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Coordination and Reactivity Study of Titanium and Zirconium Complexes of the First Imidazol-2-imine Ethenolate Ligand

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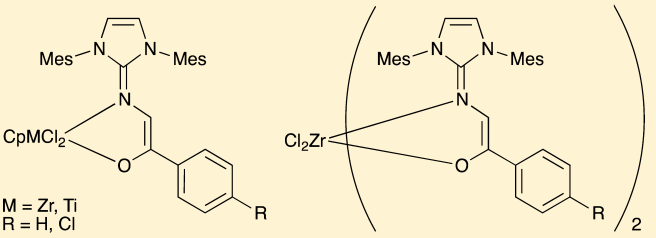
Supporting Information

ABSTRACT: The synthesis and structural characterization of group 4 transition metal complexes bearing a novel imidazol-2-imine enolate ligand with different electronic properties are reported. X-ray crystallographic studies of a cyclopentadienyl zirconium complex confirmed the coordination motif of the ligand through the imine nitrogen and ethenolate oxygen atoms, yielding a new class of formally four-electron-donor monoanionic bidentate ligands. The activities of the corresponding titanium(IV) and zirconium(IV) complexes in ethylene polymerization were assessed, resulting in activities up to 170 kg PE mol^{-1} h^{-1}.



INTRODUCTION

N-Heterocyclic carbenes (NHC) have played a dominant role as ligands in transition metal chemistry since their first isolation by Arduengo in 1991.[1] The strong σ-donating capability of NHCs results in the formation of strong metal bonds, which enhance the thermal stability of complexes.[2] This has been a key contributor to their widespread use as ancillary ligands in transition metal catalysts.[3] More recently, the reactivity of NHCs toward azides has been explored, generating a new class of anionic imidazol-2-iminate ligands that are analogous to phenoxides.[4−7] Because of the stability of imidazolium salts, these imidazol-2-iminates can exist in different mesomeric forms with unexpectedly high electron density located on the exocyclic nitrogen (Figure 1). Several groups have recently

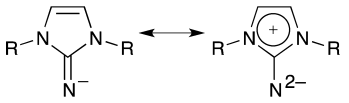
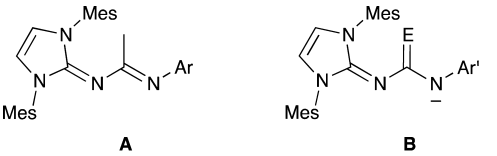


Figure 1. Mesomeric structures of substituted imidazole-2-iminate.

explored the possibility to utilize imidazol-2-iminates either as ancillary monodentate monoanionic ligands[4−7] or as neutral fragments incorporated in more complex bidentate and tridentate ligand scaffolds.[6,8]

Our group has reported the synthesis of neutral imine imidazol-2-imine ligands (**A**, Figure 2) and their coordination to titanium(IV) and palladium(II).[9,10] The structural characterization of these complexes showed two different binding modes depending on the metal center.[9] While the ligand coordinates to Ti(IV) in the expected N^N chelate, the use of Pd(II) led to the formation of a dimeric structure with monodentate coordination of the ligand to the metal through the terminal imine nitrogen. To enforce coordination of the ligand in a bidentate fashion to both early and late transition metals, we



Ar = 2,6-dimethylphenyl, Ar' = 4-methylphenyl; E = O, S

Figure 2. Neutral (**A**) and anionic (**B**) bidentate ligands with an imidazol-2-imine fragment.

recently reported the related *anionic* ureate and thioureate ligands (**B**, Figure 2).[11]

Other bidentate monoanionic systems, and most notably the substituted salicylaldiminate ligands, have proven to be extremely versatile and have led to highly active olefin polymerization catalyst precursors based on both early and late transition metals. Studied by Fujita[12] and Grubbs,[13] these salicylaldiminate ligands coordinate to the metal through the neutral imine nitrogen and anionic oxygen atoms (Figure 3). While the new anionic ureate and thioureate ligands **B** coordinated to both early and late transition metals in a bidentate fashion, thereby successfully addressing the shortcomings of the first-generation neutral ligand system **A**, both the desired $N_{p\text{-tolyl}}$^$N_{\text{imidazol-2-ylidene}}$ and the undesired $N_{p\text{-tolyl}}$^E

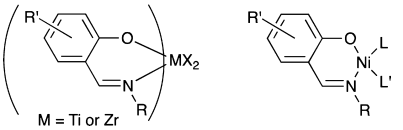


Figure 3. Early and late transition metal complexes of the salicylaldiminate ligand system.

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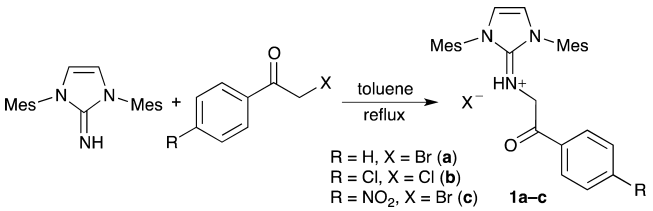
(E = O, S) chelates, with an uncoordinated imidazol-2-imine fragment, were observed. Inspired by the salicylaldiminate system, we decided to design a new ligand scaffold that could bind to the metal center in a bidentate fashion exclusively through a *neutral* imine nitrogen donor and an *anionic* oxygen donor. As such, the new ligand scaffold combines an imidazol-2-imine fragment, as the neutral nitrogen donor, and an enolate, as the anionic oxygen donor. The synthesis of these new substituted N^O ligands, their coordination to group 4 metals, and the potential of the resulting complexes as ethylene polymerization catalysts are reported.

