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Palladium(II) Complexes of 1,2,4-Triazole-Based *N*-Heterocyclic Carbenes: Synthesis, Structure, and Catalytic Activity

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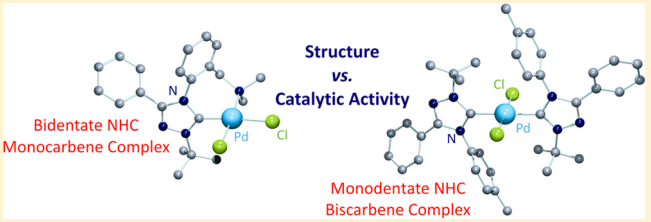
Supporting Information

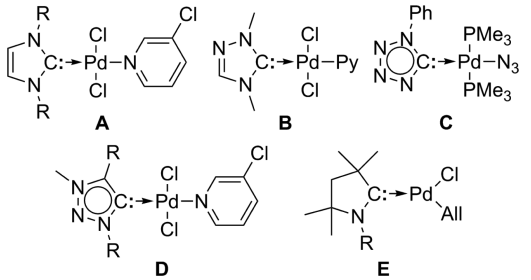
ABSTRACT: Six palladium(II) complexes bearing three different triazole-based N-heterocyclic carbene (NHC) ligands, [1-*tert*-butyl-4-{2-[(*N*,*N*-dimethylamino)methyl]phenyl}-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide, 1-*tert*-butyl-4-(2-methoxyphenyl)-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide, and 1-*tert*-butyl-4-(4-methylphenyl)-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide], were synthesized and fully characterized. NMR spectroscopy and X-ray diffraction analysis revealed that the amino-group-substituted NHC ligand is coordinated in bidentate fashion, forming a monocarbene chelate complex with an additional intramolecular Pd ← N bond with the nitrogen donor atom. The 4-methylphenyl- and 2-methoxyphenyl-substituted NHC ligands coordinate as C-monodentate donors, forming simple biscarbene Pd(II) complexes. The evaluation of the catalytic performance in the Suzuki−Miyaura cross-coupling reaction revealed very promising performance of the intramolecularly coordinated monocarbene complexes under relatively mild conditions even in direct comparison with the commercially available PEPPSI catalyst. In contrast, the biscarbene complexes proved inactive in this catalytic process. According to theoretical calculations (EDA and NOCV analysis), functionalization of the 1,2,4-triazole-based NHC with the 2-[(*N*,*N*-dimethylamino)methyl]phenyl group has a significant effect on the stability of the NHC−metal bond.



INTRODUCTION

The rapid developments in the field of palladium-catalyzed carbon−carbon and carbon−heteroatom coupling reactions are reflected by an enormous increase of interest in this topic during the last two decades.[1] The phosphine-based ligands originally employed in this field[2] have gradually been replaced by various N-heterocyclic carbene (NHC) ligands,[3−5] which have attracted exceptional attention from both academia and industry mainly because of their versatility and unique σ-donating abilities. Nowadays, the chemistry of NHC−palladium(II) complexes is rather rich with a high number of examples of highly active catalysts based on various types of such donors. A broad variety of complexes containing imidazole-, triazole-, or tetrazole-based carbene, mesoionic carbene, or cyclic alkylamino carbene (CAAC) ligands (Chart 1) have been introduced. Among them, the imidazole-based ones are widely used in catalysis as they are thermally robust and reasonably stable (see, e.g., the commercially available PEPPSI catalyst[6]), which is the major advantage compared with the phosphine-derived and other Pd catalysts.

Chart 1. Palladium Complexes with Various Carbene Ligands: (A) Imidazole-Based,[6] (B) Triazole-Based,[7] (C) Tetrazole-Based,[8] (D) Mesoionic,[9] and (E) CAAC[10]



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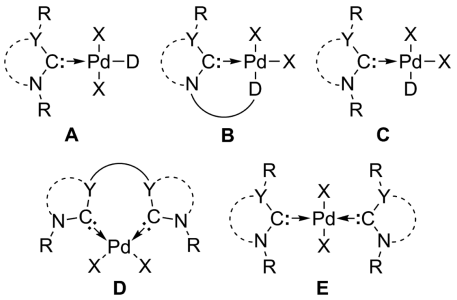
From the structural point of view, NHC-substituted PdX_2 complexes, where X is an anionic ligand (e.g., chloride or acetate) and NHC is in most cases a five-membered heterocycle or, rarely, a chain containing the carbene carbon atom, can be generally divided into two classes: monocarbene-type compounds (NHC)Pd(D)X_2 (D = donor group) and biscarbene complexes $(NHC)_2PdX_2$. All of these compounds possess the expected square-planar coordination sphere around the central palladium atom with both *cis* and *trans* arrangements of the X groups. Among the monocarbene complexes, the *trans* isomers are the most prevalent (Chart 2A),[9a,11] with the donor group usually completing the coordination of the metal center. The *cis* arrangement is less populated and is most likely to occur when the additional donor group is directly bonded to the NHC fragment, thus enabling the formation of four- to eight-membered palladacycles (Chart 2B).[12] Another example is the group of mixed NHC/triphenylphosphane Pd dibromide or diiodide complexes, where exclusive formation of the *cis* arrangement was observed (Chart 2C).[13] The Pd–X bonds in the *trans* arrangement are almost equidistant (lengths in an approximate range of 2.29–2.31 Å)[14] but in the case of *cis* isomers, the Pd–X bond located *trans* to the carbene carbon is usually elongated as a result of the *trans* influence of the NHC ligand (lengthening by ca. 0.05 Å).[14] The *cis* arrangement is also possible for the biscarbene-type compounds with either two separate NHC ligands or one bidentate ligand in which two NHCs are connected via a ring or a chain (Chart 2D).[15] When the bridge between the two carbene units is long enough, *trans* carbene complexes can be isolated as well.[16] Nonetheless, the *trans* isomers are more likely to be formed when two independent carbenes of the same or different type are present in the complex.[17] It has also been found very recently that weak CH–π and CF–π interactions can drive the conversion of the *trans* isomer to the *cis-anti* or *cis-syn* isomer of $(NHC)_2PdX_2$, depending on the weak interactions provided by the substituent groups of the NHC.[18] For the *trans* isomers, the lengths of both the Pd–X and Pd–C bonds vary only marginally. It is typically found that the Pd–C bonds (ca. 2.05 Å)[14] are slightly elongated and the Pd–X bonds (ca. 2.01 Å for Pd–O in acetates and 2.32 Å for Pd–Cl)[14] are slightly shortened in the *trans* isomers in comparison with the *cis* arrangement (ca. 1.96 Å for Pd–C, 2.07 Å for Pd–O and 2.36 Å for Pd–Cl).[14]

The use of a carbene with an adjacent donor group with potential hemilabile coordination to the metal center is quite frequent nowadays. A plethora of different strategies have been applied to the design of such NHC donors, including the use of pyridine-,[19] phosphine-,[20] or ether-based[21] donor moieties, although applications of aliphatic amino groups, as successfully implemented in the chemistry of pincer compounds,[22] still remain rare.

In this paper, we introduce a 2-[(dimethylamino)methyl]-phenyl-substituted triazole-based NHC ligand that has already been successfully applied in rhodium(I) complexes[23] into the palladium(II) chemistry. Furthermore, two analogous NHC ligands substituted with 2-methoxyphenyl and 4-methylphenyl groups were synthesized for a comparison of the bonding properties in similar complexes with the palladium(II) ion. The catalytic activities of the resulting complexes in model Suzuki–Miyaura reactions were evaluated and are discussed in comparison with the activity of the commercial PEPPSI catalyst.

