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Coordination and Reactivity Study of Group 4 and 10 Transition Metal Complexes of *N*-Imidazol-2-ylidene-*N′*-*p*-tolylureate and Thioureate Ligands

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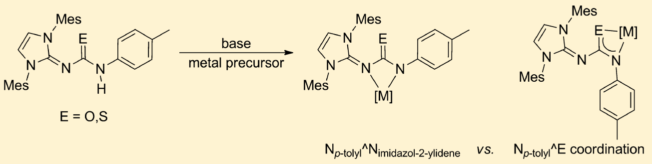
Supporting Information

ABSTRACT: The synthesis and isolation of *N*-imidazol-2-ylidene-*N′*-*p*-tolylureate and thioureate proligands is described. Titanium(IV), nickel(II), and palladium(II) complexes containing one or two equivalents of the ligand were prepared by transmetalation of the ureate or thioureate salts. The X-ray structure of titanium complexes corroborated our prediction based on spectroscopic data and showed the ureate binds in a bidentate fashion through the oxygen and nitrogen atoms of the isocyanate building block, leaving the imidazol-2-imine fragment uncoordinated. Carbon−nitrogen bond lengths indicate substantial electron delocalization from the imidazole ring to the ureate group. In contrast, the ligand adopts a different coordination mode and binds to nickel and palladium through the $N_{\text{imidazol-2-ylidene}}$ and $N_{p\text{-tolyl}}$ atoms. Surprisingly, despite the softer nature of sulfur, coordination of the thioureate was exclusively through the sulfur and nitrogen atoms of the isothiocyanate building block with all three metals studied. All complexes were tested for ethylene polymerization at ambient conditions using methylaluminoxane as cocatalyst. Titanium(IV) complexes were found to be the most active, with activities up to 60 kg PE mol^{-1} catalyst h^{-1}.



INTRODUCTION

The utility of titanium halides and alkylaluminum reagents in the polymerization of ethylene and propylene, first recognized by Ziegler and Natta,[1] has led to the development of several new homogeneous single-site olefin polymerization catalysts over the past decades.[2] Studies of well-defined group 4 metallocenes have in fact provided an excellent mechanistic understanding of the critical elementary steps involved in the formation of polyolefins.[3] Further variations on the ancillary ligands have resulted in several catalysts of group 4 transition metals with enhanced activity and exceptional control over the microstructure of simple polyolefins, such as polypropylene and polystyrene.[4,5]

The report by Brookhart that cationic α-diimine nickel and palladium complexes also gave high molecular weight polyolefins, including functionalized ones such as ethylene−acrylate copolymers, spurred a renewed interest in the field.[6] Neutral group 10 catalysts bearing salicylaldiminate ligands reported shortly thereafter also showed functional group tolerance but resulted in lower polymerization rates.[7] The versatility of these monoanionic salicylaldiminate ligands, which form six-membered chelates, was also demonstrated through their coordination to early transition metals, giving some of the most active polyolefin catalysts to date.[8,9] Our group became interested in developing a new class of bidentate monoanionic ligands that form smaller chelates with metals and exploring the activity of these new complexes in olefin polymerization.

Since the isolation of the first stable N-heterocyclic carbene (NHC),[10] several new classes of carbenes have been studied.[11] Upon coordination, these carbenes form robust transition metal complexes, an attribute that has been successfully employed in a number of catalytic transformations,[12] including olefin polymerization.[13] In addition to their role as ligands, the reactivity of these carbenes with organic azides has also been exploited, producing imidazol-2-iminates as a new class of monoanionic ligands (Figure 1).[14−16] The formation of a stable imidazolium center leads to a significant shift of the electron density to the exocyclic nitrogen, through the formation of the formally zwitterionic structure, with steric and electronic parameters easily tailored through the substituents on the azole ring. While analogous to phenoxides, the bond angles about the azole five-membered ring confer a more opened coordination sphere by positioning the 1,3-substituents farther away from the metal center, critical for the polymerization of α-olefins.

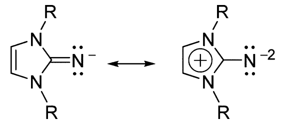


Figure 1. Mesomeric structures for imidazol-2-imine.

Our group has recently prepared a new family of neutral bidentate ligands that incorporate this imidazol-2-imine fragment in their scaffold, and we explored their coordination to titanium and palladium.[17] Solid-state structures of the imine

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imidazol-2-imine titanium and palladium complexes showed that the denticity of the ligand is highly dependent on the metal used (Figure 2). While the ligand coordinates to titanium in the expected chelating form, coordination to palladium was exclusively through the distal imine nitrogen, possibly a result of its enhanced basicity due to electron delocalization from the imidazol-2-imine fragment over the conjugated system.[17]

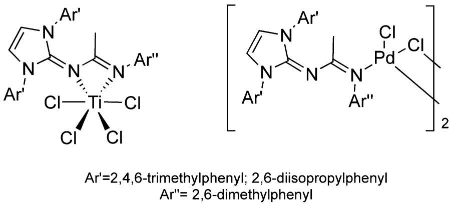


Figure 2. Titanium(IV) and palladium(II) imidazol-2-imine complexes.[17]

To enforce coordination of the ligand in the desired bidentate fashion, we prepared anionic *N*-(imidazol-2-ylidene)-*N*′-(*p*-tolyl)ureate (**A**) and thioureate (**B**) ligands (Figure 3). Herein, we report for the first time the synthesis of both ligands, their coordination to group 4 and 10 transition metals, the effect of the acyl and thioacyl groups on the coordination mode of the ligand, and the activity of these new complexes in ethylene polymerization.

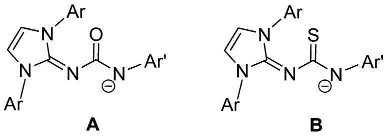


Figure 3. Ureate (**A**) and thioureate (**B**) ligands.

RESULTS AND DISCUSSION

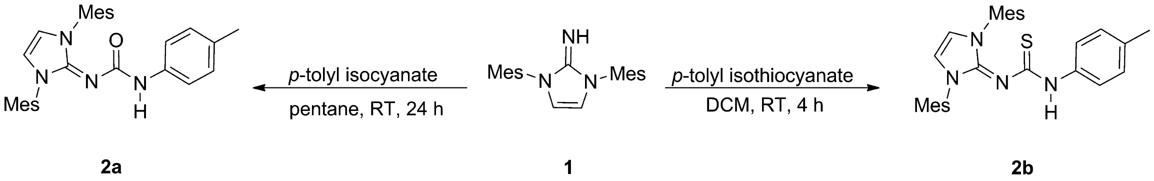
Synthesis and Characterization of the Urea and Thiourea Proligands. The urea **2a** was prepared in quantitative yield from reaction of 1,3-dimesitylimidazol-2-imine (IMes═NH) (**1**)[18] with *p*-tolyl isocyanate and isolated as a crystalline solid (Scheme 1). The imidazolium backbone protons of **2a** resonate as a singlet in the ^{1}H NMR spectrum (C_6D_6) at δ 5.83, a downfield shift from that of the imidazol-2-imine **1** (δ 5.70). The *o*- and *m*-CH protons of the *p*-tolyl group also experience a downfield shift from δ 6.54 and 6.65 in *p*-tolyl isocyanate to δ 7.02 and 6.71 in **2a**. The acyl stretching frequency of **2a** at 1642 cm^{-1} is substantially lower than that of the starting isocyanate (2274 cm^{-1}), indicating a marked decrease in C−O bond strength upon formation of the urea. This observed stretching frequency is also slightly lower than that commonly observed in organic amides,[19] a manifestation of the electron delocalization from the azole ring to the acyl group, resulting in further decreasing the C−O bond order.

The corresponding thiourea proligand analogue **2b** was similarly prepared by reacting imidazol-2-imine **1** with isothiocyanate (Scheme 1). The ^{1}H NMR (C_6D_6) resonances for the backbone imidazole protons and the *ortho* and *meta* protons of the *p*-tolyl group are observed at δ 5.89, 6.90, and 6.78, respectively, downfield from those of the starting materials. The FTIR spectrum of **2b** revealed strong absorption bands at 1400−1600 cm^{-1} assigned to the NCS group. The identification of the vibration modes responsible for these absorptions is however difficult due to mixing of bond deformation, rocking, bending, and stretching, characteristics of both organic thioureas and inorganic thioureate metal complexes.[20] Furthermore, absorption bands that are principally due to stretching of the C═S double bonds are expected at approximately 700 cm^{-1} and predicted to be weak. This was confirmed by DFT frequency calculations (B3LYP/LanL2DZ) on geometry-optimized thioureate metal complexes.[21] Thus, while infrared spectroscopy is an excellent diagnostic tool to predict the coordination mode of ureates in metal complexes, a similar use in thioureate chemistry remains highly uncertain and questionable and, therefore, will not be further discussed in this study.

