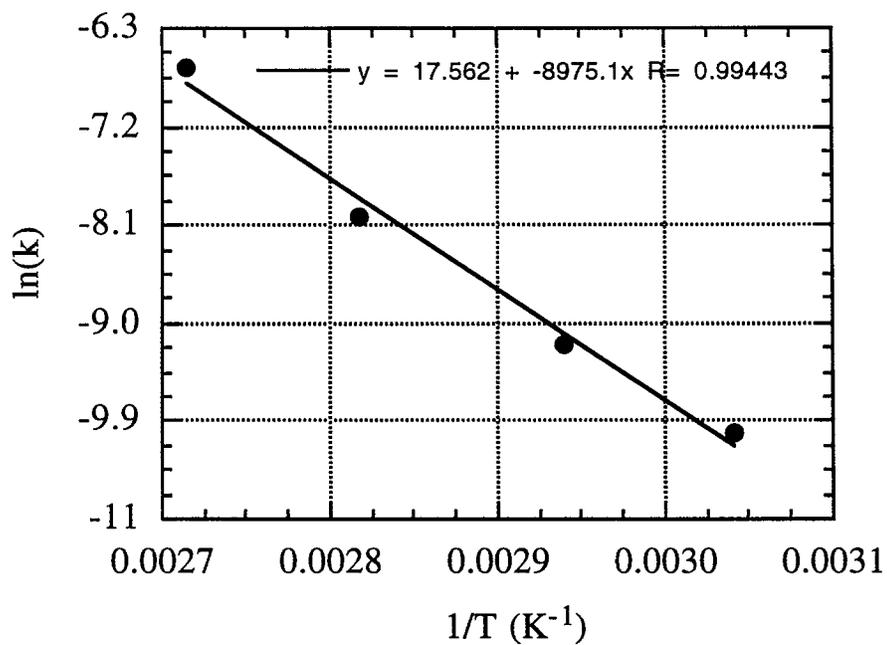


Figure 6. Arrhenius plot for the intermolecular hydroamination of  $\text{MeC}\equiv\text{CSiMe}_3$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  using  $\text{Me}_2\text{SiCp}''_2\text{NdCH}(\text{SiMe}_3)_2$  as the precatalyst in toluene- $d_8$ . The line represents the least-square fit to the data points.