Ti and Zr complexes of ferrocenyl amidinates[†]

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Preparation of a N-ferrocenyl-amidinate complex was achieved by employing $(TMEDA)Li[(CpFeC_{5}H_{4})NC(Ph)NSiMe_{3}] (1) to prepare Cp*Zr[(CpFeC_{5}H_{4})NC(Ph)NSiMe_{3}]Cl_{2} (2).$ Complex 2 exhibited poor polymerization activity and thus a series of C-ferrocenyl bis(amidinate) complexes of the type $M(L)_2Cl_2$ (M = Zr, 4; M = Ti, 5; L = (CyNC(CpFeC_5H_4)NCy) were synthesized via reaction of ferrocenyl-amidine, H(L) and $M(NMe_2)_2Cl_2$ (M = Ti, Zr·2THF). Half sandwich mono(amidinate) complexes, $Cp'ZrLCl_2$ (Cp' = Cp, 7; $Cp' = Cp^*, 8$), were prepared by the reaction of $Cp'ZrCl_3$ with Li(L) and subsequently alkylated to give M(L)₂Me₂ (M = Zr, 9; M = Ti, 11), $CpZr(L)(CH_2Ph)_2$ (12) and $Cp*Zr(L)Me_2$ (10) with the appropriate alkylating agent. Abstraction of a methyl group from 7 with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ proceeded cleanly to give $[{CyNC(CpFeC_5H_4)NCy}_2ZrMe][MeB(C_6F_5)_3]$ 13 and $[{CyNC(CpFeC_5H_4)NCy}_2ZrMe][B(C_6F_5)_4]$ 14, respectively. Similarly, the analogous CpZr and Cp*Zr derivatives LZr{CyNC(CpFeC₅H₄)-NCy}CH₂Ph] [PhCH₂B(C₆F₅)₃] L = Cp 15, Cp* 17 and [LZr{CyNC(CpFeC₅H₄)NCy}- CH_2Ph [B(C₆F₅)₄] L = Cp 16, Cp* 18 were prepared. Cyclic voltammetry studies on the metal complexes containing ferrocenyl-amidinates reveal quasi reversible oxidation and reduction waves for the ferrocene/ferrocenium couple. The dichloride complexes (4-8) activated with MAO and dialkyl complexes (9,10) activated with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ showed low ethylene polymerization activities.

Introduction

Derivatives of ferrocene have received an enormous amount of attention as components of polymeric materials and biomolecules.¹ In addition, its use as a substituent on a ligand is motivated by its high stability, low cost, facile synthesis, rigid structure, and well-behaved redox chemistry. Group 4 complexes containing ferrocene based ligands are active olefin polymerization catalysts (Scheme 1).² For example, Arnold and coworkers have prepared titanium and zirconium complexes with the bis(amino)ferrocenyl ligand (Scheme 1a), and demonstrated high ethylene polymerization activity for the zirconium complex upon activation with [Ph₃C][B(C₆F₅)₄].^{24,3} Mukaiyama and co-workers reported greater ethylene polymerization activity and superior stereoselectivity in



Scheme 1 Active olefin polymerization catalyst precursors containing ferrocene based ligands.

cyclopolymerization of 1,5-hexadiene using ferrocenyldimethylsilyl substituted zirconocene precatalysts (Scheme 1b) compared to Cp_2ZrCl_2 .⁴ Recently, we have incorporated ferrocenyl substituents on phosphinimide ligands affording a series of highly active catalysts (Scheme 1c).⁵

The incorporation of ferrocene also offers the possibility of redox tunable catalysts,⁶ in which changing the oxidation state of iron could impact the catalyst activity, co-monomer incorporation and stereoregularity of the resulting polymer. While the study of redox tunable olefin polymerization catalysts has been limited, the Fe^{III} ferrocenium derivative of the bis(amino)ferrocenyl zirconium complex (Scheme 1a) was isolated and shown to be an active catalyst.⁷ Recently, Gibson and coworkers have reported very similar ethylene polymerization activities by Fe^{III} and Fe^{III} derivatives based on ferrocenyl substituted bis(imino)pyridyl complexe.⁸

Group 4 complexes containing azaallyl⁹ and amidinates¹⁰ as ancillary ligands have been studied. For example bis(benzamidinate) complexes and half sandwich mono(benzamidinate) complexes have been reported to polymerize propylene, 1-hexene and styrene with moderate activities.¹¹ In this paper we explore species that are derived from amidinate ligands that also incorporate ferrocenyl substituents. The synthesis and characterization and electrochemical properties of these systems are presented and these complexes are evaluated in olefin polymerization.

Experimental section

All preparations were done under an atmosphere of dry, O_2 -free, N_2 employing both Schlenk-line techniques and Innovative Technology or Vacuum Atmospheres inert atmosphere glove

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boxes. Solvents were purified employing a Grubbs-type column system manufactured by Innovative Technology. ¹H, ¹³C, ³¹P, ¹¹B and ¹⁹F NMR spectroscopy spectra were recorded on Varian 200, 300, 400 MHz and Bruker 400 MHz spectrometers. ¹H and ¹³C NMR spectra are referenced to SiMe₄ using the residual solvent peak impurity of the given solvent. ³¹P, ¹¹B and ¹⁹F NMR spectra were referenced to 85% H₃PO₄, Et₂O·BF₃, and CFCl₃, respectively. Chemical shifts are reported in ppm and coupling constants in Hz. C_6D_6 , $C_6D_5CD_3$, $CDCl_3$, CD_2Cl_2 and BrC_6D_5 were used as the NMR solvents after being dried over Na/benzophenone $(C_6D_6, C_6D_5CD_3)$ or CaH₂ (the others), vacuum-transferred into Young bombs and freeze-pump-thaw degassed (three cycles). Combustion analyses were performed in house employing a Perkin Elmer 2400 Series II CHNS Analyzer. Cyclic voltammetry experiments were performed in a BASi RDE-2 cell stand for rotating disk electrochemical experiments, using a glassy carbon working electrode with a disk diameter of 3.0 mm, an aqueous Ag/AgCl reference electrode and a Pt wire auxiliary electrode. The working electrode was polished with alumina (0.05 µm) and rinsed with deionised water prior to use. $[NBu_4][PF_6]$ was used as the supporting electrolytes (0.1 M solutions). All the potentials were referenced versus Cp₂Fe^{+/0}. All electrochemical data were acquired with a computer controlled BASi Epsilon EC potentiostat, using the Epsilon EC software.

MeLi (1.6 M in ether), MeMgBr (1.4 M in toluene– THF 7:1), dicyclohexylcarbodiimide and methylaluminoxane (10% w/w in toluene) were purchased from Aldrich Chemical Company and used without further purification. [NBu₄][PF₆] and [NBu₄][BF₄], purchased from Aldrich, was recrystallized three times from absolute ethanol and ethyl acetate, respectively and dried overnight at 100 °C in *vacuo*. Cp₂Fe, CpZrCl₃ and Cp*ZrCl₃ were purchased from Strem Chemicals. CpFeC₅H₄NH₂,¹² CpFeC₅H₄NH(SiMe₃),¹³ Ti(NMe₂)₂Cl₂,¹⁴ Zr(NMe₂)₂Cl₂(THF)₂,¹⁵ CpFeC₅H₄Li¹⁶ and KCH₂Ph¹⁷ were prepared from literature methods.

