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Exceptional Rate Enhancements and Improved Diastereoselectivites through Chelating Diamide Coordination in Intramolecular Alkene Hydroaminations Catalyzed by Yttrium and Neodymium Amido Complexes

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General information: Melting points were obtained using a Met-Temp II apparatus equipped with a digital thermometer and are uncorrected. Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR. Infrared spectra of solids were obtained by standard KBr pellet procedures or by dissolving the material in a highly volatile solvent then depositing on a NaCl plate and evaporation the solvent under reduced pressure.

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: δ 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, app. = apparent), integration, coupling constants (in Hz), and assignments. ^{13}C NMR spectra were recorded on a Bruker DRX-300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). Mass spectra were obtained on a VG 70E series mass spectrometer, under electron impact conditions at 70 eV or chemical ionization .

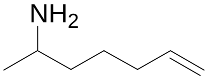
Analytical thin layer chromatography was performed on Polygram® SIL G/UV_{254}1.25 mm silica gel plates with a fluorescent indicator. Flash chromatography was performed on Merck silica gel 60. Solvents for extraction and flash chromatography were reagent grade.

All experiments were carried out under an argon atmosphere using standard anaerobic methods. Organolanthanide complexes were manipulated under argon atmosphere in a glove box. Benzene-D_6 and amino alkenes were distilled from Na and CaH_2 respectively, under an argon atmosphere, and stored at –30 °C in a glove box. Amino alkenes and the ligands, 1-methylpent-4-enylamine **(8)**[1], 2,2-dimethylhex-4-enylamine**(12)**[1], *N*,*N'*-bis(2,2-dimethylpropyl)benzene-1,2-diamine (**2a**)[2], *N*,*N'*-bis(2,6-dimethylphenyl)ethane-1,2-diamine (**3a**)[3], *N*,*N'*-bis(2,6-diethylphenyl)ethane-1,2-diamine (**3c**)[3], *N*,*N'*-bis(2-isopropylphenyl)propane-1,3-diamine (**3d**)[4] and were prepared according to reported procedures.

General Procedure for Intramolecular Alkene Hydroaminations

In an argon-filled glove box, $Ln[N(TMS)_2]_3$ (1.6×10^{-5} mol) and the appropriate diamine (1.6×10^{-5} mol) were introduced into an NMR tube (J. Young) equipped with a teflon screw cap, and then C_6D_6 or [D_8]toluene (0.7 mL) was added. The homogeneous reaction mixture was heated to 120 °C (C_6D_6) or 150 °C ([D_8]toluene) to effect ligand exchange until the peak of $Ln[N(TMS)_2]_3$ had disappeared with concomitant generation of free $(TMS)_2NH$. The appropriate amino alkene (3.2×10^{-4} mol) was added to the resulting complex and the reaction mixture was subsequently heated at 60, 120 or 125 °C in an oil bath. ^{1}H NMR spectroscopy (with a pulse delay of 10 s to avoid signal saturation) was employed to monitor the reactions.

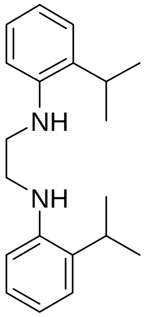
1-Methylhex-5-enylamine (10)



To a stirred suspension of $LiAlH_4$ (1g, 28 mmol) in dry Et_2O (60 mL) was added hep-6-en-2-one oxime[5] (1.8 g, 14 mmol) dropwise at room temperature. After heating at reflux overnight, the reaction mixture was cooled to 0 °C and carefully quenched via sequential addition of H_2O (2 mL), 15% aqueous NaOH (2 mL) and H_2O (4 mL). The mixture was subsequently stirred at room temperature for 2h and anhydrous $MgSO_4$ (3 g) was added. The suspension was filtered and the filtrate was concentrated in vacuo over ice-water bath. The residue was distilled to afford 1.5 g (94 %) of the title compound (b.p.101-103 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (ddt, *J* = 17.1, 10.2, 6.6 Hz, 1H; CHHC***H***=CHH), 4.97 (m, 2H; CH=C$\boldsymbol{H}_2$), 2.86 (sextet, *J* = 6.3 Hz, 1H; C***H***), 2.04 (q, *J* = 6.3 Hz, 2H; C$\boldsymbol{H}_2$), 1.46-1.32 (m, 6H; C$\boldsymbol{H}_2$, N$\boldsymbol{H}_2$), 1.03 (d, *J* = 6.3 Hz, 3H; C$\boldsymbol{H}_3$) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.83, 114.46, 46.88, 39.64, 33.81, 25.74, 23.97 ppm; **IR** (neat): ν = 3354.3, 3278.1, 3075.9,2956.6, 2926.4 (strong), 2856.9, 1822.6, 1640.2, 1584.9, 1458.8, 1373.6, 994.9, 909.8 cm^{-1}; **HRMS** (CI, NH_3): Exact mass calcd for $[C_7H_{15}N+H]^+$ 114.1283. Found 114.1283