RESULTS AND DISCUSSION

The ketone imidazol-2-imine ligand precursors **1a–c** were prepared in good yield (75–89%) by refluxing a toluene solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-imine[4] with the corresponding 2-halo-1-arylethanone for 12 h (Scheme 1). Solution NMR spectra for compounds **1a–c** are

Scheme 1. Synthesis of 2-(1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-imino)-1-arylethanone Hydrochloride (1a–c)



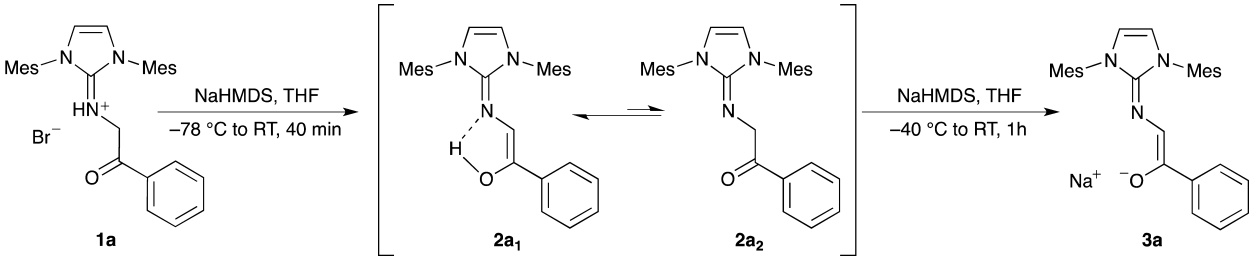
consistent with their expected structure. All ^{1}H and ^{13}C resonances were assigned using a series of one- and two-dimensional ^{1}H and ^{13}C NMR experiments, including heteronuclear single quantum correlation (HSQC) and heteronuclear multiple-bond correlation (HMBC) techniques. The characteristic iminic proton for **1a–c** appears at δ 7.99, 9.71, and 8.26, respectively, as a triplet, coupled to two vicinal methylene protons (^{3}J = 6.4–6.9 Hz). These methylene protons and those of the imidazole backbone resonate at approximately δ 4.5 and 6.7, respectively.

Deprotonation of compound **1a** with one equivalent of sodium hexamethyldisilazide (NaHMDS) gave a mixture of two tautomers, $\mathbf{2a_1}$ and $\mathbf{2a_2}$, in a 3:1 ratio (Scheme 2). The major tautomer was identified spectroscopically as the enol ($\mathbf{2a_1}$), with the characteristic vinyl proton and the corresponding carbon nucleus resonating, respectively, at δ 6.39 and 108.6 in chloroform-d_1. The methylene protons of the corresponding minor keto tautomer ($\mathbf{2a_2}$) were observed as a singlet at a lower frequency (δ 4.40), integrating to two protons, with the α-carbon atom resonating at δ 54.5. Further deprotonation of the tautomeric mixture **2a** with an additional equivalent of NaHMDS gave **3a**, as a single product, in 87% yield (Scheme 2). The proton on the α-carbon atom resonates downfield at δ 6.21 (C_6D_6), with the carbon nucleus observed in the expected vinyl region of the spectrum at δ 103.8.

The sodium ethenolate salt **3a** could also be prepared directly by addition of two equivalents of base to **1a** and used with no further purification in the preparation of titanium and zirconium complexes. Thus, addition of two equivalents of NaHMDS at −40 °C to a THF suspension of compound **1a**, with subsequent warming to room temperature, resulted in an intense yellow solution of **3a**. Without further purification, the sodium ethenolate solution was added to a THF solution of $ZrCl_4(THF)_2$ in a 2:1 stoichiometric ratio, resulting in the immediate precipitation of the desired bis(imine ethenolate) zirconium dichloride complex **4a** as a yellow solid in moderate yield (60%) (Scheme 3). Similarly, the *para*-chloro derivative **4b** could also be prepared from **1b**, albeit in slightly lower yield (42%). Attempts to synthesize the *p*-nitrophenyl analogue from **1c** resulted in a mixture of reaction products that could not be successfully isolated.

Compounds **4a** and **4b** were characterized by NMR spectroscopy and combustion analysis. The ^{1}H NMR spectrum ($CDCl_3$) of **4a** contained only one set of resonances, indicating the selective generation of a single isomer with two sets of ligands that are magnetically equivalent. As expected, the NMR spectrum of **4a** no longer displays the distinctive triplet at δ 7.99 corresponding to the imine proton of **1a**. A singlet observed at δ 5.91 for the vinylic protons of the ligand, integrating to two protons (one proton for each set of ligands), is consistent with double deprotonation of **1a** and coordination to zirconium. The azole ring backbone protons resonate at δ 6.59 as a singlet integrating to four protons (two protons for each set of ligands). As observed for compound **4a**, the ^{1}H and ^{13}C NMR spectra of **4b** show only one set of resonances for the enolate ligands, indicating the generation of a single coordination isomer. Although the structure of neither **4a** nor **4b** could be confirmed by X-ray diffraction studies, based on zirconium work using ureate and thioureate ligands[11] and substituted salicylaldiminate ligands,[14–16] we would expect the chloride atoms to adopt a *cis* conformation, with both enolate ligands coordinated to the metal with the oxygen atoms *trans* to each other. However, in bis(salicylaldiminate) metal complexes with sterically demanding substituents on the imine nitrogen, a *trans*-N/*cis*-O/*cis*-Cl isomer is in fact preferred.[14,16,17] Considering that our ethenolate ligand bears most of the bulk on the nitrogen atom, we think that complexes **4a** and **4b** may also adopt a *trans*-N/*cis*-O/*cis*-Cl arrangement. This is supported by

Scheme 2. Sequential Deprotonation of 1a to Generate a Tautomeric Mixture of 2-(1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-imine)-1-phenylethanone ($\mathbf{2a_1}$ and $\mathbf{2a_2}$) and the Corresponding Ethenolate (3a)



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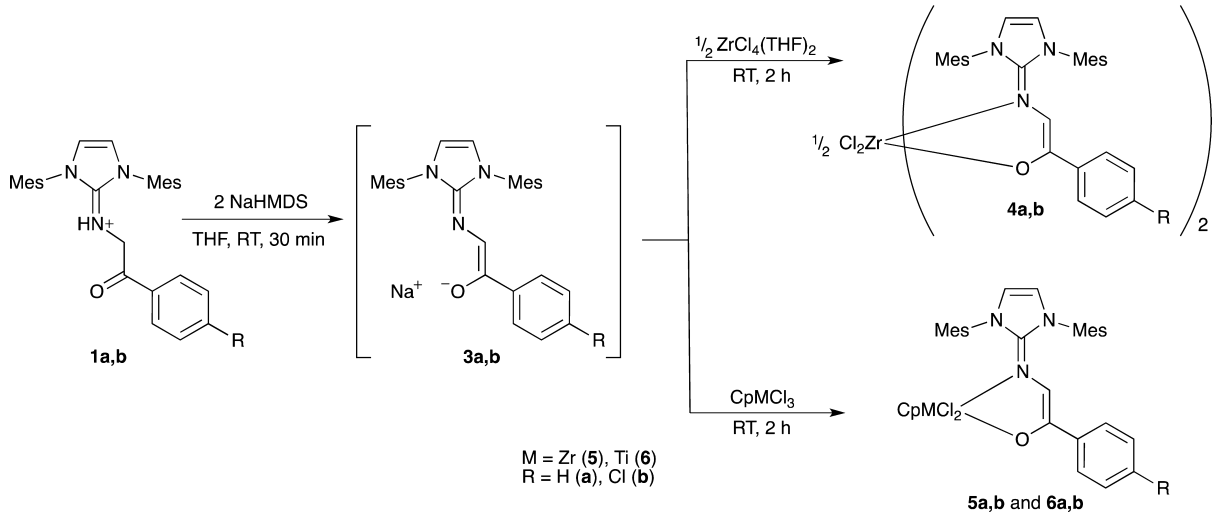
Scheme 3. Synthesis of Titanium and Zirconium Complexes of the Bis(imine ethenolate) Ligand



