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Modular Synthesis of Bidentate Triazolyl-Functionalized N-Heterocyclic Carbenes and Their Palladium Complexes

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New heterobidentate N-heterocyclic carbene-triazolyl ligands and several of their palladium(II) complexes have been synthesized in a modular fashion using click chemistry. These complexes are the first examples where triazolyl-substituted NHCs exhibit bidentate behavior, which was confirmed by NMR and X-ray diffraction studies. The synthesis of the complexes could be achieved in relatively few steps by introducing the diversity at a late stage in the synthesis. The complexes are active precatalysts in the transfer semihydrogenation of alkynes to *Z*-alkenes, with activity and selectivity depending on the triazolyl substituent and the NHC nitrogen substituent. Selectivities as high as 99% were observed.

Introduction

N-Heterocyclic carbenes (NHCs) are versatile and widely applied ligands, with strong electron-donating capacities.[1−4] Their use leads to electron-rich and often (air-)stable complexes, due to the strong carbon−metal bond.[5,6] Complexes of NHCs with transition metals (TMs) are routinely applied in catalytic transformations such as (transfer) hydrogenation, C−C and C−heteroatom couplings, and polymerization reactions.[7,8] Besides the monodentate carbene systems, a significant amount of the reported complexes involve homo- and heteropolydentate ligands. By functionalizing NHCs with secondary donors, dissymmetric bidentate complexes can be obtained.[9−15] Through the choice of an appropriate hemilabile donor, an increase in complex stability and selectivity can be obtained without loss of activity.[16] The secondary donor atoms employed are most often phosphorus, oxygen, and nitrogen. Through these donors, a large range of steric and electronic effects can be imparted on the metal center.

We have pursued the synthesis of low-valent palladium complexes incorporating one strong carbon donor and one weak nitrogen donor with excellent results.[17,18] For these complexes a marked difference in the *trans*-positions as well as an influence on complex stability and selectivity in catalysis are observed. We are interested in the use of various secondary nitrogen donors to complement the NHC, with the goal of obtaining stable, yet catalytically active complexes. Even though a lot of different donor moieties have been reported, one intuitively obvious motif has not yet been reported as a ligating moiety. The 1,2,3-triazolyl group has gained popularity through the "click" chemistry coined by Sharpless and Meldal.[19−21] This N-heterocycle can be selectively and reliably synthesized from an alkyne and an azide under copper(I) catalysis.[22−24] Because of the ease of the

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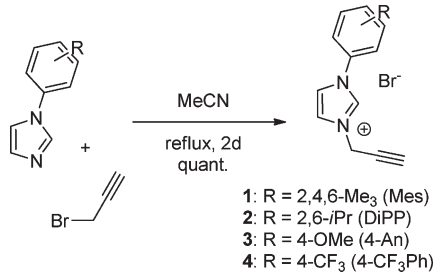
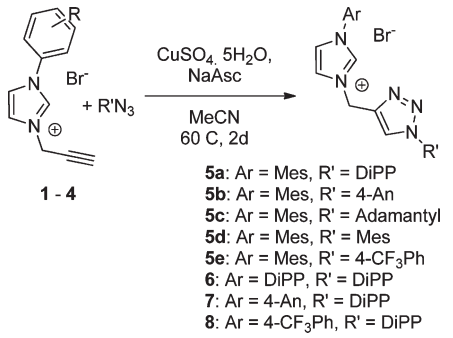
Scheme 1. Synthesis of *N*-(Prop-2-ynyl)imidazolium Salts



Scheme 2. Cu-Catalyzed Cycloaddition to Form the 1,2,3-Triazole Moiety



protocol and the high functional group tolerance, click chemistry is frequently employed in the synthesis of libraries. However, in organometallic and coordination chemistry, this versatile building block has not yet found the widespread use it has in other fields of chemistry. Most applications of click chemistry involve the use of the triazole as a linker,[25−27] except examples like Clickphine and others.[28,29] Furthermore, click chemistry is inherently suited for use in combinatorial research, which could make optimization in a catalytically active group of complexes a more facile process.

By combining the NHC and the triazole motifs in one ligand, we hope to generate a valuable new ligand type. We here report the modular synthesis and structural characterization of functionalized *N*-aryl-*N*′-propargyl imidazolium bromides and *N*-aryl-*N*′-triazolyl imidazolium bromides and their complexes with palladium(II), as well as a preliminary catalytic screening in the transfer hydrogenation of alkynes to *Z*-alkenes.

Results and Discussion

Ligand Synthesis. Easy access to the NHC-triazolyl bidentate ligands was accomplished in essentially two steps by first reacting *N*-aryl imidazoles[30] with propargyl bromide in refluxing acetonitrile, providing the alkynyl-imidazolium salts **1**−**4** in near quantitative yields, either by precipitation from or by concentration of the reaction mixture (Scheme 1).[25]

The products could easily be identified by their ^{1}H NMR spectra, where the signal characteristic for the imidazolium proton is observed at 9.57 ppm (for **1** in DMSO-d_6) or between 10.5 and 11.2 ppm (in $CDCl_3$). The propargyl substituent gives signals around 5.7 ppm for the CH_2 moiety and around 2.8 ppm for the alkynyl proton.

The propargyl imidazolium salts **1**−**4** were then reacted with several azides[31] in the presence of catalytic amounts of copper(II) sulfate and sodium ascorbate (NaAsc) to form the 1,2,3-triazolyl moiety. However, these conditions did not give the products in sufficient yield. A possibility for this discrepancy with the principles of click chemistry is the presence of the cationic charge of the imidazolium salt. With stoichiometric amounts of copper sulfate and sodium ascorbate in acetonitrile, the products **5**−**8** were obtained in acceptable to excellent yields (60−99%) and in high purity (Scheme 2).

The ^{1}H NMR signal for the imidazolium proton in $CDCl_3$ is generally found around 10.0 ppm, except in compound **8**, where the electron-poor *N*-aryl substituent induces a downfield shift to 10.86 ppm. The best indication of successful conversion is obtained from the signal of the triazolyl moiety. In the ^{1}H NMR, the triazolyl signal is observed between 8.5 and 9.0 ppm, with a notable exception for compound **5e**, where the electron-withdrawing *para*-trifluoromethylphenyl substituent induces a chemical shift of 9.44 ppm. For all ligand precursors, the methylene linker shows a slight downfield shift compared to the starting materials **1**−**4**.

An alternative approach to construct this ligand scaffold could be to first synthesize the triazole, which is then coupled to an imidazole. After several trials with propargyl bromide, it appeared that in our hands the cycloaddition suffered from side reactions.[25] Also propargyl alcohol as a building block did not give a viable route toward the desired triazolyl-substituted imidazolium salts. We abandoned this alternative for the above-mentioned, more reliable protocol.

Silver(I) NHC Complexes. With the ligand precursors in hand, the synthesis of the NHC-silver(I) complexes was attempted first. The preference for this reaction is understandable, as the desired complexes are often air stable, and generally no solvent pretreatment or additional base is required when silver(I) oxide is used to generate the carbene complexes.[32−34] Deprotonation is observed at C-2 of the NHC, and other acidic protons in the structure are generally not affected by the silver(I) oxide. However, the resulting complexes **9a**−**c** were highly unstable and could be observed only in solution. The main proof of complex formation is the disappearance of the C-2 proton signal in the ^{1}H NMR and the observation of the carbene carbon at 182.2 ppm in the ^{13}C NMR (for **9b**). On removal of the dichloromethane solvent, the complexes reverted to the imidazolium salts (Scheme 3).

One complex that could be isolated in good yield was the uncyclized silver(I) alkynyl-carbene complex **10**, which was stable for short periods under an inert atmosphere (Scheme 4).

