Catalytic Alkene Cyclohydroamination via an Imido Mechanism

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Supplementary Information

General Considerations. All manipulations were conducted using standard inert-atmosphere techniques using a dual-manifold argon/vacuum Schlenk line or an MBraun LabStar glove box. All glassware and cannulae were stored in an oven at >373 K. Solvents were (where necessary) pre-dried over sodium wire and then refluxed under nitrogen from an appropriate drying agent – toluene from sodium; pentane and diethyl ether from NaK alloy – stored in glass ampoules, and rigorously degassed before use. C_6D_6 and toluene-d_8 were refluxed *in vacuo* for 3 days over potassium metal and vacuum transferred before use. C_6D_5Br was dried similarly from CaH_2. $CDCl_3$ was purchased from Aldrich and stored over 4Å molecular sieves.

The salicyloxazoline proligands (*S*)-HL^n (*n* = 1-2),[1] Cp*Zr(NMe$_2$)$_3$,[2] Cp*Zr(NH^{t}Bu)$_3$,[3] and Zr(NMe$_2$)$_4$[4] were prepared according to published procedures. LiNMe$_2$ (99.9 % grade) was purchased from Chemat Technology and used as received. The hydroamination substrates 1-amino-2,2-dimethylpent-4-ene **I**[5] and 1-amino-2,2-dimethylaminohex-5-ene **II**[6] were prepared according to literature procedures, dried for 3 days at ambient temperature over CaH_2, vacuum transferred and stored in the glovebox. 1-amino-2,2-dimethylpent-4-ene-d_2 was prepared *via* a variation of the literature method,[7] using diethyl ether rather than dichloromethane as solvent. (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride was purchased from Acros Organics and used as received. Celite was purchased from Aldrich and stored in an oven at >150°C prior to use.

NMR spectra were recorded on Bruker DPX300 and DPX400 spectrometers. Routine NMR assignments were confirmed by ^{1}H-^{1}H (COSY) and ^{13}C-^{1}H (HMQC) correlation experiments where necessary. Elemental analyses were obtained by Warwick Analytical

Services, Coventry, UK and MEDAC Ltd, Surrey, UK. Mass Spectra were recorded on a VG Autospec Mass Spectrometer by the Department of Chemistry Mass Spectrometry Service, University of Warwick.

Complex Synthesis

(S_{Zr},S_C)-[Cp*L^{1}Zr(NMe$_2$)$_2$] 1. A Schlenk tube was charged with Cp*Zr(NMe$_2$)$_3$ (0.300 g, 0.80 mmol) and (*S*)-HL^1 (0.294 g, 0.80 mmol). Diethyl ether (10 mL) was added and the reaction stirred at ambient temperature for 1 hour, whereupon all volatiles were removed *in vacuo*. The resulting yellow solid was crystallised from the minimum amount (*ca*. 2 mL) of pentane at -30°C. Yield 0.075 g (0.11 mmol, 14 %). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.36 ppm (s, 9H, C*Me*$_3$), 1.78 (s, 9H, C*Me*$_3$), 1.93 (s, 15H, C$_5$*Me*$_5$), 2.43 (s, 6H, Zr-N*Me*$_2$), 3.28 (s, 6H, Zr-N*Me*$_2$), 3.69 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 8 Hz), 4.05 (t, 1H, OC*H*$_2$ oxazoline, $^3J_{HH}$ = 8 Hz), 4.85 (d of d, 1H, NC*H*Ph oxazoline, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 8 Hz), 6.74 - 6.77 (m, 2H, Ar C-*H* of oxazoline Ph), 6.88 – 6.91 (m, 3H, Ar C-*H* of oxazoline Ph), 7.82 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.17 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 11.4 ppm (C$_5$*Me*$_5$), 30.9, 31.7 (both C*Me*$_3$), 34.3, 36.0 (both *C*Me$_3$), 43.2, 48.1 (both Zr-N*Me*$_2$), 70.5 (N*C*HPh oxazoline), 74.7 (O*C*H$_2$ oxazoline), 112.3 (Ar C_q), 119.0 (*C*$_5$Me$_5$), 124.0, 125.9, 128.3, 128.9, 130.6 (all Ar *C*-H), 138.0, 140.4, 143.2, 166.0 (all Ar C_q), 170.9 (C_q oxazoline). Anal. Calcd for $C_{37}H_{55}N_3O_2Zr$: C, 66.82; H, 8.34; N, 6.32. Found: C, 66.73; H, 8.51; N, 5.84. MS (EI +ve): *m/z* 619 [M$^+$- NMe$_2$], 575 [M$^+$ – 2 NMe$_2$].

