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NHC Ligands with a Secondary Pyrimidyl Donor for Electron-Rich Palladium(0) Complexes

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Several (*N*-2-pyrimidyl-NHC)-palladium(0) complexes have been synthesized in very high yields and purities by transmetalation from the related silver(I) complexes with Pd^0(tBuDAB)(ma). The coordination behavior of the heteroditopic ligands was analyzed, and the structure of their complexes was confirmed by NMR and X-ray diffraction studies. The complexes are active catalysts for the transfer hydrogenation of alkynes to *Z*-alkenes, with activity and selectivity depending on the pyrimidine substituents and the NHC nitrogen substituent. Selectivities toward the *Z*-alkene as high as 97% were observed.

Introduction

N-Heterocyclic carbenes (NHCs) have been used frequently in organometallic chemistry and catalysis for almost two decades,[1,2] and the field shows no sign of saturation.[3] The high stability these ligands impart on their transition metal (TM) complexes and the catalytic activity of those complexes justify the amount of attention to this class of ligands. The strong donating character of NHCs combined with their ability to act as acceptors enables them to form complexes with a large number of TMs in various oxidation states, as well as with many main group elements.[4] The bulk of the research performed with monodentate carbenes focuses on catalysis, but also homo- and heteropolydentate ligands containing NHCs are reported frequently.[5] Currently, one of the focal points of our research concerns the development and synthesis of heterobidentate NHC ligands containing a secondary nitrogen donor.[6−8] With the combination of a strong donor and a more weakly coordinating donor we intend to gain access to a class of catalysts that benefits from the hemilabile behavior of one of its ligands.[9] Additionally, the basicity of the secondary nitrogen donor is easily varied to obtain the desired functionality. We endeavored the synthesis of electron-rich palladium complexes bearing an NHC ligand functionalized with a pyrimidyl donor because of the ease with which they are introduced and the fact that its basicity is lower than that of the more often employed pyridyl moiety. These ligands have been prepared before,[10,11] but a thorough investigation of the influence of the substituents on both the NHC and the nitrogen donor has not been performed. The pyrimidyl functionality in combination with the NHC scaffold gives rise to a five-membered chelate ring when N,C-coordinated to a metal. Because all nonmetal atoms in the ring are sp^2-hybridized, a considerable amount of strain is expected, likely enhancing the hemilability of the system.

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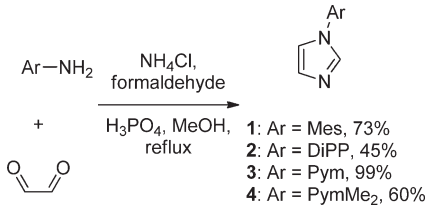
Scheme 1. Synthesis of *N*-Arylimidazoles



By combining the NHC and the pyrimidine in one ligand with various substituents, we expect to gain insight into the effects of the substituents on the coordination chemistry and, ultimately, the performance of its zerovalent palladium complexes in catalysis. We present here the synthesis and structural characterization of the *N*-pyrimidyl-functionalized imidazolium salts and the NHC complexes derived thereof with silver(I) and palladium(0). The palladium(NHC) complexes are then applied to the transfer hydrogenation of alkynes.

Results and Discussion

Ligand Synthesis. The *N*-arylimidazoles **1**−**4** were synthesized according to a literature procedure in yields higher than or equal to those reported (Scheme 1).[12]

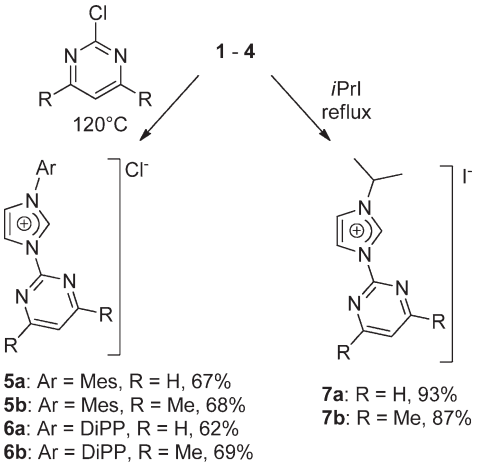
Quaternization to the imidazolium salts **5**−**7** was performed in two ways. In the case of mesityl (2,4,6-trimethylphenyl, Mes) imidazole **1** and 2,6-diisopropylphenyl (DiPP) imidazole **2**, the pyrimidyl functionality was introduced by heating the imidazole with 2-chloropyrimidine (PymCl, **a**) or 2-chloro-4,6-dimethylpyrimidine ($PymMe_2Cl$, **b**) under solvent-free conditions to obtain **5** and **6**.[11] For *N*-(2-pyrimidyl)imidazole **3** and *N*-(2-(4,6-dimethyl)pyrimidyl)imidazole **4**, quaternization with isopropyl iodide gave **7** in high yields (Scheme 2).

The progress of the reaction was monitored by ^{1}H NMR, where the imidazolium signal is observed between 10.6 and 10.4 ppm. Yields for the salts **5** and **6** are reasonably good and comparable to those reported in the literature,[11] whereas those for **7** are excellent.

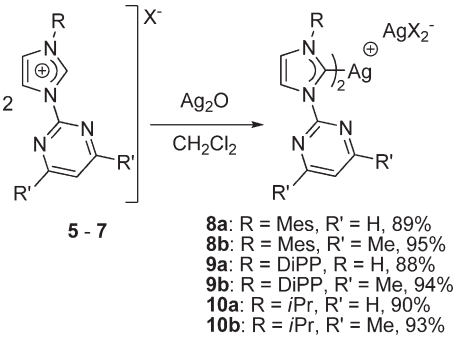
Silver(NHC) Complexes. To gain access to the NHCs, carbene generation with basic silver(I) oxide was chosen.[13] This reliable method works for most ligand precursors and generally leads to high yields and stable products.[6,7,14] With the NHC pyrimidyl scaffold this is not different; high yields are routinely obtained (Scheme 3). It has to be noted though that the solubility of complexes **10** in dichloromethane is lower than that of complexes **8** and **9**, and a precipitate was seen in the reaction mixture that disappeared upon dilution. This observation might be best explained by the formation of charged biscarbene silver complexes that are favored for ligands with small substituents. With the larger aryl substituents of **8** and **9**, the monocarbene silver(I) complex is favored. This neutral species would have a better solubility in relatively apolar solvents.