Synthesis of (TMEDA)Li[(CpFeC₅H₄)NC(Ph)NSiMe₃] (1)

The following modified literature preparation was followed.²³ A solution of *n*BuLi (0.48 mL, 0.76 mmol, 1.6 M in ether) and tetramethylethylenediamine (TMEDA) (0.11 mL, 0.74 mmol) in diethyl ether (5 mL) was added to a cooled (-30 °C) bright orange solution of CpFeC5H4NH2SiMe3 (0.21 g, 0.76 mmol) in diethylether (10 mL). The resulting suspension was warmed to room temperature and stirred overnight. The solution was concentrated to remove volatiles and then suspended in diethyl ether (10 mL) and cooled to -30 °C. Benzonitrile (0.080 g, 0.77 mmol) was added dropwise to the cooled reaction mixture, and the resultant red solution was warmed to room temperature and stirred for 2 h. The solution was filtered through a pipette plug of Celite and concentrated to an orange solid. The product was recrystallized from cold pentane to obtain an orange crystalline solid (0.326 g, 89%). ¹H NMR (C₆D₆): 7.37 (m, 2H, m-Ph), 7.21 (m, 2H, *o*-Ph), 7.11 (t, 1H, *p*-Ph), 4.14 (s, 5H, Cp), 3.79 (t, ${}^{3}J_{H-H} =$ 2.0 Hz, 2H, $H_{2,5}$ - C_5H_4), 3.51 (t, ${}^{3}J_{H-H} = 2.0$ Hz, 2H, $H_{3,4}$ - C_5H_4), 2.04 (s, 12H, NMe₂), 1.83 (s, 4H, CH₂), 0.10 (s, 9H, TMS). ¹³C{¹H} (C₆D₆): 134.9(*ipso*-C), 128.1, 127.9, 127.4, 126.9 (Ph), 69.0 (*ipso*-C₅H₄), 68.9 (C₅H₄), 63.5 (3,4-C₅H₄), 62.1 (2,5-C₅H₄), 56.5 (NMe₂), 45.6 (CH₂), 3.5 (SiMe₃). MS(EI): 376 [M⁺-TMEDA]. Anal. Calcd.

for $C_{25}H_{39}$ FeLiN₄Si: C, 62.65; H, 7.89; N, 11.24. Found: C, 61.42; H, 7.08; N, 10.01.

Synthesis of Cp*Zr[(CpFeC₅H₄)NC(Ph)NSiMe₃]Cl₂ (2)

Inside an inert atmosphere glovebox a 20 mL vial was charged with Cp*ZrCl₃ (37 mg, 0.11 mmol) and THF (5 mL). The solution was cooled to -30 °C, where a solution of 1 (56 mg, 0.11 mmol) in THF (5 mL) was added dropwise. The resultant orange solution was warmed to room temperature and stirred for 2 h. The reaction was concentrated and suspended in CH₂Cl₂ (5 mL) and filtered through a pipette plug of Celite to remove the LiCl salt. The solution was concentrated and washed 3×5 mL pentane to obtain an orange solid (55 mg, 75%). ¹H NMR (C₆D₆): 7.32 (m, 2H, m-Ph), 7.04 (m, 2H, o-Ph), 6.97 (m, 1H, p-Ph), 4.70 (br s, 1H, H₂-C₅H₄), 4.05 (s, 5H, Cp), 3.82 (br s, 1H, H₅-C₅H₄), 3.53 (br s, 1H, H₃-C₅H₄), 2.73 (br s, 1H, H₄-C₅H₄), 2.11 (s, 15H, C₅Me₅), 0.06 (s, 9H, SiMe₃). ${}^{13}C{}^{1}H{}$ (C₆D₆): 142.1(*ipso*-C), 129.8, 127.0, 126.3(Ph), 70.2 (Cp*, C₅H₅), 69.2 (*ipso*-C₅H₄), 66.8, 65.4, 64.6, 60.9 (C₅H₄), 12.9 (Cp*-Me), 3.4 (SiMe₃). MS(EI): 672 [M⁺]. Anal. Calcd. for C₃₀H₃₈Cl₂FeN₂SiZr: C, 53.56; H, 5.69; N, 4.16. Found: C, 55.12; H, 5.82; N, 4.67.

Synthesis of [CyNC(CpFeC₅H₄)NCy]H (3)

A modified literature procedure¹⁸ was developed. A 50 mL Schlenk flask was charged with monolithioferrocene (0.20 g, 1.04 mmol) and THF (10 mL). The flask was cooled to 0 °C and a solution of dicyclohexyl carbodiimide (0.21 g, 1.04 mmol) in THF (10 mL) was added dropwise. The reaction was warmed to room temperature and stirred for 1 h before quenching with water (5 mL). The aqueous portion was washed with hexanes $(2 \times 5 \text{ mL})$, and the combined organic layers were washed with water and dried over MgSO₄. The volatiles were removed in vacuo resulting in yellow solid without requiring further purification (0.31 g, 85%). The procedure can be scaled up or down without any noticeable effect on yield. The NMR data is in agreement with the literature.18 ¹H NMR (C_6D_6): 4.64 (d, ³ J_{H-H} = 6.7 Hz, 1H, NH), 4.28 (t, ³ J_{H-H} = 1.8 Hz, 2H, H_{2,5}-C₅H₄), 4.26–4.13 (m, 1H, α-H Cy), 4.01 (s, 5H, Cp), 3.94 (t, ${}^{3}J_{H-H} = 1.8$ Hz, 2H, $H_{3,4}$ -C₅ H_{4}), 3.62–3.50 (m, 1H, α-H Cy), 2.28–2.16 (m, 2H, Cy), 1.87–1.12 (m, 18H, Cy).

Synthesis of $[CyNC(CpFeC_5H_4)NCy]_2MCl_2 M = Zr$ (4), Ti (5)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 100 mL Schlenk flask was charged with Zr(NMe)₂Cl₂(THF)₂ (0.50 g, 1.3 mmol) and slight excess of 2 equiv of **3** (1.05 g, 2.7 mmol). Toluene (50 mL) was added and the orange solution was heated to reflux overnight. The volatiles were removed under reduced pressure. The solid was washed with ether (1 × 5 mL) and hexanes (3 × 10 mL) until the washings turned from orange to pale yellow indicating the complete removal of excess **3**. The orange powder was dried under vacuum (1.02 g, 85%). Crystals suitable for X-ray diffraction analysis were grown from slow evaporation of toluene solution at room temperature. (**4**): ¹H NMR (CD₂Cl₂): 4.54 (t, ³J_{H-H} = 1.7 Hz, 4H, H_{2,5}-C₅H₄), 4.37 (t,

[‡] In a number of cases repeated efforts to obtain elemental analysis resulted in satisfactory N and H analyses with carbon values that are lower than expected. This was attributed to the formation of metal carbides during the combustion process.

