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Bulky Picolyl Substituted NHC Ligands and Their Pd^0 Complexes

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Heterobidentate N-heterocyclic carbene-picolyl ligands with various substitution patterns and their palladium(0) complexes have been synthesized in excellent yields via their corresponding silver(I) complexes. These complexes are among the first examples where substitution next to the coordinating nitrogen is evaluated systematically. The complexes have been studied by NMR and X-ray diffraction, confirming their bidentate nature. The complexes are active precatalysts in the transfer semihydrogenation of alkynes to *Z*-alkenes, with activity and selectivity depending on the picolyl substituent to a high degree. Selectivities as high as 92% were observed.

Introduction

The use of *N*-heterocyclic carbenes (NHCs) in coordination chemistry and catalysis has grown tremendously in the past decade. Their strong donating powers combined with their ability to accept electron density as well makes this class of compounds excellent ligands for a range of transition metals (TMs) in various oxidation states.[1] It is well known that the introduction of multiple donors in a ligand improves the stability of a complex by the chelate effect. This approach has been successfully applied to NHCs as well, giving rise to homopolydentate carbene ligands,[2] but also to heteropolydentate scaffolds.[3] When a weaker secondary donor is introduced, the ligand can exhibit hemilabile behaviour, where the weaker donor can reversibly de- and recoordinate. This generates a free coordination site at the metal where for example a substrate can enter. After reaction and dissociation of the product the secondary donor can recoordinate to stabilize the catalyst.[4] With the appropriate choice of the secondary donor, one may tune the stability and catalytic activity of the complex. In previous publications, we have shown the effect of various nitrogen donors on the coordinative properties of the ligands and the catalytic activity and selectivity of their zero- and divalent palladium complexes.[5–7,26] The use of picoline as donor in combination with NHC ligands is also known, and the coordination chemistry of these flexible aromatic nitrogen donors is well established for various TMs.[8–11] However, relatively few reports have been published concerning the substitution pattern of the picoline ring, especially on the position directly adjacent to the nitrogen.[12–14] As this position has the largest steric influence on the coordination properties of the secondary donor, we were interested to see the effects of introducing different groups. Here we present the synthesis and structural characterization of several *N*-picolyl-NHC ligands, as well as the synthesis of their silver(I) and palladium(0) complexes. A screening of the electron-rich palladium complexes as catalysts for the transfer semi-hydrogenation of alkynes is also described.

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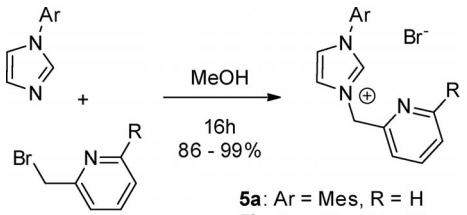
Results and Discussion

Imidazolium Bromides. After synthesis of the *N*-arylimidazoles **1**–**4**,[15,16] quaternization with 2-(bromomethyl)pyridines was performed to obtain the imidazolium salts **5**–**8** in yields between 86% and 99% (Scheme 1).[10,12,13]



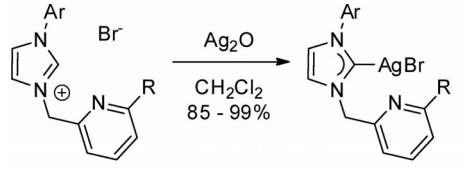
1: Ar = Mes, 73%
2: Ar = DiPP, 45%
3: Ar = 4-OMePh, 48%
4: Ar = 4-CF_3Ph, 97%

5a: Ar = Mes, R = H
5b: Ar = Mes, R = Me
5c: Ar = Mes, R = Ph
5d: Ar = Mes, R = Mes
6a: Ar = DiPP, R = H
6b: Ar = DiPP, R = Me
7: Ar = 4-OMePh, R = H
8: Ar = 4-CF_3Ph, R = H

Scheme 1. Synthesis of imidazolium bromides.

For compounds **5** and **6** the characteristic signal for the imidazolium proton was observed at a chemical shift between 10.0 and 10.4 ppm in the ^{1}H NMR spectroscopy. For **7** and **8** this signal was observed at a significantly lower field at δ = 11.0 and 11.5 ppm, respectively. For **8** this is intuitively correct, but for **7** it needs to be kept in mind that the methoxy substituent only has an inductive influence on the imidazolium core, while a mesomeric influence is prohibited. This then accounts for the deshielding of the imidazolium core, which is visible as a high-frequency shift. Yields are consistently high and appear to be independent of the substitution pattern.

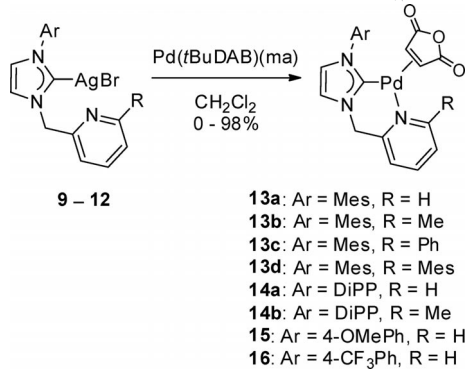
(NHC)silver(I) Complexes. Subsequently, the carbenes are generated from the imidazolium bromides by reaction with silver(I) oxide.[5,6] This reliable protocol is routinely applied and the method of choice to stabilize reactive NHCs, while simultaneously giving access to a variety of TM complexes by transmetallation.[17,18] Additionally, the silver complexes are able to transfer the NHC to another transition metal, which obviates the need for generation of the free carbene. This has the advantage that rigorously air- and moisture free reaction conditions are not necessary because the (NHC)silver(I) complexes can often be handled in air. Our results are depicted in Scheme 2.



Scheme 2. Synthesis of silver(I) NHC complexes.

The silver(I) complexes **9**–**12** were reproducibly obtained in high yields and purities. Besides the disappearance of the imidazolium signal in the proton NMR, the position of the carbene carbon in the ^{13}C NMR is indicative of carbene generation. For these silver(I) complexes a signal between 181 and 184 ppm is observed, which compares well to reported literature data.[18] The chemical change in the imidazolyl core also has an effect on the chemical shift of the methylene linker. In the imidazolium salts **5**–**8** the ^{1}H NMR signal for these benzylic protons is observed between 5.94 and 6.25 ppm, whereas in the silver(I) complexes **9**–**12** they show an upfield shift to a value between 5.40 and 5.56 ppm.

(NHC)palladium(0) Complexes. The silver(I) NHC complexes **9**–**12** were employed for subsequent transmetallation to an often employed precursor for zerovalent palladium compounds.[19] Similar to our earlier report for a different type of ligand,[5] excellent results were obtained in this instances as well (Scheme 3).



Scheme 3. Transmetallation to obtain Pd^0 NHC complexes.

