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Postmodification Approach to Charge-Tagged 1,2,4-Triazole-Derived NHC Palladium(II) Complexes and Their Applications

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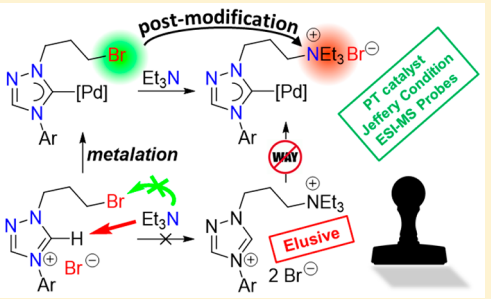
Supporting Information

ABSTRACT: Charge-tagged bis(1,2,4-triazolin-5-ylidene)palladium(II) complexes have been successfully synthesized via a postmodification strategy. Reacting $PdBr_2$ with bromo-functionalized 1,2,4-triazolium salts **A**·HBr and **B**·HBr in the presence of silver oxide afforded the bis(carbene)palladium(II) complexes *trans*-[$PdBr_2$(**A**)$_2$] (**1a**) and *trans*-[$PdBr_2$(**B**)$_2$] (**1b**), which contain tethered bromoalkyl chains. Subsequent postcoordinative nucleophilic substitution converted the bromo into ammonium groups, producing the water-soluble complexes *trans*-[$PdBr_2$(**C**)$_2$]Br_2 (**2a**) and *trans*-[$PdBr_2$(**D**)$_2$]Br_2 (**2b**), while attempts to prepare ammonium-functionalized triazolium salts for direct metalation were futile. All four complexes were fully characterized by means of multinuclear NMR spectroscopy, ESI mass spectrometry, elemental analysis, and X-ray diffraction analysis. The presence of trans-anti and trans-syn rotameric complexes in solution was elucidated by ^{1}H and ^{13}C NMR spectroscopy and theoretical calculations. Additionally, the two charge-tagged complexes, **2a**,**b**, were found to be highly active precatalysts for the Suzuki−Miyaura and Mizoroki-Heck reactions in ^{i}PrOH/H_2O and molten TBAB as an ionic liquid.



INTRODUCTION

The past few decades have witnessed remarkable advances in the development of N-heterocyclic carbenes (NHCs) for organometallic catalysis and coordination chemistry.[1] The success of NHCs is largely attributed to the extraordinary tunability of their stereoelectronic properties achievable by wingtip and backbone modifications.[1d,2]

In parallel, the development of charge-tagged ligands as valuable tools in organometallic chemistry has also received increasing interest,[3] where they have found applications in immobilization[4] and aqueous catalysis.[5] Generally, carboxylate and sulfonate or tetraalkylammonium groups can be used as anionic or cationic charge tags, respectively. However, only the latter are essentially pH independent and retain their charge regardless of reaction conditions. In addition to imparting increased solubility in polar solvents and phase-transfer capabilities, a tetraalkylammonium group may also exert a positive effect on the catalytic performance (Jeffery conditions) and act as a mass spectrometric tag.

Among the classical NHCs, imidazolin-2-ylidenes and 1,2,4-triazolin-5-ylidenes were the first to be isolated in stable free form. These two types are also most comparable in terms of reactivity and spectroscopic and structural features, since they are solely differentiated by an isolobal substitution of a CH with an N group. Moreover, Enders' 1,2,4-triazole-derived NHC was the first commercially available free NHC.[6] Despite this fact and their similarities, it is surprising to note that the organometallic chemistry of 1,2,4-triazolin-5-ylidenes is far less established and pales in comparison to their imidazolin-2-ylidene cousins. Most reported 1,2,4-triazolin-5-ylidene complexes feature carbenes with simple N substituents, such as alkyl or aryl groups,[7] but functionalized triazole-derived NHC complexes are very rare.[8]

As a contribution to a better understanding of such species and to explore their potential applications, we herein report on the syntheses of the first ammonium-functionalized 1,2,4-triazolin-5-ylidene complexes of palladium(II) via a post-functionalization approach. The postcoordinative ligand modification, which involves functional group transformations on suitable complexes, can provide efficient and versatile access to a wide range of functionalized-NHC complexes.[9] This strategy is especially advantageous when metalation conditions are incompatible with the desired functional group.[10]

RESULTS AND DISCUSSION

Synthesis and Characterization of Bromo-Functionalized Pd^{II} Bis(carbene) Complexes. Triazolium bromides **A**·HBr and **B**·HBr, were prepared in good yields by direct N-alkylation of two 4-aryl-1,2,4-triazoles with the bulky and popular 2,4,6-trimethylphenyl (Mes) and 2,6-diisopropylphenyl (Dipp) wingtips in neat 1,3-dibromopropane (Scheme 1). Formation of the triazolium salts was evidenced by the presence of downfield signals at 12.05 ppm (**A**·HBr) and

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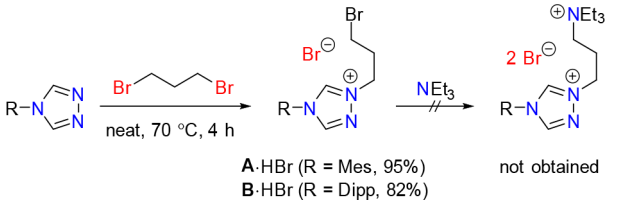
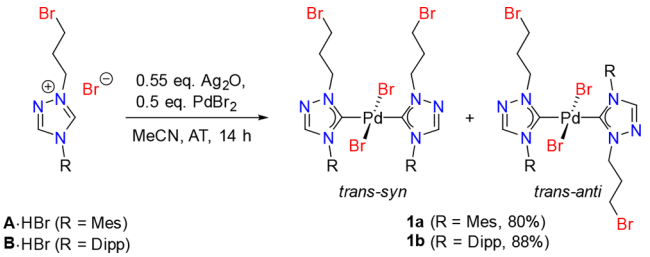
Scheme 1. Synthesis of Bromo-Functionalized Triazolium Salts A·HBr and B·HBr