 ${}^{3}J_{\text{H-H}} = 1.8 \text{ Hz}, 4\text{H}, H_{3,4}\text{--}C_{5}\text{H}_{4}), 4.29 \text{ (s, 10H, Cp-Fe), } 4.17\text{--}4.05$ (m, 4H, α-H Cy), 2.09-1.92 (m, 8H, Cy), 1.90-1.80 (m, 8H, Cy), 1.80-1.70 (m, 8H, Cy), 1.69-1.61 (m, 4H, Cy), 1.38-1.18 (m, 12H, Cy). ${}^{13}C{}^{1}H{}(CD_2Cl_2): 179.6(C_{ipso}(NCy)_2), 71.2(C_{ipso}-C_5H_4), 70.7$ (C_{3,4}-C₅H₄), 70.4 (Cp-Fe), 70.1 (C_{2,5}-C₅H₄), 57.3 (α-C Cy), 35.8 $(C_{2,6}$ -Cy), 26.5 $(C_{3,5}$ -Cy), 26.2 $(C_{4}$ -Cy). E-Chem: $E_{1/2}$ $(CH_{2}Cl_{2}) =$ 439 mV, -455 mV, $E_{1/2}$ (MeCN) = 391 mV, -400 mV. Anal. Calcd. for C₄₆H₆₂Cl₂Fe₂N₄Zr: C, 58.48; H, 6.61; N, 5.93. Found: C, 57.40;‡ H, 6.41; N, 5.90. (5): Yield: 0.84 g, 77%. Crystals suitable for Xray diffraction analysis were grown from slow diffusion of hexanes into a saturated solution of 5 in CH₂Cl₂. ¹H NMR (CD₂Cl₂): 4.56 (br, 4H, $H_{2.5}$ –C₅H₄), 4.41 (m, 2H, α -H Cy), 4.35 (br, 4H, $H_{3.4}$ – C₅H₄), 4.29 (s, 10H, Cp–Fe), 3.99 (m, 2H, α-H Cy), 2.70-2.53 (m, 2H, Cy), 2.42-2.28 (m, 2H, Cy), 2.22-1.05 (m, 36H, Cy). ¹³C{¹H} (CD₂Cl₂): 177.9 (C_{ipso}(NCy)₂), 72.0 (C_{ipso}-C₅H₄), 70.5 (C₅H₄), 70.6 (C_5H_4) , 70.4 (*Cp*-Fe), 70.0 (C_5H_4), 69.5 (C_5H_4), 61.3 (α -*C*Cy), 59.1 (α-C Cy), 35.5, 35.4, 35.0, 33.5, 26.9, 26.7, 26.3, 26.1. E-Chem: $E_{1/2}$ (CH₂Cl₂) = 351 mV, -487 mV, -1574 mV. Anal. Calcd. for C46H62Cl2Fe2N4Ti: C, 61.29; H, 6.93; N, 6.22. Found: C, 59.22;‡ H, 7.31; N, 6.48.

Synthesis of Li[CyNC(CpFeC₅H₄)NCy] (6)

The following modified literature preparation was followed.¹⁹ A bright orange solution of **3** (2.00 g, 5.1 mmol) in hexanes (50 mL) was cooled to 0 °C and treated with MeLi (3.27 mL, 5.1 mol, 1.6 M in ether). The resulting suspension was warmed to room temperature and stirred overnight. The solution was concentrated to 30 mL and filtered to provide a yellow solid. The solid was washed with hexanes and dried under vacuum (1.7 g, 84%). The NMR data is consistent with the literature preparation. ¹H NMR (C₆D₆): 4.90-4.10 (overlapping broad m, 9H, Cp–Fe–C₅H₄), 2.6-1.2 (m, 22H, Cy).

Synthesis of LZr[CyNC(CpFeC₅H₄)NCy]Cl₂ L = Cp (7), Cp* (8)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 100 mL Schlenk flask was charged with 6 (1.0 g, 2.5 mmol) and THF (25 mL), and cooled to -78 °C. The red solution of **6** was cannula transferred dropwise into a second 100 mL Schlenk flask containing a solution of CpZrCl₃ (0.66 g, 2.5 mmol) in THF (40 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 2 h, warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the solid was extracted with CH₂Cl₂. The solution was filtered through a plug of Celite on a sintered glass frit followed by removal of volatiles under reduced pressure. The resulting orange residue was washed with hexanes $(3 \times 10 \text{ mL})$ and ether $(2 \times 5 \text{ mL})$, and dried in vacuo (0.93 g, 61%). The solid was recrystallized from CH₂Cl₂ solution layered with hexanes at room temperature (0.59 g, 38%).(7): ¹H NMR (CD₂Cl₂): 6.68 (s, 5H, Cp–Zr), 4.53 (t, ${}^{3}J_{H-H} = 1.9$ Hz, 2H, $H_{2.5}$ –C₅H₄), 4.40 (t, ${}^{3}J_{H-H} = 1.9$ Hz, 2H, $H_{3,4}$ -C₅ H_{4}), 4.30 (s, 5H, Cp-Fe), 4.17-4.25 (m, 2H, α-H Cy), 1.89-1.72 (m, 8H, Cy), 1.64-1.53 (m, 6H, Cy), 1.33-1.07 (m, 6H, Cy). ${}^{13}C{}^{1}H$ NMR: 174.4 ($C_{ipso}(NCy)_2$), 116.0 (Cp-Zr), 71.0 (C_{ipso}-C₅H₄), 70.8 (C_{3,4}-C₅H₄), 70.6 (Cp-Fe), 70.1 ($C_{2,5}$ - C_5 H₄), 57.8 (α -C Cy), 35.2($C_{2,6}$ -Cy), 26.4 ($C_{3,5}$ -Cy),25.9 (C_4 -Cy). *E*-Chem: $E_{1/2}$ (CH₂Cl₂) = 430 mV, -483 mV. Anal. Calcd. for C₂₈H₃₆Cl₂FeN₂Zr·0.2CH₂Cl₂: C, 53.29; H, 5.77; N, 4.41. Found: C, 53.05; H, 5.83; N, 4.65. (8): 0.30 g, 34%. Crystals suitable for X-ray diffraction analysis were grown from hexanes solution at room temperature. ¹H NMR (CD₂Cl₂): 4.50 (t, ${}^{3}J_{\text{H-H}} = 1.8$ Hz, 2H, $H_{2,5}$ –C₅H₄), 4.35 (t, ${}^{3}J_{\text{H-H}} = 1.8$ Hz, 2H, $H_{3,4}$ –C₅H₄), 4.28 (s, 5H, Cp–Fe), 4.14-4.24 (m, 2H, α -*H* Cy), 2.21 (s, 5H, C₅*Me*₅-Zr), 1.94-1.43 (m, 12H, Cy), 1.37-0.95 (m, 8H, Cy). ¹³C{¹H} NMR: 177.2 (C_{ipso} (NCy)₂), 126.4 ($C_{5}Me_{5}$), 73.8($C_{5}H_{4}$), 70.8 ($C_{5}H_{4}$), 70.6(Cp–Fe), 69.6 ($C_{5}H_{4}$), 58.3 (α -*C* Cy), 36.1, 33.1, 26.7, 26.3, 13.6 (C₅*Me*₅). *E*-Chem: E_{1/2} (CH₂Cl₂) = 437 mV, -557 mV, E_{1/2} (MeCN) = 402 mV, E_{pa} = -399 mV. Anal. Calcd. for C₃₃H₄₆Cl₂FeN₂Zr·CH₂Cl₂: C, 52.78; H, 6.25; N, 3.62. Found: C, 52.68; ‡ H, 5.90; N, 3.58.