The carbene carbon of **10** has a resonance at 183.8 ppm in the ^{13}C NMR, which is a normal value for silver(I)-carbene species. On the basis of this signal, and the fact that the

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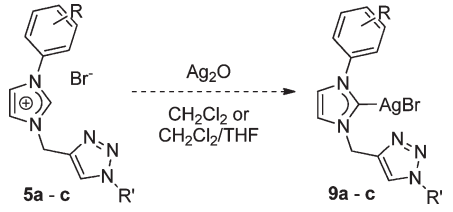
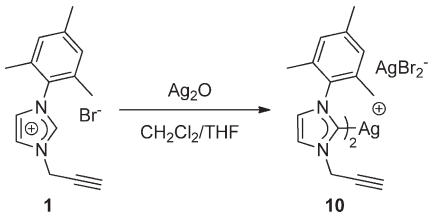
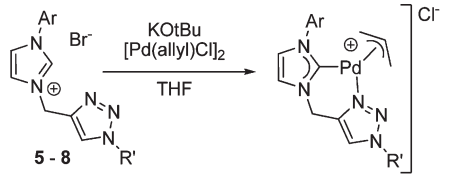
Scheme 3. Ag(I)-NHC Complexes Are Not Isolable, But Are Formed in Solution



Scheme 4. The Silver(I)-Alkynyl NHC Complex Is Moderately Stable



Scheme 5. Direct Synthesis of Palladium Allyl NHC Complexes



11a: Ar = Mes, R' = DiPP
11b: Ar = Mes, R' = 4-An
11c: Ar = Mes, R' = Adamantyl
11d: Ar = Mes, R' = Mes
11e: Ar = Mes, R' = 4-CF_3Ph
12: Ar = DiPP, R' = DiPP
13: Ar = 4-An, R' = DiPP
14: Ar = 4-CF_3Ph, R' = DiPP

propargyl signals are not shifted significantly from the imidazolium salt **1**, a silver−alkyne interaction is not likely. In mass spectrometry experiments, a bis-carbene silver species that corresponds to the cationic part of **10** was detected. This is a commonly observed structural motif for silver(I) NHC complexes.

Palladium Complexes. When the silver(I) NHC complex **9c** was treated with η^3-allylpalladium chloride dimer *in situ*, the product complex **11c** could be obtained only in a low yield of 49%. The only widely applied alternative for the silver-assisted NHC formation is deprotonation of the imidazolium salts to obtain the free carbene, which is most often treated with a TM precursor complex *in situ*. We were pleased to find that none of the ligand precursors **5**−**8** seemed to suffer any ill effects when submitted to the strongly basic conditions associated with this protocol. In contrast to earlier experiments, potassium *tert*-butoxide as base in THF smoothly gave formation of the target tethered NHC-triazolyl ligands. Subsequent metalation with η^3-allylpalladium chloride dimer yielded the desired palladium complexes **11**−**14** in high yields (Scheme 5). It has to be noted that in our hands the complexation failed with other palladium precursors such as divalent $PdCl_2$(COD) and Pd(Me)Cl(COD)[18] and zerovalent precursors such as Pd(tBuDAB)(ma).[17]

In the ^{1}H NMR spectrum of **11**−**14** the bidentate nature of the ligand could clearly be deduced from the splitting of the methylene linker signal into an AB pattern caused by dissymmetrization of the protons. Only in complex **12**, with very bulky 2,6-diisopropylphenyl substituents on both the NHC and the triazolyl donor, could a trace amount of monodentate coordinated product be observed in the ^{1}H NMR. Furthermore, the triazolyl-CH shows a resonance between 9.31 and 8.37 ppm. These two extreme values correspond to complexes bearing electron-poor and electron-rich substituents on the triazolyl moiety, respectively. The carbene carbon is found between 176 and 181 ppm in the ^{13}C NMR, which is a value commonly observed for divalent palladium(NHC) complexes.[1]

In most cases, the pure compounds could be precipitated from the reaction mixture with pentane. If minor impurities were present, the complexes could easily be purified in air by column chromatography over basic alumina with a methanol−chloroform gradient. This demonstrates the high stability of the product complexes **11**−**14**, especially viewed relative to the silver complexes **9a**−**c** and the palladium complex **15** (*vide infra*). Apparently a subtle interplay between the strong donor capability of the NHC and the weaker donicity of the triazolyl moiety as well as the metal center determines the stability of the isolated complexes. Their formation is not affected by these effects, as in all cases the products were observed in solution.

To lend more weight to this hypothesis, freshly prepared alkynyl-substituted silver-NHC complex **10** was also reacted with palladium allyl chloride dimer in THF to obtain the monodentate palladium-NHC complex **15**. The desired compound was formed in quantitative yield, but decomposed on isolation. However, the click reaction could consecutively be performed on the palladium-alkynyl complex in the same pot. This way, C−N-ligated complexes **11**−**14** can be obtained from one common precursor complex in reasonable yields (40−60%), reducing the number of reactions required for assembly of a library of precatalysts (Scheme 6). The complexation is the only step for which the yield is moderate, but the overall yields are acceptable. This one-pot procedure shows the high potential of this modular approach toward diversification of the complexes.

X-ray Crystallography. In order to be completely certain of the coordinative behavior of our complexes, we attempted to grow X-ray quality crystals. However, all attempts to obtain single crystals of the halide complexes failed. After exchange of the chloride in **11c** for the noncoordinating triflate anion to obtain complex **16**, we were able to grow crystals by slow evaporation of a dichloromethane solution (Figure 1).

The coordinative properties of the ligand in **16** do not change on anion exchange, as no significant changes are observed in the ^{1}H and ^{13}C NMR spectra. The complex crystallizes in the triclinic space group $P\bar{1}$ with one independent cationic palladium moiety and one triflate anion. The allyl fragment is disordered in the crystal, confirming that both the *syn*- and *anti*-conformers are present. The X-ray crystal structure shows that the ligand is coordinated in a bidentate fashion; along with the NMR experiments this is strong evidence of the chelating properties of the ligand. The complex adopts a square-planar geometry, with the NHC-triazolyl ligand forming a six-membered chelate ring with the TM center. The ligand has a bite angle of 86.41(10)°, a small deviation from the ideal 90°. The carbene palladium distance is 2.044(3) Å, which is a length commonly reported for NHC-palladium allyl complexes.[35] The distance between N(3) of

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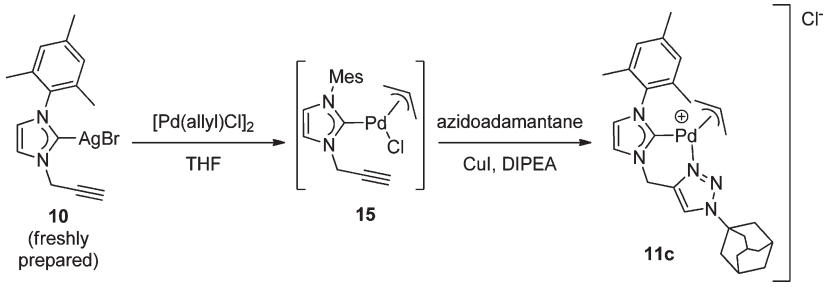
Scheme 6. Modular Approach to the Synthesis of NHC-Palladium Allyl Complexes



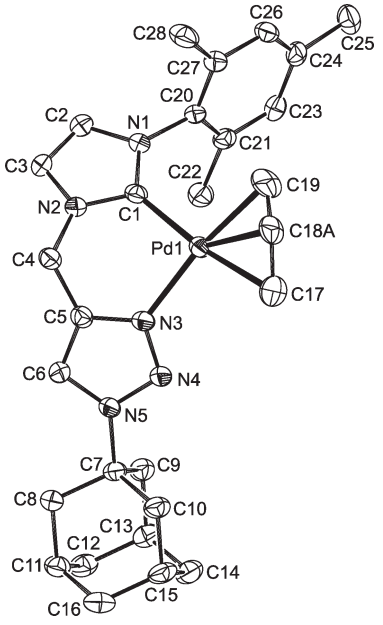


Figure 1. Displacement ellipsoid plot (50% probability level) of the cationic part of **16** in the crystal. H atoms and the triflate anion are omitted for the sake of clarity. Only the major form of the disordered allyl ligand is shown. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.044(3), Pd(1)−N(3) = 2.098(2), Pd(1)−C(17) = 2.186(3), Pd(1)−C18A = 2.163(6), Pd(1)−C18B = 2.132(8), Pd(1)−C(19) = 2.111(3); C(1)−Pd(I)−N(3) = 86.41(10).

the triazolyl donor and Pd is 2.098(2) Å; this is rather long compared to other donor moieties, reflecting the weaker donating ability of the triazole. For example, in a palladium complex bearing a picolyl-functionalized NHC, the distance between palladium and the secondary nitrogen donor is 2.042(8) Å.[36] In an analogous system with a 2-pyridyl-functionalized NHC, the distance between the nitrogen donor atom and palladium is 2.113(4) Å; this is a longer distance because the described system has a more strained geometry, with a less flexible secondary donor causing a decrease in orbital overlap (bite angle 78.44(16)°).[35] In a comparable monodentate triazole palladium complex, 2.1664(17) Å was reported for the Pd−N distance.[29] Finally, the different *trans*-influence of the donors in the bidentate ligand was qualitatively gauged in the different bond lengths between the palladium center and the distal allyl carbons. The Pd(1)−C(17) distance of the allyl-carbon in *trans*-position to the carbene is 2.186(3) Å, which is significantly longer than that of the allyl-carbon *trans* to the triazolyl donor (2.111(5) Å).