(S_{Zr},S_C)-[Cp*L^{2}Zr(NMe$_2$)$_2$] 2. A J. Young ampoule was charged with Cp*Zr(NMe$_2$)$_3$ (0.260 g, 0.71 mmol) and (*S*)-HL^2 (0.250 g, 0.71 mmol). Toluene (5 mL) was added, and the resulting yellow solution heated to 60°C for 3 days. The reaction vessel was allowed to cool to ambient temperature and all volatiles were removed *in vacuo*. The yellow oily residue was dissolved in pentane and dried *in vacuo* to remove residual toluene, and then crystallised from 2 mL of pentane at -30°C to yield the title compound as a crystalline yellow solid. Further material was obtained by concentration of the supernatant. Yield 0.198 g (0.31 mmol, 43 %). VT NMR studies gave evidence of restricted rotation of the amido units, and at low temperatures two rotamers were observed. Unusual orientations of the amido units are also noted in the molecular structure from X-ray diffraction. ^{1}H NMR (500 MHz, toluene-d_8, 243 K); major rotamer (70%): δ 0.63 ppm (s, 9H, CMe_3 oxazoline), 1.35 (s, 9H, CMe_3), 1.70 (s, 9H, CMe_3), 1.84 (s, 15H, C$_5Me_5$), 3.01 (s, 6H, Zr-NMe_2), 3.40 (s, 6H, Zr-NMe_2), 3.56 (t, 1H, OCH_2, oxazoline, $^2J_{HH}$ = 9 Hz), 3.87 (d, 1H, NCH^tBu oxazoline, $^3J_{HH}$ = 7 Hz), 3.96 (d, 1H, OCH_2, oxazoline, $^2J_{HH}$ = 9 Hz), 7.74 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.97 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). Minor rotamer: δ 0.93 ppm (s, 9H, CMe_3 oxazoline), 1.34 (s, 9H, CMe_3), 1.72 (s, 9H, CMe_3), 1.92 (s, 15H, C$_5Me_5$), 2.84 (s, 6H, Zr-NMe_2), 3.16 (s, 6H, Zr-NMe_2), 3.62 (d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz), 4.00 (t, 1H, NCH^tBu oxazoline, $^2J_{HH}$ = 9 Hz), 4.81 (d, 1H, OCH_2 oxazoline, $^3J_{HH}$ = 7 Hz), 7.74 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.65 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, toluene-d_8, 243 K); major rotamer δ 11.8 ppm (C$_5Me_5$), 25.3 (CMe_3 oxazoline), 30.3, 31.5 (both CMe_3), 34.2, 35.2, 35.8 (all *C*Me$_3$), 47.0, 50.2 (both Zr-NMe_2), 68.0 (N*C*H^{t}Bu oxazoline), 71.2 (O*C*H$_2$ oxazoline), 111.8 (Ar C_q), 119.8 (*C*$_5$Me$_5$), 122.5, 129.3 (both Ar *C*-H) 136.9, 139.9, 167.3 (all Ar C_q), 170.7 (C_q oxazoline). Minor

rotamer (30%): δ 11.2 ppm (C_5Me_5), 26.0 (CMe_3 oxazoline), 30.5, 31.4 (both CMe_3), 33.6, 35.7, 36.3 (all CMe_3), 41.8, 47.4 (both Zr-NMe_2), 70.8 (NCH^tBu oxazoline), 73.2 (OCH_2 oxazoline), 115.4 (Ar C_q), 118.8 (C_5Me_5), 126.6, 129.0 (both Ar *C*-H), 138.9, 139.4, 161.1 (all Ar C_q), 163.0 (C_q oxazoline). Anal. Calcd for $C_{35}H_{59}N_3O_2Zr$: C, 65.17; H, 9.22; N, 6.51. Found: C, 64.78; H, 9.06; N, 6.17. MS (EI +ve): *m/z* 599 [M^+- NMe_2], 555 [M^+ - 2 NMe_2].