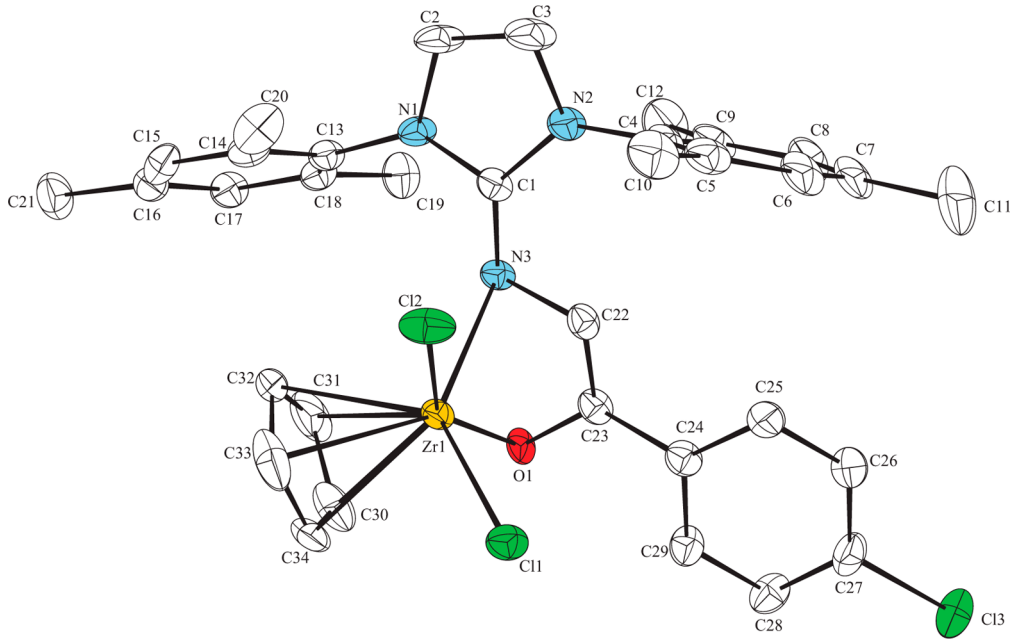


Figure 4. ORTEP drawing (50% probability) of **5b**. Only one of two independent molecules found in the asymmetric unit cell is drawn. H atoms and diethyl ether were omitted for clarity.

DFT (B3LYP/LanL2DZ) calculations on compound **4a**, which predicts this isomer to be 12.6 kcal/mol more stable than the corresponding *cis*-N/*trans*-O/*cis*-Cl isomer. Attempts to prepare the related titanium complexes using the same methodology led only to mixtures of species, possibly coordination isomers, which could not be isolated and characterized.

Cyclopentadienyl (imine ethenolate) complexes of zirconium (**5**) and titanium (**6**) were prepared by adding the ethenolate salt, prepared in situ by double deprotonation of **1** with NaHMDS, to $CpMCl_3$ (Scheme 3). The zirconium complexes **5a** and **5b** were isolated as yellow solids in 47% and 59% yield, respectively. The ^{1}H NMR spectra of both complexes showed characteristic resonances of the ethenolate ligand, with an additional resonance for the cyclopentadienyl protons at δ 6.0 in chloroform-d_1, integrating to five protons.

Crystals of compound **5b** suitable for X-ray diffraction studies were grown at −35 °C under nitrogen by slow liquid diffusion of diethyl ether into a saturated CH_2Cl_2 solution. Compound **5b** exhibits a distorted piano stool geometry with the cyclopentadienyl ligand adopting an η^5 hapticity (Figure 4; Table 1). As expected, the ligand coordinates in a bidentate fashion though the imine nitrogen and ethenolate oxygen atoms. The formation of a five-membered metallacycle leads to an O1−Zr−N3 bite angle of 75.92(9)°, which is significantly larger than that observed for the four-membered metallacycle formed in Ti(IMesN^Imine)Cl_4 (60.50(12)°). The cyclopentadienyl ligand is asymmetrically bound to zirconium, with Zr−C bond lengths ranging from 2.481(4) to 2.534(4) Å, with shorter bonds *anti* to the chloride atoms and longer ones *anti* to the imine ethenolate donor atoms. The mesityl rings of the ligand are almost orthogonal to the best plane formed by the imidazol-2-imine ring, at 84.36° and 70.21°, respectively.

The *p*-chlorophenyl and azole rings slightly deviate by 9.1° and 17.9°, respectively, from coplanarity with the best plane

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Table 1. Selected Bond Lengths and Bond Angles for Compound 5b[a]

selected bond lengths (Å)		selected bond angles (deg)	
Zr1−Cl1	2.463(1)	O1−Zr1−N3	75.92(9)
Zr1−Cl2	2.4995(9)	O1−Zr1−Cl1	90.80(7)
Zr1−O1	2.059(2)	N3−Zr1−Cl1	131.58(7)
Zr1−N3	2.276(3)	O1−Zr1−Cl2	145.06(7)
Zr1−C30	2.521(4)	N3−Zr1−Cl2	79.70(7)
Zr1−C31	2.492(4)	Cl1−Zr1−Cl2	86.95(4)
Zr1−C32	2.481(4)	Zr1−N3−C1	141.00(2)
Zr1−C33	2.503(4)	Zr1−N3−C22	83.15(2)
Zr1−C34	2.534(4)	Zr1−O1−C23	92.15(2)
N1−C1	1.363(4)	C1−N3−C22	118.65(3)
N2−C1	1.377(4)	N3−C22−C23	119.25(3)
N3−C1	1.332(4)	C22−C23−O1	117.20(3)
N3−C22	1.413(4)		
C22−C23	1.357(5)		
O1−C23	1.356(4)		