Scheme 7. Transfer Hydrogenation of Alkynes Catalyzed by Pd(NHC)allyl Complexes

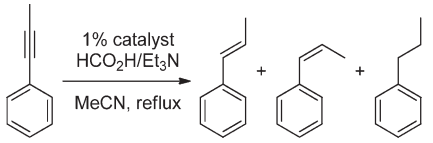


Table 1. Catalytic Transfer Hydrogenation of 1-Phenyl-1-propyne[a]

entry	precatalyst	TOF_{init}	selectivity *Z*/*E*/alkane (%)
1	**11a**	76.8	94/5/1
2	**11b**	81.4	93/5/2
3	**11c**	55.3	94/5/1
4	**11d**	62.9	94/5/1
5	**11e**	60.1	94/5/1
6	**12**	115.5	85/13/2
7	**13**	59.4	92/7/1
8	**14**	54.7	93/6/1

[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 at full conversion reported.

Catalytic Transfer Hydrogenation. As a probe for catalytic activity of **11**−**14**, the partial transfer hydrogenation of alkynes to *Z*-alkenes developed in our laboratories was used as a tool (Scheme 7).[17,37]

This remarkable transformation shows the unique reactivity of the NHC-palladium(0) systems;[37] 1-phenyl-1-propyne is converted to *Z*-1-phenyl-1-propene with a selectivity of 96% using an *in situ* generated Pd(0) complex bearing a monodentate NHC. Additionally, the chemoselectivity is very high, showing a high functional group tolerance. When a tethered secondary donor is introduced onto the NHC ligand, the selectivity could be increased to 99%, albeit at the cost of reaction rate.[17] An interesting result was that the divalent palladium species **11**−**14** did show significant catalytic activity and selectivity, where all earlier experiments indicated that a zerovalent palladium source was a prerequisite for this protocol. Most probably, reductive elimination of the auxiliary ligands takes place, leading to a zerovalent active species stabilized by the coordinating solvent. The results for the hydrogenation of our model substrate 1-phenyl-1-propyne are depicted in Table 1.

Several conclusions can be drawn from the results. First, all precatalysts show high *Z*-selectivity at full conversion. Precatalyst **12**, with two bulky 2,6-diisopropylphenyl substituents, shows the lowest selectivity toward the *Z*-alkene, but still it amounts to 85%, with mostly *E*-alkene as the

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byproduct (entry 6). The selectivity toward the desired product and the turnover frequency seem to be related; a high rate diminishes the selectivity. Apparently, a bulky substituent on the NHC gives a higher TOF; for the triazolyl donor, the electronic properties of its substituent seem to determine the rate of the reaction to some degree. For the *para*-anisyl and DiPP substituents, a beneficial effect is seen (entries 2 and 1, respectively). However, the adamantyl substituent gives the lowest TOF of all experiments (entry 3), showing the need for an aryl substituent on the triazole donor. For all complexes it is necessary to monitor the progress of the reaction, as side reactions occur after full consumption of the alkyne. After 24 h, all reactions showed between 60% and 70% *Z*-1-phenyl-1-propene with roughly equal amounts of *E*-1-phenyl-1-propene and propylbenzene as byproduct.

Conclusions

We have synthesized a series of NHC-triazolyl ligand precursors with various substitution patterns via click chemistry and successfully ligated them in a bidentate fashion to divalent palladium, resulting in very stable $C_{NHC}-N$ chelates. These complexes constitute the first example of NHC-ligand scaffolds, the weakly donating triazolyl moiety of which is employed as a secondary donor. A delicate balance was observed for the stability of the synthesized complexes: apparently the donicity of the triazole influences the stability of the palladium complexes to a high degree. This is a large contrast to our earlier research,[17,18] where the amine donor moiety stabilized the palladium irrespective of substitution pattern of the ligands or oxidation state of the transition metal. This difference demonstrates the importance of the nature of the secondary donor and supports the research performed in this area. Next to the coordinative behavior of the ligands itself, catalytic transfer hydrogenation of 1-phenyl-1-propyne was performed as a probe for the influence of the ligand on palladium. The complexes showed a relatively high activity, and the initial selectivity for the desired *Z*-1-phenyl-1-propene was high. However, products due to isomerization and further hydrogenation were formed after full consumption of the substrate. This shows that the affinity of the triazole donor for the palladium is lower than that of the *Z*-alkene product, which can then be isomerized or reduced to give the byproduct. High selectivities can be obtained if the reaction were to be monitored closely.

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.[38] All chemicals were obtained from commercial suppliers and were used as received, with the exception of *N*-aryl imidazoles **2**−**4**,[30] aryl azides,[31] and palladium allyl chloride dimer,[39] which were synthesized according to literature procedures. 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.

Synthesis of *N*-Mesitylimidazole 1. A literature procedure[30] was modified as follows: instead of purifying the crude product by column chromatography, the product (11.9 g, 64%) was obtained as off-white crystals by recrystallization from THF.

General Procedure for the Synthesis of [(1-(Prop-2-ynyl)-3-aryl)imidazolium] Bromides. A 0.3 M solution of *N*-arylimidazole was heated to reflux, after which 2.2 equiv of propargyl bromide (80% wt solution in toluene) was added. The solution was stirred at reflux for 2 days. The reaction mixture was then concentrated under reduced pressure to yield the product.

[(1-(Prop-2-ynyl)-3-mesityl)imidazolium] Bromide, 1. [25] The product was obtained as a white solid in 99% yield (5.62 g). ^{1}H NMR (DMSO-d_6): δ 9.57 (s, 1H, NCHN), 8.13 (s, 1H, CH), 7.99 (s, 1H, CH), 7.15 (s, 2H, aryl-H), 5.31 (s, 2H, CH_2), 3.91 (s, 1H, CCH), 2.50 (s, 3H, p-aryl-CH_3), 2.01 (s, 6H, o-aryl-CH_3).

[(1-(Prop-2-ynyl)-3-(2,6-diisopropylphenyl))imidazolium] Bromide, 2. The product was obtained as a white solid in 99% yield (2.78 g). ^{1}H NMR ($CDCl_3$): δ 10.51 (dd, ^4J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, NCHN), 8.05 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 7.59 (t, ^3J(HH) = 8.1 Hz, 1H, p-aryl-H), 7.36 (d, ^3J(HH) = 8.1 Hz, 1H, m-aryl-H), 7.28 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 5.86 (d, ^4J(HH) = 2.7 Hz, 2H, CH_2), 2.85 (t, ^4J(HH) = 2.7 Hz, 1H, CCH), 2.33 (dq, ^3J(HH) = 6.9 Hz, ^3J(HH) = 6.9 Hz, 2H, ^{i}Pr-CH), 1.24 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3), 1.17 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR ($CDCl_3$): δ 145.4 (o-aryl-C), 137.9 (NCN), 132.1 (i-aryl-C), 130.0 (p-aryl-C), 124.8 (m-aryl-C), 124.2 (CH), 122.8 (CH), 78.0 (alkyne), 74.4 (alkyne), 40.8 (CH_2), 28.7 (^{i}Pr-CH), 24.4 (^{i}Pr-CH). MS-(FAB+, *m*/*z*): calcd for $C_{18}H_{23}N_2$ $[M - Br]^+$ 267.1861; found 267.1857.