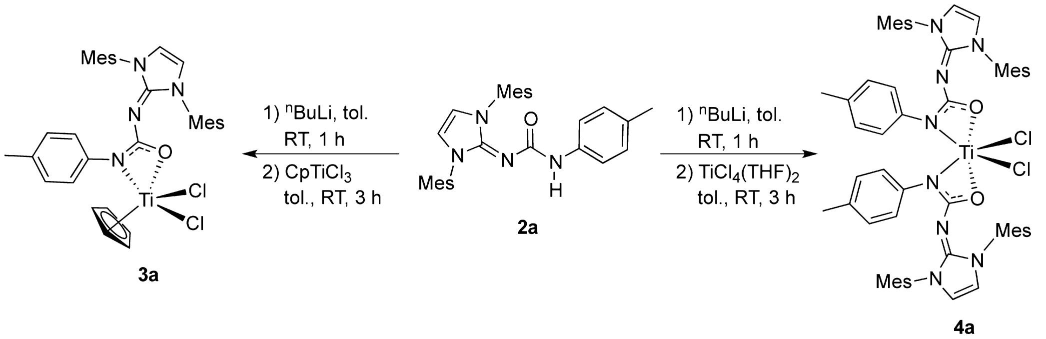
Synthesis and Characterization of *N*-Imidazol-2-ylidene-*N*′-*p*-tolylureate Titanium(IV) Complexes. The (cyclopentadienyl)(ureate)titanium(IV) dichloride complex (**3a**) was prepared by reaction of $CpTiCl_3$ with the lithiated salt of **2a** (Scheme 2). Complex **3a** was isolated in 70% yield as a bright reddish-orange crystalline solid. The ^{1}H NMR spectrum (C_6D_6) of **3a** revealed a downfield shift relative to that observed in **2a** for the *ortho* and *meta* protons of the tolyl group to δ 7.39 and 6.94, respectively, and an upfield shift for the *p*-CH_3 protons to δ 2.09. The imidazolium backbone protons resonate at δ 5.74, only slightly more upfield from that in **2a**, suggesting coordination of the ligand through the oxygen and *p*-tolyl nitrogen atoms. This is further supported by the small change in the ^{13}C NMR chemical shift for the central imidazole carbon observed (δ 148.7 for **3a** vs 149.8 for **2a**) and the more significant change in that of the *ipso*-carbon of the *p*-tolyl ring (δ 146.2 for **3a** vs 139.4 for **2a**). The carbonyl carbon nucleus resonates at δ 162.0, compared to δ 158.0 for **2a**. Furthermore, the decrease in the C═O stretching frequency ($\nu_{C=O}$ 1524 cm^{-1}) compared to that of the starting urea ($\nu_{C=O}$ 1642 cm^{-1}) strongly supports coordination through the oxygen atom.

X-ray quality crystals of complex **3a** were grown at −35 °C by slow liquid diffusion of pentane into a concentrated dichloromethane solution. Complex **3a** crystallized in the $P2_1/n$ space group (Figure 4). Selected bond lengths and angles are provided in Table 1. The solid-state structure of the four-legged piano-stool titanium complex **3a** confirmed the $N_{p\text{-tolyl}}{}^\wedge O$ coordination mode of the ligand, forming a four-membered metallacycle with a bite angle of 64.04(8)°. The cyclopentandienyl (Cp) ligand is bound to the metal center in

Scheme 1. Synthesis of Urea (2a) and Thiourea (2b) Proligands



Scheme 2. Synthesis of Mono(ureate) (3a) and Bis(ureate) (4a) Titanium(IV) Complexes



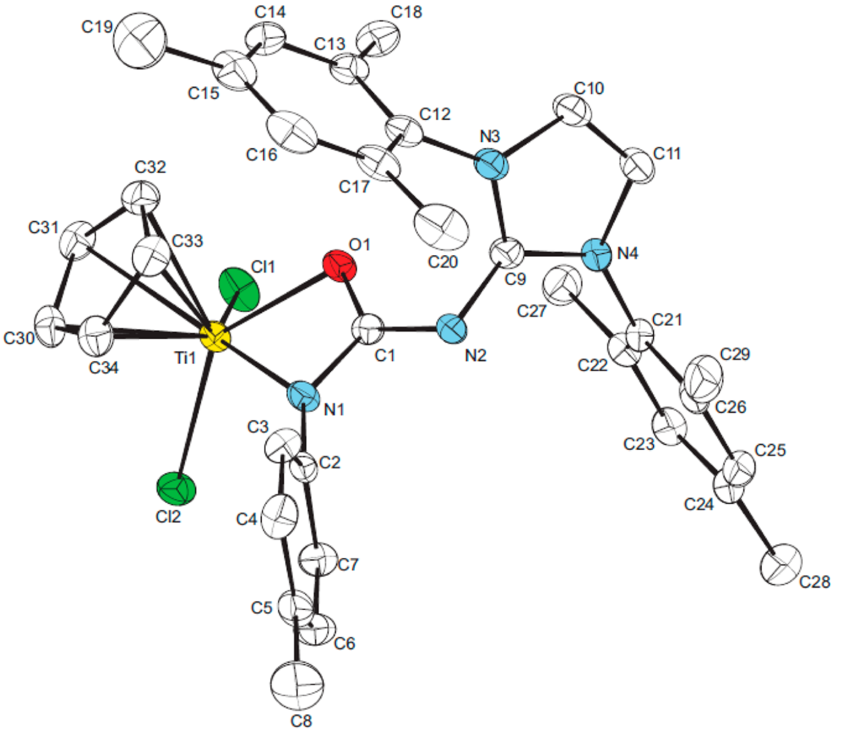


Figure 4. ORTEP diagram of complex **3a** (40% probability level). Hydrogen atoms are omitted for clarity.

the expected η^5-hapticity, with the titanium−carbon bonds ranging from 2.343(3) to 2.379(3) Å. The plane formed by the Cp ring is tilted slightly away from the chlorine atoms at a 3.4° angle from the basal plane formed by Cl1, Cl2, O1, and N1. Significant electron donation from the azole ring is evidenced by the unusually long N2−C9 (1.339(3) Å) and short N2−C1 (1.323(3) Å) bonds. Furthermore, a C1−N2−C9−N3 torsion angle of 63.9° clearly indicates significant single-bond character for N2−C9, as illustrated in the zwitterionic structure in Figure 1. Both C1−O1 and C1−N1 bond lengths are intermediate between that of a carbon−oxygen and carbon−nitrogen single bond and double bond, indicating extensive electron delocalization over O1−C1−N1.[22,23] To our knowledge, **3a** is the first reported ureate(−1) half-sandwich titanium dichloride complex. A closely related cyclopentadienyl amidate titanium dichloride complex[24] displays longer ureate C═O and C═N bond lengths (1.346(6) and 1.388(8) Å, respectively), while the exocyclic iminic bond C−$N_{p\text{-tolyl}}$ is significantly shorter (1.283(7) Å).

Reaction of two equivalents of **2a** with $TiCl_4(THF)_2$ in toluene afforded the expected bis(ureate) titanium(IV) complex **4a** (Scheme 2). The ^1H NMR (C_6D_6) spectrum shows only one set of resonances, indicating the selective formation of only one highly symmetric isomer. Similar to that observed for **3a**, the most significant changes in chemical shifts are observed for the aromatic protons of the *p*-tolyl group (δ 7.36 and 6.82 for **4a** vs δ 7.02 and 6.71 for **2a**), for the corresponding *ipso*-carbon (δ 145.3 for **4a** vs δ 139.4 for **2a**), and for the carbon nucleus of the carbonyl group (δ 167.2 for **4a** vs δ 158.0 for **2a**). In contrast, the imidazole ring backbone protons and the central carbon nuclei remain fairly unchanged at δ 5.72 (δ 5.83 for **2a**) and 149.1 (δ 149.8 for **2a**), respectively. These spectroscopic data strongly suggest $N_{p\text{-tolyl}}$^O coordination of the ligand, as observed for **3a**. This coordination motif was further substantiated by the large decrease in the C═O stretching frequency ($\nu_{C=O}$ 1506 cm^{-1}) from that of the free ligand **2a** ($\nu_{C=O}$ 1642 cm^{-1}).

X-ray quality crystals of complex **4a** were grown at −35 °C by slow liquid diffusion of pentane into a concentrated dichloromethane solution. Complex **4a** crystallized in the $P2_1/c$ space group (Figure 5). Selected bond lengths and angles are provided in Table 1. The solid-state structure is in

Table 1. Selected Bond Lengths and Bond Angles for Compounds 3a, 4a, 5a, and 7b

	3a	4a[a]	5a	7b[b]
Bond Lengths (Å)				
C1–E1[c]	1.312(3)	1.328(3)	1.211(7)	1.760(2)
C1–N1	1.329(3)	1.336(3)	1.369(8)	1.325(3)
C1–N2	1.323(3)	1.322(3)	1.431(7)	1.324(3)
C9–N2	1.339(3)	1.345(3)	1.328(7)	1.326(3)
C30–C31			1.440(13)	
C31–C32			1.305(11)	
M–E1[c]	2.056(2)	1.967(1)		2.210(6)
M–Cl1		2.317(1)		
M–N1	2.030(2)	2.063(2)	2.090(5)	1.900(17)
M–N2			2.096(4)	
M–C30			2.112(7)	
M–C32			2.104(7)	
Bond Angles (deg)				
E1–M–N1[c]	64.04(8)	65.16(6)		74.46(5)
E1–C1–N1[c]	110.2(2)	109.0(2)		107.43(16)
N1–C1–N2			104.3(5)	
N1–M–N2			63.75(18)	
C30–M–C32			69.8(3)	

[a] Average bond lengths and angles for both ureate ligands that are not related by any symmetry operation. [b] Average bond lengths and angles of both independent molecules of **7b** found in the asymmetric unit cell. [c] E1 = O1 in **3a**, **4a**, and **5a** and E1 = S1 in **7b**.

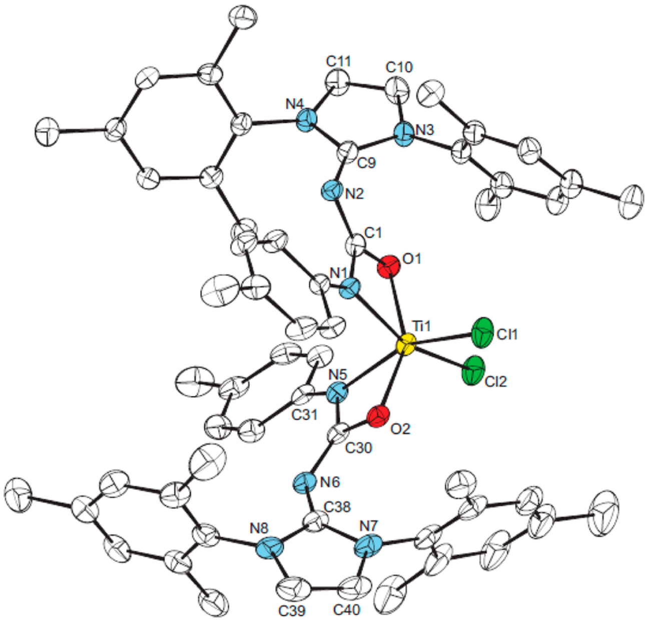


Figure 5. ORTEP diagram of complex **4a** (40% probability level). Hydrogen atoms and one molecule of dichloromethane are omitted for clarity.