It appears that substituents on the *ortho* positions of the NHC aryl group are crucial for the stability of the product. Complexes **15** and **16** were formed in solution and could be observed by ^{1}H NMR, but rapid decomposition did not allow full characterization of these complexes. In stark contrast, the complexes **13**–**14** were isolated in yields over 95% and were obtained pure by precipitation with pentane. Principal proof for coordination of the secondary picolyl donor is the splitting of the methylene signal to an AB system in the ^{1}H NMR spectroscopy. However, due to ring inversion of the chelating ligand, these signals are broadened at room temperature. The carbene carbons of **13**–**14** are observed at a chemical shift between 188.7 and 191.5 ppm in the ^{13}C NMR spectroscopy. This is significantly higher than the values reported for divalent palladium complexes bearing analogous ligands,[9,11,14] reflecting the higher electron density on palladium.

X-ray Crystallography. To establish the molecular structure of our complexes, we attempted to grow X-ray quality crystals. However, it appeared that the complexes lacking a substituent on the picolyl donor were not stable enough to yield crystals. In contrast, when pentane was allowed to diffuse into a concentrated solution of **13b** in dichloromethane, suitable crystals were obtained (Figure 1).

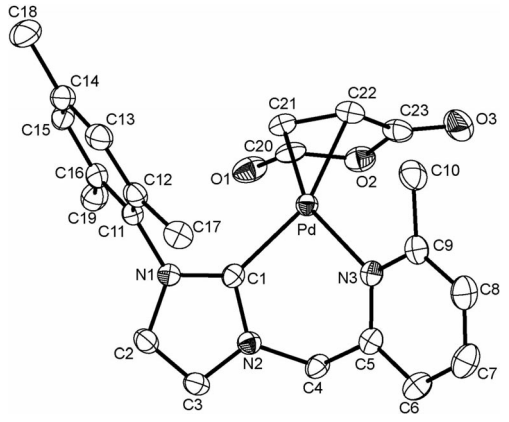
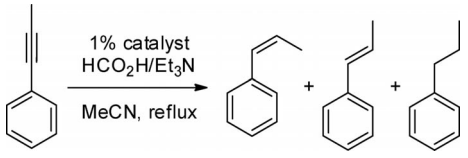


Figure 1. Displacement ellipsoid plot (50% probability level) of **13b**. H-atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Pd–C1 2.030(2), Pd–C21 2.049(2), Pd–C22 2.129(2), Pd–N3 2.183(2); C1–Pd1–N3 84.75(6).

The coordination geometry around palladium is virtually planar, with the angles totalling 360°. The Pd–C1 bond has a length of 2.030(2) Å, which is a length commonly reported for zerovalent palladium NHC complexes,[5] but longer than for neutral Pd^{II} complexes bearing NHC-picolyl ligands.[9] The length of the bond between the palladium and the nitrogen donor is 2.183(2) Å, which is shorter than that in related zerovalent complexes [2.2019(12) Å and 2.197(2) Å],[5] but comparable to divalent analogues that have been reported.[9,11,14] The complex is Y-shaped, with a bite angle of 84.75(7)° for the bidentate NHC-picolyl ligand. This is smaller than the bite angle for a similar ligand where a value of 92.06(5)° was reported.[5] Apparently, the ligand is not so flexible as to allow for the predicted coordination angle of 90°, an effect which has been noted before.[9,11,14] These *N*-picolyl-NHC ligands seem to be of intermediate rigidity. There is a significant difference between the bond lengths of Pd–C21 and Pd–C22 [2.049(2) and 2.128(2) Å, respectively], showing the difference in *trans* influence of the carbene and the nitrogen donor, with the former being the stronger donor.

Catalytic Transfer Hydrogenation. As a probe for the activity and selectivity of the complexes **13**–**14**, transfer hydrogenation of 1-phenyl-1-propyne was performed (Scheme 4).



Scheme 4. Transfer hydrogenation of 1-phenyl-1-propyne with NHC-picolyl palladium complexes.

In previously reported research we have found that mono- and heterobidentate (NHC)palladium(0) complexes are excellent catalysts for the conversion of alkynes to the corresponding *Z*-alkene.[20] This transformation shows a high chemo- and stereoselectivity which is unique to this type of complexes. With a secondary amine donor, selectivities of more than 99% towards (*Z*)-1-phenyl-1-propene were observed.[5] A significant influence of the nitrogen donor on the activity and selectivity were found.[7] The results of our screening with differently substituted NHC-picolyl ligands are summarized in Table 1.

The catalysts show a good to very good selectivity towards the *Z*-alkene product, with the corresponding *E*-alkene and alkane being the only byproducts. The substitution on the secondary picolyl donor clearly has a large impact on the activity of the catalyst, and to a lesser extent on the selectivity for (*Z*)-1-phenyl-1-propene. The unsubstituted complexes (entries 1 and 5) show a lower activity than the methyl-substituted analogues (entries 2 and 6). However, when the substituent is larger (entries 3 and 4), a dramatic decrease of activity was observed; the conversion after 24 h did not exceed 80%. Further research has to show whether this is due to the steric bulk imparted by the ligand,

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	**13a**	26.1	71:10:19
2	**13b**	46.6	91:3:6
3	**13c**	15.5	88:7:5
4	**13d**	12.9	92:2:6
5	**14a**	23.1	82:10:8
6	**14b**	46.4	86:6:8

[a] Reaction conditions: 1 mol-% Pd complex, 150 mM alkyne, 750 mM triethylammonium formate and 150 mM *p*-xylene (internal standard) in 14 mL refluxing acetonitrile. Selectivity measured at full conversion, or after 24 h (entries 3 and 4).

or that it is caused by an electronic effect of the aryl substituent. The structure of a related complex has been determined by X-ray diffraction.[14] It can be seen that the π-system of the aryl substituent is oriented towards the metal, possibly influencing the catalytic behaviour. The reaction times for the fastest catalysts **13b** and **14b** are around 3 h, but it was observed that significant amounts of the undesired *E*-alkene and alkane were formed after full consumption of the substrate (entries 2 and 5), which means that close monitoring of the reaction progress is required. With the unsubstituted analogues **13a** and **14a** full conversion was reached after roughly 10 h, but side reactions occurred to a lesser degree.