[a]Average bond lengths and angles for both molecules present in the asymmetric unit cell.

formed by N3, C22, C23, and O1, possibly indicating little electron delocalization from the imidazole ring to the exocyclic atoms (N3, C22, C23, and O1). However, the C1−N3 bond is only slightly shorter than C1−N1, C1−N2, and C22−N3. Furthermore, the length of these bonds, as well as those for C22−C23 and O1−C23, are all intermediate to those expected for single and double bonds,[18] indicating significant bond conjugation. Interestingly, despite the relatively long Zr1···C22 and Zr1···C23 distances (2.5 Å), the position of zirconium with respect to the ethenolate ligand in fact resembles that of metal bound to an η^4-1,4-butadiene ligand, perhaps another manifestation of the double-bond character between N3 and C22, and O1 and C23, which would arise from electron delocalization from the imidazole ring through the conjugated system. The orientation of the ethenolate ligand results in a fold angle between the best plane containing Zr1, N3, and O1 and the one containing N3, C22, C23, and O1 of 68.74°.

While the steric influence of the bulky imidazole ring cannot be ruled out, the weaker Coulombic interactions between the formally charged metal center and the neutral nitrogen donor, in constrast to the negatively charged oxygen atom, likely account for the longer Zr1−N3 bond (2.276(3) Å), compared to Zr1−O1. Furthermore, π-donation of the oxygen atom to the Lewis acidity metal center leads to a Zr1−O1 bond length of 2.059(2), which is intermediate between those for Zr−O single (2.17 Å) and Zr═O double (1.84 Å) bonds.[18]

Addition of one equivalent of sodium ethenolate **3a** and **3b**, prepared in situ, to $CpTiCl_3$ resulted in an immediate color change of the THF solution from yellow to deep blue, indicative of a ligand-to-metal charge transfer, with formation of complexes **6a** and **6b** in 74% and 56% yield, respectively. NMR spectra of both complexes are in agreement with their structure, with resonances and chemical shifts similar to those observed for compounds **5a** and **5b**. Attempts to prepare the cyclopentadienyl zirconium and titanium complexes of the *p*-nitrophenyl derivative resulted in a mixture of reaction products that could not be successfully isolated.

All titanium and zirconium complexes were evaluated for their activity in ethylene polymerization. Complexes were activated with methylaluminoxane (MAO) as cocatalyst in toluene, at room temperature and at one atmosphere of ethylene. While all four zirconium complexes gave only trace amounts of polyethylene (PE), titanium complex **6a** gave polymer at a moderate rate of 110 kg PE mol cat^{-1} h^{-1}. The small electronic perturbation arising from replacing the *para* hydrogen atom with the more electronegative chlorine atom led to a slight enhancement in catalytic activity for complex **6b** (170 kg PE mol cat^{-1} h^{-1}). These activities favorably compare to the best ones reported by Lancaster and Bochmann for a series of titanium and zirconium cyclopentadienyl salicylaldiminate complexes.[19] While they are also comparable to those reported for bis(salicylaldiminate)$ZrCl_2$ complexes that have small alkyl substituents on the phenol ring, these activities are orders of magnitude lower than those of related complexes with larger *tert*-butyl, adamantyl, and cumyl groups.[14] The lower activity observed in our complexes may therefore be a result of an unoptimized substitution pattern on the ethenolate ligand. Alternatively, it may also be a result of either the different ligand arrangement (*trans*-N/*cis*-O/*cis*-Cl vs *cis*-N/*trans*-O/*cis*-Cl) or a less electrophilic metal center, a result of electron delocalization from the imidazole ring to the exocyclic nitrogen atom.[7,9−11]

CONCLUSIONS

The synthesis of a new monoanionic bidentate ligand structure that incorporates the electron-rich imidazol-2-imine fragment was reported for the first time and coordinated to zirconium and titanium. Bis(ethenolate) and (cyclopentadienyl)(ethenolate) metal dichloride complexes were successfully prepared and fully characterized. The solid-state structure of the cyclopentadienyl zirconium complex **5b** confirmed the targeted bidentate coordination of the ligand, resulting in a four-legged piano stool configuration. The synthesis of the bis(imine ethenolate) zirconium dichloride complexes furthermore proved to be very selective, with the formation of one single highly symmetric molecule. While all zirconium complexes tested showed no activity in ethylene polymerization, both titanium complexes **6a** and **6b** were effective catalysts at room temperature, with activities up to 170 kg PE mol cat^{-1} h^{-1}. A decrease in the electron-donating capabilities of the ligand through the inductive effect of a more electronegative chlorine atom led to enhanced catalyst activities. Work aimed at determining the effect of other ligand subtitution patterns on catalyst performance will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere in a drybox or using standard Schlenk techniques. Solvents used in the preparation of air- and/or moisture-sensitive compounds were dried using an MBraun Solvent Purification System fitted with alumina columns and stored over molecular sieves under a positive pressure of argon. Toluene for polymerization was distilled under argon after being dried with the MBraun SPS. Deuterated solvents were degassed using three freeze−pump−thaw cycles. C_6D_6 and $CDCl_3$ were vacuum distilled from sodium and CaH_2, respectively, and stored under nitrogen. NMR spectra were recorded on a Bruker DRX 600 (^{1}H at 600 MHz, ^{13}C at 150.9 MHz), Bruker AV 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), or Bruker AV 300 (^{1}H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances, and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Elemental compositions were determined by Guelph Chemical Laboratories Inc. located in Guelph, Ontario.

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All metal precursors were purchased from either BDH or Sigma-Aldrich. All acetophenones and NaHMDS were purchased from Sigma-Aldrich and used as received. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. MAO was graciously donated by Albemarle Corp. Lastly, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-imine[4] and $ZrCl_4(THF)_2$[20] were prepared using published procedures.

General Procedure for the Synthesis of 2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(aryl)ethanone Hydrochloride Salt, IMesN^ethanone·HX, 1a–c. In a typical procedure, the substituted 2-halo-1-(4-substituted phenyl)ethanone (3.65 mmol) was added as a solid to a toluene (20 mL) solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-imine (3.28 mmol). The solution was refluxed for a few hours, resulting in the formation of a precipitate. The reaction mixture was then cooled to room temperature and filtered. The solid was washed with pentane (2 × 15 mL) and dried in vacuo to yield the product as a powder.

