ORGANOMETALLICS

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Reactivity Study of Imino-*N*-Heterocyclic Carbene Palladium(II) Methyl Complexes

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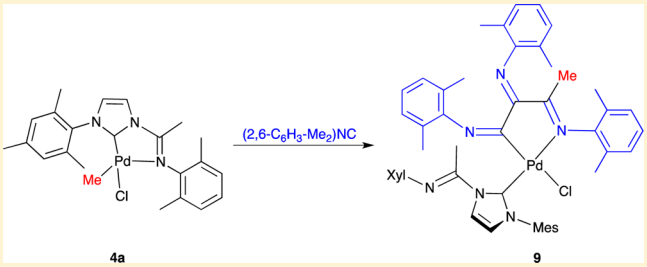
Supporting Information

ABSTRACT: Neutral and cationic palladium(II) complexes containing three different heteroditopic bis(aryl)-substituted imino-*N*-heterocyclic carbene ligands have been synthesized and structurally characterized. Modifications made to the substituent at the iminic carbon allow for independent tuning of the steric and electronic environment around the metal center. The nature of this substituent profoundly affects the thermal stability of the neutral palladium complexes. While the *tert*-butyl derivative decomposes at 60 °C over a period of 24 h to give the corresponding 1-mesityl-2-methyl-1H-imidazole and the corresponding imidoyl chloride as the major products, the phenyl and methyl analogues show no sign of decomposition. Likewise, the corresponding cationic complexes of all three carbene derivatives are stable under the same conditions, with no evidence of decomposition. While inactive for ethylene polymerization, these palladium methyl complexes react with CO and isocyanides to form a variety of products, including structurally characterized simple adducts and single and multiple insertion products.



INTRODUCTION

The reactivity of the metal−carbon bond plays a critical role in the stoichiometric and catalytic synthesis of organic compounds.[1] While carbon monoxide has historically played an important role as substrate due to its role in hydroformylation,[2] the related isocyanide has received relatively far less attention.[3] Isocyanides are of special interest thanks to the addition of a biologically important nitrogen atom and thanks to the presence of a new iminic reactive site for subsequent reaction on the molecule. Palladium methyl complexes of chelating nitrogen[4−8] and phosphine[9−11] ligands have proven capable of inserting not only one but also multiple equivalents of aryl and alkyl isocyanides.[8] In many cases, the use of excess isocyanide, however, leads to dissociation of the ancillary ligand used, such as monodentate phosphine,[11] and chelating P−P[9] and N−N[5,9] ligands, with a decrease in control over the reactivity of the transition metal complex.

Coordination of strong σ donors such as N-heterocyclic carbenes (NHCs) may mitigate or eliminate this undesired dissociation of the ancillary ligand. To our knowledge, only one NHC palladium methyl complex has been shown to insert one equivalent of isocyanide, even when used in excess.[12] In the absence of an alkyl migratory group, the isocyanide inserts into the palladium−carbene bond in palladium iodide dimers coordinated with remote N-heterocyclic carbenes.[13] Interestingly, addition of 2,6-dimethylaniline to dibromo(NHC)(isocyanide)palladium gives a complex that contains a new acyclic carbene, the result of a nucleophilic attack of the aniline on the coordinated isocyanide.[14]

We have recently reported the synthesis and coordination of aryl-substituted heteroditopic imino-N-heterocyclic carbenes (C^Imine).[15−17] These are closely related to the α-diimine ligands that have been installed on nickel and palladium to form catalysts capable of copolymerizing ethylene and functionalized olefins, such as acrylates.[18,19] The C^Imine ligands are conceptually a hybrid of the α-diimine ligands in which one of the two imine fragments has been replaced by a stronger σ-donor and a poorer π-acceptor carbene. The NHC moiety was chosen due to its demonstrated ability to impart thermal stability in several complexes used in a variety of catalytic applications.[20−22] Nickel complexes of these C^Imine ligands were however found to be inactive for ethylene polymerization.[15]

Considering the importance of palladium catalysts in cross-coupling reactions[20,21,23] and their ability to polymerize functionalized olefins,[18,19,24] we decided to extend our study to diamagnetic palladium−methyl complexes to gain insight into their thermal stability and into their insertion chemistry. Herein, we present the synthesis, structural characterization, thermal stability, and reactivity of both neutral and cationic Pd(II) methyl complexes of C^Imine$_R$ (where R = Me, Ph, or *t*Bu) ligands toward ethylene, isocyanides, and carbon monoxide.

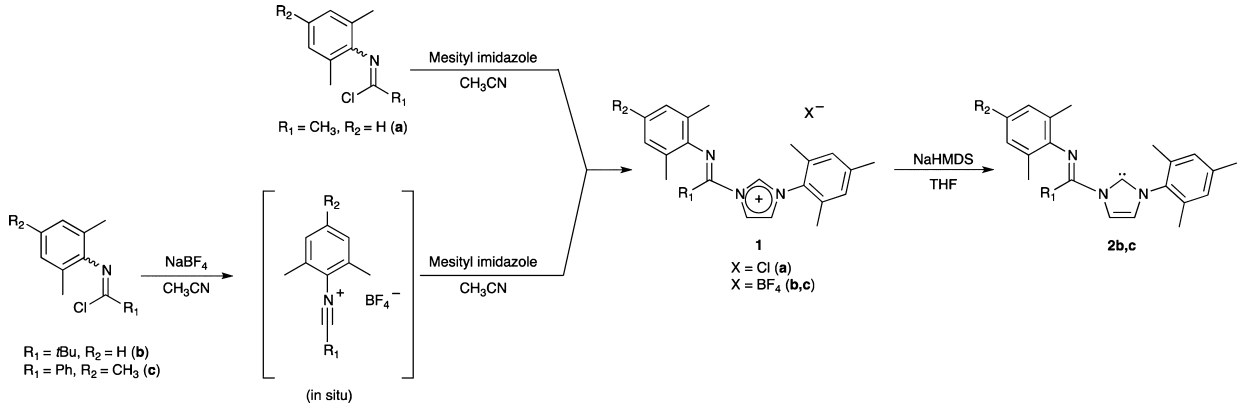
RESULTS AND DISCUSSION

Synthesis and Characterization of Palladium(II) Imino−NHC Complexes. Imidazolium salts, **1a** and **1b**, were synthesized following literature procedures (Scheme 1).[16] The phenyl derivative C^Imine$_{Ph}$·HBF$_4$ (**1c**) was prepared in 67% and necessitated activation of the imidoyl chloride by reaction with sodium tetrafluoroborate to form the corresponding nitrilium salt in situ. The ^{1}H NMR ($CDCl_3$) resonance for the central imidazolium proton of **1c** is observed at δ 8.81, while

Received: June 10, 2013

   dx.doi.org/10.1021/om400533d | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of Imidazolium Salts (1a−1c) and of the Corresponding Free Carbenes (2b and 2c)



Scheme 2. Synthesis of Neutral (4a−4c) and Cationic (5a−5c) Palladium Complexes

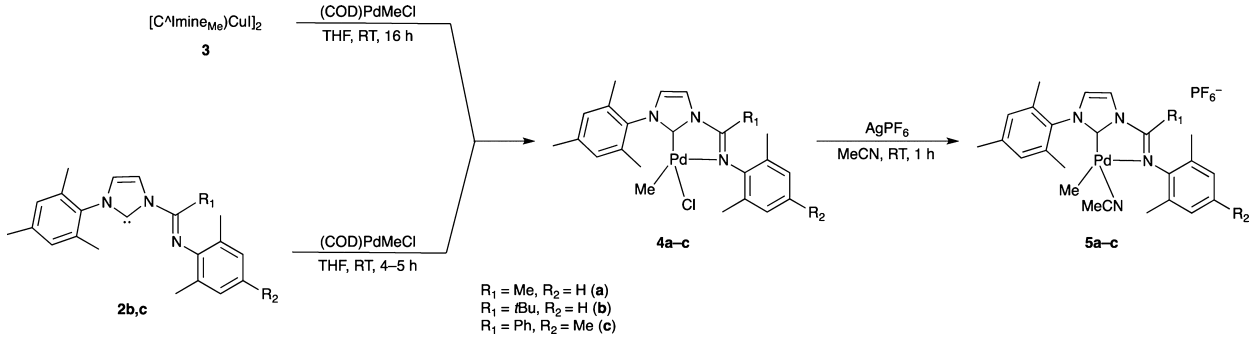


Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 4a−4c, 5b, and 12

	4a	4b	4c	5b	12
bond lengths					
Pd1−C1	1.969(4)	1.939(5)	1.969(3)	1.949(3)	1.977(4)
Pd1−N3	2.184(3)	2.165(4)	2.170(3)	2.146(2)	2.191(3)
Pd1−N4	—	—	—	—	—
Pd1−Cl1	2.3605(10)	2.3612(12)	2.3237(9)	—	2.3268(12)
Pd1−C_{Me}	2.033(4)	2.036(5)	2.040(4)	2.039(3)	—
Pd1−C27	—	—	—	—	1.972(5)
Pd1−C42	—	—	—	—	—
C4−N1	1.406(5)	1.449(6)	1.412(4)	1.435(3)	1.436(5)
C4−N3	1.273(5)	1.295(6)	1.295(4)	1.278(3)	1.282(5)
C27−O1	—	—	—	—	1.205(6)
C32−C24	—	—	—	—	—
bond angles					
C1−Pd1−N3	77.93(14)	77.22(17)	78.54(13)	77.47(10)	77.45(14)
C1−Pd1−Cl1	174.97(12)	172.75(16)	174.26(18)	—	172.69(12)
C42−Pd1−Cl1	—	—	—	—	—
Pd1−N3−C_{ipso}	127.8(2)	117.1(3)	126.0(2)	116.27(16)	117.0(2)

those for the inequivalent backbone protons of the heterocycle appear at δ 8.09 and 7.52. The iminic and the central imidazolium carbon nuclei resonate at δ 148.1 and 136.1, respectively. The Fourier transform-infrared (FT-IR) stretching frequency for the imine group of **1c** was observed at 1675 cm^{-1}, consistent with values reported for **1a** and **1b**.[16] Deprotonation of **1c** with NaHMDS cleanly gave the free carbene C^$Imine_{Ph}$ (**2c**) in 72% yield, with ^1H and ^{13}C NMR spectra consistent with the desired product. The stretching frequency of the imine group has decreased from that observed in **1c** to 1652 cm^{-1}.

The neutral palladium complexes were prepared in good yields, 80%−98%, either from copper(I) transmetalation[15,25] (for **4a**) or ligand displacement (for **4b** and **4c**) (Scheme 2). In contrast to the corresponding (C^$Imine_R$)$NiBr_2$ complexes,[15] these complexes are diamagnetic, indicating a square planar geometry. All three complexes are stable in solution on exposure to air and moisture at room temperature. Their ^1H NMR spectra showed one set of resonances, consistent with the formation of only one isomer, with the methyl group attached to the metal center resonating at δ 0.23−0.42 in $CDCl_3$. The conformation of all complexes was determined by one-dimensional (1D)-nuclear Overhauser effect spectroscopy (NOESY) nuclear magnetic resonance (NMR) experiments. Selective excitation on the methyl group bound to palladium resulted in a nuclear

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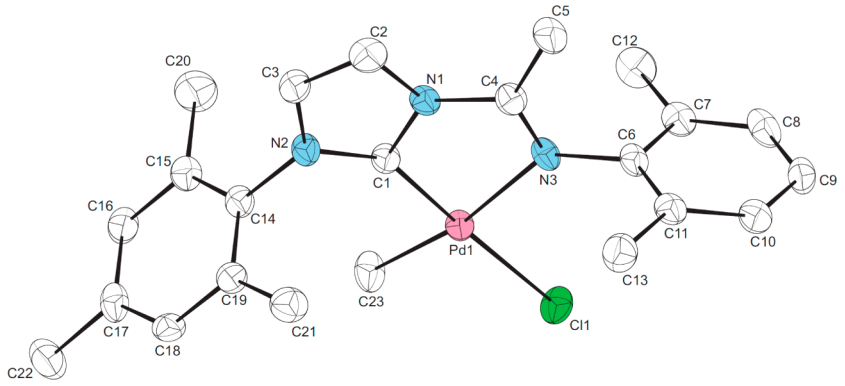

Figure 1. ORTEP plot of the molecular structure of (C^Imine$_{Me}$)PdMeCl (**4a**) (50% probability level). Hydrogen atoms and a solvent molecule of chloroform omitted for clarity.

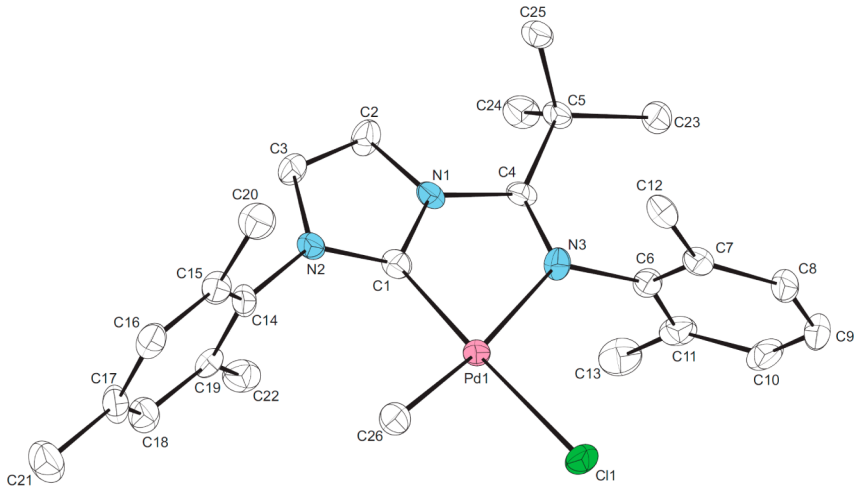

Figure 2. ORTEP plot of the molecular structure of (C^Imine$_{t\text{-}Bu}$)PdMeCl (**4b**) (50% probability level). Hydrogen atoms and a solvent molecule of chloroform omitted for clarity.

Overhauser effect (NOE) for the mesityl ring directly attached to the azole ring, consistent with the methyl group trans to the imine nitrogen and the chloro ligand trans to the carbene.