[(1-(Prop-2-ynyl)-3-(4-methoxyphenyl))imidazolium] Bromide, 3. The product was obtained as a white solid in 99% yield (0.66 g). ^{1}H NMR ($CDCl_3$): δ 10.97 (dd, ^4J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, NCHN), 7.70 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 7.64 (d, ^3J(HH) = 6.9 Hz, 2H, aryl-CH), 7.54 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 7.05 (d, ^3J(HH) = 6.9 Hz, 2H, aryl-CH), 5.63 (d, ^4J(HH) = 2.4 Hz, 2H, CH_2), 3.86 (s, 3H, OMe), 2,70 (t, ^4J(HH) = 2.4 Hz, 1H, CCH). ^{13}C NMR ($CDCl_3$): δ = 161.1 (p-aryl-C), 136.1 (i-aryl-C), 127.3 (NCHN), 123.6 (o-aryl-C), 122.0 (CH), 120.7 (CH), 115.7 (m-aryl-C), 77.9 (alkyne), 77.2 (alkyne), 55.8 (OMe), 40.4 (CH_2). MS(FAB+, *m*/*z*): calcd for $C_{13}H_{13}N_2O$ $[M - Br]^+$ 213.1028; found 213.1031.

[(1-(Prop-2-ynyl)-3-(4-trifluoromethylphenyl))imidazolium] Bromide, 4. The product was obtained as a white solid in 99% yield (0.94 g). ^{1}H NMR ($CDCl_3$): δ 11.14 (dd, ^4J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, NCHN), 8.03 (d, ^3J(HH) = 8.4 Hz, 2H, aryl-H), 7.92 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 7.84 (d, ^3J(HH) = 8.4 Hz, 2H, aryl-H), 7.84 (dd, ^3J(HH) = 1.8 Hz, ^4J(HH) = 1.8 Hz, 1H, CH), 5.62 (d, ^4J(HH) = 2.4 Hz, 2H, CH_2), 2.76 (t, ^4J(HH) = 2.4 Hz, 1H, CCH). ^{13}C NMR ($CDCl_3$): δ = 137.1 (NCHN), 136.5 (p-aryl-C), 132.6 (CF_3), 128.0 (aryl-C), 125.0 (i-aryl-C), 123.1 (CH), 122.8 (aryl-C), 120.9 (CH), 78.4 (alkyne), 73.9 (alkyne), 40.7 (CH_2). MS(FAB+, *m*/*z*): calcd for $C_{13}H_{11}N_2BrF_3$ $[M + H]^+$ 331.0058; found 331.0057.

General Procedure for the Cycloaddition of Alkynyl-Imidazolium Salts with Azides. Copper sulfate pentahydrate (4 mmol) and 1.5 equiv of sodium ascorbate were suspended to 0.1 M in acetonitrile. The mixture was stirred for 20 min at 60 °C, after which 1 equiv of alkynyl-imidazolium salt was added and stirred for an hour. Azide (1 equiv) was then added in a small volume of

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(39) Angelici, R. J. *Inorganic Syntheses*; Wiley: New York, 1990; Vol. *28*, p 342.

acetonitrile. The reaction was stirred at 60 °C for 2 days. The reaction mixture was filtered after cooling to room temperature and the solvent removed under reduced pressure. The residue was dissolved in 50 mL of dichloromethane and was washed with 3 × 30 mL of water. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated to yield the product.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazolium] Bromide, 5a. The product was obtained as a yellow solid in 96% yield (1.92 g). ^{1}H NMR (DMSO-d_6): δ 9.63 (s, 1H, NCHN), 8.62 (s, 1H, triazole-H), 8.14 (s, 1H, CH), 7.98 (s, 1H, CH), 7.58 (t, ^3J(HH) = 7.5 Hz, 1H), 7.40 (d, ^3J(HH) = 7.5 Hz, 2H), 7.15 (s, 2H, Mes), 5.78 (s, 2H, CH_2), 2.32 (s, 3H, p-aryl-CH_3), 2.04 (dq, ^3J(HH) = 6.9 Hz, ^3J(HH) = 6.9 Hz, 2H, ^{i}Pr-CH), 1.99 (s, 6H, o-aryl-CH_3), 1.06 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3), 1.04 (d, ^3J(HH) = 6.9 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR (DMSO-d_6): δ 145.0 (o-aryl-C), 140.0 (p-Mes-C), 137.7 (NCN), 134.0 (o-Mes-C), 132.6 (i-aryl-C), 132.4 (m-Mes-C), 131.1 (p-aryl-C), 130.9 (i-Mes-C), 129.0 (m-aryl-C), 127.0 (triazole-C), 123.7, 123.2 (2 CH), 54.7 (CH_2), 44.2 (triazole-CH), 27.7 (^{i}Pr-CH), 23.5, 23.4 (^{i}Pr-CH_3), 20.4 (o-Mes-CH_3), 16.5 (p-aryl-CH_3). MS(FAB+, m/z): calcd for $C_{27}H_{33}BrN_5$ $[M]^+$ 508.1903; found 508.1909.

[1-((4-(4-Methoxyphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazolium] Bromide, 5b. The product was obtained as a brown solid in 99% yield (1.92 g). ^{1}H NMR ($CDCl_3$): δ 10.33 (s, 1H, NCHN), 9.02 (s, 1H, triazole-H), 8.09 (s, 1H, CH), 7.68 (d, $^3J_{HH}$ = 9 Hz, 2H, aryl-H), 7.12 (s, 1H, CH), 6.98 (d, $^3J_{HH}$ = 9 Hz, 2H, aryl-H), 6.96 (s, 2H, aryl-H), 6.18 (s, 2H, CH_2), 3.84 (s, 3H, OMe), 2.31 (s, 3H, p-aryl-CH_3), 2.02 (s, 6H, o-aryl-CH_3). ^{13}C NMR ($CDCl_3$): δ 160.2 (p-aryl-C), 141.7 (p-Mes-C), 138.1 (NCN), 134.4 (o-Mes-C), 130.9 (aryl-CH), 130.4 (i-Mes-C), 130.1 (m-Mes-C), 125.2 (triazole-C), 123.6 (CH), 123.3 (CH), 122.6 (i-aryl-C), 115.0 (aryl-CH), 77.5 (OMe), 55.9 (CH_2), 44.7 (triazole-CH), 21.3 (o-aryl-CH_3), 18.4 (p-aryl-CH_3). MS(FAB+, m/z): calcd for $C_{22}H_{24}N_5O$ $[M - Br]^+$ 374.1981; found 374.1979.

[1-((4-Adamantyl-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazolium] Bromide, 5c. The product was obtained as a light brown foam in 72% yield (0.72 g). ^{1}H NMR (MeCN-d_3): δ 8.82 (s, 1H, NCHN), 8.10 (s, 1H, triazole-H), 7.71 (s, 1H, CH), 7.44 (s, 1H, CH), 7.11 (s, 2H, aryl-H), 5.57 (s, 2H, CH_2), 2.35 (s, 3H, p-aryl-CH_3), 2.24 (m, 9H, α/β-Ad), 2.02 (s, 6H, o-aryl-CH_3), 1.80 (m, 6H, γ-Ad). ^{13}C NMR (MeCN-d_3): δ 142.9 (p-aryl-C), 138.3 (NCN), 136.3, (o-aryl-C), 132.6 (i-aryl-C), 131.0 (m-aryl-C), 125.7 (CH), 124.9 (CH), 123.1 (triazole-C), 68.2 (1-Ad-C), 61.6 (CH_2), 46.6 (triazole-CH), 44.1 (2-Ad-C), 37.0 (4-Ad-C), 31.1 (3-Ad-C), 21.7 (p-aryl-CH_3), 18.1 (o-aryl-CH_3). MS-(FAB+, m/z): calcd for $C_{25}H_{32}N_5$ $[M - Br]^+$ 402.2658; found 402.5648.