Chart 2. Possible Bonding Modes and Structural Motifs in NHC–Pd Complexes[a]

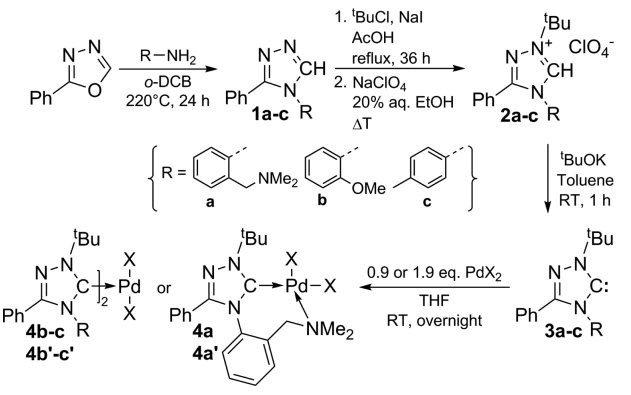


[a]D = donor group; X = an electronegative substituent; Y = C, N, P, or Si.

RESULTS AND DISCUSSION

Three carbene precursors, 1-*tert*-butyl-4-{2-[(dimethylamino)-methyl]phenyl}-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**2a**), 1-*tert*-butyl-4-(2-methoxyphenyl)-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**2b**), and 1-*tert*-butyl-4-(4-methylphenyl)-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**2c**), were synthesized in two steps in moderate (**2a**) to high (**2b** and **2c**) overall yields according to the procedure reported in our recent work (**2a**)[23] or by means of the general procedures published earlier (**2b** and **2c**).[24] Triazoles **1** were formed via the recyclization[25] reaction of 2-phenyl-1,3,4-oxadiazole with the respective anilines in 1,2-dichlorobenzene (*o*-DCB) at elevated temperature. The next step of the reaction sequence was a quaternization with the 2-chloro-2-methylpropane (^{t}BuCl) under reflux conditions in acetic acid to give triazolium perchlorates **2**, which were finally crystallized and isolated as white powders. The formation of **2** was clearly manifested in the ^{1}H and ^{13}C NMR spectra, where the characteristic peaks due to N–C*H*–N moieties were observed at 10.58 (**2a**), 10.75 (**2b**), and 10.57 (**2c**) ppm and at 143.3 (**2a**), 153.2 (**2b**), and 142.6 (**2c**) ppm in the ^{1}H and ^{13}C NMR spectra, respectively, similar to those reported for the related *N*-alkyl(aryl)triazolium salts.[26] The final two steps leading to the formation of NHC–Pd complexes were the generation of the free carbenes from the respective triazolium salts with a strong base (potassium *tert*-butoxide) and the subsequent in situ complexation with Pd(II) precursors in the appropriate molar ratios (Scheme 1).

Scheme 1. Synthesis of the Carbene Precursors, Generation of the Free Carbenes, and Subsequent Formation of the Pd Complexes[a]



[a]X = Cl for **4a–c**, OAc for **4a′–c′**.

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On the basis of the previous results obtained for the Rh(I) complexes,[23] the formation of a very rare (with only two previously published examples[12d]) seven-membered diazametallacycle via strong intramolecular coordination of the pendant amino group was expected for the products **4a** and **4a′**. This assumption was at first confirmed by ^{1}H and ^{13}C NMR spectroscopy. The generation of the free carbene and the subsequent formation of the NHC−Pd complex were unambiguously confirmed by the absence of the ^{1}H NMR resonance due to the imidazolium proton (N−C*H*−N) and by the appearance of the low-field resonance of the Pd-bound carbene carbon (157.6 ppm for **4a**, 159.0 ppm for **4a′**) in the ^{13}C NMR spectrum. The coordination of the amino nitrogen atom was indicated by the ^{1}H NMR spectra, in which the NMe_2 protons appeared as two singlets and the NCH_2 protons gave rise to an AB spin pattern. The same trend was noticed in the ^{13}C NMR spectra, where two resonances were present for the NMe_2 carbons. These NMR-based conclusions were unequivocally corroborated by X-ray structure determination in both cases.

The geometry of complex **4a** (Figure 1) is essentially square-planar with an C1−Pd1−N4 bite angle of almost ideally 90°,

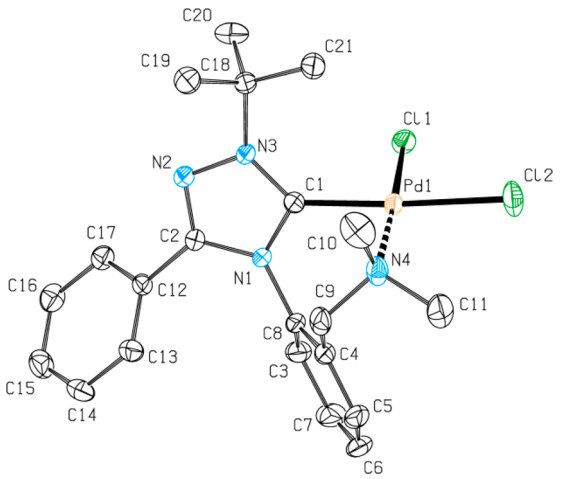

Figure 1. Molecular structure (ORTEP, 30% probability level) of **4a**. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd1−C1 1.968(4), Pd1−N4 2.123(3), Pd1−Cl1 2.3034(9), Pd1−Cl2 2.3509(11), C1−N3 1.335(4), C1−N1 1.360(5), C1−Pd1−N4 90.38(14), C1−Pd1−Cl1 85.40(10), N4−Pd1−Cl2 93.93(9), Cl1−Pd1−Cl2 90.44(4), N3−C1−N1 103.6(3), N3−C1−Pd1 134.8(3), N1−C1−Pd1 121.1(3).

thus proving the flexibility of the aliphatic amino group compared with the rigid geometry of the oxazoline-based NHC ligands.[12a] On the other hand, the C1−Pd1−Cl1 and N4−Pd1−Cl2 angles are slightly more distorted. The elongation of the Pd1−Cl2 bond *trans* to the carbene ligand compared with the Pd−Cl1 bond *trans* to the amino-N donor group [2.3509(11) vs 2.3034(9) Å] indicates a greater *trans* influence of the NHC ligand. This is consistent with previous structural studies.[12a,27] The interplanar angle between the plane defined by the triazole ring and the plane of the square-planar environment of the Pd atom is 72.94(13)°. The values of the remaining Pd−C [1.968(4) Å] and Pd−N [2.123(3) Å] distances lie within the expected ranges.[23]

The molecular structure of **4a′** (Figure 2) resembles that of **4a**, having the same conformation and interplanar angle

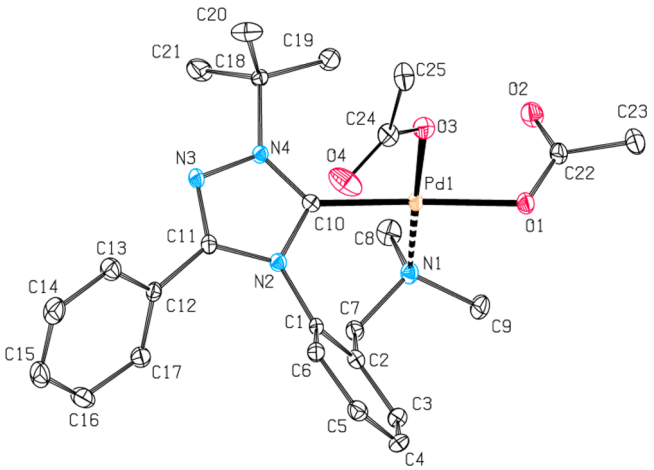

Figure 2. Molecular structure (ORTEP, 30% probability level) of **4a′**·H_2O. H atoms and the water molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd1−C10 1.968(3), Pd1−O3 2.033(2), Pd1−O1 2.063(2), Pd1−N1 2.085(3), C10−N4 1.325(4), C10−N2 1.371(4), C10−Pd1−O3 90.18(11), O3−Pd1−O1 84.41(10), C10−Pd1−N1 91.24(12), O1−Pd1−N1 94.52(10), N4−C10−N2 104.3(3), N4−C10−Pd1 134.6(2), N2−C10−Pd1 120.1(2).

between the triazole ring and the plane determined by the Pd atom and its four ligating atoms. The Pd−C bond in **4a′** is similar in length to that in **4a**, whereas the Pd−N distance involving the amino-N donor atom is shorter than in **4a**, suggesting stronger coordination of the pendant arm in the acetate complex. Again, a lengthening of the Pd−O1 bond located *trans* to the carbene unit with respect to the Pd−O3 bond *trans* to the amino-N donor group [2.063(2) vs 2.033(2) Å] due to the larger *trans* influence of the carbene ligand is observed. This is in contrast to structural features found in the previously published NHC-substituted palladium acetates with either an internal[28] or an external[29] phosphane donor group, where the *trans* influence exerted by the electron-donating phosphane group overpowers that of the carbene.