Conclusions

We have successfully synthesized picolyl-substituted NHC ligands with varying bulk and electronic properties. Thus far, a limited number of examples had been reported where substituents are present on the secondary picolyl donor. We have also synthesized their zerovalent palladium complexes in high yields and purities via the corresponding silver(I) complexes. We found that *ortho* substituents on the NHC aryl group are a necessity for isolation of the stable electron-rich complexes; for ligands without the required substitution the products were only observed in solution. All stable compounds were fully characterized and a representative palladium complex has also been characterized by X-ray crystallography, showing the bidentate nature of the ligand and the difference in *trans* influence imparted by its two distinct donors. The denticity was also inferred from the ^{1}H NMR, where splitting of the methylene signal into two doublets was observed. As a probe for the catalytic behaviour of the complexes, transfer hydrogenation of 1-phenyl-1-propyne was performed. It appeared that the substitution on the picolyl donor has a larger influence on the results than the NHC substituent. For the unsubstituted picolyl donor, full conversion of the alkyne was generally observed after 10 h, with selectivities as high as 82% for the *Z*-alkene product. The use of methyl-substituted ligands resulted in faster and more selective catalysts; however, the selectivity dropped after full consumption of the substrate, making monitoring mandatory. When aryl substituents were present on the picolyl donor, similar selectivities were

observed, but the rate of reaction was diminished dramatically. We have shown that the substitution pattern of the secondary donor has a profound effect on catalytic behaviour and we will continue to study this subject, as well as the use of different donor moieties.

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.[21] All chemicals were used as received, except for the bis(*tert*-butyldiazabutadiene maleic anhydride)–palladium complex, which was synthesized according to a literature procedure.[19] 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 1–4: 1-(2,6-Diisopropylphenyl)imidazole (**2**), 1-(4-methoxyphenyl)imidazole (**3**)[15] and 1-(4-trifluoromethylphenyl)imidazole (**4**)[16] were synthesized according to literature procedures. 1-(2,4,6-Methylphenyl)imidazole (**1**) was synthesized according to a modified literature procedure.[15]

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, 1 H, NCH), 7.28 (s, 1 H, NCH), 6.96 (s, 2 H, aryl-CH), 6.93 (s, 1 H, NCHN), 2.36 (s, 3 H, *p*-aryl-CH_3), 2.01 (s, 6 H, *o*-aryl-CH_3) ppm.

General Synthesis of Imidazolium Bromides 5–8: Compounds **1**–**4** were synthesized according to literature procedures.[10,12]

[1-(2-Pyridyl)methylene-3-mesityl]imidazolium Bromide (5a): The product (1.11 g, 86%) was obtained as a dark pink solid.[10] ^{1}H NMR ($CDCl_3$): δ = 10.34 [dd, ^4J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, NCHN], 8.54 [d, ^3J(H,H) = 4.8 Hz, 1 H, 6-pyr-H], 8.04 [dd, ^3J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, CH], 7.88 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-pyr-H], 7.71 [dt, ^3J(H,H) = 7.8, ^4J(H,H) = 1.5 Hz, 1 H, 4-pyr-H], 7.24 [dd, ^3J(H,H) = 7.5 and ^4J(H,H) = 4.8 Hz, 1 H, 5-pyr-H], 7.15 [dd, ^3J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, CH], 7.00 (s, 2 H, aryl-H), 6.16 (s, 2 H, CH_2), 2.37 (s, 3 H, *p*-aryl-CH_3), 2.06 (s, 6 H, *o*-aryl-CH_3) ppm.

{1-[2-(6-Methyl)pyridyl]methylene-3-mesityl}imidazolium Bromide (5b): The product (0.49 g, 98%) was obtained as a orange/red solid. ^{1}H NMR ($CDCl_3$): δ = 10.18 [dd, ^4J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, NCHN], 8.02 [dd, ^3J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, CH], 7.69 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-pyr-H], 7.62 [t, ^3J(H,H) = 7.8 Hz, 1 H, 4-pyr-H], 7.12 [d, ^3J(H,H) = 7.8 Hz, 1 H, 5-pyr-H], 7.11 [d, ^3J(H,H) = 1.5 Hz, 1 H, CH], 6.99 (s, 2 H, Aryl-H), 6.07 (s, 2 H, CH_2), 2.47 (s, 3 H, pyr-CH_3), 2.33 (s, 3 H, *p*-aryl-CH_3), 2.07 (s, 6 H, *o*-aryl-CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.7 (6-pyr-C), 151.7 (2-pyr-C), 141.2 (*p*-aryl-C), 138.0 (4-pyr-C), 137.8 (NCN), 134.4 (*o*-aryl-C), 130.7 (*i*-aryl-C), 129.8 (m-aryl-C), 124.0 (CH), 123.5 (5-pyr-C), 122.7 (CH), 120.9 (3-pyr-C), 54.0 (CH_2), 24.3 (pyr-CH_3), 21.1 (*p*-aryl-CH_3), 17.6 (*o*-aryl-CH_3) ppm. MS (FAB$^+$, *m*/*z*): calcd. for $C_{19}H_{22}N_3$ [M – Br]$^+$ 292.1814; found 292.1808.

{1-[2-(6-Phenyl)pyridyl]methylene-3-mesityl}imidazolium Bromide (5c): The product (0.42 g, 94%) was obtained as a white powder.[12] ^{1}H NMR ($CDCl_3$): δ = 10.21 (s, 1 H, NCHN), 7.96 [dd, ^3J(H,H) = 8, ^4J(H,H) = 1.6 Hz, 2 H, Ph], 7.94 [dd, ^3J(H,H) = 8, ^4J(H,H) = 1.6 Hz, 2 H, Ph], 7.89 [d, ^3J(H,H) = 7.2 Hz, 1 H, 3-pyr-H], 7.81 [dd, ^3J(H,H) = 7.2, ^3J(H,H) = 7.2 Hz, 1 H, 4-pyr-H], 7.71 [d, ^3J(H,H) = 7.6 Hz, 1 H, 5-pyr-H], 7.53–7.44 (m, 4 H, CH, Ph), 7.11 (s, 1 H, CH), 6.92 (s, 2 H, aryl-H), 6.22 (s, 2 H, CH_2), 2.30 (s, 3 H, *p*-aryl-CH_3), 1.96 (s, 6 H, *o*-aryl-CH_3) ppm.

{1-[2-(6-Mesityl)pyridyl]methylene-3-mesityl}imidazolium Bromide (5d): The product (0.45 g, 96%) was obtained as a white solid.[12] ^{1}H NMR ($CDCl_3$): δ = 10.22 (s, 1 H, NCHN), 8.00 (s, 1 H, CH), 7.95 [d, ^3J(H,H) = 7.2 Hz, 1 H, 3-pyr-H], 7.81 [dd, ^3J(H,H) = 7.2, ^3J(H,H) = 7.2 Hz, 1 H, 4-pyr-H], 7.18 [d, ^3J(H,H) = 7.2 Hz, 1 H, 5-pyr-H], 7.03 (s, 1 H, CH), 6.94 (s, 2 H, aryl-H), 6.88 (s, 2 H, aryl-H), 6.19 (s, 2 H, CH_2), 2.29 (s, 6 H, 2 *p*-aryl-CH_3), 1.94 (s, 6 H, *o*-aryl-CH_3), 1.90 (s, 6 H, *o*-aryl-CH_3) ppm.