Synthesis of [CyNC(CpFeC₅H₄)NCy]₂ZrMe₂ (9), Cp*Zr[CyNC(CpFeC₅H₄)NCy]Me₂ (10)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. Methyllithium (0.40 mL, 0.64 mmol, 1.6 M in ether) was added dropwise to an orange suspension of 7 (0.30 g, 0.32 mmol) in toluene (18 mL) at -30 °C and stirred for 6 h at room temperature. The solution was concentrated to 10 mL under reduced pressure and filtered through a plug of Celite on a sintered glass frit. The volatiles were removed under reduced pressure and the orange residue was washed with ether $(3 \times 1 \text{ mL})$ and dried in *vacuo* (0.22 g, 75%). Crystals suitable for X-ray diffraction analysis were grown from slow evaporation of toluene solution at -30 °C. (9): ¹H NMR (C₆D₆): 4.31 (t, ³J_{H-H} = 1.7 Hz, 4H, H_{2.5}-C₅H₄), 4.28-4.19 (m, 4H, α-H Cy), 4.15 (s, 10H, Cp–Fe), 4.07 (t, ${}^{3}J_{H-H} = 1.8$ Hz, 4H, $H_{3,4}$ –C₅H₄), 2.19-2.05 (m, 8H, Cy), 2.02-1.92 (m, 8H, Cy), 1.87-1.76 (m, 8H, Cy), 1.70-1.59 (m, 4H, Cy), 1.41-1.23 (m, 12H, Cy), 1.12 (s, 6H, Zr-Me₂). ¹³C{¹H} (C_6D_6) : 178.1 $(C_{ipso}(NCy)_2)$, 73.5 $(C_{ipso}-C_5H_4)$, 70.2 $(C_{3,4}-C_5H_4)$, 70.0 (*Cp*-Fe), 69.1 ($C_{2.5}$ - C_5 H₄), 56.7 (α -*C* Cy), 45.3(Zr-*Me*₂), 36.3 $(C_{2,6}-Cy)$, 26.6 $(C_{3,5}-Cy)$, 26.3 (C_4-Cy) . *E*-Chem: $E_{1/2}$ $(CH_2Cl_2) =$ 447 mV, 108 mV, Anal. Calcd. for C₄₈H₆₈FeN₂Zr: C, 63.77; H, 7.58; N, 6.20. Found: C, 62.18; H, 7.34; N, 6.31. (10): 0.13 g, 32%. ¹H NMR (CD₂Cl₂): 4.42 (t, ${}^{3}J_{H-H} = 1.8, 2H, H_{2,5}-C_{5}H_{4}$), 4.28 (t, ${}^{3}J_{H-H} = 1.8, 2H, H_{3,4} - C_{5}H_{4}, 4.23 (s, 5H, Cp-Fe), 4.09-3.98 (m, 2H, Cp-Fe)$ α-H Cy), 2.07 (s, 15H, C₅Me₅), 1.75-0.94 (m, 20H, Cy), -0.10 (s, 6H, Zr-Me₂). ¹³C{¹H} NMR (CD₂Cl₂): 176.7 (C_{inso}(NCy)₂), 120.2 (C₅Me₅), 74.9 (C_{ipso}-C₅H₄), 70.7 (C_{3,4}-C₅H₄), 70.3 (Cp-Fe), 68.9 $(C_{2,5}-C_5H_4)$, 57.8 (α -C Cy), 46.9 (Zr-Me₂), 35.9 (br, C_{2,6}-Cy), 26.6 $(C_{3,5}-Cy)$, 26.2 (C_4-Cy) , 12.5 (C_5Me_5) . E-Chem: $E_{1/2}$ $(CH_2Cl_2) =$ 334 mV, $E_{pa} = 170$ mV. Anal. Calcd. for $C_{35}H_{52}FeN_2Zr \cdot 0.5CH_2Cl_2$: C, 61.76; H, 7.74; N, 4.06. Found: C, 61.08; H, 7.72; N, 4.18.

Synthesis of [CyNC(CpFeC₅H₄)NCy]₂TiMe₂ (11)

All glassware was covered with aluminium foil due to the light sensitive nature of the product. A 100 mL Schlenk flask was charged with **5** (0.3 g, 0.33 mmol) and toluene (50 mL). The flask was cooled to -78 °C and methyl magnesium bromide (0.48 mL, 0.67 mmol, 1.4 M in toluene–tetrahydrofuran 7:1) was added to the suspension dropwise over a 5 min period. A colour change from pink to dark yellow was observed immediately. After stirring for 5 min, the solution was concentrated to 25 mL under reduced pressure. The solution was filtered through a plug of Celite on a sintered glass frit and the volatiles were removed in *vacuo*. The yellow solid was washed with hexanes (3 × 4 mL) resulting in 90%

pure product (0.086 g, 30%). Dilute conditions and stirring time are crucial to minimize the decomposition products. ¹H NMR (CD₂Cl₂): 4.47 (t, ³*J*_{H-H} = 1.8 Hz, 4H, *H*_{2.5}–C₅H₄), 4.36 (t, ³*J*_{H-H} = 1.8 Hz, 4H, *H*_{3.4}–C₅H₄), 4.26 (s, 10H, Cp–Fe), 4.19-4.08 (m, 4H, α-*H* Cy), 2.05-1.58 (m, 30H, Cy), 1.38-1.17 (m, 16H, Cy), 1.23 (s, 6H, Ti–*Me*₂). ¹³C{¹H} (CD₂Cl₂, partial): 178.6 (s, *C*_{*ipso*}(NCy)₂), 69.2 (C₅H₄), 64.7 (Ti–*Me*₂), 70.3 (*Cp*–Fe), 70.4 (C₅H₄), 35.7 (br, Cy), 26.7-26.4 (overlapping peaks, Cy). Sufficient elemental analysis could not be obtained due to the thermal instability and the light sensitive nature of the product.

Synthesis of CpZr[CyNC(CpFeC₅H₄)NCy](CH₂Ph)₂ (12)

A 50 mL Schlenk flask was charged with 7 (0.25 g, 0.40 mmol) and KCH₂Ph (0.11 g, 0.80 mmol), and cooled to -30 °C. Toluene (20 mL), precooled to -30 °C, was added to the Schlenk flask and the suspension was stirred for 1 h at -30 °C. Then, the suspension was warmed to room temperature and stirred overnight. The red suspension changed to a yellow solution over time. The solution was filtered through a plug of Celite on a sintered glass frit and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with hexanes $(3 \times 2 \text{ mL})$ and ether $(3 \times 2 \text{ mL})$ 2 mL) and dried in vacuo (0.14 g, 47%). Crystals suitable for X-ray diffraction analysis were grown from slow evaporation of hexanes solution at room temperature. ¹H NMR (CD₂Cl₂): 7.15 (t, ³J_{H-H} = 7.7 Hz, 4H, *m*-*Ph*), 6.89 (d, ${}^{3}J_{H-H} = 7.3$ Hz, 4H, *o*-*Ph*), 6.81 (t, ${}^{3}J_{H-H} = 7.3$ Hz, 2H, *p-Ph*), 6.01 (s, 5H, Cp-Zr), 4.52 (t, ${}^{3}J_{H-H} = 1.7$ Hz, 2H, $H_{2,5}$ -C₅H₄), 4.40 (t, ${}^{3}J_{H-H} = 1.8$ Hz, 2H, $H_{3,4}$ -C₅H₄), 4.31 (s, 5H, Cp–Fe), 4.19-4.10 (m, 2H, α -*H* Cy), 2.35 (d, ${}^{3}J_{H-H} = 10.4$ Hz, 2H, CH_2 Ph), 1.87 (d, ${}^{3}J_{H-H} = 10.6$ Hz, 2H, CH_2 Ph), 1.81-1.48 (m, 16H, Cy), 1.36-1.07 (m, 4H, Cy). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂): 176.6 (s, C_{ipso}(NCy)₂), 151.7 (C_{ipso}-Ph), 128.6 (m-Ph), 125.9 (o-Ph), 121.0 (p-Ph), 114.4 (Cp-Zr), 73.3 (C_{ipso}-C₅H₄), 71.9 (CH₂Ph), 70.7 (C_{3,4}-C₅H₄), 70.5 (Cp-Fe), 69.5 (C_{2,5} -C₅H₄), 58.3 (α-C Cy), 36.2 $(C_{2,6}-Cy)$, 26.6 $(C_{3,5}-Cy)$, 26.1 (C_4-Cy) . E-Chem.: $E_{1/2}$ $(CH_2Cl_2) =$ 4257 mV, 95 mV, Anal. Calcd. for C42H50FeN2Zr: C, 69.11; H, 6.90; N, 3.84. Found: C, 68.56; H, 6.65; N, 3.67.