In order to operate with a broader set of compounds for the sake of comparison of their structural properties and possible catalytic activities, two new simplified NHC ligands were synthesized, and similar reactions with Pd(II) precursors were successfully performed to generate the complexes **4b**/**4b′** and **4c**/**4c′** (see Scheme 1). The two complexes possessing the 2-methoxyphenyl-substituted NHC ligands (**4b** and **4b′**) were prepared in order to distinguish between the formation of either biscarbene or monocarbene complexes. The formation of the carbene complexes was established by means of ^{1}H and ^{13}C NMR spectroscopy in the same way as in the case of **4a** and **4a′**. The ^{1}H NMR spectra of **4b** and **4b′** lacked the resonance due to the imidazolium proton (N−C*H*−N), while the low-field-shifted resonance of the carbene carbon appeared in the ^{13}C NMR spectra (172.0 ppm for **4b**, 171.9 ppm for **4b′**). Unambiguous proof of the formation of *trans* biscarbene complexes came from the X-ray structure determinations (Figure 3 for **4b**; Figure S1 in the Supporting Information for **4b′**). When the ^{1}H and ^{13}C NMR spectra of samples of **4b** and **4b′** dissolved in $CDCl_3$ were measured after a few days at room temperature, another set of signals with a similar spectral pattern appeared in each NMR spectrum. This is in line with the very recent work of Hong[18] describing the possible *trans* to *cis* conversion of analogous biscarbene complexes in $CDCl_3$. To

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confirm this assumption, the spectra of **4b** in $CDCl_3$ were measured immediately after preparation and then again after 24 h of heating at 40 °C. The spectra of the former sample showed only one set of signals attributed to the *trans* isomer, while the spectra of the latter contained signals of both isomers in an approximate ratio of 1:1 (for comparison, see Figures S10–S13 in the Supporting Information).

Compound **4b** is a square-planar Pd(II) complex showing a *trans* geometry and a coplanar arrangement of the NHC ligands in *anti* positions, with the Pd atom residing at the inversion center (Figure 3). The methoxy group of the NHC ligand is

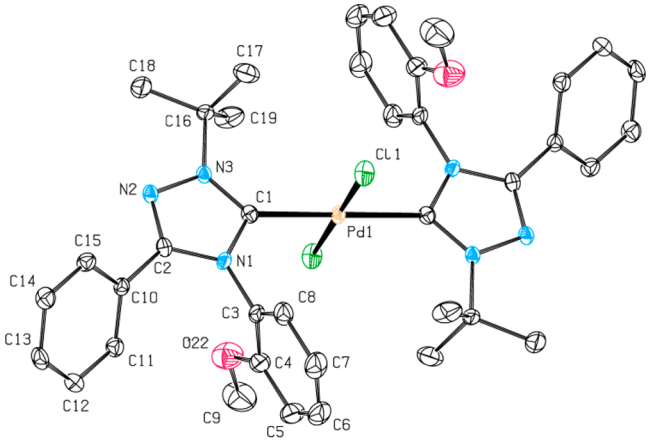

Figure 3. Molecular structure (ORTEP, 40% probability level) of **4b**·$CHCl_3$. H atoms and the chloroform molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd1–C1 2.025(4), Pd1–Cl1 2.3145(11), C1–N3 1.336(5), C1–N1 1.366(5), C1–Pd1–Cl1 88.89(11) [91.12(11)], N3–C1–N1 103.1(3), N3–C1–Pd1 134.8(3), N1–C1–Pd1 122.1(3).

directed away from the metal center and does not take part in intra- or intermolecular coordination. This is in good agreement with the results published earlier for similar O-functionalized NHCs.[30] The lengths of the Pd–C and Pd–Cl bonds are comparable to those in other related structurally characterized NHC–Pd complexes with chloride auxiliary ligands.[30,31]

The third and most simplified version of the NHC ligand having only a *p*-tolyl substituent was finally synthesized and employed in the same manner as the previous two ligands, completing the set of studied compounds. A comparison with the above-mentioned methoxy-substituted ligand left no doubt about the formation of the biscarbene complexes **4c** and **4c′**. The ^1H and ^{13}C NMR spectra provided clear signs supporting the formation of these products. The ^{13}C NMR chemical shifts for the carbene carbon atoms in **4c** and **4c′** were similar to those in **4b** and **4b′** (171.4 ppm for **4c**, 171.5 ppm for **4c′**). In both cases, single crystals suitable for X-ray structure determination were obtained, and the complexes were structurally characterized. The X-ray structure of **4c** (Figure 4) has an almost identical *trans-anti* arrangement as in the case of **4b** with bond distances and angles within the expected ranges. On the other hand, the X-ray structure of **4c′** has quite interesting features (Figure 5). First of all, there are very few known examples of palladium complexes with two monodentate-bonded acetate ligands with a *trans-anti*-type conformation of coplanar NHC ligands.[32] The square-planar geometry of **4c′** is slightly distorted with a deviation of about

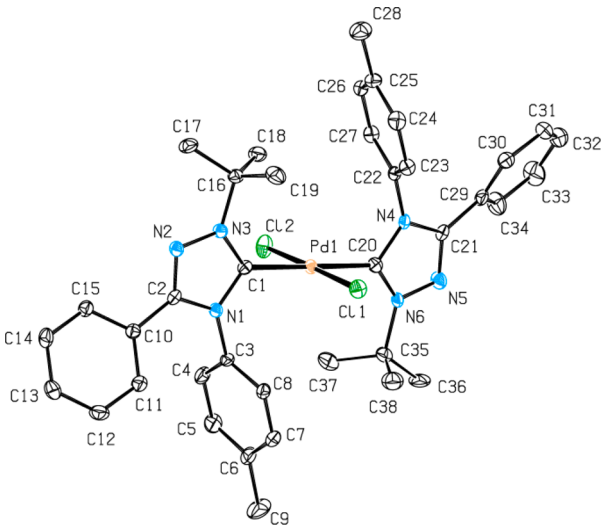

Figure 4. Molecular structure (ORTEP, 40% probability level) of **4c**·$2CHCl_3$. H atoms and the solvent molecules have been omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd1–C20 2.023(5), Pd1–C1 2.033(5), Pd1–Cl2 2.3249(14), Pd1–Cl1 2.3328(13), N1–C1 1.361(6), C1–N3 1.329(6), C20–N6 1.338(6), C20–N4 1.373(6), C20–Pd1–Cl2 88.26(14), C1–Pd1–Cl2 89.95(13), C20–Pd1–Cl1 91.38(14), C1–Pd1–Cl1 90.42(13), N3–C1–N1 104.1(4), N3–C1–Pd1 132.3(4), N1–C1–Pd1 123.5(3), N6–C20–N4 103.8(4), N6–C20–Pd1 132.5(4), N4–C20–Pd1 123.4(3).