[1-(2-Pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazolium Bromide (6a): The product (0.94 g, 94%) was obtained as a red solid.[10] ^{1}H NMR ($CDCl_3$): δ = 10.16 [dd, ^4J(H,H) = 1.8, ^4J(H,H) = 1.8 Hz, 1 H, NCHN], 8.52 [d, ^3J(H,H) = 3.9 Hz, 6-pyr-H], 8.26 [dd, ^3J(H,H) = 1.8, ^4J(H,H) = 1.8 Hz, 1 H, CH], 8.03 [d, ^3J(H,H) = 7.5 Hz, 3-pyr-H], 7.78 [dt, ^3J(H,H) = 7.5, ^4J(H,H) = 1.8 Hz, 1 H, 4-pyr-H], 7.54 [t, ^3J(H,H) = 7.8 Hz, 1 H, *p*-aryl-H], 7.31 [d, ^3J(H,H) = 7.8 Hz, 1 H, *m*-aryl-H], 7.29 (m, 1 H, 5-pyr-H), 6.25 (s, 2 H, CH_2), 2.31 [dq, ^3J(H,H) = 6.9, ^3J(H,H) = 6.9 Hz, 2 H, *i*Pr-H], 1.22 [d, ^3J(H,H) = 6.9 Hz, 6 H, *i*Pr-CH_3], 1.14 [d, ^3J(H,H) = 6.9 Hz, 6 H, *i*Pr-CH_3] ppm.

{1-[2-(6-Methyl)pyridyl]methylene-3-(2,6-diisopropylphenyl)}imidazolium Bromide (6b): The product (0.57 g, 99%) was obtained as red crystals. ^{1}H NMR ($CDCl_3$): δ = 10.02 [dd, ^4J(H,H) = 1.5, 1.5 Hz, 1 H, NCHN], 8.24 [dd, ^3J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, CH], 7.72 [d, ^3J(H,H) = 7.5 Hz, 1 H, 3-pyr-H], 7.62 [dd, ^3J(H,H) = 7.5, 7.5 Hz, 1 H, 4-pyr-H], 7.52 [t, ^3J(H,H) = 7.8 Hz, 1 H, *p*-aryl-H], 7.29 [d, ^3J(H,H) = 7.8 Hz, 2 H, *m*-aryl-H], 7.14 [dd, ^3J(H,H) = 1.5, ^4J(H,H) = 1.5 Hz, 1 H, CH], 7.12 [d, ^3J(H,H) = 7.5 Hz, 1 H, 5-pyr-H], 6.14 (s, 2 H, CH_2), 2.46 (s, 3 H, pyr-CH_3), 2.32 [dd, ^3J(H,H) = 6.9, 6.9 Hz, 2 H, *i*Pr], 1.20 [d, ^3J(H,H) = 6.9 Hz, 6 H, *i*Pr], 1.12 [d, ^3J(H,H) = 6.9 Hz, 6 H, *i*Pr] ppm. ^{13}C NMR ($CDCl_3$): δ = 158.7 (6-pyr-C), 151.7 (2-pyr-C), 145.4 (*o*-aryl-C), 138.2 (4-pyr-C), 137.9 (m-aryl-C), 137.8 (NCN), 131.9 (*i*-aryl-C), 130.2 (*p*-aryl-C), 124.7 (CH), 124.1 (CH), 123.5 (5-pyr-C), 121.1 (3-pyr-C), 53.9 (CH_2), 28.6 (*i*Pr-CH), 24.4 (*i*Pr-CH_3), 24.2 (pyr-CH_3) ppm. MS (FAB$^+$, *m*/*z*): calcd. for $C_{22}H_{28}N_3$ [M – Br]$^+$ 334.2283; found 334.2284.

[1-(2-Pyridyl)methylene-3-(4-methoxyphenyl)]imidazolium Bromide (7): The product (0.88 g, 99%) was obtained as a red solid. ^{1}H NMR ($CDCl_3$): δ = 11.02 [dd, ^4J(H,H) = 2.1, ^4J(H,H) = 2.1 Hz, 1 H, NCHN], 8.57 [dd, ^3J(H,H) = 4.8, 1.8 Hz, 1 H, 6-pyr-H], 7.90 [dd, ^3J(H,H) = 7.8, ^4J(H,H) = 1.2 Hz, 1 H, 3-pyr-H], 7.83 [dd, ^3J(H,H) = 2.1, ^4J(H,H) = 2.1 Hz, 1 H, CH], 7.79 [ddd, ^3J(H,H) = 7.8, 7.5, ^4J(H,H) = 1.8 Hz, 1 H, 4-pyr-H], 7.65 [d, ^3J(H,H) = 9.0 Hz, 2 H, aryl-H], 7.58 [dd, ^3J(H,H) = 2.1, ^4J(H,H) = 2.1 Hz, 1 H, CH], 7.32 [ddd, ^3J(H,H) = 7.5, 4.8, ^4J(H,H) = 1.2 Hz, 1 H, 5-pyr-H], 7.07 [d, ^3J(H,H) = 9.0 Hz, 2 H, aryl-H], 5.95 (s, 2 H, CH_2),

3.86 (s, 3 H, OMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 180.9 (*p*-aryl-C), 152.8 (2-pyr-C), 149.8 (6-pyr-C), 137.6 (4-pyr-C), 136.1 (NHCN), 127.6 (*i*-aryl-C), 124.1 (CH), 124.0 (CH), 123.8 (5-pyr-C), 123.4 (aryl-C), 120.4 (3-pyr-C), 115.4 (aryl-C), 55.8 (OMe), 54.0 (CH_2) ppm. MS (FAB^+, *m*/*z*): calcd. for $C_{16}H_{16}N_3OAg$ $[M - Br]^+$ 266.1293; found 266.1294.

[1-(2-Pyridyl)methylene-3-(4-trifluoromethylphenyl)]imidazolium Bromide (8): The product (0.39 g, 97%) was obtained as a red solid. ^1H NMR ($CDCl_3$): δ = 11.52 [dd, ^4J(H,H) = 1.8, ^4J(H,H) = 1.8 Hz, 1 H, NCHN], 8.51 (m, 1 H, 6-pyr-H), 8.03 [d, ^3J(H,H) = 8.1 Hz, 2 H, aryl-H], 7.94 [dd, ^3J(H,H) = 1.8, ^4J(H,H) = 1.8 Hz, 1 H, CH], 7.91 [dd, ^3J(H,H) = 1.8, ^4J(H,H) = 1.8 Hz, 1 H, CH], 7.84 (m, 1 H, 3-pyr-H), 7.80 [d, ^3J(H,H) = 8.1 Hz, 2 H, aryl-H], 7.72 (m, 1 H, 4-pyr-H), 7.27 (m, 1 H, 5-pyr-H), 5.94 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0 (2-pyr-C), 149.8 (6-pyr-C), 137.9 (4-pyr-C), 137.0 (NCHN), 136.7 (*p*-aryl-C), 132.3 (CF_3), 127.9 (*i*-aryl-C), 124.9, 124.2 (*o*- and *m*-aryl-C), 124.3 (5-pyr-C), 122.4 (CH), 122.3 (CH) 120.2 (3-pyr-C), 54.3 (CH_2) ppm. MS (FAB^+, *m*/*z*): calcd. for $C_{16}H_{13}F_3N_3$ $[M - Br]^+$ 304.1062; found 304.1067.