N,N'-Bis(2-isopropylphenyl)ethane-1,2-diamine (3b)

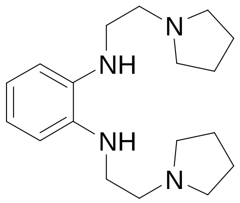


To a solution of 2-isopropylaniline (97%, 2.5 mL, 17.4 mmol) and Et_3N (2.6 mL, 19 mmol) in THF (60 mL) was added oxalyl chloride (1g, 7.9 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and then heated at reflux for 1h. After cooling to room temperature, the mixture was diluted with EtOAc (50 mL) and washed with 1N HCl (2 x 10 mL), sat. $NaHCO_3$ (2 x 10 mL) and brine (10 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated to furnish *N,N'*-bis(2-isopropylphenyl)oxalamide quantitatively (R_f = 0.54 ; 20 % ethyl acetate in *n*-hexane) m.p.= 179.3-181.0.

N,N'-Bis(2-isopropylphenyl)oxalamide (2.0 g, 6.16 mmol) was reduced by addition to $LiAlH_4$ (0.47 g, 12.3 mmol) in dry THF (30 mL) at room temperature and then heating the resulting mixture at reflux overnight. The reaction mixture was cooled to 0 °C and carefully quenched via sequential addition of H_2O (0.5 mL), 15% aqueous NaOH (0.5 mL) and H_2O (1 mL). The mixture was stirred at room temperature for 2h, and anhydrous $MgSO_4$ (1 g) was added, followed by filtration and concentration of the filtrate by simple distillation. The residue was purified by preparative TLC (20 % ethyl acetate in *n*-hexane, $R_f = 0.47$) to afford 1 g (55 %) of the title compound as a white solid (m.p. = 47-48 ^{o}C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (m, 4H; Ar***H***), 6.76 (m, 4H; Ar***H***), 4.03 (bs, 2H; N***H***), 3.50 (s, 4H; C***H***$_2$), 2.85 (septet, *J* = 6.9 Hz, 2H; C***H***), 1.22 (d, *J* = 6.9 Hz, 12H; *C**H**$_3$*) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 144.59, 132.78, 126.76, 125.09, 117.95, 110.78, 43.54, 27.18, 22.32 ppm; **IR** (KBr): ν = 3421.3, 2959.5(strong), 2867.5, 1602.3, 1582.1, 1504.7(strong), 1449.1, 1305.6, 1256.8, 744.7 (strong) cm^{-1}; **HRMS** (CI, NH_3): Exact mass calcd for $[C_{20}H_{28}N_2+H]^+$ 297.2331. Found 297.2368.

***N,N'*-Bis(2-pyrrolidin-1-ylethyl)benzene-1,2-diamine (2b)**

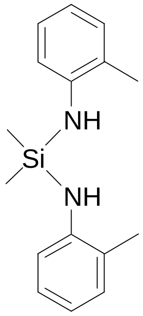


This compound was prepared in a fashion analogous to **3b**, but utilizing (2-oxo-1-pyrrolidinyl)acetyl chloride[6].