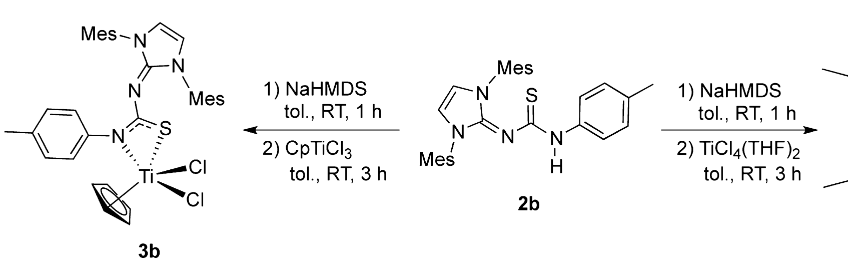
agreement with the high symmetry predicted by NMR spectroscopy. The solid-state structure also confirms the $\mathrm{N}_{p\text{-tolyl}}$^O coordination mode of the ligand. As observed in other bis(ureate) complexes[25] and in the well-studied salicylaldiminato complexes,[26] complex **4a** exhibits a distorted octahedral geometry with the oxygen atoms *trans* to each other and a *cis* arrangement for the chloride atoms, ideal for use as olefin polymerization catalysts.[9,16] The shorter Ti–O bonds compared to Ti–N bonds,[22,23] as observed in **4a** (Table 1), are believed to favor the *trans* arrangement of the oxygen atoms (and, consequently, the *cis* arrangement of the nitrogen atoms) by minimizing the overall steric congestion of these complexes.[9] The mesityl groups generate a pseudo-C_2-symmetric reaction pocket, with potential face selectivity for prochiral α-olefins and formation of stereoregular poly(α-olefins), while providing enough steric bulk in the secondary coordination sphere to prevent bimolecular decomposition. As observed in complex **3a**, the longer N2–C9/N6–C38 bonds (1.345(3) Å) compared to N1–C1/N5–C30 (1.336(3) Å) and N2–C1/N6–C30 (1.322(3) Å) bond lengths strongly suggest extensive electron delocalization from the imidazol-2-ylidene. This is further supported by the C1–N2–C9–N3 (55.9°) and O1–C1–N2–C9 (10.8°) torsion angles, each indicating significant single- and double-bond character for N2–C9 and N2–C1, respectively. The values for both C1–O1 and C1–N1 bond lengths also indicate significant electron delocalization over O1–C1–N1.

Synthesis and Characterization of *N*-Imidazol-2-ylidene-*N*′-*p*-tolylthioureate Titanium(IV) Complexes. Titanium complexes of the related thioureate ligand were also prepared to determine the impact of the softer sulfur on the coordination mode to the metal and on the activity of the complexes. Thioureate complexes of early transition metals have previously been prepared by migratory insertion of a metal imide[27] or iminate[16] into an isothiocyanate, resulting in the formation of N^N metal chelates. However, our attempts to adopt this procedure using (1,3-bis(mesityl)imidazol-2-iminato)titanium(IV) trichloride led only to the formation of unidentifiable products.[15]

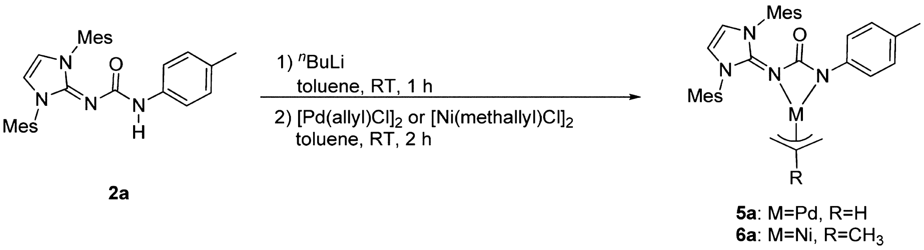
Similar to the ureate titanium(IV) complexes **3a** and **4a**, the thioureate complexes **3b** and **4b** were thus prepared by addition of the thioureate salt, generated in situ by deprotonation of **2b** with sodium hexamethyldisilazide, to the appropriate metal precursor (Scheme 3). Complex **3b** was isolated in 65% yield as a bright reddish-orange crystalline solid. The protons of the cyclopentadienyl ring resonate at δ 6.18 in benzene-d_6, a downfield shift from that of $\mathrm{CpTiCl_3}$ (δ 5.93). Surprisingly, the ^{1}H NMR spectrum is consistent with coordination of the soft sulfur to the hard titanium(IV) metal center, resulting in an $\mathrm{N}_{p\text{-tolyl}}$^S coordination mode. As observed in the ureate series, the *o*- and *m*-CH protons of the *p*-tolyl group both experienced a downfield shift to δ 7.12 and 6.98, respectively, from δ 6.90 and 6.78 for **2b**. The upfield shift for the backbone imidazolium protons to 5.67 in complex **3b**, as observed in **3a** and **4a**, both structurally characterized, suggests an uncoordinated imidazol-2-imine fragment.

The predicted $\mathrm{N}_{p\text{-tolyl}}$^S binding motif is supported by ^{13}C NMR data. The resonance for the *ipso*-carbon of the *p*-tolyl ring is shifted by approximately 9 ppm from that observed of **2b**. This change in chemical shift is consistent with the *p*-tolyl nitrogen atom coordinated to titanium.[16] Coordination through the sulfur atom is substantiated by the thioacyl carbon resonance at δ 169.5, significantly lower than that observed for **2b** (δ 181.0). Coordination of the ligand in an $\mathrm{N}_{p\text{-tolyl}}$^$\mathrm{N}_{\text{iminate}}$ mode would have resulted in the thioacyl carbon nucleus resonating at a *higher* frequency, around 190 ppm.[16] The chemical shift of the thioacyl carbon is furthermore within the range reported for transition metal complexes for which the thioureate ligand coordinates in an N^S fashion.[28,29] Multiple attempts to generate single crystals of **3b** suitable for X-ray diffraction studies were unsuccessful. However, the related fluorinated [*N*-(1,3-dimesitylimidazol-2-ylidene)-*N*′-(4-trifluoromethylphenyl)thioureato]cyclopentadienyl titanium di-

Scheme 3. Synthesis of Mono(ureate) (3b) and Bis(thioureate) (4b) Titanium(IV) Complexes



Scheme 4. Synthesis of Palladium(II) (5a) and Nickel(II) (6a) Ureate Complexes



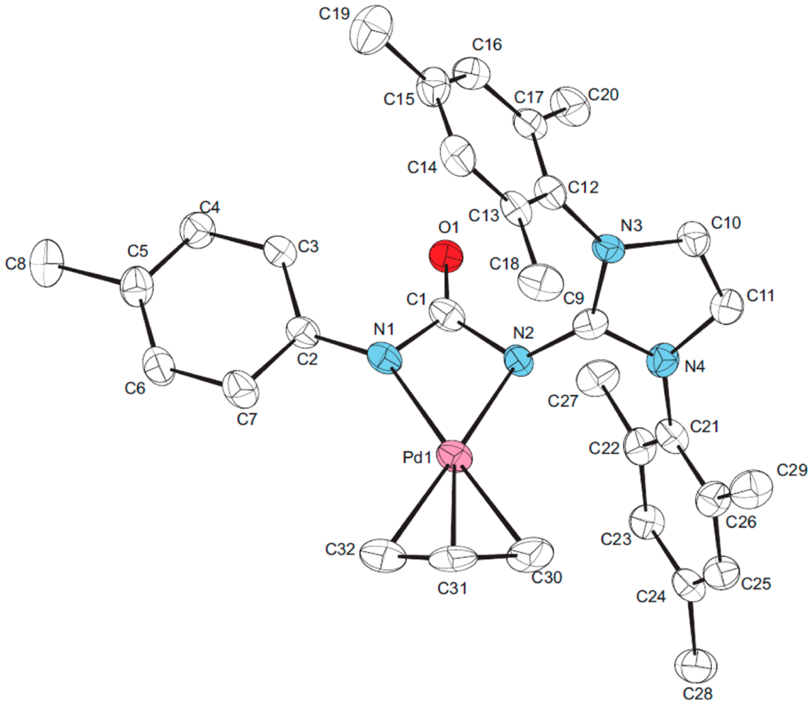
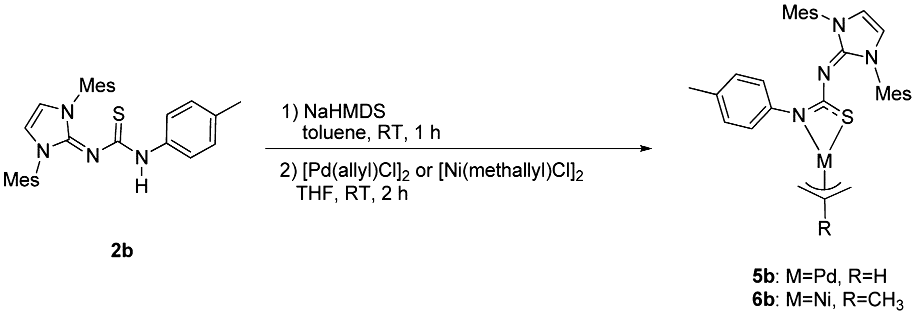


Figure 6. ORTEP diagram of complex **5a** (40% probability level). Hydrogen atoms and minor allyl configuration are omitted for clarity.

chloride (**3b′**) was successfully isolated, and the ligand was found to be bound to the metal center in an $N_{p\text{-tolyl}}$^S coordination mode (see Supporting Information). Considering the similarities in NMR spectroscopic features between both compounds, we conclude that the thioureate ligand in **3b** also adopts an $N_{p\text{-tolyl}}$^S coordination mode.