(S_{Zr},S_C)-[Cp*L$^{1'}$Zr(NH^{t}Bu)] 3. A J. Young ampoule was charged with Cp*Zr(NH^{t}Bu)$_3$ (0.400 g, 0.90 mmol) and (*S*)-HL[1] (0.380 g, 1.20 mmol). Toluene (5 mL) was added and the yellow solution heated to reflux for 3 days whereupon the reaction vessel was allowed to cool to ambient temperature. All volatiles were removed *in vacuo* and the residue transferred to a sublimation tube with the aid of 5 mL of pentane. The crude compound was sublimed at 235°C and 10^{-6} mm Hg. Yield 0.152 g (0.23 mmol, 26 %). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.28 ppm (s, 9H, CMe_3), 1.30 (s, 9H, CMe_3), 1.74 (s, 9H, CMe_3), 1.82 (s, 15H, C_5Me_5), 3.79 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 8 Hz), 4.36 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 10 Hz, 8 Hz), 4.91 (s, br, 1H, N*H*^{t}Bu), 5.48 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 10 Hz), 6.56 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.12 (t, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.24 (t, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.80 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.99 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.04 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 11.7 ppm (C_5Me_5), 31.6, 31.7, 33.0 (all CMe_3), 34.3, 36.2 (both CMe_3), 55.1 (NHCMe_3), 74.0 (OCH_2 oxazoline), 74.6 (N*C*HPh oxazoline), 112.2 (Ar C_q), 118.9 (C_5Me_5), 121.5 (Ar *C*-H of metallated Ph), 123.5 (Ar *C*-H), 125.3, 126.1 (both Ar *C*-H of metallated Ph), 130.6 (Ar

C-H), 138.5, 139.9 (both Ar C_q), 143.5 (Ar *C*-H of metallated Ph), 150.8, 164.5 (both Ar C_q), 168.9 (C_q oxazoline), 188.4 (Zr-C_{Ar}). Anal. Calcd for $C_{37}H_{52}N_2O_2Zr$: C, 68.57; H, 8.09; N, 4.32. Found: C, 68.00; H, 7.85; N, 3.94. MS (EI +ve): *m/z* 646 [M^+], 631 [M^+-Me], 574 [M^+ - NH^{t}Bu].

(S_{Zr},S_C)-[Cp*L$^{2'}$Zr(NH^{t}Bu)] 4. An NMR tube fitted with J. Young concentric stopcock was charged with Cp*Zr(NH^{t}Bu)$_3$ (20.0 mg, 45.2 μmol) and (*S*)-HL^2 (15.0 mg, 45.2 μmol). Toluene-d_8 (0.4 mL) was added and the yellow solution heated to 110°C for 36 hours whereupon the reaction vessel was allowed to cool to ambient temperature. The compound was characterised by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.35 ppm (d, 1H, Zr-C*H*$_2$CMe$_2$, $^2J_{HH}$ = 14 Hz), 0.67 (s, 3H, Zr-CH$_2$C*Me*$_2$), 0.68 (s, 3H, Zr-CH$_2$C*Me*$_2$), 1.30 (s, 9H, C*Me*$_3$), 1.41 (m, 10H, C*Me*$_3$ and C*H*$_2$CMe$_2$, overlapping), 1.68 (s, 9H, NHC*Me*$_3$), 1.85 (s, 15H, C$_5$*Me*$_5$), 3.80-3.93 (m, 3H, NCHCMe$_2$ and OCH$_2$ oxazoline, overlapping), 4.55 (s, 1H, N*H*CMe$_3$), 7.73 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.94 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 11.8 ppm (C$_5$*Me*$_5$), 23.5, 25.7 (both Zr CH$_2$C*Me*$_2$), 31.2, 31.6, 33.4 (all C*Me*$_3$), 34.4, 36.1, 43.7 (all *C*Me$_3$), 54.8 (Zr-*C*H$_2$CMe$_2$), 68.3 (O*C*H$_2$ oxazoline), 78.0 (N*C*HMe$_2$ oxazoline), 112.1 (Ar C_q), 117.6 (*C*$_5$Me$_5$), 123.4, 130.0 (both Ar *C*-H), 138.6, 139.9, 163.9 (all Ar C_q), 166.1 (oxazoline C_q).

(S_{Zr},S_C)-[Cp*L^{1}Zr(NH^{t}Bu)][B(C$_6$F$_5$)$_4$] 5. In the glovebox, a 2 mL sample vial was charged with **3** (29.1 mg, 45 μmol). C_6D_5Br (0.2 mL) was added. In a separate vial, [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (40.0 mg, 50 μmol, 1.1 equivalents) was slurried in C_6D_5Br (0.2