2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethanone hydrobromide salt, ***1a:*** 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): *major isomer (keto form, 82%)* δ 7.99 (t, 1H, J = 6.9 Hz, NH), 7.49 (t, 1H, J = 7.8 Hz, *p*-$CH_{(phenyl)}$), 7.46 (d, 1H, J = 7.8 Hz, *o*-$CH_{(phenyl)}$), 7.30 (t, 1H, J = 7.8 Hz, *m*-$CH_{(phenyl)}$), 6.89 (s, 4H, *m*-$CH_{(mesityl)}$), 6.77 (s, 2H, −NC*H*C*H*N−), 4.48 (d, 2H, J = 6.9 Hz, =NH−CH_2−C−), 2.23 (s, 12H, *o*-$CH_{3(mesityl)}$), 2.21 (s, 6H, *p*-$CH_{3(mesityl)}$); *minor isomer (enol form, 18%; some resonances are missing due to accidental overlap with those of the major isomer)* δ 7.06 (s, 4H, *m*-$CH_{(mesityl)}$), 6.83 (s, 2H,, −NC*H*C*H*N−), 6.69 (s + br, 2H, =N*H*−C*H*=CPh−), 4.97 (s + br, 1H, −C(Ph)O*H*), 2.35 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.16 (s, 12H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *major isomer* δ 192.2 (O=*C*), 144.8 (−NCN−), 141.4 (*ipso*-$C_{(mesityl)}$), 136.0 (*o*-$C_{(mesityl)}$), 133.7 (*p*-$C_{(phenyl)}$), 130.0 (*p*-$C_{(mesityl)}$), 128.4 (*o*-$C_{(phenyl)}$), 127.5 (*m*-$C_{(phenyl)}$), 117.7 (−NCHCHN−), 48.6 (=NH−CH_2−C−), 21.1 (*p*-$CH_{3(mesityl)}$), 17.8 (*p*-$CH_{3(mesityl)}$); *minor isomer (some resonances are missing due to accidental overlap with those of the major isomer)* δ 145.2 (−NCN−), 141.4 (*o*-$C_{(mesityl)}$), 135.6 ($C_{(mesityl)}$), 130.4 (*p*-$C_{(mesityl)}$), 117.2 (−NCHCHN−), 21.2 (*p*-$CH_{3(mesityl)}$), 17.6 (*p*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{29}H_{32}BrN_3O$ (%): C, 67.18; H, 6.22; N, 8.10. Found (%): C, 67.20; H, 6.31; N, 8.35.

2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(4-chlorophenyl)ethanone hydrochloride salt, ***1b:*** 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (t, 1H, J = 6.4 Hz, N*H*), 7.42 (d, 2H, J = 8.7 Hz, *o*-$CH_{(phenyl)}$), 7.28 (d, 2H, J = 8.7 Hz, *m*-$CH_{(phenyl)}$), 6.91 (s, 4H, *m*-$CH_{(mesityl)}$), 6.67 (s, 2H, −NC*H*C*H*N−), 4.47 (d, 2H, J = 6.4 Hz, =NH−CH_2−C−), 2.22 (s, 18H, *p*-$CH_{3(mesityl)}$ + *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.4 (O=*C*), 145.2 (−NCN−), 141.3 (*p*-$C_{(mesityl)}$), 140.0 (*ipso*-$C_{(phenyl)}$), 132.2 (*p*-$CH_{(phenyl)}$), 130.4 (*o*-$C_{(mesityl)}$), 130.1 (*m*-$CH_{(mesityl)}$), 128.9 (*ipso*-$C_{(mesityl)}$), 128.8 (*o*-$CH_{(phenyl)}$), 128.7 (*m*-$CH_{(phenyl)}$), 117.3 (−NCHCHN−), 48.5 (=NH−CH_2−C−), 21.1 (*p*-$CH_{3(mesityl)}$), 17.7 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{29}H_{31}Cl_2N_3O$ (%): C, 68.50; H, 6.14; N, 8.26. Found (%): C, 68.66; H, 5.95; N, 8.44.

2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(4-nitrophenyl)ethanone hydrobromide salt, ***1c:*** 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (t, 1H, J = 6.4 Hz, N*H*), 8.16 (d, 2H, J = 8.7 Hz, *m*-$CH_{(nitrophenyl)}$), 7.68 (d, 2H, J = 8.7 Hz, *o*-$CH_{(nitrophenyl)}$), 6.93 (s, 4H, *m*-$CH_{(mesityl)}$), 6.74 (s, 2H, NC*H*C*H*N), 4.60 (d, 2H, J = 6.4 Hz, =NH−CH_2−C−), 2.22 (s, 12H, *p*-$CH_{3(mesityl)}$) 2.16 (s, 6H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.6 (O=*C*), 144.8 (−NCN−), 150.5 (*p*-$C_{(nitrophenyl)}$), 138.3 (*ipso*-$C_{(nitrophenyl)}$), 136.0 (*ipso*-$C_{(mesityl)}$), 135.6 (*p*-$C_{(mesityl)}$), 130.2 (*o*-$C_{(mesityl)}$), 128.6 (*o*-$CH_{(nitrophenyl)}$), 123.5 (*m*-$CH_{(nitrophenyl)}$), 117.6 (−NCHCHN−), 49.0 (=NH−CH_2=C−), 17.7 (*o*-$CH_{3(mesityl)}$), 17.6 (*p*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{29}H_{31}BrN_4O_3$ (%): C, 61.81; H, 5.55; N, 9.94. Found (%): C, 61.85; H, 5.38; N, 10.12.

