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Synthesis and Structure of Imine−N-Heterocyclic Carbene Palladium Complexes and Their Catalytic Behavior in Norbornene Polymerization

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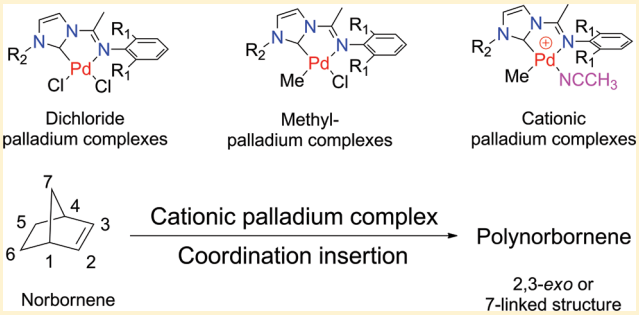
Supporting Information

ABSTRACT: On the basis of the steric effects of ligand, a series of imine−N-heterocyclic carbene (NHC) ligands and their corresponding five-membered palladium complexes with bulky substituents on both the imine and the NHC moieties were synthesized and characterized. Transpalladation of silver carbene complexes with (COD)$PdCl_2$ and (COD)PdMeCl afforded the palladium dichloride and methylpalladium complexes, respectively. Bulky cationic palladium complexes were further obtained by treatment of the methylpalladium complexes with sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (NaBAF) in CH_3CN. Well-defined cationic palladium complexes were confirmed by X-ray crystal diffraction to have trans forms. Palladium dichloride complexes and methylpalladium complexes after activation with MMAO show high activity for norbornene polymerization, whereas cationic palladium complexes can polymerize norbornene alone without any cocatalysts and exhibit a high thermostability. Norbornene polymerization with the cationic palladium catalyst was proven to proceed through a coordination−insertion mechanism by NMR studies. Analysis of oligomers obtained by polymerizing the monomer in the presence of H_2 reveals the existence of a C7 linkage in the polynorbornene (PNB) by σ-bond metathesis, which may be the reason for the insolublity of polynorbornenes obtained by palladium catalysts.



INTRODUCTION

Over the past decade, the chemistry of N-heterocyclic carbenes (NHCs) and their metal complexes have attracted considerable attention in the field of organometallics and catalysis since the precursory work of Arduengo.[1] The strong σ-donor ability of NHC leads to complexes that are more thermodynamically robust than those of the ubiquitous phosphine ligands.[2] All of the transition metals from group 7 to group 11 in the periodic table can nearly be coordinated with the NHC ligand.[3] Although transition-metal complexes containing NHCs are now widely used in the field of C−C cross-coupling reactions,[4] olefin metathesis,[5] hydrosilylation,[6] [3 + 2] cycloaddition reactions,[7] atom transfer radical polymerization,[8] Wacker oxidation,[9] and CO/ethylene copolymerization,[10] successful applications of NHC-derived complexes for olefin polymerizations are rather rare so far.[11]

Recently, late-transition-metal catalysts for olefin polymerization have been extensively developed.[12,13] Brookhart reported that nickel and palladium complexes bearing a bulky α-diimine ligand exhibited high catalytic activity for olefin polymerization.[14] Specifically, well-defined cationic α-diimine palladium catalysts (**A** in Figure 1) can afford polyethylenes with different topologies by a chain-walking approach and functional polyethylenes.[15] Despite the early promising results, cationic α-diimine palladium catalysts are often thermally unstable and prone to deactivation

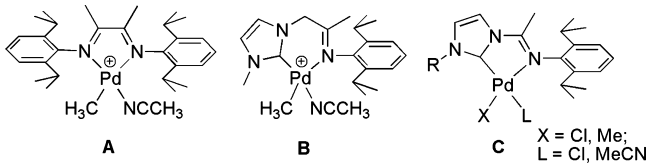


Figure 1. α-Diimine palladium complex (**A**), six-membered imine−NHC palladium complex (**B**), and five-membered imine−NHC palladium complex (**C**).

under comparatively mild conditions.[13f,16] In view of the improved thermal stability of the complexes and superior donor ability of NHC, our interests lie in the design and synthesis of new imine−N-heterocyclic carbene ligands and the corresponding cationic palladium complexes, which are seemingly similar to the α-diimine analogues. Although cationic methylpalladium species are well-defined active initiators for a number of polymerization and catalysis reactions, the literature reports showed that alkylpalladium−NHC complexes are prone to deactivation by reductive elimination of 2-alkylimidazolium salts; such a mode of decomposition is often more facile with cationic complexes.[17] Increasing the steric bulk of the NHC can

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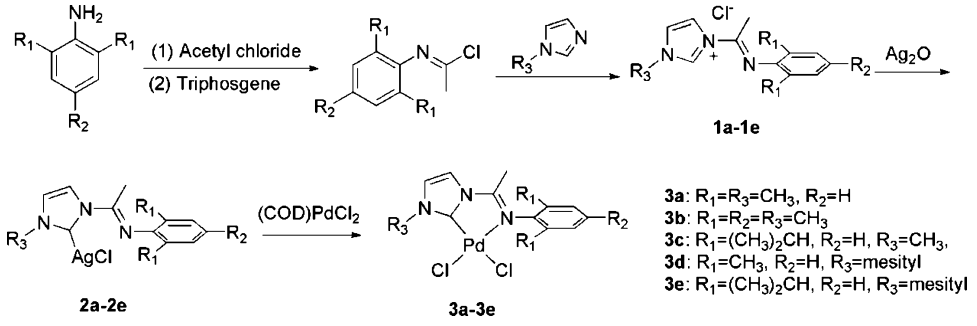
Scheme 1. Synthesis of Imine-NHC Ligands and Palladium Complexes 3a−e



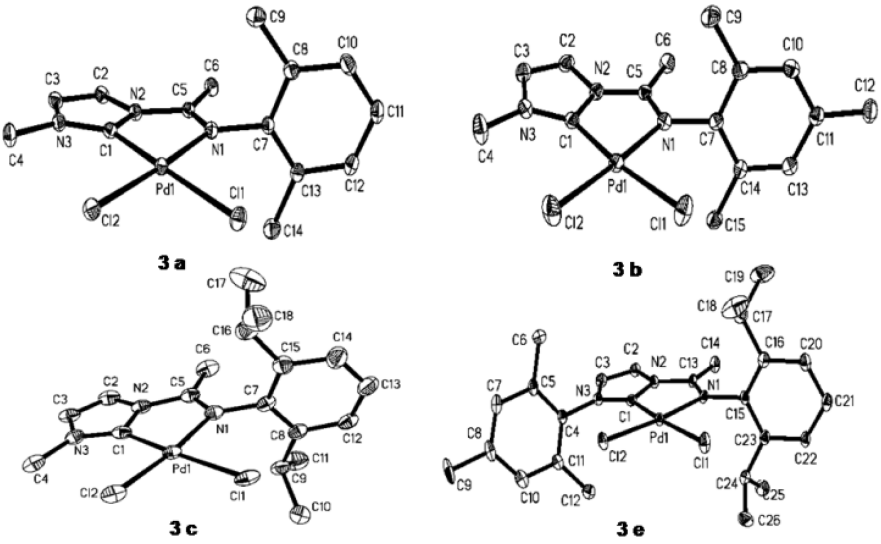


Figure 2. ORTEP drawing of the molecular structures of **3a−c,e**. All thermal ellipsoids are at the 50% probability level, and hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

prevent this decomposition pathway, and a few cationic methylpalladium−NHC complexes with six-membered [N,C]-metal chelates (**B** in Figure 1) have been synthesized in this way.[18] In addition, NHCs with a directly N-bonded imine group are also unstable because of a [1,2] rearrangement of the imidoyl moiety.[19] Therefore, the synthesis of cationic methylpalladium−NHC complexes with a directly N bonded imine group still remains a challenge.