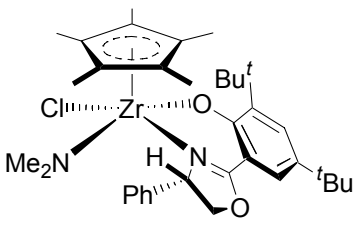
mL). The Zr complex solution was added to the borate slurry, resulting in the dissolution of the borate reagent. The reaction was monitored by ^{1}H NMR spectroscopy and judged to be complete after *ca*. 3h at ambient temperature. The compound was monitored by ^{1}H NMR spectroscopy at regular intervals to assess stability and found to be stable for several days at room temperature. A colour change to blue/turquoise/green was often observed, with no discernable effect on spectroscopic properties. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 0.52 ppm (s, 9H, C*Me*$_3$), 1.31 (s, 9H, C*Me*$_3$), 1.33 (s, 9H, C*Me*$_3$), 1.73 (s, 15H, C_5*Me*$_5$), 4.36 (d of d, 1H, OC*H*$_2$ oxazoline, $^{2}J_{HH}$ = 9 Hz, $^{3}J_{HH}$ = 5 Hz), 4.54 (t, 1H, OC*H*$_2$ oxazoline, $^{2}J_{HH}$ = 9 Hz), 4.83 (d of d, 1H, NC*H*Ph oxazoline, $^{3}J_{HH}$ = 9 Hz, 5 Hz), 6.78 (s, br, 1H, NHCMe$_3$), 7.06-7.19 (m, 5H, Ar C-*H* of Ph), 7.85 (d, 1H, Ar C-*H*, $^{4}J_{HH}$ = 3 Hz), 8.17 (d, 1H, Ar C-*H*, $^{4}J_{HH}$ = 3 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_5Br, 298 K): δ 10.5 ppm (C_5Me_5), 29.9, 30.9, 32.1 (all CMe_3), 34.5, 35.2, 56.6 (all CMe_3), 67.7 (NCHPh) oxazoline), 76.5 (OCH_2 oxazoline), 111.4 (C_5Me_5), 118.9 (Ar C_q) 129.2, 129.8 (both Ar *C*-H), 134.0, 138.8, 144.8, 159.7 (all Ar C_q), 171.8 (oxazoline C_q). ^{19}F{^{1}H} NMR (282.4 MHz, C_6D_5Br, 298 K): δ -131.6 ppm (d, *o*-F), -161.7 (t, *m*-F), -165.7 (t, *p*-F).

(*S*$_{Zr}$,*S*$_C$)-[Cp*L^{2}Zr(NH^{t}Bu)][B(C$_6$F$_5$)$_4$] 6. The metallated complex **4** was prepared as described above. The solvent was removed *in vacuo* and replaced with C_6D_5Br, before addition to 1 equivalent of [HNMe$_2$Ph][B(C_6F_5)$_4$] (as a slurry in C_6D_5Br). Conversion to the cation was monitored by NMR spectroscopy and judged to be complete after *ca*. 3 h. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 0.57 ppm (s, 9H, C*Me*$_3$), 1.00 (s, 9H, C*Me*$_3$), 1.27 (s, 9H, C*Me*$_3$), 1.35 (s, 9H, C*Me*$_3$), 1.72 (s, 15H, C_5*Me*$_5$), 3.75 (d of d, 1H, NC*H*^{t}Bu oxazoline, $^{3}J_{HH}$ = 10, 5 Hz), 4.16 (t, 1H OC*H*$_2$ oxazoline, $^{3}J_{HH}$ = 5 Hz), 4.36 (d of d, 1H,

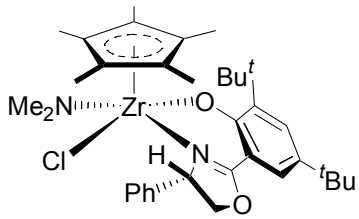
OC*H*$_2$ oxazoline, $^3J_{HH}$ = 10, 5 Hz), 6.64 (s, br, 1H N*H*CMe$_3$), 7.81 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.04 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_5Br, 298 K): δ 10.8 ppm (C_5*Me*$_5$), 25.1, 30.2, 30.9, 32.4 (all C*Me*$_3$), 33.7, 34.4, 35.2 (all *C*Me$_3$), 57.6 (NH*C*Me$_3$), 70.0 (N*C*H^{t}Bu oxazoline), 74.9 (O*C*H$_2$ oxazoline), 113.1 (*C*$_5$Me$_5$), 123.6 (Ar *C*$_q$), 129.2, 133.8 (both Ar *C*-H), 138.5, 144.8, 159.1 (all Ar *C*$_q$), 173.6 (oxazoline *C*$_q$). ^{19}F{^{1}H} NMR (282.4 MHz, C_6D_5Br, 298 K): δ -131.3 ppm (d, *o*-F), -161.5 (t, *m*-F), -165.4 (t, *p*-F).