The palladium methyl carbon and the central imidazolium (NCN) carbon nuclei resonate at approximately δ 9 and 177, respectively, for complexes **4a**–**4c**. While the resonance of the iminic carbon for both **4a** and **4c** appear at δ 156, that of the *tert*-butyl derivative **4b** is found downfield at δ 161.2. The decrease in the FTIR $\nu_{C=N}$ absorption for **4a**–**4c** (1626–1652 cm^{-1}) from the corresponding imidazolium salt strongly suggests coordination of the ligand through both the carbenoid carbon and the iminic nitrogen atoms. These values are also in agreement with those observed in the related nickel complexes.[8]

The crystal structures for all three palladium complexes **4a**–**4c** were obtained, and the selected bond angles and bond lengths are provided in Table 1. Complexes **4a** (Figure 1) and **4c** (Figure 3) both crystallized in the space group $P2_1/n$, while complex **4b** crystallized in the space group $P2_12_12_1$ (Figure 2). All three complexes show a slightly distorted square planar structure where the chloro ligand is trans to the carbene, in agreement with the assignment based on solution NMR spectroscopy and consistent with the trans influence. The palladium–methyl bond lengths are observed in the range of 1.939(5)–1.969(4) Å, similar to those reported for related complexes of NHC^pyridine bidentate ligands.[26] The palladium–chloride bond lengths are in the range of 2.3237(9)–2.3612(12) Å. In all three complexes **4a**–**4c**, the C1–Pd1–N3 bite angles are comparable, with values ranging from 77.22(17)° to 78.54(13)°. In contrast, the nature of the substituent has a marked impact on the Pd1–N3–C$_{ipso}$ angles, with the large *tert*-butyl group pushing the xylyl ring toward the metal, resulting in the smallest angle of 117.1(3)°. The smaller methyl group yields a larger angle of 127.8(2)°, which is only slightly further reduced to 126.0(2)° upon substituting the iminic carbon with a phenyl ring. These differences further manifest themselves in the yaw distortion,[27] with the smallest one observed in the *tert*-butyl derivative (θ = 11.9°) and the largest ones in the methyl (θ = 13.5°) and phenyl (θ = 13.6°) analogues. This is consistent with our previous report on nickel analogues.[15] The Pd1–N3 bond length is the smallest for the *tert*-butyl [**4b**, 2.165(4) Å] and the phenyl [**4c**, 2.170(3) Å] derivatives and the largest [2.184(3) Å] for the methyl derivative (**4a**). Interestingly, the Pd–C1 bond length in **4a** and **4c** are also statistically equivalent and longer at 1.969 Å compared to **4b** [1.939(5) Å]. These metrics clearly impact the coordination sphere around the metal, possibly resulting in differences in reactivity toward various substrates. Finally, the solid-state structures clearly show the axial positions of the square planar structures well-protected by the ortho-methyl substituents of both aryl rings, which are tilted by 85.8° and 74.0° (**4a**), 87.2° and 84.6°(**4b**), and 79.0° and 69.8° (**4c**), with respect to the mean plane formed by the metallacycle. Protection of the axial positions is well-known to be essential for α-diimine

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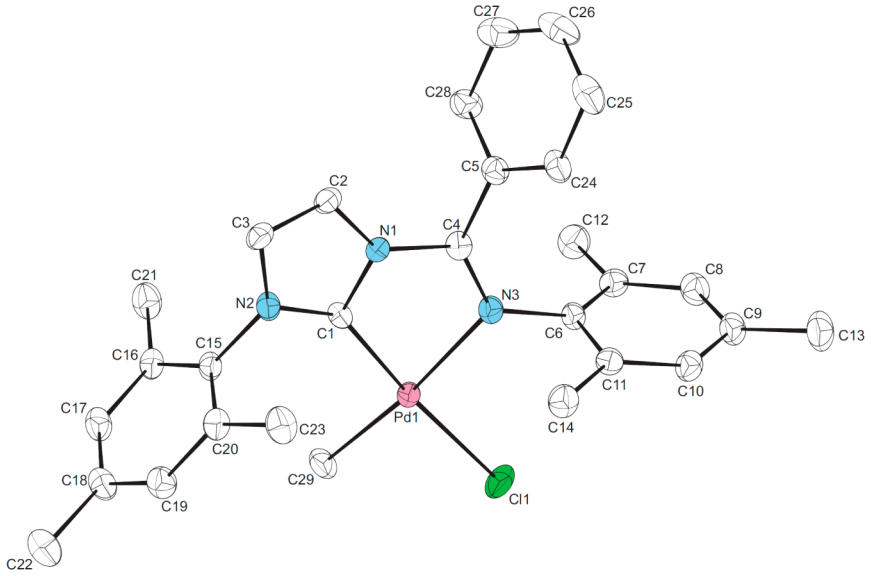

Figure 3. ORTEP plot of the molecular structure of (C^Imine$_{Ph}$)PdMeCl (**4c**) (50% probability level). Hydrogen atoms omitted for clarity.

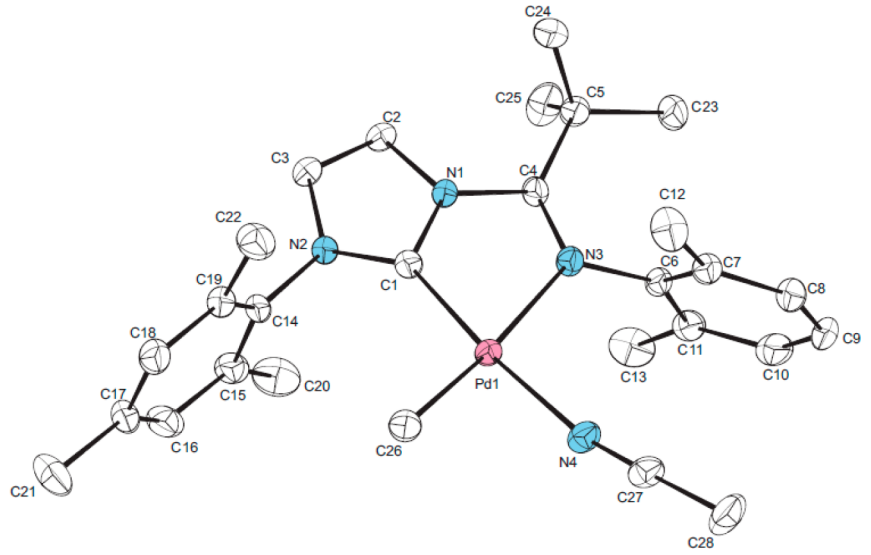

Figure 4. ORTEP diagram of [(C^Imine$_{t\text{-}Bu}$)PdMe(MeCN)]PF_6 (**5b**) (50% probability level). Counteranion (PF_6^-) and hydrogen atoms omitted for clarity.

palladium (and nickel) catalysts to achieve high molecular weight polymer, effectively mitigating chain transfer from an associative displacement of an alkene terminated polymer chain by an incoming monomer.[28]

The related cationic methyl complexes were also prepared as model compounds for the cationic hydrocarbyl propagating species that are present in the catalytic cycle of olefin polymerization. Addition of one equivalent of silver hexafluorophosphate to compounds **4a**−**4c** in acetonitrile resulted in the formation of the cationic complexes **5a**−**5c** in excellent yields (Scheme 2). Similar to the neutral complexes, all cationic complexes are stable in solution on exposure to air and moisture at room temperature. Similarly, only one set of resonances is observed in the proton NMR spectra, consistent with the presence of only one isomer. 1D-NOESY NMR spectra are consistent with the methyl group trans to the imine nitrogen, with an acetonitrile molecule trans to the carbene.

The palladium-bound methyl protons in **5a**−**5c** resonate at lower frequencies to those of the neutral analogues **4a**−**4c**, with chemical shifts in chloroform-*d* ranging from δ −0.10 to 0.10. The acetronitrile protons appears at approximately δ 1.6 for all three cationic complexes, consistent with its coordination to the metal center. The carbenoid carbon (NCN) nucleus of compounds **5a**−**5c** resonates at approximately δ 172 and upfield shift from that of **4a**−**4c**. Interestingly, no significant changes in chemical shifts were observed for the palladium methyl carbon nucleus. The lower electron density on the cationic metal center of compounds **5a**−**5c** led to a decrease in π-backdonation, as evidenced by the FTIR $\nu_{C=N}$ stretching frequencies (1635−1660 cm^{-1}) that are 5−9 cm^{-1} larger than those observed in **4a**−**4c**. The values of these stretching frequencies are also consistent with bidentate coordination of the ligand through the carbenoid carbon and the imine nitrogen.

X-ray quality crystals of **5b** were successfully grown at room temperature by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution. Compound **5b** crystallized in a monoclinic crystal system in the $P2_1/n$ space group. The complex adopts a distorted square planar geometry, with the

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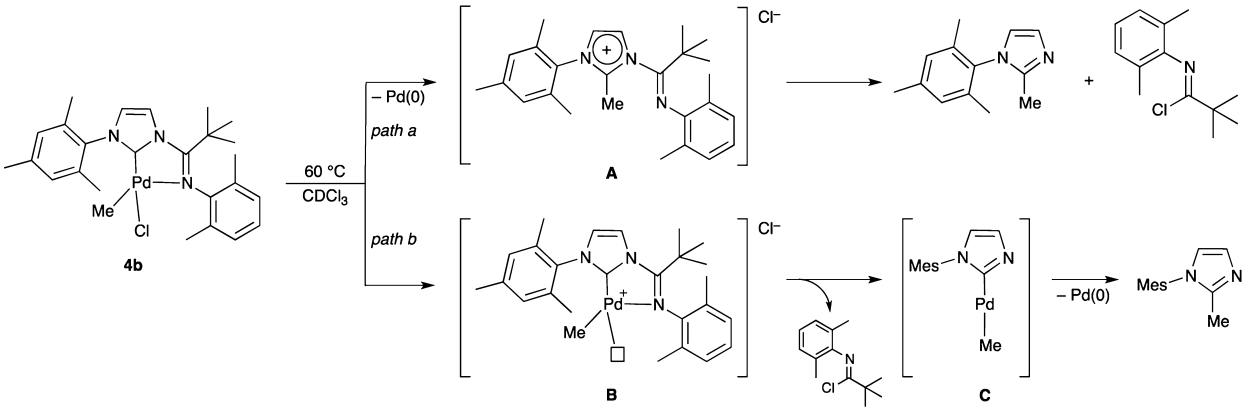
Scheme 3. Proposed Mechanisms for the Thermal Decomposition of Neutral 4b



acetonitrile bound trans to the carbene, as predicted from NMR spectroscopy experiments (Figure 4). Abstraction of the chloro ligand and its replacement with a molecule of acetonitrile caused a decrease in both the Pd1–N3 and C4–N3 bond lengths from 2.165(4) Å in **4b** to 2.146(2) Å in **5b** and from 1.295(6) Å in **4b** to 1.278(3) Å in **5b**, respectively, with very little change to the Pd1–C1 bond length. This substitution also resulted in the Pd1–N3–C_{ipso} bond angle decreasing from 117.1(3) to 116.27(16)°, with little change to either the C1–Pd1–N3 bite angle or the yaw distortion (θ 12.2° in **5b** compared to θ 11.9° in **4b**).

Reactivity Studies of Palladium Complexes 4 and 5. The activity of the compounds **4a–4c** in the polymerization of ethylene was tested at atmospheric pressure and room temperature using 1000 equivalents methylaluminoxane (MAO) as cocatalyst to generate in situ the putative catalytically active cationic species. Palladium black readily formed and no ethylene uptake was noted in any of the trials. While palladium black was not observed in reactions with **5a–5c**, these complexes did not either produce polyethylene with and without MAO added. Considering reports of reductive elimination in other NHC palladium alkyl complexes,[12,29,30] thermal studies of complexes **4** and **5** were undertaken to determine whether these complexes also suffered from this undesired side-reaction, limiting their utility in catalysis involving migratory insertion of an alkyl group.

All complexes were heated to 60 °C in $CDCl_3$ and monitored over time for any sign of decomposition. The nature of the substituent on the iminic carbon impacted the thermal stability of the neutral complexes **4a–4c**. In the case of the *tert*-butyl derivative **4b**, *N*-(2,6-dimethylphenyl)pivalimidoyl chloride and 1-mesityl-2-methyl-1H-imidazole[31] were produced as the major species after 30 min, with complete decomposition of **4b** within 24 h. In contrast, both the methyl (**4a**) and phenyl (**4c**) derivatives and the cationic complexes (**5a–5c**) showed no evidence of decomposition when heated to 60 °C in $CDCl_3$. This is in stark contrast to other palladium alkyl systems for which the cationic species undergo reduction elimination more readily than their neutral analogues.[29,30,32]

Two mechanisms for the formation of *N*-(2,6-dimethylphenyl)pivalimidoyl chloride and 1-mesityl-2-methyl-1H-imidazole from **4b** are proposed in Scheme 3. In path a, complex **4b** undergoes reductive elimination to generate Pd(0) and the 2-methylimidazolium salt (**A**), which then reacts with the chloride anion to produce the observed products. While chloride is a very poor nucleophile, we have observed similar cleavage of the imidazole–imine bond in other related systems.[33] In path b, the chloride first dissociates from **4b** to form complex **B**. Coordination of the imine to the cationic metal center enhances the electrophilicity of the carbon atom, making it more susceptible to nucleophilic attack of the chloride to generate the observed imidoyl chloride and a reactive two-coordinate (imidazolyl)(methyl)palladium complex **C** that undergoes reductive elimination to give the substituted imidazole.

To get a better understanding of the actual decomposition mechanism, the imidazolium tetrafluoroborate salt **1b** and both the neutral (**4b**) and cationic (**5b**) palladium methyl complexes were treated with chloride ions. Addition of tetrabutylammonium chloride to **1b** gave no reaction, even at elevated temperature, ruling out the formation of compound **A**, and consequently of path a. Compound **1b**, however, rapidly decomposed to *N*-mesitylimidazole and to the imidoyl chloride upon addition of HCl in diethyl ether at room temperature, supposedly due to protonation of the imine nitrogen, effectively activating the imine carbon for nucleophilic attack by the chloride.