Typically, palladium complexes are highly efficient catalyst precursors for the vinyl polymerization of norbornene (NB).[20] Although numerous palladium catalysts have been developed for the polymerization of norbornene, current studies are mostly limited to various ligand or substituent effects of palladium catalysts on polymerization activity by employment of empirical methods. This is largely due to a lack of understanding of the activation mechanism and the nature of the active species and a lack of understanding of the activity trends as well as the microstructure and origin of the insolubility of the polynorbornene (PNB).[21] Studies on the activation process still remain a great challenge due to the ill-defined structure of MAO used as cocatalyst, palladium(II) reduction, and the formation of insoluble gel-like products.[22] Exceptions are cationic palladium(II) complexes such as $[Pd(NCCH_3)_4](BF_4)_2$ and $[Pd(PPh_3)_3(NCCH_3)](BF_4)_2$, which require no cocatalyst for their activation toward norbornene polymerization, but a "classical" coordination−insertion mechanism cannot be applied to explain this polymerization because of the lack of a Pd−C bond.[23]

In this paper, we synthesized and characterized a series of imine−N-heterocyclic carbene ligands and their corresponding palladium complexes by the introduction of bulky substituents on both the imine and the NHC moieties (**C** in Figure 1). The first sample of a cationic five-membered imine-functionalized methylpalladium complex was synthesized and exhibited good stability. These imine−N-heterocyclic carbene palladium complexes and well-defined cationic NHC−palladium complexes were also used as catalyst precursors for norbornene polymerization. A preliminary study on the activation mechanism and structure of the polymer was also performed by NMR analysis.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. The synthetic routes to imine−NHC ligands and palladium complexes are shown in Scheme 1. A series of imine-functionalized NHC ligands with different substituents on both the imine moiety and the imidazole moiety was synthesized by a coupling reaction of imidoyl chlorides with N-substituted imidazole. Imidazolium salts (C^imine·HCl) (**1a−e**) containing different substituents were obtained in high yield. Imine−NHC silver complexes were usually used as effective transfer reagents to obtain other transition-metal complexes. Stirring **1a−e** with Ag_2O in dichloromethane at room temperature for 6 h afforded the silver N-heterocyclic complexes **2a−e**. Lavoie and co-workers once reported that C^imine·HCl (**1d**) showed no reactivity toward Ag_2O under various experimental conditions,

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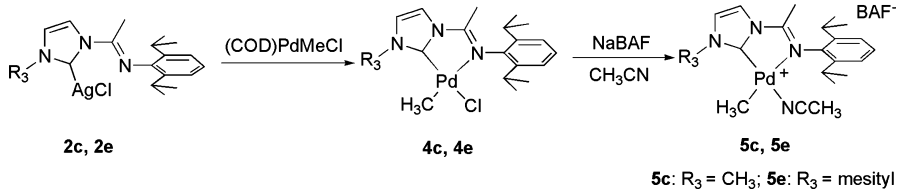
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Palladium Dichloride Complexes 3a−c,e

	3a	3b	3c	3e
Pd(1)−C(1)	1.962(3)	1.959(6)	1.957(4)	1.958(4)
Pd(1)−N(1)	2.039(2)	2.056(5)	2.049(4)	2.048(3)
Pd(1)−Cl(1)	2.3437(7)	2.3409(18)	2.3418(11)	2.3423(10)
Pd(1)−Cl(2)	2.2926(7)	2.3012(18)	2.2888(12)	2.2812(10)
C(1)−Pd−N(1)	79.33(9)	79.2(2)	79.49(16)	79.92(14)
C(1)−Pd−Cl(2)	96.47(8)	96.94(19)	97.00(13)	95.72(11))
C(1)−Pd−Cl(1)	170.96(8)	172.36(19)	173.71(11)	173.08(11)
N(1)−Pd−Cl(1)	93.19(6)	93.21(15)	93.73(10)	93.23(9)

Scheme 2. Synthesis of Methylpalladium Complexes 4c,e and Cationic Palladium Complexes 5c,e



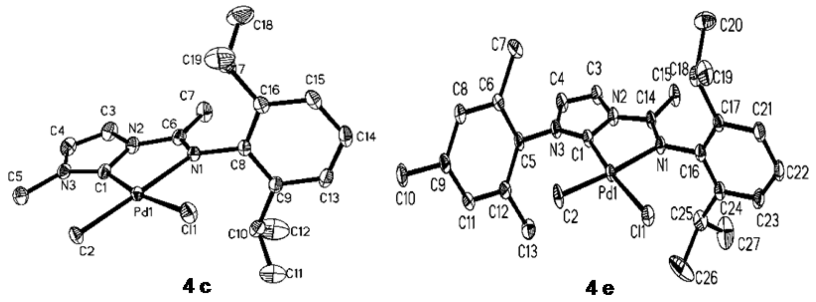


Figure 3. ORTEP drawings of complexes **4c,e**. All thermal ellipsoids are at the 50% probability level, and hydrogen atoms and cocrystallized solvent molecule CH_2Cl_2 are omitted for clarity.

and Ag_2CO_3 was thereby used instead of Ag_2O.[24] However, the imine−NHC silver complex **2d** was herein readily prepared by reaction of the imidazolium salt **1d** with Ag_2O under mild reaction conditions in a good yield of 83%. Elemental analyses (EA) of the obtained silver complexes show C/H/N ratios consistent with the corresponding (NHC)AgCl complex. ESI-MS mass spectra display a molecular ion of the silver bis(NHC) monocation, which is a result of an occurrence of conversion between $[Ag^{-}(NHC)Cl]$ and $[Ag(NHC)_2]^{+}$ under the adopted conditions.[25] No interaction between the imine nitrogen atoms and the Ag center is observed on the basis of the presence of the $\nu_{C=N}$ absorption at 1678 cm^{-1} (see the Experimental Section). The formation of the carbene Ag complexes can be further established by the absence of the resonance for the 2*H*-imidazolium proton in ^1H NMR spectra.[18]

The N-heterocyclic carbene Ag complexes can be smoothly converted to the corresponding palladium dichloride complexes **3a−e** by transpalladation with $(COD)PdCl_2$(COD = 1,5-cyclooctadiene). All of the palladium dichloride complexes bearing imine−-NHC ligands were fully characterized by EA, ESI-MS, ^1H NMR, and ^{13}C NMR analyses. For instance, the carbene-C resonances of **3c,e** are located at around 165 ppm in the ^{13}C NMR, and this shift in comparison to the Ag complexes (183.3 ppm for **2c** and 151.4 ppm for **2e**) indicates the formation of Pd−C(carbene) bonding. In the ^1H NMR spectra of **3c,e**, separations of the doublets (δ 1.36, 1.12 ppm for **3c** and δ 1.28, 1.13 ppm for **3e**) from the diastereotopic methyl on isopropyl groups are over 0.15 ppm, which is somewhat greater than the values for the corresponding Ag carbene complexes (δ 1.18, 1.11 ppm for **2c** and δ 1.20, 1.16 ppm for **2e**). The greater separation between the two methyl doublets on isopropyl groups is indicative of coordination between imine and palladium metal.[18]

The chelated structure was further confirmed by the X-ray crystal determination. Crystals of **3a−c,e** suitable for X-ray diffraction studies were obtained by layering a saturated CH_2Cl_2 solution with *n*-hexane at room temperature. ORTEP drawings of the palladium complexes are depicted in Figure 2, and selected bond lengths (Å) and angles (deg) are given in Table 1. All palladium dichloride complexes display a distorted-square-planar coordination around the palladium center. Pd−C(carbene) bond lengths are around 1.96 Å, while Pd−N(imine) bond lengths are around 2.04 Å.