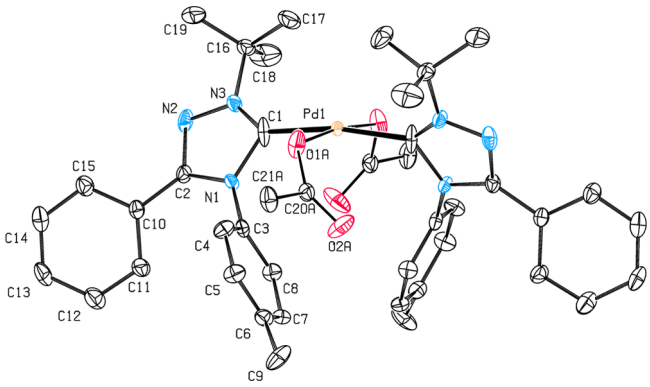

Figure 5. Molecular structure (ORTEP 30%, probability level) of **4c′**. H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd1–O1A 2.007(3), Pd1–C1 2.024(5), C1–N1 1.455(15), N1–C3 1.431(8), O1A–Pd1–C1 85.74(18) [93.58(17)], N3–C1–N1 101.2(5), N3–C1–Pd1 139.3(9), N1–C1–Pd1 119.2(7).

0.127 Å, which does not have any significant effect on the Pd–C bond distances compared with the previous complexes. The most surprising feature is seen in the mutual twisting of the carbene ligands. The interplanar angle of 59.48(11)° is, to the best of our knowledge, unprecedented among complexes of this kind.

Cross-coupling reactions, including the Suzuki–Miyaura reaction, have become some of the most important and widely used methods in fine chemical synthesis during the last decades.[1] Therefore, the catalytic activity of carbene complexes **4** was evaluated in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid to give the corresponding biphenyls as the model reaction (Scheme 2). In the tested series, only the *N*-chelated carbene complexes **4a** and **4a′**

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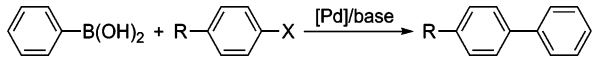
Scheme 2. Suzuki–Miyaura Cross-Coupling of Aryl Halides with Phenylboronic Acid



showed some catalytic activity, whereas the biscarbene complexes **4b**/**4b′** and **4c**/**4c′** were totally inactive in this reaction. This contrasts with the previously published results,[30,31b,c,33] among which the most surprising is the good catalytic activity of [1-(2-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$,[30] which features a structural motif very similar to that in **4b**.

Figures 6 and 7 show the kinetic profiles for the coupling reactions of 4-bromotoluene with phenylboronic acid per-

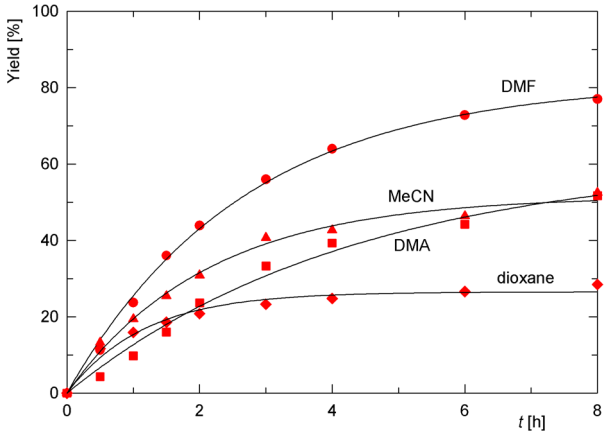


Figure 6. Kinetic profiles for the Suzuki–Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid in the presence of K_2CO_3 and 0.5 mol % **4a** in various solvents.

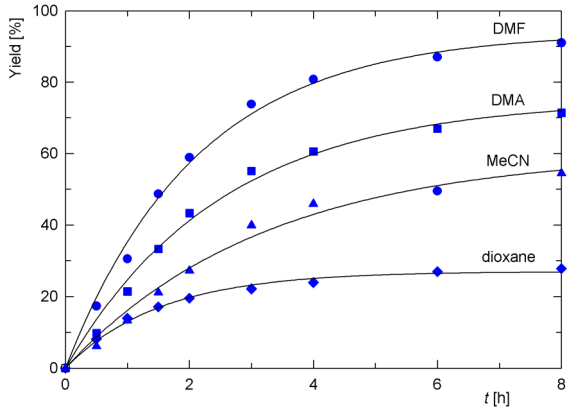


Figure 7. Kinetic profiles for the Suzuki–Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid in the presence of K_2CO_3 and 0.5 mol % **4a′** in various solvents.

formed in the presence of 0.5 mol % **4a** and **4a′**, respectively, and K_2CO_3 as the base at 80 °C in various solvents. In dioxane and MeCN, the complexes performed practically identically, affording the coupling product in yields of ca. 30% and 55%, respectively, after 8 h. In contrast, the reactions in DMF proceeded considerably faster and also differentiated the catalysts (conversions of 77% for **4a** and 91% for **4a′** after 8 h). A similar difference was observed in *N*,*N*-dimethylacetamide (DMA), where the yields of the biphenyl were 52% and 71% after 8 h for **4a** and **4a′**, respectively. Finally, the best results were achieved in azeotropic ethanol. The reaction in this solvent, which is the cheapest and least environmentally demanding among the tested solvents, proceeded very rapidly, giving the coupling product in essentially quantitative yield (>95%) within 30 min at 80 °C for both catalysts **4a** and **4a′** (0.5 mol %). This solvent was therefore applied in all of the subsequent reaction tests.

The dependence of the yield of 4-methylbiphenyl on the reaction temperature is illustrated in Figure 8, which

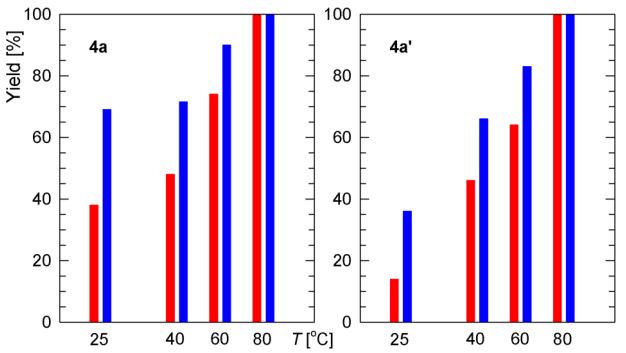


Figure 8. Dependence of the yield of the coupling product (4-methylbiphenyl) on the reaction temperature after 1 h (red bars) and 6 h (blue bars) using (left) **4a** and (right) **4a′** as the catalyst. Conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.2 mmol), and **4** (0.5 mol %) in ethanol (5 mL).

summarizes the results achieved with catalysts **4a** and **4a′** in ethanol. The conversions increased with the reaction temperature as expected and were rather similar for the two complexes.

Furthermore, we studied the possible influence of the base additive. For this purpose, the model coupling reaction was carried out with 0.5 mol % **4a** in the presence of various bases (1.2 molar equiv. with respect to the aryl halide) in 96% ethanol at room temperature for 1 h. In the reactions performed with anhydrous alkali-metal carbonates, the yield of the coupling product increased practically linearly with the square of the ionic radius of the alkali-metal cation[34] (Figure 9). In other words, salts with larger, more polarizable cations that

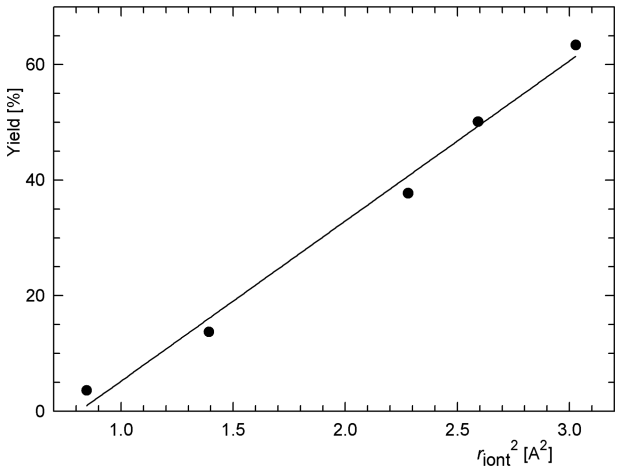


Figure 9. Dependence of the yield of 4-methylbiphenyl in the model coupling reaction on the square of the ionic radius of the alkali-metal cation (M) in M_2CO_3 used as the base. Conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.2 mmol), M_2CO_3 (1.2 mmol), and 0.5 mol % **4a** in ethanol (5 mL) at 25 °C for 1 h.

