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Rigid pyridyl substituted NHC ligands, their Pd(0) complexes and their application in selective transfer semihydrogenation of alkynes

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The synthesis of an air-stable series of Pd^0 complexes with unsymmetric bidentate *N*-pyridine N-heterocyclic carbene ligands has been described. The carbenes were generated by synthesis of the silver(I) complexes from the imidazolium salts, followed by transmetallation of the C-N ligands to obtain the target electron-rich zerovalent palladium compounds. The bidentate coordination behaviour of the ligands was confirmed by ^1H, ^{13}C NMR and X-ray spectroscopy. The complexes are active precatalysts for the selective transfer semihydrogenation of alkynes to *Z*-alkenes, with selectivities up to 99%.

Keywords: carbene complexes; organometallic compounds; palladium; transmetallation; hydrogenation

Introduction

N-heterocyclic carbenes (NHCs) have been at the forefront of organometallic chemistry and catalysis for a number of years[1] and new developments are published regularly.[2] The high stability they impart on their transition metal (TM) complexes and the catalytic activity of those complexes make this class of ligands an exceedingly valuable addition to the field.[3] The strong donating character, combined with their ability to act as acceptors as well, enables NHCs to ligate to a large number of TMs in various oxidation states, as well as to many main group elements.[4] Next to monodentate carbenes, also homo- and heteropolydentate ligands containing NHCs and their complexes are reported frequently.[5]

Our current interest lies in the development and synthesis of heterobidentate NHC ligands containing a nitrogen moiety as secondary donor.[6–8] By combining the strong carbon-based donor with a more weakly coordinating nitrogen donor, we hope to gain access to a class of catalysts which benefits from the hemilabile behaviour of one of its ligands.[9] We endeavoured the synthesis of electron rich palladium complexes bearing an NHC ligand functionalized with a pyridine nitrogen donor, where the pyridine ring is attached directly to the NHC. These ligands have been prepared before,[10–12] but an investigation into the influence of the substituents on both the NHC and the nitrogen donor has not been thoroughly performed. The pyridine functionality is a commonly used motif in coordination chemistry,[13] and gives rise to a five-membered chelate ring in combination with the NHC scaffold. Because all non-metal atoms in the ring are sp^2-hybridized, a considerable amount of strain is expected, which is likely to enhance the hemilability of the tethered C-N ligand.

By combining the NHC and the pyridine in one bidentate ligand, varying the substituents on both the NHC and the pyridyl moieties, we hope to gain insight in effects of the substituents on the coordination chemistry and, ultimately, the performance of the zerovalent palladium complexes in catalysis. As a probe for the catalytic performance we employed the transfer hydrogenation of alkynes to *Z*-alkenes, in which (NHC)Pd(0) complexes have shown to be excellent catalysts.[14] This reaction is important in organic chemistry, because it is the only selective and reproducible method of obtaining *Z*-alkenes. This reaction constitutes a valuable tool for materials sciences, as well as for the synthesis of pharmaceuticals, fragrance chemicals and natural products, where selective synthesis of only one isomer is a prerequisite.It appeared that the choice of the secondary nitrogen donor has a marked influence on the results.[6,8]

We present here the synthesis of the imidazolium salts from which the zerovalent palladium carbene complexes are generated by intermediacy of their silver(I) complexes. The NHCs are then transmetallated onto palladium(0). Finally, we verify whether (*N*-pyridyl-NHC)Pd(0) complexes catalyze the transfer hydrogenation of alkynes to *Z*-alkenes and compare their putative reactivity and selectivity with previously investigated catalysts.

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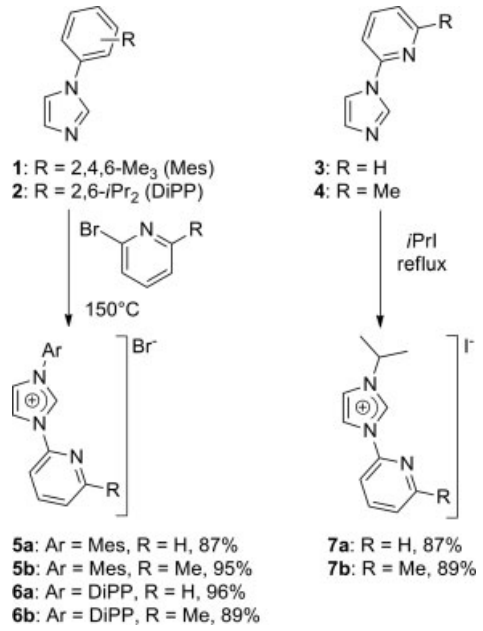
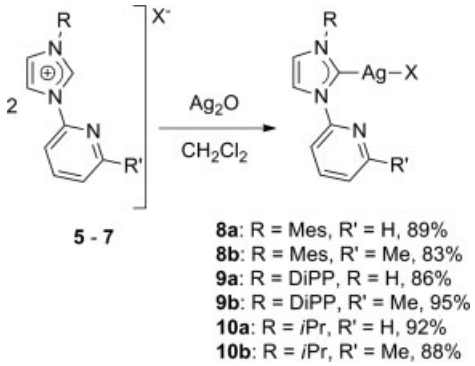
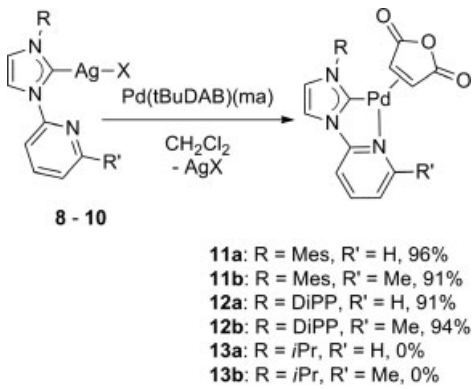


Scheme 1. Synthesis of imidazolium salts.



Scheme 2. Silver(I) carbene complex synthesis.



Scheme 3. Synthesis of zerovalent Pd(NHC) complexes.