While palladium complex **4b** remains intact at room temperature when exposed to Bu_4NCl, formation of *N*-(2,6-dimethylphenyl)pivalimidoyl chloride and 1-mesityl-2-methyl-1H-imidazole was observed upon heating the reaction mixture to 60 °C. The lower decomposition rate compared to that observed in the absence of additional chloride ions is consistent with the cationic metal complex **B** being a key intermediate in the decomposition of **4b**. These results, coupled with the rapid decomposition of the cationic complex **5b** observed upon addition of Bu_4NCl, support the mechanism proposed in path b (Scheme 3). While dissociation of the chloride in **4a** and **4c** may also occur, the stronger imidazole–imine bond in these two complexes, indicated by their short C4–N1 bond lengths [1.406(5) and 1.412(4) Å, respectively, compared to 1.449(6) in **4b**], may prevent further decomposition to compound **C**, resulting in the reversible coordination of the chloride anion to regenerate the stable four-coordinate neutral palladium complex.

The stability of all three cationic complexes **5a–5c** at 60 °C, however, suggested that the inability of these complexes to catalyze the polymerization of ethylene was not due to decomposition of a cationic metal alkyl propagating species but possibly arose from their inability to undergo migratory insertion. To get further insight into the ability of the palladium methyl group to insert into electrophiles, reaction of complexes **4** and **5** toward isocyanides was investigated. Interestingly, despite using similar experimental conditions, reaction of neutral complexes **4a–4c** with *tert*-butyl isocyanide in toluene all led to different reaction products, further highlighting the important role of the substituent on the imine carbon (Scheme 4). Addition

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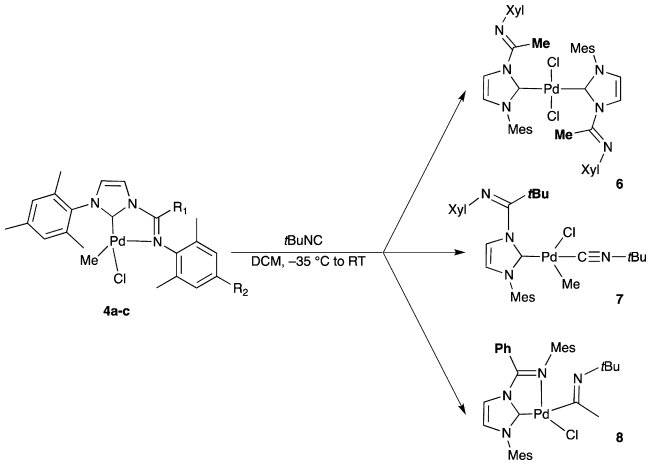
Scheme 4. Reactivity of Neutral Complexes 4a−4c with *tert*-Butyl Isocyanides



of one equivalent of *tert*-butyl isocyanide to (C^Imine$_{Me}$)-PdMeCl (**4a**) in toluene at −35 °C, with subsequent warming to room temperature and standard workup, resulted a yellow solid. The ^{1}H NMR spectrum was surprisingly simple, with only resonances assigned to the coordinated C^Imine$_{Me}$ ligand present, with no other proton coming from either the palladium methyl group of the isocyanide. The FTIR $\nu_{C=N}$ stretching frequency at 1674 cm^{-1} strongly suggests coordination of the C^Imine$_{Me}$ ligand exclusively through the carbenoid carbon atom. X-ray quality crystals of the isolated product were successfully obtained by slow vapor diffusion of pentane into a concentrated solution of dichloromethane.

The compound crystallized in the centrosymmetric P$\bar{1}$ space group, with the solid-state structure consistent with the spectroscopic data, in which two C^Imine$_{Me}$ ligands are bound to the metal center through the carbene, with the iminic arm remaining uncoordinated (Figure 5), similar to that observed in (C^Imine$_{Me}$)$_2$NiCl$_2$.[8] Compound **6** adopts a slightly distorted square planar geometry, with both carbene ligands coordinated trans to each other. The palladium atom lies on an inversion center, which results in two sets of crystallographically equivalent ligand sets and chlorine atoms, with linear angles for C1−Pd−C1a and Cl1−Pd1−Cl1a. Other angles around the metal range from 89.7(2)° to 90.3(2)° and add up to 180(3)°. The Pd1−C1 bond length is of 2.027(4) Å, within the range reported for other (NHC)$_2$PdCl$_2$ complexes.[34] The N3−C4 bond length measures 1.252(5) Å, statistically equivalent to that observed in **1a**.[17]

Under similar conditions, when *tert*-butyl isocyanide was added to (C^Imine$_{t\text{-Bu}}$)PdMeCl (**4b**) in toluene at −35 °C and allowed to warm up to room temperature, a gradual color change from tan to yellow was observed, with the final product identified as the coordinated isocyanide adduct (C^Imine$_{t\text{-Bu}}$)PdMe(*t*-BuNC)Cl (**7**) (Scheme 4). The ^{1}H NMR spectrum (C_6D_6) of compound **7** is consistent with coordination of the isocyanide with no insertion, as evidenced by a new resonance at δ 0.70 attributed to the protons of the coordinated isocyanide and the palladium methyl protons remaining upfield at δ −0.50. Migratory insertion would have resulted in the latter resonating at a higher frequency (δ 1.6−2.3), characteristic of the iminoacyl complex.[9] In the ^{13}C NMR spectrum, the isocyanide carbon atom that is directly attached to the metal center is observed at δ 119.6, consistent with simple coordination.[7,35] The IR spectrum shows a strong band at 2189 cm^{-1}, assigned to the coordinated isocyanide. Heating the reaction mixture to 70 °C to enforce migratory insertion of the methyl group into the coordinated isocyanide led to the formation of palladium black and unidentified products presumably through decomposition (vide supra).

In contrast, reaction of *tert*-butyl isocyanide with (C^Imine$_{Ph}$)-PdMeCl (**4c**) at room temperature yielded the insertion product **8**, as a light orange solid (Scheme 4). The ^{1}H NMR spectrum (C_6D_6) of **8** is consistent with the structure, as evidenced by a new resonance at δ 2.49 for the iminoacyl methyl protons, and the disappearance of the initial Pd−Me resonance at δ −0.50. The imine bond stretching frequency at 1638 cm^{-1} furthermore indicates that C^Imine$_{Ph}$ remains coordinated in a bidentate fashion to satisfy the preferred electronics and tetracoordinate nature of palladium(II).

Replacing the *tert*-butyl group of the isocyanide by an aryl ring has a profound effect on the chemistry displayed by complexes

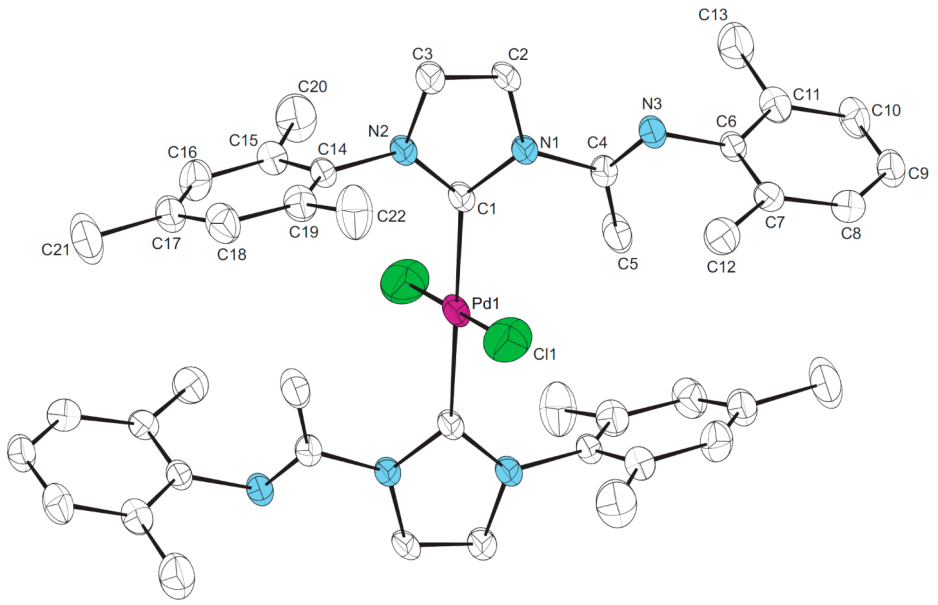


Figure 5. ORTEP plot of (C^Imine$_{Me}$)$_2$PdCl$_2$ (**6**) (50% probability level). Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−C1 2.027(4), Pd1−Cl1 2.413(10), C4−N1 1.445(5), C4−N3 1.254(5), and C1−Pd1−Cl1 89.7(2).

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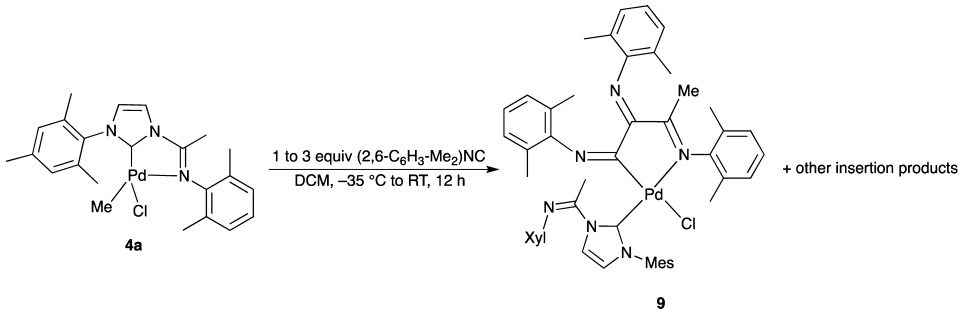
Scheme 5. Reactivity of Complex 4a with 2,6-Dimethylphenyl Isocyanide



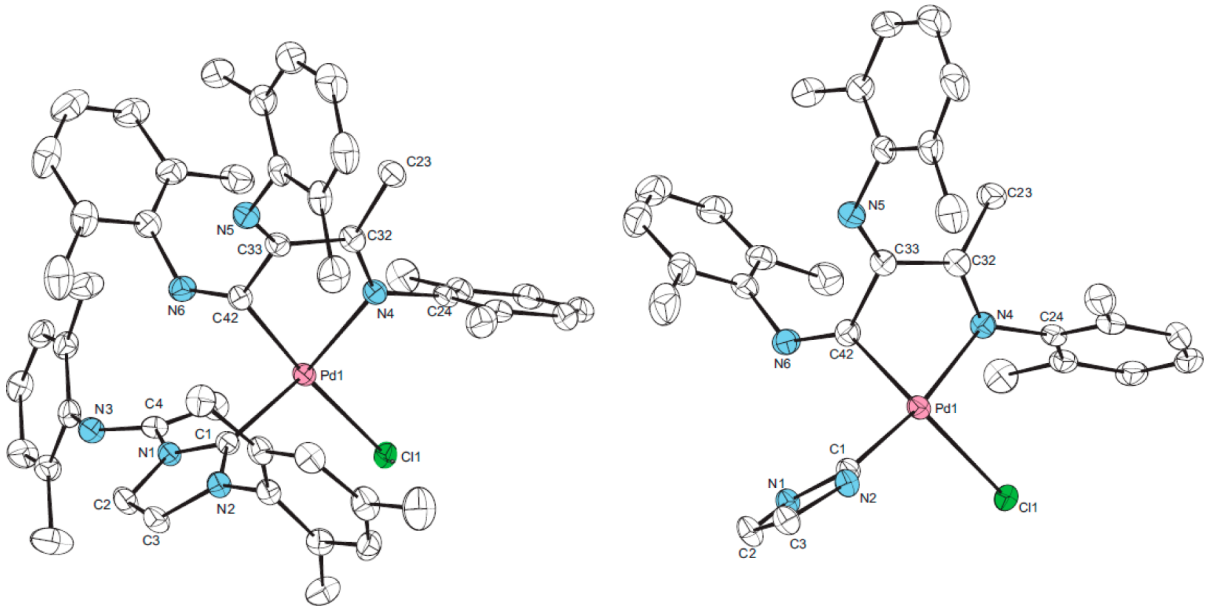


Figure 6. ORTEP plot of chloro(C^Imine$_{Me}$)(1,2-bis[(2,6-dimethylphenyl)imino]-3-[(2,6-dimethylphenyl)imino-κ-*N*]butyl-κ-*C*]palladium(II) (**9**) (50% probability level). Left: Full structure. Right: N1/N2 substituents are omitted for clarity. Hydrogen atoms and one solvent molecule of chloroform omitted in both views for clarity. Selected bond distances (Å) and angles (deg): Pd1−C1 1.996(3), Pd1−N4 2.103(3), Pd1−Cl1 2.400(19), Pd1−C42 1.971(3), C4−N1 1.446(4), C4−N3 1.265(4), C24−C32 1.290(4), C1−Pd1−N3 79.71(12), C1−Pd1−Cl1 94.7(6), C42−Pd1−Cl1 166.9(5), Pd1−N4−C24 123.6(2).

4a−**4c**. Reaction with an excess of 2,6-dimethylphenyl isocyanide gave spectroscopic evidence of several products of multiple insertions (Scheme 5). X-ray quality crystals were successfully isolated from the reaction mixture with **4a**. Compound **9** selectively crystallized in a monoclinic crystal system in the $P2_1/c$ space group. The palladium center adopts a distorted square planar geometry with three molecules of isocyanide inserted into the Pd−Me bond, and forming a new five-membered metallacycle, effectively breaking the chelate formed by C^Imine$_{Me}$ in **4a** (Figure 6). This demonstrates the hemilability of the imine fragment, easily dissociating from the metal center to accommodate the steric and electronic properties of the other ligands. This feature may prove invaluable in catalytic transformations when reactive coordinatively- and electronically unsaturated intermediates are produced. These intermediates could effectively be stabilized through coordination of the imine nitrogen atom before re-entering the catalytic cycle upon associative displacement of the nitrogen donor by an incoming substrate.

Complex **9** resulted from three consecutive insertions of 2,6-dimethylphenyl isocyanide into the palladium−methyl bond, as previously observed and structurally characterized by other groups.[8,9,11,36] Interestingly, formation of a five-membered metallacycle through coordination of the isocyanide nitrogen atom N4 is preferred over coordination of N3 from C^Imine$_{Me}$, possibly due to the higher strain that would otherwise result based on the yaw distortion for **4** and **5** (vide supra). The formation of the observed metallacycle furthermore generates a more favorable metal bite angle of 79.71(12)°, compared to the more acute 77.93(14)° in **4a**. This also leads to a Pd−N4 bond length of 2.103(3) Å markedly shorter than Pd1−N3 [2.184(3) Å] in complex **4a**, with enhanced π-backdonation from the metal to the C=N π^* orbital, resulting in a C32−N4 bond [1.290(4) Å] slightly longer than C4−N3 in **4a** [1.273(5) Å].