Transpalladation of silver carbene complexes **2** with a (COD)PdMeCl precursor instead of $(COD)PdCl_2$ is expected to afford the methylpalladium complexes (Scheme 2).[11b,c] Our experimental results show that transpalladation of silver carbene complexes **2a,b,d** with a (COD)PdMeCl precursor did not afford the corresponding methylpalladium complexes. Reaction of **2a,b,d** with (COD)PdMeCl even at −20 °C afforded a trace of white methylpalladium complexes. The bulk of generated products was black insoluble substances, presumably palladium black (Pd(0)). ESI-MS analysis of organic compounds in solution also showed the presence of 2-methylimidazolium salts. Methylpalladium complexes with ligands **1a,b,d** were not obtained because the methylpalladium complexes were prone to deactivation by reductive elimination.[17] The reaction between **2c**

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and (COD)PdMeCl at above 0 °C afforded only a small amount of white methylpalladium complex **4c** in a very low yield. When the reaction temperature was set below −20 °C, only **4c** was obtained in 50% yield. However, the reaction of the more bulky **2e** with (COD)PdMeCl could smoothly proceed at room temperature to produce white **4e** in 75% yield. Introduction of bulky substituent groups on imine−NHC ligands can improve the stability of five-membered methylpalladium complexes and suppress reductive elimination which may cause alkylpalladium−NHC complex decomposition.[26] Methylpalladium complexes **4c,e** have better solubility in organic solvents than palladium dichloride complexes, and purifications of methylpalladium complexes are thereby facile.

The structures of these two methylpalladium complexes have been proven by EA, ESI-MS, ^{1}H NMR, and ^{13}C NMR. The signals at 0.83 and 0.27 ppm in the ^{1}H NMR spectra can be assigned to the palladium-bound methyl groups of **4c,e**, respectively. The ^{13}C NMR resonances of carbene-C of **4c,e** lie at −5.01 and −5.97 ppm, respectively, which shift to low field in comparison to the chemical shift of a methylpalladium complex with a pyridine−NHC ligand.[11] The single set of resonances observed for **4c,e** indicates the presence of a single isomer. Single-crystal X-ray diffraction analysis of **4c,e** (Figure 3) further confirmed that methylpalladium complexes are present in the trans form and feature the methyl group trans to the imine group. Bond lengths and angles around the palladium center are highly similar to those in the corresponding palladium dichloride complexes **3c,e** except for the Pd−N(imine) bond length (Table 2). The Pd−N(imine) bond lengths of methylpalladium complexes are substantially longer (2.051(5) Å in **3c** vs 2.172(2) Å in **4c**, 2.049(4) Å in **3e** vs 2.176(3) Å in **4e**), which is a result of the strong structural trans effect of the methyl group.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Methylpalladium Complexes 4c,e

	4c	4e
Pd(1)−C(1)	1.967(3)	1.964(3)
Pd(1)−C(2)	2.053(2)	2.041(3)
Pd(1)−N(1)	2.172(2)	2.176(3)
Pd(1)−Cl(1)	2.3587(7)	2.3436(8)
C(1)−Pd(1)−C(2)	96.03(11)	96.22(13)
C(1)−Pd(1)−Cl(1)	171.71(8)	173.77(9)
C(2)−Pd(1)−Cl(1)	90.75(7)	89.98(10)
C(1)−Pd(1)−N(1)	78.89(9)	78.69(11)
Cl(1)−Pd(1)−N(1)	94.49(5)	95.10(7)
C(2)−Pd(1)−N(1)	174.50(9)	174.77(13)

Treatment of complexes **4c,e** with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF) in CH_3CN readily yields the corresponding cationic palladium complexes **5c,e** as white solids. Pure cationic complexes can be almost quantitatively obtained. The cationic complex **5c,e** solids are stable to air and moisture and remained unchanged for over 3 days in open air. Also, the cationic palladium complexes show the best solubility in toluene and dichloromethane among the three types of palladium complexes.

For the cationic palladium complexes **5c,e**, methyl bonded to palladium metal can be still observed at around 0 ppm in the ^{1}H NMR spectra, while a new methyl signal of the coordinated CH_3CN is also identified on the basis of the resonance around 1.6 ppm. Like the neutral methylpalladium complex, only one isomer of the cationic palladium complex is present in solution on the basis of a single set of methyl resonances in ^{1}H NMR and ^{13}C NMR spectra (see the Experimental Section). Crystals of **5c,e** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into palladium complex solutions in CH_2Cl_2. ORTEP drawings of **5c,e** are given in Figure 4, and selected bond distances and angles are given in Table 3. The molecular structures of the cationic complexes support the connectivity pattern deduced from NMR analyses in solution. The cationic palladium complexes also feature the methyl group trans to the imine and the coordinated CH_3CN trans to the NHC. Note that the coordination of CH_3CN is not linear (Pd−N_4−C_3 is 166.9° for **5c** and 163.5° for **5e**) and is also bent out of the metal coordination plane.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Cationic Palladium Complexes 5c,e

	5c	5e
Pd(1)−C(1)	1.957(5)	1.965(7)
Pd(1)−C(2)	2.028(5)	2.031(8)
Pd(1)−N(1)	2.136(4)	2.160(6)
Pd(1)−N(4)	2.041(4)	2.053(6)
C(1)−Pd(1)−C(2)	98.0(2)	97.1(3)
C(1)−Pd(1)−N(4)	170.69(18)	171.8(3)
C(2)−Pd(1)−N(4)	91.0(2)	91.1(3)
C(1)−Pd(1)−N(1)	78.99(16)	79.2(3)
N(4)−Pd(1)−N(1)	92.17(15)	92.6(2)
C(2)−Pd(1)−N(1)	175.5(2)	176.4(3)

Norbornene Polymerization. Experimental results of norbornene polymerization with palladium complexes **3a−e**,

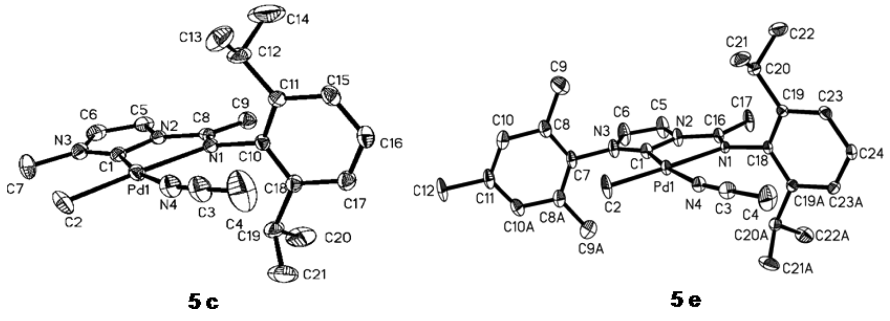

Figure 4. ORTEP drawing of the molecular structures of **5c,e**. All thermal ellipsoids are at the 50% probability level, and hydrogen atoms, cocrystallized solvent molecule CH_2Cl_2, and counterion BAF^- are omitted for clarity.