2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethanone, IMesN^ethanone, 2a. Compound **1a** (2.6 g, 5.0 mmol) was suspended in THF (30 mL), and a solution of NaHMDS (938 mg, 5.11 mmol) in THF (10 mL) was added dropwise at −78 °C. The reaction mixture was stirred for 10 min, subsequently slowly warmed to room temperature, and stirred for an additional 30 min. The pale yellow solution was filtered, evaporated to dryness, and extracted with pentane (2 × 30 mL). The off-white solid was dried in vacuo, and the pale yellow pentane solution was concentrated to 15 mL and left at −78 °C for 4 h to collect additional product through precipitation. The precipitated off-white solid was washed with cold (−78 °C) pentane (10 mL) and dried in vacuo. Yield: 1.8 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$): *major isomer (enol form 75%)* δ 7.41 (d, 1H, J = 7.7 Hz, *o*-$CH_{(phenyl)}$), 7.08 (t, 1H, J = 7.7 Hz, *p*-$CH_{(phenyl)}$), 6.94–6.84 (m, 2H, *m*-$CH_{(phenyl)}$), 6.71 (s, 4H, *m*-$CH_{(mesityl)}$), 6.39 (s, 1H, =N−C*H*=C−), 5.60 (s, 2H, −NC*H*C*H*N−), 2.13 (s, 12H, *o*-$CH_{3(mesityl)}$), 2.11 (s, 6H, *p*-$CH_{3(mesityl)}$); *minor isomer (keto form, 25%)* δ 7.57 (d, 1H, J = 7.7 Hz, *o*-$CH_{(phenyl)}$), 7.04–6.84 (m, 2H, *m*-$CH_{(phenyl)}$ + 1H, *p*-$CH_{(phenyl)}$), 6.62 (s, 4H, *m*-$CH_{(mesityl)}$), 5.65 (s, 2H, −NC*H*C*H*N−), 4.40 (s, 2H, =N−CH_2−C−), 2.35 (s, 12H, *o*-$CH_{3(mesityl)}$), 1.98 (s, 6H, *p*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *major isomer* δ 141.9 (−NCN−), 136.4 ($C_{(mesityl)}$), 136.2 (O−*C*), 133.9 (*o*-$C_{(mesityl)}$), 128.9 (*p*-$C_{(mesityl)}$), 126.1 (*p*-$C_{(phenyl)}$), 129.1 (*m*-$C_{(phenyl)}$), 123.2 (*o*-$C_{(phenyl)}$), 108.6 (=N−CH=C−), 114.7 (−NCHCHN−), 21.6 (*p*-$CH_{3(mesityl)}$), 18.6 (*o*-$CH_{3(mesityl)}$); *minor isomer* δ 196.6 ($C_{(ketone)}$), 145.5 (−NCN−), 136.7 ($C_{(mesityl)}$), 136.3 ($C_{(phenyl)}$) 132.7 (*m*-$C_{(phenyl)}$), 129.1 (*p*-$C_{(mesityl)}$), 128.8 (*o*-$C_{(mesityl)}$), 128.7 (*p*-$C_{(phenyl)}$), 123.2 (*o*-$C_{(phenyl)}$), 114.2 (−NCHCHN−), 54.5 (=N−CH_2−C−), 21.5 (*p*-$CH_{3(mesityl)}$), 18.9 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{29}H_{31}N_3O$ (%): C, 79.60; H, 7.14; N, 9.60. Found (%): C, 79.35; H, 7.17; N, 9.38.

Sodium 2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethenolate, Na[IMesN^ethenolate], 3a. To a THF (2 mL) suspension of NaH (11.5 mg, 480 μmol) at −40 °C slowly was added a cold (−40 °C) solution of **2a** (150 mg, 343 μmol) in THF (5 mL). The reaction mixture was slowly warmed to room temperature and stirred for 60 min, resulting in the color slowly changing to intense yellow. Pentane (5 mL) was added to precipitate the product, which was filtered, washed with pentane (2 × 5 mL), and dried in vacuo to yield a yellow solid. Yield: 137 mg (87%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.26 (t, 2H, J = 7.4 Hz, *m*-$CH_{(phenyl)}$), 7.08 (t, 1H, J = 7.4 Hz, *p*-$CH_{(phenyl)}$), 6.98 (s, 1H, *m*-$CH_{(mesityl)}$), 6.82 (d, 2H, J = 7.4 Hz, *o*-$CH_{(phenyl)}$), 6.75 (s, 1H, *m*-$CH_{(mesityl)}$), 6.30 (s, 1H, *m*-$CH_{(mesityl)}$), 6.21 (s, 1H, =N−C*H*=C−), 6.08 (s, 1H, *m*-$CH_{(mesityl)}$), 5.61 (d, 1H, J = 2.7 Hz −NC*H*C*H*N−), 5.58 (d, 1H, J = 2.7 Hz −NC*H*C*H*N−), 2.49 (s, 3H, $CH_{3(mesityl)}$), 2.28 (s, 3H, $CH_{3(mesityl)}$), 2.16 (s, 3H, $CH_{3(mesityl)}$), 2.15 (s, 3H, $CH_{3(mesityl)}$), 2.05 (s, 3H, $CH_{3(mesityl)}$), 1.89 (s, 3H, $CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 150.3 (O−*C*), 146.5 (*ipso*-$C_{(mesityl)}$), 141.5 (−NCN−), 137.9 (aromatic *C*H), 137.7 (aromatic *C*H), 137.4 (aromatic *C*H), 136.9 (aromatic *C*H), 135.8 (aromatic *C*H), 135.5 (aromatic *C*H), 135.2 (aromatic *C*H), 133.3 (*ipso*-$C_{(mesityl)}$), 130.3 (aromatic *C*H), 129.6 (aromatic *C*H), 129.0 (aromatic *C*H), 128.7 (*m*-$CH_{(mesityl)}$), 127.7 (*m*-$CH_{(phenyl)}$), 124.5 (*o*-$CH_{(phenyl)}$), 122.5 (*p*-$CH_{(phenyl)}$), 114.3 (−NCHCHN−), 113.8 (−NCHCHN−), 103.8 (=N−C*H*=C−), 21.1 ($CH_{3(mesityl)}$), 20.7 ($CH_{3(mesityl)}$), 19.3 ($CH_{3(mesityl)}$), 18.8 ($CH_{3(mesityl)}$), 18.4 ($CH_{3(mesityl)}$), 16.9 ($CH_{3(mesityl)}$). Anal. Calcd for $C_{29}H_{30}N_3NaO$ (%): C, 75.79; H, 6.58; N, 9.14. Found (%): C, 76.04; H, 6.62; N, 8.87.

General Procedure for the Synthesis of Bis(2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(aryl)ethenolate) Zirconium Dichloride, $ZrCl_2$(IMesNethenolate)$_2$, 4a and 4b. NaHMDS (0.773 mmol) was slowly added at room temperature as a solid to a THF (5 mL) suspension of compound **1** (0.386 mmol). The solution immediately turned a bright yellow, and the reaction mixture was allowed to stir for 30 min. The solution was then added to a THF (2 mL) solution of $ZrCl_2(THF)_2$ (0.386 mmol). A white precipitate formed immediately. The yellow solution was stirred for 2 h, subsequently filtered through a pad of Celite, and dried under reduced pressure. The product was washed with Et_2O (2 × 5 mL) and dried in vacuo to yield a yellow powder.