Considering the better thermal stability of the palladium complexes **5** and the importance of cationic complexes in olefin polymerization catalysis, the reactivity of these complexes in isocyanide insertion was also explored. Addition of one equivalent of either *tert*-butyl or 2,6-dimethylphenyl isocyanide to the palladium complex produced the isocyanide adduct in good yield (83−96%) (Scheme 6). The ^{1}H NMR spectra of the *tert*-butyl isocyanide reaction products (**10**) showed sharp upfield resonances (δ 0.01 to −0.10) integrating to three protons, characteristic of the palladium methyl group. The FTIR $\nu_{C=N}$ absorption of the coordinated isocyanide were observed as a strong sharp band at 2208−2211 cm^{-1}, approximately 74 cm^{-1}

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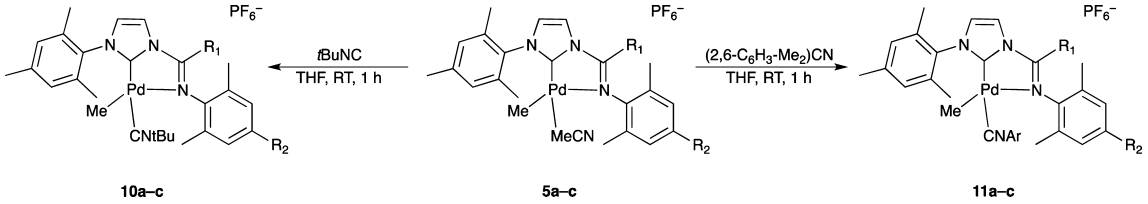
Scheme 6. Reactivity of Cationic Complexes 5a−5c with Isocyanides

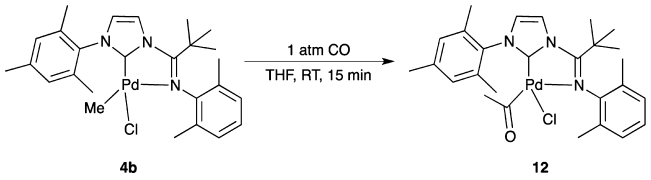


higher than that of free isocyanide.[6] The ^{1}H NMR spectra for **11** are also consistent with isocyanide coordination with no evidence of migratory insertion of the methyl group, as indicated by the corresponding FTIR $\nu_{C\equiv N}$ absorption at 2181−2184 cm^{-1}. The C═N stretching frequency for the C^Imine$_R$ ligand in **10** and **11** ranged from 1626 to 1656 cm^{-1}, indicating bidentate coordination.

Addition of two to five equivalents of *tert*-butyl or 2,6-dimethylphenyl isocyanide to **5a−5c** resulted in multiple products. While unable to isolate each individual component, mass spectrometry on the reaction mixture shows signals corresponding to the isocyanide adduct of the palladium methyl complex **5** and of palladium *N*-(2,6-dimethylphenyl)iminoacyl insertion products, which are a result of single and multiple insertion of the methyl group into the isocyanide. Signals from the organic isocyanide oligomers, generated by cleavage of the growing chain from the metal center by protonolysis, were also observed.

Considering the ability of isocyanide to insert multiple times into a metal−carbon bond made and the challenge in isolating and characterizing the reaction mixture, we decided to explore the reactivity of complexes **4** and **5** toward CO, which does not undergo multiple insertions. The *tert*-butyl derivative **4b** reacts with CO within a few minutes to form the acyl complex **12** in 77% yield (Scheme 7). The low energy FTIR $\nu_{C\equiv N}$ stretching

Scheme 7. Reactivity of Complexes 4b with CO



frequency of complex **12** (1631 cm^{-1}) indicates chelation of the iminic nitrogen atom. The $\nu_{C=O}$ absorption at 1689 cm^{-1} is consistent with a related NHC palladium acyl complex reported by Jordan.[12] In contrast, neutral complexes **4a** and **4c**, and all cationic **5a−5c** remained intact upon exposure to one atmosphere of carbon monoxide, with no evidence of CO coordination, insertion, or reductive elimination, as observed by Elsevier in a related system.[37]

X-ray quality crystals of **12** were grown at room temperature by slow vapor diffusion of pentane in a saturated dichloromethane solution. Compound **12** crystallized in a monoclinic crystal system in the $P2_1/n$ space group. The palladium center adopts a distorted square planar geometry with one equivalent of CO inserted into the Pd−Me bond (Figure 7). The acyl group (C27−O1−C26) is approximately orthogonal (85.2°) to the mean plane formed by C1, N3, Pd1, and C27, allowing for interactions with the metal dπ orbitals. This competing π-accepting capability of the acyl group may account for the greater Pd1−N3 and Pd1−C1 bond lengths compared to those in the palladium methyl precursor **4b** (Table 1). While the chelate angle of 77.45(14)° remained practically unchanged from that of the starting *tert*-butyl derivative complex **4b**, the greater bulk of the acyl group further distorts the Pd−NHC bond, as suggested by a larger yaw distortion angle of 12.6°.

CONCLUSIONS

Several neutral and cationic palladium complexes with an aryl-substituted acyclic imino-*N*-heterocyclic carbene were prepared, isolated, and characterized to get insight into the inactivity of related nickel complexes in ethylene polymerization.[15] None of the new palladium complexes gave polyethylene at 1 atm C_2H_4 and room temperature. Their thermal stability and reactivity toward electrophiles were thus studied. All three cationic palladium methyl complexes **5**, model compounds for active olefin polymerization catalysts, and both neutral complexes **4a** and **4c** were found to be stable at elevated temperatures. In contrast, the *tert*-butyl derivative **4b** rapidly decomposed under similar conditions, possibly through dissociation of the chloride followed by a series of nucleophilic attack and reductive elimination to yield palladium black, 1-mesityl-2-methyl-1H-imidazole, and the corresponding imidoyl chloride. Addition of MAO to **4** at room temperature also caused formation of palladium black. We further demonstrated the significant role of the substituent on the imine carbon on the reactivity of **4** and **5** with isocyanides and carbon monoxide. Compounds **4** and **5** reacted with these electrophiles to give a variety of products, including structurally characterized simple adducts and single and multiple insertion products. On the basis of these observations, the inactivity of these palladium methyl complexes in ethylene polymerization may thus stem from their inability to insert ethylene, rather than from their intrinsic instability, especially for the cationic species.

EXPERIMENTAL SECTION

All manipulations were performed under a dinitrogen atmosphere in a glovebox 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 dinitrogen. 1-(2,4,6-Trimethylphenyl)imidazole,[38] *N*-(2,6-dimethylphenyl)acetimidoyl chloride, *N*-(2,6-dimethylphenyl)pivalimidoyl chloride, *N*-(2,4,6-trimethylphenyl)benzimidoyl chloride,[39] **2b**[16] and **3**[15] were prepared according to published procedures. $PdCl_2$ and Pd(COD)MeCl were purchased from Strem and used without further purification. Silver hexafluorophosphate was purchased from Alfa Aesar and used as received. *tert*-Butyl isocyanide, 2,6-dimethylphenyl isocyanide, sodium bis(trimethylsilyl)amide were purchased from Sigma-Alrich and used as received. 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 (^{1}H at 400 MHz and ^{13}C at 100 MHz) or Bruker AV 300 (^{1}H at 300 MHz and ^{13}C at 75.5 MHz) spectrometer and are at room temperature, unless otherwise stated. The spectra were

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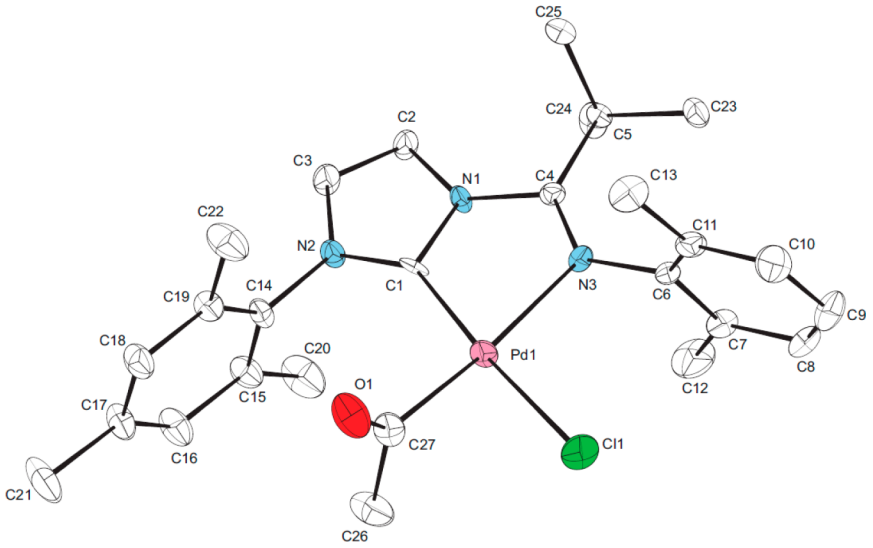

Figure 7. ORTEP plot of (C^Imine$_{Me}$)Pd(COMe)Cl (**12**) (50% probability level). Hydrogen atoms omitted for clarity.

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. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental composition was determined by Guelph Chemical Laboratories Incorporated.

1-[1-(2,4,6-Trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate, C^Imine$_{Ph}$·HBF$_4$ (1c). *N*-(2,4,6-Dimethylphenyl)benzimidoyl chloride (3.63 g, 16.2 mmol) was dissolved in a minimal amount of acetonitrile and added to a suspension of acetonitrile (70 mL) solution of $NaBF_4$ (1.78 g, 16.2 mmol) at room temperature and stirred for 36 h. 2,4,6-Trimethylphenylimidazole (3.03 g, 16.3 mmol) was subsequently added, and the reaction mixture was stirred for an additional 12 h. Volatiles were then removed under vacuum, and the resulting brown solid was dissolved in a minimal amount of dichloromethane. The solution was filtered and pentane was added to the filtrate to precipitate the product. The solid was further washed with pentane and dried under vacuum, giving the product as a light brown solid (5.38 g, 10.9 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H, NC*H*N$_{(azole)}$), 8.09 (s, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 7.52 (s, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 7.37 (m, 5H, C*H*$_{(phenyl)}$), 7.01 (s, 2H, *m*-C*H*$_{(azole\text{-}mesityl)}$), 6.74 (s, 2H, *m*-C*H*$_{(N\text{-}mesityl)}$), 2.33 (s, 3H, *p*-C*H*$_{3(azole\text{-}mesityl)}$), 2.20 (s, 3H, *p*-C*H*$_{3(N\text{-}mesityl)}$), 2.17 (s, 6H, *o*-C*H*$_{3(N\text{-}mesityl)}$), 2.02 (s, 6H, *o*-C*H*$_{3(azole\text{-}mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.1 (*C*═N), 141.8 (*p*-*C*$_{(azole\text{-}mesityl)}$), 140.7 (*C*$_{ipso(N\text{-}mesityl)}$), 134.5 (*C*$_{(phenyl)}$), 134.4 (*o*-*C*$_{(azole\text{-}mesityl)}$), 132.6 (*C*$_{(phenyl)}$), 130.7 (*C*$_{ipso(azole\text{-}mesityl)}$), 130.1 (*m*-CH$_{(azole\text{-}mesityl)}$), 130.0 (*p*-*C*$_{(N\text{-}mesityl)}$), 129.5 (*C*$_{(phenyl)}$), 129.0 (*m*-CH$_{(N\text{-}mesityl)}$), 128.0 (*C*$_{(phenyl)}$), 126.6 (*o*-*C*$_{(N\text{-}mesityl)}$), 124.9 (NCCN$_{(azole\text{-}mesityl)}$), 121.9 (NCCN$_{(azole\text{-}mesityl)}$), 21.2 (*p*-CH$_{3(azole\text{-}mesityl)}$), 20.8 (*p*-CH$_{3(N\text{-}mesityl)}$), 18.4 (*o*-CH$_{3(N\text{-}mesityl)}$), 17.6 (*o*-CH$_{3(azole\text{-}mesityl)}$). FT-IR (cast-$CDCl_3$) $\nu_{C=N}$ 1675 cm^{-1}. Anal. Calcd for $C_{28}H_{30}N_3BF_4$ (%): C, 67.89; H, 6.10; N, 8.48. Found (%): C, 68.13; H, 5.86; N, 8.33.

1-[1-(2,4,6-Trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene, C^Imine$_{Ph}$ (2c). A suspension of C^Imine$_{Ph}$·HBF$_4$ **1c** (96.7 mg, 0.195 mmol) and KN[Si(CH$_3$)$_3$]$_2$ (39.1 mg, 0.196 mmol) in toluene (15 mL) was cooled to −78 °C and stirred at this temperature for 30 min. The flask was then removed from the bath and stirred at room temperature for an additional 1.5 h. Volatiles were removed under reduced pressure, and pentane (20 mL) was added to extract the product. The pentane solution was filtered and the filtrate was dried under reduced pressure to give a yellow solid (57.2 mg, 0.140 mmol, 72%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (d, ^3J = 7.5 Hz, 2H, *p*-C*H*$_{(phenyl)}$), 7.32 (s, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 6.94−6.89 (m, 3H, *m*-C*H*$_{(phenyl)}$ + *o*-C*H*$_{(phenyl)}$), 6.65 (s, 2H, *m*-C*H*$_{(azole\text{-}mesityl)}$), 6.48 (s, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 6.48 (s, 2H, *m*-C*H*$_{(N\text{-}mesityl)}$), 2.07 (s, 6H, *o*-C*H*$_{3(azole\text{-}mesityl)}$), 1.97 (s, 3H, *p*-C*H*$_{3(azole\text{-}mesityl)}$), 1.94 (s, 3H, *p*-C*H*$_{3(azole\text{-}mesityl)}$), 1.80 (s, 6H, *o*-C*H*$_{3(N\text{-}mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 158.2 (*C*═N), 146.0 (*C*$_{ipso(N\text{-}mesityl)}$), 137.9 (*p*-*C*$_{(azole\text{-}mesityl)}$), 136.8 (*C*$_{ipso(azole\text{-}mesityl)}$), 135.3 (*o*-*C*$_{(azole\text{-}mesityl)}$), 131.8 (*p*-*C*$_{(N\text{-}mesityl)}$), 130.1 (NCCN$_{(azole\text{-}mesityl)}$), 129.7 (*o*-*C*$_{(phenyl)}$), 129.3 (*p*-*C*$_{(phenyl)}$), 129.1 (*C*$_{ipso(phenyl)}$), 128.9 (NCCN$_{(azole\text{-}mesityl)}$), 128.8 (*m*-CH$_{(azole\text{-}mesityl)}$), 127.6 (*m*-*C*$_{(phenyl)}$), 125.0 (*o*-*C*$_{(N\text{-}mesityl)}$), 123.7 (*m*-CH$_{(N\text{-}mesityl)}$), 21.0 (*p*-CH$_{3(azole\text{-}mesityl)}$), 20.7 (*p*-CH$_{3(N\text{-}mesityl)}$), 18.4 (*o*-CH$_{3(N\text{-}mesityl)}$), 18.0 (*o*-CH$_{3(azole\text{-}mesityl)}$); resonance for NCN was not observed. FT-IR (cast-solvent) $\nu_{C=N}$ 1652 cm^{-1}. Anal. Calcd for $C_{28}H_{29}N_3$ (%): C, 82.52; H, 7.17; N, 10.31. Found (%): C, 82.26; H, 6.90; N, 10.58.