Results and Discussion

Imidazolium bromides. *N*-arylimidazoles **1**–**4**[15] were quaternized in two ways; heating with 2-bromopyridine **a** or 2-bromo-6-methylpyridine **b** to obtain the imidazolium bromides **5** and **6**,[11] or refluxing in 2-iodopropane to obtain **7** in high yields (scheme 1). The latter method has to our knowledge not been employed in this fashion, which is remarkable in view of the good results and ease of the procedure.

All compounds were obtained pure and in high yields after washing the precipitated crude products with diethyl ether. The characteristic signal of the imidazolium proton is observed between 11.4 ppm and 10.8 ppm in the ^{1}H NMR.

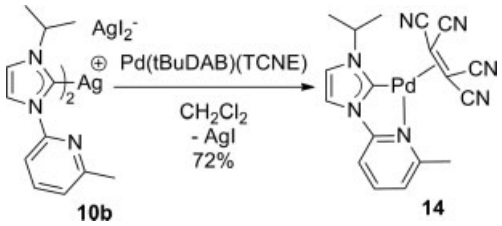
(NHC)Silver(I) complexes. After the ligand precursors were obtained, the *N*-heterocyclic carbenes were generated using a well described method.[16–18] In this instance, we employed silver(I) oxide as the base and as the metal precursor under mild conditions, giving the target complexes in high yields for this scaffold (scheme 2). It has to be noted that the exact structure of the NHC silver complexes is hard to deduce, as dynamic exchange processes can take place in solution, and the solid state structure is influenced by the method of isolation.[17] We depict these complexes as monocarbene silver(I) halide species, as this shows the one to one ratio of the NHC and the silver ion.

The protocol for the synthesis of these silver(I) complexes is simple without being deleterious to the yield or purity of the complexes, because there is no need for inert solvents or atmosphere with these ligands. It has to be noted that the less sterically encumbering substituents on the ligand in **10a** and **10b** probably cause the complex to exist predominantly as the silver(I) biscarbene species in solution, as opposed to the monocarbene complex. As the former is charged, its solubility in the dichloromethane reaction solvent is presumably lower than that of the latter; hence a precipitate is sometimes seen. Further dilution of the reaction mixture and sufficient washing of the celite pad ensures high isolated yields of the products. The disappearance of the signal for the imidazolium proton in the ^{1}H NMR and the appearance of a peak for the carbene carbon between 175 ppm and 183 ppm in the ^{13}C NMR are indicative of product formation.

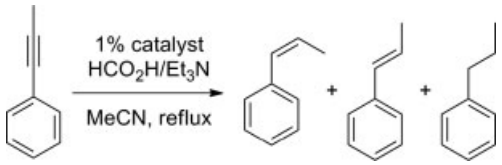
For the complexes **8b** and **9b**, a slight broadening of the carbene signal was observed, indicating that slow exchange of the carbene ligands takes place in solution. However, the coupling of the carbene carbon with the silver ion was not resolved.[19] This observation is supported by the fact that this broadening is only observed with the complexes bearing the most bulky ligands. This causes the dynamic ligand exchange to be slower than in the other complexes bearing less bulky ligands.

(NHC)Palladium(0) complexes. The silver(I) NHC complexes were used for transmetallation to the target palladium(0) complexes, which was performed according to a previously reported protocol.[6] In this reaction the relatively air-stable palladium precursor palladium(bis-*tert*-butyldiazabutadiene)(maleic anhydride) (Pd(tBuDAB)(ma)) was used;[20] the precipitation of the silver(I) halide is the driving force for the reaction. The pure products were obtained after filtration of the reaction mixture by precipitation with pentane (scheme 3).

Yields for this transformation are excellent, except for the *N*-isopropyl substituted NHC ligands in **10a** and **10b**, where only decomposition was observed. We believe that this is mostly due to the fact that the isopropyl substituent is a more electron-donating group than the Mes or DiPP substituents, which causes a higher electron density on the palladium center. As these zerovalent palladium complexes containing two donor ligands are already very electron-rich, a destabilizing effect is the likely result. The electronic influence of the ligand on the palladium can be countered by changing the other ligand so the electron-density at palladium is lowered; we routinely use the electron-poor



Scheme 4. Less electron-rich complexes can be isolated.



Scheme 5. Catalytic transfer hydrogenation of 1-phenyl-1-propyne.

maleic anhydride to stabilize the complex. However, even more electron-poor alkenes like tetracyanoethylene (TCNE) are also used.[20] When the silver(I) complex **10b** was reacted with a precursor bearing this alkene, the product **14** could be obtained in reasonable yield (scheme 4).

All spectral data are congruous with the results obtained for complexes **11** and **12**, except for the value of the carbene carbon in the ^{13}C NMR, which is found at 179.7 ppm, which is a higher field shift by about 15 ppm. We have observed a similar effect before when employing TCNE,[6] and relate this to the fact that the extremely electron-poor alkene renders the palladium only formally zerovalent. The chemical shift of the carbene carbon is closer to that of a divalent complex.[12]

X-ray structure determination. To unequivocally establish the structure of this type of complexes, a crystal structure analysis of complex **13b** was performed. X-ray quality crystals were obtained by slow evaporation of a dichloromethane solution of **13b** (figure 1).

The complex crystallizes in the triclinic spacegroup P −1 with four complex molecules in the asymmetric cell. On viewing the molecular structure it is apparent that the bidentate coordination of the C-N ligand causes the carbene ring, the pyridine ring and the palladium atom to lie virtually in one plane. Also the two carbon atoms of the maleic anhydride double bond lie in this plane. The bond length between palladium and the carbene carbon (Pd1-C1) is 2.042(3) Å, which is a normal value for palladium(0) NHC complexes.[6] The Pd1-N3 bond length is 2.173(2) Å, which to our knowledge is the shortest palladium nitrogen bond in a zerovalent complex bearing bidentate nitrogen donor functionalized NHC ligands. The bite angle of the C-N ligand is 77.73(9)°, which shows the rigid nature of the ligand.[21] Because of the planar nature of the coordination sphere around palladium, the difference in *trans* influence of the pyridine nitrogen and carbene carbon donors can be qualitatively gauged by the lengths of the bonds between palladium and the maleic anhydride carbons. The bond trans to the NHC (Pd1-C21) has a length of 2.104(3) Å, which is longer than the bond trans to the nitrogen donor (Pd1-C20, 2.068(3) Å). This indicates the stronger donating character of the carbene donor over the pyridine donor.