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4c,e, and **5c,e** are summarized in Table 4. Palladium dichloride complexes **3a−e** and methylpalladium complexes **4c,e** do not afford any polymer in the absence of cocatalyst. After activation with MMAO, all of these palladium complexes can catalyze norbornene polymerization with high activity. Increasing the steric hindrance of the NHC moiety leads to a slight decrease in catalytic activity. It may be that the bulky mesityl substituent retards the coordination and insertion of the norbornene monomer.[27] Palladium dichloride complexes **3c,e** show higher activities in comparison to methylpalladium analogues **4c,e**, indicating that palladium dichloride complexes are more easily activated by MMAO than the corresponding methylpalladium complexes.

Table 4. Results of Norbornene Polymerization with Palladium Catalysts[a]

entry	catalyst	temp (°C)	yield (mg)	conversion (%)	activity[b]
1	**3a**/MMAO	30	858	71.5	34.3
2	**3b**/MMAO	30	876	73.0	35.0
3	**3c**/MMAO	30	847	70.5	33.8
4	**3d**/MMAO	30	785	65.4	31.4
5	**3e**/MMAO	30	778	64.8	31.1
6	**4c**/MMAO	30	650	54.1	26.0
7	**4e**/MMAO	30	636	53.0	25.4
8	**5c**	30	164	13.6	6.56
9	**5c**	60	210	17.5	8.40
10	**5c**	80	192	16.0	7.68
11	**5c**	110	80	6.7	3.20
12	**5e**	60	110	9.2	4.40
13	α-diimine Pd[c]	60			

[a]Polymerization conditions: palladium complex, 5 μmol; monomer, 1.2 g; time, 30 min; total volume, 10 mL; solvent, *o*-dichlorobenzene; Al(MMAO)/Pd ratio, 3000. [b]In units of 10^4 g of PNB/((mol of Pd) h). [c]The cationic α-diimine−Pd catalyst structure is given as **A** in Figure 1.

Differently from the neutral palladium complexes, cationic palladium complexes **5c,e** can polymerize norbornene alone without any cocatalysts. However, a "classical" Brookhart-type cationic α-diimine palladium analogue (**A** in Figure 1) was found to be basically inactive for norbornene polymerization (entry 13). Although the cationic palladium complexes exhibit lower activities than the corresponding **3c,e**, the experimental data (entries 8−11) demonstrate that cationic palladium complexes **5c** are thermally stable for norbornene polymerization because of the strong σ-donor ability of NHC ligand. Even at 80 °C, it still maintains a stable activity, and at 110 °C, the activity is significantly reduced. As was previously reported in the literature for other palladium catalyst systems,[21] the PNBs obtained herein with these palladium catalysts bearing NHC ligands are also insoluble in organic solvents such as cyclohexane, toluene, chlorobenzene, dichlorobenzene, and trichlorobenzene even at elevated temperature.

Currently, two crucial questions, the nature of the active species for norbornene polymerization and the insolubility origin of the PNB obtained by palladium catalyst, remain unanswered. Well-defined cationic palladium complexes **5c,e** herein used to catalyze norbornene polymerization without any cocatalysts are suitable for research on the polymerization mechanism.

The norbornene polymerization processes in 0.75 mL of $CDCl_3$ solution containing 0.5 μmol of **5e** and different concentrations of norbornene monomer (NB/Pd = 10/1, 20/1, 50/1) were monitored by ^{1}H NMR spectroscopy (Figure 5). For **5e** solution without NB monomer, the integral ratio of two

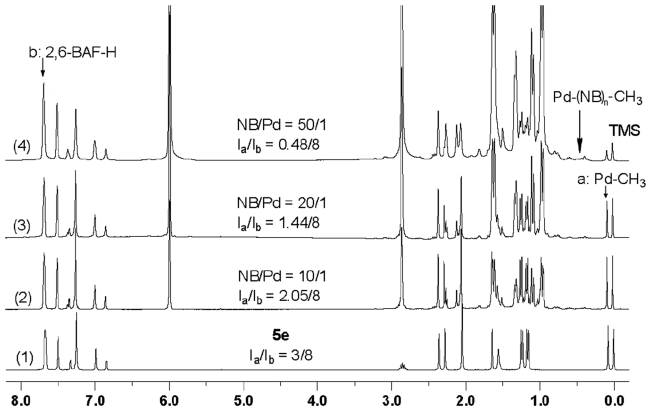

Figure 5. ^{1}H NMR of the cationic catalyst **5e** in combination with different norbornene concentrations at 5 min: (1) **5e**, I_a/I_b = 3/8; (2) NB/**5e** = 10/1, I_a/I_b = 2.05/8; (3) NB/**5e** = 20/1, I_a/I_b = 1.44/8; (4) NB/**5e** = 50/1, I_a/I_b = 0.48/8.

peaks at 0.08 and 7.68 ppm assigned to Pd−CH_3 protons and 2,6-H of the BAF group is quite consistent with the theoretical value of 3/8. When norbornene monomer was added, these two characteristic peaks were still observed, but the integral ratio of two peaks obviously changed. An integral ratio reduction from 3/8 to 0.48/8 was observed with an increase in NB/Pd ratio from 0 to 50, suggesting a consumption of the Pd−CH_3 bond because of norbornene insertion into the Pd−CH_3 bond. At the same time, new signals for the PNB sequence appear at 0.9−2.5 ppm.[28b] More importantly, a set of resonances at 0.3−0.8 ppm is clearly observed, which can be assigned to the end group CH_3 of the growing chain (Me−$(NB)_n$−Pd). The NMR results undoubtedly prove that norbornene polymerization with well-defined cationic palladium catalysts proceeds through a coordination−insertion mechanism.[22c,28]

The norbornene polymerization at low norbornene concentration (NB/Pd = 10/1) was further monitored by ^{1}H NMR spectroscopy at different times (see Figure S9 in the Supporting Information). Generally, norbornene polymerization was slowly initiated on the basis of the full disappearance of Pd−Me at ∼7 h because of coordination completion between norbornene and CH_3CN. When the polymerization time wa prolonged, norbornene monomer was gradually consumed on the basis of decreasing integral ratio (I_c/I_b), and ∼60% of monomer was consumed at 7 h. No obvious decomposition and elimination of catalyst were observed in the test time scale, suggesting that the palladium catalyst is stable under the tested conditions.