The reactions could be monitored visually by the uptake of silver(I) oxide, but optimum results were obtained for all

Scheme 2. Synthesis of Pyrimidyl−Imidazolium Salts



Scheme 3. Carbene Generation with Silver(I) Oxide



complexes with a reaction time of 16 h. The pure products were obtained after filtration and concentration of the reaction mixture. Successful conversion is observed in the ^{1}H NMR, where the disappearance of the signal of the acidic imidazolium proton signifies carbene formation. However, positive proof is seen only in ^{13}C NMR and MS experiments. For the complexes **8**−**10**, the signal for the carbene carbon is observed around 184 ppm in the ^{13}C NMR, which is a common value for Ag(NHC) complexes. In solution, dynamic exchange processes can take place; this is the reason that instead of doublets due to ^{107,109}Ag coupling, a singlet is the only observed signal for the carbene carbon.[15] In contrast, this coupling is observed in more rigid polydentate systems.[16] In mass spectrometry experiments a biscarbene silver cation was observed, which is an often seen architecture. However, the results from MS experiments cannot be directly correlated with a solution structure because of the dynamic nature of Ag(NHC) silver complexes in the solution phase.

Palladium(NHC) Complexes. The silver complexes were then subjected to transmetalation with a zerovalent palladium precursor[17] to obtain the zerovalent NHC palladium complexes **11**−**13**.[6] Yields were consistently high (91−99%), as we have observed before, and excellent purities were

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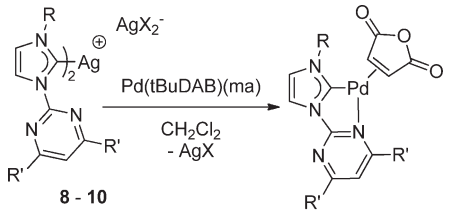
Scheme 4. Transmetalation to Zerovalent Palladium



11a: R = Mes, R' = H, 91%
11b: R = Mes, R' = Me, 99%
12a: R = DiPP, R' = H, 93%
12b: R = DiPP, R' = Me, 87%
13a: R = *i*Pr, R' = H, 93%
13b: R = *i*Pr, R' = Me, 91%

obtained by precipitation of the products with pentane (Scheme 4).

The signal for the carbene carbon in **11**−**13** exhibits a low-field shift compared to that of the silver(I) complexes and is observed between 188 and 194 ppm in the ^{13}C NMR. Because of the dissymmetry of the complexes, all hydrogens and carbons give unique signals in the NMR. For the methylpyrimidyl-substituted ligands **11b**−**13b**, the signal for the methyl *ortho* to the coordinating nitrogen shows a downfield shift to around 2.8 ppm in the ^{1}H NMR, as opposed to the other methyl, which does not show a significant difference in chemical shift from the corresponding silver complex (2.6 ppm). In the nonsubstituted cases **11a**−**13a** the difference in chemical shift for the hydrogens neighboring the nitrogen is smaller, from around 8.8 ppm in the silver complexes to 8.9 ppm in the palladium complexes. However, we do observe that the signals for the two protons are not fully resolved on the NMR time scale. This is probably due to dynamic processes at room temperature, involving exchange of the two nitrogen donor atoms of the *N*-pyrimidyl-NHC ligand. This hemilability is also expected to occur in the methyl-substituted ligands, but the activation barrier is apparently too high to let this process occur at room temperature. As for the maleic anhydride ligand, we observe that in the less bulky **11a**−**13a** the two signals coalesce to a broad singlet at room temperature in the ^{1}H NMR spectra, whereas for the more bulky **11b**−**13b** the signals are resolved into two doublets with a coupling of 3.6 Hz. We attribute this to rotation of the maleic anhydride facilitated by decoordination of the secondary donor. For **11b** and **12b** the two alkene signals are very close together, whereas for **13b** they are over 0.5 ppm apart. The origin of this difference remains obscure. In ^{13}C NMR the same trends are observed, albeit less pronounced.

X-ray Crystallography. To unequivocally establish the structure of this type of complex, a crystal structure analysis of complex **11a** was performed. X-ray quality crystals were obtained by vapor diffusion of diethyl ether into a dichloromethane solution of **11a** (Figure 1).

The solid-state structure of **11a** exhibits structural similarities that are consistent with those of other NHC-Pd derivatives featuring a maleic anhydride ligand.[6] The bidentate carbene ligand and the double bond of the maleic anhydride define a plane where the anhydride moiety is coordinated side-on, with an angle of 108.4° with respect to the coordination plane. The geometrical parameters of the maleic anhydride molecule with the Pd center resemble features that lie between a Pd metallacycle and a metal−olefin bond. Two slightly different bond lengths between the maleic anhydride ligand and the Pd center, C18−Pd1 (2.110(2) Å) and C19−Pd1 (2.054(3) Å), reflect the difference in *trans* influence of the two donors in the bidentate NHC ligand. The alkene bond length C5−C19 (1.424(3) Å) is elongated compared to the free ligand (1.332(3) Å), indicating a lower bond order caused by a significant d−π* back-bonding. The NHC is a stronger donor than the pyrimidine moiety, and as a consequence, the alkene is tilted away from the NHC ligand. The bite angle (C1−Pd1−N3 76.97(8)°) of the NHC ligand is similar to that observed in an analogous divalent palladium complex.[11] The distances between the atoms C1−Pd1 and N1−Pd1 (2.045(2) and 2.197(2) Å) are longer compared to the divalent analogue, reflecting a higher electron density of the zerovalent palladium.