Catalytic transfer hydrogenation. As a probe for the activity and selectivity of the complexes **11–12**, transfer hydrogenation of 1-phenyl-1-propyne was performed (scheme 5).

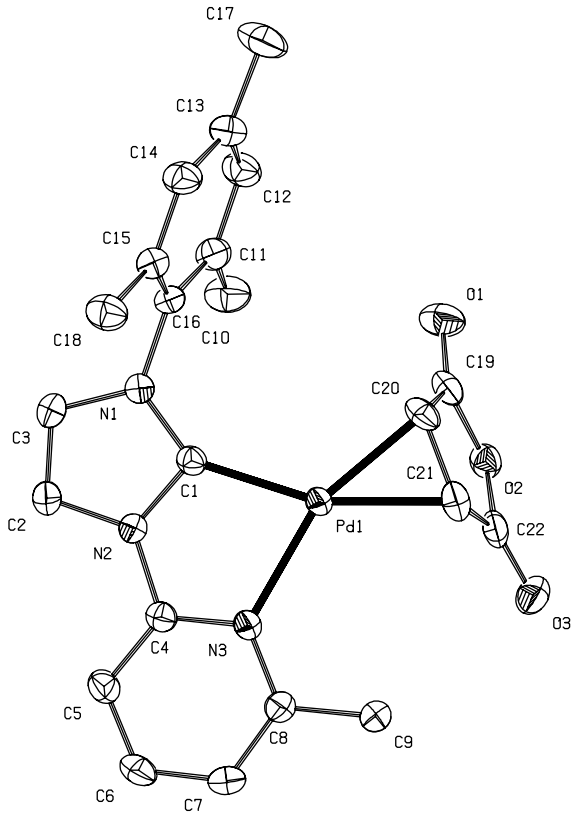


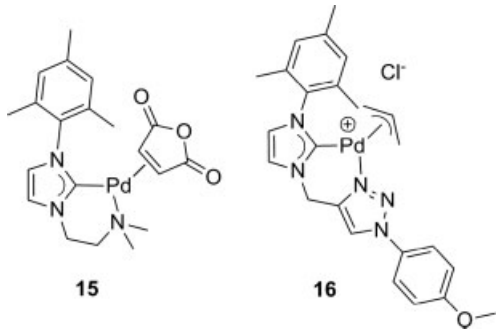
Figure 1. Displacement ellipsoid plot (50% probability level) of **13b**. H-atoms are omitted for the sake of clarity. Selected bond lengths (´Å) and angles (°): Pd1-C1 2.042(3), Pd1-N3 2.173(2), Pd1-C20 2.068(3), Pd1-C21 2.104(3), C20-C21 1.434(4); C1- Pd1-N3 77.73(9), C20-Pd1-C21 40.21(12), N1-C1-Pd1 143.3(2), N2-C1-Pd1 113.55(18).

Table 1. Catalytic transfer hydrogenation of 1-phenyl-1-propyne

entry	complex	Initial TOF (mol sub/ mol cat/h)	Selectivity *Z*/*E*/alkane (%)	Full conversion reached (h)
1	**11a**	83.7	99/1/0	2
2	**11b**	35.9	96/3/1	6
3	**12c**	68.5	95/4/1	3
4	**12d**	20.4	97/2/1	10
5	**15**	24.9	95/4/1	24
6	**16**	81.4	93/5/2	2.3

Reaction conditions: 1% 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. Initial TOF was determined with the initial linear part of the reaction profiles.

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.[14] This transformation shows a high chemo- and stereoselectivity which is unique to this type of complexes. With a secondary amine donor tethered to the NHC, selectivities of more than 99% towards *Z*-1-phenyl-1-propene were observed.[6] The results of our screening with differently substituted *N*-pyridyl-NHC ligands are summarized in table 1, together with results from complexes reported earlier (scheme 6).[6,8]



Scheme 6. Other catalysts used in transfer semihydrogenation.

Indeed, all Pd(*N*-pyridyl-NHC) complexes are very selective and fast catalysts in the transfer hydrogenation of 1-phenyl-1-propyne. The difference between the substitution patterns is also visible; the complexes with a methyl substituted pyridyl donor show a much lower TOF than their unsubstituted counterparts (entries 2 and 4 compared with entries 1 and 3). The aryl substituent on the NHC also has an influence on the TOF, but it is much less pronounced; the Mes substituent (entries 1 and 2) shows a higher rate than the DiPP substituent (entries 3 and 4). The selectivities are excellent for all four complexes, but it has to be noted that isomerization and overreduction occur for all complexes after full consumption of the alkyne. Apparently, the pyridyl donor does not displace the product alkene from the palladium. The affinity of the alkyne for palladium exceeds that of the alkene product, which is why the sidereactions only occur after full conversion of the substrate. Careful monitoring of the reaction is therefore necessary. When these results are compared to those obtained employing complexes bearing other chelating nitrogen donors on the NHC (entry 5 and 6), the selectivity is similarly high. However, a profound difference in the TOF and the behaviour after full consumption of the substrate is noted. Whereas complex **16** shows the same overreduction and isomerisation as observed with **11** and **12**, the slower catalyst **15** does not give any overreduction after full conversion. This is attributed to the higher donor strength of the tethered tertiary amine donor compared to the pyridine or the triazole donors. This implies a stronger coordination, which could also account for the lower reaction rate.