12.16 ppm (**B**·HBr) in their ^{1}H NMR spectra, which are assigned to the acidic C5 protons of the heterocyclic rings. Furthermore, base peaks for the molecular $[M - Br]^+$ cations were observed in their ESI mass spectra at m/z 308 (**A**·HBr) and m/z 350 (**B**·HBr), respectively, confirming the identity of the salts. The alkylations also produced propylene-bridged ditriazolium salts as minor side products. Nevertheless, this side reaction is minimized when 10 equiv of 1,3-dibromopropane is used. Excess 1,3-dibromopropane was recovered by distillation at 80 °C and 50 mbar. It is noted that, even with an excess of 1,3-dibromopropane, only one of the two cyclic imine nitrogen atoms was alkylated and no 1,2-bis(3-bromopropyl)-1,2,4-triazolium dibromides were observed. In fact, to alkylate the third ring nitrogen, much stronger electrophiles, e.g. trialkyl oxonium salts, are required.[11]

Initial attempts to install an ammonium function on the carbene precursors as a cationic tag via direct nucleophilic substitution reactions between **A**·HBr or **B**·HBr and triethylamine were futile and only led to decomposition. This is probably due to the interference of the rather acidic C5 proton of the triazolium salts with the amine base. To circumvent this problem, a postmodification strategy was pursued as an elegant alternative instead.[9a,b] Accordingly, bromopropyl-substituted complexes *trans*-$[PdBr_2(\mathbf{A})_2]$ (**1a**) and *trans*-$[PdBr_2(\mathbf{B})_2]$ (**1b**) were obtained in good yields by reacting $PdBr_2$ with the respective salts **A**·HBr and **B**·HBr and Ag_2O at ambient temperature (AT) in acetonitrile (Scheme 2) for subsequent

Scheme 2. Synthesis of Complexes 1a,b



postcoordinative modification. The two complexes were purified by column chromatography (SiO_2) using dichloromethane as eluent and isolated as pale yellow solids. They are soluble in common polar organic solvents, such as dichloromethane, chloroform, and acetonitrile, but insoluble in hexane or diethyl ether. In their ESI mass spectra, base peaks at m/z 803 (**1a**) and m/z 887 (**1b**) were observed for the $[M - Br]^+$ fragments, corroborating the formation of the desired complexes. Furthermore, the absence of downfield signals in their ^{1}H NMR spectra characteristic for the acidic C5 protons in their salt precursors supports their successful palladation.

Moreover, two sets of signals were observed in the ^{1}H and ^{13}C NMR spectra of both **1a** and **1b**, indicating the presence of two isomers. The $^{13}C_{carbene}$ signals are marginally separated and appear at 172.8/172.7 ppm (**1a**) and 173.6/173.2 ppm (**1b**), suggestive of a trans orientation of the two triazolin-5-ylidenes. A more upfield shift is expected when the carbenes are trans to the weaker donating bromido ligands.[12] Considering the unsymmetrical nature of the two NHC ligands, the two sets of signals can be assigned to trans-anti and trans-syn rotamers. Notably, the ^{1}H NMR resonances of the bromopropyl side chains of the two isomers are well separated with one set distinctively shifted more to high field. This set of signals is assignable to the trans-anti rotamer, in which the bromopropyl tethers are exposed to the magnetic anisotropic shielding from the aromatic rings (Figure 1). In contrast, the bromopropyl chains in the syn isomer are free from such shielding.[9b,13]

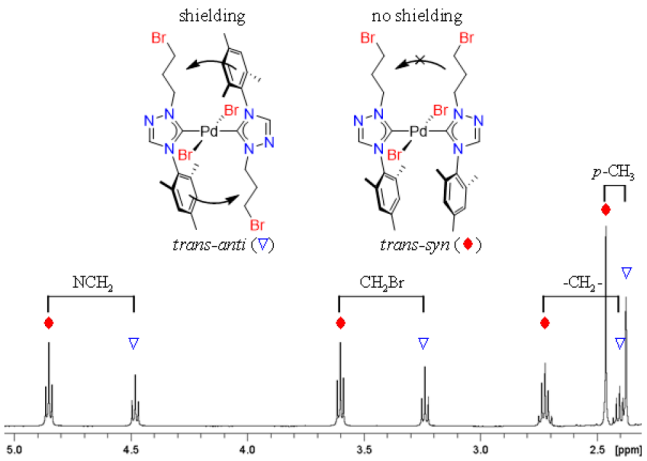


Figure 1. ^{1}H NMR spectrum of **1a** in CD_3CN from ~2.3−5.1 ppm.

The differences in resonances induced by the aromatic rings as "built-in sensors" allow for an unambiguous spectral assignment and easy determination of the relative anti:syn ratio in solution. For example, in $CDCl_3$ solutions, the ratios amount to 0.9:1 and 0.8:1 for **1a,b**, respectively. The ratios were found to vary from one solvent to another. For example, the anti:syn ratio for **1a** changes from 0.9:1 in $CDCl_3$ to 0.6:1 in CD_3CN and 0.5:1 in DMSO-d_6. A similar trend is also observed for **1b**, for which anti:syn ratios of 0.6:1 and 0.4:1 were found in CD_3CN and DMSO-d_6, respectively. The predominance of the trans-syn isomers for both **1a** and **1b** suggests that they are more stable in $CDCl_3$ than their trans-anti counterparts, and more polar solvents (i.e., CD_3CN, DMSO) stabilize them even further.