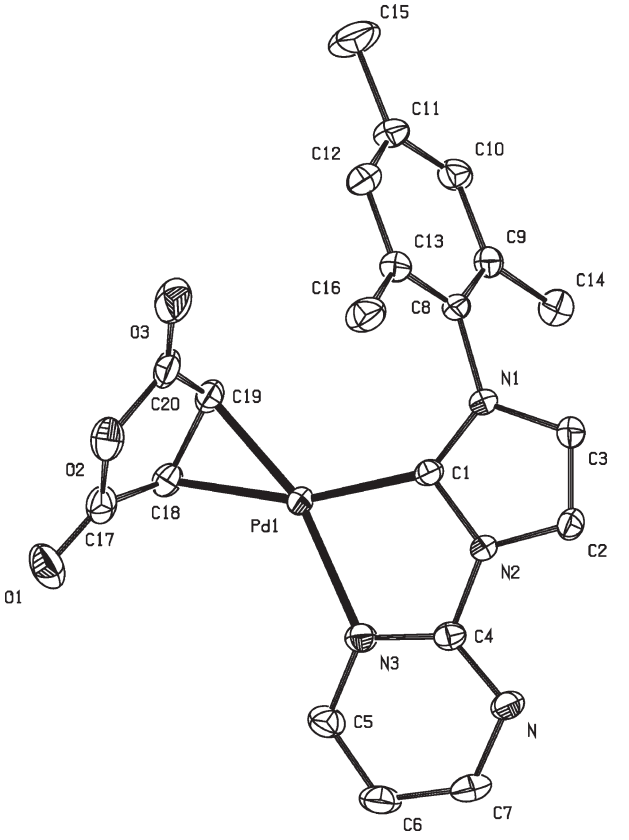
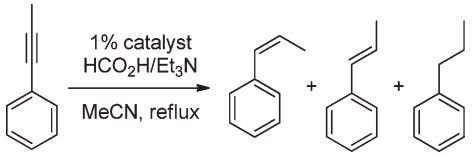


Figure 1. Displacement ellipsoid plot (50% probability level) of **11a**. H atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1 2.045(2), Pd1−C19 2.054(2), Pd1−C18 2.110(2), Pd1−N3 2.197(2); C1−Pd1−N3 76.99(8), C1−Pd1−C19 120.38(9), C1−Pd1−C18 160.16(9), C19−Pd1−C18 39.7(1), C19−Pd1−N3 162.60(9), C18−Pd1−N3 122.74(9), C5−N3−Pd1 131.1(2), C4−N3−Pd1 113.5(2), C20−C19−Pd1 108.4(2), N1−C1−Pd1 141.6(2), N2−C1−Pd1 115.0(2).

Scheme 5. Transfer Hydrogenation of Alkynes Catalyzed by Pd(NHC)(ma) Complexes



Catalytic Transfer Hydrogenation. As a probe for the activity and selectivity of complexes **11**−**13**, transfer hydrogenation of 1-phenyl-1-propyne was performed (Scheme 5).

Table 1. Catalytic Transfer Hydrogenation of 1-Phenyl-1-propyne[a]

entry	complex	initial TOF (mol sub/mol cat/h)	selectivity *Z*/*E*/alkane (%)
1	**11a**	43.9	90/6/4
2	**11b**	29.8	95/3/2
3	**12a**	24.0	97/2/1
4	**12b**	14.4	97/2/1
5	**13a**	35.1	85/3/12
6	**13b**	18.7	90/3/7

[a] Reaction conditions: 1% Pd complex, 150 mM alkyne, 750 mM triethylammonium formate, and 150 mM *p*-xylene (internal standard) in 15 mL of refluxing acetonitrile. Selectivity measured at full conversion, or after 24 h (entries 5 and 6).

In previous research we have found that mono- and heterobidentate (NHC)palladium(0) complexes are excellent catalysts for the conversion of the alkyne to the *Z*-alkene.[8,18,19] This transformation shows a high chemo- and stereoselectivity that is unique to this type of complexes. When a secondary amine donor is tethered to the NHC, selectivities of more than 99% toward (*Z*)-1-phenyl-1-propene were observed.[6] The results of our screening with differently substituted *N*-pyrimidyl-NHC ligands are summarized in Table 1.

For the catalysts tested, introduction of methyl groups onto the pyridimyl donor leads to lower reaction rates (entries 1, 3, 5 compared to entries 2, 4, 6, respectively). At the same time, the reaction selectivity increased when moving from iPr (entries 5 and 6) to Mes (entries 1 and 2) and DiPP (entries 3 and 4). The major drawback of this ligand type in catalysis seems to be that overreduction and isomerization after full conversion take place. In contrast, we did not observe any overreduction or isomerization when a tertiary amine donor was tethered to the NHC;[6] selectivity and activity were comparable to entries 2 and 3 for this type of complex. The occurrence of side reactions in the system described here implies that the affinity of the complex for the *Z*-alkene product is high enough relative to the secondary donor and the solvent, acetonitrile, for further reaction to take place.[18] As long as any alkyne is present, this coordinates preferentially to palladium, precluding unwanted side reactions. The donor strength of the pyrimidyl N atom is not large enough to preclude this secondary reaction from occurring. For the iPr-substituted ligands (entries 5 and 6) it has to be noted that a deactivation takes place and complete conversion is not reached after 24 h, whereas the aryl-substituted ligands show full conversion within 12 hours.

Conclusions

We have synthesized electron-rich zerovalent palladium complexes containing one maleic anhydride ligand and a heteroditopic NHC-pyrimidine ligand. These spatially very open complexes were obtained in high yields and purities. Complete characterization has been performed, and a representative compound has also been characterized by X-ray crystallography, showing the very planar nature of the ligand and the coordination sphere. From the ^{1}H NMR of the palladium complexes it was concluded that the secondary donor shows hemilabile behavior at room temperature, evidenced by the broadening of the signals of the pyrimidyl hydrogens. For the methyl-substituted pyrimidine donor, this behavior was not seen at room temperature. Catalytic transfer hydrogenation of 1-phenyl-1-propyne to (*Z*)-1-phenyl-1-propene has been performed to gauge the influence of the substituents on activity and selectivity. It appeared that more bulk on either the secondary nitrogen donor or the carbene nitrogen was beneficial for selectivity, but impeded the conversion. The donor strength of the pyrimidyl functionality appeared to be not sufficient to retain high selectivity after full consumption of the starting material. The results from the catalytic experiments show that the substrate binds in the position occupied by the *N*-pyrimidyl donor, which is in line with the hemilabile behavior observed in NMR experiments. For the smaller *N*-isopropyl substituent, deactivation took place. The large influence of the *N*-pyrimidyl donor on the catalytic results supports our interest in the effect of different nitrogen donors in this type of complex on reactivity and stability.