[1-((4-Mesityl-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazolium] Bromide, 5d. The product was obtained as a brown solid in 85% yield (89 mg). ^{1}H NMR ($CDCl_3$): δ 10.08 (s, 1H, NCHN), 8.66 (s, 1H, triazole-H), 8.16 (s, 1H, CH), 7.13 (s, 1H, CH), 6.98 (s, 2H, aryl-H), 6.94 (s, 2H, aryl-H), 6.24 (s, 2H, CH_2), 2.32 (s, 6H, 2 p-aryl-CH_3), 2.03 (s, 6H, o-aryl-CH_3 NHC), 1.89 (s, 6H, o-aryl-CH_3 triazole). ^{13}C NMR ($CDCl_3$): δ 141.5, 140.4 (2 p-aryl-C), 137.4 (NCHN), 134.7, 134.2 (2 o-aryl-C), 133.0 (i-aryl-C NHC), 130.6 (i-aryl-C triazole), 129.9, 129.2 (2 m-aryl-C), 128.0 (triazole-C), 123.7, 123.1 (2 CH), 77.4 (CH_2), 44.7 (triazole-CH), 21.1 (2 p-aryl-CH_3), 17.7, 17.4 (2 m-aryl-CH_3). MS(FAB+, m/z): calcd for $C_{24}H_{28}N_5$ $[M - Br]^+$ 386.2345; found 386.2348.

[1-((4-(4-Trifluoromethylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazolium] Bromide, 5e. The product was obtained as an orange solid in 78% yield (0.13 g). ^{1}H NMR ($CDCl_3$): δ 9.81 (s, 1H, NCHN), 9.44 (s, 1H, triazole-H), 8.12, s, 1H, CH), 8.05 (d, ^3J(HH) = 7.2 Hz, 2H, aryl-H), 7.76 (d, ^3J(HH) = 7.2 Hz, 2H, aryl-H), 7.13 (s, 1H, CH), 6.97 (s, 2H, aryl-H), 6.21 (s, 2H, CH_2), 2.32 (s. 3H, p-aryl-CH_3), 2.05 (s, 6H, o-aryl-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5 (p-Mes-C), 139.0 (p-aryl-C), 137.7 (NCHN), 134.3 (o-Mes-C), 131.9 (CF_3), 130.6 (i-Mes-C), 129.9 (m-Mes-C), 129.1 (triazole-C), 127.1 (aryl-C), 125.2 (i-aryl-C), 123.7 (CH), 123.3 (CH), 120.6 (aryl-C), 77.8 (CH_2), 44.8 (triazole-CH), 21.1 (p-aryl-CH_3), 17.8 (o-aryl-CH3). MS(FAB+, m/z): calcd for $C_{22}H_{21}F_3N_5$ $[M - Br]^+$ 412.1749; found 412.1742.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(2,6-diisopropylphenyl))imidazolium] Bromide, 6. The product was obtained as an orange solid in 93% yield (0.23 g). ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H, NCHN), 8.58 (s, 1H, triazole-H), 8.20 (s, 1H, CH), 7.53 (m, 2H, 2 p-aryl-H), 7.30 (m, 4H, 4 m-aryl-H), 7.23 (s, 1H, CH), 5.68 (s, 2H, CH_2), 2.32 (m, 2H, ^{i}Pr), 2.13 (m, 2H, ^{i}Pr), 1.16−1.00 (m, 24H, ^{i}Pr). ^{13}C NMR ($CDCl_3$): δ 145.6, 145.3 (2 o-aryl-C), 137.6 (NCHN), 132.7, 132.0 (2 i-aryl-C), 131.1, 130.1 (2 p-aryl-C), 128.5 (triazole-C), 124.7 (m-aryl-C), 124.7, 124.2 (2 CH), 123.9 (m-aryl-C), 77.4 (CH_2), 44.7 (triazole-CH), 28.7, 28.5 (2 ^{i}Pr), 24.5, 24.3, 24.1, 23.5 (4 ^{i}Pr). MS(FAB+, m/z): calcd for $C_{30}H_{40}N_5$ $[M - Br]^+$ 470.3284; found 470.3278.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(4-methoxyphenyl))imidazolium] Bromide, 7. The product was obtained as a yellow solid in 60% yield (93 mg). ^{1}H NMR ($CDCl_3$): δ 10.17 (s, 1H, NCHN), 8.50 (s, 1H, triazole-H), 7.96 (s, 1H, CH), 7.63 (d, ^3J(HH) = 8.1 Hz, 2H, aryl-H), 7.49 (t, ^3J(HH) = 7.5 Hz, 1H, p-aryl-H), 7.28 (d, ^3J(HH) = 7.5 Hz, 2H, m-aryl-H), 7.25 (s, 1H, CH), 7.06 (d, ^3J(HH) = 8.1 Hz, 2H, aryl-H), 6.10 (s, 2H, CH_2), 3.86 (s, 3H, OMe), 2.14 (m, 2H, 2 ^{i}Pr), 1.11 (m, 12H, 2 ^{i}Pr). ^{13}C NMR ($CDCl_3$): δ 161.1 (p-aryl-C), 146.1 (o-DiPP-C), 135.7 (NCN), 132.9 (i-DiPP-C), 131.1 (p-DiPP-C), 129.0 (m-DiPP-C), 127.6 (CH), 125.9 (triazole-C), 124.2 (aryl-CH), 123.7 (CH), 121.4 (i-aryl-C), 115.9 (aryl-CH), 77.6 (OMe), 56.1 (CH_2), 45.0 (triazole-CH), 28.7 (^{i}Pr-CH), 24.5, 24.3 (^{i}Pr-CH_3). MS(FAB+, m/z): calcd for $C_{25}H_{30}N_5O$ $[M-Br]^+$ 416.2450; found 416.2449.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(4-trifluoromethylphenyl))imidazolium] Bromide, 8. The product was obtained as a green solid in 63% yield (0.32 g). ^{1}H NMR ($CDCl_3$): δ 10.86 (s, 1H, NCHN), 8.57 (s, 1H, triazole-H), 8.01 (s, 1H, CH), 7.90−7.65 (m, 4H, aryl-H), 7.48 (t, ^3J(HH) = 7.5 Hz, 1H, p-aryl-H), 7.35−7.18 (m, 3H, CH and m-aryl-H), 6.19 (s, 2H, CH_2), 2.13 (m, 2H, 2 ^{i}Pr), 1.10 (m, 12H, 2 ^{i}Pr). ^{13}C NMR ($CDCl_3$): δ 145.9 (o-DiPP-C), 143.1 (p-aryl-C), 136.4 (NCHN), 132.7 (i-DiPP-C), 131.1 (p-DiPP-C), 127.9 (m-DiPP-C), 127.1 (aryl-CH), 126.8 (i-aryl-C), 126.4 (triazole-C), 123.9 (aryl-CH), 123.0 (CH), 120.8 (CH), 77.3 (CH_2), 45.2 (triazole-CH), 28.5 (^{i}Pr-CH), 24.2 (^{i}Pr-CH_3). MS(FAB+, m/z): calcd for $C_{25}H_{27}F_3N_5$ $[M - Br]^+$ 454.2219; found 474.2227.

[Bis((1-(prop-2-ynyl)-3-mesityl)imidazol-2-ylidene)silver(I)]silver(I) Dibromide, 10. [25] A Schlenk flask was charged with **1** and 1 equiv of silver(I) oxide under a N_2 atmosphere and suspended in a 1:1 dichloromethane/THF mixture to 0.1 M. The suspension was stirred for 2 days and filtered over Celite, and the solvent was removed *in vacuo*. Traces of THF were co-evaporated twice with dichloromethane. The product is obtained as a light brown foam in 84% yield (0.233 g). ^{1}H NMR (CD_2Cl_2): δ 7.44 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.04 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.03 (s, 2H, aryl-H), 5.05 (d, ^4J(HH) = 2,7 Hz, 2H, CH_2), 2.62 (t, ^4J(HH) = 2.7 Hz, 1H, CCH), 2.34 (s, 3H, p-aryl-CH_3), 2.00 (s, 6H, o-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ 183.8 (NCN), 141.8 (p-aryl-C), 137.7 (i-aryl-C), 137.0 (o-aryl-C), 131.4 (m-aryl-C), 125.2 (CH), 123.0 (CH), 78.7 (alkyne), 78.0 (alkyne), 43.5 (CH_2), 23.0 (p-aryl-CH_3), 19.6 (o-aryl-CH_3). MS(FAB+, m/z): calcd for $C_{30}H_{32}N_4Ag$ $[NHC_2Ag]^+$ 555.1678; found 555.1675.