PNBs obtained with palladium catalysts bearing NHC ligands are insoluble in organic solvents, even at elevated temperature. The IR spectra of the PNBs revealed the missing absorption of a double bond at 1600−1700 cm^{-1} and the existence of vibration bands of bicyclics of norbornene at 941 cm^{-1}, indicating that the PNBs are not ROMP polymers. The wide-angle X-ray diffraction analysis of the obtained PNBs showed two major broad peaks (2θ = 9−11 and 17−19°), which implies the obtained PNBs are noncrystalline and cannot provide more information on the microstructure.[29]

In order to obtain a soluble product and gain an insight into the microstructure of polynorbornene obtained by the palladium catalyst, a hydrogen-regulated polymerization of norbornene was performed with **5e** under the conditions of 1 atm of H_2 pressure,

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50 °C, and low norbornene monomer concentration (NB/Pd = 100). A small amount of a toluene-soluble fraction was extracted from the polymerization product. The soluble fraction as an oligomer with number-average molecular weight (M_n) of 1500 determined by GPC analysis allowed us to its their microstructure and probe the origin of the insolubility of PNB obtained by palladium catalysts. As shown in Figure 6, the ^{1}H NMR

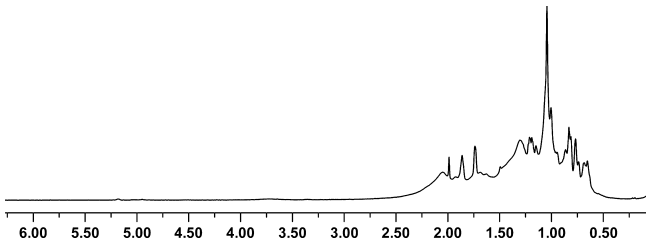

Figure 6. ^{1}H NMR spectrum of the oligomer of norbornene.

spectrum of the soluble fraction is in a range from 0.6 to 2.5 ppm, and no traces of any double bond at 5−7 ppm are observed. The absence of a double bond proves the formation of a saturated oligomer.

The ^{13}C NMR spectrum of the norbornene oligomer would provide a basis for a model of the microstructure of the PNBs obtained by these palladium catalysts. Figure 7 shows a few sets

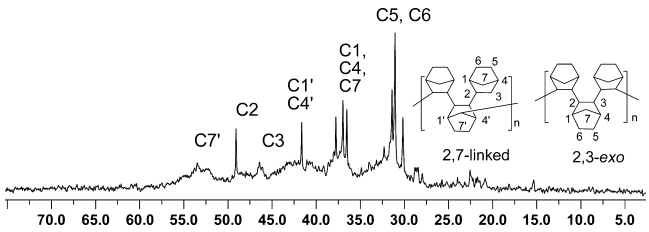

Figure 7. ^{13}C NMR spectrum of the oligomers of norbornene.

of sharp resonances, which differ distinctly from the spectra of 2,3-*exo*-disyndiotactic and 2,3-*exo*-diheterotactic PNBs obtained by $TiCl_4/Al(Et)_2Cl$[30a,b] and $CrCl_2(dppa)/MAO$[30c] catalytic systems. On the basis of the assignments in previous work, the resonances of methenes and methines appear at 29.3−32.5 ppm for C5 and C6, ∼35.8 ppm for C7, 36.3−40.4 ppm for C1 and C4, 46.4 ppm for C3, and 49.1 ppm for C2.[31] Two significant differences are the occurrence of a sharp peak at 41.6 ppm and a broad peak at low field of 53.8 ppm, which can be assigned to a 7-linked norbornene unit as a result of σ-bond metathesis.[32] The microstructure of the insoluble PNB was also determined and analyzed by a ^{13}C cross-polarization (CP)/magic-angle-spinning (MAS) spectrum (^{13}C-CP/MAS). The ^{13}C-CP/MAS spectrum shown in Figure 8 is similar to the reported spectrum of insoluble PNB with a C7-linkage structure obtained by a Zr catalyst.[32] Six

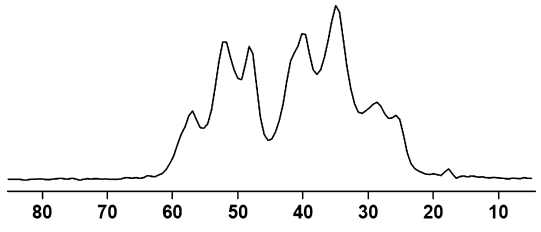

Figure 8. ^{13}C-CP/MAS spectrum of insoluble PNB.

broad resonances are observed at 20−60 ppm, and the peaks at very low field (52−57 ppm) are a result of C7 linkage. Moreover, two characteristic peaks of the norbornene oligomer in Figure 7 are also overlapped in ^{13}C-CP/MAS spectroscopy. These agreements support the existence of a C7 linkage in the insoluble PNB obtained by the cationic palladium catalyst.[32] Intramolecular σ-bond metathesis leads to a rigid helical structure of the PNB obtained by palladium catalysts, which strongly affects its solubility. It must be acknowledged that such reactions may occur much more frequently with palladium catalysts than with zirconium catalysts on the basis of the frequent existence of C−H activation reactions for palladium catalysts.[33] Therefore, intermolecular σ-bond metathesis cannot be excluded, and insoluble PNB with cross-linking structure may be formed.

CONCLUSIONS

In summary, a series of new palladium complexes bearing an NHC ligand with a directly N-bonded imine group, including palladium dichloride, methylpalladium, and cationic palladium complexes, has been successfully synthesized and fully characterized. The reductive elimination of methylpalladium complexes containing an NHC donor is effectively suppressed by introduction of a bulky substituent group on both the imine and the NHC moiety. Neutral palladium complexes activated by MMAO are highly active toward norbornene polymerization, whereas well-defined cationic palladium complexes can polymerize norbornene alone without any cocatalysts and show a high thermostability. Norbornene polymerization with the cationic palladium catalyst **5e** proceeds through a coordination−insertion mechanism. Analysis of the oligomer from a hydrogen-regulated polymerization of norbornene reveals the existence of a palladium-catalyzed C7 linkage in the polynorbornene (PNB) by σ-bond metathesis. The origin of the insolubility of PNB obtained by palladium catalysts may come from a rigid helical structure or cross-linking structure. Our study provides deep insight into Pd-catalyzed norbornene polymerization and the microstructure of the PNB obtained by a palladium catalyst.

EXPERIMENTAL SECTION

General Considerations. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line Schlenk techniques.

Materials. 2, -Dimethylaniline, 2,4,6-trimethyaniline, and 2,6-diisopropylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before being used. Modified methylaluminoxane (MMAO, 2.0 M in hexane) was purchased from Akzo Nobel Corp. Toluene, *n*-hexane, and diethyl ether were refluxed over metallic sodium for 24 h before being used. Dichloromethane and dichlorobenzene were dried over phosphorus pentoxide for 8 h and distilled under a nitrogen atmosphere. Norbornene was dried over potassium metal prior to use in polymerization. Methylimidazole was purchased from Alfa Aesar and used as received. The intermediate products mesityl-substituted imidazole, imidoyl chlorides, (COD)-$PdCl_2$, and (COD)PdMeCl were prepared according to literature methods.[12a] The cationic α-diimine palladium compound was synthesized according to the reported methods.[12a]

Characterizations. Elemental analyses were performed with a Vario EL series elemental analyzer from Elementar. ESI-MS spectra were obtained with a Shimadzu LCMS-2010A instrument. IR spectra were recorded on a Nicolet NEXUS-670 spectrometer. The NMR data of ligands and complexes were obtained on a Varian Mercury-Plus 300 MHz spectrometer at ambient temperature, using $CDCl_3$, DMSO-d_6, CD_3CN, or dichlorobenzene-d_4 as solvent and referenced versus TMS as standard. The molecular weight of the norbornene oligomer were

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determined on an Agilent Technologies PL-GPC220 instrument at 150 °C with polystyrene as standard, and 1,2,4-trichlorobenzene was employed as the eluent. ^{13}C-CP/MAS measurements were performed on a Bruker AVANCE 400 spectrometer using adamantine as standard.

