Supplementary Information For:

Scandium Catalyzed Intramolecular Hydroamination. The Development of a Highly Active Cationic Catalyst

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Experimental

General. ^1H , and ^{13}C and spectra were recorded on either a Bruker 300 MHz or 400 MHz Avance spectrometer at ambient temperature and chemical shifts are given relative to residual solvent. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source. HRMS determinations were performed at the Department of Chemistry, University of British Columbia.

All reactions were carried out using standard Schlenk line and glove box techniques, under an atmosphere of nitrogen, unless otherwise stated. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under inert atmosphere. Hexanes and toluene were purified by passage through a column of activated alumina and degassed with nitrogen. C_6D_6 was degassed and dried over 4Å-molecular sieves. *p*-Xylene as standard was distilled from sodium under an atmosphere of argon and stored over 4Å-molecular sieves.

All amino alkenes were distilled from CaH_2 under reduced pressure or under an argon atmosphere and stored in a glove box. Aminoalkyne 5-phenyl-4-pentyn-1-amine (**3**)¹ and aminoalkenes 2,2-diphenyl-4-pentenylamine (**5**),² 2,2-dimethyl-4-pentenylamine (**7**),³ 2-methyl-4-pentenylamine (**9**),³ 2,2-diphenyl-5-hexenylamine (**11**),² and 1-methyl-4-pentenylamine (**13**)³ were prepared as described in the literature. The complexes **1a**, **1b**, **2a** and **2b** were synthesized according to published procedures.⁴

General Procedure for Intramolecular Aminoalkene Hydroamination:

All hydroamination reactions were carried out in an N_2 -filled glove box on an NMR-tube scale. The NMR-tubes were equipped with a Teflon screw cap. The aminoalkene, the standard (1,3,5-trimethoxybenzene or p-xylene) and the catalysts were dissolved in C_6D_6 . The reactions were heated in an oil bath to the corresponding temperature or kept outside the glove box at room temperature (25 °C). Heterocyclic products 2-benzyl-1-pyrroline (**4**),¹ 2-methyl-4,4-diphenylpyrrolidine (**6**),⁵ 2-methyl-4,4-dimethylpyrrolidine (**8**),³ 2-methyl-4-methylpyrrolidine (**10**)³ were characterized by ^1H NMR spectroscopy and LRMS and compared with literature data.

2-Methyl-5,5-diphenyl-piperidine (**12**). Colorless liquid: ^1H -NMR (300 MHz, CDCl_3) δ = 1.01-1.03 (d, J = 6.4 Hz, 3 H, $-\text{CH}_3$), 1.10-1.24 (m, J = 3.1, 10.9 Hz, 1H, $-\text{CHH}-\text{CHCH}_3$), 1.61-1.67 (dd, J = 3.1, 13.3 Hz, 1 H, $\text{CHH}-\text{CHCH}_3$), 2.10-2.30 (m, 2 H, N- H , $\text{CPh}_2\text{CHHCH}_2-$), 2.60-2.74 (dq, J = 3.1, 13.6 Hz, 1 H, $\text{CPh}_2\text{CHHCH}_2-$) 2.75-2.90 (m, 1 H, $-\text{CHCH}_3$), 3.05-3.15 (d, J = 13.7, 1 H, $-\text{CHHNH}$), 3.85-3.99 (dd, J = 2.9, 13.6 Hz, 1 H, CHHNH) 7.05-7.43 (m, 10 H, $\text{H}_{\text{arom.}}$) – ^{13}C -NMR (75 MHz, CDCl_3): δ = 22.07 ($-\text{CH}_3$), 32.60 ($-\text{CH}_2\text{CH}(\text{CH}_3)$),

36.71 (-CH₂CH₂CH(CH₃)), 46.62 (-CH₂CPh₂CH₂-), 53.77 (-CHCH₃), 56.88 (-CH₂NH), 127.32, 127.84, 129.59, 129.67, 130.13, 145.86, 149.99 (C_{arom.}). – EI-MS (50eV): m/z (%) = 252 (2) [M⁺], 251 (7) [M], 236 (2), 221 (2), 205 (2), 180 (20), 165 (18), 91 (8), 71 (6), 58 (100).– HR-EIMS: calc. 251.1674, found 251.1673.