General Procedure for Synthesis of NHC-Triazolyl Palladium Allyl Chloride Complexes. Imidazolium salt, potassium *tert*-butoxide (1.1 equiv), and palladium allyl chloride dimer (0.5 equiv) were charged into a Schlenk flask and suspended in THF to 0.1 M. The reaction mixture was stirred for 4 h, filtered over Celite, and concentrated *in vacuo*. The crude product was dissolved in dichloromethane and precipitated by addition of pentane. Because of a small amount of halide scrambling, elemental analysis of the complexes did not give reliable results.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 11a. The product was obtained as a yellow solid in 92% yield (0.212 g). ^{1}H NMR (CD_2Cl_2): δ 8.37 (s, 1H, triazole-H), 7.80 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.59 (t ^3J(HH) = 7.8 Hz, 1H, p-aryl-H), 7.31 (d, ^3J(HH) = 1.8 Hz, 2H, m-aryl-H), 7.07 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.05 (s, 1H, Mes-H), 6.97 (s, 1H, Mes-H), 5.92 (d ^2J(HH) = 15.5 Hz, 1H, CH_2), 5.59 (d, ^2J(HH) = 15.5 Hz, 1H, CH_2), 5.07 (m, 1H, allyl-H), 4.07 (d, ^3J(HH) = 7.5 Hz, 1H, allyl-H), 3.10 (d, ^3J(HH) = 6.3 Hz, 1H, allyl-H), 3.04 (d, ^3J(HH) = 13.5 Hz, 1H, allyl-H), 2.33 (s, 3H, p-Mes-CH_3), 2.17 (m, 2H, ^{i}Pr-H), 2.12 (s, 3H, o-Mes-CH_3), 2.02 (s, 3H, o-Mes-CH_3), 1.85 (d, ^3J(HH) = 12 Hz, 1H, allyl-H), 1.12 (d, ^3J(HH) = 2.1 Hz, 6H, ^{i}Pr-CH_3), 1.10 (d, ^3J(HH) = 2.1 Hz, 6H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 180.5 (NCN), 143.5 (o-aryl-C), 139.3 (p-Mes-C), 136.6 (i-Mes-C), 135.9 (o-Mes-C), 135.3 (o-Mes-C), 133.3 (i-aryl-C), 131.2 (p-aryl-C), 129.2 (m-Mes-C), 129.0 (m-Mes-C), 127.6 (m-aryl-C), 124.1 (CH), 122.9 (CH), 122.1 (triazole-C), 115.7 (allyl), 78.0 (allyl), 71.9 (CH_2), 49.4 (allyl), 46.0 (triazole-CH), 28.7 (^{i}Pr-CH, br), 24.1 (^{i}Pr-CH_3), 24.0 (^{i}Pr-CH_3), 23.9 (^{i}Pr-CH_3), 23.8 (^{i}Pr-CH_3), 21.1 (p-Mes-CH_3), 18.2 (o-Mes-CH_3), 17.9 (o-Mes-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{30}H_{55}N_5Pd$ $[M - Cl]^+$ 574.2162; found 574.2168.

[1-((4-(4-Methoxyphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 11b. The product was obtained as a beige solid in a yield of 93% (0.10 g). ^{1}H NMR (CD_2Cl_2): δ 8.80 (s, 1H, triazole-H), 7.71 (d, ^3J(HH) = 15 Hz, 2H, aryl-H), 7.56 (d ^3J(HH) = 2.5 Hz, 1H, CH), 7.04 (d, ^3J(HH) = 15 Hz, 2H, aryl-H), 6.98 (s, 2H, Mes-H), 6.97 (d ^3J(HH) = 2.5 Hz, 1H, CH), 5.85 (d, ^2J(HH) = 15.0 Hz, 1H, CH_2), 5.76 (d, ^2J(HH) = 15.0 Hz, 1H, CH_2), 5.07 (m, 1H, allyl), 4.15 (d, ^3J(HH) = 12.5 Hz, 1H, allyl), 3.86 (s, 3H), 3.21 (d, ^3J(HH) = 10.5 Hz, 1H, allyl), 3.03 (d, ^3J(HH) = 22.5 Hz, 1H, allyl), 2.33 (s, 3H, p-Mes-CH_3), 2.12 (s, 3H, o-Mes-CH_3), 2.03 (s, 3H, o-Mes-CH_3), 1.93 (d, ^3J(HH) = 20.5 Hz, 1H, allyl). ^{13}C NMR (CD_2Cl_2): δ 176.6 (NCN), 160.9 (p-aryl-C), 139.9 (p-Mes-C), 136.8 (i-Mes-C), 135.6 o-Mes-C), 135.2 (o-Mes-C), 129.6 (aryl-CH), 129.3 (m-Mes-C), 129.2 (m-Mes-C), 123.9, 123.2, 122.1 (2 CH, triazole-C), 122.8 (i-aryl-C), 119.0 (allyl), 115.2 (aryl-CH), 72.3 (CH_2), 68.0 (allyl), 56.2 (OMe), 50.1 (allyl), 45.4 (triazole-CH), 21.2 (p-Mes-CH_3), 18.0 (o-Mes-CH_3), 17.9 (o-Mes-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{25}H_{28}ON_5Pd$ $[M - Cl]^+$ 520.1329; found 520.1344.

[1-((4-(Adamantyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 11c. The product was obtained as a yellow solid in a yield of 94% (0.24 g). ^{1}H NMR (CD_2Cl_2): δ 8.54 (s, 1H, triazole-H), 7.78 (d, ^3J(HH) = 0.9 Hz, 1H, CH), 7.02 (s, 2H, aryl-H), 6.98 (d, ^3J(HH) = 0.9 Hz, 1H, CH), 5.95 (d, ^2J(HH) = 15.0 Hz, 1H, CH_2), 5.70 (d, ^2J(HH) = 15.0 Hz, 1H, CH_2), 5.14 (m, 1H, allyl-H), 4.27 (d, ^3J(HH) = 3.9 Hz, 1H, allyl-H), 3.17 (d, ^3J(HH) = 8.1 Hz, 1H, allyl-H), 3.02 (br s, 1H, allyl-H), 2.37 (s, 3H, p-aryl-CH_3), 2.28 (m, 9H, α/β-Ad), 2.09 (s, 3H, o-aryl-CH_3), 2.02 (s, 3H, o-aryl-CH_3), 1.90 (d, ^3J(HH) = 6 Hz, 1H, allyl-H), 1.83 (m, 9H, γ-Ad). ^{13}C NMR (CD_2Cl_2): δ 177.0 (NCN), 139.8 (p-aryl-C), 136.8 (i-aryl-C), 135.7 (o-aryl-C), 135.3 (o-aryl-C), 129.2 (m-aryl-C), 129.1 (m-aryl-C), 123.5 (triazole-C), 122.0 (CH), 121.5 (CH), 118.4 (allyl), 71.7 (CH_2), 68.1 (1-Ad-C), 62.3 (allyl), 50.6 (allyl), 45.6 (triazole-CH), 42.8 (2-Ad-C), 35.8 (4-Ad-C), 29.8 (3-Ad-C), 21.1 (p-aryl-CH_3), 18.0, 17.8 (o-aryl-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{28}H_{36}N_5Pd$ $[M - Cl]^+$ 548.2006; found 548.2001.