To rationalize the above observation, theoretical calculations were carried out to assess the relative energy of trans-anti and trans-syn rotamers for **1a** as a representative. The structures of both anti and syn rotamers were first optimized in the gas phase, and then single-point calculations were performed with solvation described by an implicit solvent effect model (see the Supporting Information for more calculation details). Optimized structures of the two rotamers are presented in Figure S1 in the Supporting Information. Structural parameters of the optimized geometries of the anti rotamer agree well with the molecular structure determined by single-crystal X-ray diffraction studies (vide infra).

The calculation results show that *trans-anti*-**1a** is 4.5 kJ/mol lower in energy in comparison to *trans-syn*-**1a** in the gas phase, likely due to steric repulsion of the two mesityl substituents.

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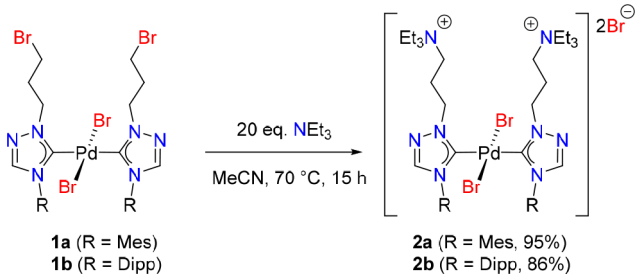
However, the symmetrical trans-anti isomer has an overall zero dipole moment, whereas the trans-syn isomer possesses a dipole moment of 8.2 D. The larger dipole moment leads to a significant stabilization of the trans-syn isomer in polar solvents, where it can become the major species. In fact, the syn form is lower in energy than the anti counterpart by 1.8, 3.7, and 3.8 kJ/mol in chloroform, acetonitrile, and dimethyl sulfoxide, respectively. These energy differences translate into the anti:syn ratios of 0.48:1, 0.22:1, and 0.21:1 for their respective solutions in chloroform, acetonitrile, and dimethyl sulfoxide. Although the calculations underestimate the anti:syn ratio, they do predict and rationalize the experimentally observed stabilization of the syn isomer in polar solvents.

Synthesis and Characterization of Charge-Tagged Complexes via Postfunctionalization Approach. Since suitably ammonium functionalized carbene precursors were not accessible, a postfunctionalization approach had to be explored for the preparation of the charge-tagged NHC complexes *trans*-$[PdBr_2(\mathbf{C})_2]Br_2$ (**2a**; **C** = 1-(3-triethylammonium)propyl-4-mesityl-1,2,4-triazolin-5-ylidene) and *trans*-$[PdBr_2(\mathbf{D})_2]Br_2$ (**2b**; **D** = 1-(3-triethylammonium)propyl-4-(2,6-diisopropyl)-phenyl-1,2,4-triazolin-5-ylidene). Indeed, these were successfully prepared with ease by nucleophilic substitution reactions between the bromo-functionalized complexes **1a,b** and triethylamine (Scheme 3). The reactions were complete after stirring

Scheme 3. Synthesis of Complexes 2a,b



1a (R = Mes)
1b (R = Dipp)

2a (R = Mes, 95%)
2b (R = Dipp, 86%)

at 70 °C for 15 h, affording white solids of **2a,b** in very good yields. Both complexes are insoluble in nonpolar solvents, such as hexane and diethyl ether, but they display good solubilities in dichloromethane, methanol, acetonitrile, and dimethyl sulfoxide. Notably, both complexes also dissolve in water with solubilities of 1.3 mg/mL (1.2 mmol/L, **2a**) and 1.7 mg/mL (1.5 mmol/L, **2b**).

Generally, mass spectroscopic analysis of neutral bis(carbene) complexes of the type $[PdX_2(NHC)_2]$ is not straightforward and often only shows base peaks for azolium cations from NHC decomposition and minor patterns for complex fragments, such as the $[PdX(NHC)_2]^+$ cation (vide supra). Desirable molecular cations such as $[M + H]^+$ are rarely detected,[9b,14] and thus evidence for the full square-planar coordination sphere around a metal center cannot be directly obtained. Complexes **2a,b** are decorated with ammonium functions, and harsh ionization processes in the gas phase are not required, which makes them much more ESI-MS responsive. This should allow for an easy detection of the intact molecular complex cation. Indeed, the ESI mass spectra of **2a,b** show base peaks for their molecular cations $[PdBr_3(\mathbf{C})_2]^+$ and $[PdBr_3(\mathbf{D})_2]^+$ at *m/z* 1005 (**2a**) and *m/z* 1089 (**2b**), respectively. In addition, peaks for the intact dications $[PdBr_2(\mathbf{C})_2]^{2+}$ and $[PdBr_2(\mathbf{D})_2]^{2+}$ at *m/z* 462 (**2a**) and *m/z* 504 (**2b**) are also observed at 50% and 40%, respectively. All of these peaks exhibit isotopic distribution patterns identical with the theoretical ones, confirming the identities of the two complexes. A representative comparison for the $[PdBr_2(\mathbf{D})_2]^{2+}$ cation of **2b** is depicted in Figure 2.

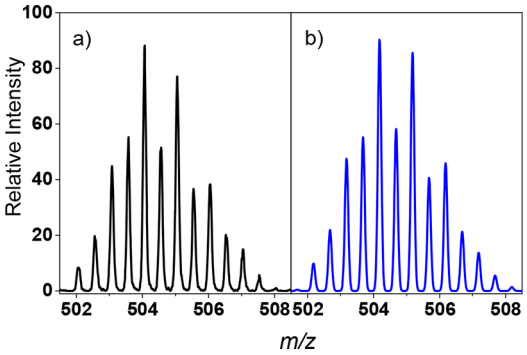


Figure 2. Experimental (a) and theoretical (b) isotopic patterns of the $[PdBr_2(D)_2]^{2+}$ cation of **2b**.