General Synthesis of Silver(I) N-Heterocyclic Carbene Complexes 9–12: In a typical experiment, 1 mmol of the imidazolium bromide and 0.55 equiv. of silver(I) oxide were suspended in dichloromethane to 0.1 M and the reaction mixture was stirred for 16 h. It was then filtered through a celite pad and concentrated in vacuo to yield the product.

Bis{[1-(2-Pyridyl)methylene-3-mesityl]imidazol-2-ylidene}silver(I) Silver(I) Dibromide (9a): The product (0.20 g, 87%) was obtained as a light brown solid.[10] ^1H NMR ($CDCl_3$): δ = 8.58 [d, ^3J(H,H) = 5.7 Hz, 1 H, 6-pyr-H], 7.72 [dt, ^3J(H,H) = 7.5, ^4J(H,H) = 1.8 Hz, 1 H, 4-pyr-H], 7.37 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 7.34 [d, ^3J(H,H) = 7.5 Hz, 1 H, 3-pyr-H], 7.27 (m, 1 H, 5-pyr-H), 6.96 (m, 3 H, aryl-H, CH), 5.50 (s, 2 H, CH_2), 2.32 (s, 3 H, *p*-aryl-CH_3), 1.94 (s, 6 H, *o*-aryl-CH_3) ppm.

bis({1-[2-(6-methyl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)-silver(I) Silver(I) Dibromide 9b: The product (0.27 g, 94%) was obtained as a brown solid. ^1H NMR (CD_2Cl_2): δ = 7.61 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 7.8 Hz, 1 H, 4-pyr-H], 7.37 [d, ^3J(H,H) = 1.5 Hz, 1 H, CH], 7.14 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-pyr-H], 7.02–6.98 (m, 4 H, CH, aryl-H and 5-pyr-H), 5.40 (s, 2 H, CH_2), 2.52 (s, 3 H, pyr-CH_3), 2.36 (s, 3 H, *p*-aryl-CH_3), 1.97 (s, 6 H, *o*-aryl-CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 183.1 (NCN), 158.8 (6-pyr-C), 154.7 (2-pyr-C), 139.4 (*p*-aryl-C), 137.3 (4-pyr-C), 135.6 (*i*-aryl-C), 134.9 (*o*-aryl-C), 129.2 (m-aryl-C), 122.9 (5-pyr-C), 122.7 (CH), 122.2 (CH), 118.6 (3-pyr-C), 56.9 (CH_2), 24.2 (pyr-CH_3), 20.9 (*p*-aryl-CH_3), 17.5 (*o*-aryl-CH_3) ppm. MS (FAB^+, *m*/*z*): calcd. for $C_{19}H_{21}N_3Ag$ $[M - Br]^+$ 398.0786; found 398.0786.

bis({1-[2-(6-phenyl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)-silver(I) Silver(I) Dibromide (9c): The product (0.10 g, 99%) was obtained as a beige solid.[12] ^1H NMR ($CDCl_3$): δ = 7.97 [dd, ^3J(H,H) = 8, ^4J(H,H) = 1.6 Hz, 2 H, Ph], 7.77 [dd, ^3J(H,H) = 7.6, ^3J(H,H) = 7.6 Hz, 1 H, 4-pyr-H], 7.70 [d, ^3J(H,H) = 7.6 Hz, 1 H, 5-pyr-H], 7.5–7.4 (m, 5 H, CH, Ph, 3-pyr-H), 6.95 [d, ^3J(H,H) = 1.6 Hz, 1 H, CH], 6.93 (s, 2 H, aryl-H), 5.55 (s, 2 H, CH_2), 2.32 (s, 3 H, *p*-aryl-CH_3), 1.98 (s, 6 H, *o*-aryl-CH_3) ppm.

bis({1-[2-(6-mesityl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)-silver(I) Silver(I) Dibromide (9d): The product (0.18 g, 99%) was obtained as a beige solid.[12] ^1H NMR ($CDCl_3$): δ = 7.77 [dd, ^3J(H,H) = 7.6, ^3J(H,H) = 7.6 Hz, 1 H, 4-pyr-H], 7.37 [d, ^3J(H,H) = 1.6 Hz, 1 H, CH], 7.34 [d, ^3J(H,H) = 7.6 Hz, 1 H, 3-pyr-H], 7.18 [d, ^3J(H,H) = 7.6 Hz, 1 H, 5-pyr-H], 6.92 (s, 4 H, aryl-H), 6.88 [d, ^3J(H,H) = 1.6 Hz, 1 H, CH], 5.50 (s, 2 H, CH_2), 2.31 (s, 6 H, 2 *p*-aryl-CH_3), 1.95 (s, 6 H, *o*-aryl-CH_3), 1.91 (s, 6 H, *o*-aryl-CH_3) ppm.

bis{[1-(2-Pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazol-2-ylidene}silver(I) Silver(I) Dibromide (10a): The product (0.13 g, 85%) was obtained as a light yellow solid.[10] ^1H NMR ($CDCl_3$): δ = 8.60 [d, ^3J(H,H) = 4.2 Hz, 1 H, 6-pyr-H], 7.76 (m, 1 H, 5-pyr-H), 7.6–7.0 (m, 7 H, pyr-H, CH, aryl-H), 5.52 (s, 2 H, CH_2), 2.39 (m, 2 H, *i*Pr-CH), 1.20 (br. d, 6 H, *i*Pr-CH_3), 1.12 (br. d, 6 H, *i*Pr-CH_3) ppm.