$$\{[\text{ArNC}(\text{'Bu})\text{CHC}(\text{'Bu})\text{NAr}] \text{ScNCH}_2\text{CPh}_2\text{CH}_2\text{CHMe}\}^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$$
 (**D**). Complex **2b** (0.018 g, 0.017 mmol) was placed in an NMR tube with 0.3 mL C₆D₅Br and cooled to –35 °C. A C₆D₅Br solution (0.3 mL) containing NH₂CH₂CPh₂CH=CH₂ (0.0040 g, 0.017 mmol) was added dropwise to the cold NMR tube. The tube was gradually warmed to 330K for 10 minutes and then allowed to cool to room temperature. – ¹H NMR (C₆D₅Br): δ = 7.09-6.82 (ov m, 4 H, Ph), 6.70 (d, *J*_{H-H} = 8.2 Hz, 2 H, Ph), 5.71 (s, 1 H, CH), 4.37 (d, *J*_{H-H} = 11.7 Hz, 1 H, ScNCH₂), 4.28 (d, *J*_{H-H} = 11.7 Hz, 1 H, ScNCH₂), 3.83 (m, 1 H, ScNCHMe), 2.74 (sp, *J*_{H-H} = 6.4 Hz, 2 H, CH(CH₃)₂), 2.40 (sp, *J*_{H-H} = 6.4 Hz, 2 H, CH(CH₃)₂), 1.78 (dd, *J*_{H-H} = 12.6, 5.5 Hz, 1 H, NC(H)(Me)CH₂CPh₂), 1.48 (dd, *J*_{H-H} = 12.1, 5.5 Hz, 1 H, NC(Me)(H)CH₂CPh₂), 1.39 (br s, 3 H, B-Me), 1.21 (d, *J*_{H-H} = 6.4 Hz, 6 H, CH(CH₃)₂), 1.18 (d, *J*_{H-H} = 6.4 Hz, 6 H, CH(CH₃)₂), 1.05 (d, *J*_{H-H} = 6.4 Hz, 6 H, CH(CH₃)₂), 1.02 (s, 18 H, C(CH₃)₃), 0.72 (d, *J*_{H-H} = 6.7 Hz, 6 H, CH(CH₃)₂), 0.37 (d, *J*_{H-H} = 6.2 Hz, 3 H, ScNCHMe). – ¹³C{¹H} NMR (C₆D₅Br): δ = 176.34 (NCCH₃), 149.25, 148.87, 141.86, 140.06, 139.96 (C_{ipso}), 131.52, 128.09, 127.80, 127.00, 126.62, 124.37, 124.21, 122.45, 121.80 (C₆H₅), 86.79 (CH), 62.87 (NCH₂), 56.28 (ScNCHMe), 56.12 (NCH₂CPh₂), 45.81 (NC(H)(Me)CH₂CPh₂), 44.59 (C(CH₃)₃), 31.49 (C(CH₃)₃), 29.80, 28.78 (CH(CH₃)₂), 25.57, 25.09, 24.19, 23.77 (CH(CH₃)₂), 21.38 (ScNCHMe), 18.78 (B-Me). – ¹⁹F NMR (C₆D₅Br): δ = -132.9 (d, ³*J*_{F-F} =

21 Hz, *ortho*-F)-164.9(t, $^3J_{\text{F-F}} = 21$ Hz, *para*-F), -167.4 t, $^3J_{\text{F-F}} = 21$ Hz, *meta*-F). $-^{11}\text{B}\{^1\text{H}\}$

NMR (C₆D₅Br): $\delta = -14.9$.

Figure S.1

^1H NMR:

Figure S.2

2D HMQC:

Figure S.3

^{11}B NMR:

Figure S.4

^{13}C NMR:

Figure S.5

^{19}F NMR:

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