$\begin{array}{l} Synthesis of [\{CyNC(CpFeC_5H_4)NCy\}_2ZrMe][MeB(C_6F_5)_3] (13), \\ [\{CyNC(CpFeC_5H_4)NCy\}_2ZrMe][B(C_6F_5)_4] (14), \\ [LZr\{CyNC(CpFeC_5H_4)NCy\}CH_2Ph][PhCH_2(C_6F_5)_3] L = Cp \\ (15), Cp^* (17), [LZr\{CyNC(CpFeC_5H_4)NCy\}CH_2Ph] [B(C_6F_5)_4] \\ L = Cp (16), Cp^* (18) \end{array}$

These compounds were prepared in a similar fashion and thus only one preparation is detailed. $B(C_6F_5)_3$ (5.7 mg, 11 µmol) was added to a solution of **9** (10 mg, 11 µmol) in C_6D_5Br at -35 °C. The solution was transferred to Teflon sealed J-Young NMR tube. NMR data support the quantitative formation of the cationic metal monoalkyl species paired with borate anions. (**13**): ¹H (C_6D_5Br): 4.55-3.70 (m, 22H, α -*H* Cy and CpFeC₅*H*₄), 4.39 (br, 4H, $H_{2,5}$ -C₅H₄-Fe), 4.33 (br, 4H, $H_{3,4}$ -C₅H₄-Fe), 4.13 (s, 10H, Cp-Fe), 2.05-0.60 (m, 43H, Cy and Zr-*Me*), 0.75 (s, 3H, B-*Me*). ¹⁹F (C_6D_5Br): -132.6 (br, 6F, o-C₆F₅), -162.2 (br, 3F, p-C₆F₅), -165.3 (br, 6F, *m*-C₆F₅) (m,p-F) = 3.07. ¹¹B (C₆D₅Br): -14.4. (**14**):. ¹H (C_6D_5Br): 7.18-7.04 (m, 15H, *Ph*₃CMe), 4.53-3.97 (m, 22H, α -*H* Cy and CpFeC₅*H*₄), 4.42 (br, 4H, $H_{2,5}$ -C₅H₄Fe), 4.33 (br, 4H, $H_{3,4}$ -C₅H₄Fe), 4.31 (br, 4H, $H_{3,4}$ -C₅H₄Fe), 4.12 (s, 10H, CpFe), 2.04 (s, 3H, Ph₃CMe), 1.94-1.02 (m, 43H, Cy and Zr-*Me*), 0.85 (br, 3H, Zr-*Me*). ¹⁹F

 (C_6D_5Br) : -132.1 (br, 6F, o-C₆F₅), -161.5 (br, 3F, p-C₆F₅), -165.5 $(br, 6F, m-C_6F_5)(m, p-F gap) = 4.0 ppm. {}^{11}B(C_6D_5Br): -16.1.$ (15): ¹H (C₆D₅Br): 7.25-6.77 (overlapping m, 8H, m, p-ZrCH₂C₆H₅ and BCH₂C₆H₅), 6.49 (d, ${}^{3}J_{H-H}$ = 6.9 Hz, 2H, *o*-ZrCH₂C₆H₅), 5.90 (s, 5H, Cp-Zr), 4.42 (br, 2H, H_{2,5}-C₅H₄-Fe), 4.32 (br, 2H, H_{3,4}-C₅H₄-Fe), 4.13 (br, 5H, Cp–Fe), 3.37 (s, 2H, BCH₂), 2.90 (s, 2H, ZrCH₂), 1.97-0.67 (m, 20H, Cy). ¹⁹F (C₆D₅Br): -129.9 (d, ³ $J_{F-F} = 22$ Hz, 6F, $o-C_6F_5$, -163.4 (t, ${}^{3}J_{F-F} = 21$ Hz, 3F, $p-C_6F_5$), -166.1 (t, ${}^{3}J_{F-F} = 21$ Hz, 6F, m-C₆F₅) (m,p-F gap) = 2.8 ppm. ¹¹B (C₆D₅Br): -12.2. (16): ¹H (C₆D₅Br): 7.23-6.85 (overlapping m, 23H, PhCH₂CPh₃ and m_{p} -ZrCH₂C₆ H_{5}), 6.49 (d, ${}^{3}J_{H-H}$ = 6.5 Hz, 2H, o-CH₂C₆ H_{5} -Zr), 5.91 (s, 5H, Cp-Zr), 4.42 (br, 2H, H_{2.5}-C₅H₄-Fe), 4.33 (br, 2H, H_{3,4}-C₅H₄-Fe), 4.13 (br, 5H, Cp-Fe), 3.84 (s, 2H, PhCH₂CPh₃), 2.89 (s, 2H, ZrCH₂), 1.89-0.77 (m, 20H, Cy). ¹⁹F (C₆D₅Br): -131.6 $(d, {}^{3}J_{F-F} = 10 \text{ Hz}, 6F, o-C_{6}F_{5}), -161.7 (t, {}^{3}J_{F-F} = 21 \text{ Hz}, 3F, p-C_{6}F_{5}),$ -165.7 (t, ${}^{3}J_{F-F} = 18$ Hz, 6F, $m-C_{6}F_{5}$) (m,p-F gap) = 4.0 ppm. ${}^{11}B$ (C_6D_5Br) : -16.2. (17): ¹H (C_6D_5Br) : 4.40 (br, 2H, $H_{2.5}$ - C_5H_4 -Fe), 4.28 (br, 2H, H_{34} -C₅H₄-Fe), 4.21-4.07 (overlapping m, 7H, α -H Cy and CpFe), 4.10 (s, 5H, Cp-Fe), 1.94 (br, 15H, C₅Me₅), 1.82-0.70 (overlapping m, 23H, Cy and Zr-Me), 1.13 (br, 3H, Zr-Me), 0.64 (s, 3H, BMe). ¹⁹F (C₆D₅Br): -132.1 (d, ${}^{3}J_{F-F} = 24$ Hz, 6F, o- C_6F_5 , -163.5 (t, ${}^{3}J_{F-F}$ = 21 Hz, 3F, p- C_6F_5), -166.0 (t, ${}^{3}J_{F-F}$ = 19 Hz, $6F, m-C_6F_5$ (m,p-F gap) = 2.5 ppm. ¹¹B (C_6D_5Br): -14.4. (18): ¹H (C₆D₅Br): 7.18-7.04 (m, 15H, Ph₃CMe), 4.43 (br, 2H, H_{2,5}-C₅H₄-Fe), 4.32 (br, 2H, H₃₄-C₅H₄-Fe), 4.20-4.06 (overlapping m, 7H, α-H Cy and CpFe), 4.09 (s, 5H, Cp–Fe), 2.04 (br, 3H, Ph₃CCH₃), 1.90 (s, 15H, C₅Me₅), 1.79-0.93 (m, 20H, Cy), 0.61 (s, 3H, Zr-Me). 19 F (C₆D₅Br): -131.7 (d, $^{3}J_{F-F} = 9$ Hz, 6F, o-C₆F₅), -161.9 (t, $^{3}J_{F-F} =$ 21 Hz, 3F, p-C₆F₅), -165.7 (t, ${}^{3}J_{F-F} = 19$ Hz, 6F, m-C₆F₅) (m,p-F gap) = 3.8 ppm. ¹¹B (C₆D₅Br): -16.2.