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are more soluble in the reaction medium showed better results, which is indeed in line with previous observations.[35] Variation of the anion was then performed for a small series of sodium salts. However, with the exception of Na_3PO_4 (23% conversion), common sodium salts (NaF, CH_3CO_2Na) afforded only poor yields (≲10%; see Table S1 in the Supporting Information).

The results of the "preparative" reaction tests summarized in Table 1 confirmed that the coupling reactions with aryl

Table 1. Summary of Preparative Catalytic Experiments[a]

substrate	temp./time	yield of biphenyl
4-bromoacetophenone	1 h/25 °C	65%
4-bromoacetophenone	24 h/25 °C	84%
4-bromoacetophenone	1 h/80 °C	100%
4-bromoanisole	1 h/25 °C	37%
4-bromoanisole	24 h/25 °C	35%
4-bromoanisole	1 h/80 °C	100%
1-bromo-4-(trifluoromethyl)benzene	1 h/25 °C	100%
4-bromo-1-nitrobenzene	1 h/25 °C	82%[b]
4-bromobenzonitrile	1 h/25 °C	100%
4-chloroacetophenone	3 h/80 °C	24%
4-chloroanisole	3 h/80 °C	3%
1-chloro-4-(trifluoromethyl)benzene	3 h/80 °C	75%
4-chloro-1-nitrobenzene	3 h/80 °C	ca. 73%
4-chlorobenzonitrile	3 h/80 °C	ca. 25%

[a]Conditions: Substrate (1.0 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol; K_2CO_3 for aryl bromides, Cs_2CO_3 for aryl chlorides), and catalyst **4a** (0.5 mol %) in azeotropic ethanol (5 mL). [b]Nitrobenzene, a dehalogenation product, was formed in 18% yield.

bromides mediated by catalyst **4a** (0.5 mol %) can be performed well at room temperature. The activated substrates were fully converted to the biphenyl products within 1 h, while the deactivated ones achieved only partial conversions. Extending the reaction time to 24 h improved the yields only partially. Eventually, complete conversions were obtained within 1 h upon heating to 80 °C. The corresponding aryl chlorides afforded considerably lower yields of the coupling products. The catalytic performance of complex **4a** thus appears to be slightly worse than that of the commercial catalyst PEPPSI, which is also a chloro−carbene Pd(II) complex.[6] This was indeed confirmed by a series of comparative experiments. For instance, the reaction of phenylboronic acid with 4-chlorotoluene as a deactivated aryl chloride afforded 4-methylbiphenyl in 54% yield when performed with 1 mol % **4a**. A similar reaction in the presence of PEPPSI-IPr afforded the coupling product in 69% yield (for the kinetic profiles, see Figure 10). On the other hand, catalyst **4a** maintained its catalytic activity for a longer time. Whereas the reaction with the PEPPSI-IPr catalyst practically stopped within ca. 30 min, compound **4a** maintained its activity for ca. 3 h.[36]

In another series of experiments (Figure 11), we focused on the nature of the actual catalytic species.[37] Thus, the reaction of 4-bromotoluene with phenylboronic acid was allowed to proceed in the presence of catalyst **4a** (0.5 mol %) at 80 °C for 1 h, and then the reaction mixture was filtered while hot through a PTFE syringe filter (pore size 0.45 μm). The filtration did not apparently affect the reaction, which proceeded similarly in the filtrate and the nonfiltered part of the reaction mixture. However, when a small amount of mercury (0.1 mL) was added after reaction for 1 h, the reaction

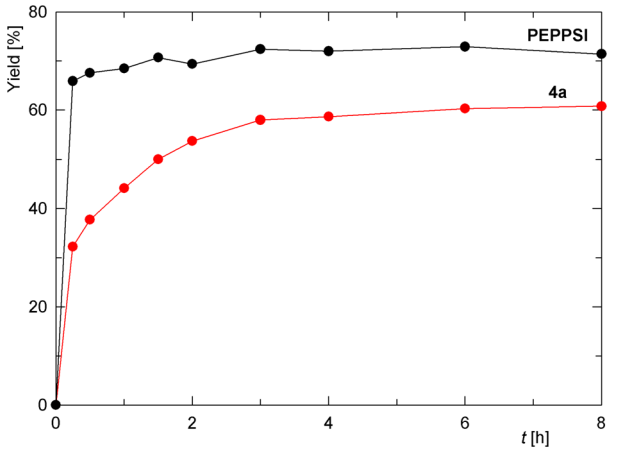

Figure 10. Comparison of the catalytic activity of **4a** (red circles) with that of the commercial catalyst PEPPSI (black circles). Conditions: 4-chlorotoluene (1.0 mmol), phenylboronic acid (1.2 mmol), Cs_2CO_3 (1.2 mmol), and catalyst (0.5 mol %) in azeotropic ethanol (5 mL) at 80 °C. The lines connecting the experimental points are shown only as guides to the eye.

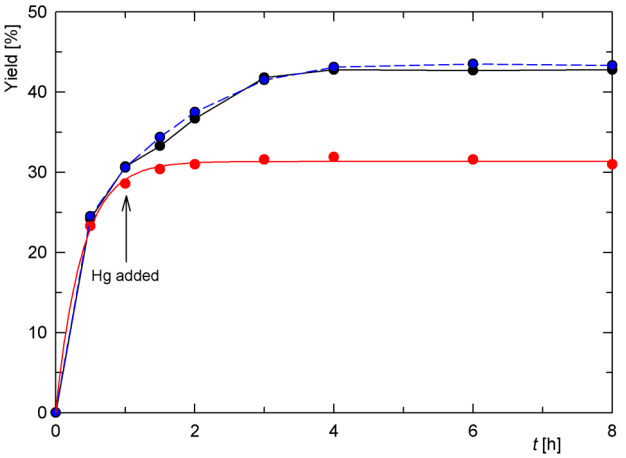

Figure 11. Comparison of the kinetic profiles for a standard reaction mixture (black circles), a reaction mixture that was filtered after 1 h (blue circles), and a reaction mixture to which mercury metal was added after 1 h (red circles). Conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.2 mmol), and **4a** (0.5 mol %) in azeotropic ethanol (5 mL) at 80 °C. The lines connecting the black and blue experimental points are shown only as guides to the eye.

stopped as a result of the metal scavenging effect of the mercury metal, which suggests the formation of fine palladium(0) particles[38] or a heterogeneous nature for the catalyst formed in the reaction mixture from complex **4a**. This observation is indeed in line with those made earlier for similar, PEPPSI-like catalysts.[9] In order to rule out possible degradation of complex **4a** under the given reaction conditions, neat **4a** was heated in ethanol at 80 °C for 4 h. This stability test, which mimicked the most severe reaction conditions used in any of catalytic experiments of this study, showed no signs of the decomposition of **4a**.

In order to gain more detailed insight into the nature of the bonding situation in the complexes reported in this paper, a theoretical survey was performed. The first part of this study was conducted on compounds **4a** and **4b**, starting from their structures determined by X-ray diffraction analysis. Next, the

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donating ability of the different types of NHC ligands was explored in the model PEPPSI-type[6] complex. A similar approach as in our study on coinage metal−NHC complexes was adopted,[39] using energy decomposition and natural orbital for chemical valence (NOCV) analyses[40] of the optimized structures (for details, see the Experimental Section). For calculation purposes, the *tert*-butyl and phenyl substituents on the carbene ligand were replaced by methyl groups, as these groups exhibit only a minor influence on the metal−carbene bonding.