The related bis(thioureate) titanium complex **4b** was prepared by addition of two equivalents of the thioureate salt to $TiCl_4(THF)_2$ and isolated in 90% yield as a red solid. As observed for the related bis(ureate) complex **4a**, both ligands are magnetically equivalent, with only one set of resonances observed in the NMR spectra, indicating a highly symmetric molecule. The key ^{1}H and ^{13}C NMR spectroscopic data suggest an $N_{p\text{-tolyl}}$^S binding motif, with an uncoordinated imidazo-2-ylidene-substituted nitrogen atom as observed in **4a**. Considering the hardness of Ti(IV) and the softness of sulfur, we were quite surprised to conclude a coordination of the thioureate ligand through sulfur. However, out of all the thioureate transition metal complexes structurally characterized and registered with the Cambridge Structural Database,[28−30] only two cases with an N^N coordination mode were found.[16,27] Our system thus provides further evidence of the shortcomings

Scheme 5. Synthesis of Palladium(II) (5b) and nickel(II) (6b) Thioureate Complexes



of the concept of hard and soft acids and bases, recently documented by Mayr.[31] Multiple attempts to grow single crystals for X-ray diffraction studies using several solvent combinations were not successful.

Synthesis and Characterization of Palladium(II) and Nickel(II) Allyl Ureate Complexes. Our coordination study of the ureate and thioureate ligands to titanium demonstrated the challenge in enforcing the desired $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ binding mode with this new class of ligands. We thus became interested in exploring coordination of both ligands to nickel(II) and palladium(II) and assessing the effect of using late transition metals on the binding mode selectivity.

The palladium(II) allyl imidazol-2-imine ureate complex (**5a**) was synthesized according to Scheme 4. A downfield shift in the resonances for the *ortho*- and *meta*-CH *p*-tolyl protons to δ 7.66 and 7.01, respectively, from that of **2a** was observed in the ^{1}H NMR (C_6D_6) spectrum of **5a**, similar to that noted for **3a** and **4a**. The *ipso*-carbon of the *p*-tolyl ring resonates at δ 147.4, an upfield shift from that of **2a**, further suggesting coordination of $N_{p\text{-tolyl}}$ to the metal center. The ^{1}H and ^{13}C resonances for the imidazole ring only marginally change from those observed in the ligand precursor **2a**, with the imidazole backbone protons and the central carbon nucleus resonating at δ 5.80 (compared to δ 5.83 for **2a**) and 148.7 (compared to δ 149.8 for **2a**), respectively. In contrast, the acyl carbon resonance shifted upfield by 6.3 ppm to δ 164.3. The small decrease in the C═O stretching frequency (1636 cm^{-1}) from that of the free ligand **2a** ($\nu_{C=O}$ 1642 cm^{-1}) is however inconsistent with an $N_{p\text{-tolyl}}$^O binding motif, which should have resulted in a much larger decrease (>100 cm^{-1}) in stretching frequency (vide supra). These spectroscopic data thus suggest the formation of an $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ chelate upon coordination of the ligand despite the absence of any significant changes in the ^{1}H and ^{13}C chemical shifts for both the imidazole backbone protons and the central carbon.

X-ray quality crystals of **5a** were grown at room temperature by slow vapor diffusion of pentane into a saturated THF solution. Compound **5a** crystallized in a monoclinic crystal system in the $P2_1/n$ space group, with the central carbon atom of the allyl group disordered over two positions (Figure 6). The complex adopts a square planar geometry with the metal positioned on the plane formed by N1, N2, C30, and C31. Selected bond lengths and angles are provided in Table 1. The solid-state structure of **5a** confirmed our prediction based on NMR and IR spectroscropic data, with the ureate ligand bound to the metal center through both nitrogen atoms, forming a four-membered metallacycle with a N−Pd−N bite angle of 63.75(18)°. The C1−O1 bond length is significantly shorter than those observed in compounds **3a** and **4a**, in which the ureate is bound in an $N_{p\text{-tolyl}}$^O fashion, and is in agreement with the expected values for carbon−oxygen double bonds.[23] The observed C1−O1 bond length is also consistent with the marginally unchanged ν_{CO} stretching frequency upon coordination. The imidazole ring also displays less zwitterionic character, as evidenced by the shorter C9−N2 bond compared to those in **3a** and **4a** and by the substantially smaller C1−N2−C9−N3 torsion angle (36.7° vs 55.9° and 63.9° for **3a** and **4a**, respectively). As a result of the N^N coordination mode, the C1−N1 and C1−N2 bonds are also significantly longer than the corresponding bonds in **3a** and **4a**. Surprisingly, both Pd1−N1 and Pd1−N2 bond lengths are statistically equivalent despite N1 and N2 being formally anionic and neutral, respectively.

The related nickel(II) complex (**6a**) was prepared under similar conditions by reaction of the ureate salt with nickel(methylallyl) chloride dimer (Scheme 4). The diamagnetic nature of the complex indicates that a square planar geometry is also adopted. As seen for **5a**, the *ortho* and *meta* protons of the *p*-tolyl ring experience a significant downfield shift to δ 7.53 and 6.95, respectively, from that for **2a**, indicating coordination of the $N_{p\text{-tolyl}}$ atom. The ^{13}C nuclei for the central azole carbon, the *ipso*-carbon of the *p*-tolyl ring, and the acyl carbon all resonate at frequencies comparable to those of the palladium analogue **5a**. More importantly, the $\nu_{C=O}$ stretching frequency ($\nu_{C=O}$ 1645 cm^{-1}) marginally differs from that of compound **5a** (1636 cm^{-1}) and of the proligand **2a** (1642 cm^{-1}), but it is clearly larger than that of **3a** (1524 cm^{-1}) and **4a** (1506 cm^{-1}), for which the ligand was unambiguously shown to bind through the acyl oxygen atom (vide supra). The similarities in NMR and FTIR spectroscopic data for both **5a** and **6a** thus strongly suggest an $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ coordination mode to nickel.

Synthesis and Characterization of Palladium(II) and Nickel(II) Allyl Thioureate Complexes. Considering the change in coordination mode of the ureate from $N_{p\text{-tolyl}}$^O on titanium to $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ for both nickel and palladium, we were interested in determining whether the thioureate ligand would also preferentially adopt the $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ coordination mode with nickel and palladium.

The palladium(II) (**5b**) and nickel(II) (**6b**) thioureate complexes were prepared in excellent yields (85%) by reacting the thioureate salt of **2b** with the corresponding metal allyl (Scheme 5). The ^{1}H NMR (C_6D_6) spectra of both complexes showed striking similarities to those for titanium complexes **3b** and **4b**. First, the *ortho* and *meta* protons of the *p*-tolyl group and the backbone protons of the azole ring all resonated at a higher frequency upon coordination. Second, the resonance for the imine carbon for **5b** and **6b** appears at chemical shifts (δ 146.3 and 146.6, respectively) similar to those for the titanium complexes **3b** and **4b** (δ 147.3 and 147.2, respectively). The thioacyl carbon for **5b** and **6b** resonates at δ 176.8 and 175.7, respectively, upfield from that observed in **2b**, consistent with sulfur coordination.[16,28,29] These NMR spectroscopic data strongly suggest coordination of the $N_{p\text{-tolyl}}$ atom and of sulfur. Crystals of **6b** were grown at −35 °C by liquid diffusion of pentane into a saturated THF solution. While the quality of the diffraction data acquired on the nonmerohedral twinned crystal prevented satisfactory refinement, the atoms' connectivity in **6b** could nonetheless be established, unequivocally confirming the $N_{p\text{-tolyl}}$^S coordination mode for **6b** (Figure 7).

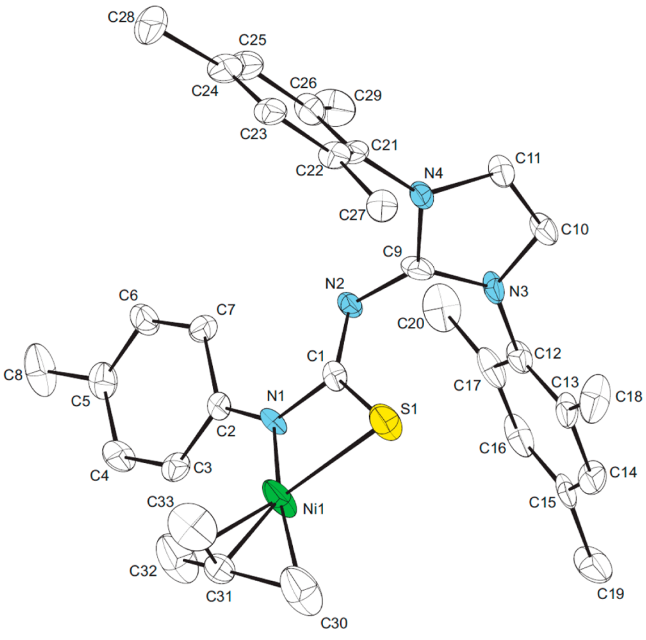


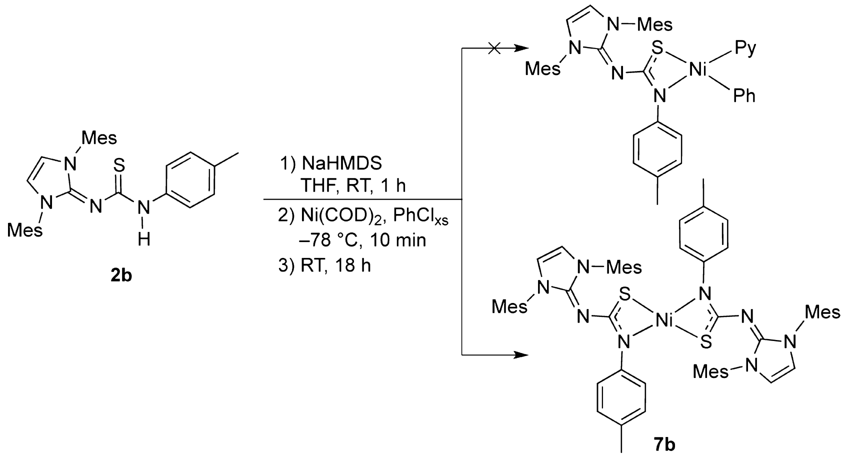
Figure 7. ORTEP diagram of complex **6b** (40% probability level). Hydrogen atoms, a solvent molecule of THF, and pentane are omitted for clarity, and only one of two symmetrically independent molecules in the asymmetric unit cell is shown.