bis({1-[2-(6-Methyl)pyridyl]methylene-3-(2,6-diisopropylphenyl)}-imidazol-2-ylidene)silver(I) Silver(I) Dibromide (10b): The product (0.27 g, 94%) was obtained as a red solid. ^1H NMR (CD_2Cl_2): δ = 7.61 [dd, ^3J(H,H) = 7.6, ^3J(H,H) = 7.6 Hz, 1 H, 4-pyr-H], 7.48 [t, ^3J(H,H) = 8.1 Hz, 1 H, *p*-aryl-H], 7.39 [d, ^3J(H,H) = 1.8 Hz, 1 H, CH], 7.28 [d, ^3J(H,H) = 8.1 Hz, 2 H, *m*-aryl-H], 7.15 [d, ^3J(H,H) = 7.6 Hz, 1 H, 3-pyr-H], 7.1–7.0 (m, 3 H, CH, 5-pyr-H), 5.49 (s, 2 H, CH_2), 2.52 (s, 3 H, pyr-CH_3), 2.41 (m, 2 H, *i*Pr-CH), 1.3–1.1 (m, 12 H, *i*Pr-CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 184.1 (NCN), 158.9 (6-pyr-C), 154.4 (2-pyr-C), 146.0 (*o*-aryl-C), 137.4 (*i*-aryl-C), 137.2 (4-pyr-C), 137.3 (*p*-aryl-C), 130.4 (m-aryl-C), 124.1 (5-pyr-C), 122.7 (CH), 122.2 (CH), 118.5 (3-pyr-C), 56.7 (CH_2), 28.2 (*i*Pr-CH), 24.3 (pyr-CH_3), 23.9 (*i*Pr-CH_3) ppm. MS (FAB^+, *m*/*z*): calcd. for $C_{22}H_{27}N_3Ag$ $[M - Br]^+$ 440.1256; found 440.1250.

bis{[1-(2-Pyridyl)methylene-3-(4-methoxyphenyl)]imidazol-2-ylidene}silver(I) Silver(I) Dibromide (11): The product (0.82 g, 85%) was obtained as a red solid. ^1H NMR (CD_2Cl_2): δ = 8.58 (m, 1 H, 6-pyr-H), 7.73 (m, 1 H, 4-pyr-H), 7.49 [d, ^3J(H,H) = 9.0 Hz, 2 H, aryl-H], 7.37 (m, 1 H, 3-pyr-H), 7.36 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 7.29 (m, 1 H, 5-pyr-H), 7.29 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 6.97 [d, ^3J(H,H) = 9.0 Hz, 2 H, aryl-H], 5.49 (s, 2 H, CH_2), 3.84 (s, 3 H, OMe) ppm. ^{13}C NMR (CD_2Cl_2): δ = 181.4 (NCN), 159.8 (6-pyr-C), 155.2 (2-pyr-C), 149.8 (*p*-aryl-C), 137.3 (3-pyr-C), 133.1 (*i*-aryl-C), 1235.4 (aryl-CH), 123.4 (CH), 123.0 (5-pyr-C), 122.7 (CH), 122.2 (4-pyr-C), 114.6 (aryl-CH), 57.3 (CH_2), 55.6 (OMe) ppm. MS (FAB^+, *m*/*z*): calcd. for $C_{16}H_{15}N_3Ag$ $[M - Br]^+$ 372.0266; found 372.0260.

bis{[1-(2-pyridyl)methylene-3-(4-trifluoromethylphenyl)]imidazol-2-ylidene}silver(I) Silver(I) Dibromide (12): The product (0.10 g, 88%) was obtained as a brown solid. ^1H NMR (CD_2Cl_2): δ = 8.59 (m, 1 H, 6-pyr-H), 7.84–7.77 (m, 5 H, aryl-H and 3-pyr-H), 7.74 (m, 1 H, 4-pyr-H), 7.44 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 7.38 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 7.30 (m, 1 H, 5-pyr-H), 5.56 (s, 2 H, CH_2). ^{13}C NMR (CD_2Cl_2): δ = 182.6 (NCN), 154.8 (6-pyr-C), 149.9 (2-pyr-C), 137.3 (3-pyr-C), 135.4 (*p*-aryl-C), 130.9 (CF_3), 127.0 (*i*-aryl-C), 124.4 (aryl-C), 123.5 (5-pyr-C), 123.1 (CH), 122.9 (aryl-C), 121.5 (CH), 121.2 (4-pyr-C), 57.5 (CH_2). MS (FAB^+, *m*/*z*): calcd. for $C_{32}H_{24}F_6N_6Ag$ $[M - AgBr_2]^+$ 713.1018; found 713.1019.

General Synthesis of (N-Heterocyclic Carbene)(Maleic Anhydride)–Palladium(0) Complexes 13–16: In a typical experiment, silver(I)(NHC) complex (0.5 mmol with respect to the carbene) and 0.9 equiv. Pd(*t*BuDAB) were dissolved in dichloromethane to 0.1 M and stirred for 1 h. The reaction mixture was then filtered of a pad of celite and concentrated to a small volume. It is then layered with pentane, allowing the product to precipitate. After decanting the solution, the product is washed with pentane and dried in vacuo.

{[1-(2-Pyridyl)methylene-3-mesityl]imidazol-2-ylidene}palladium(0) Maleic Anhydride (13a): The product (0.27 g, 98%) was obtained as a yellow solid. ^1H NMR (CD_2Cl_2): δ = 8.92 [d, ^3J(H,H) = 5.1 Hz, 1 H, 6-pyr-H], 7.85 [dt, ^3J(H,H) = 7.2, ^3J(H,H) = 1.2 Hz, 1 H, 4-pyr-H], 7.56 [d, ^3J(H,H) = 7.2 Hz, 1 H, 3-pyr-H], 7.35 [dt, ^3J(H,H) = 6.0, ^3J(H,H) = 1.2 Hz, 1 H, 5-pyr-H], 7.25 [d, ^3J(H,H) = 2.1 Hz, 1

H, CH], 7.08 (s, 1 H, aryl-H), 6.91 (s, 1 H, aryl-H), 6.85 [d, ^3J(H,H) = 1.2 Hz, 1 H, CH], 5.41 [d, ^2J(H,H) = 15 Hz, 1 H, CH_2], 5.12 [d, ^2J(H,H) = 15 Hz, 1 H, CH_2], 3.30 (br. s, 1 H, ma), 3.08 (br. s, 1 H, ma), 2.37 (s, 3 H, *p*-aryl-CH_3), 2.05 (s, 3 H, *o*-aryl-CH_3), 1.92 (s, 3 H, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ = 188.7 (NCN), 173.6 (CO), 173.5 (CO), 155.9 (6-pyr-C), 154.3 (2-pyr-CH), 139.8 (4-pyr-C), 139.1 (*p*-aryl-C), 137.1 (*i*-aryl-C), 136.1 (*o*-aryl-C), 135.6 (*o*-aryl-C), 129.6 (m-aryl-CH), 128.9 (m-aryl-CH), 125.4 (CH), 125.2 (CH), 123.4 (5-pyr-CH), 121.8 (3-pyr-CH), 55.9 (CH_2), 41.5 (alkene), 40.4 (alkene), 21.4 (*p*-aryl-CH_3), 18.1 (br., *o*-aryl-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{22}H_{22}N_3O_3Pd$ [M + H]$^+$ 482.0696; found 482.0675.