Conclusion

We have successfully synthesized zerovalent palladium complexes bearing heterobidentate pyridine functionalized NHC ligands and maleic anhydride *via* their silver(I) complexes. All complexes were obtained in excellent yields and purities. Only the palladium complexes with ligands containing *N*-isopropyl substituents could not be isolated. However, when a more electron-poor alkene was used as the ancillary ligand, the C-N ligated complex could be obtained in a reasonable yield. This implies that the high electron density on palladium was deleterious to the stability of the maleic anhydride complex. All stable compounds were fully characterized by NMR and MS measurements and a representative palladium(0) complex was analyzed by X-ray crystallography. Screening of four of the complexes in the catalytic transfer hydrogenation of 1-phenyl-1-propyne to *Z*-1-phenyl-1-propene showed that all complexes are good catalysts for this conversion, with high TOFs and excellent selectivities. As a secondary donor, the 2-pyridyl moiety is not the ideal choice for this catalytic conversion, as the affinity of its N-donor is apparently lower than that of the alkene product. This results in isomerization of the *Z*- to the *E*-alkene after full conversion of the substrate and hence an apparent lower selectivity.

Experimental Section

General procedures and instrumentation

All reactions involving palladium complexes were performed using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled using standard procedures.[22] All chemicals were used as received, with the exception of palladium bis-*t*-butyldiazabutadiene maleic anhydride, which was synthesized according to a literature procedure.[20] 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 3KeV. 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

The imidazoles **1–4** were synthesized according to a literature procedure.[15]

General synthesis of 1-aryl-3-pyridylimidazolium bromides

Compounds **5–6** were prepared according to a literature procedure.[11]

1-mesityl-3-(2-pyridyl)-imidazolium bromide 5a

The product (1.17 g, 87%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$):δ = 11.38 (s, 1H, NCHN), 9.20 (d, ^{3}J(HH) = 8.1 Hz, 1H, 6-pyr-H), 8.91 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 8.53 (dd, ^{3}J(HH) = 6.6 Hz, ^{4}J(HH) = 1.5 Hz, 1H, 3-pyr-H), 8.11 (dd, ^{3}J(HH) = 6.6 Hz, ^{3}J(HH) = 1.5 Hz, 1H, 4-pyr-H), 7.49 (m, 1H, 5-pyr-H), 7.32 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 7.03 (s, 2H, m-aryl-H), 2.33 (s, 3H, p-aryl-CH_3), 2.17 (s, 6H, o-aryl-CH_3).

1-mesityl-3-(6-methyl-2-pyridyl)-imidazolium bromide 5b

The product (3.27 g, 95%) was obtained as an off-white powder. ^{1}H NMR ($CDCl_3$):δ = 11.10 (s, 1H, NCHN), 8.97 (s, 1H, CH), 8.94 (d, ^{3}J(HH) = 7.5 Hz, 1H, 3-pyr-H), 7.96 (dd, 1H, ^{3}J(HH) = 7.5 Hz, ^{3}J(HH) = 7.8 Hz, 4-pyr-H), 7.33 (d, ^{3}J(HH) = 7.8 Hz, 1H, 5-pyr-H), 7.30 (s, 1H, CH), 7.04 (s, 2H, m-aryl-H), 2.59 (s, 3H, 6-pyr-CH_3), 2.34 (s, 3H, p-aryl-CH_3), 2.17 (s, 6H, o-aryl-CH_3). ^{13}C NMR ($CDCl_3$):δ = 160.3 (6-pyr-C), 146.5 (2-pyr-C), 142.9 (4-pyr-CH), 142.3 (p-aryl-C), 135.5 (o-aryl-C), 132.6 (i-aryl-C), 132.1 (NCHN), 131.0 (m-aryl-CH), 121.6, 126.1, 126.6 (2 CH, 5-pyr-CH), 114.1 (3-pyr-CH), 25.3 (6-pyr-CH_3), 22.6 (p-aryl-CH_3), 18.6 (o-aryl-CH_3). MS(FAB+): m/z = 278.1656 for $C_{18}H_{20}N_3$ $[M - Br]^+$.

1-(2,6-diisopropylphenyl)-3-(2-pyridyl)-imidazolium bromide 6a

The product (0.53 g, 96%) was obtained as a brown solid. ^{1}H NMR ($CDCl_3$):δ = 11.01 (s, 1H, NCHN), 9.30–9.34 (m, 2H, CH, 6-pyr-H), 8.51 (d, ^{3}J(HH) = 5.1 Hz, 1H, 3-pyr-CH), 8.14 (dd, ^{3}J(HH) = 8.1 Hz, ^{3}J(HH) = 5.1 Hz, 1H, 4-pyr-CH), 7.57 (t, ^{3}J(HH) = 8.1 Hz, 1H, p-aryl-CH), 7.49 (dd, ^{3}J(HH) = 4.8 Hz, ^{3}J(HH) = 8.1 Hz, 1H, 5-pyr-CH), 7.34 (m, 3H, m-aryl-CH, CH), 2.41 (dq, ^{3}J(HH) = 6.9 Hz, ^{3}J(HH) = 6.9 Hz, 2H, ^{i}Pr-CH), 1.28 (d, ^{3}J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3), 1.17 (d, ^{3}J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR ($CDCl_3$):δ = 148.7 (6-pyr-CH), 145.9 (2-pyr-C), 145.1 (o-aryl-C), 141.4 (4-pyr-CH), 135.4 (i-aryl-C), 132.3 (NCHN), 130.0 (p-aryl-CH), 125.7 (5-pyr-CH), 124.9 (m-aryl-CH), 123.8 (CH), 121.0 (CH), 116.6 (3-pyr-CH), 28.9 (^{i}Pr-CH), 24.3 (^{i}Pr-CH_3).