Bis(2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethenolate) zirconium dichloride, ***4a:*** 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (m, 12H, *m*-$CH_{(mesityl)}$ + *m*-$CH_{(phenyl)}$), 6.88 (d, 2H, J = 7.4 Hz, *p*-$CH_{(phenyl)}$), 6.74 (d, 4H, J = 7.4 Hz, *o*-$CH_{(phenyl)}$), 6.58 (s, 4H, −NC*H*C*H*N−), 5.93 (s, 2H, =N−C*H*=C−), 2.30 (s, 12H, *p*-$CH_{3(mesityl)}$), 2.24 (s, 24H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz,

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$CDCl_3$): δ 145.5 (O−*C*), 139.2 (*p*-$C_{(mesityl)}$), 137.1 (*ipso*-$C_{(phenyl)}$), 136.3 (*ipso*-$C_{(mesityl)}$), 132.3 (−NCN−), 129.6 (*m*-$CH_{(mesityl)}$), 126.9 (*m*-$CH_{(phenyl)}$), 124.3 (*p*-$CH_{(phenyl)}$), 123.5 (*o*-$CH_{(phenyl)}$), 117.4 (−NCHCHN−), 113.0 (=N−*CH*=C−), 21.1 (*p*-$CH_{3(mesityl)}$), 19.2 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{58}H_{60}Cl_2N_6O_2Zr$ (%): C, 67.29; H, 5.84; N, 8.12. Found (%): C, 67.48; H, 6.02; N, 7.94.

Bis(2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(4-chlorophenyl)ethenolate) zirconium dichloride, ***4b:*** 42% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 6.96 (s, 8H, *m*-$CH_{(mesityl)}$) 6.92 (d, 4H, *J* = 8.4 Hz, *m*-$CH_{(chlorophenyl)}$), 6.64 (d, 4H, *J* = 8.4 Hz, *o*-$CH_{(chlorophenyl)}$), 6.59 (s, 4H, −NC*HCH*N−), 5.91 (s, 2H, =N−*CH*=C−), 2.30 (s, 12H, *p*-$CH_{3(mesityl)}$), 2.21 (s, 24H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.4 (O−*C*), 139.3 (*p*-$C_{(mesityl)}$), 136.2 (*ipso*-$C_{(mesityl)}$ + *o*-$C_{(mesityl)}$), 135.6 (*p*-$C_{(chlorophenyl)}$), 132.2 (−NCN−), 129.6 (*m*-$CH_{(mesityl)}$), 129.5 (*ipso*-$C_{(chlorophenyl)}$), 127.1 (*m*-$CH_{(chlorophenyl)}$), 124.5 (*o*-$CH_{(chlorophenyl)}$), 117.5 (−NCHCHN−), 113.4 (=N−CH=C−), 21.1 (*p*-$CH_{3(mesityl)}$), 19.2 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{58}H_{58}Cl_4N_6O_2Zr$ (%): C, 63.09; H, 5.29; N, 7.61. Found (%): C, 63.32; H, 5.01; N, 7.43.

General Procedure for the Synthesis of Cyclopentadienyl (2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(aryl)-ethenolate) Zirconium Dichloride, $CpZrCl_2$(IMesN^ethenolate), 5a and 5b. NaHMDS (0.773 mmol) was slowly added as a solid to a THF (5 mL) suspension of compound **1** (0.386 mmol). The solution immediately turned a bright yellow, and the reaction mixture was allowed to stir for 30 min. The solution was then added to a THF (2 mL) solution of $CpZrCl_3$ (0.386 mmol). A white precipitate immediately formed, and the reaction mixture was allowed to stir for 2 h. The reaction mixture was then filtered through a pad of Celite and dried under reduced pressure. The product was washed with diethyl ether (2 × 5 mL) and dried in vacuo to yield a yellow powder.

Cyclopentadienyl (2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethenolate) zirconium dichloride, ***5a:*** 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13−7.09 (m, 7H, *m*-$CH_{(mesityl)}$ + *o*-$CH_{(phenyl)}$ + *p*-$CH_{(phenyl)}$), 6.92 (dd, 2H, *J* = 7.2, 6.0 Hz, *m*-$CH_{(phenyl)}$), 6.53 (s, 2H, −NC*HCH*N−), 6.10 (s, 1H, =N−*CH*=C−), 6.04 (s, 5H, Cp), 2.34 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.31 (s, 12H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.8 (O−*C*), 147.4 (−NCN−), 140.5 (*p*-$C_{(mesityl)}$), 136.2 (*o*-$C_{(mesityl)}$), 132.9 (*ipso*-$C_{(phenyl)}$), 132.7 (*ipso*-$C_{(mesityl)}$), 130.1 (*m*-$CH_{(mesityl)}$), 128.3 (*p*-$CH_{(phenyl)}$), 127.5 (*o*-$CH_{(phenyl)}$), 125.6 (*m*-$CH_{(phenyl)}$), 117.7 (−NCHCHN−), 115.8 (Cp), 103.9 (=N−CH=C−), 21.0 (*p*-$CH_{3(mesityl)}$), 18.7 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{34}H_{35}Cl_2N_3OZr$ (%): C, 61.52; H, 5.31; N, 6.33. Found (%): C, 61.30; H, 5.24; N, 6.10.

Cyclopentadienyl (2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(4-chlorophenyl)ethenolate) zirconium dichloride, ***5b:*** 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 4H, *m*-$CH_{(mesityl)}$), 7.06 (d, 2H, *J* = 8.5 Hz, *o*-$CH_{(chlorophenyl)}$), 6.84 (d, 2H, *J* = 8.5 Hz, *m*-$CH_{(chlorophenyl)}$), 6.55 (s, 2H, −NC*HCH*N−), 6.09 (s, 1H, =N−*CH*=C−), 6.02 (s, 5H, Cp), 2.34 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.30 (s, 12H, *o*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.5 (−NCN−), 146.6 (O−*C*), 140.5 (*p*-$C_{(mesityl)}$), 136.1 (*o*-$C_{(mesityl)}$), 133.8 (*p*-$C_{(chlorophenyl)}$), 132.6 (*ipso*-$C_{(mesityl)}$), 131.6 (*ipso*-$C_{(chlorophenyl)}$), 130.3 (*m*-$CH_{(mesityl)}$), 127.7 (*o*-$CH_{(chlorophenyl)}$), 126.8 (*m*-$CH_{(chlorophenyl)}$), 117.8 (−NCHCHN−), 115.9 (Cp), 104.71 (=N−CH=C−), 21.0 (*p*-$CH_{3(mesityl)}$), 18.7 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{34}H_{34}Cl_3N_3OZr$ (%): C, 58.49; H, 4.91; N, 6.02. Found (%): C, 58.64; H, 4.72; N, 5.76.