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75 (dd, *J* = 5.7, 3.6 Hz, 2H; Ar***H***), 6.64 (dd, *J* = 5.7, 3.6 Hz , 2H; Ar***H***), 3.88 (bs, 2H; N***H***), 3.19 (app. d, *J* = 3.2 Hz, 4H; NC***H***$_2$), 2.77 (t, *J* = 6.3 Hz, 4H; NC***H***$_2$), 2.54 (m, 8H; NC***H***$_2$), 1.78 (m, 8H; C***H***$_2$) ppm; **^{13}H NMR** (75 MHz, $CDCl_3$): δ = 137.47, 118.78, 111.36, 55.15, 54.09, 43.12, 23.52 ppm; **IR** (neat) : ν =

3322.2 (NH), 2959.9, 2794.5, 1691.1, 1599.3, 1517.3, 1441.3, 1256.8, 1145.5, 732.8 cm^{-1} ; **HRMS** (EI): Exact mass calcd for $[C_{18}H_{30}N_4]^+$ 302.2470. Found 302.2474.

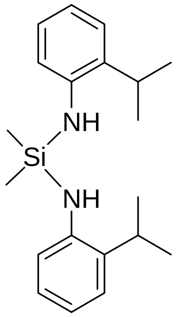
Bis[(2-methyl)phenylamino]dimethylsilane (4a)



To a stirred solution of 2-methylaniline (3 mL, 28 mmol) and Et_3N (3.9 mL, 28 mmol) in THF (30 mL) was added dichlorodimethylsilane (1.7 mL, 14 mmol) dropwise at 0 ^{o}C. The mixture was stirred at room temperature for 30 min and then heated at reflux for 1h. The mixture was diluted with ethyl acetate (50 mL), washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue by bulb-to-bulb distillation (120-125 ^{o}C / 0.02 torr) afforded the title compound (2.5 g, 66 %) as a white solid (m.p. = 56-57 ^{o}C).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.00$ (m, 6H; Ar***H***), 6.67 (dt, *J* = 1.5, 7.2 Hz, 2H; Ar***H***), 3.53 (bs, 2H; N***H***), 2.16 (s, 6H; ArC$\boldsymbol{H}_3$), 0.45 (s, 6H; Si(C$\boldsymbol{H}_3)_2$) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): $\delta = 144.49$, 130.46, 126.92, 124.02, 118.32, 115.42, 17.82, -0.883 ppm; **IR** (KBr) : $\nu =$ 3202 (bs), 2961.0, 1622.3, 1496.5, 1256.6 (s), 1062.8, 904.0, 870.8 (s), 198.9, 750.0 cm^{-1}.

Bis[(2- isopropyl)phenylamino]dimethylsilane (4b)



To a stirred solution of 2-isopropylaniline (97 %, 3 mL, 22.5 mmol), Et_3N (3.8 mL, 27 mmol) and DMAP (274 mg, 2.2 mmol) in 1,2-DME (30 mL) was added dichlorodimethylsilane (1.37 mL, 11.2 mmol) dropwise at 0 ^oC. The reaction mixture was stirred at room temperature for 30 min and then heated at reflux overnight. The mixture was diluted with ethyl acetate (50 mL), washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue by distillation (120-125 ^oC / 0.02 torr) afforded the title compound (2.6 g, 70.5 %) as a colorless oil.

^{1}H NMR (300 MHz, [D_6]Acetone): $\delta = 7.07$ (app. t, *J* = 8.4 Hz, 4H; Ar***H***), 6.86 (app. t, *J* = 8.1 Hz, 2H; Ar***H***), 6.76 (app. t, *J* = 7.2 Hz, 2H; Ar***H***), 4.3 (bs, 2H; N***H***), 3.12 (septet, *J* = 6.9 Hz, 2H; C***H***$(CH_3)_2$), 1.17 (d, *J* = 6.9 Hz, 12H; C***H***$_3$), 0.41 (s, 6H; Si(C***H***$_3$)$_2$) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): $\delta = 143.13$, 134.24, 126.37, 125.36, 118.75, 116.41, 27.51, 22.46, -0.80 ppm; **IR** (neat) : ν = 3372.5, 3063.1, 2960.2 (strong), 1620.1, 1495.5 (strong), 1453.9, 1293.6, 1256.2, 906.9, 873.7, 747.4 cm^{-1}.

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