1-(2,6-diisopropylphenyl)-3-(6-methyl-2-pyridyl)-imidazolium bromide 6b

The product (0.25 g, 89%) was obtained as a brown solid. ^{1}H NMR ($CDCl_3$):δ = 10.81 (s, 1H, NCHN), 9.41 (s, 1H, CH), 9.02 (d, ^{3}J(HH) = 8.4 Hz, 1H, 3-pyr-CH), 7.99 (dd, ^{3}J(HH) = 8.4 Hz, ^{3}J(HH) = 7.8 Hz, 1H, 4-pyr-CH), 7.58 (t, ^{3}J(HH) = 7.8 Hz, 1H, p-aryl-CH), 7.32 (m, 4H, CH, m-aryl-CH, 5-pyr-CH), 2.59 (s, 3H, 6-pyr-CH_3), 2.41 (dq, ^{3}J(HH) = 6.9 Hz, ^{3}J(HH) = 6.6 Hz, 2H, ^{i}Pr-CH), 1.28 (d, ^{3}J(HH) = 6.6 Hz, 6H, ^{i}Pr-CH_3), 1.17 (d, ^{3}J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$):δ = 157.7 (6-pyr-C), 144.1 (2-pyr-C), 143.4 (o-aryl-C), 140.6 (4-pyr-CH), 137.5 (i-aryl-C), 133.8 (NCHN), 131.3 (p-aryl-CH), 129.1 (5-pyr-CH), 124.2 (m-aryl-CH), 123.7 (CH), 120.2 (CH), 112.2 (3-pyr-CH), 27.7 (^{i}Pr-CH), 23.9 (6-pyr-CH_3), 23.3 (^{i}Pr-CH_3). MS(FAB+): m/z = 320.2122 for $C_{21}H_{26}N_3$ $[M - Br]^+$.

General synthesis of imidazolium iodides 7

The pyridylimidazole was stirred in 10 equivalents of 2-iodopropane at reflux for 16 hours. The product precipitates from the reaction mixture and was washed with diethyl ether until the supernatant was colourless.

1-isopropyl-3-(2-pyridyl)-imidazolium iodide 7b

The product (0.90 g, 87%) was obtained as a beige solid. ^{1}H NMR ($CDCl_3$):δ = 11.10 (s, 1H, NCHN), 8.57 (d, ^{3}J(HH) = 7.8 Hz, 1H, 6-pyr-C), 8.50 (d, ^{3}J(HH) = 1.8 Hz, 1H, 3-pyr-CH), 8.32 (s, 1H, CH), 8.03 (dd, ^{3}J(HH) = 7.8 Hz, ^{4}J(HH) = 1.8 Hz, 1H, 5-pyr-CH), 7.68 (s, 1H, CH), 7.45 (m, 1H, 4-pyr-CH), 5.24 (septet, ^{3}J(HH) = 6.9 Hz, 1H, ^{i}Pr-CH), 1.72 (d, ^{3}J(HH) = 6.6 Hz, 12H, ^{i}Pr-CH_3). ^{13}C NMR ($CDCl_3$):δ = 149.1 (4-pyr-CH), 145.9 (5-pyr-CH), 140.5 (3-pyr-CH), 133.4 (NCHN), 125.3 (6-pyr-CH), 121.1 (CH), 119.5 (CH), 115.2 (2-pyr-CH), 54.4 (^{i}Pr-CH), 23.3 (^{i}Pr-CH_3). MS(FAB+): m/z = 188.1186 for $C_{11}H_{14}N_3$ $[M - I]^+$.

1-isopropyl-3-(6-methyl-2-pyridyl)-imidazolium iodide 7b

The product (1.72 g, 89% based on the imidazole) was obtained as a yellow crystalline solid. ^{1}H NMR ($CDCl_3$):δ = 11.04 (s, 1H, NCHN), 8.33 (s, 1H, CH), 8.31 (d, ^{3}J(HH) = 8.1 Hz, 1H, 3-pyr-CH), 7.89 (dd, ^{3}J(HH) = 8.1 Hz, ^{3}J(HH) = 7.8 Hz, 1H, 4-pyr-CH), 7.66 (s, 1H, CH), 7.28 (d, ^{3}J(HH) = 7.8 Hz, 1H, 5-pyr-CH), 5.26 (septet, ^{3}J(HH) = 6.3 Hz, 1H, ^{i}Pr-CH), 1.72 (d, ^{3}J(HH) = 6.3 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$):δ = 159.1 (4-pyr-CH), 145.1 (5-pyr-CH), 140.4 (3-pyr-CH), 133.0 (NCHN), 128.4 (6-pyr-C), 121.14 (CH), 119.4 (CH), 111.7 (2-pyr-C), 54.2 (^{i}Pr-CH), 24.1 (6-pyr-CH_3), 23.3 (^{i}Pr-CH_3). MS(FAB+): m/z = 202.1344 for $C_{12}H_{16}N_3$ [M-I]$^+$.

General procedure for the synthesis of silver(I) N-heterocyclic carbene complexes

Complexes **8–10** were synthesized according to a literature procedure.[16]

[1-mesityl-3-(2-pyridyl)-imidazol-2-ylidene] silver(I) bromide 8a

The product (0.23 g, 89%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2):δ = 8.52 (d, ^{3}J(HH) = 4.5 Hz, 1H, 6-pyr-CH), 8.31 (d, ^{3}J(HH) = 8.7 Hz, 1H, 3-pyr-CH), 8.12 (m, 1H, CH), 7.91 (m, 1H, 4-pyr-CH), 7.39 (dd, ^{3}J(HH) = 6.6 Hz, ^{3}J(HH) = 5.7 Hz, 1H, 5-pyr-CH), 7.08 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 6.96 (s, 2H, m-aryl-CH), 2.33 (s, 3H, p-aryl-CH_3), 2.02 (s, 6H, o-aryl-CH_3). ^{13}C NMR (CD_2Cl_2):δ = 182.4 (NCN), 150.7 (2-pyr-C), 148.5 (6-pyr-CH), 139.7 (p-aryl-C), 139.3 (4-pyr-CH), 135.8 (i-aryl-C), 134.8 (o-aryl-C), 129.4 (m-aryl-CH), 123.9 (CH), 123.4 (5-pyr-CH), 120.1 (CH), 115.2 (3-pyr-CH), 20.9 (p-aryl-CH_3), 17.6 (o-aryl-CH_3). MS(FAB+): m/z = 635.1900 for $C_{34}H_{34}N_6Ag$ $[M - Br]^+$.