The nickel (**5a,b**) and palladium (**6a,b**) complexes gave valuable insight into the coordination mode of the ureate and thioureate ligands. We however suspected that these allyl complexes might be poor catalysts for olefin polymerization at 1 atm of ethylene and at room temperature due to poor initiation kinetics. Indeed, nickel and palladium allyl complexes all require elevated temperatures and pressures and long reaction times to produce polymer in moderate yields, if at all.[32] We thus became interested in preparing the nickel phenyl complexes, by adaptation of a published procedure developed for a monoanionic chelating NHC ligand.[33] Attempts to prepare the ureate complex were unsuccessful. In contrast, the salt of **2b** reacted cleanly with $Ni(COD)_2$ and chlorobenzene. To our surprise, the bis(thioureate)nickel(II) complex **7b** was isolated as the main reaction product in 61% yield (Scheme 6). A related bis(α-iminocarboxamide)nickel(II) complex was reported by Bazan, albeit as a minor product from the reaction of a potassium amidate with $Ni(COD)_2$ and benzoyl chloride.[34] NMR spectroscopy data of **7b** are consistent with the selective generation of only one isomer, with the ligand bound to the metal in an $N_{p\text{-tolyl}}$^S coordination mode.

X-ray quality crystals of **7b** were grown at room temperature by slow vapor diffusion of ether into a saturated THF solution. Compound **7b** crystallized in a triclinic crystal system in the $P\bar{1}$ space group, with nickel located at an inversion center (Figure 8). The complex adopts a square planar geometry with the metal positioned on the plane formed by S1, C1, N1 and S1′, C1′, N1′. Selected bond lengths and angles are provided in Table 1. The solid-state structure of **7b** confirmed our prediction based on spectroscopic data, with the thioureate ligand bound to the metal center through the sulfur atom, forming a four-membered metallacycle with an S1−Ni1−N1 bite angle of 74.46(5)°. The imidazole ring displays significant zwitterionic character, as evidenced by the large and statistically equivalent N2−C9 and N2−C1 bond lengths and by the C1−N2−C9−N3 torsion angle (74.3°), which deviates greatly from the expected value (0°). This torsion angle is also significantly larger than those observed for **3a** (55.9°) and **4a** (63.9°).

In an attempt to generate a mono(thioureate)nickel complex, complex **7b** was treated with methanol and HCl. Surprisingly, complex **7b** was found to be very stable to protonolysis. Addition of a large excess of methanol to a solution of **7b** in air led to no reaction. Similarly, attempts to prepare a thioureate nickel chloride complex by addition of one or two equivalents of ethereal HCl to a THF solution of **7b** led to no reaction. In contrast, addition of a larger excess of HCl led to uncontrolled decomposition of the complex.

Scheme 6. Synthesis of Bis(thioureato) nickel(II) Complex (7b)



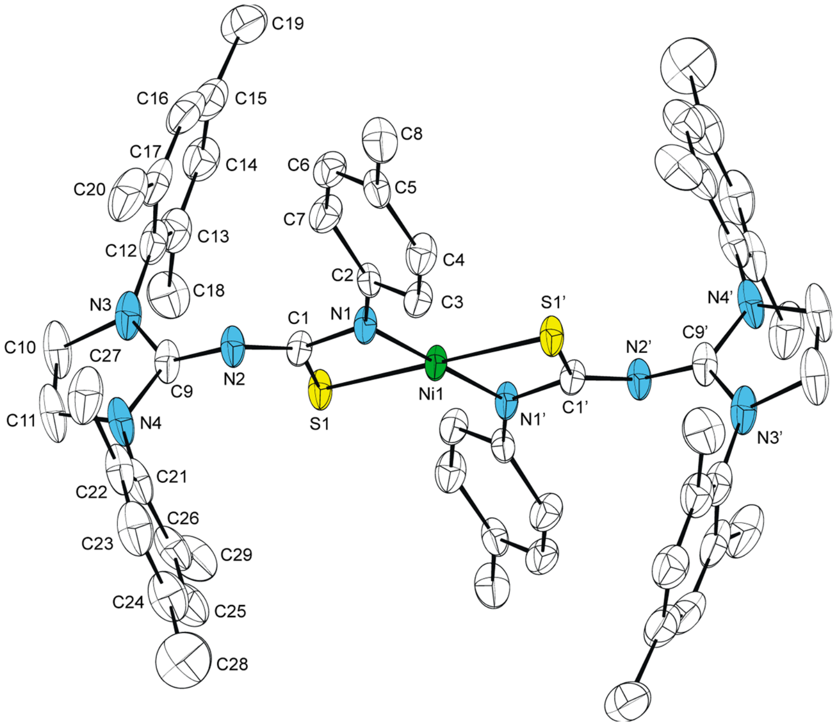


Figure 8. ORTEP diagram of complex **7b** (40% probability level). Hydrogen atoms and a solvent molecule of diethyl ether are omitted for clarity. Only one of two symmetrically independent molecules in the asymmetric unit cell is shown.

Ethylene Polymerization. The catalytic activity of all complexes was evaluated for ethylene polymerization (1 atm C_2H_4, room temperature) with 1000 equivalents of methylaluminoxane (MAO) as cocatalyst. Complexes **3a**, **3b**, and **4a** all gave polyethylene in comparable productivities of 60 kg mol^{-1} catalyst over 10 min. Complex **4b** gave only trace amounts of polymer. The maximum melting endotherm for the polymer produced by these complexes was determined by differential scanning calorimetry and was found to be in the range 134−136 °C, indicating the production of linear polyethylene. Related group 4 complexes of mono- and bis(amidinato)[35] and bis(guanidinato)[36] also exhibited relatively low activity.[5,37] Neither the palladium(II) (**5a** and **5b**) nor the nickel(II) (**6a** and **6b**) allyllic complexes showed any activity under the exact conditions. Prolonged reaction times (19 h) led to the formation of black particulates, indicative of catalyst decomposition, and gave very little polyethylene, with a maximum productivity of 2 kg mol^{-1} catalyst. The inactivity of the late transition metal complexes **5** and **6** is likely a result of the unfavorable formation of the η^1-allyl species to create an open coordination site for binding of the monomer,[32] and of the poor thermal stability of the catalytic species. Unfortunately, decomposition of complexes **5** and **6** even at room temperature precludes the use of elevated temperatures to improve initiation kinetics. The bis(thioureato) nickel(II) complex **7b** also showed no activity, likely due to the inability of MAO to generate the cationic nickel methyl initiator. In all the trials, no wax or oligomer was detected in the reaction medium.

■ CONCLUSIONS

In contrast to our first-generation neutral imine imidazol-2-imine ligands, the new homologous monoanionic ureate and thioureate ligands coordinate to both early and late transition metals in a bidentate fashion. Interestingly, the binding mode greatly depends on both the metal and the ligand used. The ureate ligand coordinates to titanium in an $N_{p\text{-tolyl}}$^O binding mode, while an $N_{\text{imidazol-2-ylidene}}$^$N_{p\text{-tolyl}}$ chelate is produced upon coordination to nickel and palladium. In contrast, the thioureate ligand exclusively coordinates to both early and late transition metals in an $N_{p\text{-tolyl}}$^S binding mode. The nature of the chelate was determined by a combination of NMR and FTIR spectroscopy and, in many cases, confirmed by solid-state structures. The titanium complexes were active in the polymerization of ethylene, albeit at rates considerably lower than those reported for metallocenes and salicylaldiminate-based group 4 metal complexes.[9]

■ EXPERIMENTAL SECTION

All manipulations involving air-sensitive materials were carried out in oven-dried glassware and performed under nitrogen using standard Schlenk line techniques or in a nitrogen atmosphere glovebox. All glassware and cannulae were dried overnight at 160 °C for at least 12 h prior to use. 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 dinitrogen. Cyclopentadienyltitanium(IV) trichloride, allylpalladium chloride dimer, and methallylnickel chloride dimer were purchased from Strem and used without further purification. Sodium bis(trimethylsilyl)amide, *p*-tolyl isocyanate, and *p*-tolyl isothiocyanate were purchased from Sigma-Aldrich and used as received. Compounds **1**[18] and $TiCl_4(THF)_2$[38] were prepared using published procedures. Methylaluminoxane was graciously donated by Albermarle Corp. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories and 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 dinitrogen. NMR spectra were recorded on a Bruker AV 400 (^1H at 400 MHz, ^{13}C at 100 MHz) or Bruker AV 300 (^1H 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 (^1H) and solvent (^{13}C) resonances, and chemical shifts are reported with respect to $\delta = 0$ for tetramethylsilane. J-coupling constants are reported in hertz (Hz). The multiplicity of signals is reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), or a combination of any of these. Where ^{13}C spectra are reported, the ^{1}H and ^{13}C assignments were confirmed by two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H correlation NMR experiments. The proton or carbon attributed to the resonance is sometimes italicized for clarity. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental composition was determined by Guelph Chemical Laboratories Incorporated.