Experimental Section

General Procedures and Instrumentation. All reactions involving transition metal complexes were performed using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled using standard procedures.[20] All chemicals were used as received, with the exception of palladium bis-*tert*-butyldiazabutadiene maleic anhydride, which was synthesized according to a literature procedure.[17] NMR measurements were performed on Varian Mercury 300 (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz), Bruker DRX 300 (^{1}H: 300.11 MHz, ^{13}C: 75.47 MHz), and Varian Inova 500 (^{1}H: 499.86 MHz, ^{13}C: 125.70 MHz) spectrometers. ^{13}C NMR spectra were measured with ^{1}H decoupling. Positive chemical shifts (δ) are denoted for high-frequency shifts relative to the external TMS reference. High-resolution mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer; mass samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. During the high-resolution FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used. Gas chromatography analyses were performed with a Carlo Erba HRGC 8000 Top instrument using a DB-5 capillary column and *p*-xylene as internal standard.

General Synthesis of *N*-Arylimidazoles. 1-(2,6-Diisopropylphenyl)imidazole **2** and 1-(2-(4,6-dimethylpyrimidyl))imidazole **4** were synthesized according to a literature procedure.[12] 1-(2,4,6-Methylphenyl)imidazole and 1-(2-pyrimidyl)imidazole were synthesized according to a modified literature procedure.[12]

1-Mesityl-1*H*-imidazole 1. The product (27.3 g, 73%) was obtained as a light beige crystalline solid after recrystallization of the crude product from tetrahydrofuran. ^{1}H NMR ($CDCl_3$): δ 7.53 (s, 1H, NCH), 7.28 (s, 1H, NCH), 6.96 (s, 2H, aryl-CH), 6.93 (s, 1H, NCHN), 2.36 (s, 3H, *p*-aryl-CH_3), 2.01 (s, 6H, *o*-aryl-CH_3).

1-(2-Pyrimidyl)imidazole 3.[21] The product (1.34 g, 99%) was obtained as a pale yellow solid from the reaction mixture without the need for column chromatography. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, ^3J(HH) = 4.8 Hz, 2H, *m*-pym-H), 8.62 (s, 1H, NCHN), 7.89 (d, ^3J(HH) = 1.2 Hz, 1H, NCH), 7.20 (t, ^3J(HH) = 4.8 Hz, 1H, *p*-pym-H), 7.17 (d, ^3J(HH) = 1.2 Hz, 1H, NCH).

General Synthesis of (1-(2-Pyrimidyl)-3-aryl)imidazolium Salts. A literature procedure[11] was modified as follows: equimolar

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amounts of *N*-aryl imidazole and the 2-chloropyrimidine were heated overnight in a sealed vessel at 120 °C. The reaction mixture was then allowed to cool to room temperature and washed with diethyl ether until the supernatant was colorless. The product was then dried *in vacuo*.

(1-(2-Pyrimidyl)-3-mesityl)imidazolium Chloride 5a.[11]. The product (2.45 g, 67%) was obtained as a beige solid. ^{1}H NMR (DMSO-d_6): δ 10.45 (s, 1H, NCHN), 9.11 (d, ^3J(HH) = 4.5 Hz, 2H, *m*-pym-H), 8.81 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 8.16 (t, ^3J(HH) = 1.8 Hz, 1H, CH), 7.79 (t, ^3J(HH) = 4.5 Hz, 1H, *p*-pym-H), 7.14 (s, 2H, aryl-H), 2.32 (s, 3H, *p*-aryl-CH$_3$), 2.08 (s, 6H, *o*-aryl-CH$_3$).

(1-(2-(4,6-Dimethylpyrimidyl))-3-mesityl)imidazolium Chloride 5b. The product (0.30 g, 68%) was obtained as a purple solid. ^{1}H NMR (DMSO-d_6): δ 10.41 (dd, ^4J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, NCHN), 8.70 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 8.15 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 7.57 (s, 1H, pym-H), 7.16 (s, 2H, aryl-H), 2.58 (s, 6H, pym-CH$_3$), 2.34 (s, 3H, *p*-aryl-CH$_3$), 2.10 (s, 6H, *o*-aryl-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 170.8 (*m*-pym-C), 151.7 (*i*-pym-C), 141.8 (*p*-aryl-C), 135.2 (*i*-aryl-C), 134.3 (NCHN), 130.8 (*o*-aryl-C), 130.2 (*m*-aryl-C), 126.9 (CH), 121.8 (*p*-pym-CH), 120.9 (CH), 24.1 (pym-CH$_3$), 21.4 (*p*-aryl-CH$_3$), 18.0 (*o*-aryl-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{18}H_{21}N_4$ [M − Cl]$^+$ 293.1766; found 293.1762.

(1-(2-Pyrimidyl)-3-(2,6-diisopropylphenyl))imidazolium Chloride 6a.[11] The product (1.87 g, 62%) was obtained as a light brown solid. ^{1}H NMR (DMSO-d_6): δ 10.60 (s, 1H, NCHN), 9.11 (d, ^3J(HH) = 4.5 Hz, 2H, *m*-pym-H), 8.82 (s, 1H, CH), 8.35 (s, 1H, CH), 7.83 (t, ^3J(HH) = 4.5 Hz, 1H, *p*-pym-H), 7.66 (t, ^3J(HH) = 7.8 Hz, 1H, *p*-aryl-H), 7.49 (d, ^3J(HH) = 7.8 Hz, 2H, *m*-aryl-H), 2.49 (m, 2H, ^{i}Pr-CH), 1.17 (d, ^3J(HH) = 6.9 Hz, 12H, ^{i}Pr-CH$_3$).