Chloromethyl{1-[1-(2,6-dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium, Pd(C^Imine$_{Me}$)MeCl (4a). A solution of [Cu(C^Imine$_{Me}$)I]$_2$ (**3**) (233 mg, 0.224 mmol) in THF (12 mL) was added to a solution of chloromethyl(1,5-cyclooctadiene)palladium(II) (118 mg, 0.447 mmol) in THF (4 mL). The resulting mixture was stirred at room temperature for 16 h, and then the solution was filtered through Celite. The mixture was concentrated down to 6 mL and pentane was added to precipitate the product. A beige solid was recovered and further washed with pentane (2 × 6 mL) and dried under reduced pressure (173 mg, 0.354 mmol, 80%). Crystals suitable for X-ray diffraction were grown at room temperature by slow vapor diffusion of pentane into a saturated chloroform solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, ^3J = 1.9 Hz, 1H, NC*H*CN$_{(mesityl)}$), 7.07−7.06 (m, 3H, *p*-C*H*$_{(2,6\text{-}xylyl)}$ + *m*-C*H*$_{(2,6\text{-}xylyl)}$), 6.98 (s, 2H, *m*-C*H*$_{(mesityl)}$), 6.83 (d, ^3J = 1.9 Hz, 1H, NCC*H*N$_{(mesityl)}$), 2.35 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.22 (s, 9H, C*H*$_{3(imine)}$ + *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 2.13 (s, 6H, *o*-C*H*$_{3(mesityl)}$), 0.30 (s, 3H, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.0 (NCN), 156.2(C═N), 142.2 (*C*$_{ipso(2,6\text{-}xylyl)}$), 140.1 (*p*-*C*$_{(mesityl)}$), 134.8 (*C*$_{ipso(mesityl)}$), 134.5 (*o*-*C*$_{(mesityl)}$), 129.7 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 129.4 (*m*-CH$_{(mesityl)}$), 128.2 (*m*-CH$_{(2,6\text{-}xylyl)}$), 126.2 (*p*-CH$_{(2,6\text{-}xylyl)}$), 124.2 (NCCN$_{(mesityl)}$), 116.9 (NCCN$_{(mesityl)}$), 21.4 (*p*-CH$_{3(mesityl)}$), 18.9 (*o*-CH$_{3(2,6\text{-}xylyl)}$), 18.0 (*o*-CH$_{3(mesityl)}$), 14.8 (CH$_{3(imine)}$), −8.9 (Pd−CH$_3$). FT-IR (cast-DCM): $\nu_{C=N}$ 1652 cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_3ClPd$ (%): C, 56.57; H, 5.78; N, 8.60. Found (%): C, 56.42; H, 6.07; N, 8.42.

Chloromethyl{1-[1-(2,6-dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium, Pd(C^Imine$_{t\text{-}Bu}$)MeCl (4b). A solution of C^Imine$_{t\text{-}Bu}$ (**2b**) (323 mg, 0.864 mmol) in THF (8 mL) and was added to a solution of chloromethyl(1,5-cyclooctadiene)palladium(II) (207 mg, 0.782 mmol) in THF (6 mL). The reaction mixture was stirred for 5 h. Volatiles were removed under reduced pressure, and a pentane wash (2 × 8 mL) was performed to give a beige solid (415 mg, 0.766 mmol, 98%). Crystals suitable for X-ray diffraction were grown at room temperature by slow vapor diffusion of pentane into a saturated chloroform solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, ^3J = 2.0 Hz, 1H, NC*H*CN$_{(mesityl)}$), 6.70 (m, 3H, *p*-C*H*$_{(2,6\text{-}xylyl)}$ + *m*-C*H*$_{(2,6\text{-}xylyl)}$), 6.97 (s, 2H, *m*-C*H*$_{(mesityl)}$),

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6.81 (d, ^3J = 2.2 Hz, 1H, NCC*H*N$_{(mesityl)}$), 2.34 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.29 (s, 6H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 2.15 (s, 6H, *o*-C*H*$_{3(mesityl)}$), 1.39 (s, 9H, C(C*H*$_3$)$_{3(imine)}$), 0.23 (s, 3H, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.8 (NCN$_{(mesityl)}$), 161.2 (*C*=N), 143.7 (C$_{ipso(2,6\text{-}xylyl)}$), 139.9 (*p*-*C*$_{(mesityl)}$), 135.1 (C$_{ipso(mesityl)}$), 134.5 (*o*-*C*$_{(mesityl)}$), 129.4 (*m*-*C*H$_{(mesityl)}$), 128.8 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 127.3 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 125.4 (*p*-*C*H$_{(2,6\text{-}xylyl)}$), 122.7 (NC*C*N$_{(mesityl)}$), 119.5 (NC*C*N$_{(mesityl)}$), 39.9 (*C*(CH$_3$)$_{3(imine)}$), 30.0 (C(*C*H$_3$)$_{3(imine)}$), 21.3 (*p*-*C*H$_{3(mesityl)}$), 19.4 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$), 18.02 (*o*-*C*H$_{3(mesityl)}$), −8.6 (Pd−*C*H$_3$). FT-IR (cast-DCM): $\nu_{C=N}$ 1626 cm^{-1}. Anal. Calcd for $C_{26}H_{34}N_3ClPd$ (%): C, 58.87; H, 6.46; N, 7.92. Found (%): C, 59.10; H, 6.32; N, 8.09.

Chloromethyl{1-[1-(2,4,6-trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium, Pd(C^Imine$_{Ph}$)MeCl (4c). C^Imine$_{Ph}$ (**2c**) (259 mg, 0.635 mmol) dissolved in THF (8 mL) and was added to a solution of chloromethyl(1,5-cyclooctadiene)palladium(II) (159 mg, 0.601 mmol) in THF (8 mL). The reaction mixture was stirred for 4 h. Volatiles were removed under reduced pressure, and a pentane wash was performed to give a light cream solid (307 mg, 0.544 mmol, 91%). Crystals suitable for X-ray diffraction were grown at room temperature by slow diffusion of pentane into a saturated chloroform solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, ^3J = 7.5 Hz, 1H, *p*-C*H*$_{(phenyl)}$), 7.42 (t, ^3J = 7.5 Hz, 2H, *m*-C*H*$_{(phenyl)}$), 7.35 (d, ^3J = 7.5 Hz, 2H, *o*-C*H*$_{(phenyl)}$), 7.08 (d, ^3J = 2.0 Hz, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 7.02 (s, 2H, *m*-C*H*$_{(azole\text{-}mesityl)}$), 6.75 (s, ^3J = 2.0 Hz, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 6.73 (s, 2H, *m*-C*H*$_{(N\text{-}mesityl)}$), 2.38 (s, 3H, *p*-C*H*$_{3(azole\text{-}mesityl)}$), 2.25 (s, 6H, *o*-C*H*$_{3(N\text{-}mesityl)}$), 2.21 (s, 6H, *o*-C*H*$_{3(azole\text{-}mesityl)}$), 2.19 (s, 3H, *p*-C*H*$_{3(N\text{-}mesityl)}$), 0.42 (s, 3H, Pd−C*H*$_3$).^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 176.5 (NCN$_{(azole\text{-}mesityl)}$), 156.5 (*C*=N), 140.1 (*p*-*C*$_{(azole\text{-}mesityl)}$), 139.6 (C$_{ipso(N\text{-}mesityl)}$), 135.1 (*p*-*C*$_{(N\text{-}mesityl)}$), 134.9 (C$_{ipso(azole\text{-}mesityl)}$), 134.5 (*o*-*C*$_{(azole\text{-}mesityl)}$), 131.8 (*p*-*C*H$_{(phenyl)}$), 129.4 (*m*-*C*H$_{(azole\text{-}mesityl)}$), 129.0 (*m*-*C*H$_{(phenyl)}$), 128.6 (*m*-*C*H$_{(N\text{-}mesityl)}$), 128.3 (*o*-*C*H$_{(phenyl)}$), 128.1 (C$_{ipso(phenyl)}$), 123.5 (NC*C*N$_{(azole\text{-}mesityl)}$), 118.7 (NC*C*N$_{(azole\text{-}mesityl)}$), 21.4 (*p*-*C*H$_{3(azole\text{-}mesityl)}$), 21.1 (*p*-*C*H$_{3(N\text{-}mesityl)}$), 19.2 (*o*-*C*H$_{3(N\text{-}mesityl)}$), 18.0 (*o*-*C*H$_{3(azole\text{-}mesityl)}$), −8.8 (Pd−*C*H$_3$), resonance for (*o*-*C*$_{(N\text{-}mesityl)}$) was not observed. FT-IR (cast-DCM): $\nu_{C=N}$ 1635 cm^{-1}. Anal. Calcd for $C_{29}H_{32}N_3ClPd$ (%): C, 61.71; H, 5.71; N, 7.44. Found (%): C, 61.49; H, 5.45; N, 7.18.

{1-[1-(2,6-Dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl Acetonitrile Hexafluorophosphate, Pd(C^Imine$_{Me}$)(Me)(MeCN)]PF$_6$ (5a). A solution of (C^Imine$_{Me}$)PdMeCl (**4a**) (202 mg, 0.414 mmol) in MeCN (6 mL) was added to a suspension of silver hexafluorophosphate (105 mg, 0.415 mmol) in MeCN (4 mL) and stirred at room temperature for 1 h in the absence of light. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting tan residue was washed with pentane (2 × 4 mL) and dried under reduced pressure to give a light beige solid (236 mg, 0.369 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, ^3J = 2.0 Hz, 1H, NC*H*CN$_{(mesityl)}$), 7.13 (m, 3H, *p*-C*H*$_{(2,6\text{-}xylyl)}$ + *m*-C*H*$_{(2,6\text{-}xylyl)}$), 6.98 (s, 2H, *m*-C*H*$_{(mesityl)}$), 6.93 (d, ^3J = 2.0 Hz, 1H, NCC*H*N$_{(mesityl)}$), 2.43 (s, 3H, C*H*$_{3(imine)}$), 2.35 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.23 (s, 6H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 2.09 (s, 6H, *o*-C*H*$_{3(mesityl)}$), 1.72 (s, 3H, *C*H$_3$CN), 0.00 (s, 3H, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.3 (NCN$_{(mesityl)}$), 160.1 (*C*=N), 141.1 (C$_{(2,6\text{-}xylyl)}$), 140.4 (*p*-*C*$_{(mesityl)}$), 134.4 (*o*-*C*$_{(mesityl)}$), 134.3 (C$_{(mesityl)}$), 129.8 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 129.5 (*m*-*C*H$_{(mesityl)}$), 128.6 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 126.9 (*p*-*C*H$_{(2,6\text{-}xylyl)}$), 124.9 (NC*C*N$_{(mesityl)}$), 120.1 (NC*C*N$_{(mesityl)}$), 117.2 (*C*H$_3$CN), 21.3 (*p*-*C*H$_{3(mesityl)}$), 18.3 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$), 17.8 (*o*-*C*H$_{3(mesityl)}$), 14.7 (*C*H$_{3(imine)}$), 1.6 (*C*H$_3$CN), −9.1 (Pd−*C*H$_3$). FT-IR (cast-DCM): $\nu_{C=N}$ 1662 cm^{-1}. Anal. Calcd for $C_{25}H_{31}N_4F_6PPd$ (%): C, 47.00; H, 4.89; N, 8.77. Found (%): C, 46.90; H, 5.15; N, 8.52.

{1-[1-(2,6-Dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl Acetonitrile Hexafluorophosphate, [Pd(C^Imine$_{t\text{-}Bu}$)(Me)(MeCN)]PF$_6$ (5b). A solution of (C^Imine$_{t\text{-}Bu}$)PdMeCl (**4b**) (122 mg, 0.230 mmol) in MeCN (8 mL) was added to a suspension of silver hexafluorophosphate (60.0 mg, 0.237 mmol) in MeCN (2 mL) and stirred at room temperature for 1 h in the absence of light. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting brown residue was washed with pentane and dried under reduced pressure to give a champagne-colored solid (140 mg, 0.206 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, ^3J = 2.1 Hz, 1H, NC*H*CN$_{(mesityl)}$), 7.11 (d, ^3J = 7.4 Hz, 2H, *m*-C*H*$_{(2,6\text{-}xylyl)}$), 7.06 (m, 1H, *p*-C*H*$_{(2,6\text{-}xylyl)}$), 7.03 (d, ^3J = 2.1 Hz, 1H, NCC*H*N$_{(mesityl)}$), 6.97 (s, 2H, *m*-C*H*$_{(mesityl)}$), 2.34 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.30 (s, 6H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 2.10 (s, 6H, *o*-C*H*$_{3(mesityl)}$), 1.71 (s, 3H, *C*H$_3$CN), 1.43 (s, 9H, C(C*H*$_3$)$_{3(imine)}$), −0.08 (s, 3H, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.1 (NCN$_{(mesityl)}$), 164.5 (C=N), 143.6 (C$_{ipso(2,6\text{-}xylyl}$), 140.4 (*p*-*C*$_{(mesityl)}$), 134.5 (C$_{ipso(mesityl)}$), 134.2 (*o*-*C*$_{(mesityl)}$), 129.5 (*m*-*C*H$_{(mesityl)}$), 128.3 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 128.0 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 126.0 (*p*-*C*H$_{(2,6\text{-}xylyl)}$), 124.5 (NC*C*N$_{(mesityl)}$), 122.2 (NC*C*N$_{(mesityl)}$), 118.7 (*C*H$_3$CN), 40.4 (*C*(CH$_3$)$_{3(imine)}$), 29.7 (C(*C*H$_3$)$_{3(imine)}$), 21.3 (*p*-*C*H$_{3(mesityl)}$), 19.0 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$), 17.9 (*o*-*C*H$_{3(mesityl)}$), 1.6 (*C*H$_3$CN), −8.2 (Pd−*C*H$_3$). FT-IR (cast-DCM): $\nu_{C=N}$ 1634 cm^{-1}. Anal. Calcd for $C_{28}H_{37}N_4F_6PPd$ (%): C, 49.38; H, 5.48; N, 8.23. Found (%): C, 49.09; H, 5.41; N, 8.05.