***N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)urea, IMesN(CO)N(H)-*p*-tolyl (2a).** To a toluene solution of 1,3-dimesitylimidazol-2-imine (**1**) (300 mg, 0.940 mmol) was added a 5% excess of *p*-tolyl isocyanate (124 μL, 0.990 mmol), and the reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated in vacuo, and the recovered beige solid was purified by an *n*-pentane wash to afford a spectroscopically pure light beige solid (404 mg, 0.890 mmol, 95%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.02 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.73−6.70 (m, 6H, *m*-CH$_{(\text{mesityl})}$ + *m*-CH$_{(p\text{-tolyl})}$), 6.36 (br s, 1H, NH), 5.83 (s, 2H, NCHCHN), 2.27 (s, 12H, *o*-CH$_{3(\text{mesityl})}$), 2.06 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 1.94 (s, 3H, CH$_{3(p\text{-tolyl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 158.0 (C═O), 149.8 (C═N), 139.4 (C$_{\text{ipso}(p\text{-tolyl})}$), 138.3 (*p*-CCH$_{3(\text{mesityl})}$), 135.9 (C$_{\text{ipso}(\text{mesityl})}$), 134.0 (*o*-CCH$_{3(\text{mesityl})}$), 129.4 (*m*-CH$_{(\text{mesityl})}$), 129.4 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.0 (*m*-CH$_{(p\text{-tolyl})}$), 118.2 (*o*-CH$_{(p\text{-tolyl})}$), 115.4 (NCHCHN), 21.0 (*p*-CCH$_{3(\text{mesityl})}$), 20.6 (*p*-CCH$_{3(p\text{-tolyl})}$), 18.2 (*o*-CCH$_{3(\text{mesityl})}$). FTIR (cast film): $\nu_{C=O}$ 1642 cm^{-1}. Anal. Calcd for $C_{29}H_{31}N_4O$: C, 76.96; H, 7.13; N, 12.38. Found: C, 77.23; H, 6.89; N, 12.15.

***N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)thiourea, IMesN(CS)N(H)-*p*-tolyl (2b).** To a dichloromethane solution of 1,3-dimesitylimidazol-2-imine (**1**) (170 mg, 0.540 mmol) was added a 5% excess of *p*-tolyl isothiocyanate (78.8 μL, 0.500 mmol), and the reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated in vacuo, and the recovered beige solid was purified by an *n*-pentane wash to afford a spectroscopically pure light beige solid (250 mg, 0.520 mmol, 97%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (br s, 1H, NH), 6.90 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.78 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.67 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.89 (s, 2H, NCHCHN), 2.36 (s, 12H, *o*-CH$_{3(\text{mesityl})}$), 2.02 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 1.96 (s, 6H, *p*-CH$_{3(\text{mesityl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 181.0 (C═S), 151.4 (C═N), 139.2 (*p*-CCH$_{3(\text{mesityl})}$), 138.9 (C$_{\text{ipso}(p\text{-tolyl})}$), 135.9 (*o*-CCH$_{3(\text{mesityl})}$), 132.5 (C$_{\text{ipso}(\text{mesityl})}$), 130.5 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.6 (*m*-CH$_{(\text{mesityl})}$), 128.7 (*m*-CH$_{(p\text{-tolyl})}$), 119.9 (*o*-CH$_{(p\text{-tolyl})}$), 117.1 (NCHCHN), 20.9 (*p*-CCH$_{3(\text{mesityl})}$), 20.7 (*p*-CCH$_{3(p\text{-tolyl})}$), 18.8 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for $C_{29}H_{32}N_4S$: C, 74.32; H, 6.88; N, 11.95. Found: C, 74.11; H, 6.75; N, 12.16.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)ureato]cyclopentadienyl titanium Dichloride, CpTiCl$_2$[IMesN(CO)N-*p*-tolyl] (3a). To a solution of **2a** (103 mg, 0.230 mmol) in 2 mL of toluene was slowly added *n*-butyllithium (100 μL, 0.250 mmol). The solution was stirred at room temperature for 1 h before a 2 mL toluene solution of cyclopentadienyltitanium(IV) trichloride (76.4 mg, 0.230 mmol) was added. A color change to an orange solution was observed. The reaction mixture was stirred for 2 h and filtered, and the volatiles were removed under reduced pressure. The recovered brownish-red solid was purified by crystallization using dichloromethane and *n*-pentane to afford a spectroscopically pure orange solid (102 mg, 0.160 mmol, 70%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.39 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.94 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.65 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 6.18 (s, 5H, C_5H_5), 5.74 (s, 2H, NCHCHN), 2.12 (s, 12H, *o*-CH$_{3(\text{mesityl})}$), 2.09 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 2.00 (s, 6H, *p*-CH$_{3(\text{mesityl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 162.0 (C═O), 148.7 (C═N), 146.2 (C$_{\text{ipso}(p\text{-tolyl})}$), 139.7 (*p*-CCH$_{3(\text{mesityl})}$), 135.9 (*o*-CCH$_{3(\text{mesityl})}$), 132.2 (C$_{\text{ipso}(\text{mesityl})}$), 131.8 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.7 (*m*-CH$_{(\text{mesityl})}$), 128.7 (*m*-CH$_{(p\text{-tolyl})}$), 123.8 (*o*-CH$_{(p\text{-tolyl})}$), 120.2 ($C_5H_5$), 117.1 (NCHCHN), 21.0 (*p*-CCH$_{3(\text{mesityl})}$), 20.9 (*p*-CCH$_{3(p\text{-tolyl})}$), 18.0 (*o*-CCH$_{3(\text{mesityl})}$). FTIR (cast film): $\nu_{C=O}$ 1524 cm^{-1}. Anal. Calcd for $C_{34}H_{36}N_4OTiCl_2$: C, 64.26; H, 5.71; N, 8.82. Found: C, 64.01; H, 5.55; N, 8.63.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)thioureato]cyclopentadienyl titanium Dichloride, CpTiCl$_2$[IMesN(CS)N-*p*-tolyl] (3b). To a solution of **2b** (105 mg, 0.220 mmol) in 2 mL of toluene was added bis(trimethylsilyl)amide (45.2 mg g, 0.250 mmol) in 1 mL of toluene. The solution was stirred at room temperature for 1 h before a 2 mL toluene solution of cyclopentadienyltitanium(IV) trichloride (50.4 mg, 0.220 mmol) was added. The reaction mixture was stirred for 1 h and filtered, and the volatiles were removed under reduced pressure. The recovered brownish-red solid was purified by slow diffusion using dichloromethane and *n*-pentane to afford a spectroscopically pure red solid (93.1 mg, 0.140 mmol, 65%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.12 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.98 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.69 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 6.18 (s, 5H, C_5H_5), 5.67 (s, 2H, NCHNCHN), 2.12 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 2.05 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 2.02 (s, 12H, *o*-CH$_{3(\text{mesityl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 169.5 (C═S), 147.5 (C$_{\text{ipso}(p\text{-tolyl})}$), 147.3 (C═N), 139.9 (*p*-CCH$_{3(\text{mesityl})}$), 135.8 (*o*-CCH$_{3(\text{mesityl})}$), 133.6 (*p*-CCH$_{3(p\text{-tolyl})}$), 131.6 (C$_{\text{ipso}(\text{mesityl})}$), 129.7 (*m*-CH$_{(\text{mesityl})}$), 128.7 (*m*-CH$_{(p\text{-tolyl})}$), 126.6 (*o*-CH$_{(p\text{-tolyl})}$), 119.7 ($C_5H_5$), 117.1 (NCHCHN), 21.1 (*p*-CCH$_{3(p\text{-tolyl})}$), 21.0 (*p*-CCH$_{3(\text{mesityl})}$), 18.4 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for $C_{34}H_{36}Cl_2N_4STi$: C, 62.68; H, 5.57; N, 8.60. Found: C, 62.42; H, 5.30; N, 8.37.

Bis[*N*-(1,3-dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)ureato]titanium Dichloride, TiCl$_2$[IMesN(CO)N-*p*-tolyl]$_2$ (4a). To a solution of **2a** (104 mg, 0.230 mmol) in 2 mL of toluene was slowly added *n*-butyllithium (100 μL, 0.250 mmol). The solution was stirred at room temperature for 1 h before a 2 mL toluene solution of TiCl$_4$·2THF (38.2, 0.120 mmol) was added. The yellow solution gradually turned deep red. The reaction mixture was stirred for 2 h and filtered, and the volatiles were removed under reduced pressure. The recovered red solid was purified by crystallization using dichloromethane and *n*-pentane to afford a spectroscopically pure red solid (160 mg, 0.160 mmol, 68%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.36 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.82 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.6 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.72 (s, 2H, NCHCHN), 2.17 (s, 12H, *o*-CH$_{3(\text{mesityl})}$), 2.08 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 2.04 (s, 3H, *p*-CH$_{3(\text{mesityl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 167.2 (C═O), 149.1 (C═N), 145.3 (C$_{\text{ipso}(p\text{-tolyl})}$), 139.6 (*p*-CCH$_{3(\text{mesityl})}$), 135.5 (C$_{\text{ipso}(\text{mesityl})}$), 131.8 (*o*-CCH$_{3(\text{mesityl})}$), 131.0 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.8 (*m*-CH$_{(\text{mesityl})}$), 128.1 (*m*-CH$_{(p\text{-tolyl})}$), 123.0 (*o*-CH$_{(p\text{-tolyl})}$), 116.8 (NCHCHN), 21.1 (*p*-CCH$_{3(\text{mesityl})}$), 21.0 (*p*-CCH$_{3(p\text{-tolyl})}$), 18.1 (*o*-CCH$_{3(\text{mesityl})}$). FTIR (cast film): $\nu_{C=O}$ 1506 cm^{-1}. Anal. Calcd for $C_{58}H_{62}N_8OTiCl_2$: C, 68.17; H, 6.12; N, 10.96. Found: C, 68.10; H, 5.93; N, 11.15.