Similar to the case for **1a,b**, the ^1H and ^{13}C NMR spectra of **2a,b** also show two sets of signals assignable to the trans-anti and trans-syn rotamers of the palladium(II) bis(carbene) complexes. The $^{13}C_{carbene}$ signals remain largely unaffected by the remote postfunctionalization. Again, unambiguous signal assignment was made convenient by the anisotropic effect exerted by the aromatic ring as "built-in sensors", which causes the propylene ^1H NMR signals of the trans-anti isomers to shift distinctly upfield in comparison to those of the trans-syn forms. The relative ratios of anti:syn rotamers were determined to be 0.3:1 (**2a**) and 0.5:1 (**2b**) in acetonitrile, suggesting a better stabilization of the syn rotamers in comparison to their anti counterparts, which was also observed for **1a,b** and attributed to their larger dipole moments in line with theoretical calculations (vide supra). The same preference for the syn forms for **2a,b** is somewhat surprising, since one would expect intramolecular charge repulsion between the ammonium moieties.[9b] On the other hand, $\pi-\pi$ stacking interactions between the aromatic substituents could contribute to a stabilization of the trans-syn rotamers. The only compound that crystallized in the trans-syn conformation was complex **2a** (vide infra). In its solid-state structure, the shortest interplanar C−C distance between two aromatic mesityl rings is 3.51 Å. This distance is slightly smaller than the sum of the van der Waals radius (1.77 Å) of two carbon atoms[15] and is well within the optimal distance for a significant $\pi-\pi$ stacking interaction (3.3−3.8 Å).[16] This could indeed point to the contributing factor of $\pi-\pi$ stacking interactions.

Additionally, in order to probe the syn preference more deeply, we set out to examine the molecular dipole moments of the complexes. However, a routine geometry optimization for **2a,b** in the gas phase would be computationally inefficient, as both molecules possess multiple flexible alkyl chains and mobile bromide anions. Alternatively, their dipole moments were assessed using solid-state molecular structures determined by X-ray diffraction (vide infra). Using these for calculations, dipole moments of 34 and 0 D were found for *trans-syn*-**2a** and *trans-anti*-**2b**, respectively. It is noted that the predominant species in acetonitrile are syn isomers, which possess much larger dipole moments. In addition, the syn preference in solution could also be attributed to favorable electrostatic attractions. The syn arrangement of the two tethered

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ammonium cations can be further supported by electrostatic attraction to a small bromide anion in the interstitial space. If this electrostatic interaction is one of the contributing factors, replacement of bromide with a larger and more charge diffused anion, such as hexafluorophosphate, would reduce the favoritism for the syn arrangement. To test this notion, an anion exchange was carried out, which gave *trans*-$[PdBr_2(\mathbf{C})_2](PF_6)_2$ (**2a′**) and $[PdBr_2(\mathbf{D})_2](PF_6)_2$ (**2b′**). The ^{1}H NMR spectra of **2a′**,**b′** also show two sets of signals, indicating the presence of two rotamers. The protons on alkyl chains of the two isomers are well separated, and therefore, the anti:syn ratios can be determined with ease. Indeed, their respective anti:syn ratios in acetonitrile solutions have increased from 0.3:1 (**2a**) to 0.7:1 (**2a′**) and from 0.5:1 (**2b**) to 1.2:1 (**2b′**), respectively, supporting the aforementioned notion. The $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ spectra of **2a′**,**b′**, on the other hand, show only one set of signal for hexafluorophosphate counteranions, suggesting the absence of any significant interactions between the counteranions with the complex cations in solution.

Molecular Structures. Single crystals of complexes **1a**,**b**, **2a**·CH_2Cl_2, and **2b**·$2CHCl_3$ were grown by slow evaporation of concentrated solutions in $CHCl_3$/hexane (**1a**,**b**), chloroform (**2a**), or dichloromethane (**2b**). The molecular structures of the four complexes are shown in Figure 3, and selected bond lengths and bond angles are given in Table 1.

In the crystals of **1a** and **2a**,**b**, one independent molecule was found, whereas two independent molecules were found in crystals of **1b**. In all of the structures, the palladium(II) center is coordinated by two carbene and two bromido ligands in an essentially square planar coordination geometry. All of the complexes adopt the trans configuration, which is in line with conclusions drawn from solution NMR data. The molecular structures of **1a**,**b** and **2b** show a trans-anti arrangement for the two unsymmetrical carbene ligands, whereas a trans-*syn* orientation is displayed by **2a**. Notably, a bromide anion is located in the space between the two ammonium groups of *trans-syn*-**2a** (Figure 3), which is in line with the notion given above. In addition, the Pd−$C_{carbene}$ bond distances are identical within 3σ, ranging from 2.00(1) to 2.027(6) Å, which are close to the range reported for Pd−$C_{carbene}$ distances in *trans*-bis(triazolin-5-ylidene)palladium(II) complexes (2.017(5)−2.034(5) Å).[17] In complexes **1a**,**b** and **2b**, the two NHC rings are coplanar but they are twisted from the coordination plane, with dihedral angles of 67° (**1a**), 87° and 79° (**1b**), and 68° (**2b**). On the other hand, the NHC rings of *trans-syn*-**2a** are twisted by 34° from each other due to steric repulsion of the ammonium moieties. The two NHC ring planes are nearly perpendicular to the coordination plane with dihedral angles of 72 and 74°.