({1-[2-(6-Methyl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)palladium(0) Maleic Anhydride (13b): The product (0.13 g, 96%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 7.72 [dd, *J*(HH) = 7.5, ^3J(HH) = 7.8 Hz, 1 H, 4-pyr-H], 7.37 [d, ^3J(HH) = 7.5 Hz, 1 H, 3-pyr-H], 7.34 ^3J(HH) = 7.8 Hz, 1 H, 5-pyr-H(), 7.29 [d, ^3J(HH) = 1.8 Hz, 1 H, CH], 7.09 (br. s, 1 H, aryl-H), 6.97 (br. s, 1 H, aryl-H), 6.91 [d, ^3J(HH) = 1.8 Hz, 1 H, CH], 5.50 [br. d, ^2J(HH) = 13.5 Hz, 1 H, CH_2], 5.09 [br. d, ^2J(HH) = 13.5 Hz, 1 H, CH_2], 3.36 (br. s, 1 H, ma), 3.10 (br. s, 1 H, ma), 2.81 (s, 3 H, pyr-CH_3), 2.37 (s, 3 H, *p*-aryl-CH_3), 2.15 (br. s, 3 H, *o*-aryl-CH_3), 1.86 (br. s, 3 H, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ = 190.0 (NCN), 174.0 (CO), 173.3 (CO), 161.8 (6-pyr-C), 154.1 (2-pyr-C), 138.8 (*p*-aryl-C), 138.4 (4-pyr-CH), 136.7 (*i*-aryl-C), 135.9 (*o*-aryl-C), 135.6 (*o*-aryl-C), 129.0 (m-aryl-CH), 128.7 (m-aryl-CH), 124.5 (5-pyr-CH), 122.1 (CH), 121.6 (3-pyr-CH), 121.2 (CH), 56.2 (CH_2), 39.3 (alkene), 39.2 (alkene), 29.0 (pyr-CH_3), 21.1 (*p*-aryl-CH_3), 17.9 (*o*-aryl-CH_3), 17.7 (*o*-aryl-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{23}H_{24}N_3O_3Pd$ [M + H]$^+$ 496.0852; found 496.0866. $C_{23}H_{23}N_3O_3Pd$ (495.08): calcd. C 55.71, H 4.68, N 8.47; found C 55.70, H 4.74, N 8.23.

({1-[2-(6-Phenyl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)palladium(0) Maleic Anhydride (13c): The product (48 mg, 98%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 8.09 [d, ^3J(H,H) = 4.5 Hz, 2 H, Ph], 7.78 [dd, ^3J(H,H) = 4.5, ^3J(H,H) = 4.5 Hz, 1 H, 4-pyr-H], 7.70 [d, ^3J(H,H) = 4.5 Hz, 1 H, 3-pyr-H], 7.5–7.4 (m, 3 H, 5-pyr-H, Ph), 7.14 (s, 1 H, CH), 7.08 (s, 2 H, aryl-H), 6.90 (s, 1 H, CH), 4.9–4.6 (br. s, 2 H, CH_2), 3.02 (br. s, 1 H, ma), 2.41 (s, 3 H, *p*-aryl-CH_3), 2.11 (s, 1 H, ma), 1.92 (br. s, 6 H, *o*-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ = 191.5 (NCN), 174.1 (CO), 157.8 (6-pyr-C), 156.6 (2-pyr-C), 139.3 (4-pyr-CH), 139.0, 138.0, 136.9, 136.7 (*p*-aryl-C, *p*-Ph–CH, *i*-aryl-C, *i*-Ph–C), 136.2 (*o*-aryl-C), 135.9 (*o*-aryl-C), 129.4 (m-aryl-CH), 129.2 (m-aryl-CH), 128.8 (Ph-CH), 127.0 (Ph-CH), 123.4 (5-pyr-CH), 121.3 (CH), 121.0 (3-pyr-CH), 119.1 (CH), 55.9 (CH), 39.4 (alkene), 21.0 (*p*-aryl-CH_3), 18.0 (*o*-aryl-CH_3), 17.6 (*o*-aryl-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{24}H_{23}N_3Pd$ [M – ma]$^+$ 459.0927; found 459.0930.

({1-[2-(6-Mesityl)pyridyl]methylene-3-mesityl}imidazol-2-ylidene)palladium(0) Maleic Anhydride (13d): The product (83 mg, 95%) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2): δ = 7.90 [dd, ^3J(H,H) = 7.8, ^3J(H,H) = 7.8 Hz, 1 H, 4-pyr-H], 7.54 [d, ^3J(H,H) = 7.8 Hz, 1 H, 3-pyr-H], 7.35 [d, ^3J(H,H) = 7.8 Hz, 1 H, 5-pyr-H], 7.30 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 7.06 (br. s, 2 H, pyr-aryl-H), 6.95 (br. s, 1 H, aryl-H), 6.89 [d, ^3J(H,H) = 2.1 Hz, 1 H, CH], 6.87 (br. s, 1 H, aryl-H), 5.66 [d, ^2J(H,H) = 14.4 Hz, 1 H, CH_2], 5.12 [d, ^2J(H,H) = 14.4 Hz, 1 H, CH_2], 2.83 (br. s, 1 H, ma), 2.36 (s, 3 H, *p*-aryl-CH_3), 2.32 (s, 3 H, *p*-aryl-CH_3), 2.06 (s, 3 H, *o*-aryl-CH_3), 1.99 (s, 3 H, *o*-aryl-CH_3), 1.89 (s, 3 H, *o*-aryl-CH_3), 1.86 (s, 3 H, *o*-aryl-CH_3), 1.61 (br. s, 1 H, ma). ^{13}C NMR (CD_2Cl_2): δ = 190.4 (NCN), 173.9 (CO), 172.6 (CO), 163.7 (6-pyr-C), 154.6 (2-pyr-C), 139.1 (4-pyr-CH), 138.4, 138.2, 138.0, 136.6, 136.4, 136.0, 134.6 (2 *p*-aryl-C, 2 *i*-aryl-C, 4 *o*-aryl-C), 128.9, 128.5, 128.2, 127.3 (4 *m*-aryl-CH), 125.9 (CH), 122.7 (5-pyr-CH), 121.7 (3-pyr-CH), 120.9 (CH), 56.4 (CH_2), 39.9 (alkene), 37.8 (alkene), 20.8 (2 *p*-aryl-CH_3), 20.5, 20.3 (2 *o*-aryl-CH_3), 17.7, 17.6 (2 *o*-aryl-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{27}H_{29}N_3Pd$ [M – ma]$^+$ 501.1396; found 501.1410.