Polymerization protocol

In all cases, trials were done in duplicate and the average activity is reported. Solutions of precatalyst and cocatalyst were prepared inside a glovebox and stored at -30 °C freezer. A 250 mL Schlenk flask was charged with toluene (50 mL) and MAO (1000 equivalents of precatalyst). The flask was connected to a Schlenk line, briefly evacuated and refilled with dry ethylene gas (repeated 5 times) A solution of dichloride precatalyst (10 µmol) in toluene (3 mL) was added to the stirring solution (500 rpm) in the Schlenk flask. The pressure of ethylene used for these trials was 1 atm. The mixture was stirred for 20 min. at room temperature and quenched with 10% HCl (v/v) in methanol solution. The polymer was filtered, washed with methanol and dried under vacuum overnight.

For dimethylated precatalysts, the Schlenk flask was charged with toluene (50 mL). After placing it under ethylene atmosphere, $iBu_3Al(10\% \text{ w/w} \text{ in toluene}, 0.5 \text{ mL}, 200 \,\mu\text{mol})$ was added and the solution was stirred for 5 min. The precatalyst (10 μ mol in 1 mL toluene) was added to the solution immediately followed by the cocatalyst solution (10 μ mol in 1 mL toluene). The mixture was quenched after stirring for 20 min. and the polymer was collected as described above.

X-ray data collection and reduction

Crystals were manipulated and suspended in Paratone inside a glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2 -free environment for

each crystal. The data for crystals were collected on a Bruker Apex II diffractometer with Mo-K α radiation ($\lambda = 0.71069$ Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS). Subsequent solution and refinement were performed using the SHELXTL solution package.

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.²⁰ The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $\omega (F_o - F_c)^2$ where the weight ω is defined as $4F_0^2/2\sigma(F_0^2)$ and F_0 and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. Hatom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the supplementary data.

Results and discussion

Incorporation of ferrocenyl-fragments into amidinate ligands was achieved employing a synthetic strategy similar to that used to prepared dissymmetric amidinates (Scheme 2).²¹ The species $CpFeC_5H_4NH_2^{12}$ was prepared and subsequently converted to $CpFeC_5H_4NH(SiMe_3)$.¹³ Lithiation and reaction with benzonitrile afforded (TMEDA)Li[($CpFeC_5H_4NC(Ph)NSiMe_3$] (1). Spectroscopic data for 1 were consistent with this formulation and this reagent was used without further purification. Initial



Scheme 2 Synthesis of 1,2.

attempts were made to make a Zr complex by transmetallation were performed with CpZrCl₃. While spectroscopic data suggested the formation of the desired product, it could not be obtained in a pure form. Similar problems were encountered in efforts to prepare the Ti analog. In contrast the species $Cp*Zr[(CpFeC_5H_4)NC(Ph)NSiMe_3]Cl_2$ (2) was readily prepared and isolated as an orange solid in 75% yield. The ¹H NMR and ¹³C{¹H} were as expected. A preliminary test of the polymerization activity, employing 1 and 1000 equiv of MAO led only to traces of polyethylene. It was speculated that this poor performance was attributed to ligand degradation *via* Cp–C–H bond activation by the transient cationic Zr complex. While such C–H activation has been demonstrated recently for the reactions of zirconocene cations and ferrocene,²² effort to probe this in the present system were plagued by problems with scale up of the ligand synthesis.

Adopting an alternative synthetic strategy, N,N'-dicyclohexyl ferrocenyl-amidine and the corresponding lithium amidinate salt were synthesized by a modified literature procedure.¹⁸ Subsequently *bis*(amidinate) complexes were successfully prepared by treatment of M(NMe₂)₂Cl₂ (M = Zr·2THF, Ti; Scheme 3) with 2.05 equivalents of **3** after refluxing in toluene. The species [CyNC(CpFeC₅H₄)NCy]₂ZrCl₂ **4** was isolated as an orange solid in high yields (85%) by trituration of the resulting reaction mixture with hexanes followed by subsequent washings with hexanes and ether. Hexane washings are required to completely remove the unreacted amidine, **3**. The titanium analog **5** was isolated in 77% yield as a purple solid using the same workup procedure as for **4**.



Scheme 3 Synthesis of 4–12.

The ¹H NMR spectra are consistent with the formation of **4** and **5** and assignments were assisted by DEPT135 and HSQC experiments. Sharp resonances for the unsubstituted Cp ring of the ferrocene for both bis(amidinate) complexes are similar at *ca.* 4.29 ppm. The resonances for the substituted Cp rings and the *alpha*-proton of the cyclohexyl ring are observed in the 4.6-4.0 ppm region while broad resonances are observed in 2.5-1.0 ppm region for the cyclohexyl protons. In the case of **5** the C_2 symmetry of the bis(amidinate) complexes results in inequivalent nitrogen atoms as evidenced by two multiplets at 4.41 ppm and 3.99 ppm attributed to the *alpha*-protons of the cyclohexyl rings. Similarly, two resonances were observed in the ¹³C NMR spectra at 61 ppm and 59 ppm corresponding to the *alpha*-carbon atoms. In contrast, the NMR spectra of **4** shows single resonances arsing from the corresponding protons and

Table 1 Crystallographic data

	4	5 (CH ₅ l ₂)	7	$8(0.5C_6H_{16})$	9
Formula	$C_{46}H_{62}Cl_2Fe_2N_4Zr$	$C_{47}H_{64}Cl_4Fe_2N_4Ti$	C ₂₈ H ₃₆ Cl ₂ FeN ₂ Zr	$C_{72}H_{106}Cl_4Fe_2Zr_2$	$C_{48}H_{68}Fe_2N_4Z$
Formula wt	944.82	986.42	618.56	1463.55	903.98
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Pna2_1$	$Pca2_1$
a/Å	11.0872(3)	10.7232(5)	19.1426(13)	19.7051(12)	18.6543(10)
b/Å	18.5813(7)	22.1321(11)	18.5720(14)	14.5964(10)	11.9951(6)
c/Å	21.3216(6)	19.1676(9)	7.4148(5)	24.6497(16)	19.4642(10)
α (°)					
β(°)	95.434(2)	93.048(2)	96.285(4)		
γ (°)					
$V/Å^3$	4372.8(2)	4542.6(4)	2620.2(3)	7089.8(8)	4355.3(4)
Ζ	4	4	4	4	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
$d_{\rm (calc)}/{\rm g~cm^{-3}}$	1.435	1.442	1.568	1.371	1.379
R(int)	0.0685	0.0720	0.0408	0.0434	0.0916
μ/cm^{-1}	1.048	1.075	1.175	0.880	0.930
, Total data	40303	75328	62648	113245	36674
Data > $3\sigma(F_0^2)$	10062	10329	8715	12881	9775
Variables	496	523	307	769	498
$R(>3\sigma)$	0.0413	0.0408	0.0269	0.0341	0.0533
R _w	0.0951	0.0912	0.0690	0.0786	0.1099
GOF	1.006	1.008	1.021	1.008	0.981

carbons atoms. This infers facile interchange of the dissimilar cyclohexyl groups in 4 at room temperature. Upon cooling a CD₂Cl₂ solution of 4 to 230 K, the ¹H NMR signals for the alpha-proton broadened and the signals for the substituted Cpprotons split presumably a result of restricted rotation of the ferrocene moiety. This was also observed for 5. Further cooling to 200 K did not afford a limiting spectrum and thus the kinetic parameters for the interconversion were not determined. Xue and coworkers have previously described similar behavior for the bis(amidinate) complexes M(NMe₂)₂(CyNC(Me)NCy)₂ (M = Zr; Ti)²³ where the smaller titanium center is static, and the larger Zr species fluxional at room temperature. Richeson and coworkers proposed that bulky substituents on the central carbon also inhibits the fluxionality.^{24,25} The mechanism of the fluxional process for 4 could involve a dissociative pathway or an intramolecular twist mechanism. The latter twist mechanism involving a trigonal prismatic intermediate has been proposed for related group 4 metal bis(amidinate) and bis(ketenimine) complexes.23,26-28