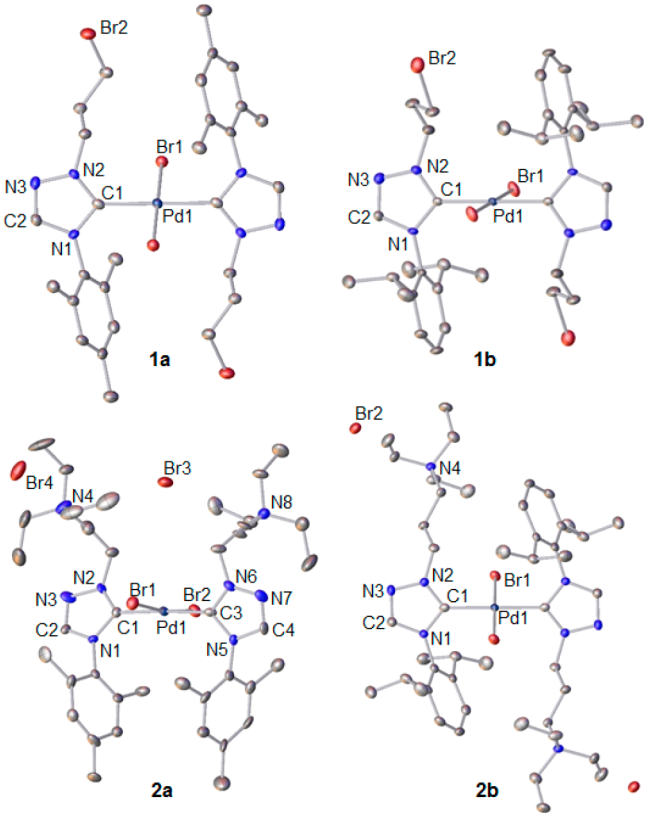

Figure 3. Molecular structures of **1a**,**b**, **2a**·CH_2Cl_2, and **2b**·$2CHCl_3$. Thermal ellipsoids are plotted at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in Structures of 1a,b, 2a·CH_2Cl_2, and 2b·$2CHCl_3$

param	1a	1b	2a·CH_2Cl_2	2b·$2CHCl_3$
Pd1−C1	2.027(6)	2.021(6)	2.04(1)	2.016(3)
Pd1−Br1	2.4452(5)	2.4235(7)	2.448(2)	2.4424(3)
Pd1−C3			2.00(1)	
Pd1−Br2			2.446(2)	
C1−Pd1−Br1	90.9(1)	91.7(2)	89.3(3)	90.43(9)
C1−Pd1−Br1A	89.1(1)	88.3(2)		89.57(9)
C1−Pd1−C1A	180.00	180.0		180.0(1)
Br1−Pd1−Br1A	180.00(3)	180.0		180.0
C1−Pd1−Br2			90.3(3)	
C1−Pd1−C3			177.3(4)	
Br1−Pd1−Br2			172.25(3)	

Catalytic Applications. N-heterocyclic carbene complexes of palladium(II) have been shown to be efficient catalysts for a wide range of organic reactions, especially C−C and C−heteroatom couplings.[1e,f,2c] Among the lesser explored palladium(II) triazolin-5-ylidene complexes, several demonstrated good catalytic activities in Mizoroki−Heck coupling,[7b] Sonogashira[8a]/cyclic hydroalkoxylation[7c] reactions, and hydroamination of olefins.[7d] Notably, these reactions were performed in water-free media. Thus, the water-soluble complexes **2a**,**b** were tested for their catalytic activities in the Suzuki−Miyaura and Mizoroki−Heck coupling reactions using water as a cosolvent and in molten TBAB as an ionic liquid.

Suzuki−Miyaura Coupling Reactions. In order to determine the optimal reaction conditions, several experiments were performed using 4-bromoacetophenone or 4-bromoanisole and phenylboronic acid, as model substrates, at a low catalyst loading of 0.03 mol %. The optimization results are summarized in Table 2. Initially, no conversion was observed when the reaction was conducted in DMF/H_2O (1/1 v/v) at room temperature using catalyst **2a** (entry 1). However, a yield of 60% was achieved when the reaction temperature was increased to 80 °C (entry 2). A sharp decrease in the yield was noted when either DMF or water was used as the sole solvent (entries 3 and 4). Notably, excellent yields were observed when the reactions were carried out in an ^{i}PrOH/H_2O (1/1 v/v) mixture at 80 °C (entry 7). A decrease in reaction temperature from 80 to 60 °C or room temperature was accompanied by a

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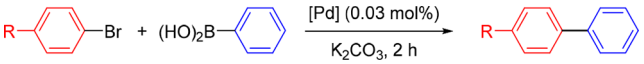
Table 2. Optimization of Suzuki–Miyaura Coupling Reaction Conditions[a]



entry	R	solvents	T (°C)	catalyst	yield (%)[b]
1	$COCH_3$	DMF/H_2O	room temp	**2a**	traces
2	$COCH_3$	DMF/H_2O	80	**2a**	60
3	$COCH_3$	DMF	80	**2a**	traces
4	$COCH_3$	H_2O	80	**2a**	traces
5	$COCH_3$	$^iPrOH/H_2O$	r.t.	**2a**	25
6	$COCH_3$	$^iPrOH/H_2O$	60	**2a**	51
7	$COCH_3$	$^iPrOH/H_2O$	80	**2a**	96
8	$COCH_3$	^iPrOH	80	**2a**	traces
9	OCH_3	$^iPrOH/H_2O$	80	**2a**	96
10	OCH_3	$^iPrOH/H_2O$	80	**2b**	95

[a]Reaction conditions: 8.0 mmol of aryl bromide, 10 mmol (1.25 equiv) of arylboronic acid, 0.03 mol % of precatalyst **2a**/**2b**, 12 mmol (1.5 equiv) of K_2CO_3, solvent (24 mL), H_2O (24 mL), 80 °C, 2 h. [b]Isolated yield for an average of two runs.