Cp*L^{1}ZrCl(NMe$_2$) 7. In the glovebox, a vial was charged with Cp*ZrL^{1}Cl$_2$ (20.0 mg, 31.0 μmol) and LiNMe$_2$ (1.6 mg, 31.0 μmol). C_6D_6 was added and the yellow suspension transferred to a J. Young NMR tube and allowed to stand overnight, yielding a clear yellow solution. The sample was characterised by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_6, 298 K): (major isomer only) δ 1.47 ppm (s, 9H, C*Me*$_3$), 1.78 (s, 6H, Zr-N*Me*$_2$), 1.85 (s, 15H, C_5*Me*$_5$), 1.95 (s, 9H, C*Me*$_3$), 3.93 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz), 4.25 (t, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 8 Hz), 5.12 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 8, 2 Hz), 7.00 (m, 5H, Ar C-*H* of Ph), 7.92 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.28 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): (major isomer only) δ 11.5 ppm (*C*$_5$Me$_5$), 31.1 (C*Me*$_3$), 31.6 (br, Zr-N*Me*$_2$), 31.7 (C*Me*$_3$), 35.8, 36.1 (both *C*Me$_3$), 68.3 (N*C*HPh oxazoline), 70.9 (O*C*H$_2$ oxazoline), 111.6 (Ar *C*$_q$), 118.8 (*C*$_5$Me$_5$), 123.4 (Ar *C*-H of Ph), 126.7 (Ar *C*-H), 128.9 (Ar *C*-H of Ph), 129.3 (Ar *C*-H), 130.7 (Ar *C*-H of Ph), 138.2, 140.8, 143.1, 165.9 (all Ar *C*$_q$), 171.7 (oxazoline *C*$_q$).

From the NMR spectra in Figure S1 it is apparent that no starting material Cp*L[1]$ZrCl_2$ is present in the product mixture, and neither is any diamido catalyst Cp*L[1]$Zr(NMe_2)_2$ **1** produced. Two sets of peaks in the ratio 2.3:1 for the mixed amide/chloride are assigned to the diastereomers **7(a)** and **(b)**. On the basis that the most sterically accessible site for substitution is that adjacent to the oxazoline unit, the predominant diastereomer is expected to be **(a)**.



7(a)



7(b)

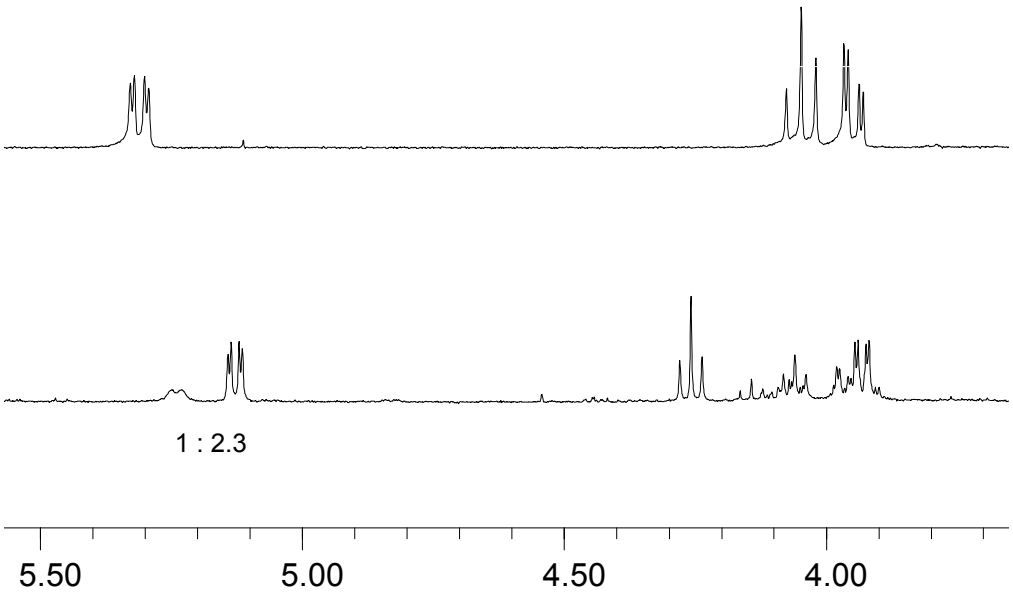


Figure S1. [1]H NMR spectra of oxazoline region of Cp*L[1]$ZrCl_2$ (upper) and diastereomers Cp*L[1]$ZrCl(NMe_2)$ (lower).