Bis[*N*-(1,3-dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)thioureato]titanium Dichloride, TiCl$_2$[IMesN(CS)N-*p*-tolyl]$_2$ (4b). To a solution of **2b** (95.0 mg, 0.200 mmol) in 2 mL of toluene was added sodium bis(trimethylsilyl)amide (40.9 mg, 0.220 mmol) in 2 mL of toluene. The solution was stirred at room temperature for 1 h before a 2 mL toluene solution of TiCl$_4$·2THF (33.8, 0.110 mmol) was added. The reaction mixture was stirred for 1 h and filtered, and the volatiles were removed under reduced pressure. The recovered red solid was purified by slow diffusion using dichloromethane and *n*-pentane to afford a spectroscopically pure red solid (104.6 mg, 0.090 mmol, 90%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.86 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.81 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.71 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.64 (s, 2H, NCHNCHN), 2.18 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 2.15 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 1.94 (s, 12H, *o*-CH$_{3(\text{mesityl})}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 174.3 (C═S), 148.3 (C$_{\text{ipso}(p\text{-tolyl})}$), 147.2 (C═N), 139.4 (*p*-CCH$_{3(\text{mesityl})}$), 135.5 (*o*-CCH$_{3(\text{mesityl})}$), 132.2 (*p*-CCH$_{3(p\text{-tolyl})}$), 131.5 (C$_{\text{ipso}(\text{mesityl})}$), 129.7 (*m*-CH$_{(\text{mesityl})}$), 125.2 (*o*-CH$_{(p\text{-tolyl})}$), 116.9 (NCHCHN), 21.3 (*p*-CCH$_{3(p\text{-tolyl})}$), 21.2 (*p*-CCH$_{3(\text{mesityl})}$), 18.3 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for $C_{58}H_{62}Cl_2N_8S_2Ti$: C, 66.09; H, 5.93; N, 10.63. Found: C, 65.78; H, 5.75; N, 10.39.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)ureato]palladium Allyl, Pd(η^3-C_3H_5)[IMesN(CO)N-*p*-tolyl] (5a). To a solution of **2a** (112 mg, 0.250 mmol) in 2 mL of toluene was slowly added *n*-butyllithium (109 μL, 0.270 mmol). The solution was stirred at room temperature for 2 h before being added to a 3 mL toluene suspension of palladium allyl chloride dimer (45.4 mg, 0.124 mmol). The reaction mixture was stirred for 2 h, filtered, concentrated to approximately 2 mL, and precipitated using 5 mL of *n*-pentane. The supernatant was decanted, and the remaining solid was dried under reduced pressure. The recovered yellow powder was purified by crystallization using THF and *n*-pentane to afford a spectroscopically pure yellow solid (120 mg, 0.200 mmol, 81%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.66 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 7.01 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.68 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.80 (s, 2H, NCHCHN), 4.38 (m, 1H, CH$_2$C*H*CH$_{2(\text{allyl})}$), 3.53 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 1H, C*H*$_2$CHCH$_{2(\text{allyl})}$), 2.91 (d, $^3J_{\mathrm{HH}}$ = 5.0 Hz, 1H, CH$_2$CHC*H*$_{2(\text{allyl})}$), 2.30 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 1H, C*H*$_2$CHCH$_{2(\text{allyl})}$), 2.22 (s, 6H, *o*-CH$_{3\ (\text{mesityl})}$), 2.21 (s, 6H, *o*-CH$_{3(\text{mesityl})}$), 2.15 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 2.06 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 1.84 (d, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 1H, CH$_2$CHC*H*$_{2(\text{allyl})}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 164.3 (C═O), 148.7 (C═N), 147.4 (C$_{\text{ipso}(p\text{-tolyl})}$), 138.4 (*p*-CCH$_{3(\text{mesityl})}$), 135.4 (*o*-CCH$_{3(\text{mesityl})}$), 133.2 (C$_{\text{ipso(mesityl)}}$), 129.3 (*m*-CH$_{(\text{mesityl})}$), 128.8 (*m*-CH$_{(p\text{-tolyl})}$), 127.3 (*p*-CCH$_{3(p\text{-tolyl})}$), 122.6 (*o*-CH$_{(p\text{-tolyl})}$), 116.3 (NCHCHN), 107.4 (*CH*$_2$CH*CH*$_2$), 53.1 (CH$_2$CHCH$_2$), 51.6 (CH$_2$CHCH$_2$), 20.9 (*p*-CCH$_{3(\text{mesityl}}$), 20.9 (*p*-CCH$_{3(\text{p-tolyl})}$), 18.6 (*o*-CCH$_{3(\text{mesityl})}$). FTIR (cast film): $\nu_{\mathrm{C=O}}$ 1636 cm^{-1}. Anal. Calcd for C$_{32}$H$_{36}$N$_4$OPd: C, 64.16; H, 6.06; N, 9.35. Found: C, 64.10; H, 5.87; N, 9.12.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)thioureato]-palladium Allyl, Pd(η^3-C$_3$H$_5$)[IMesN(CS)N-*p*-tolyl] (5b). To a solution of **2b** (50.0 mg, 0.110 mmol) in 2 mL of THF was added sodium bis(trimethylsilyl)amide (21.0 mg, 0.110 mmol) in 2 mL of THF. The reaction mixture was stirred for 1 h before being added to a 2 mL THF solution of palladium allyl chloride dimer (19.4 mg, 0.050 mmol). The reaction mixture was stirred for 2 h and filtered, and the volatiles were removed under reduced pressure. The recovered brown solid was purified by slow diffusion using THF and *n*-pentane to afford a spectroscopically pure red solid (57 mg, 0.094 mmol, 85%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.52 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 7.01 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.67 (s, 2H, *m*-CH$_{(\text{mesityl})}$), 6.63 (s, 2H, *m*-CH$_{(\text{mesityl})}$), 5.78 (s, 2H, NCHCHN), 4.24 (m, 1H, CH$_2$C*H*CH$_{2(\text{allyl})}$), 3.50 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 1H, C*H*$_2$CHCH$_{2(\text{allyl})}$), 3.24 (d, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 1H, CH$_2$CHC*H*$_{2(\text{allyl})}$), 2.31 (s, 6H, *o*-CH$_{3(\text{mesityl})}$), 2.26 (s, 6H, *o*-CH$_{3(\text{mesityl})}$), 2.20 (s, 3H, *p*-CH$_{3(\text{p-tolyl})}$), 2.08 (d, $^3J_{\mathrm{HH}}$ = 4.5 Hz, 1H, CH$_2$CHC*H*$_{2(\text{allyl})}$), 1.93 (s, 6H, *p*-CH$_{3(\text{mesityl})}$). ^{13}C{1H} NMR (100 MHz, C$_6$D$_6$): δ 176.8 (C═S), 146.4 (C$_{\text{ipso}(p\text{-tolyl})}$), 146.3 (C═N), 138.8 (*p*-CCH$_{3(\text{mesityl})}$), 135.7 (*o*-CCH$_{3(\text{mesityl})}$), 135.2 (*o*-CCH$_{3(\text{mesityl})}$), 132.4 (C$_{\text{ipso(mesityl)}}$), 131.7 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.4 (*m*-CH$_{(\text{mesityl})}$), 124.1 (*o*-CH$_{(p\text{-tolyl})}$), 116.1 (NCHCHN), 67.6 (CH$_2$CCH$_2$), 59.2 (CH$_2$CCH$_2$), 48.7 (CH$_2$CCH$_2$), 20.8 (*p*-CCH$_{3(\text{mesityl})}$) + *p*-CCH$_{3(p\text{-tolyl})}$), 18.5 (*o*-CCH$_{3(\text{mesityl})}$), 18.4 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for C$_{32}$H$_{36}$N$_4$SPd: C, 62.48; H, 5.90; N, 9.11. Found: C, 62.75; H, 5.72; N, 8.86.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)ureato]nickel Methylallyl, Ni(η^3-C$_3$H$_4$CH$_3$)[IMesN(CO)N-*p*-tolyl] (6a). To a solution of **2a** (84.8 mg, 0.190 mmol) in 2 mL of toluene was slowly added *n*-butyllithium (82.5 μL, 0.206 mmol). The solution was stirred at room temperature for 1 h before being added to a 3 mL toluene suspension of nickel methallyl chloride dimer (28.0 mg, 0.090 mmol). A color change from a dark orange to a reddish-orange solution was observed. The reaction mixture was stirred for 2 h, filtered, concentrated to approximately 2 mL, and precipitated using 5 mL of *n*-pentane. The supernatant was decanted, and the remaining solid was dried under reduced pressure. The recovered orange powder was spectroscopically pure (98.7 mg, 0.180 mmol, 93%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.53 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.95 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.70 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.77 (s, 2H, NCHCHN), 2.82 (d, $^3J_{\mathrm{HH}}$ = 2.5 Hz, 1H, C*H*$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 2.24 (s, 12H, *o*-C*H*$_{3\ (\text{mesityl})}$), 2.10 (s, 3H, *p*-C*H*$_{3(p\text{-tolyl})}$), 2.05 (s, 6H, *p*-C*H*$_{3(\text{mesityl})}$), 1.90 (d, $^3J_{\mathrm{HH}}$ = 3.2 Hz, 1H, CH$_2$C(CH$_3$)C*H*$_{2(\text{allyl})}$), 1.72 (s, 1H, CH$_2$C(CH$_3$)C*H*$_{2(\text{allyl})}$), 1.68 (s, 3H, CH$_2$C(C*H*$_3$)CH$_{2(\text{allyl})}$), 1.10 (s, 1H, CH$_2$CHC*H*$_{2(\text{allyl})}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.1 (C═O), 149.5 (C═N), 147.6 (C$_{\text{ipso}(p\text{-tolyl})}$), 138.5 (*p*-CCH$_{3(\text{mesityl})}$), 135.3 (*o*-CCH$_{3(\text{mesity)l}}$), 135.2 (*o*-CCH$_{3(\text{mesityl})}$), 133.2 (*C*$_{\text{ipso(mesityl)}}$), 129.7 (*m*-CH$_{(\text{mesityl})}$), 128.6 (*m*-CH$_{(p\text{-tolyl})}$), 127.0 (*p*-CCH$_{3(p\text{-tolyl})}$), 122.8 (*o*-CH$_{p\text{-tolyl}}$), 116.8 (CH$_2$C(CH$_3$)CH$_2$), 116.6 (NCHCHN), 47.7 (CH$_2$C(CH$_3$)CH$_2$), 46.3 (CH$_2$C(CH$_3$)CH$_2$), 22.9 (CH$_2$C(*C*H$_3$)CH$_2$), 20.9 (*p*-CCH$_{3(\text{mesityl}}$ + *p*-CCH$_{3(p\text{-tolyl})}$), 18.4 (*o*-CCH$_{3(\text{mesityl})}$). FTIR (cast film): $\nu_{\mathrm{C=O}}$ 1645 cm^{-1}. Anal. Calcd for C$_{33}$H$_{38}$N$_4$ONi: C, 70.10; H, 6.77; N, 9.91. Found: C, 69.86; H, 6.52; N, 10.18.