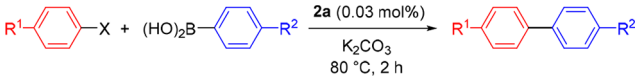
significant drop in yield (entries 5 and 6). Moreover, only trace amounts of the product were obtained when the reaction was conducted in only isopropyl alcohol (entry 8). Therefore, subsequent reactions were carried out in $^iPrOH/H_2O$ at 80 °C. Under these conditions, phenylboronic acid reacted smoothly with both activated (entry 7) and deactivated (entry 9) aryl bromides to give the products in excellent yields.

Complex **2b** was also tested as catalyst against **2a** for the coupling reaction between less reactive 4-bromoanisole and phenylboronic acid under the same reaction conditions. The reaction went smoothly, giving the desired product in equally high yield (95%; Table 2, entry 12) in comparison to **2a**.

Since **2b** was not distinctively superior in performance, complex **2a** was chosen for a substrate scope study. Various arylboronic acids were reacted with a diverse array of aryl bromides and aryl chlorides using **2a** as catalyst under the optimized conditions (Table 3). Activated as well as deactivated aryl bromides reacted smoothly, affording the respective substituted biphenyl in excellent yields (92–96%) (entries 1–12). The coupling reactions can tolerate various functional groups on either the aryl halide or arylboronic acid. The coupling of activated aryl chlorides was also successful, forming products in excellent yields (95–96%), although higher catalyst loading and more forcing conditions (120 °C, 24 h) were required (entries 13 and 14). Notably, decent yields were still observed for coupling reactions between phenylboronic acid and unactivated (chlorobenzene) or deactivated aryl chlorides (4-chloroanisole) (entries 14–17). The high catalytic activity of the charge-tagged complex **2a** was found to be comparable to those of reported sulfonate-tethered imidazolin-2-ylidene palladium(II) complexes under very similar reaction conditions.[18] However, it is interesting to note that these required the addition of excess tetrabutylammonium bromide (1.5 equiv), while complexes **2a**,**b** contain built-in and only "catalytic amounts" of tetraalkylammonium functions. In addition, their preparation by the postmodification approach avoided harsh experimental conditions, such as prolonged heating at high temperatures in DMSO.[18]

Mizoroki–Heck Coupling Reactions between Aryl Bromides and Substituted Styrenes. In addition to Suzuki–Miyaura coupling reactions, catalytic activities of the complexes

Table 3. Suzuki–Miyaura Coupling of Aryl Halides[a]



entry	R^1	X	R^2	yield (%)[b]	TON
1	$COCH_3$	Br	H	96	3200
2	$COCH_3$	Br	CH_3	96	3200
3	$COCH_3$	Br	OH	95	3170
4	NO_2	Br	H	92	3070
5	H	Br	H	95	3170
6	H	Br	OH	94	3130
7	H	Br	CH_3	92	3070
8	OCH_3	Br	H	96	3200
9	NH_2	Br	H	94	3130
10	CHO	Br	H	95	3170
11	CN	Br	H	95	3170
12	CH_3	Br	H	93	3100
13[c]	CHO	Cl	H	95	95
14[c]	$COCH_3$	Cl	H	96	96
15[d]	H	Cl	H	72	72
16[d]	H	Cl	OCH_3	74	74
17[d]	OCH_3	Cl	OCH_3	69	69

[a]Reaction conditions unless specified otherwise: 8.0 mmol of aryl halide, 10 mmol (1.25 equiv) of arylboronic acid, 0.03 mol % of **2a**, 12 mmol (1.5 equiv) of K_2CO_3, ^iPrOH (24 mL), H_2O (24 mL), 80 °C, 2 h. [b]Isolated yield for an average of two runs. [c]Catalyst loading 1.0 mol % of **2a**, 120 °C, 24 h. [d]Catalyst loading 1.0 mol % of **2a**, 140 °C, 24 h.

2a,**b** were also tested in the Mizoroki–Heck reaction, which usually requires harsher conditions. The coupling of 4-bromoacetophenone and styrene was chosen as the standard reaction for optimization (Table 4). The reaction was initially tested at 100 °C in the presence of catalyst **2a** using biphasic toluene/H_2O (entry 1) or DMF/H_2O (entry 2) mixtures. These two preliminary reactions gave no coupling product after 20 h.

However, a sharp increase in the product yield to 71% was observed when reaction temperature was increased to 120 °C (entry 3). Again, the best conversion was achieved in $^iPrOH/H_2O$ (1/1 v/v) where a high isolated yield of 92% was obtained (entry 5). Using these conditions ($^iPrOH/H_2O$, 120 °C, 20 h), the coupling with the less reactive 4-bromoanisole was tested, and a decent yield (80%) was obtained when K_2CO_3 was used as a base (entry 6). Our previous study of the Mizoroki–Heck coupling reaction catalyzed by Pd^{II}-bis(oxazoline) complexes has demonstrated that KOH could be a more efficient base in comparison to K_2CO_3.[19] In this regard, KOH was then tested under otherwise identical conditions, and the reaction gave an excellent yield of 93% after 12 h at 120 °C (entry 8). Notably, the reaction did not initiate at 100 °C (entry 7). A more detailed examination shows that the reaction was essentially complete after 4 h (entries 9 and 10) with KOH. On the other hand, the coupling using K_2CO_3 only gave a 32% yield after 4 h (entry 11). The set of reaction conditions ($^iPrOH/H_2O$, KOH, 120 °C, 4 h) were then considered as optimal conditions, under which a good yield was also achieved with catalyst precursor **2b** (entry 13).