Crystal Structure Determination. The X-ray diffraction data of single crystals were obtained with the $\omega-2\theta$ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Norbornene Polymerization. In a typical procedure, 1.20 g of norbornene in 5.5 mL of *o*-dichlorobenzene and 2.5 mL of MMAO (2 M) (**5c**,**e** without MMAO) were added into a flask (100 mL) with stirring under an N_2 atmosphere. After the mixture was kept at the desired temperature for 2 min, 5 μmol of the palladium complex in 1 mL of dichloromethane was injected into the flask via syringe, and the total reaction volume kept at 10 mL by variation of the added *o*-dichlorobenzene when necessary. The reaction mixture was continuously stirred at polymerization temperature, which was controlled with an external oil bath in polymerization experiments. After 30 min, the polymerization was terminated by addition of acidic ethanol (ethanol/HCl, 95/5). The precipitated polymer was washed with ethanol and dried at 60 °C under vacuum to a constant weight.

Hydrogen-Regulated Polymerization of Norbornene. Eight milliliters of a norbornene solution in toluene (100 mg of NB) was added into a flask (100 mL) under an H_2 pressure of 1 atm. After the mixture was stirred at 50 °C for 2 min, 1 mL of a **5e** (10 μmol) solution in dichloromethane was injected into the flask via syringe. After the reaction mixture was continuously stirred at 50 °C for 30 min, the reaction was terminated by addition of 5 mL of ethanol. The obtained solid products were fractionated by extraction with toluene, and the small mass of soluble fraction was concentrated to low volume. Then addition of ethanol to the solution afforded a white solid. The precipitated solid was dried and used for characterization by NMR and GPC.

Synthesis of Ligands. *Synthesis of [3-Me-1-(2,6-dimethylphenyl)iminyl-$C_3H_3N_2$]$^+$Cl$^-$ (**1a**).* Methylimidazole (0.33 g, 4.0 mmol) was added dropwise to a solution of the dimethylphenyliminyl chloride (0.71 g, 3.90 mmol) in dry THF (20 mL) over a period of 5 min. The mixture was stirred at ambient temperature for 20 h, and the product slowly precipitated as a white solid. The crude product was obtained by filtration, washed with dry THF (3 × 15 mL), and dried under reduced pressure. **1a** was isolated as a white solid in 98% yield (1.03 g, 3.92 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.7 (s, 1H, NCHN), 7.93 (s, H, imidazole-H), 7.74 (s, H, imidazole-H), 6.73 (m, 3H, Ar-H), 3.99 (s, 3H, N-CH_3), 2.18 (s, 3H, imine CH_3), 1.73 (d, 6H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 145.3, 136.2, 130.5, 129.7, 127.4, 123.5, 118.1, 36.1, 17.3, 16.2.

*Synthesis of [3-Me-1-(2,4,6-trimethylphenyl)iminyl-$C_3H_3N_2$]$^+$Cl$^-$ (**1b**).* Following the above procedure, **1b** was isolated in 96% yield (1.1 g, 3.8 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 1H, NCHN), 8.33 (s, H, imidazole-H), 7.86 (s, H, imidazole-H), 7.17 (m, 2H, Ar-H), 3.94 (s, 3H, N-CH_3), 2.28 (s, 3H, *p*-Ar-CH_3), 2.27 (s, 3H, imine-CH_3), 1.95 (s, 6H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 145.7, 137.3, 132.5, 128.4, 125.5, 121.9, 119.6, 37.5, 23.1, 19.5, 16.8.

*Synthesis of [3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_3N_2$]$^+$Cl$^-$ (**1c**).* Following the above procedure, **1c** was isolated in 90% yield (1.2 g, 3.6 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.9 (s, 1H, NCHN), 8.19 (d, H, imidazole-HN), 7.55 (d, H, imidazole-H), 7.16 (m, 3H, Ar-H), 4.32 (s, 3H, N-CH_3), 2.59 (m, 2H, ^{i}Pr-CH), 2.53 (s, 3H, imine-CH_3), 1.13 (m, 12H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 140.7, 138.4, 136.5, 125.6, 124.7, 123.6, 117.7, 37.57, 28.8, 23.5, 17.1. IR: $\nu_{C=N}$ 1678 cm^{-1}, $\nu_{imidazole\text{-}H}$ 3495 cm^{-1}.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-dimethylphenyl)iminyl-$C_3H_3N_2$]$^+$Cl$^-$ (**1d**).* Following the above procedure, **1d** was isolated in 94% yield (1.4 g, 3.7 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.2 (s, 1H, NCHN), 8.15 (d, H, imidazole-H), 7.84 (d, H, imidazole-H), 6.92 (m, 6H, C_6H_3, C_6H_2), 2.55 (s, 3H, imine-CH_3), 2.25 (s, 3H, *p*-Ar-CH_3), 1.86 (d, 12H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 148.7, 135.7, 134.5, 129.8, 128.4, 127.5, 127.9, 126.9, 126.1, 117.1, 116.7, 21.3, 18.2, 17.9, 17.6.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)iminyl-$C_3H_3N_2$]$^+$Cl$^-$ (**1e**).* Following the above procedure, **1e** was isolated in 93% yield (1.6 g, 3.7 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.1 (s, 1H, NCHN), 7.28 (s, 1H, imidazole-H), 8.51 (s, 1H, imidazole-H), 7.12 (m, 5H, Ar-H), 2.78 (s, 3H, imine-CH_3), 2.67 (m, 2H, ^{i}Pr-CH_3), 2.34 (s, 3H, *p*-Ar-CH_3), 2.25 (s, 6H, *o*-Ar-CH_3), 1.16 (dd, 12 H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.9, 137.2, 134.9, 130.4, 130.1, 126.0, 124.4, 124.1, 123.9, 118.8, 29.0, 23.7, 21.5, 18.2, 18.4, 17.7.

Synthesis of Ag(I) Complexes. *Synthesis of [3-Me-1-(2,6-dimethylphenyl)iminyl-$C_3H_2N_2$]AgCl (**2a**).* The dimethylphenylimidazolium salt **1a** (0.789 g, 3 mmol) was dissolved in 30.0 mL of dry dichloromethane and the solution added, under nitrogen, to a Schlenk containing activated powdered 4 A molecular sieves. Ag_2O (0.450 g, 2 mmol) was then added and the reaction mixture stirred in the absence of light for 6 h. The reaction mixture was then filtered in the dark and the volume of the solution reduced to 5.0 mL. Pentane was added to afford the product **2a** as an off-white solid in 63% yield (694 mg, 1.9 mmol). Anal. Calcd for $C_{14}H_{17}N_3AgCl$: C, 45.37; H, 4.62; N, 11.34. Found: C, 45.04; H, 4.57; N, 10.87. ESI-MS (*m*/*z*): 563, [Ag(ligand)$_2$]$^+$ 563. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (s, 1H, imidazole-H), 7.18 (s, 1H, imidazole-H), 6.88 (m, 3H, Ar-H), 3.86 (s, 3H, N-CH_3), 2.34 (s, 3H, imine-CH_3), 1.98 (d, 6H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 152.2, 144.6, 128.3, 126.4, 124.2, 123.1, 119.7, 40.3, 20.3, 18.5.

*Synthesis of [3-Me-1-(2,4,6-trimethylphenyl)iminyl-$C_3H_2N_2$]AgCl (**2b**).* Following the above procedure, **2b** was isolated in 70% yield (804 mg, 2.1 mmol). Anal. Calcd for $C_{15}H_{19}N_3AgCl$: C, 46.84; H, 4.98; N, 10.92. Found: C, 46.94; H, 4.72; N, 10.83. ESI-MS (*m*/*z*): 626, [Ag(ligand)$_2$]$^+$ 626. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, H, imidazole-H), 7.88 (s, H, imidazole-H), 7.62 (m, 2H, Ar-H), 4.08 (s, 3H, N-CH_3), 2.31 (s, 3H, imine-CH_3), 2.31 (d, 6H, *o*-Ar-CH_3), 2.012 (s, 3H, *p*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.9, 152.7, 147.2, 132.3, 128.3, 126.8, 121.1, 116.3, 38.4, 30.6, 21.3, 18.7.