The molecular structures of 4 and 5 (Fig. 1, Table 1) illustrate the pseudo octahedral environment of the metal centers comprised of four N- and two Cl- atoms. The bidentate amidinate ligands are positioned cis to each other. In complex 5, the Ti-N bond distance differ for the NCy groups cis and trans to Cl. The former Ti-N bonds (2.041(2) Å, 2.037(2) Å) are shorter than those *trans* to Cl (2.079(2) Å, 2.103(2) Å), consistent with the *trans* effect. However, interestingly this trend is not evident for Zr-N bond distances in 4. The amidinate bite angles in 5 $(63.94(8)^\circ, 63.76(8)^\circ)$ are larger than those in 4 (60.02(8)°, 59.86(8)°). This phenomenon has been previously observed.²⁹ Charge delocalization and partial double bond character in the amidinate NCN backbone is evident from the C-N bond distances in 4 and 5 which range from 1.323(3) Å to 1.350(4) Å. The average M–N– C_{alpha} angle in 4 is 139.4° and is smaller than the corresponding average angle in [CyNC(Me)NCy]₂ZrCl₂ (142.4°), suggesting the bulk of the ferrocenyl group pressures the Cy-groups closer to the metal

center. The M–Cl bond distances in **4** (2.4311(7) Å, 2.4413(9) Å) are longer than those in **5** (2.3069(8) Å, 2.3204(7) Å). The Cl–M–Cl angles in both complexes are similar (93.92(3)° for **4**; 93.84(3)° for **5**) and smaller than that in Cp₂ZrCl₂ (97.1°),³⁰ This angle in **4** is similar compared to that see in [CyNC(Me)NCy]₂ZrCl₂ (93.1(1)°) and significantly smaller than the corresponding angle in [Me₃SiNC(Ph)NSiMe₃]₂ZrCl₂ (103.71°).^{29,10h} In this description, two of the vertices are defined as the vectors that bisect the amidinate ligand at the central carbons and the other two vertices as the Zr–Cl vectors.³¹ Using the Richeson description of *bis*(amidinate) complexes as pseudotetrahedral complexes,²⁹ the C–M–C angles is in **4** and **5** are 115.46° and 115.85°, respectively, significantly smaller than the Cp–Zr–Cp angle of 134° in Cp₂ZrCl₂.

The zirconium mono(amidinate) half sandwich complexes $LZr[CyNC(CpFeC_5H_4)NCy]Cl_2 L = Cp 7, Cp* 8$ were synthesized by salt metathesis using Cp'ZrCl₃ (Cp' = Cp; Cp*) and 1 equiv of **6**. These products were isolated in 60% and 55% yields, respectively (Scheme 3). It is noteworthy that initial attempts using Na[CyNC(CpFeC_5H_4)NCy], were unsuccessful. The ¹H NMR spectra of **7** and **8** show the resonances for the unsubstituted Cp ring of ferrocene at *ca.* 4.30 ppm, which is shifted downfield from the protonated amidine, **6**. Only one resonance for the *alpha*-proton of the cyclohexyl ring is observed due to the *C_s* symmetry of the complex. Furthermore, this resonance appears as a triplet of triplets due to difference in coupling between the neighbouring axial and equatorial protons on the cyclohexyl ring.

The molecular structure of **7** and **8** (Fig. 2) display the expected pseudotetrahedral geometry about Zr. The amidinate binding in **7** is asymmetric with Zr–N distances of 2.224(1) Å and 2.110(1) Å. In contrast, the Zr–N bond distances in **8** are indistinguishable (2.215(3) Å, (2.217(3) Å). Nonetheless, the amidinate bite angles in **7** (59.99(4)°) and **8** (60.18(9)°) are very similar. The ferrocenyl-Cp plane is tilted relative to the amidinate NCN plane by 52.09(15)° for **7** and 52.39(11)° for **8**, indicating no π conjugation. The species [CyNC(CpFeC₅H₄)NCy]₂ZrMe₂ (**9**) and Cp*Zr[CyNC(CpFeC₅H₄)NCy]Me₂ (**10**) were prepared



Fig. 1 ORTEP drawing of 4; 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°) for 4: Zr–Cl(1) 2.4311(7), Zr–Cl(2) 2.4413(9), Zr–N(1) 2.189(2), Zr–N(2) 2.209(2), Zr–N(3) 2.186(2), Zr–N(4) 2.238(3), N(1)–C(1) 1.339(4), N(2)–C(1) 1.338(3), C(1)–C(15) 1.487(4), N(3)–C(2) 1.350(4), N(4)–C(2) 1.328(3), C(2)–C(37) 1.477(4), N(1)–Zr–N(2) 60.02(8), N(3)–Zr–N(4) 59.86(8), Cl(1)–Zr–Cl(2) 93.92(3), N(1)–C(1)–N(2) 110.51(24), N(3)–C(1)–N(4) 111.04(25), The structure of 5 is analogous: Ti–Cl(1) 2.3069(8), Ti–Cl(2) 2.3204(7), Ti–N(1) 2.079(2), Ti–N(2) 2.041(2), Ti–N(3) 2.037(2), Ti–N(4) 2.103(2), N(1)–C(1) 1.329(3), N(2)–C(1) 1.347(3), C(1)–C(15) 1.484(4), N(3)–C(2) 1.363(3), N(4)–C(2) 1.323(3), C(2)–C(37) 1.475(4), N(1)–Ti–N(2) 63.94(8), N(3)–Ti–N(4) 63.76(8), Cl(1)–Ti–Cl(2) 93.84(3), N(1)–C(1)–N(2) 109.25(22), N(3)–C(1)–N(4) 109.03(22).

in 75% and 71% isolated yields, respectively, by treatment of a toluene solution of 4 with MeLi. The ¹H and ¹³C NMR spectra of 9 and 10 show the Zr–Me resonances at 1.12 ppm and 45 ppm, and –0.21 ppm and 47 ppm, respectively. The molecular structure of 9 (Fig. 3) is structurally similar to 4 with Zr–C bond distances of 2.269(6) Å and 2.277(6) Å. The corresponding C–Zr–C' bond angle in 9 is 88.22(21)°, significantly smaller than the Cl–Zr–Cl' angle in 4 and also smaller than the corresponding angles in [CyNC(Me)NCy]₂ZrMe₂ (92.4(3)°) and Cp₂ZrMe₂ (95.6°).^{29,32} Similarly the amidinate bite angle in 9 (58.49(16)°, 58.45(17)°) is smaller than the bite angle in 4.

Alkylation of **5** was initially attempted using MeLi, even at -78 °C in the dark resulted black mixtures after a few minutes. However, reaction of **5** with MeMgBr in toluene at -78 °C afforded [CyNC(CpFeC₅H₄)NCy]₂TiMe₂ (**11**) albeit in low yields (32%). Complex **11** proved to be difficult to purify as it was both thermally unstable and light sensitive. Although the mechanistic details of decomposition were not investigated, ¹H NMR data after 1 day



Fig. 2 ORTEP drawings of 7 and 8; 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°) for 7: Zr–Cl(1) 2.4404(4), Zr–Cl(2) 2.4375(4), Zr–N(1) 2.224(1), Zr–N(2) 2.110(1), N(1)–C(6) 1.341(2), N(2)–C(6) 1.341(2), C(6)–C(19) 1.487(2), N(1)–Zr–N(2) 59.99(4), Cl(1)–Zr–Cl(2) 90.65(2), N(1)–C(1)–N(2) 111.07(12), 8. Zr–Cl(1) 2.4426(9), Zr–Cl(2) 2.4245(9), Zr–N(1) 2.215(3), Zr–N(2) 2.217(3), N(1)–C(6) 1.334(4), N(2)–C(6) 1.343(4), C(6)–C(19) 1.485(4), N(1)–Zr–N(2) 60.18(9), Cl(1)–Zr–Cl(2) 89.80(3), N(1)–C(1)–N(2) 112.18(27).

at room temperature in the presence of light in d_8 -toluene showed the liberation of methane, ferrocene and protonated ligand. This thermal instability of **11** is not surprising as Cp₂TiMe₂ exhibits similar characteristics.