The formation of the metal−carbene bond in the complex is associated with an electron density reorganization. The eigenvectors that diagonalize this deformation density are the NOCVs, which can be shown to occur in pairs, each pair describing a contribution to the total charge transfer upon bonding. For each of the NOCV pairs, one can also compute the energetic contribution to the charge transfer component of bonding (or orbital interaction contribution) and the number of electrons transferred. We found that for the analogues of compounds **4a** and **4b** (Figure 12) the density depletion (red)/accumulation (blue) patterns of the two most dominant NOCV pairs similarly describe the strong σ bonding (NOCV-1) and the weak π back-bonding (NOCV-2) of the carbene with the palladium dichloride fragment. In the case of **4a**, we found an additional important NOCV pair (NOCV-3) showing very clearly a strong contribution of the coordinated amino group to the overall bond formation. For the exact determination of the donating ability of the nitrogen atom itself, the fact that a minor part of this contribution is also expressed in NOCV-1 must be taken into account (for the whole set of results of these calculations, see the Supporting Information). The conclusion from both studies is that even though the triazole-based carbene itself has the second-lowest stabilizing effect in the series of six different NHCs, the presence of the amino group with the extra donating ability significantly improves the performance of the whole carbene ligand.

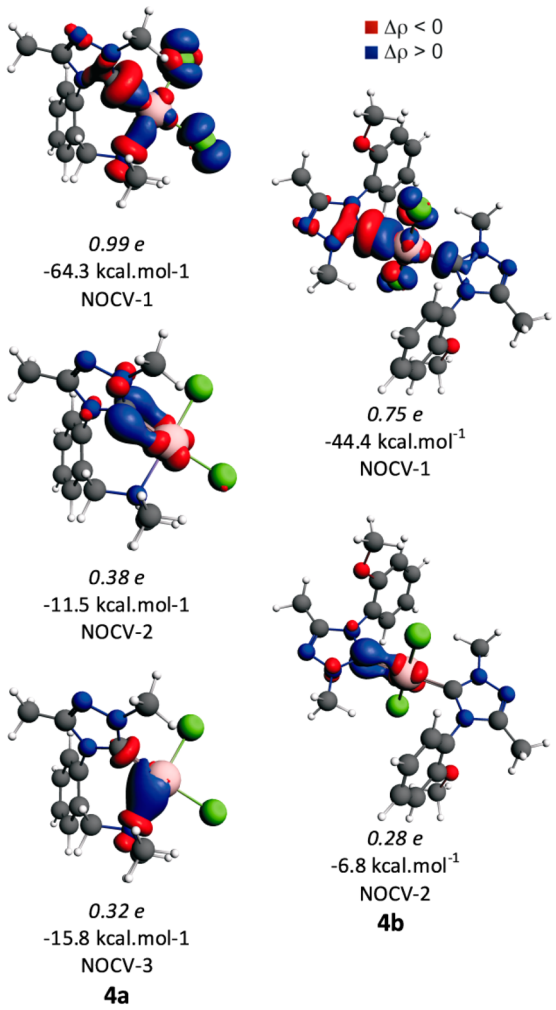

Figure 12. Relevant NOCV pairs with the corresponding density changes, numbers of electrons transferred, and contributions to the total orbital interaction energy component of the binding energy for the simplified models of **4a** and **4b**.

CONCLUSION

Six novel palladium complexes containing three different triazole-based NHCs were synthesized and structurally characterized. Among these compounds, only $PdCl_2$ and $Pd(OAc)_2$ derivatives bearing the 2-[(dimethylamino)methyl]-phenyl-substituted NHC ligand revealed a configuration involving a monocarbene-type complex with a strong intramolecular (i.e., chelating) coordination of the pendant amino group, resulting in the formation of an unusual seven-membered diazapalladacycle. On the other hand, the other two ligands bearing a 2-methoxyphenyl or 4-methylphenyl substituent form the usual biscarbene complexes. The catalytic activity evaluation revealed that only the monocarbene complexes **4a** and **4a′** are active in the Suzuki−Miyaura cross-coupling of aryl halides with phenylboronic acid. However, in comparison with other systems, the catalytic performance of **4a** and **4a′** can be achieved under "greener" conditions (lower temperature, shorter time, azeotropic ethanol as a solvent). Nonetheless, the catalytic performance of **4a** was slightly worse than that of the commercially available catalyst PEPPSI-IPr. Theoretical calculations revealed that the functionalization of the triazole backbone with the amino group has a significant stabilizing effect on the NHC−metal bonding and changes the overall coordinating ability of the modified NHC ligand.

EXPERIMENTAL SECTION

General Comments. All of the reactions leading to free carbenes and their Pd(II) complexes were performed under an argon atmosphere using standard Schlenk techniques. A solvent purification system was used to dry the solvents, which were then degassed and stored under an argon atmosphere.

Materials. *N*,*N*-Dimethyl-1-[2-(3-phenyl-4*H*-1,2,4-triazol-4-yl)-phenyl]methanamine (**1a**) and 1-*tert*-butyl-4-{2-[(dimethylamino)-methyl]phenyl}-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**2a**) were prepared according to the previously published procedures.[23]

NMR Spectroscopy. Samples for NMR measurements were obtained by dissolving ca. 40 mg of the analyzed compound in ca. 0.7 mL of a suitable deuterated solvent (DMSO-d_6, $CDCl_3$, or CD_2Cl_2). The ^{1}H chemical shifts are given relative to internal tetramethylsilane [$\delta(^1H) = 0.00$ ppm] or to residual solvent signals [DMSO-d_6, $\delta(^1H) = 2.50$ ppm; $CDCl_3$, $\delta(^1H) = 7.26$ ppm; CD_2Cl_2, $\delta(^1H) = 5.32$ ppm]. The ^{13}C chemical shifts were calibrated similarly [DMSO-d_6, $\delta(^{13}C) = 39.52$ ppm; $CDCl_3$, $\delta(^{13}C) = 77.16$ ppm; CD_2Cl_2, $\delta(^{13}C) = 53.84$ ppm]. All of the ^{13}C NMR spectra were measured using the standard proton-decoupled experiment, and CH and CH_3 versus C and CH_2 groups were distinguished by the APT method.[41]

Elemental Analysis. Elemental compositions were determined under an argon atmosphere using an automatic combustion analyzer.

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Analysis could not be performed for compound **2** because of the possibly explosive nature of the perchlorate salts.

X-ray Crystallography. The diffraction data (see Table S2 in the Supporting Information) were obtained at 150(2) K on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a graphite monochromator and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[42] The data were corrected for absorption by integration methods.[43] The structures were solved by direct methods (SIR92)[44] and refined by full matrix least-squares based on F^2 (SHELXL97).[45] Hydrogen atoms could be mostly localized on the difference Fourier maps. However, to ensure uniformity of the treatment of the crystal structures, all of the hydrogen atoms were recalculated into their idealized positions (riding model) and assigned temperature factors of $U_{iso}(H) = 1.2U_{eq}$ (pivot atom) or $1.5U_{eq}$ (methyl moiety), with C−H distances of 0.96, 0.97, and 0.93 Å for methyl, methylene, and aromatic ring or allyl moieties, respectively.

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under CCDC deposition numbers 921181−921186. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax: +44−1223−336033; e-mail: deposit@ccdc.cam.ac.uk; Web: http://www.ccdc.cam.ac.uk).

Preparation of 1 (Recyclization). Compounds **1b** and **1c** were prepared according to the published general procedure.[24a]

*4-(2-Methoxyphenyl)-3-phenyl-4H-1,2,4-triazole (**1b**).* Yield: 68%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75 (s, 1H, C*H*), 7.52 (td, 1H, ^3J = 7.8, ^4J = 1.6 Hz, Ar*H*), 7.44−7.33 (m, 6H, Ar*H*), 7.22 (dd, 1H, ^3J = 8.4, ^4J = 0.8 Hz, Ar*H*), 7.08 (td, 1H, ^3J = 7.6, ^4J = 0.8 Hz, Ar*H*), 3.58 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9 (N*C*N), 152.9 (N*C*HN), 146.0 (Ar*C*), 131.4 (Ar*C*), 129.7 (Ar*C*), 128.6 (Ar*C*), 128.4 (Ar*C*), 127.4 (Ar*C*), 127.2 (Ar*C*), 123.2 (Ar*C*), 121.1 (Ar*C*), 113.1 (Ar*C*), 55.8 (O*C*H$_3$). Anal. Calcd (%) for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.20; N, 17.72. Found: C, 71.78; H, 5.23; N, 17.69. Mp: 107−110 °C.