[1-mesityl-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] silver(I) bromide 8b

The product (0.38 g, 83%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2):δ = 8.06 (s, 1H, CH), 7.92 (d, ^{3}J(HH) = 8.1 Hz, 1H, 3-pyr-H), 7.79 (m, 1H, 4-pyr-H), 7.26 (dd, ^{3}J(HH) = 7.8 Hz, ^{4}J(HH) = 2.7 Hz, 1H, 5-pyr-H), 7.22 (s, 1H, CH), 7.08 (s, 2H, m-aryl-H), 2.60 (s, 3H, 6-pyr-CH_3), 2.35 (s, 3H, p-aryl-CH_3), 2.02 (s, 6H, o-aryl-CH_3). ^{13}C NMR (CD_2Cl_2):δ = 183.2 (NCN), 159.1 (6-pyr-C), 150.0 (2-pyr-C), 139.9 (4-pyr-CH), 139.7 (i-aryl-C), 136.2 (p-aryl-C), 135.0 (o-aryl-C), 129.5 (m-aryl-CH), 123.6 (CH), 119.8 (5-pyr-CH), 111.7 (3-pyr-CH), 24.1 (6-pyr-CH_3), 21.1 (p-aryl-CH_3), 17.8 (o-aryl-CH_3). MS(FAB+): m/z = 384.0630 for $C_{18}H_{19}N_3Ag$ $[M - Br]^+$.

[1-(2,6-diisopropylphenyl)-3-(2-pyridyl)-imidazol-2-ylidene] silver(I) bromide 9a

The product (0.33 g, 86%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2):δ = 8.60 (m, 1H, 4-pyr-H), 8.10 (s, 1H, CH), 7.97 (d, ^{3}J(HH) = 7.5 Hz, 1H, 6-pyr-H), 7.29–7.54 (m, 5H, 5-pyr-H, 3-pyr-H, m-aryl-H, p-aryl-H), 7.26 (s, 1H, CH), 2.42 (septet, 2H, ^{3}J(HH) = 6.9 Hz, ^{i}Pr-CH), 1.12–1.31 (m, 12H, ^{i}Pr-CH_3).

[1-(2,6-diisopropylphenyl)-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] silver(I) bromide 9b

The product (0.75 g, 95%) was obtained as a brown solid. ^{1}H NMR (CD_2Cl_2):δ = 8.03 (s, 1H, CH), 7.84 (m, 1H, 4-pyr-H), 7.54 (t, 1H, ^{3}J(HH) = 3.6 Hz, p-aryl-CH), 7.24–7.44 (m, 4H, m-aryl-H, 3-pyr-H, 5-pyr-H), 7.21 (s, 1H, CH), 2.66 (s, 3H, 6-pyr-CH_3), 2.51 (m, 2H, ^{i}Pr-CH), 1.12–1.27 (m, 12H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2):δ = 183.4 (NCN), 159.3 (6-pyr-C), 150.0 (2-pyr-C), 145.9 (o-aryl-C), 139.6 (4-pyr-CH), 135.5 (i-aryl-C), 130.8 (p-aryl-CH), 124.7 (CH), 124.5 (m-aryl-CH), 123.7 (5-pyr-CH), 119.7 (CH), 111.9 (3-pyr-CH), 28.5 (^{i}Pr-CH), 28.4 (6-pyr-CH_3), 24.3 (^{i}Pr-CH_3). MS(FAB+): m/z = 426.1101 for $C_{21}H_{25}N_3Ag$ $[M - Br]^+$.

[1-isopropyl-3-(2-pyridyl)-imidazol-2-ylidene] silver(I) iodide 10a

The product (0.14 g, 92%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2):δ = 8.46 (d, ^{3}J(HH) = 6.0 Hz, 1H, 6-pyr-H), 8.14 (d, ^{3}J(HH) = 7.5 Hz, 1H, 3-pyr-H), 7.87 (dd, ^{3}J(HH) = 6.0 Hz, ^{3}J(HH) = 4.5 Hz,

1H, 5-pyr-H), 7.80 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 7.30–7.46 (dd, ^{3}J(HH) = 7.5 Hz, ^{3}J(HH) = 4.5 Hz, 1H, 4-pyr-H), 7.17 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 4.94 (septet, ^{3}J(HH) = 6.6 Hz, 1H, ^{i}Pr-CH), 1.52 (d, ^{3}J(HH) = 6.6 Hz, 6H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 174.9 (NCN), 148.8 (2-pyr-C), 148.0 (6-pyr-CH), 137.6 (4-pyr-CH), 123.6 (5-pyr-CH), 120.1 (CH), 117.9 (CH), 115.5 (3-pyr-CH), 55.0 (^{i}Pr-CH), 23.8 (^{i}Pr-CH$_3$). MS(FAB+): m/z = 294.0166 for $C_{11}H_{13}N_3Ag$ [M − I]$^+$.

[1-isopropyl-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] silver(I) iodide 10b

The product (0.30 g, 88%) was obtained as a white solid. ^{1}H NMR (CD_2Cl_2):δ = 7.78 (dd, ^{3}J(HH) = 7.8 Hz, ^{3}J(HH) = 8.1 Hz, 1H, 4-pyr-CH), 7.76 (d, ^{3}J(HH) = 2.1 Hz, 1H, CH), 7.59 (d, ^{3}J(HH) = 8.1 Hz, 1H, 5-pyr-CH), 7.26 (d, ^{3}J(HH) = 2.1 Hz, 1H, CH), 7.21 (d, ^{3}J(HH) = 7.8 Hz, 1H, 3-pyr-CH), 4.87 (septet, ^{3}J(HH) = 6.6 Hz, 1H, ^{i}Pr-CH), 2.53 (s, 3H, 6-pyr-CH$_3$), 1.55 (d, ^{3}J(HH) = 6.6 Hz, 6H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 181.4 (NCN), 158.4 (6-pyr-C), 150.1 (2-pyr-C), 139.6 (4-pyr-CH), 119.6 (CH), 118.6 (CH), 112.9 (5-pyr-CH), 111.6 (3-pyr-CH), 55.1 (^{i}Pr-CH), 24.0 (6-pyr-CH$_3$), 23.5 (^{i}Pr-CH$_3$). MS(FAB+): m/z = 308.0320 for $C_{12}H_{15}N_3Ag$ [M-I]$^+$.