{[1-(2-Pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazol-2-ylidene}palladium(0) Maleic Anhydride (14a): The product (83 mg, 98%) was obtained as yellow crystals. ^{1}H NMR (CD_2Cl_2): δ = 8.83 (m, 1 H, 6-pyr-H), 7.88 (m, 1 H, 4-pyr-H), 7.57 (m, 1 H, 3-pyr-H), 7.48 [t, *J*(HH) = 7.8 Hz, 1 H, *p*-aryl-H], 7.39 (m, 1 H, 5-pyr-H), 7.29 [d, ^3J(HH) = 7.8 Hz, 2 H, *m*-aryl-H], 7.26 [d, ^3J(HH) = 1.8 Hz, 1 H, CH], 6.95 [d, ^3J(HH) = 1.8 Hz, 1 H, CH], 5.27 (br. s, 2 H, CH_2), 3.34 (br. s, 2 H, ma), 2.58–2.24 (2 br. m, 2 H, *i*Pr), 1.28 [br. d, ^3J(HH) = 6.6 Hz, 6 h, *i*Pr], 1.05 [br. d, ^3J(HH) = 6.9 Hz, 6 h, *i*Pr]. ^{13}C NMR (CD_2Cl_2): δ = 190.1 (NCN), 172.6 (CO), 172.3 (CO), 154.1 (6-pyr-CH), 153.8 (2-pyr-C), 145.8 (*o*-aryl-CH), 138.7 (4-pyr-CH), 136.2 (*i*-aryl-C), 129.8 (*p*-aryl-C), 125.0 (m-aryl-C), 124.0 (CH), 123.8 (CH), 123.0 (5-pyr-CH), 121.1 (3-pyr-CH), 55.7 (CH_2), 41.2 (alkene), 40.8 (alkene), 29.9 (*i*Pr-CH), 24.6 (*i*Pr-CH_3), 23.7 (*i*Pr-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{25}H_{28}N_3O_3Pd$ [M + H]$^+$ 524.1165; found 524.1174. $C_{25}H_{27}N_3O_3Pd$ (537.12): calcd. C 54.39, H 5.19, N 8.02; found C 54.50, H 5.31, N 7.69.

({1-[2-(6-Methyl)pyridyl]methylene-3-(2,6-diisopropylphenyl)}imidazol-2-ylidene)palladium(0) Maleic Anhydride (14b): The product (0.13 g, 98%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 7.74 [dd, ^3J(HH) = 7.5, ^3J(HH) = 7.8 Hz, 1 H, 4-pyr-H], 7.47 [t, ^3J(HH) = 7.8 Hz, 1 H, *p*-aryl-H], 7.37 [d, ^3J(HH) = 7.5 Hz, 1 H, 3-pyr-H], 7.35 {d, [d, ^3J(HH) = 7.8 Hz, 1 H, 5-pyr-H]}, 7.30 (m, 2 H, *m*-aryl-H), 7.25 [d, ^3J(HH) = 2.1 Hz, 1 H, CH], 6.95 [d, ^3J(HH) = 2.1 Hz, 1 H, CH], 5.50 (br. s, 1 H, CH_2), 5.23 (br. s, 1 H, CH_2), 3.32 (s, 2 H, ma), 2.78 (s, 3 H, pyr-CH_3), 2.64 (br. m, 1 H, *i*Pr-H), 2.37 (br. m, 1 H, *i*Pr-H), 1.4–1.0 (br. m, 12 H, *i*Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ = 191.4 (NCN), 173.4 (CO), 173.2 (CO), 162.3 (6-pyr-C), 154.0 (2-pyr-C), 146 (br., *o*-aryl-C), 138.3 (4-pyr-CH), 136.3 (*i*-aryl-C), 129.6 (*p*-aryl-CH), 126.8 (m-aryl-CH), 125.2 (m-aryl-CH), 124.5 (5-pyr-CH), 123.8 (CH), 121.8 (3-pyr-CH), 120.8 (CH), 56.4 (CH_2), 39.4 (alkene), 39.2 (alkene), 29.3 (*i*Pr-CH), 28.8 (*i*Pr-CH), 28.5 (pyr-CH_3), 26.0 (*i*Pr-CH_3), 25.1 (*i*Pr-CH_3), 24.1, (*i*Pr-CH_3), 23.6 (*i*Pr-CH_3). MS (FAB$^+$, *m*/*z*): calcd. for $C_{22}H_{27}N_3Pd$ [M – ma]$^+$ 439.1240; found 439.1251.

{[1-(2-Pyridyl)methylene-3-(4-methoxyphenyl)]imidazol-2-ylidene}palladium(0) Maleic Anhydride: The product could be identified in ^{1}H NMR, although decomposition was too rapid to assign the spectrum.

{[1-(2-Pyridyl)methylene-3-(4-trifluoromethylphenyl)]imidazol-2-ylidene}palladium(0) Maleic Anhydride: The product (18 mg, 26%) was obtained as a yellow solid which decomposed over the course of several hours. ^{1}H NMR (CD_2Cl_2): δ = 8.88 (m, 1 H, 6-pyr-H), 7.92–7.81 (m, 6 H, aryl-H, CH, 4-pyr-H), 7.55 (m, 1 H, 3-pyr-H), 7.40 (m, 1 H, 5-pyr-H), 7.29 [d, ^3J(HH) = 2.1 Hz, 1 H, CH], 5.40–5.16 (2 br. d, 2 H, CH_2), 3.80–3.40 (2 br. d, 2 H, ma).

X-ray Data Collection, Reduction, and Refinement: A suitable single crystal of **13b** was coated with Paratone-N oil, mounted using a glass fibre 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-K_α radiation (λ = 0.71073 Å) with a scan width of 0.3° and exposure time of 15 s. The generator setting was 50 kV and 160 mA. Diffraction data was 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 SA-

DABS routine (empirical multi-scan 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[24] and was refined with SHELXL-97[25] 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 aromatic protons of the maleic anhydride moiety the protons (H21, H22) 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 significance. **13b** ($C_{23}H_{23}N_3O_3Pd$): FW = 495.84, monoclinic, space group $P\bar{1}$, Z = 2, a = 10.4832(3), b = 10.7456(3), c = 10.8393(3), α = 63.8842(4) β = 78.1875(4), β = 71.1702(4), V = 1034.87(5), $F(000)$ = 504, T = 153(2), μ = 0.927, 10634 reflections collected, 4929 reflections unique (R_{int} = 0.0166), 4608 reflections observed [$F > 2\sigma(F)$]. The final was R_1 = 0.0231 and wR_2 = 0.0608 (all data).

CCDC-784029 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Experimental Procedure for Catalytic Transfer Semi-Hydrogenation of Phenyl Propyne Using Formic Acid as Hydrogen Donor: A solution of 150 mM 1-phenyl-1-propyne, 750 mM triethylammonium formate and 150 mM *p*-xylene in 12 mL acetonitrile was heated to reflux. At t = 0, a solution of 1 mol-% catalyst in 2 mL acetonitrile was added to the reaction mixture. Periodically, samples were taken over a period of 24 h. Reaction mixtures were analyzed by GC to determine conversions. Reactions were quenched by dilution with EtOH.

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