*Synthesis of [3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$]AgCl (**2c**).* Following the above procedure, **2c** was isolated in 75% yield (956 mg, 2.2 mmol). Anal. Calcd for $C_{18}H_{25}N_3AgCl$: C, 50.66; H, 5.90; N, 9.85. Found: C, 50.37; H, 5.78; N, 9.76. ESI-MS (*m*/*z*): 675, [Ag(ligand)$_2$]$^+$ 675. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H, imidazole-H), 7.23 (s, 1H, imidazole-H), 7.13 (m, 3H, Ar-H), 3.97 (s, 3H, N-CH_3), 2.68 (m, 2H, ^{i}Pr-CH), 2.50 (s, 3H, imine-CH_3), 1.14 (dd, 12H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.3, 151.6, 142.1, 136.7, 124.9, 123.5, 119.7, 40.45, 28.8, 23.6, 18.4. IR: $\nu_{C=N}$ 1678 cm^{-1}.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-dimethylphenyl)iminyl-$C_3H_2N_2$]AgCl (**2d**).* Following the above procedure, **2d** was isolated in 83% yield (1.2 g, 2.5 mmol). Anal. Calcd for $C_{22}H_{25}N_3AgCl$: C, 55.65; H, 5.31; N, 8.85. Found: C, 55.27; H, 5.04; N, 8.61. ESI-MS (*m*/*z*): 769, [Ag(ligand)$_2$]$^+$ 769. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.307 (s, 1H, imidazole-H), 7.11 (s, 1H, imidazole-H), 6.97 (m, 5H, C_6H_3, C_6H_2), 2.60 (s, 3H, imine-CH_3), 2.36 (s, 3H, *p*-Ar-CH_3), 2.09 (d, 12H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 144.6, 139.9, 134.9, 129.7, 128.3, 126.3, 124.3, 123.0, 119.7, 21.4, 18.6, 18.2.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$]AgCl (**2e**).* Following the above procedure, **2e** was isolated in 80% yield (1.3 g, 2.4 mmol). Anal. Calcd for $C_{26}H_{33}N_3AgCl$: C, 58.82; H, 6.27; N, 7.92. Found: C, 58.70; H, 6.07; N, 7.65. ESI-MS (*m*/*z*): 883, [Ag(ligand)$_2$]$^+$ 883. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H, imidazole-H), 7.20 (s, 1H, imidazole-H), 7.10 (m, 6H, C_6H_3, C_6H_2), 2.71 (m, 2H, ^{i}Pr-CH), 2.62 (s, 3H, imine-CH_3), 2.09 (m, 9H, *p*-Ar-CH_3, *o*-Ar-CH_3), 1.16 (m, 12H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 142.6, 140.4, 136.7, 135.8, 134.9, 130.8, 125.1, 123.6, 119.4, 28.7, 23.5, 21.3, 18.8.

Synthesis of Pd(II) Complexes. *Synthesis of [3-Me-1-(2,6-dimethylphenyl)iminyl-$C_3H_2N_2$]PdCl$_2$ (**3a**).* A cooled solution (−20 °C) of the silver complex **2a** (100 mg, 0.230 mmol) in dry dichloromethane (10 mL) was slowly transferred to a similarly cooled solution of (COD)PdCl$_2$ (0.061 mg, 0.21 mmol) in dichloromethane (15 mL). The mixture was slowly warmed to ambient temperature and

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stirred overnight before removal of the volatiles under vacuum. The crude product was dissolved in acetonitrile (15 mL) and filtered to remove precipitated silver chloride. The solvent was removed under vacuum, and the crude product was recrystallized from a pentane/dichloromethane mixture. **3a** was isolated in 85% yield (79 mg, 1.9 mmol). ESI-MS (m/z): 403, MW 403. Anal. Calcd for $C_{14}H_{18}N_3PdCl_2$: C, 41.45; H, 4.47; N, 10.36. Found: C, 41.64; H, 4.51; N, 10.28. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.05 (d, 1H, imidazole-H), 7.52 (d, 1H, imidazole-H), 7.07 (m, 3H, Ar-H), 4.11 (s, 3H, N-CH_3), 2.25 (s, 3H, imine-CH_3), 2.15 (s, 6H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.5, 157.2, 142.1, 131.8, 128.4, 125.6, 119.4, 38.0, 18.9, 15.4.

*Synthesis of [3-Me-1-(2,4,6-trimethylphenyl)iminyl-$C_3H_2N_2$]PdCl$_2$ (**3b**).* Following the above procedure, **3b** was isolated in 74% yield (71.1 mg, 0.2 mmol). ESI-MS (m/z): 418, MW 418. Anal. Calcd for $C_{15}H_{20}N_3PdCl_2$: C, 42.93; H, 4.80; N, 10.01. Found: C, 42.99; H, 4.72; N, 10.12. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.03 (d, 2H, imidazole-H), 7.51 (d, 2H, imidazole-H), 6.87 (m, 2H, Ar-H), 4.10 (s, 3H, N-CH_3), 2.22 (s, 6H, *o*-Ar-CH_3), 2.11 (m, 3H, imine-CH_3), 2.09 (m, 3H, *p*-Ar-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.6, 150.6, 146.1, 139.8, 138.3, 135.4, 131.5, 129.0, 125.6, 117.5, 38.3, 21.4, 18.9, 15.4.

*Synthesis of [3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$]PdCl$_2$ (**3c**).* Following the above procedure, **3c** was isolated in 77% yield (81.4 mg, 0.2 mmol). ESI-MS (m/z): 458, MW 458. Anal. Calcd for $C_{18}H_{26}N_3PdCl_2$: C, 46.82; H, 5.68; N, 9.10. Found: C, 46.98; H, 5.75; N, 8.98. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.73 (s, 1H, imidazole-H), 7.33 (s, 1H, imidazole-H), 7.10 (m, 3H, Ar-H), 4.26 (s, 3H, N-CH_3), 3.08 (m, 2H, ^{i}Pr-CH), 2.31 (s, 3H, imine-CH_3), 1.25 (d, 12H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.3, 157.1, 142.6, 139.1, 136.4, 129.0, 125.7, 123.9, 120.7, 119.5, 38.4, 28.3, 24.5, 16.3.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-dimethylphenyl)-iminyl-$C_3H_2N_2$]PdCl$_2$ (**3d**).* Following the above procedure, **3d** was isolated in 80% yield (94 mg, 0.18 mmol). ESI-MS (m/z): 506, MW 506. Anal. Calcd for $C_{22}H_{26}N_3PdCl_2$: C, 51.83; H, 5.14; N, 8.24. Found: C, 51.92; H, 5.22; N, 8.13. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.31 (s, 1H, imidazole-H), 7.51 (s, 1H, imidazole-H), 7.08 (m, 5H, C_6H_3, C_6H_2), 2.29 (s, 3H, imine-CH_3), 2.19 (s, 3H, *p*-Ar-CH_3), 2.06 (m, 12H, *o*-Ar-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.1, 159.7, 142.0, 139.0, 134.4, 131.8, 128.4, 125.3, 123.9, 21.5, 18.9, 18.4, 15.7.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)-iminyl-$C_3H_2N_2$]PdCl$_2$ (**3e**).* Following the above procedure, **3e** was isolated in 85% yield (110 mg, 0.20 mmol). ESI-MS (m/z): 562, MW 562. Anal. Calcd for $C_{26}H_{34}N_3PdCl_2$: C, 55.18; H, 6.06; N, 7.43. Found: C, 55.25; H, 6.13; N, 7.32.^{1}H NMR (300 MHz, DMSO-d_6): δ 8.24 (d, 1H, imidazole-H), 7.53 (d, 1H, imidazole-H), 7.18 (m, 5H, C_6H_3, C_6H_2), 3.08 (m, 2H, ^{i}Pr-CH), 2.39 (s, 3H, imine-CH_3), 2.07 (s, 6H, *o*-Ar-CH_3), 1.28 (d, 12H,^{i}Pr-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.4, 159.9, 145.2, 141.7, 139.1, 134.3, 129.1, 125.3, 124.0, 120.4, 109.9, 28.8, 24.5, 24.1, 21.5, 18.4, 16.4.