General synthesis of palladium(0) N-heterocyclic carbene complexes

Complexes **11–12** and **14** were synthesized according to a literature procedure.[6]

[1-mesityl-3-(2-pyridyl)-imidazol-2-ylidene] palladium(0) maleic anhydride anhydride 11a

The product (0.30 g, 96%) was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2):δ = 8.75 (d, 1H, ^{3}J(HH) = 7.5 Hz, 6-pyr-H), 8.07 (dd, ^{3}J(HH) = 5.4 Hz, ^{4}J(HH) = 7.5 Hz, 1H, 5-pyr-H), 7.70 (d, 1H, ^{3}J(HH) = 1.8 Hz, CH), 7.57 (d, 1H, ^{3}J(HH) = 7.5 Hz, 3-pyr-H), 7.42 (dd, ^{3}J(HH) = 7.5 Hz, ^{3}J(HH) = 5.4 Hz, 1H, 4-pyr-H), 7.10 (d, ^{3}J(HH) = 1.8 Hz, 1H, CH), 7.07 (broad s, 2H, m-aryl-CH), 3.55 (broad s, 1H, ma), 3.50 (broad s, 1H, ma), 2.40 (s, 3H, p-aryl-CH$_3$), 2.06 (s, 6H, o-aryl-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 192.7 (NCN), 173.1 (CO), 172.3 (CO), 152.4 (2-pyr-CH), 151.9 (6-pyr-C), 140.82 (4-pyr-CH), 139.0 (p-aryl-C), 135.6 (i-aryl-C), 134.7 (o-aryl-C), 133.9 (o-aryl-C), 129.4 (m-aryl-CH), 128.6 (m-aryl-CH), 124.4 (CH), 123.7 (5-pyr-CH), 115.5 (CH), 111.0 (3-pyr-CH), 42.2 (alkene), 39.9 (alkene), 20.9 (p-aryl-CH$_3$), 17.6 (o-aryl-CH$_3$), 17.4 (o-aryl-CH$_3$). MS(FAB+): m/z = 369.0464 for $C_{17}H_{17}N_3Pd$ [M − $C_4H_2O_3$]$^+$. Anal. Calcd. for $C_{21}H_{19}N_3O_3Pd$ C, 53.92; H, 4.09; N, 8.98. Found: C, 54.07; H, 4.35; N, 9.12.

[1-mesityl-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] palladium(0) maleic anhydride anhydride 11b

The product (50 mg, 91%) was obtained as a pale yellow solid. ^{1}H NMR (CD_2Cl_2):δ = 7.89–7.95 (m, 1H, 5-pyr-H), 7.68 (s, 1H, CH), 7.39 (m, 2H, 3-pyr-H, 4-pyr-H), 7.01–7.13 (m, 3H, CH, m-aryl-CH), 3.46 (broad s, 2H, ma), 2.87 (s, 3H, 6-pyr-CH$_3$), 2.42 (s, 3H, p-aryl-CH$_3$), 2.07 (s, 6H, o-aryl-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 191.7 (NCN), 174.0 (CO), 173.4 (CO), 161.3 (6-pyr-C), 151.9 (2-pyr-C), 140.8 (4-pyr-CH), 139.1 (p-aryl-C), 135.8 (i-aryl-C), 134.1 (o-aryl-C), 129.8 (m-aryl-CH), 128.7 (m-aryl-CH), 124.4 (CH), 122.9 (CH), 115.8 (5-pyr-CH), 107.8 (3-pyr-CH), 41.3 (alkene), 39.9 (alkene), 28.3 (6-pyr-CH$_3$), 17.9 (o-aryl-CH$_3$), 17.6 (o-aryl-CH). MS(FAB+): m/z = 383.0623 for $C_{18}H_{19}N_3Pd$ [M − $C_4H_2O_3$]$^+$. Anal. Calcd. for $C_{22}H_{22}N_3O_3Pd$ C, 54.84; H, 4.39; N, 8.72. Found: C, 54.63; H, 4.21; N, 9.05.

[1-(2,6-diisopropylphenyl)-3-(2-pyridyl)-imidazol-2-ylidene] palladium(0) maleic anhydride anhydride 12a

The product (49 mg, 91%) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2):δ = 8.77 (d, ^{3}J(HH) = 5.1 Hz, 1H, 6-pyr-CH), 8.09 (dd, ^{3}J(HH) = 8.4 Hz, ^{4}J(HH) = 1.5 Hz, 1H, 5-pyr-H), 7.74 (s, 1H, CH), 7.61 (d, ^{3}J(HH) = 7.8 Hz, 1H, 3-pyr-H), 7.55 (t, 1H, ^{3}J(HH) = 7.5 Hz, p-aryl-H), 7.44 (m, 1H, 4-pyr-H), 7.36 (d, ^{3}J(HH) = 7.5 Hz, 2H, m-aryl-H), 7.19 (s, 1H, CH), 3.48–3.53 (broad s, 2H, ma), 2.37–2.68 (m, 2H, ^{i}Pr-CH), 1.05–1.42 (m, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 198.3 (NCN), 173.4 (CO), 152.5 (2-pyr-C), 151.9 (6-pyr-CH), 145.6 (m-aryl-C), 144.9 (m-aryl-C), 140.7 (4-pyr-CH), 135.4 (i-aryl-CH), 130.0 (p-aryl-C), 125.5 (o-aryl-C), 124.1 (CH), 123.7 (CH), 115.1 (5-pyr-CH), 111.0 (3-pyr-CH), 42.8 (alkene), 40.4 (alkene), 28.4 (^{i}Pr-CH), 24.1 (^{i}Pr-CH$_3$), 23.6 (^{i}Pr-CH$_3$), 23.0 (^{i}Pr-CH$_3$), 22.3 (^{i}Pr-CH$_3$). MS(FAB+): m/z = 411.0938 for $C_{20}H_{23}N_3Pd$ [M − $C_4H_2O_3$]$^+$. Anal. Calcd. for $C_{24}H_{25}N_3O_3Pd$ C, 56.53; H, 4.94; N, 8.24. Found: C, 56.08; H, 4.91; N, 8.37.