$L^1_2Zr(NMe_2)_2$ 8. A J. Young NMR tube was charged with $Zr(NMe_2)_4$ (7.6 mg, 28.5 μmol) and (*S*)-HL[1] (20.0 mg, 56.9 μmol). C_6D_6 (0.4 mL) was added, and the sample immediately characterised by NMR spectroscopy. For similar compounds, see ref. 1. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.37 ppm (s, 18H, 2 x C*Me*$_3$), 1.62 (s, 18H, 2 x C*Me*$_3$), 3.00 (s, 12H, 2 x Zr-N*Me*$_2$), 3.70 (m, 4H, 2 x OC*H*$_2$ oxazoline, overlapping), 4.80 (d of d, 2H, NC*H*Ph of oxazoline, $^3J_{HH}$ = 9 Hz, 5 Hz), 6.87 (m, 4H, 2 x *o*-Ar C-*H* of Ph), 6.95 (m, 6H, 2 x *m*- and *p*-Ar C-*H* of Ph), 7.86 (d, 2H, 2 x Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.20 (d, 2H, 2 x Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 30.2, 31.7 ppm (both C*Me*$_3$), 34.5, 36.0 (both *C*Me$_3$), 45.0 (Zr-N*Me*$_2$), 68.7 (N*C*HPh oxazoline), 74.4 (O*C*H$_2$ oxazoline), 113.4 (Ar C_q), 123.6, 126.6, 127.7, 128.4, 130.2 (all Ar *C*-H), 139.0, 140.5, 141.3, 162.2 (all Ar C_q), 168.9 (C_q oxazoline).

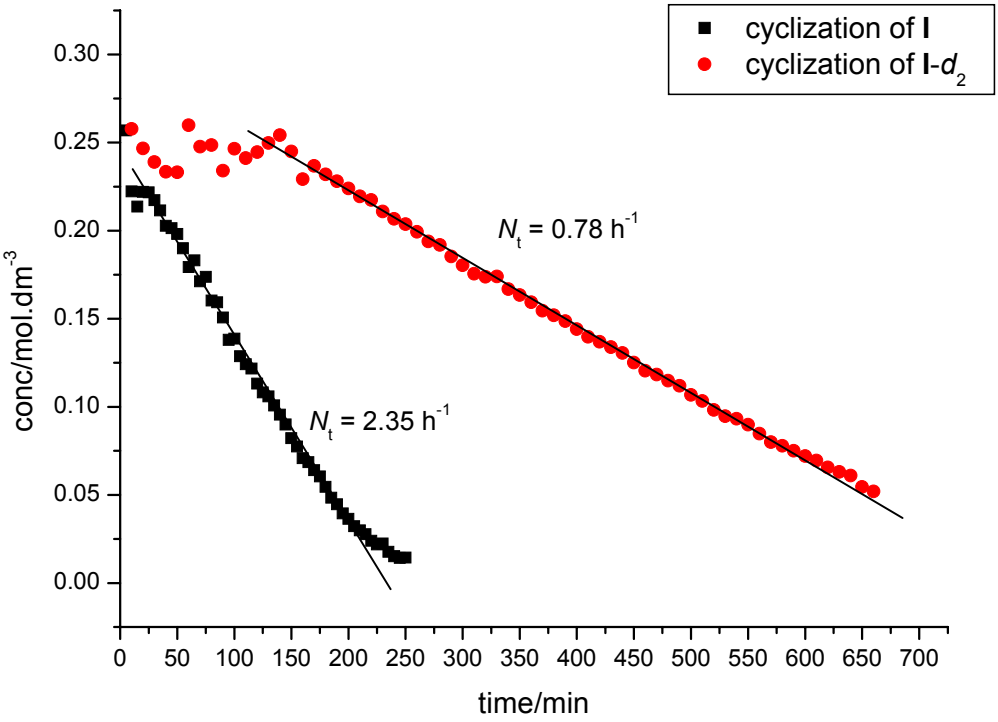
Hydroamination Procedure. In the glovebox, a 2 mL sample vial was charged with the appropriate catalyst **1**/**2** (15 μmol). A second vial was charged with the appropriate substrate (150 μmol). Toluene-d_8 (0.2 mL) was added to each vial and the contents mixed for 5 minutes before transfer to a J. Young NMR tube. The initial room temperature ^{1}H NMR spectrum was recorded and the sample then placed in a heating block at 110°C and the ^{1}H NMR spectrum recorded at regular intervals thereafter to accurately determine the time taken for complete conversion.