Attempts to methylate 7 led to an unexpected ligand redistribution affording Cp₂ZrMe₂ and 9. Such reactivity has been observed previously for other half sandwich zirconium mono(amidinate) complexes.^{10f,33} Attempts to alkylate 7 with a benzyl Grignard reagent led to CpZr[CyNC(CpFeC5H4)NCy](CH₂Ph)₂ 12 in low yields (< 10%). However, 12 was readily synthesized and isolated in 60% yield *via* alkylation with KCH₂Ph. The difference in yields with the alkylating agent has been observed before in the alkylation



Fig. 3 ORTEP drawings of 9, 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°) for 9: Zr-C(47) 2.269(6), Zr-C(48) 2.277(6), Zr-N(1) 2.246(5), Zr-N(2) 2.273(4), Zr-N(3) 2.262(5), Zr-N(4) 2.235(5), N(1)-C(1) 1.338(6), N(2)-C(1) 1.330(6), C(1)-C(15) 1.488(8), N(3)-C(2) 1.335(7), N(4)-C(2) 1.322(7), C(2)-C(37) 1.492(8), N(1)-Zr-N(2) 58.49(16), N(3)-Zr-N(4) 58.45(17), C(47)-Zr-C(48) 88.22(21), N(1)-C(1)-N(2) 111.66(49), N(3)-C(2)-N(4) 111.43(50).

of iron amidinates by Hessen and coworkers. 34 It was postulated that $Mg^{\rm 2+}$ cations may facilitate ligand redistribution.

The cyclic voltammograms of (4–8) show a quasi-reversible oxidation of Fe^{II} in dichloromethane solution using [ⁿBu₄N][PF₆] as the electrolyte. The voltammograms also show a second redox couple at $E_{1/2}$ ranging from –400 mV to –487 mV (Fig. 4). Complex 5 shows an irreversible reduction at –1574 mV corresponding to the reduction of titanium from Ti^{IV} to Ti^{III} as commonly observed with other titanium complexes. The $E_{1/2}$ of Fe^{II}/Fe^{III} redox couple



Fig. 4 Cyclic voltammogram of 4. $(10^{-3} \text{ M in } CH_2Cl_2, 10^{-1} \text{ M } [^{n}Bu_4N][PF_6]$, scan rates: 50 mV s⁻¹ (grey) and 250 mV s⁻¹ (black).

in 4, 7 and 8 is similar at *ca*. 430 mV, while the $E_{1/2}$ for 5 is 88 mV lower and E_p is broader by 134 mV in comparison to 4. These complexes exhibit Fe oxidations at higher potentials compared to the protonated amidine, 3 (quasi-reversible, $E_{1/2}$ of 310 mV).¹⁹ This is consistent with the withdrawal of electron density from the amidinate by complexation. Complex 9 and 12 shows similar $E_{1/2}$ as their corresponding dichloride complexes, whereas, 10 shows lower $E_{1/2}$ by 100 mV compared to 8. The quasi-reversible nature of the Fe^{II} oxidations results in a cathodic to anodic peak ratio that is significantly lower in amidinate complexes compared to the ferrocene standard. This loss of current in the return wave suggests that the oxidized Fe^{III} species undergo a subsequent chemical reaction before reduction. The lack of stability of the ferrocenium species may be due to an attack by Lewis basic substituents, solvent or supporting electrolyte.35 although use of MeCN as the solvent or [ⁿBu₄N][BF₄] as the electrolyte had minimal impact on the nature of the observed wave.

Abstraction of a methyl group from **9** with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)]_4$ in C_6D_5Br proceeded cleanly to form $[\{CyNC(CpFeC_5H_4)NCy\}_2ZrMe][MeB(C_6F_5)_3]$ **13** and $[\{CyNC-(CpFeC_5H_4)NCy\}_2ZrMe][B(C_6F_5)_4]$ **14**, respectively (Scheme 4). The ¹H NMR spectra of **13** and **14** show broad overlapping resonances in the 4.0–4.5 ppm and 2.0-0.6 ppm region arising form the Cp and cyclohexyl substituents, respectively. For **13**, the ¹¹B NMR signal at –14.4 ppm and the difference in the resonances from *meta* and *para*-fluorines³⁶ in the ¹⁹F NMR spectrum is consistent with the formation of $MeB(C_6F_5)_3^-$. In contrast,



attempts to characterize the analogous titanium complexes were unsuccessful as the generation of a mixture of products was evident. However, the analogous CpZr and Cp*Zr derivatives LZr{CyNC(CpFeC₃H₄)NCy}CH₂Ph] [PhCH₂B(C₆F₅)₃] L = Cp **15**, Cp* **17** and [LZr{CyNC(CpFeC₃H₄)NCy}CH₂Ph] [B(C₆F₅)₄] L = Cp **16**, Cp* **18** were cleanly generated by methyl and benzyl group abstraction as evidenced by NMR data. In the case of the benzyl cationic species **15** and **17**, the upfield resonance of the *ortho*-proton of the benzyl group at 6.49 ppm in the ¹H NMR spectrum, suggested an η^2 bonding to Zr.³⁷ Decomposition of **15** and **16** was observed in solution after 24 h but other ion pairs were stable for few days.

Catalysts derived from the activation of the complex **4**, **5**, **7** and **8** with MAO showed low polymerization activity of 66, 27, 36 and 8 g (mmol h atm)⁻¹, respectively. These activities are significantly lower than the Cp₂ZrCl₂ standard (627 g (mmol h atm)⁻¹. The trend for the higher activity of the Zr derivative **4** in comparison to the Ti species **5** has been observed for benzamidinate complexes.^{29,10h}

Similarly, polymerizations were conducted using 10 μ mol of the respective precatalyst (**9**,**10**), one equivalent of either B(C₆F₅)₃ or [Ph₃C][B(C₆F₅)₄] and twenty equivalents of ⁱBu₃Al as a solvent scrubber in 50 mL of toluene. Again, only moderate activities at best were observed. It is noted that the catalysts generated from **9** and **10** showed activities of 45 and 43 g (mmol h atm)⁻¹ upon activation with B(C₆F₅)₃ and 87 and 57 g (mmol h atm)⁻¹ upon activation with [Ph₃C][B(C₆F₅)₄]. The activities derived from **11** and **12** were very low even at elevated temperatures and could not be measured reproducibly.

Conclusions

Herein we have shown that ferrocenyl-(amidinate) complexes of Ti and Zr are readily prepared. *Bis*-ligand dichloride complexes as well as cyclopentadienyl derivatives are reported. Subsequent alkylation and alkyl group abstraction affords neutral dialkyland monoalkyl cationic derivatives. Electrochemical studies revealed quasi reversible oxidation and reduction waves for the ferrocene/ferrocenium couple. These complexes are also shown to be precursors for ethylene polymerization catalysts that show low activities. Building on these observations we are now targeting new ferrocenyl-based ligands for the development of more active catalysts. The results of these studies will be reported in due course.

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