[*N*-(1,3-Dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)thioureato] nickel Methylallyl, Ni(η^3-C$_3$H$_4$CH$_3$)[IMesN(CS)N-*p*-tolyl] (6b). To a solution of **2b** (75.0 mg, 0.200 mmol) in 2 mL of THF was added sodium bis(trimethylsilyl)amide (32.3 mg, 0.210 mmol) in 2 mL of THF. The reaction mixture was stirred for 1 h before being added to a 2 mL THF solution of nickel methallyl chloride dimer (23.9 mg, 0.10 mmol). The reaction mixture was stirred for 2 h and filtered, and the volatiles were removed under reduced pressure. The recovered brown solid was purified by crystallization using THF and *n*-pentane to afford a spectroscopically pure orange solid (79.5 mg, 0.106 mmol, 85%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.28 (d, $^3J_{\mathrm{HH}}$ = 8.3 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 7.00 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.70 (s, 2H, *m*-CH$_{(\text{mesityl})}$), 6.63 (s, 2H, *m*-CH$_{(\text{mesityl})}$), 5.74 (s, 2H, NCHCHN), 2.73 (d, $^3J_{\mathrm{HH}}$ = 2.8, 1H, C*H*$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 2.41 (d, $^3J_{\mathrm{HH}}$ = 2.6 Hz, 1H, CH$_2$C(CH$_3$)C*H*$_{2(\text{allyl})}$), 2.29 (s, 6H, *o*-CH$_{3(\text{mesityl})}$), 2.20 (s, 6H, *o*-CH$_{3(\text{mesityl})}$), 2.18 (s, 3H, *p*-CH$_{3(p\text{-tolyl})}$), 1.99 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 1.70 (s, 1H, C*H*$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 1.69 (s, 3H, CH$_2$C(C*H*$_3$)-CH$_{2(\text{allyl})}$), 1.51 (s, 1H, CH$_2$C(CH$_3$)C*H*$_{2(\text{allyl})}$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 175.7 (C═S), 147.6 (C$_{\text{ipso}(p\text{-tolyl})}$), 146.6 (C═N), 139.1 (*p*-CCH$_{3(\text{mesityl})}$), 136.0 (*o*-CCH$_{3(\text{mesityl})}$), 135.9 (*o*-CCH$_{3(\text{mesityl})}$), 132.6 (C$_{\text{ipso(mesityl)}}$), 130.2 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.7 (*m*-CH$_{(\text{mesityl})}$), 129.6 (*m*-CH$_{(\text{mesityl})}$), 123.6 (*o*-CH$_{(p\text{-tolyl})}$), 117.2 (CH$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 116.5 (NCHCHN), 53.1 (CH$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 44.9 (CH$_2$C(CH$_3$) CH$_{2(\text{allyl})}$), 23.5 (CH$_2$C(CH$_3$)CH$_{2(\text{allyl})}$), 21.1 (*p*-CCH$_{3(\text{mesityl})}$), 21.3 (*p*-CCH$_{3(\text{mesityl})}$), 18.7 (*o*-CCH$_{3(\text{mesityl})}$), 18.6 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for C$_{33}$H$_{38}$N$_4$SNi: C, 68.17; H, 6.59; N, 9.64. Found: C, 67.89; H, 6.32; N, 9.78.

Bis[*N*-(1,3-dimesitylimidazol-2-ylidene)-*N*′-(*p*-tolyl)-thioureato]nickel, bis[IMesN(CS)N-*p*-tolyl]Ni (7b). Compound **2b** (51.0 mg, 0.110 mmol) and sodium bis(trimethylsilyl)amide (40.0 mg, 0.210 mmol) were added to a Schlenk tube and dissolved in THF. The resulting solution was stirred for 1 h. In a separate Schlenk tube, a solution of bis(cyclooctadiene)nickel(0) (14.8 mg, 0.060 mmol) in THF was prepared and cooled to −78 °C, and an excess of chlorobenzene (119 mg, 1.06 mmol) subsequently added. After 10 min, the solution containing the ureate salt was added to the solution of the nickel precursor and stirred for 18 h. The reaction mixture was filtered, and the volatiles were removed in vacuo. The recovered dark green solid was purified by crystallization using THF and diethyl ether to give a spectroscopically pure green solid (64 mg, 0.07 mmol, 61% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.93 (d, $^3J_{\mathrm{HH}}$ = 8.3 Hz, 2H, *o*-CH$_{(p\text{-tolyl})}$), 6.75 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, *m*-CH$_{(p\text{-tolyl})}$), 6.72 (s, 4H, *m*-CH$_{(\text{mesityl})}$), 5.63 (s, 2H, NCHCHN), 2.14 (s, 6H, *p*-CH$_{3(\text{mesityl})}$), 2.04 (s, 15H, *o*-CH$_{3(\text{mesityl})}$ + *p*-CH$_{3(\text{p-tolyl})}$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 173.3 (C═S), 145.0 (C$_{\text{ipso}(p\text{-tolyl})}$), 143.6 (C═N), 138.5 (*p*-CCH$_{3(\text{mesityl})}$), 135.7 (*o*-CCH$_{3(\text{mesityl})}$), 132.3 (C$_{\text{ipso(mesityl)}}$), 129.9 (*p*-CCH$_{3(p\text{-tolyl})}$), 129.2 (*m*-CH$_{(\text{mesityl})}$), 124.7 (*o*-CH$_{(p\text{-tolyl})}$), 115.6 (NCHCHN), 20.9 (*p*-CCH$_{3(\text{mesityl})}$), 20.6 (*p*-CCH$_{3(p\text{-tolyl})}$), 18.1 (*o*-CCH$_{3(\text{mesityl})}$). Anal. Calcd for C$_{58}$H$_{64}$N$_8$S$_2$Ni: C, 69.94; H, 6.48; N, 11.25. Found: C, 70.18 ; H, 6.63; N, 10.98.

General Procedure for Ethylene Polymerization. Polymerization trials were performed under 1 atm of ethylene at room temperature in a Schlenk-type flask containing a magnetic stir bar. The flask was conditioned at 160 °C for at least 12 h prior to use. The flask was evacuated, backfilled with ethylene, and charged with toluene (20 mL) and methylaluminoxane (2 M Al in toluene; 1000 equiv of Al). After vigorously stirring for 15 min under 1 atm of C$_2$H$_4$, the catalyst (9 μmol) dissolved in 1 mL of toluene was added. The reaction mixture was vigorously stirred for an additional 10 min. The reaction mixture was quenched with a 50:50 mixture of methanol/HCl. The resulting mixture was filtered, and any solid collected was washed with distilled water and dried for 24 h in a vacuum oven. The polymer yields were determined by gravimetry.

Table 2. Crystal Data and Structure Refinement Details for **3a**, **4a**, **5a**, and **7b**

	3a	4a	5a	7b
empirical formula	$C_{34}H_{36}Cl_2N_4OTi$	$C_{59}H_{61}Cl_4N_8O_2Ti$	$C_{32}H_{36}N_4OPd$	$C_{62}H_{72}N_8NiOS_2$
fw/g mol^{-1}	635.47	1103.86	599.05	1068.11
cryst size/mm	0.26 × 0.15 × 0.12	0.35 × 0.35 × 0.12	0.16 × 0.12 × 0.10	0.22 × 0.20 × 0.13
θ range/deg	2.60−27.52	2.62−27.62	2.73−27.49	1.45−27.55
h; k; l range	±13; ±20; −24, 25	±20; ±18; −25, 33	±11; ±18; ±30	±14; ±19; ±23
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	10.7126(4)	15.8799(2)	8.82619(3)	11.5188(14)
b/Å	15.6730(5)	14.5184(3)	14.1257(4)	15.159(2)
c/Å	19.6255(7)	25.9490(6)	23.4966(9)	17.772(2)
α/deg	90	90	90	96.840(3)
β/deg	98.552(2)	102.0350(10)	93.891(2)	93.540(3)
γ/deg	90	90	90	110.670
Z	4	4	4	2
D_{calc}/Mg m^{-3}	1.295	1.253	1.361	1.238
$F(000)$	1328	2308	1240	1136
no. of reflns collected/unique	22 519/7427	48 686/13 332	26 613/6681	49 175/13 097
R_{int}	0.0624	0.0769	0.1013	0.0403
no. data/restraints/params	7427/0/386	13 332/0/680	6681/3/354	13 097/0/686
final R indices [$F^2 < 2\sigma(F^2)$]: R_1, wR_2	0.0541, 0.1129	0.0566, 0.1299	0.0703, 0.1665	0.0476, 0.1217
R indices (all data): R_1, wR_2	0.1203, 0.1396	0.1356, 0.1652	0.1652, 0.2185	0.0695, 0.1337
goodness-of-fit on F^2	1.017	1.019	1.021	1.030

X-ray Crystallography. Selected details of the X-ray crystal data and structure refinement for **3a**, **4a**, **5a**, and **7b** are listed in Table 2. Other detailed crystallographic data (tables of atomic coordinates with isotropic and anisotropic displacement parameters, bond lengths, and angles) are provided as Supporting Information. Crystallographic data for **3a**, **4a**, and **5a** 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.[39] Absorption corrections were carried out using SORTAV.[40] Data for **3b′** and **7b** were collected on a Bruker Kappa APEX-DUO diffractometer using a copper ImuS (microsource) tube with multi layer optics and a monochromated Mo-Kα radiation (Bruker Triumph), respectively. Data were measured using a combination of ϕ scans and ω scans, and were processed using APEX2 and SAINT.[41] Absorption corrections were carried out using SADABS.[41] Structure **3b′** was solved and refined using OLEX2 (v. 1.2)[42] with SHELXS-97 for full-matrix least-squares refinement that was based on F^2.[43] Compound **3a**, **4a**, **5a** and **7b** was solved using Superflip[44] and refined using WinGX[45] with SHELXS-97 for full-matrix least-squares refinement that was based on F^2.[43] 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 **3a**, **3b′**, **4a**, **5a**, and **7b** (CCDC reference numbers 928501−928505). 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 displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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