*Synthesis of [3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$]-PdMeCl (**4c**).* A solution of **2c** (425 mg, 1 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a solution of (COD)PdMeCl (263 mg, 1 mmol) in CH_2Cl_2 (40 mL) and stirred at −30 °C temperature for 15 h with exclusion from light. The reaction mixture was then filtered through Celite, and volatiles were removed under reduced pressure. The resulting light white solid was washed with *n*-hexane and dried under vacuum. **4c** was isolated in 50% yield (214 mg, 0.5 mmol). ESI-MS (m/z): 440, MW 440. Anal. Calcd for $C_{19}H_{29}N_3PdCl$: C, 51.71; H, 6.62; N, 9.52. Found: C, 51.62; H, 6.69; N, 9.47. ^{1}H NMR (300 MHz, CD_3CN): 7.85 (d, 1H, imidazole-H), 7.46 (d, 1H, imidazole-H), 7.12 (m, 3H, C_6H_3), 3.75 (s, 3H, NCH_3), 2.89 (m, 2H, ^{i}Pr-CH), 2.19 (s, 3H, imine-CH_3), 1.18 (d, 6H, ^{i}Pr-CH_3), 1.04 (d, 6H, ^{i}Pr-CH_3), 0.83 (s, 3H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 176.1, 164.8, 145.8, 131.7, 130.1, 128.9, 128.5, 43.1, 33.8, 28.7, 28.6, 20.7, −5.4.

*Synthesis of [3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)-iminyl-$C_3H_2N_2$]PdMeCl (**4e**).* Following the above procedure, **4e** was isolated in 75% yield (408 mg, 0.75 mmol). ESI-MS (m/z): 544, MW 544. Anal. Calcd for $C_{27}H_{37}N_3PdCl$: C, 59.45; H, 6.84; N, 7.70. Found: C, 59.32; H, 6.83; N, 7.69. ^{1}H NMR (300 MHz, CD_3CN): 7.60 (d, 1H, imidazole-H), 7.15 (m, 3H, imidazole-H, C_6H_2), 6.95 (s, 2H, C_6H_3), 6.78 (s, 1H, C_6H_3), 3.00 (m, 2H, ^{i}Pr-CH), 2.35 (s, 3H, imine-CH_3), 2.22 (m, 3 H, *p*-Ar-CH_3), 2.13 (s, 6H, *o*-Ar-CH_3), 1.34 (d, 6H, ^{i}Pr-CH_3), 1.14 (d, 6H, ^{i}Pr-CH_3), 0.27 (s, 3H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 179.1, 164.1, 145.8, 140.1, 134.3, 131.7, 129.3, 128.5, 124.1, 33.8, 28.8, 28.6, 25.9, 22.6, 20.9, −5.9.

*Synthesis of [(3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$)-PdMeCH$_3$CN]$^+$BAF$^-$ (**5c**).* NaBAF (443 mg, 0.5 mmol) was added to a solution of **4c** (220 mg, 0.5 mmol) in MeCN (10 mL) and stirred at room temperature for 16 h with exclusion from light. The reaction mixture was then filtered through Celite, and the volatiles were removed under reduced pressure. The resulting off-white solid was dissolved in CH_2Cl_2 (5 mL), and the solution was stirred with activated charcoal for 30 min. The mixture was then filtered through Celite and concentrated to 2 mL. An off-white solid was precipitated by addition of excess *n*-hexane, filtered, and dried under vacuum. **5c** was isolated in 95% yield (640 mg, 0.48 mmol). ESI-MS (m/z): 405, [NHC-Pd-CH_3]$^+$ 405. Anal. Calcd for $C_{53}H_{44}N_4BF_{24}Pd$: C, 48.44; H, 3.68; N, 4.26. Found: C, 48.33; H, 3.56; N, 4.24. ^{1}H NMR (300 MHz, CD_3Cl): 7.68 (s, 12H, BAF Ar-H), 7.51 (m, 3H, Ar-H), 7.11 (s, 1H, imidazole-H), 6.71 (s, 1H, imidazole-H), 3.73 (s, 3H, N−CH_3), 2.85 (m, 2H, ^{i}Pr-CH), 2.22 (s, 3H, imine-CH_3), 1.59 (s, 3H, CH_3CN), 1.23 (d, 6H, ^{i}Pr-CH_3), 1.13 (d, 6H, ^{i}Pr-CH_3), 0.87 (s, 3H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 173.5, 168.0, 167.4, 166.7, 166.4, 145.5, 143.9, 140.1, 134.6, 134.2, 131.7, 129.2, 128.1, 43.3, 33.8, 28.5, 28.4, 20.6, −6.3.

*Synthesis of [(3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$)PdMeCH$_3$CN]$^+$BAF$^-$ (**5e**).* Following the above procedure, **5e** was isolated in 98% yield (704 mg, 0.49 mmol). ESI-MS (m/z): 509, [NHC-Pd-CH_3]$^+$ 509. Anal. Calcd for $C_{61}H_{52}N_4BF_{24}Pd$: C, 51.66; H, 3.98; N, 3.95. Found: C, 51.47; H, 3.88; N, 3.85. ^{1}H NMR (300 MHz, CD_3Cl): δ 7.67 (s, 8H, BAF Ar-H), 7.50 (m, 4H, BAF Ar-H), 7.32 (m, 3H, Ar-H), 6.98 (s, 3H, imidazole-H, Ar-H), 6.84 (s, 1H, imidazole-H), 2.85 (m, 2H, ^{i}Pr-CH), 2.36 (s, 3H, imine-CH_3), 2.28 (m, 3H, *p*-Ar-CH_3), 1.64 (s, 3H, CH_3CN), 1.23 (d, 6H, ^{i}Pr-CH_3), 1.18 (d, 6H, ^{i}Pr-CH_3), 0.07 (s, 3H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 175.4, 168.1, 167.4, 166.7, 166.1, 165.9, 145.5, 140.2, 135.1, 134.7, 134.5, 134.3, 132.8, 131.8, 130.0, 129.3, 128.2, 125.4, 33.8, 28.5, 25.7, 22.3, 20.6, −5.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving detailed NMR sepctra, crystallographic data of palladium complexes **3a**−**c**,**e**, **4c**,**e**, and **5c**,**e**, ^{1}H NMR spectroscopy of **5e** with norbornene at different times, and IR and WAXD of the PNB. 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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