*4-(4-Methylphenyl)-3-phenyl-4H-1,2,4-triazole (**1c**).* Yield: 73%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.84 (s, 1H, C*H*), 7.43−7.35 (m, 5H, Ar*H*), 7.32−7.30 (m, 2H, Ar*H*), 7.28−7.25 (m, 2H, Ar*H*), 2.35 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.3 (N*C*N), 145.7 (N*C*HN), 138.97 (Ar*C*), 132.07 (Ar*C*), 130.27 (Ar*C*), 129.77 (Ar*C*), 128.77 (Ar*C*), 128.47 (Ar*C*), 126.87 (Ar*C*), 125.97 (Ar*C*), 20.77 (*C*H$_3$). Anal. Calcd (%) for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.49; H, 5.62; N, 17.88. Mp: 144−146 °C.

Preparation of 2 (Quaternization). Compounds **2b** and **2c** were prepared according to the published general procedure.[24b]

*1-tert-Butyl-4-(2-methoxyphenyl)-3-phenyl-4H-1,2,4-triazol-1-ium Perchlorate (**2b**).* Yield: 84%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.75 (s, 1H, C*H*), 7.81 (dd, 1H, ^3J = 7.9, ^4J = 1.6 Hz, Ar*H*), 7.66 (td, 1H, ^3J = 7.8, ^4J = 1.6 Hz, Ar*H*), 7.61−7.57 (m, 1H, Ar*H*), 7.52−7.44 (m, 4H, Ar*H*), 7.29−7.23 (m, 2H, Ar*H*), 3.56 (s, 3H, OCH_3), 1.76 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.4 (N*C*N), 153.2 (N*C*HN), 143.1 (Ar*C*), 133.3 (Ar*C*), 132.1 (Ar*C*), 129.1 (Ar*C*), 128.4 (Ar*C*), 128.1 (Ar*C*), 123.4 (Ar*C*), 121.4 (Ar*C*), 120.6 (Ar*C*), 113.4 (Ar*C*), 63.8 (*C*(CH$_3$)$_3$), 56.1 (O*C*H$_3$), 28.1 (C(*C*H$_3$)$_3$).

*1-tert-Butyl-4-(4-methylphenyl)-3-phenyl-4H-1,2,4-triazol-1-ium Perchlorate (**2c**).* Yield: 87%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.57 (s, 1H, C*H*), 7.59−7.55 (m, 1H, Ar*H*), 7.53−7.51 (m, 2H, Ar*H*), 7.48−7.46 (m, 4H, Ar*H*), 7.42−7.40 (m, 2H, Ar*H*), 2.39 (s, 3H, CH_3), 1.75 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.6 (N*C*N), 142.6 (N*C*HN), 141.1 (Ar*C*), 131.9 (Ar*C*), 130.4 (Ar*C*), 129.9 (Ar*C*), 129.3 (Ar*C*), 129.1 (Ar*C*), 126.5 (Ar*C*), 123.1 (Ar*C*), 63.4 (*C*(CH$_3$)$_3$), 28.1 (C(*C*H$_3$)$_3$), 20.8 (*C*H$_3$).

General Procedure for the Generation of Free Carbenes (3a−c) and the Preparation of (NHC)$_n$PdX$_2$ Complexes (4a−c and 4a′−c′). Free carbene **3** was generated at room temperature from the reaction of **2** with *t*-BuOK (**2**:*t*-BuOK molar ratio = 1.05:1) in dry toluene (ca. 30 mL). After 1 h of stirring, the resulting precipitate was filtered off, and the colorless to light-yellow filtrate was evaporated to dryness to afford free carbene **3**. Another Schlenk tube was charged with the precursor Pd(II) complex ([PdCl$_2$(CH$_3$CN)$_2$] for **4a−c** or Pd(OAc)$_2$ for **4a′−c′**), which was mixed with dry THF (ca. 10 mL). The solution of the freshly prepared free carbene **3** dissolved in 30 mL of dry THF was added dropwise to a stirred suspension of the Pd(II) complex at room temperature (**3**:Pd(II) complex molar ratio = 1:0.9 for **4a**/**4a′** and 1:1.9 for **4b**/**4b′** and **4c**/**4c′**). After the reaction mixture was stirred overnight, the solid residue was filtered off, and the filtrate was evaporated to dryness. The crude product was washed with hexane to give pure **4** as a yellow to yellow-brown powder. Single crystals suitable for X-ray diffraction were obtained by gas-phase diffusion of hexane into a solution of **4** in dichloromethane.

*(1-tert-Butyl-4-{2-[(N,N-dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide)palladium(II) Dichloride (**4a**).* Yield: 32%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.61−7.57 (m, 2H, Ar*H*), 7.46−7.43 (m, 2H, Ar*H*), 7.31 (t, 2H, ^3J = 8.0 Hz, Ar*H*), 7.18 (d, 1H, ^3J = 8.0 Hz, Ar*H*), 7.08 (d, 2H, ^3J = 7.0 Hz, Ar*H*), 3.39, 3.31 (AB spin system, $\Delta\delta$ = 0.08 ppm = 38 Hz, ^2J = 12 Hz, 2H, NCH_2), 2.95 (s, 3H, NCH_3), 2.89 (s, 3H, NCH_3), 2.16 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 158.0 (N*C*$_{carb}$N), 152.2 (N*C*N), 135.8 (Ar*C*), 133.3 (Ar*C*), 131.2 (Ar*C*), 130.9 (Ar*C*), 130.6 (Ar*C*), 130.0 (Ar*C*), 128.9 (Ar*C*), 127.3 (Ar*C*), 124.2 (Ar*C*), 67.7 (N*C*H$_2$), 64.2 (*C*(CH$_3$)$_3$), 54.5 (NCH$_3$), 52.5 (NCH$_3$), 31.1 (C(*C*H$_3$)$_3$). Anal. Calcd (%) for $C_{21}H_{26}Cl_2N_4Pd$: C, 49.28; H, 5.12; N, 10.95; Cl, 13.85. Found: C, 49.22; H, 5.02; N, 10.87; Cl, 13.94. Mp: 230 °C (dec.).

*(1-tert-Butyl-4-{2-[(N,N-dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide)palladium(II) Diacetate (**4a′**).* Yield: 48%. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.59 (t, 1H, ^3J = 7.5 Hz, Ar*H*), 7.53−7.49 (m, 2H, Ar*H*), 7.44 (t, 1H, ^3J = 7.5 Hz, Ar*H*), 7.33 (t, 2H, ^3J = 8.0 Hz, Ar*H*), 7.27 (d, 1H, ^3J = 7.5 Hz, Ar*H*), 7.20 (d, 1H, ^3J = 7.5 Hz, Ar*H*), 3.34, 3.19 (AB spin system, $\Delta\delta$ = 0.15 ppm = 76 Hz, ^2J = 12.5 Hz, 2H, NCH_2), 2.99 (s, 3H, NCH_3), 2.43 (s, 3H, NCH_3), 2.07 (s, 9H, C(CH_3)$_3$), 1.78 (s, 3H, CH_3COO$^-$), 1.67 (s, 3H, CH_3COO$^-$). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$): δ 177.2 (CH$_3$*C*OO$^-$), 175.6 (CH$_3$*C*OO$^-$), 159.6 (N*C*$_{carb}$N), 152.1 (N*C*N), 137.3 (Ar*C*), 132.4 (Ar*C*), 131.1 (Ar*C*), 130.6 (Ar*C*), 130.5 (Ar*C*), 129.7 (Ar*C*), 129.1 (Ar*C*), 129.0 (Ar*C*), 128.9 (Ar*C*), 125.1 (Ar*C*), 67.3 (N*C*H$_2$), 63.5 (*C*(CH$_3$)$_3$), 55.1 (NCH$_3$), 50.3 (NCH$_3$), 30.5 (C(*C*H$_3$)$_3$), 24.3 (*C*H$_3$COO$^-$), 22.7 (*C*H$_3$COO$^-$). Anal. Calcd (%) for $C_{25}H_{32}N_4O_4Pd$: C, 53.72; H, 5.77; N, 10.02. Found: C, 53.75; H, 5.80; N, 10.11. Mp: 196−197 °C (dec.).