[1-((4-(Mesityl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 11d. The product was obtained as a yellow solid in a yield of 90% (90 mg). ^{1}H NMR (CD_2Cl_2): δ 8.49 (s, 1H, triazole-H), 7.82 (s, 1H, CH), 7.06 (s, 2H, aryl-H), 7.03 (s, 1H, CH), 7.01 (bs, 2H, aryl-H NHC), 6.02 (d, ^2J(HH) = 13.2 Hz, 1H, CH_2), 5.73 (d, ^2J(HH) = 13.2 Hz, 1H, CH_2), 5.21 (m, 1H, allyl-CH), 4.33 (m, 1H, allyl-CH_2), 4.05 (m, 1H, allyl-CH_2), 3.27 (m, 1H, allyl-CH_2), 2.95 (m, 1H, allyl-CH_2), 2.38 (s, 3H, p-aryl-CH_3), 2.36 (s, 3H, p-aryl-CH_3), 2.05 (s, 3H, o-aryl-CH_3 NHC), 2.02 (s, 3H, o-aryl-CH_3 NHC), 1.99 (s, 6H, o-aryl-CH_3 triazole). ^{13}C NMR (CD_2Cl_2): δ 177.6 (NCN), 141.1 (p-aryl-C triazole), 139.5 (p-aryl-C), 136.5 (i-aryl-C), 135.5, 135.1 (o-aryl-C), 134.8 (o-aryl-C triazole), 132.7 (i-aryl-C triazole), 129.3 (m-aryl-C triazole), 129.1, 128.9 (m-aryl-C), 127.0 (CH), 123.4 (CH), 122.0 (triazole-C), 117.8 (allyl), 71.7 (CH_2), 62.3 (allyl), 50.2 (allyl), 45.6 (triazole-CH), 22.3 (p-aryl-CH_3 triazole), 20.8 (p-aryl-CH_3), 17.8, 17.6 (o-aryl-CH_3), 17.2 (o-aryl-CH_3 triazole). MS(FAB+, *m*/*z*): calcd for $C_{27}H_{32}N_5Pd$ $[M - Cl]^+$ 532.1693; found 532.1706.

[1-((4-(4-Trifuoromethylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 11e. The product was obtained as an orange solid in a yield of 94% (0.138 g). ^{1}H NMR (CD_2Cl_2): δ 9.31 (s, 1H, triazole-H), 8.12 (d, ^3J(HH) = 8.4 Hz, 2H, aryl-H), 7.88 (d, ^3J(HH) = 8.4 Hz, 2H, aryl-H), 7.76 (s, 1H, CH), 7.04 (s, 1H, CH), 7.02 (s, 3H, Mes-H), 5.97 (d, ^2J(HH) = 15.9 Hz, 1H, CH_2), 5.73 (d, ^2J(HH) = 15.9 Hz, 1H, CH_2), 5.23 (m, 1H, allyl-CH), 4.41 (m, 1H, allyl-CH_2), 4.09 (m, 1H, allyl-CH_2), 3.32 (m, 1H, allyl-CH_2), 3.00 (m, 1H, allyl-CH_2), 2.36 (s, 3H, p-aryl-CH_3), 2.05 (s, 3H, o-aryl-CH_3), 2.01 (s, 3H, o-aryl-CH_3). ^{13}C NMR (CD_2Cl_2): δ 177.6 (NCN), 142.9 (p-Mes-C), 139.6 (p-aryl-C), 136.4 (i-Mes-C), 135.5, 135.0 (m-Mes-C), 131.2 (CF_3), 129.1, 128.9 (o-Mes-C), 127.3 (aryl-CH), 125.4 (i-aryl-C), 123.7 (triazole-C), 123.2 (CH), 122.1 (CH), 121.2 (aryl-CH), 117.8 (allyl), 72.0 (CH_2), 62.5 (allyl), 50.6 (allyl), 45.5 (triazole-CH), 20.9 (p-Mes-CH_3), 17.9, 17.7 (o-Mes-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{25}H_{25}F_3N_5Pd$ $[M - Cl]^+$ 558.1097; found 558.1116.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(2,6-diisopropylphenyl))imidazol-2-ylidenepalladium(II)allyl] Chloride, 12. The product was obtained as a brown solid in a yield of 99% (0.258 g). ^{1}H NMR (CD_2Cl_2): δ 8.63 (s, 1H, triazole-H), 8.03 (s, 1H, CH), 7.59 (t, ^3J(HH) = 7.8 Hz, 1H, p-aryl-H), 7.53 (t, ^3J(HH) = 7.8 Hz, 1H, p-aryl-H), 7.36 (d, ^3J(HH) = 7.8 Hz, 2H, m-aryl-H), 7.32 (d, ^3J(HH) = 7.8 Hz, 2H, m-aryl-H), 7.13 (s, 1H, CH), 6.06 (d, ^2J(HH) = 15.9 Hz, 1H, CH_2), 5.81 (d, ^2J(HH) = 15.9 Hz, 1H, CH_2), 5.22 (m, 1H, allyl-CH), 4.38 (m, 1H, allyl-CH_2), 3.99 (m, 1H, allyl-CH_2), 3.33 (m, 1H, allyl-CH_2), 2.91 (m, 1H, allyl-CH_2), 2.45 (m, 2H, ^{i}Pr), 2.20 (m, 2H, ^{i}Pr), 1.30−1.00 (m, 24H, ^{i}Pr). ^{13}C NMR (CD_2Cl_2): δ 177.3 (NCN), 146.2 (o-aryl-C), 145.8 (o-aryl-C), 136.3 (i-aryl-C NHC), 132.3 (i-aryl-C triazole), 131.7 (p-aryl-C NHC), 130.4 (p-aryl-C triazole), 127.6 (m-Aryl-C NHC), 124.2 (m-aryl-C triazole), 124.1 (CH), 123.9 (CH), 123.1 (triazole-C), 118.4 (allyl), 71.9 (CH_2), 62.0 (allyl), 50.6 (allyl), 45.4 (triazole-CH), 28.7 (^{i}Pr-CH NHC), 28.5 (^{i}Pr-CH triazole), 28.3 (^{i}Pr-CH NHC), 25.0 (^{i}Pr-CH_3 NHC), 24.8 (^{i}Pr-CH_3 NHC), 24.1 (^{i}Pr-CH_3 triazole), 23.5 (^{i}Pr-CH_3 triazole), 23.3 (^{i}Pr-CH_3 NHC), 23.0 (^{i}Pr-CH_3 NHC). MS(FAB+, *m*/*z*): calcd for $C_{33}H_{44}N_5Pd$ $[M - Cl]^+$ 616.2632; found 616.2646.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(4-methoxyphenyl))imidazol-2-ylidenepalladium(II)allyl] Chloride, 13. The product was obtained as a yellow solid in a yield of 91% (0.054 g). ^{1}H NMR (CD_2Cl_2): δ 8.38 (s, 1H, triazole-H), 7.72 (s, 1H, CH), 7.55 (t, ^3J(HH) = 12 Hz, 1H, p-aryl-H), 7.34 (d, ^3J(HH) = 9 Hz, 2H, aryl-H), 7.32 (d, ^3J(HH) = 12 Hz, 2H, m-aryl-H), 7.02 (d, ^3J(HH) = 9 Hz, aryl-H), 6.97 (s, 1H, CH), 5.94 (d, ^2J(HH) = 15.3 Hz, 1H, CH_2), 5.77 (d, ^2J(HH) = 15.3 Hz, 1H, CH_2), 5.18 (m, 1H, allyl-CH), 4.29 (d, ^3J(HH) = 5.4 Hz, 1H, allyl-CH_2), 3.87 (s, 3H, OMe), 3.27 (d, ^3J(HH) = 14.1 Hz, 1H, allyl-CH_2), 2.3−2.1 (m, 3H, allyl-CH_2, ^{i}Pr-CH), 1.2−1.1 (m, 12 H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 177.4 (NCN), 159.9 (p-aryl-C), 145.9 (o-DiPP-C), 133.6 (i-DiPP-C), 131.5 (p-DiPP-C), 131.1 (m-DiPP-C), 126.9 (triazole-C), 124.1 (aryl-CH), 123.4 (CH), 123.0 (i-aryl-C), 122.1 (CH), 117.0 (allyl), 114.2 (aryl-CH), 70.7 (CH_2), 63.2 (allyl), 55.8 (OMe), 51.9 (allyl), 46.0 (triazole-CH), 28.6 (^{i}Pr-CH), 24.1, 23.6 (^{i}Pr-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{28}H_{34}N_5OPd$ $[M - Cl]^+$ 562.1798; found 562.1799.