Determination of Enantioselectivities. Using the samples from the catalytic reactions described above, the volatile contents of the NMR tube were transferred to a small Rotaflo/Young's reaction ampoule (containing a magnetic stirrer bar) by vacuum transfer.

Pentane (2 mL) and triethylamine (0.2 mL) were added. A separate vial was charged with a solution of (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (1 equivalent based on the amount of catalysis substrate used) in pentane (1 mL). The solutions were mixed, with the almost immediate precipitation of a white solid, and the reaction stirred at ambient temperature for 3 hours. The suspension was then filtered through a glass pipette filled with Celite (*ca*. 2 cm depth) to remove insoluble material, and the filter-cake washed with pentane (5 mL). All volatiles were removed under high vacuum to yield the mixture of (*R*,*R*)- and (*R*,*S*)-Mosher amides as colourless solids. Enantioselectivities were determined by comparison of well resolved resonances in either the ^{1}H NMR (25°C, $CDCl_3$) or ^{19}F NMR spectra (60°C) against racemic samples prepared using $Zr(NMe_2)_4$ as catalyst.[8]

Kinetic Studies. The probe of a Bruker AC400 NMR spectrometer was pre-set to 90°C and the temperature confirmed by a calibrated thermocouple prior to the run. The kinetic samples were prepared according to the general hydroamination procedure described above, with the additional inclusion of an internal standard of ferrocene (purified by Soxhlet extraction in hexane prior to use). Spectra were recorded at an interval of 5 min. Data processing and calculation of turnover frequency (N_t, h^{-1}) were performed according to the method of Marks and co-workers as described elsewhere.[9] Scatter in the measurements apparent at the start of each run, but particularly for the *N*-deuteriated substrate, is a result of an induction period during which time the diamido precatalyst fully releases NMe_2H.

Figure S2. Kinetic plot (90 °C) of [substrate] versus time for cyclisation of **I** and **I-*d*$_2$**



X-ray Crystallography. Colourless plates of **2** suitable for X-ray diffraction were grown from a saturated pentane solution at room temperature after prolonged standing. A suitable crystal was immersed in an inert oil prior to transfer to the cold nitrogen gas stream on a Siemens SMART CCD area detector diffractometer equipped with Mo-Kα radiation (λ = 0.7107 Å). Data were collected using narrow (0.3° in ω) frame exposures, and intensities corrected using SADABS.[10] The structures were solved using direct methods via SHELXS[11] and refined using SHELXL.[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms placed in calculated positions using a riding model (with free rotation for methyl groups). All H-atoms were assigned isotropic

thermal parameters 1.2 x (1.5 x for methyl groups) the equivalent isotropic displacement parameter of the parent atom.

Figure S3. Molecular Structure of **2**. Displacement ellipsoids are at the 50% probability level. Second molecule of asymmetric unit and hydrogen atoms omitted for clarity.