Catalyst **2a** (1 mol %) was further tested in a substrate scope study using the optimal conditions (Table 5). Nonactivated, activated, and deactivated aryl bromides reacted smoothly with styrene, affording the cross-coupling products in good to excellent yields (89–93%). Various functional groups were

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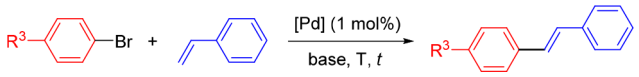
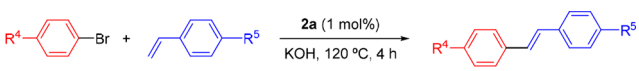
Table 4. Optimization of Reaction Conditions for the Mizoroki–Heck Coupling Reactions of Aryl Bromides with Styrene[a]



entry	R^3	base	solvent	T (°C)	t (h)	cat.	yield (%)[b]
1	$COCH_3$	K_2CO_3	toluene/H_2O	100	20	**2a**	
2	$COCH_3$	K_2CO_3	DMF/H_2O	100	20	**2a**	
3	$COCH_3$	K_2CO_3	DMF/H_2O	120	20	**2a**	71
4	$COCH_3$	K_2CO_3	^{i}PrOH/H_2O	100	20	**2a**	
5	$COCH_3$	K_2CO_3	^{i}PrOH/H_2O	120	20	**2a**	92
6	OCH_3	K_2CO_3	^{i}PrOH/H_2O	120	20	**2a**	80
7	OCH_3	KOH	^{i}PrOH/H_2O	100	20	**2a**	traces
8	OCH_3	KOH	^{i}PrOH/H_2O	120	20	**2a**	93
9	OCH_3	KOH	^{i}PrOH/H_2O	120	12	**2a**	92
10	OCH_3	KOH	^{i}PrOH/H_2O	120	4	**2a**	90
11	OCH_3	K_2CO_3	^{i}PrOH/H_2O	120	4	**2a**	32
13	OCH_3	KOH	^{i}PrOH/H_2O	120	4	**2b**	87

[a]Reaction conditions: 1.0 mmol of aryl bromide, 1.5 mmol (1.5 equiv) of styrene, 1.0 mol % of catalyst **2a**/**2b**, 2.0 mmol (2 equiv) of base, solvent/H_2O (3.0 mL/3.0 mL). [b]Isolated yield for an average of two runs.

Table 5. Mizoroki–Heck Coupling Reactions of Aryl Bromides with Substituted Styrenes[a]



entry	R^4	R^5	yield (%)[b]	TON
1	H	H	90	90
2	$COCH_3$	H	93	93
3	$COCH_3$	OCH_3	93	93
4	$COCH_3$	Cl	90	90
5	CN	H	92	92
6	OCH_3	H	90	90
7	H	OCH_3	92	92
8	H	Cl	89	89
9	H	$C(CH_3)_3$	92	92

[a]Reaction conditions: 1.0 mmol of aryl bromide, 1.5 mmol (1.5 equiv) of alkene, 1.0 mol % of catalyst **2a**, 2.0 mmol (2 equiv) of KOH, ^{i}PrOH/H_2O (3.0 mL/3.0 mL), 120 °C, 4 h. [b]Isolated yield for an average of two runs.

tolerated, and the effect of varying the substituents on both the aryl bromides and the styrene derivatives was found to be insignificant.

Mizoroki–Heck Coupling Reactions between Aryl Chlorides and Substituted Styrenes. The catalytic activity of **2a** was also tested for less reactive aryl chloride substrates (Table 6). Unfortunately, no coupling product was obtained under the optimized reaction conditions for aryl bromides (entries 1–3). However, the coupling reaction was successful when it was carried out at 140 °C in tetrabutylammonium bromide (TBAB) as an ionic liquid (IL), using cesium carbonate as a base, and run for 20 h. It is anticipated that the ammonium tethers of the complex allow for efficient anchoring onto the IL and facilitating formation of ion pairs. These modified conditions gave the desired product in 72% yield (entry 4). Under similar reaction conditions, a minimally lower yield was obtained when **2b** was used as a catalyst (entry 5). Additionally, **2a** shows good catalytic performance for the coupling of several activated and deactivated aryl chlorides (entries 6–10).

The catalytic performance of **2a** in Mizoroki–Heck coupling reactions between aryl bromides and styrene is comparable to that reported for nonfunctionalized Pd-bis(NHC) complexes containing imidazolin-2-ylidenes and mesoionic 1,2,3-triazolin-5-ylidenes in pure organic solvents.[7b,9b,20] However, **2a** outperforms these in the coupling of more challenging aryl chlorides.[20b,c]

CONCLUSION

A series of four functionalized bis(1,2,4-triazolin-5-ylidene)-palladium(II) complexes (**1a**,**b** and **2a**,**b**) have been successfully synthesized and fully characterized by various spectroscopic and spectrometric means, including single-crystal X-ray diffraction. Complexes **1a**,**b**, containing tethered bromoalkyl chains, were conveniently transformed into ammonium-functionalized complexes **2a**,**b**, respectively, via a postmodification approach. Notably, the respective ammonium-functionalized triazolium salts are still elusive, making a direct palladation impossible. All four complexes are rare examples of functionalized 1,2,4-triazole-derived NHC complexes, and their rotameric ratios in solution have been obtained by ^{1}H NMR spectroscopy. The preference for the syn rotamers in all cases has been rationalized by DFT calculations and can be traced back to their larger dipole moments. Moreover, complexes **2a**,**b** contain cationic tethers, which can serve as (i) ESI MS-responsive tags for the mild mass-spectrometric detection of complete complex spheres, (ii) built-in phase-transfer catalysts, and (iii) built-in Jeffery-type cocatalysts for palladium catalysis. Thus, their catalytic activities in the Suzuki–Miyaura and Mizoroki–Heck couplings of aryl bromides and chlorides have been examined as well. Overall, excellent yields were obtained for all the aryl bromide substrates, while average to good yields were observed for aryl chlorides. These results show that the postmodification approach allows the preparation of useful complexes that are otherwise not obtainable using conventional methods. Current research in our laboratory is concerned with the extension of this approach to complexes with more elaborate multidentate ligands.