[1-((4-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazolyl)methylene-3-(4-trifluoromethylphenyl))imidazol-2-ylidenepalladium(II)allyl] Chloride, 14. The product was obtained as a dark yellow solid in a yield of 97% (0.125 g). ^{1}H NMR (CD_2Cl_2): δ 8.34 (s, 1H,

triazole-H), 7.9−7.3 (m, 9H, DiPP, aryl, 2 CH), 6.0−5.8 (br m, 2H, CH_2), 5.25 (m, 1H, allyl), 4.31 (m, 1H, allyl), 3.27 (m, 1H, allyl), 2.2−2.1 (m, 4H, allyl, ^{i}Pr-CH), 1.3−1.0 (m, 12H, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2): δ 179.8 (NCN), 145.9 (o-DiPP-C), 143.3 (p-aryl-C), 132.6 (i-DiPP-C), 132.1 (CF_3), 131.3 (p-DiPP-C), 131.1 (m-DiPP-C), 127.7 (triazole-C), 126.0 (aryl-CH), 125.4 (i-aryl-C), 124.0 (aryl-CH), 121.8 (CH), 120.5 (CH), 115.9 (allyl), 71.21 (CH_2), 63.3 (allyl), 46.4 (allyl), 38.8 (triazole-CH), 28.6 (^{i}Pr-CH), 24.0 (^{i}Pr-CH_3), 23.7 (^{i}Pr-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{28}H_{31}F_3N_5Pd$ $[M - Cl]^+$ 600.1566; found 600.1570.

[(1-(Prop-2-ynyl)-3-mesityl)imidazol-2-ylidenepalladium(II)allyl] Chloride, 15. Freshly prepared **10** (0.183 g, 0.207 mmol) was dissolved in 10 mL of THF. Then palladium allyl chloride dimer (1 equiv) was added, upon which a white precipitate formed. The reaction was stirred for 20 min and filtered over Celite, and the yellow solution was concentrated *in vacuo*. The product was obtained as a brown foam in 98% yield (0.18 g). ^{1}H NMR (CD_2Cl_2): δ 7.43 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 7.02 (s, 2H), 6.98 (d, ^3J(HH) = 1.8 Hz, 1H, CH), 5.30 (d, ^4J(HH) = 2.4 Hz, 2H, CH_2), 5.03 (m, 1H, allyl), 4.00 (dd, ^3J(HH) = 7.5 Hz, ^3J(HH) = 2.1 Hz, 1H, allyl), 3.28 (m, 1H, allyl), 2.94 (d, ^3J(HH) = 13.5 Hz, 1H, allyl), 2.58 (t, $^4J_{HH}$ = 2.4 Hz, 1H, CH), 2.33 (s, 3H, p-aryl-CH_3), 2.04 (s, 6H, o-aryl-CH_3), 1.87 (d, ^3J(HH) = 10.8 Hz, 1H, allyl). ^{13}C NMR (CD_2Cl_2): δ 187.2 (NCN), 139.9 (p-aryl-C), 136.4 (i-aryl-C), 135.3 (o-aryl-C), 129.3 (m-aryl-CH), 127.0 (CH), 122.9 (CH), 117.5 (allyl), 77.9, 74.5 (alkyne), 57.8 (allyl), 41.1 (CH_2), 36.6 (allyl), 21.1 (p-aryl-CH_3), 18.0 (o-aryl-CH_3). MS(FAB+, *m*/*z*): calcd for $C_{18}H_{21}N_2Pd$ $[M - Cl]^+$ 371.0740; found 371.0752.

[1-((4-(Adamantyl)-1*H*-1,2,3-triazolyl)methylene-3-mesityl)-imidazol-2-ylidenepalladium(II)allyl]trifluoromethane Sulfonate, 16. Silver triflate was added to a 0.1 M dichloromethane solution of **11c** (1 equiv). A white precipitate formed immediately, and the suspension was filtered over Celite. After removal of the solvent *in vacuo*, the product (45 mg, 97%) was obtained as a colorless solid. ^{1}H NMR (CD_2Cl_2): δ 8.36 (s, 1H, triazole-H), 7.63 (d, ^3J(HH) = 2.1 Hz, 1H, CH), 7.03 (s, 2H, aryl-H), 7.01 (d ^3J(HH) = 2.1 Hz, 1H, CH), 5.73 (d, ^2J(HH) = 15.6 Hz, 1H, CH_2), 5.43 (d, ^2J(HH) = 15.6 Hz, 1H, CH_2), 5.23 (m, 1H, allyl), 4.44 (dd, ^3J(HH) = 7.5 Hz, ^2J(HH) = 2.4 Hz, 1H, allyl), 3.32 (d, ^3J(HH) = 13.5 Hz, 1H, allyl), 2.73 (dd, ^3J(HH) = 6.9 Hz, ^2J(HH) = 2.4 Hz, 1H, allyl), 2.38 (s, 3H, p-aryl-CH_3), 2.28 (m, 9H, α/β-Ad), 1.98 (m, 7H, o-aryl-CH_3, allyl), 1.82 (m, 6H, γ-Ad). ^{13}C NMR (CD_2Cl_2): δ 176.9 (NCN), 139.8 (p-aryl-C), 136.8 (i-aryl-C), 135.6 (o-aryl-C), 129.2 (m-aryl-C), 123.5 (triazole-C), 122.0 (CH), 121.5 (CH), 118.4 (allyl), 71.7 (1-Ad-C), 68.0 (allyl), 62.3 (CH_2), 50.1 (allyl), 45.6 (triazole-CH), 42.9 (2-Ad-C), 34.3 (4-Ad-C), 25.9 (3-Ad-C), 21.0 (p-aryl-CH_3), 18.0, 17.8 (o-aryl-CH_3). The signal for the carbon of the triflate anion was not observed. MS(FAB+, *m*/*z*): calcd for $C_{28}H_{36}N_5Pd$ $[M - OTf]^+$ 548.2006; found 548.1994.

X-ray Crystal Structure Determination of 16. $[C_{28}H_{36}N_5Pd](CF_3O_3S)$, fw = 698.09, colorless plate, 0.24 × 0.24 × 0.06 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 9.5963(2) Å, b = 11.0135(2) Å, c = 16.1259(4) Å, α = 70.3568(10)°, β = 76.7089(11)°, γ = 67.2874(10)°, V = 1470.81(6) Å^3, Z = 2, D_x = 1.576 g/cm^3, μ = 0.76 mm^{-1}; 16 083 reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} at a temperature of 150(2) K. Intensity integration was performed with HKL2000.[40] The SORTAV[41] program was used for absorption correction and scaling based on multiple measured reflections (0.85−0.96 correction range). A total of 5283 reflections were unique (R_{int} = 0.054), of which 4604 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SHELXS-97.[42] The structure was refined with SHELXL-97[42] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The coordinated allyl ligand was refined with a disorder model with occupancies of 0.58:0.42 for the two disordered components. All hydrogen atoms were introduced in calculated positions and refined with a riding model. A total of 392 parameters were refined with 14 restraints concerning the disordered allyl ligand (distance restraints and restraints to approximate isotropic behavior of the displacement parameters). R1/wR2 [$I > 2\sigma(I)$]: 0.0337/0.0831. R1/wR2 [all reflns]: 0.0404/0.0888. S = 1.060. Residual electron density is between −0.76 and 0.92 e/Å^3. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[43]

General Experimental Procedure for Catalytic Transfer Semihydrogenation of Phenylpropyne Using Formic Acid As Hydrogen Donor. [37] A solution of 12 mL of MeCN containing 150 mM 1-phenyl-1-propyne, 750 mM triethylammonium formiate, and 150 mM *p*-xylene was heated to reflux. A solution of 1 mol % catalyst in 2 mL of MeCN was added to the reaction mixture. Periodically, samples were taken over 24 h. Reaction mixtures were analyzed by GC to determine conversions. Reactions were quenched by dilution with EtOH.

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Supporting Information Available: X-ray crystallographic data in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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