General Procedure for the Synthesis of Cyclopentadienyl (2-(1,3-Bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(aryl)-ethenolate) Titanium Dichloride, $CpTiCl_2$(IMesN^ethenolate), 6a and 6b. Compounds **6a** and **6b** were prepared using the same procedure used for the preparation of compounds **5a** and **5b**, with the exception that the $CpTiCl_3$ was used as metal precursor. The product was purified by redissolving it in toluene, filtering the mixture, and removing the volatiles in vacuo to yield blue powders. Analytically pure samples were obtained by recrystallization from THF and pentane at −35 °C.

Cyclopentadienyl (2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-phenylethenolate) titanium dichloride, ***6a:*** 74% yield; ^{1}H NMR (400 MHz, C_6D_6): δ 7.19−7.17 (m, 4H, *o*-$CH_{(phenyl)}$ + *m*-$CH_{(phenyl)}$), 6.90 (d, 1H, *J* = 8.5 Hz, *p*-$CH_{(phenyl)}$), 6.78 (s, 1H, =N−*CH*=C−), 6.73 (s, 4H, *m*-$CH_{(mesityl)}$), 6.12 (s, 5H, Cp), 5.56 (s, 2H, −NC*HCH*N−), 2.12 (s, 12H, *o*-$CH_{3(mesityl)}$), 2.09 (s, 6H, *p*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 156.8 (O−*C*), 144.8 (−NCN−$_{(mesityl)}$), 139.1 (*p*-$C_{(mesityl)}$), 137.7 (*ipso*-$C_{(phenyl)}$), 136.5 (*o*-$C_{(mesityl)}$), 133.9 (*ipso*-$C_{(mesityl)}$), 129.6 (*m*-$CH_{(mesityl)}$), 127.0 (*m*-$CH_{(phenyl)}$), 125.4 (*p*-$CH_{(phenyl)}$), 124.2 (N−CH=C), 122.3 (*o*-$CH_{(phenyl)}$), 120.5 (Cp), 115.0 (−NCHCHN−), 20.9 (*p*-$CH_{3(mesityl)}$), 18.0 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{34}H_{35}Cl_2N_3OTi$ (%): C, 65.82; H, 5.69; N, 6.77. Found (%): C, 66.10; H, 5.90; N, 7.02.

Cyclopentadienyl (2-(1,3-bis(2,4,6-trimethylphenyl)imizadol-2-imine)-1-(4-chlorophenyl)ethenolate) titanium dichloride, ***6b:*** 56% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 (d, 2H, *J* = 8.6 Hz, *m*-$CH_{(chlorophenyl)}$), 6.97 (d, 2H, *J* = 8.6 Hz, *o*-$CH_{(chlorophenyl)}$), 6.71 (s, 4H, *m*-$CH_{(mesityl)}$), 6.68 (s, 1H, =N−*CH*=C−), 6.05 (s, 5H, Cp), 5.56 (s, 2H, −NC*HCH*N−), 2.09 (s, 12H, *o*-$CH_{3(mesityl)}$), 2.06 (s, 6H, *p*-$CH_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 155.6 (O−*C*), 144.8 (−NCN−), 139.2 (*p*-$C_{(mesityl)}$), 136.4 (*o*-$C_{(mesityl)}$), 136.3 (*p*-$C_{(chlorophenyl)}$), 133.8 (*ipso*-$C_{(mesityl)}$), 130.7 (*ipso*-$C_{(chlorophenyl)}$), 129.9 (*m*-$CH_{(mesityl)}$), 128.6 (*m*-$CH_{(chlorophenyl)}$), 124.6 (=N−*CH*=C−), 123.4 (*o*-$CH_{(chlorophenyl)}$), 120.6 (Cp), 115.1 (−NCHCHN−), 20.9 (*p*-$CH_{3(mesityl)}$), 17.9 (*o*-$CH_{3(mesityl)}$). Anal. Calcd for $C_{34}H_{34}Cl_3N_3OTi$ (%): C, 62.36; H, 5.23; N, 6.42. Found (%): C, 62.15; H, 5.09; N, 6.38.

General Procedure for Ethylene Polymerization. Ethylene polymerization was performed at atmospheric pressure and room temperature in a 200 mL Schlenk flask containing a magnetic stir bar. The flask was conditioned in an oven at 160 °C for at least 12 h prior to use. The hot flask was brought to room temperature under dynamic vacuum and backfilled with ethylene. This cycle was repeated a total of three times. Under an atmosphere of ethylene, the flask was charged with 20 mL of dry toluene and 1000 equivalents of MAO. The solution was stirred for 15 min before a solution of the catalyst precursor in toluene was introduced into the flask via a syringe. The reaction mixture was vigorously stirred for 10 min and subsequently quenched with a 50:50 mixture of concentrated hydrochloric acid and methanol. The resulting mixture was filtered, and any solid collected was washed with distilled water. Solids collected were dried under vacuum at approximately 60 °C for several hours.

Computational Details. DFT calculations were carried out at the hybrid B3LYP level of theory with LanL2DZ as basis set using Gaussian 9[21] and GaussView 3[22] for computing and molecular visualization, respectively. These calculations were performed on the Shared Hierarchical Academic Research Computing Network (SHARCNET: www.sharcnet.ca).

X-ray Crystallography. Detailed crystallographic data for compound **5b** (tables of atomic coordinates with isotropic and anisotropic displacement parameters, bond lengths and angles) are provided as Supporting Information. Crystallographic data for **5b** were collected at the University of Toronto on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K and were measured using a combination of φ scans and ω scans with κ offsets, to fill the Ewald sphere. Intensity data were processed using the Denzo-SMN package.[23] Absorption corrections were carried out using SORTAV.[24] The structure was solved using Superflip[25] and refined using WinGX[26] with SHELXS-97[27] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **5b** (CCDC reference number 940710). Crystallographic data in CIF and other electronic format, including tables of crystal data and structure refinement, bond lengths, angles, atomic coordinates and equivalent isotropic displacement parameters, and anisotropic displace-

ment parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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