(1-(2-(4,6-Dimethylpyrimidyl))-3-(2,6-diisopropylphenyl))imidazolium Chloride 6b. The product (0.26 g, 69%) was obtained as a dark brown solid. ^{1}H NMR (DMSO-d_6): δ 10.55 (s, 1H, NCHN), 8.73 (s, 1H, CH), 8.30 (s, 1H, CH), 7.64 (t, ^3J(HH) = 7.6 Hz, 1H, *p*-aryl-H), 7.57 (s, 1H, pym-H), 7.46 (d, ^3J(HH) = 7.6 Hz, 2H, *m*-aryl-H), 2.59 (s, 6H, pym-CH$_3$), 2.44 (m, 2H, ^{i}Pr-CH), 1.18 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH$_3$), 1.14 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 171.0 (*m*-pym-C), 151.6 (*i*-pym-C), 145.3 (*o*-aryl-CH), 134.7 (*i*-aryl-C), 132.5 (NCHN), 130.3 (*p*-aryl-C), 127.9 (CH), 125.0 (*m*-aryl-CH), 122.1 (CH), 121.4 (*p*-pym-CH), 29.0 (^{i}Pr-CH), 24.6 (^{i}Pr-CH$_3$), 24.5 (^{i}Pr-CH$_3$), 24.1 (pym-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{21}H_{27}N_4$ [M − Cl]$^+$ 335.2236; found 335.2231.

General Synthesis of 1-(2-Pyrimidyl)-3-isopropyl)imidazolium Salts. The *N*-(2-pyrimidyl)imidazole was dissolved in 10 equiv of 2-iodopropane and heated to reflux for 16 h. After the reaction mixture was allowed to cool, all volatiles were removed under reduced pressure. The resulting solid was washed with diethyl ether until the supernatant was colorless. The product was then dried *in vacuo*.

(1-(2-Pyrimidyl)-3-isopropyl)imidazolium Iodide 7a. The product (0.43 g, 93%) was obtained as an ochre solid. ^{1}H NMR ($CDCl_3$): δ 10.49 (dd, ^4J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, NCHN), 8.88 (d, ^3J(HH) = 4.8 Hz, 2H, *m*-pym-H), 8.26 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 7.85 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 7.55 (t, ^3J(HH) = 4.8 Hz, 1H, *p*-pym-H), 5.51 (septet, ^3J(HH) = 6.6 Hz, 1H, ^{i}Pr), 1.72 (d, ^3J(HH) = 6.6 Hz, 6H, ^{i}Pr). ^{13}C NMR ($CDCl_3$): δ 160.0 (*m*-pym-CH), 152.2 (*i*-pym-C), 134.0 (NCHN), 122.8 (CH), 122.5 (CH), 119.5 (*p*-pym-CH), 54.8 (^{i}Pr-CH), 23.2 (^{i}Pr-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{10}H_{13}N_4$ [M − I]$^+$ 189.1140; found 189.1144.

(1-(2-(4,6-Dimethylpyrimidyl)-3-isopropyl)imidazolium Iodide 7b. The product (0.19 g, 87%) was obtained as a gray solid. ^{1}H NMR ($CDCl_3$): δ 10.37 (dd, ^4J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, NCHN), 8.24 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 7.89 (dd, ^3J(HH) = 1.6 Hz, ^4J(HH) = 1.6 Hz, 1H, CH), 7.17 (s, 1H, pym-H), 5.47 (septet, ^3J(HH) = 6.6 Hz, 1H, ^{i}Pr), 2.60 (s, 6H, pym-CH$_3$), 1.72 (d, ^3J(HH) = 6.6 Hz, 6H, ^{i}Pr). ^{13}C NMR ($CDCl_3$): δ 170.6 (*m*-pym-C), 151.7 (*i*-pym-C), 133.8 (NCHN), 122.3 (CH), 122.4 (CH), 119.4 (*p*-pym-C), 54.7 (^{i}Pr-CH), 24.2 (pym-CH3), 23.3 (^{i}Pr-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{12}H_{17}N_4$ [M − I]$^+$ 217.1453; found 217.1456.

General Synthesis of (NHC)Silver(I) Complexes. A literature procedure[11] was modified as follows: imidazolium salt and silver(I) oxide (0.55 equiv) were suspended in dichloromethane to 0.1 M. After stirring overnight at room temperature, the reaction mixture was filtered through Celite. The products were obtained by concentrating the resulting solution *in vacuo*. Yields are calculated on the basis of the imidazolium salt.

Bis[(1-(2-pyrimidyl)-3-mesityl)imidazol-2-ylidene]silver(I) Dichloroargentate(I) 8a.[11] The product (0.12 g, 89%) was obtained as a pale yellow solid. ^{1}H NMR (CD_2Cl_2): δ 8.84 (d, ^3J(HH) = 4.8 Hz, 2H, *m*-pym-H), 8.35 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 7.46 (t, ^3J(HH) = 4.8 Hz, 1H, *p*-pym-H), 7.15 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 7.07 (s, 2H, aryl-H), 2.39 (s, 3H, *p*-aryl-CH$_3$), 2.07 (s, 6H, *o*-aryl-CH$_3$).

Bis[(1-(2-(4,6-dimethylpyrimidyl))-3-mesityl)imidazol-2-ylidene]-silver(I) Dichloroargentate(I) 8b. The product (0.12 g, 95%) was obtained as an orange solid. ^{1}H NMR (CD_2Cl_2): δ 8.29 (d, ^3J(HH) = 1.5 Hz, 1H, CH), 7.07 (s, 1H, pym-H), 7.02 (d, ^3J(HH) = 1.5 Hz, 1H, CH), 6.95 (s, 2H, aryl-H), 2.59 (s, 6H, pym-CH$_3$), 2.33 (s, 3H, *p*-aryl-CH$_3$), 2.01 (s, 6H, o-aryl-CH$_3$). ^{13}C NMR (CD_2Cl_2): δ = 183.4 (NCN), 169.4 (*m*-pym-C), 154.7 (*i*-pym-C), 139.6 (*p*-aryl-C), 136.1 (*i*-aryl-C), 134.8 (*o*-aryl-C), 129.2 (*m*-aryl-CH), 123.0 (CH), 119.6 (CH), 119.0 (*p*-pym-CH), 23.3 (pym-CH$_3$), 21.0 (*p*-aryl-CH$_3$), 17.6 (*o*-aryl-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{36}H_{40}N_8Ag$ [M − $AgCl_2$]$^+$ 693.2423; found 693.2432.