*trans-Bis[1-tert-butyl-4-(2-methoxyphenyl)-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide]palladium(II) Dichloride (**4b**).* Yield: 62%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, 2H, ^3J = 7.6 Hz, Ar*H*), 7.49 (t, 2H, ^3J = 7.8 Hz, Ar*H*), 7.31−7.14 (m, 12H, Ar*H*), 6.94 (d, 2H, ^3J = 8.4 Hz, Ar*H*), 3.52 (s, 6H, OCH_3), 1.67 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 172.0 (N*C*$_{carb}$N), 155.6 (N*C*N), 152.4 (Ar*C*), 132.0 (Ar*C*), 131.1 (Ar*C*), 129.9 (Ar*C*), 128.3 (Ar*C*), 128.2 (Ar*C*), 126.6 (Ar*C*), 121.2 (Ar*C*), 112.8 (Ar*C*), 62.0 (*C*(CH$_3$)$_3$), 56.1 (O*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$). Anal. Calcd (%) for $C_{38}H_{42}Cl_2N_6O_2Pd$: C, 57.62; H, 5.34; N, 10.61; Cl, 8.95. Found: C, 57.63; H, 5.40; N, 10.68; Cl, 9.06. Mp: 295−297 °C (dec.).

*trans-Bis[1-tert-butyl-4-(2-methoxyphenyl)-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide]palladium(II) Diacetate (**4b′**).* Yield: 67%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.64 (dd, 2H, ^3J = 8.0, ^4J = 1.6 Hz, Ar*H*), 7.53 (td, 2H, ^3J = 7.7, ^4J = 1.6 Hz, Ar*H*), 7.36−7.23 (m, 12H, Ar*H*), 6.88 (dd, 2H, ^3J = 8.4, ^4J = 0.8 Hz, Ar*H*), 3.42 (s, 6H, OCH_3), 1.76 (s, 18H, C(CH_3)$_3$), 1.69 (s, 6H, CH_3COO$^-$). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$): δ 175.5 (CH$_3$*C*OO$^-$), 171.9 (N*C*$_{carb}$N), 155.2 (N*C*N), 152.3 (Ar*C*), 132.0 (Ar*C*), 131.0 (Ar*C*), 130.0 (Ar*C*), 128.4 (Ar*C*), 128.3 (Ar*C*), 127.0 (Ar*C*), 121.7 (Ar*C*), 112.1 (Ar*C*), 62.1 (*C*(CH$_3$)$_3$), 55.8 (O*C*H$_3$), 30.4 (C(*C*H$_3$)$_3$), 23.1 (*C*H$_3$COO$^-$). Anal. Calcd (%) for $C_{42}H_{48}N_6O_6Pd$: C, 60.10; H, 5.76; N, 10.01. Found: C, 60.03; H, 5.83; N, 10.15. Mp: 255 °C (dec.).

*trans-Bis[1-tert-butyl-4-(4-methylphenyl)-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide]palladium(II) Dichloride (**4c**).* Yield: 65%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51−7.49 (m, 4H, Ar*H*), 7.33−7.29 (m, 6H, Ar*H*), 7.23−7.22 (m, 8H, Ar*H*), 2.50 (s, 6H, CH_3), 1.62 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 171.4 (N*C*$_{carb}$N), 151.7 (N*C*N), 139.4 (Ar*C*), 134.8 (Ar*C*), 130.2 (Ar*C*), 129.9 (Ar*C*), 129.6 (Ar*C*), 128.6 (Ar*C*), 128.3 (Ar*C*), 125.7 (Ar*C*), 61.8 (*C*(CH$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 21.3 (*C*H$_3$). Anal. Calcd (%) for $C_{38}H_{42}Cl_2N_6Pd$: C,

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60.05; H, 5.57; N, 11.06; Cl, 9.33. Found: C, 59.98; H, 5.52; N, 11.21; Cl, 9.40. Mp: 299−301 °C (dec.).

*trans-Bis[1-tert-butyl-4-(4-methylphenyl)-3-phenyl-1H-1,2,4-triazol-4-ium-5-ide]palladium(II) Diacetate (**4c′**).* Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.53 (m, 4H, Ar*H*), 7.31−7.26 (m, 10H, Ar*H*), 7.22−7.19 (m, 4H, Ar*H*), 2.49 (s, 6H, CH_3), 1.73 (s, 6H, CH_3COO^-), 1.63 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5 (CH_3COO^-), 171.5 ($NC_{carb}N$), 151.2 (NCN), 138.9 (Ar*C*), 135.0 (Ar*C*), 129.7 (Ar*C*), 129.6 (Ar*C*), 129.5 (Ar*C*), 128.8 (Ar*C*), 128.1 (Ar*C*), 126.1 (Ar*C*), 61.5 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$), 23.5 (CH_3COO^-), 21.4 (CH_3). Anal. Calcd (%) for $C_{42}H_{48}N_6O_4Pd$: C, 62.49; H, 5.99; N, 10.41. Found: C, 62.51; H, 6.03; N, 10.37. Mp: 340−345 °C (dec.).

Catalytic Tests. A Schlenk tube was charged with the respective aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), the base (1.2 mmol), and the Pd catalyst, flushed with nitrogen, and sealed. The solvent was introduced, and the reaction vessel was transferred to a parallel batch reactor. The progress of the coupling reactions was monitored by gas chromatography.

The reaction mixtures resulting from the "preparative" experiments (Table 1) were diluted with water and extracted into dichloromethane. The organic layer was dried over $MgSO_4$ and passed through a short silica gel column. The eluate was evaporated and analyzed by ^{1}H and/or ^{19}F NMR spectroscopy ($CDCl_3$ was used as the solvent).

Computational Details. Density functional theory (DFT)[46] geometry optimizations of the molecules were performed with the Gaussian 09 program[47] using the B3LYP hybrid functional[48] with the Dunning-type basis set cc-pVDZ[49] for carbon, hydrogen, nitrogen, and chlorine and the cc-pVDZ-pp[50] basis set for palladium. Frequency calculations were carried out to confirm that the obtained structures corresponded to minima on the potential energy surface. Next, the Ziegler−Rauk-type energy decomposition[51] and NOCV analyses were carried out on the B3LYP/cc-pVDZ(-pp)-optimized structures using the PBE[52]/TZ2P (small-core) functional/basis set combination as implemented in ADF2012.02.[53] Relativistic effects as well as dispersion corrections were taken into account using the zeroth-order regular approximation (ZORA)[54] and Grimme's revised DFT-D3 method.[55]

■ ASSOCIATED CONTENT

Supporting Information

Molecular structure of complex **4b′**, additional results from catalytic tests, crystallographic tables and details (CIF) for compounds **4a−c** and **4a′-c′**, an extended discussion of the computational survey, NMR spectra for compounds **4a−c** and **4a′-c′**, and a text file containing all of the computed molecule Cartesian coordinates in a format for convenient visualization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(36) In another experiment (see Scheme S1 in the Supporting Information), 1,4-dibromobenzene was allowed to react in the presence of 0.5 mol % **4a** sequentially with (4-acetylphenyl)boronic acid and then 4-tolueneboronic acid (1 equiv each). When the second boronic acid reagent was added after 1 h of the reaction of 1,4-dibromobenzene with (4-acetylphenyl)boronic acid and the reaction was continued for another 1 h, GC−MS analysis revealed that the reaction mixture contained products with all possible substituent combinations and some unreacted 1,4-dibromobenzene. When the reaction was carried out similarly for 3 h [longer reaction with (4-acetylphenyl)boronic acid] and 1 h (with 4-tolueneboronic acid), the relative amount of residual 1,4-dibromobenzene increased, suggesting some catalyst deactivation.

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