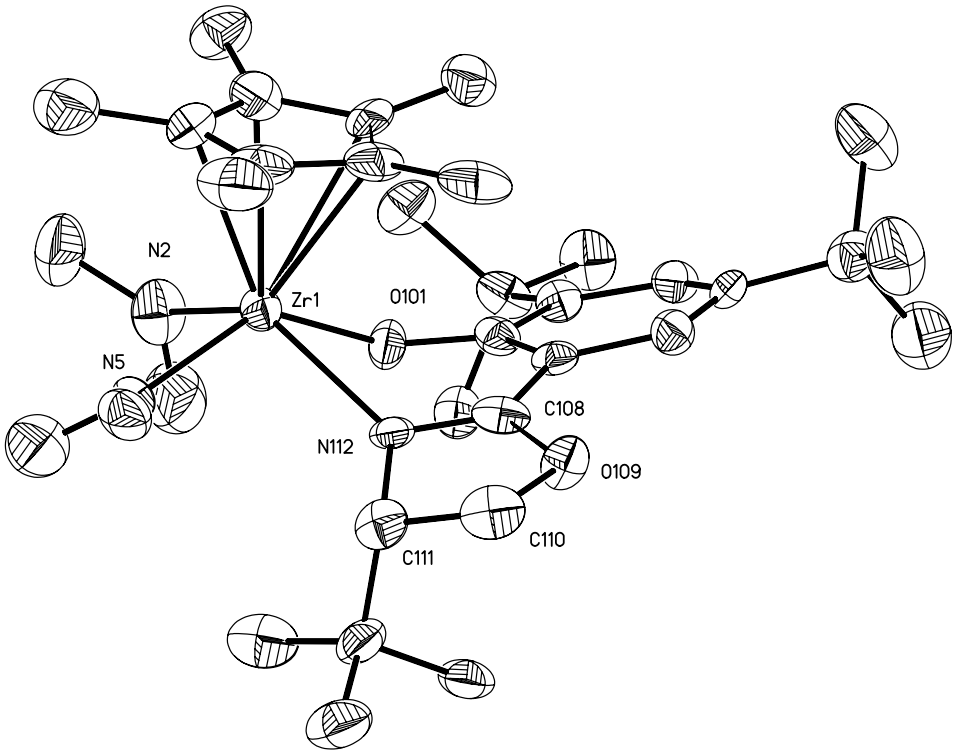


Table S1. Data collection and refinement parameters for **2**.

	$Cp^*Zr(L^2)(NMe_2)_2$ **2**
formula	$C_{35}H_{59}N_3O_2Zr$
formula weight	645.07
crystal morphology	colourless block
crystal dimensions/ mm	0.22 x 0.20 x 0.04
crystal system	monoclinic
space group	$P2_1$
a/ Å	9.9465(7)
b/ Å	9.9106(7)
c/ Å	36.050(3)
α/ °	90
β/ °	95.098(2)
δ/ °	90
V/ $Å^3$	3539.6(4)
Z	4
d(calc)/ $mg.m^3$	1.211
μ(MoKα)/ mm^{-1}	0.343
T/K	180 K
F_{000}	1384
reflections measured	21778
unique reflections	9976 [*R*(int) = 0.0631]
R_1 [$I > 2\sigma(I)$]	0.0804
wR_2	0.1649
data/restraints/parameters	9976/ 55/ 776
goodness of fit on F^2	1.105
largest peak and hole/ e. $Å^3$	1.437 and -0.720

Table S2. Selected Bond Lengths and Angles for **2**.

	Length/Å		Length/Å
Zr(1)-N(2)	2.078(9)	Zr(1)-N(5)	2.144(9)
Zr(1)-O(101)	2.140(7)	Zr(1)-N(112)	2.361(8)
C(108)-N(112)	1.324(13)	C(108)-O(109)	1.339(12)
C(111)-N(112)	1.507(12)	C(110)-C(111)	1.535(15)
O(109)-C(110)	1.432(11)	O(101)-C(102)	1.319(11)
Zr(1)-C(301)	2.630(10)	Zr(1)-C(302)	2.667(10)
Zr(1)-C(303)	2.612(12)	Zr(1)-C(304)	2.532(11)
Zr(1)-C(305)	2.553(12)	Zr(1)-Cp*$_{cent}$	2.305
	Angle/°		Angle/°
N(2)-Zr(1)-N(5)	88.7(4)	N(5)-Zr(1)-N(112)	87.3(3)
O(101)-Zr(1)-N(112)	71.9(3)	N(2)-Zr(1)-O(101)	82.0(3)
C(108)-N(112)-Zr(1)	120.7(6)	C(102)-O(101)-Zr(1)	131.3(6)
N(112)-C(108)-O(109)	115.1(8)	C(108)-O(109)-C(110)	108.2(8)
O(109)-C(110)-C(111)	102.8(7)	N(112)-C(111)-C(110)	101.5(8)
C(108)-N(112)-C(111)	105.3(8)		

References

1 I. Westmoreland, I. J. Munslow, A. J. Clarke, G. Clarkson, R. J. Deeth, and P. Scott, *J. Organomet. Chem.*, 2006, **691**, 2228.

2 A. M. Irigoyen, A. Martin, M. Mena, F. Palacios, and C. Yelamos, *J. Organomet. Chem.*, 1995, **494**, 255.

3 H. Bai, H. W. Roesky, M. Noltemeyer, and M. Witt, *Chem. Ber.*, 1992, **125**, 825.

4 D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.

5 P. H. Martinez, K. C. Hultzsch, and F. Hampel, *Chem. Commun.*, 2006, 2221.

6 P. D. Knight, I. Munslow, P. N. O'Shaughnessy, and P. Scott, *Chem. Commun.*, 2004, 894.

7 B. D. Stubbert and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 6149.

8 J. A. Bexrud, J. D. Beard, D. C. Leitch, and L. L. Schafer, *Org. Lett.*, 2005, **7**, 1959.

9 M. R. Gagne, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 275.

10 G. M. Sheldrick, SADABS, *Program for Area Detector Absorption Correction*, 1996.

11 G. M. Sheldrick, *Acta. Crystallogr.*, 1990, **A46**, 467.

12 G. M. Sheldrick, Madison, WI, 1997.