Bis[(1-(2-pyrimidyl)-3-(2,6-diisopropylphenyl))imidazol-2-ylidene]-silver(I) Dichloroargentate(I) 9a.[11] The product (0.17 g, 88%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2): δ 8.84 (d, ^3J(HH) = 4.8 Hz, 2H, *m*-pym-H), 8.33 (s, 1H, CH), 7.50−7.38 (m, 2H, *p*-aryl-H, *p*-pym-H), 7.26 (d, ^3J(HH) = 8.0 Hz, 2H, *m*-aryl-H), 7.10 (s, 1H, CH), 2.48 (septet, ^3J(HH) = 6.8 Hz, 1H, ^{i}Pr-CH), 2.38 (septet, ^3J(HH) = 6.8 Hz, 1H, ^{i}Pr-CH), 1.24 (d, ^3J(HH) = 6.8 Hz, 6H, ^{i}Pr-CH$_3$), 1.11 (d, ^3J(HH) = 6.8 Hz, 6H, ^{i}Pr-CH$_3$).

Bis[(1-(2-(4,6-dimethylpyrimidyl))-3-(2,6-diisopropylphenyl))-imidazol-2-ylidene] Dichloroargentate(I) 9b. The product (0.24 g, 94%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2): δ 8.32 (s, 1H, CH), 7.45 (d, ^3J(HH) = 5.7 Hz, 1H, *p*-aryl-H), 7.25 (t, ^3J(HH) = 5.7 Hz, 2H, *m*-aryl-H), 7.08 (s, 1H, pym-H), 7.06 (s, 1H, CH), 2.63 (s, 6H, pym-CH$_3$), 2.49 (septet, ^3J(HH) = 5.1 Hz, 2H, ^{i}Pr-CH), 1.23 (d, ^3J(HH) = 5.1 Hz, 2H, ^{i}Pr-CH$_3$), 1.12 (d, ^3J(HH) = 5.1 Hz, 2H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2): δ 184.3 (NCN), 169.7 (*m*-pym-C), 155.1 (*i*-pym-C), 145.8 (*o*-aryl-CH), 135.8 (*i*-aryl-C), 130.6 (*p*-aryl-C), 124.8 (CH), 124.4 (*m*-aryl-CH), 119.9 (CH), 119.0 (*p*-pym-CH), 28.5 (^{i}Pr-CH$_3$), 24.4 (pym-CH$_3$), 24.1 (^{i}Pr-CH$_3$), 23.8 (^{i}Pr-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{42}H_{52}N_8Ag$ [M − $AgCl_2$]$^+$ 777.3362; found 777.3380.

Bis[(1-(2-pyrimidyl)-3-isopropyl)imidazol-2-ylidene]silver(I) Diiodoargentate(I) 10a. The product (90%, 0.16 g) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2): δ 8.77 (d, ^3J(HH) = 4.8 Hz, 2H, *m*-pym-H), 8.16 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.41 (t, ^3J(HH) = 4.8 Hz, 1H, *p*-pym-H), 7.23 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 4.88 (septet, ^3J(HH) = 6.9 Hz, 1H, ^{i}Pr), 1.57 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr). ^{13}C NMR (CD_2Cl_2): δ 183.8 (NCN), 159.1 (*m*-pym-CH), 155.9 (*i*-pym-C), 121.0 (CH), 119.6 (CH), 118.9 (*p*-pym-CH), 55.7 (^{i}Pr-CH), 23.6 (^{i}Pr-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{20}H_{24}N_8Ag$ [M − AgI_2]$^+$ 483.1175; found 483.1180.

Bis[(1-(2-(4,6-dimethylpyrimidyl))-3-isopropyl)imidazol-2-ylidene]-silver(I) Diiodoargentate(I) 10b. The product (93%, 32 mg) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 8.15 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 7.19 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 7.08 (s, 1H, pym-H), 4.86 (septet, ^3J(HH) = 6.6 Hz, 1H, ^{i}Pr), 2.57 (s, 6H, pym-CH$_3$), 1.55 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr). ^{13}C NMR (CD_2Cl_2): δ 183.9 (NCN), 169.5 (*m*-pym-C), 155.1 (*i*-pym-C), 119.5 (CH), 119.4 (CH), 118.3 (*p*-pym-CH), 55.5 (^{i}Pr-CH), 23.9 (pym-CH$_3$), 23.5 (^{i}Pr-CH$_3$). MS(FAB+, *m*/*z*): calcd for $C_{24}H_{32}N_8Ag$ [M − AgI_2]$^+$ 539.1801; found 539.1809.

General Procedure for the Synthesis of [NHC-pyrimidyl]-palladium(0) Maleic Anhydride Complexes. Palladium (bis-*tert*-butyldiazabutadiene)(maleic anhydride) and bis[NHC-pyrimidyl]-silver(I) complex (0.55 equiv) were dissolved in dichloromethane to 0.1 M. Immediate precipitation of silver(I) halide was observed.

After 1 h, the reaction mixture was filtered through Celite and concentrated to a small volume at reduced pressure. The solution was then layered with pentane to precipitate the product. After decanting the supernatant, the product was washed with a small volume of pentane and dried *in vacuo*. Alternatively, the reaction mixture can be fully concentrated and only then washed with pentane. This procedure is preferable if the product is less stable in solution. Yields are calculated on the basis of palladium.

[(1-(2-Pyrimidyl)-3-mesityl)imidazol-2-ylidene]palladium(0) Maleic Anhydride 11a. The product (0.11 g, 91%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 8.93 (bd, ^3J(HH) = 5.1 Hz, 2H, *m*-pym-H), 8.01 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 7.45 (t, ^3J(HH) = 5.1 Hz, 1H, *p*-pym-H), 7.16−7.02 (2 br s, 2H, aryl-H), 7.07 (d, ^3J(HH) = 2.1 Hz, 2H, CH), 3.65−3.50 (2 br s, 2H, ma), 2.42 (s, 3H, *p*-aryl-CH_3), 2.07 (br s, 6H, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ 193.4 (NCN), 173.4, 172.4 (2 CO), 160.8, 160.7 (2 *m*-pym-C), 158.0 (*i*-pym-C), 139.6 (*p*-aryl-C), 135.8 (*i*-aryl-C), 134.5, 134.4 (2 *o*-aryl-C), 129.9, 129.1 (2 *m*-aryl-C), 124.8 (CH), 120.8 (CH), 117.2 (*p*-pym-C), 43.2, 40.7 (2 alkene-CH), 21.3 (*p*-aryl-CH_3), 17.9 (br, *o*-aryl-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{20}H_{19}N_4O_3Pd$ $[M + H]^+$ 469.0492; found 469.0493. Anal. Calcd for $C_{20}H_{18}N_4O_3Pd$ C, 51.24; H, 3.87; N, 11.95. Found: C, 51.30; H, 4.01; N, 11.76.