{1-[1-(2,4,6-Trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladiummethyl Acetonitrile Hexafluorophosphate, [Pd(C^Imine$_{Ph}$)(Me)(MeCN)]PF$_6$ (5c). A solution of (C^Imine$_{Ph}$)PdMeCl (**4c**) (125 mg, 0.221 mmol) in MeCN (10 mL) was added to a suspension of silver hexafluorophosphate (57.1 mg, 0.226 mmol) in MeCN (2 mL) and stirred at room temperature for 1 h in the absence of light. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting brown residue was washed with pentane and dried under reduced pressure to give a brown solid (148 mg, 0.207 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, ^3J = 7.4 Hz, 1H, *p*-C*H*$_{(phenyl)}$), 7.48 (t, ^3J = 7.4 Hz, 2H, *m*-C*H*$_{(phenyl)}$), 7.41 (d, ^3J = 7.4 Hz, 2H, *o*-C*H*$_{(phenyl)}$), 7.37 (d, ^3J = 2.0 Hz, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 7.00 (s, 2H, *m*-C*H*$_{(azole\text{-}mesityl)}$), 6.98 (s, ^3J = 2.0 Hz, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 6.83 (s, 2H, *m*-C*H*$_{(N\text{-}mesityl)}$), 2.36 (s, 3H, *p*-C*H*$_{3(azole\text{-}mesityl)}$), 2.22 (s, 3H, *p*-C*H*$_{3(N\text{-}mesityl)}$), 2.21 (s, 6H, *o*-C*H*$_{3(N\text{-}mesityl)}$), 2.01 (s, 6H, *o*-C*H*$_{3(azole\text{-}mesityl)}$), 1.75 (s, 3H, *C*H$_3$CN), −0.10 (s, 3H, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.3 (NCN$_{(mesityl)}$), 158.8 (*C*=N), 140.5 (*p*-*C*$_{(azole\text{-}mesityl)}$), 138.9 (C$_{ipso(N\text{-}mesityl)}$), 136.4 (*p*-*C*$_{(N\text{-}mesityl)}$), 134.4 (*o*-*C*$_{(azole\text{-}mesityl)}$), 133.0 (*p*-*C*H$_{(phenyl)}$), 129.8 (*o*-*C*$_{(N\text{-}mesityl)}$), 129.6 (*m*-*C*H$_{(azole\text{-}mesityl)}$), 129.5 (*m*-*C*H$_{(phenyl)}$ + C$_{ipso(azole\text{-}mesityl)}$), 129.1 (*m*-*C*$_{(N\text{-}mesityl)}$), 128.5 (*o*-*C*H$_{(phenyl)}$), 126.2 (C$_{ipso(phenyl)}$), 125.0 (NC*C*N$_{(azole\text{-}mesityl)}$), 121.1 (NC*C*N$_{(azole\text{-}mesityl)}$), 119.5 (*C*H$_3$CN), 21.3 (*p*-*C*H$_{3(azole\text{-}mesityl)}$), 20.8 (*p*-*C*H$_{3(N\text{-}mesityl)}$), 18.7 (*o*-*C*H$_{3(N\text{-}mesityl)}$), 17.9 (*o*-*C*H$_{3(azole\text{-}mesityl)}$), 1.6 (*C*H$_3$CN), −8.9 (Pd−*C*H$_3$). FT-IR (cast-DCM): $\nu_{C=N}$ 1640 cm^{-1}. Anal. Calcd for $C_{31}H_{35}N_4F_6PPd$ (%): C, 52.07; H, 4.93; N, 7.84. Found (%): C, 51.86; H, 4.70; N, 8.01.

Dichloro(bis{1-[1-(2,6-dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene})palladium, Pd(C^Imine$_{Me}$)$_2$Cl$_2$ (6). *tert*-Butyl isocyanide (6.0 μL, 0.053 mmol) was syringed into a cooled (−35 °C) solution of **4a** (26.0 mg, 0.053 mmol) in toluene (4 mL) and stirred at room temperature for 16 h. Volatiles were removed under reduced pressure, and a pentane wash was performed to give a yellow-cream-colored solid. Sample was further purified by slow vapor diffusion of pentane onto a saturated dichloromethane solution over a period of several days to provide small yellow crystals (14.2 mg, 0.0169 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H, NC*H*CN$_{(mesityl)}$), 7.16 (d, ^3J = 7.4 Hz, 2H, *m*-C*H*$_{(2,6\text{-}xylyl)}$), 7.07 (m, 1H, *p*-C*H*$_{(2,6\text{-}xylyl)}$), 6.97 (s, 2H, *m*-C*H*$_{(mesityl)}$), 6.67 (s, 1H, NCC*H*N$_{(mesityl)}$), 3.61 (s, 3H, C*H*$_{3(imine)}$), 2.19 (s, 6H, *o*-C*H*$_{3(mesityl)}$), 2.10 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.07 (s, 6H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.2 (NCN), 155.1 (*C*=N), 145.2 (C$_{ipso(2,6\text{-}xylyl)}$), 139.3 (*p*-*C*$_{(mesityl)}$), 137.0 (*o*-*C*$_{(mesityl)}$), 135.7 (C$_{ipso(mesityl)}$), 128.9 (*m*-*C*H$_{(mesityl)}$), 127.6 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 126.5 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 123.2 (*p*-*C*H$_{(2,6\text{-}xylyl)}$), 122.6 (NC*C*N$_{(mesityl)}$), 119.5 (NC*C*N$_{(mesityl)}$), 20.4 (*p*-*C*H$_{3(mesityl)}$), 20.1 (*C*H$_{3(imine)}$), 18.6 (*o*-*C*H$_{3(mesityl)}$), 18.9 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$). FT-IR (cast-DCM): $\nu_{C=N}$ 1700 cm^{-1}. Anal. Calcd for $C_{44}H_{50}N_6Cl_2Pd$ (%): C, 62.90; H, 6.00; N, 10.00. Found (%): C, 62.67; H, 5.74; N, 10.17.

Chloromethyl{1-[1-(2,6-Dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium *tert*-Butyl Isocyanide Adduct, Pd(C^Imine$_{t\text{-}Bu}$)Me(*tert*-BuNC)Cl (7). *tert*-Butyl isocyanide (30.0 μL, 0.265 mmol) was syringed into a cooled (−35 °C) solution of **4b** (67.5 mg, 0.127 mmol) in toluene

dx.doi.org/10.1021/om400533d | *Organometallics* XXXX, XXX, XXX−XXX

(6 mL) and stirred at room temperature for 16 h. Volatiles were removed under reduced pressure and a pentane wash was performed to give a cream-colored solid (60.0 mg, 0.0978 mmol, 77%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.09 (s + br, 1H, p-C$H_{(2,6\text{-xylyl})}$), 6.91 (d, ^3J = 7.2 Hz, 2H, m-C$H_{(2,6\text{-xylyl})}$), 6.62 (s, 1H, m-C$H_{(\text{mesityl})}$), 6.61 (d, ^3J = 1.6 Hz, 1H, NCHCN$_{(\text{mesityl})}$), 6.58 (s, 1H, m-C$H_{(\text{mesityl})}$), 5.98 (s, 1H, NCCHN$_{(\text{mesityl})}$), 3.19 (s, 3H, o-C$H_{3(2,6\text{-xylyl})}$), 2.60 (s, 3H, p-C$H_{3(\text{mesityl})}$), 1.96 (s, 3H, o-C$H_{3(\text{mesityl})}$), 1.80 (s, 3H, o-C$H_{3(\text{mesityl})}$), 1.79 (s, 9H, C(CH_3)$_{3(\text{imine})}$ + 3H, o-C$H_{3(2,6\text{-xylyl})}$), 0.70 (s, 9H, CNC(CH_3)$_{3(\text{isocyanide})}$, −0.50 (s, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 157.6 (C═N), 144.7 ($C_{\text{ipso}(2,6\text{-xylyl})}$), 138.6 ($o$-$C_{(\text{mesityl})}$), 137.5 ($p$-$C_{(\text{mesityl})}$), 136.6 ($o$-$C_{(\text{mesityl})}$), 134.3 ($C_{\text{ipso}(\text{mesityl})}$), 130.1 ($m$-C$H_{(\text{mesityl})}$), 129.0 ($p$-C$H_{(2,6\text{-xylyl})}$), 128.5 ($m$-C$H_{(\text{mesityl})}$), 128.0 ($m$-C$H_{(2,6\text{-xylyl})}$), 124.2 ($m$-C$H_{(\text{mesityl})}$), 123.2 ($o$-$C_{(2,6\text{-xylyl})}$), 122.8 ($o$-$C_{(2,6\text{-xylyl})}$), 120.5 (NC$CN_{(\text{mesityl})}$), 120.2 (NC$CN_{(\text{mesityl})}$), 119.6 (CNC(CH$_3$)$_{3(\text{isocyanide})}$, 55.8 (CNC(CH$_3$)$_{3(\text{isocyanide})}$), 41.4 (C(CH$_3$)$_{3(\text{imine})}$), 30.3 (C(C$H_3$)$_{3(\text{imine})}$), 29.5 (CNC(C$H_3$)$_{3(\text{isocyanide})}$), 21.9($o$-C$H_{3(2,6\text{-xylyl})}$), 21.0 ($o$-C$H_{3(\text{mesityl})}$), 20.0 ($p$-C$H_{3(\text{mesityl})}$), 19.0 ($o$-C$H_{3(2,6\text{-xylyl})}$), 18.1 ($o$-C$H_{3(\text{mesityl})}$), −14.9 (Pd-C$H_3$); resonance for NC$N_{(\text{mesityl})}$ was not observed. FT-IR (cast-DCM): $\nu_{\text{C═N-ligand}}$ 1696 and 1684 cm^{-1}, $\nu_{\text{C═N-isocyanide}}$ 2189 cm^{-1}. Anal. Calcd for $C_{31}H_{43}N_4$ClPd (%): C, 60.68; H, 7.06; N, 9.13. Found (%): C, 60.42; H, 7.22; N, 8.85.

Chloromethyl{1-[1-(2,4,6-trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}[1-(*tert*-butylimino)-ethyl]palladium, Pd(C^Imine$_{Ph}$)Me(tBuNC)Cl (8). *tert*-Butyl isocyanide (22 μL, 0.20 mmol) was syringed into a cooled (−35 °C) solution of **4c** (54.2 mg, 0.0960 mmol) in toluene (8 mL) and stirred at room temperature for 24 h. Volatiles were removed under reduced pressure to give a light orange solid. A minimal amount of DCM was added to dissolve the crude material that was then filtered through a plug of Celite. Pentane was added to precipitate the product as an orange solid, which was further washed with pentane. The solid was dried under reduced pressure to give the desired product and was a light orange solid (42.9 mg, 0.0555 mmol, 69%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.84 (m, 1H, p-C$H_{(\text{phenyl})}$), 6.80 (m, 4H, m-C$H_{(\text{phenyl})}$ + o-C$H_{(\text{phenyl})}$), 6.72 (s, 1H, m-C$H_{(\text{azole-mesityl})}$), 6.71 (s, 1H, m-C$H_{(\text{azole-mesityl})}$), 6.62 (s, 1H, m-C$H_{(N\text{-mesityl})}$), 6.54 (s, 1H, m-C$H_{(N\text{-mesityl})}$), 6.31 (s, 1H, NCHCN$_{(\text{azole-mesityl})}$), 5.80 (s, 1H, NCC$HN_{(\text{azole-mesityl})}$), 2.48 (s, 3H, p-C$H_{3(\text{azole-mesityl})}$), 2.19 (s, 3H, o-C$H_{3(\text{azole-mesityl})}$), 2.18 (s, 3H, Pd−C═N(CCH$_3$)$_3$CH_3), 2.16 (s, 3H, o-C$H_{3(N\text{-mesityl})}$), 2.07 (s, 3H, o-C$H_{3(\text{azole-mesityl})}$), 2.03 (s, 3H, p-C$H_{3(N\text{-mesityl})}$), 2.01 (s, 3H, o-C$H_{3(N\text{-mesityl})}$), 1.89 (s, 9H, Pd−C═N(CH_3)$_3$CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 156.1 (C═N), 140.2 (p-$C_{(\text{N-mesityl})}$), 140.1 (p-$C_{(\text{azole-mesityl})}$), 135.4 ($o$-$C_{(\text{azole-mesityl})}$), 135.3 ($C_{\text{ipso}(\text{azole-mesityl})}$), 134.8 ($o$-$C_{(N\text{-mesityl})}$), 134.2 ($o$-$C_{(N\text{-mesityl})}$), 131.4 (CH$_{(\text{phenyl})}$), 131.3 (CH$_{(\text{phenyl})}$), 129.9 ($m$-CH$_{(N\text{-mesityl})}$), 129.6 ($m$-CH$_{(\text{azole-mesityl})}$), 129.1 ($m$-CH$_{(\text{azole-mesityl})}$), 129.0 ($m$-CH$_{(N\text{-mesityl})}$), 128.8 (CH$_{(\text{phenyl})}$), 128.5 (CH$_{(\text{phenyl})}$), 123.0 (NC$CN_{(\text{azole-mesityl})}$), 118.8 (NC$CN_{(\text{azole-mesityl})}$), 55.5 (Pd−C═N(C$CH_3$)$_3CH_3$), 32.7 (Pd−C═N(CCH$_3$)$_3CH_3$), 32.5 (Pd−C═N(C$CH_3$)$_3CH_3$), 21.0 ($p$-C$H_{3(N\text{-mesityl})+}$ 19.2 o-C$H_{3(N\text{-mesityl})}$), 19.8 (p-C$H_{3(\text{azole-mesityl})}$), 18.9 ($o$-CH$_{3\ (\text{azole-mesityl})+}$ o-C$H_{3(N\text{-mesityl})}$), 18.3 (o-C$H_{3(\text{azole-mesityl})}$); resonances for NC$N_{(\text{azole-mesityl})}$, ipso-$C_{(\text{phenyl})}$, and Pd−C═N(CCH$_3$)$_3CH_3$ were not observed. FTIR (cast-DCM): $\nu_{\text{C═N}}$ 1638 cm^{-1}. Anal. Calcd for $C_{34}H_{41}N_4$ClPd (%): C, 63.06; H, 6.38; N, 8.65. Found (%): C, 62.86; H, 6.32; N, 8.49.