[1-(2,6-diisopropylphenyl)-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] palladium(0) maleic anhydride anhydride 12b

The product (0.10 g, 94%) was obtained as an ochre solid. ^{1}H NMR (CD_2Cl_2):δ = 7.95 (d, ^{3}J(HH) = 7.8 Hz, 1H, 5-pyr-H), 7.69 (s, 1H, CH), 7.56 (dd, ^{3}J(HH) = 7.8 Hz, ^{3}J(HH) = 7.8 Hz, 1H, p-aryl-H), 7.35–7.41 (m, 4H, m-aryl-H, 3-pyr-H, 4-pyr-H), 7.16 (s, 1H, CH), 3.53 (d, ^{3}J(HH) = 3.9 Hz, 1H, CH), 3.41 (d, ^{3}J(HH) = 3.9 Hz, 1H, ma), 2.88 (s, 3H, 6-pyr-CH$_3$), 2.53 (m, 2H, ^{i}Pr-CH), 1.10–1.33 (m, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 192.4 (NCN), 173.2 (CO), 172.0 (CO), 161.4 (6-pyr-C), 151.7 (2-pyr-C), 145.5 (o-aryl-C), 144.7 (o-aryl-C), 140.5 (4-pyr-CH), 135.5 (p-aryl-CH), 129.9 (i-aryl-C), 125.5 (m-aryl-C), 124.4 (m-aryl-CH), 123.5 (CH), 115.2 (5-pyr-CH), 112.9 (CH), 107.7 (3-pyr-CH), 41.8 (alkene), 40.1 (alkene), 29.1 (^{i}Pr-CH), 28.6 (^{i}Pr-CH), 28.2 (6-pyr-CH$_3$), 24.4 (^{i}Pr-CH$_3$), 23.2 (^{i}Pr-CH$_3$), 22.8 (^{i}Pr-CH$_3$), 22.3 (^{i}Pr-CH$_3$). MS(FAB+): m/z = 425.1088 for $C_{21}H_{25}N_3Pd$ [M − $C_4H_2O_3$]$^+$. Anal. Calcd. for $C_{25}H_{27}N_3O_3Pd$ C, 57.31; H, 5.19; N, 8.02. Found: C, 57.77; H, 4.91; N, 8.24.

[1-isopropyl-3-(6-methyl-2-pyridyl)-imidazol-2-ylidene] palladium(0) tetracyanoethylene 14

The product (0.10 g, 72%) was obtained as a dark orange solid. ^{1}H NMR (CD_2Cl_2):δ = 8.02 (dd, 1H, ^{3}J(HH) = 7.8 Hz, ^{3}J(HH) = 8.1 Hz, 4-pyr-CH), 7.62 (d, ^{3}J(HH) = 2.1 Hz, 1H, CH), 7.45 (d, ^{3}J(HH) = 7.8 Hz, 31H, -pyr-H), 7.38 (d, ^{3}J(HH) = 8.1 Hz, 1H, 5-pyr-H), 7.29 (d, ^{3}J(HH) = 2.1 Hz, 1H, CH), 4.85 (septet, ^{3}J(HH) = 6.6 Hz, 1H, ^{i}Pr-CH), 2.99 (s, 3H, 6-pyr-CH$_3$), 1.64 (d, ^{3}J(HH) = 6.6 Hz, 6H, ^{i}Pr-CH$_3$). ^{13}C NMR (CD_2Cl_2):δ = 179.7 (NCN), 161.2 (6-pyr-C), 151.7 (2-pyr-C), 142.5 (4-pyr-CH), 123.7 (CH), 119.4 (CH), 117.0 (5-pyr-CH), 115.8 (TCNE), 114.9 (TCNE), 108.5 (3-pyr-CH), 55.6 (^{i}Pr-CH), 27.9 (6-pyr-CH$_3$), 23.4 (^{i}Pr-CH$_3$). MS(FAB+): m/z = 436.0512 for $C_{18}H_{16}N_7Pd$ [M + H]$^+$. Anal. Calcd. for $C_{27}H_{25}N_7O_3Pd$ C, 58.54; H, 4.55; N, 17.70. Found: C, 58.36; H, 4.89; N, 18.03.

X-ray data collection, reduction, and refinement

A Suitable single crystal of **11b** 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

35 sec. The generator setting was 50 kV and 180 mA. Diffraction data was collected over the full sphere and the frames were integrated using the Bruker SMART[23] software package using the narrow frame algorithm. Data were corrected for absorption effects using the SADABS routine (empirical multi-scan method). Atomic scattering factors for non-hydrogen elements were taken from the literature tabulations.[24] The structure solution was found by using direct methods as implemented in the SHELXS-97 package[25] and was refined with SHELXL-97[26] 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. **11b** ($C_{22}H_{21}N_3O_3Pd$): FW = 481.82, triclinic, space group $P-1$, $Z = 4$, $a = 9.9708(4)$, $b = 12.1777(5)$, $c = 17.6335(7)$, $\alpha = 80.365(1)$, $\beta = 76.437(1)$, $\gamma = 75.693(1)$, $V = 2003.17(14)$, $F000 = 976$, $T = 153(2)$, $\mu = 0.927$, 21223 reflections collected, 9931 reflections unique ($R_{int} = 0.0277$), 7729 reflections observed ($F > 2\sigma(F)$). The final was $R_1 = 0.0339$ and $wR_2 = 0.0845$ (all data). CCDC 789503 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: 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 2 mmol 1-phenyl-1-propyne, 10 mmol triethylammonium formiate and 10 mmol p-xylene in 12 ml acetonitrile was heated to reflux. A solution of 1 mol-percent of catalyst (relative to the alkyne substrate) in 2 ml acetonitrile was added to the reaction mixture. Periodically, samples were taken over a period of 24 hours. Aliquots from the reaction mixtures were quenched by dilution with EtOH and were analyzed by GC to determine conversions and composition.

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