[(1-(2-(4,6-Dimethylpyrimidyl))-3-mesityl)imidazol-2-ylidene]-palladium(0) Maleic Anhydride 11b. The product (0.12 g, 99%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.95 (d, ^3J(HH) = 1.6 Hz, 1H, CH), 7.17 (s, 1H, pym-H), 7.12 (s, 1H, aryl-H), 6.98 (s, 1H, aryl-H), 6.96 (d, ^3J(HH) = 1.6 Hz, 1H, CH), 3.53 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 3.49 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 2.80 (s, 3H, pym-CH_3), 2.59 (s, 3H, pym-CH_3), 2.40 (s, 3H, *p*-aryl-CH_3), 2.06 (s, 3H, *o*-aryl-CH_3), 2.04 (s, 3H, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ 191.8 (NCN), 173.1 (CO), 171.9 (CO), 170.2 (*m*-pym-C), 170.0 (*m*-pym-C), 157.8 (*i*-pym-C), 139.0 (*p*-aryl-C), 135.3 (*i*-aryl-C), 133.9 (*o*-aryl-C), 129.5 (*m*-aryl-C), 128.5 (*m*-aryl-C), 123.8 (CH), 118.8 (CH), 117.0 (*p*-pym-C), 41.4 (alkene-CH), 39.6 (alkene-CH), 27.0 (pym-CH_3), 23.9 (pym-CH_3), 20.9 (*p*-aryl-CH_3), 17.6 (*o*-aryl-CH_3), 17.3 (*o*-aryl-CH_3). MS-(FAB+, *m*/*z*): calcd for $C_{18}H_{20}N_4Pd$ $[M - ma]^+$ 398.0723; found 398.0730. Anal. Calcd for $C_{22}H_{22}N_4O_3Pd$: C, 53.18; H, 4.46; N, 11.28. Found: C, 53.30; H, 4.61; N, 11.06.

[(1-(2-Pyrimidyl)-3-(2,6-diisopropylphenyl))imidazol-2-ylidene]-palladium(0) Maleic Anhydride 12a. The product (80 mg, 93%) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2): δ 8.95 (bd, ^3J(HH) = 8.0 Hz, 2H, *m*-pym-H), 8.04 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 7.58 (t, ^3J(HH) = 8.0 Hz, 1H, *p*-aryl-H), 7.48 (t, ^3J(HH) = 5.0 Hz, 1H, *p*-pym-H), 7.38 (d, ^3J(HH) = 8.0 Hz, 1H, *m*-aryl-H), 7.16 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 3.58 (br s, 2H, ma), 2.68 (br s, 1H, ^{i}Pr-CH), 2.57 (br s, 1H, ^{i}Pr-CH), 1.29 (br s, 3H, ^{i}Pr-CH_3), 1.20 (br s, 3H, ^{i}Pr-CH_3), 1.16 (d, ^3J(HH) = 7.0 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 193.9 (NCN), 173.2 (CO), 172.0 (CO), 161.1 (*m*-pym-CH), 160.0 (*m*-pym-CH), 157.8 (*i*-pym-C), 145.8 (*o*-aryl-C), 145.1 (*o*-aryl-C), 135.4 (*i*-aryl-C), 130.3 (*p*-aryl-CH), 125.7 (CH), 124.4 (*m*-aryl-CH), 123.9 (*m*-aryl-CH), 120.7 (*p*-pym-CH), 116.7 (CH), 43.6 (alkene), 40.8 (alkene), 28.8 (br, ^{i}Pr-CH), 24.3 (^{i}Pr-CH_3), 23.9 (^{i}Pr-CH_3), 23.3 (^{i}Pr-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{19}H_{22}N_4Pd$ $[M - ma]^+$ 412.0879; found 412.0889. Anal. Calcd for $C_{23}H_{24}N_4O_3Pd$ C, 54.07; H, 4.74; N, 10.97. Found: C, 53.81; H, 4.62; N, 11.13.

[(1-(2-(4,6-Dimethylpyrimidyl))-3-(2,6-diisopropylphenyl))-imidazol-2-ylidene]palladium(0) Maleic Anhydride 12b. The product (0.19 g, 87%) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2): δ 7.97 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 7.54 (dd, ^3J(HH) = 7.6 Hz, 1H, *p*-aryl-H), 7.36 (dd, ^3J(HH) = 7.6 Hz, 1H, *m*-aryl-H), 7.31 (dd, ^3J(HH) = 7.6 Hz, 1H, *m*-aryl-H), 7.18 (s, 1H, pym-H), 7.04 (d, ^3J(HH) = 2.0 Hz, 1H, CH), 3.59 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 3.50 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 2.80 (s, 3H, pym-CH_3), 2.70 (dq, ^3J(HH) = 6.8 Hz, ^3J(HH) = 6.8 Hz, 1H, ^{i}Pr-CH), 2.59 (s, 3H, pym-CH_3), 2.47 (dq, ^3J(HH) = 6.8 Hz, ^3J(HH) = 6.8 Hz, 1H, ^{i}Pr-CH), 1.27 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH_3), 1.20 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH_3), 1.14 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH_3), 1.10 (d, ^3J(HH) = 6.8 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 192.7 (NCN), 173.3 (CO), 172.0 (CO), 170.6 (*m*-pym-C), 157.5 (*i*-pym-C), 145.8 (*o*-aryl-C), 145.0 (*o*-aryl-C), 135.5 (*i*-aryl-C), 130.1 (*p*-aryl-CH), 125.3 (CH), 124.5 (*m*-aryl-CH), 123.7 (*m*-aryl-CH), 119.1 (*p*-pym-CH), 116.9 (CH), 42.2 (alkene), 40.2 (alkene), 29.3 (pym-CH_3), 28.8 (^{i}Pr-CH), 28.6 (^{i}Pr-CH), 27.2 (pym-CH_3), 24.5 (^{i}Pr-CH_3), 24.1 (^{i}Pr-CH_3), 23.6 (^{i}Pr-CH_3), 23.1 (^{i}Pr-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{21}H_{26}N_4Pd$ $[M - ma]^+$ 440.1192; found 440.1196. Anal. Calcd for $C_{25}H_{28}N_4O_3Pd$ C, 55.71; H, 5.24; N, 10.40. Found: C, 56.06; H, 4.85; N, 10.82.