Chloro{1-[1-(2,6-dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}{1,2-bis[(2,6-dimethylphenyl)imino]-3-[(2,6-dimethylphenyl)imino-*κ*-*N*]-butyl-*κ*-*C*}palladium, (9). A cooled solution (−35 °C) solution of 2,6-dimethylphenyl isocyanide (13.3 mg, 0.101 mmol) in THF (4 mL) was added to a cooled (−35 °C) partially soluble solution of **4a** (24.5 mg, 0.0502 mmol) in THF (2 mL). The mixture was dried in vacuo and washed with pentane to give the product as an orange-pink solid (mass recovered 32.4 mg). Crystals suitable for X-ray diffraction were grown at room temperature by slow vapor diffusion of pentane into a saturated chloroform solution. ^{1}H NMR (400 MHz, $CDCl_3$): major isomer (80%) δ 8.35 (d, ^3J = 1.3 Hz, 1H, NCHCHN$_{(\text{mesityl})}$), 7.04 (s + br; accidental overlap with minor isomer), 6.98 (m; accidental overlap with minor isomer), 6.88 (m; accidental overlap with minor isomer), 6.78 (m; accidental overlap with minor isomer), 3.35 (s, 3H, C$H_{3(\text{C^Imine})}$), 2.37 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 1.97 (s, 6H), 1.91 (s, 3H), 1.77 (s, 3H), 1.58 (s, 3H), 1.41 (s, 3H), 1.15 (s, 3H); minor isomer (20%) δ 8.40 (s, 1H, NCHCHN$_{(\text{mesityl})}$), 7.04 (s + br, 3H; accidental overlap with major isomer), 6.98 (m; accidental overlap with major isomer), 6.88 (m; accidental overlap with major isomer), 6.78 (m; accidental overlap with major isomer), 3.32 (s, 3H, C$H_{3(\text{C^Imine})}$), 2.37 (s, 3H; accidental overlap with major isomer), 2.35 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.91 (s, 3H; accidental overlap with major isomer), 1.77 (s, 3H; accidental overlap with major isomer), 1.58 (s, 3H; accidental overlap with major isomer), 1.41 (s, 6H; accidental overlap with major isomer), 1.15 (s, 6H; accidental overlap with major isomer). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$; only resonances for the major isomer are reported) δ 180.5, 170.9, 164.6, 154.3, 150.3, 146.8, 145.3, 143.0, 138.9, 137.7, 136.5, 135.2, 129.9, 129.5, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 126.9, 124.0, 123.5, 122.3, 122.1, 120.4 (NCCN), 59.7 {Pd−[C(═NXyl)]$_3$CH$_3$}, 21.2 (C$H_{3(\text{C^Imine})}$), 19.7, 19.5, 19.0, 18.6, 18.4, 17.5, 16.8. Anal. Calcd for $C_{50}H_{55}N_6$ClPd (%): C, 68.10; H, 6.29; N, 9.53. Found (%): C, 67.89; H, 6.24; N, 9.35.

{1-[1-(2,6-Dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl *tert*-Butyl Isocyanide Hexafluorophosphate, [Pd(C^Imine$_{Me}$)(Me)(*t*-BuNC)]PF$_6$ (10a). *tert*-Butyl isocyanide (8.0 μL, 0.071 mmol) was syringed into a solution of **5a** (45.5 mg, 0.0712 mmol) in THF (6 mL) and stirred at room temperature for 1 h. Volatiles were removed under reduced pressure, and a pentane wash was performed to give a brown solid (46.1 mg, 0.0677 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, ^3J = 1.8 Hz, 1H, NCHCN$_{(\text{mesityl})}$), 7.12 (m, 3H, p-C$H_{(2,6\text{-xylyl})}$ + m-C$H_{(2,6\text{-xylyl})}$), 6.99 (s, 2H, m-C$H_{(\text{mesityl})}$), 6.97 (d, ^3J = 1.8 Hz, 1H, NCCHN$_{(\text{mesityl})}$), 2.41 (s, 3H, C$H_{3(\text{imine})}$), 2.35 (s, 3H, p-C$H_{3(\text{mesityl})}$), 2.24 (s, 6H, o-C$H_{3(2,6\text{-xylyl})}$), 2.10 (s, 6H, o-C$H_{3(\text{mesityl})}$), 1.11 (CNC-(CH_3)$_{3(\text{isocyanide})}$, 0.01 (s, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 177.2 (NC$N_{(\text{mesityl})}$), 162.0 (C═N), 143.9 ($C_{\text{ipso}(2,6\text{-xylyl})}$), 140.4 ($p$-$C_{(\text{mesityl})}$), 135.0 (CNC(CH$_3$)$_{3(\text{isocyanide})}$, 134.3 ($o$-$C_{(\text{mesityl})}$), 134.0 ($C_{\text{ipso}(\text{mesityl})}$), 129.5 ($m$-CH$_{(\text{mesityl})}$), 129.4 ($o$-$C_{(2,6\text{-xylyl})}$), 128.7 ($m$-CH$_{(2,6\text{-xylyl})}$), 126.9 ($p$-CH$_{(2,6\text{-xylyl})}$), 124.9 (NC$CN_{(\text{mesityl})}$), 120.4 (NC$CN_{(\text{mesityl})}$), 57.95 (CNC(CH$_3$)$_{3(\text{isocyanide})}$, 29.7 (CNC-(C$H_3$)$_{3(\text{isocyanide})}$, 21.3 ($p$-C$H_{3(\text{mesityl})}$), 18.4 ($o$-C$H_{3(2,6\text{-xylyl})}$), 17.8 ($o$-C$H_{3(\text{mesityl})}$), 14.5 C$H_{3(\text{imine})}$), −12.6 (Pd−C$H_3$). FT-IR (cast-DCM): $\nu_{\text{C═N(ligand)}}$ 1656 cm^{-1}, $\nu_{\text{C═N(isocyanide)}}$ 2208 cm^{-1}. Anal. Calcd for $C_{28}H_{37}F_6N_4$PPd (%): C, 49.38; H, 5.48; N, 8.23. Found (%): C, 49.14; H, 5.52; N, 7.95.

{1-[1-(2,6-Dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl *tert*-Butyl Isocyanide Hexafluorophosphate, [Pd-(C^Imine$_{t\text{-Bu}}$)(Me)(*t*-BuNC)]PF$_6$ (10b). *tert*-Butyl isocyanide (5.3 μL, 0.047 mmol) was syringed into a solution of **5b** (31.9 mg, 0.0468 mmol) in THF (4 mL) and stirred at room temperature for 1 h. Volatiles were removed under reduced pressure, and a pentane wash was performed to give a brown solid (31.2 mg, 0.0431 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, ^3J = 1.4 Hz, 1H, NCHCN$_{(\text{mesityl})}$), 7.08 (m, 3H, p-C$H_{(2,6\text{-xylyl})}$ + m-C$H_{(2,6\text{-xylyl})}$), 7.07 (s, 1H, NCCHN$_{(\text{mesityl})}$), 6.97 (s, 2H, m-C$H_{(\text{mesityl})}$), 2.34 (s, 9H, p-C$H_{3(\text{mesityl})}$ + o-C$H_{3(2,6\text{-xylyl})}$), 2.10 (s, 6H, o-C$H_{3(\text{mesityl})}$), 1.41 (s, 9H, C(CH_3)$_{3(\text{imine})}$), 1.13 (CNC(CH_3)$_{3(\text{isocyanide})}$, −0.07 (s, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.5 (NC$N_{(\text{mesityl})}$), 166.1 (C═N), 147.0 ($C_{\text{ipso}(2,6\text{-xylyl})}$), 140.3 ($p$-$C_{(\text{mesityl})}$), 134.7 (CNC(CH$_3$)$_{3(\text{isocyanide})}$, 134.3 ($o$-$C_{(\text{mesityl})}$), 134.2 ($C_{\text{ipso}(\text{mesityl})}$), 129.5 ($m$-CH$_{(\text{mesityl})}$), 128.2 ($m$-CH$_{(2,6\text{-xylyl})}$), 127.8 ($o$-$C_{(2,6\text{-xylyl})}$), 126.1 ($p$-CH$_{(2,6\text{-xylyl})}$), 124.6 (NC$CN_{(\text{mesityl})}$), 122.7 (NC$CN_{(\text{mesityl})}$), 57.8 CNC(CH$_3$)$_{3(\text{isocyanide})}$, 40.6 (C(CH$_3$)$_{3(\text{imine})}$), 29.9 (C(C$H_3$)$_{3(\text{imine})}$), 29.7 (CNC(CH$_3$)$_{3(\text{isocyanide})}$, 21.3 ($p$-C$H_{3(\text{mesityl})}$), 19.1 ($o$-C$H_{3(2,6\text{-xylyl})}$), 17.8 ($o$-C$H_{3(\text{mesityl})}$), −11.4 (Pd-C$H_3$). FT-IR (cast-DCM): $\nu_{\text{C═N(ligand)}}$ 1626 cm^{-1}, $\nu_{\text{C═N(isocyanide)}}$ 2211 cm^{-1}. Anal. Calcd for $C_{31}H_{43}N_4F_6$PPd (%): C, 51.49; H, 5.99; N, 7.75. Found (%): C, 51.58; H, 6.12; N, 8.02.

{1-[1-(2,4,6-Trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)-imidazol-2-ylidene}palladium Methyl *tert*-Butyl Isocyanide Hexafluorophosphate, [Pd(C^Imine$_{Ph}$)(Me)(*t*BuNC)]-PF$_6$ (10c). *tert*-Butyl isocyanide (7.0 μL, 0.062 mmol) was syringed into a solution of **5c** (43.9 mg, 0.0614 mmol) in THF (6 mL) and stirred at room temperature for 1 h. Volatiles were removed under reduced pressure, and a pentane wash was performed to give a light brown solid (38.8 mg, 0.0512 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54

dx.doi.org/10.1021/om400533d | *Organometallics* XXXX, XXX, XXX−XXX

(t, ^3J = 7.5 Hz, 1H, *p*-$CH_{(phenyl)}$), 7.46 (t, ^3J = 7.5 Hz, 2H, *m*-$CH_{(phenyl)}$), 7.40 (d, ^3J = 7.5 Hz, 2H, *o*-$CH_{(phenyl)}$), 7.36 (d, ^3J = 1.8 Hz, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 7.03 (s, ^3J = 1.8 Hz, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 7.00 (s, 2H, *m*-$CH_{(azole\text{-}mesityl)}$), 6.80 (s, 2H, *m*-$CH_{(N\text{-}mesityl)}$), 2.36 (s, 3H, *p*-$CH_{3(azole\text{-}mesityl)}$), 2.23 (s, 6H, *o*-$CH_{3(N\text{-}mesityl)}$), 2.20 (s, 3H, *p*-$CH_{3(N\text{-}mesityl)}$), 2.15 (s, 6H, *o*-$CH_{3(azole\text{-}mesityl)}$), 1.13 (CNC-$(CH_3)_{3(isocyanide)}$, −0.10 (s, 3H, Pd−$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.2 (N*C*N$_{(mesityl)}$), 160.5 (*C*=N), 141.7 ($C_{ipso(N\text{-}mesityl)}$), 140.4 (*p*-$C_{(azole\text{-}mesityl)}$), 136.3 (*p*-$C_{(N\text{-}mesityl)}$), 134.90 (CNC-$(CH_3)_{3(isocyanide)}$, 134.4 (*o*-$C_{(azole\text{-}mesityl)}$), 134.1 ($C_{ipso(azole\text{-}mesityl)}$), 133.0 (*p*-$CH_{(phenyl)}$), 129.5 (*m*-$CH_{(azole\text{-}mesityl)}$), 129.5 (*m*-$CH_{(phenyl)}$), 129.1 (*m*-$C_{(N\text{-}mesityl)}$), 129.1 (*o*-$C_{(N\text{-}mesityl)}$), 128.5 (*o*-$CH_{(phenyl)}$), 126.0 ($C_{ipso(phenyl)}$), 125.2 (NC*C*N$_{(azole\text{-}mesityl)}$), 121.5 (NC*C*N$_{(azole\text{-}mesityl)}$), 58.0 (CNC$(CH_3)_{3(isocyanide)}$, 29.6 (CNC$(CH_3)_{3(isocyanide)}$, 21.3 (*p*-$CH_{3(azole\text{-}mesityl)}$), 20.8 (*p*-$CH_{3(N\text{-}mesityl)}$), 18.8 (*o*-$CH_{3(N\text{-}mesityl)}$), 17.9 (*o*-$CH_{3(azole\text{-}mesityl)}$), −12.0 (Pd−$CH_3$). FT-IR (cast-DCM): $\nu_{C=N(ligand)}$ 1636 cm^{-1}, $\nu_{C=N(isocyanide)}$ 2208 cm^{-1}. Anal. Calcd for $C_{34}H_{41}F_6N_4PPd$ (%): C, 53.94; H, 5.46; N, 7.40. Found (%): C, 54.02; H, 5.71; N, 7.28.