[(1-(2-Pyrimidyl)-3-isopropyl)imidazol-2-ylidene]palladium(0) Maleic Anhydride 13a. The product (40 mg, 93%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 8.89 (bd, ^3J(HH) = 5.0 Hz, 2H, *m*-pym-H), 7.84 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.40 (t, ^3J(HH) = 5.0 Hz, 1H, *p*-pym-H), 7.16 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 4.86 (septet, ^3J(HH) = 7.0 Hz, 1H, ^{i}Pr-H), 4.00 (br s, 2H, ma), 1.56 (d, ^3J(HH) = 7.0 Hz, 6H, ^{i}Pr-CH_3), 1.43 (s, 6H, pym-CH_3). ^{13}C NMR (CD_2Cl_2): δ 189.4 (NCN), 173.1 (CO), 160.6 (*m*-pym-CH), 157.7 (*i*-pym-C), 120.2 (CH), 119.1 (*p*-pym-CH), 117.2 (CH), 54.8 (^{i}Pr-CH), 41.1 (alkene-CH), 23.2 (^{i}Pr-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{14}H_{15}N_4O_3Pd$ $[M + H]^+$ 393.0179; found 393.0186. Anal. Calcd for $C_{14}H_{14}N_4O_3Pd$ C, 42.82; H, 3.59; N, 14.27. Found: C, 43.29; H, 4.01; N, 14.11.

[(1-(2-(4,6-Dimethylpyrimidyl))-3-isopropyl)imidazol-2-ylidene]-palladium(0) Maleic Anhydride 13b. The product (30 mg, 91%) was obtained as pale yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 7.82 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 7.18 (s, 1H, pym-H), 7.12 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 4.91 (septet, ^3J(HH) = 6.6 Hz, 1H, ^{i}Pr-H), 4.21 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 3.67 (d, ^3J(HH) = 3.6 Hz, 1H, ma), 2.79 (s, 3H, pym-CH_3), 2.56 (s, 3H, pym-CH_3), 1.54 (d, ^3J(HH) = 6.6 Hz, 3H, ^{i}Pr-CH_3), 1.52 (d, ^3J(HH) = 6.6 Hz, 3H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 188.4 (NCN), 173.5 (br, CO), 170.4 (br, *m*-pym-C), 157.4 (*i*-pym-C), 119.0 (CH), 118.4 (*p*-pym-C), 117.2 (CH), 55.1 (^{i}Pr-CH), 42.1 (alkene), 39.7 (alkene), 27.4 (pym-CH_3), 24.1 (pym-CH_3), 23.2 (^{i}Pr-CH). MS(FAB+, *m*/*z*): calcd for $C_{16}H_{19}N_4O_3Pd$ $[M + H]^+$ 421.0492; found 421.0492. Anal. Calcd for $C_{16}H_{18}N_4O_3Pd$ C, 45.67; H, 4.31; N, 13.32. Found: C, 45.30; H, 4.21; N, 13.21.

X-ray Data Collection, Reduction, and Refinement. A suitable single crystal of **11a** was coated with Paratone-N oil, mounted using a glass fiber pin, and frozen in the cold nitrogen stream of the goniometer. X-ray diffraction data was collected on a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with a scan width of 0.3° and exposure time of 1 s. The generator setting was 50 kV and 180 mA. Diffraction data were collected over the full sphere, and the frames were integrated using the Bruker SMART[22] software package using the narrow frame algorithm. Data were corrected for absorption effects using the SADABS routine (empirical multiscan method). Atomic scattering factors for non-hydrogen elements were taken from the literature tabulations.[23] The structure solution was found by using direct methods as implemented in the SHELXS-97 package and was refined with SHELXL-97[24] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. C−H atom positions were calculated and allowed to ride on the carbon atom to which they are bonded, assuming C−H bond length of 0.95 Å for aromatic protons and 0.98 Å for methyl groups. H atom temperature factors were fixed at 1.20 (arom-H) or 1.50 (CH_3) times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated but not refined. In the case of the protons of the maleic anhydride moiety the protons (H18, H19) were refined isotropically. The locations of the largest peaks in the final difference Fourier map calculated as well as the magnitude of the residual electron densities in each case were of no chemical

(22) *SMART*; Bruker AXS: Madison, WI, 2000.
(23) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.
(24) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.

significance. **11a** ($C_{20}H_{18}N_4O_3Pd$): fw = 468.78, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.271(1)$ Å, $b = 10.2858(8)$ Å, $c = 14.300(1)$ Å, $\beta = 105.392(1)°$, $V = 1882.1(3)$ Å^3, $F000 = 944$, $T = 153(2)$ °C, $\mu = 1.015$, 19 366 reflections collected, 4687 reflections unique ($R_{int} = 0.0403$), 3871 reflections observed ($F > 2\sigma(F)$). The final was $R_1 = 0.0287$ and $wR_2 = 0.0694$ (all data).

General Experimental Procedure for Catalytic Transfer Semihydrogenation of Phenyl Propyne Using Formic Acid As Hydrogen Donor. A solution of 150 mM 1-phenyl-1-propyne, 750 mM triethylammonium formiate, and 150 mM *p*-xylene in 12 mL of acetonitrile was heated to reflux. A solution of 1 mol % of catalyst (Table 1) in 2 mL of acetonitrile was added to the reaction mixture. Periodically, samples were taken over a period of 24 h. Aliquots from the reaction mixtures were quenched by dilution with EtOH and were analyzed by GC to determine conversions and composition.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.