{1-[1-(2,6-Dimethylphenylimino)ethyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl 2,6-Dimethylphenyl Isocyanide Hexafluorophosphate, [Pd(C^Imine$_{Me}$)(Me)(ArNC)]PF$_6$ (11a). A solution of 2,6-dimethylphenyl isocyanide (10.7 mg, 0.0816 mmol) in THF (6 mL) was added to a solution of **5a** (52.0 mg, 0.0814 mmol) in THF (4 mL) and stirred at room temperature for 1 h. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting brown solid was further washed with pentane and dried under reduced pressure to give the desired product (52.7 mg, 0.888 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, ^3J = 1.6 Hz, 1H, NC*H*CN$_{(mesityl)}$), 7.19 (t, ^3J = 7.7 Hz, 1H, *p*-$CH_{(2,6\text{-}xylyl)}$), 7.09 (m, 3H, *p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$ + *m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 7.02 (s, 2H, *m*-$CH_{(mesityl)}$), 7.00 (s + br, 3H, NCC*H*N$_{(mesityl)}$ + *m*-$CH_{(2,6\text{-}xylyl)}$), 2.42 (s, 3H, $CH_{3(imine)}$), 2.37 (s, 3H, *p*-$CH_{3(mesityl)}$), 2.29 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 2.14 (s, 6H, *o*-$CH_{3(mesityl)}$), 1.93 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 0.23 (s, 3H, Pd−$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.7 (N*C*N$_{(mesityl)}$), 162.5 (*C*=N), 144.2 ($C_{ipso(2,6\text{-}xylyl)}$), 140.4 (*p*-$C_{(mesityl)}$), 135.7 (*o*-$C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 134.5 (*o*-$C_{(mesityl)}$), 134.0 ($C_{ipso(mesityl)}$), 130.4 (*p*-$CH_{(2,6\text{-}xylyl)}$), 129.5 (*m*-$CH_{(mesityl)}$), 129.2 (*o*-$C_{(2,6\text{-}xylyl)}$), 129.0 (*m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 128.2 (*m*-$CH_{(2,6\text{-}xylyl)}$), 127.0 (*p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 124.1 (NC*C*N$_{(mesityl)}$ + $C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 120.6 (NC*C*N$_{(mesityl)}$), 21.3 (*p*-$CH_{3(mesityl)}$), 18.4 (*o*-$CH_{3(2,6\text{-}xylyl)}$), 18.3 (*o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 17.8 (*o*-$CH_{3(mesityl)}$), 14.5 $CH_{3(imine)}$), −11.8 (Pd-CH_3); CN-(2,6-dimethylphenyl) carbon resonances not observed. FTIR (cast-DCM): $\nu_{C=N(ligand)}$ 1653 cm^{-1}, $\nu_{C=N(isocyanide)}$ 2181 cm^{-1}. Anal. Calcd for $C_{32}H_{37}N_4F_6PPd$ (%): C, 52.72; H, 5.12; N, 7.68. Found (%): C, 52.49; H, 5.03; N, 7.41.

{1-[1-(2,6-Dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl 2,6-Dimethylphenyl Isocyanide Hexafluorophosphate, [Pd(C^Imine$_{t\text{-}Bu}$)(Me)(ArNC)]PF$_6$ (11b). A solution of 2,6-dimethylphenyl isocyanide (22.3 mg, 0.170 mmol) in THF (8 mL) was added to a solution of **5b** (112 mg, 0.165 mmol) in THF (6 mL) and stirred at room temperature for 1 h. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting brown solid was further washed with pentane and dried under reduced pressure to the desired product (114 mg, 0.148 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, ^3J = 1.8 Hz, 1H, NC*H*CN$_{(mesityl)}$), 7.19 (t, ^3J = 7.8 Hz, 1H, *p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 7.13 (d, ^3J = 1.8 Hz, 1H, NCC*H*N$_{(mesityl)}$), 7.19 (d, ^3J = 7.8 Hz, 2H, *m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 7.00 (s, 2H, *m*-$CH_{(mesityl)}$), 6.95 (d, ^3J = 7.6 Hz, 2H, *m*-$CH_{(2,6\text{-}xylyl)}$), 6.80 (t, ^3J = 7.6 Hz, 3H, *p*-$CH_{(2,6\text{-}xylyl)}$), 2.38 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 2.35 (s, 3H, *p*-$CH_{3(mesityl)}$), 2.14 (s, 6H, *o*-$CH_{3(mesityl)}$), 2.04 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 1.43 (s, 9H, C$(CH_3)_{3(imine)}$), 0.11 (s, 3H, Pd−$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 177.9 (N*C*N$_{(mesityl)}$), 166.5 (*C*=N), 146.8 ($C_{ipso(2,6\text{-}xylyl)}$), 140.4 (*p*-$C_{(mesityl)}$), 135.2 ($C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 134.3 (*o*-$C_{(mesityl)}$), 134.2 ($C_{ipso(mesityl)}$), 130.3 (*p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 129.6 (*m*-$CH_{(mesityl)}$), 128.2 (*m*-$CH_{(2,6\text{-}xylyl)}$ + *m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 127.5 (*o*-$C_{(2,6\text{-}xylyl)}$), 126.1 (*p*-$CH_{(2,6\text{-}xylyl)}$), 125.1 (*o*-$C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 124.9 (NC*C*N$_{(mesityl)}$ + *o*-$C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 123.0 (NC*C*N$_{(mesityl)}$), 40.7 (*C*$(CH_3)_{3(imine)}$), 29.9 (C$(CH_3)_{3(imine)}$), 21.3 (*p*-$CH_{3(mesityl)}$), 19.2 (*o*-$CH_{3(2,6\text{-}xylyl)}$), 18.6 (*o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 17.9 (*o*-$CH_{3(mesityl)}$), −10.8 (Pd−$CH_3$), (CN-(2,6-dimethylphenyl) carbon missing. FT-IR (cast-DCM): $\nu_{C=N(ligand)}$ 1628 cm^{-1}, $\nu_{C=N(isocyanide)}$ 2184 cm^{-1}. Anal. Calcd for $C_{35}H_{43}F_6N_4PPd$ (%): C, 54.51; H, 5.62; N, 7.27. Found (%): C, 54.26; H, 5.45; N, 7.00.

{1-[1-(2,4,6-Trimethylphenylimino)benzyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium Methyl 2,6-Dimethylphenyl Isocyanide Hexafluorophosphate, [Pd(C^Imine$_{Ph}$)(Me)(ArNC)]PF$_6$ (11c). A solution of 2,6-dimethylphenyl isocyanide (9.20 mg, 0.070 mmol) in THF (4 mL) was added to a solution of **5c** (50.0 mg, 0.070 mmol) in THF (6 mL) and stirred at room temperature for 1 h. The solution was filtered through a plug of Celite, and the volatiles were removed under reduced pressure. The resulting brown solid was further washed with pentane and dried under reduced pressure to the desired product (48.6 mg, 0.0604 mmol, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, ^3J = 7.4 Hz, 1H, *p*-$CH_{(phenyl)}$), 7.46 (t, ^3J = 7.4 Hz, 2H, *m*-$CH_{(phenyl)}$), 7.41 (d, ^3J = 7.4 Hz, 2H, *o*-$CH_{(phenyl)}$), 7.39 (d, ^3J = 1.8 Hz, 1H, NC*H*CN$_{(azole\text{-}mesityl)}$), 7.20 (t, ^3J = 7.7 Hz, 1H, *p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 7.07 (s, ^3J = 1.8 Hz, 1H, NCC*H*N$_{(azole\text{-}mesityl)}$), 7.03 (s, 2H, *m*-$CH_{(azole\text{-}mesityl)}$), 7.01 (m, 2H, *m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 6.72 (s, 2H, *m*-$CH_{(N\text{-}mesityl)}$), 2.37 (s, 3H, *p*-$CH_{3(azole\text{-}mesityl)}$), 2.27 (s, 6H, *o*-$CH_{3(N\text{-}mesityl)}$), 2.20 (s, 6H, *o*-$CH_{3(azole\text{-}mesityl)}$), 2.11 (s, 3H, *p*-$CH_{3(N\text{-}mesityl)}$), 1.97 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 0.31 (s, 3H, Pd−$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 177.3 (N*C*N$_{(mesityl)}$), 161.0 (*C*=N), 141.9 ($C_{ipso(N\text{-}mesityl)}$), 140.5 (*p*-$C_{(azole\text{-}mesityl)}$), 136.4 (*p*-$C_{(N\text{-}mesityl)}$), 135.7 ($C_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 134.5 (*o*-$C_{(azole\text{-}mesityl)}$), 134.1 ($C_{ipso(azole\text{-}mesityl)}$), 133.0 (*p*-$CH_{(phenyl)}$), 130.4 (*p*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 129.6 (*m*-$CH_{(azole\text{-}mesityl)}$), 129.4 (*m*-$CH_{(phenyl)}$), 129.3 (*m*-$C_{(N\text{-}mesityl)}$), 128.9 (*o*-$C_{(N\text{-}mesityl)}$), 128.6 (*o*-$CH_{(phenyl)}$), 128.2 (*m*-$CH_{(2,6\text{-}xylyl)\text{-}isocyanide}$), 126.0 ($C_{(phenyl)}$), 125.4 (NC*C*N$_{(azole\text{-}mesityl)}$), 121.7 (NC*C*N$_{(azole\text{-}mesityl)}$), 21.3 (*p*-$CH_{3(azole\text{-}mesityl)}$), 20.7 (*p*-$CH_{3(N\text{-}mesityl)}$), 18.9 (*o*-$CH_{3(N\text{-}mesityl)}$), 18.2 (*o*-$CH_{3(2,6\text{-}xylyl)\text{-}isocyanide}$), 17.9 (*o*-$CH_{3(azole\text{-}mesityl)}$), −11.3 (Pd−$CH_3$). FT-IR (cast-DCM): $\nu_{C=N(ligand)}$ 1635 cm^{-1}, $\nu_{C=N(isocyanide)}$ 2181 cm^{-1}. Anal. Calcd for $C_{38}H_{41}N_4F_6PPd$ (%): C, 56.69; H, 5.13; N, 6.96. Found (%): C, 56.91; H, 4.97; N, 7.10.

{Acetylchloro[1-(2,6-dimethylphenylimino)-2,2-dimethylpropyl]-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}palladium, Pd(C^Imine$_{t\text{-}Bu}$)(C=OMe)Cl (12). A Schlenk tube containing a solution of **4b** (32.5 mg, 0.0613 mmol) in 6 mL of THF was backfilled with CO and stirred for 15 min at atmospheric pressure and room temperature. The reaction was dried under vacuum and brought inside the glovebox. The solid residue was dissolved in a minimal amount of THF, filtered through a plug of Celite, and the yellow solution was dried under vacuum. The solid was washed with pentane and dried under vacuum to give a yellow-green solid (26.5 mg, 0.0474 mmol, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, ^3J = 1.3 Hz, 1H, NC*H*CN$_{(mesityl)}$), 6.97 (m, 3H, *p*-$CH_{(2,6\text{-}xylyl)}$ + *m*-$CH_{(2,6\text{-}xylyl)}$), 6.94 (m, 2H, *m*-$CH_{(mesityl)}$), 6.87 (s + br, 1H, NCC*H*N$_{(mesityl)}$), 2.31 (s, 3H, *p*-$CH_{3(mesityl)}$), 2.29 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 2.14 (s, 6H, *o*-$CH_{3(mesityl)}$), 1.71 (s, 3H, Pd−CO−CH_3), 1.36 (s, 9H, C$(CH_3)_{3(imine)}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 228.5 (Pd−*C*O−CH_3), 179.4 (N*C*N$_{(mesityl)}$), 161.7 (*C*=N), 143.1 ($C_{(2,6\text{-}xylyl)}$), 140.3 (*p*-$C_{(mesityl)}$), 135.5 (*o*-$C_{(mesityl)}$), 134.4 ($C_{(mesityl)}$), 129.4 (*m*-$CH_{(mesityl)}$), 127.9 (*o*-$C_{(2,6\text{-}xylyl)}$), 127.4 (*m*-$C_{(2,6\text{-}xylyl)}$), 125.2 (*p*-$CH_{(2,6\text{-}xylyl)}$), 122.2 (NC*C*N$_{(mesityl)}$), 120.0 (NC*C*N$_{(mesityl)}$), 40.2 (*C*$(CH_3)_{3(imine)}$), 38.7 (Pd−CO−*C*H_3), 29.9 (C$(CH_3)_{3(imine)}$), 21.3 (*p*-$CH_{3(mesityl)}$), 19.6 (*o*-$CH_{3(2,6\text{-}xylyl)}$), 18.1 (*o*-$CH_{3(mesityl)}$). FT-IR (cast-DCM): $\nu_{C=N}$ 1632 cm^{-1}, $\nu_{C=O}$ 1690 cm^{-1}. Anal. Calcd for $C_{27}H_{34}N_3OClPd$ (%): C, 58.07; H, 6.14; N, 7.52. Found (%): C, 58.19; H, 6.28; N, 7.24.

General Procedure for Ethylene Polymerization. Ethylene polymerization was performed at atmospheric pressure and room temperature in a 500 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 25 mL of dry toluene and 1000 equivalents of methylaluminoxane (2 M in toluene). The solution was stirred for 15 min before the catalyst (10.3 μmol) in 1 mL of toluene was introduced into the flask via syringe. The reaction mixture was vigorously stirred for 10 min after the addition

dx.doi.org/10.1021/om400533d | *Organometallics* XXXX, XXX, XXX−XXX

of the catalyst 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, if any, were dried under vacuum at approximately 60 °C for several hours.

X-ray Crystallography. Detailed crystallographic data for **4a**−**4c**, **6**, and **9** (tables of atomic coordinates with isotropic and anisotropic displacement parameters, bond lengths, and angles) are provided as Supporting Information. Crystallographic data for **4a**−**4c**, **6**, and **9** 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 Denzo−SMN.[40] Absorption corrections were carried out using SORTAV.[41] Crystallographic data for **5b** and **12** were collected at the University of Toronto on a Bruker Kappa APEX-DUO diffractometer using monochromated Mo Kα radiation (Bruker Triumph) and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX2 and SAINT.[42] Absorption corrections were carried out using SADABS.[42] All structures were solved and refined using Superflip[43] and refined with SHELXS-97[44] 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 **4a, 4b, 4c, 5b, 6, 9**, and **12** (CCDC reference numbers 940711−940717). Crystallographic data in CIF and other electronic format, including tables of crystal data and structure refinement, bond lengths, angles, atomic coordinates, 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.

■ ACKNOWLEDGMENTS

G.G.L. gratefully acknowledges financial support from the Ontario Ministry of Research and Innovation for an Early Researcher Award, the Natural Sciences and Engineering Research Council for a Discovery Grant and a Research and Tools Instrumentation Grant, the Canadian Foundation for Innovation and the Ontario Research Fund for infrastructure funding, and York University for start-up funds. A.C.B. wishes to thank York University for a Provost Dissertation Scholarship. The authors wish to thank Dr. Alan J. Lough of the University of Toronto (Toronto, Ontario) and Dr. James F. Britten of McMaster University (Hamilton, Ontario) for X-ray data acquisition and/or for assistance in solving and refining the solid-state structures.

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