EXPERIMENTAL SECTION

General Considerations. All syntheses were carried out without precautions to exclude air and moisture unless otherwise stated. Solvents used for syntheses and spectroscopic measurements were used as received. 4-Mesityl-1,2,4-triazole[21] and 4-(2,6-diisopropylphenyl)-1,2,4-triazole[21] were synthesized following reported procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ACF 300, Advance III, or AMX 500 spectrometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane. Electrospray ionization mass spectra (ESI-MS) were obtained using a Finnigan LCQ spectrometer. Elemental analyses were carried out at the Elemental Analysis Laboratory in the Department of Chemistry, National University of Singapore.

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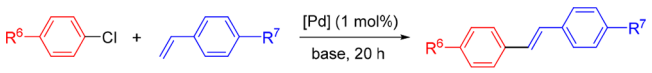
Table 6. Mizoroki−Heck Coupling Reactions of Aryl Chlorides and Substituted Styrene[a]



entry	R^6	R^7	base	solvent	T (°C)	cat.	yield (%)[b]	TON
1	CHO	H	KOH	^{i}PrOH/H_2O	120	**2a**	0	0
2	$COCH_3$	H	KOH	^{i}PrOH/H_2O	120	**2a**	0	0
3	H	H	KOH	^{i}PrOH/H_2O	120	**2a**	0	0
4[c]	H	H	Cs_2CO_3	TBAB	140	**2a**	72	72
5[c]	H	H	Cs_2CO_3	TBAB	140	**2b**	70	70
6[c]	$COCH_3$	H	Cs_2CO_3	TBAB	140	**2a**	90	90
7[c]	CHO	H	Cs_2CO_3	TBAB	140	**2a**	89	89
8[c]	OCH_3	H	Cs_2CO_3	TBAB	140	**2a**	70	70
9[c]	H	OCH_3	Cs_2CO_3	TBAB	140	**2a**	74	74
10[c]	H	Cl	Cs_2CO_3	TBAB	140	**2a**	72	72

[a]Reaction conditions unless specified otherwise: 1.0 mmol of aryl chloride, 1.5 mmol (1.5 equiv) of styrene, 1.0 mol % of catalyst, 2.0 mmol (2 equiv) of base, solvent/H_2O (3.0 mL/3.0 mL), 20 h. [b]Isolated yield for an average of two runs. [c]TBAB (2.0 g).

4-Mesityl-1-(3-bromopropyl)-1,2,4-triazolium Bromide (A·HBr). A mixture of 4-mesityl-1,2,4-triazole (374 mg, 2 mmol) and 1,3-dibromopropane (2.1 mL, 20 mmol) was heated at 70 °C for 4 h. The reaction mixture was cooled to ambient temperature, and diethyl ether (20 mL) was added to precipitate the triazolium salt. The precipitate was then filtered and washed with diethyl ether (3 × 5 mL) to give the product as an off-white powder (740 mg, 1.9 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.05 (s, 1 H, NCHN), 8.37 (s, 1 H, NCHN), 7.05 (s, 2 H, Ar-H), 5.12 (t, 2 H, NCH_2), 3.61 (t, 2 H, CH_2Br), 2.72 (m, 2 H), 2.35 (s, 3 H, CH_3), 2.13 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 145.2 (NCHN), 143.6 (NCHN), 142.6, 134.3, 130.5, 127.4 (Ar-C), 52.3, 31.7, 29.1, 21.3, 18.2. Anal. Calcd for $C_{14}H_{19}Br_2N_3$: C, 43.21; H, 4.92; N, 10.80. Found: C, 43.17; H, 5.47; N, 11.13.[22] MS (ESI): calcd for $[M - Br]^+$, $C_{14}H_{19}BrN_3$, m/z 308; found, m/z 308.

4-(2,6-Diisopropylphenyl)-1-(3-bromopropyl)-1,2,4-triazolium Bromide (B·HBr). The triazolium salt **B**·HBr was prepared in a manner similar to that for **A**·HBr from 4-(2,6-diisopropylphenyl)-1,2,4-triazole (458 mg, 2 mmol) and 1,3-dibromopropane (2.1 mL, 20 mmol). The product was obtained as a pale yellow solid (707 mg, 1.64 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.16 (s, 1 H, NCHN), 8.43 (s, 1 H, NCHN), 7.58 (t, ^3J(H−H) = 8.0 Hz, 1 H, Ar-H), 7.33 (d, ^3J(H−H) = 8.0 Hz, 2 H, Ar-H), 5.21 (t, 2 H, NCH_2), 3.64 (t, 2 H, CH_2Br), 2.73 (m, 2 H, $CH_2CH_2CH_2$), 2.27 (m, ^3J(H−H) = 6.8 Hz, 2 H, $CH(CH_3)_2$), 1.24 (d, ^3J(H−H) = 6.8 Hz, 6 H, CH_3), 1.14 (d, ^3J(H−H) = 6.8 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 145.4 (NCHN), 145.1 (NCHN), 144.2, 132.9, 126.7, 125.2 (Ar-C), 52.3, 31.6, 29.1, 24.3, 24.2. Anal. Calcd for $C_{17}H_{25}Br_2N_3$: C, 47.35; H, 5.84; N, 9.74. Found: C, 49.39; H, 6.58; N, 10.26.[22] MS (ESI): calcd for $[M - Br]^+$, $C_{17}H_{25}BrN_3$, m/z 350; found, m/z 350.

***trans*-[$PdBr_2$(A)$_2$] (1a).** A mixture of **A**·HBr (390 mg, 1 mmol), Ag_2O (128 mg, 0.55 mmol), and $PdBr_2$ (133 mg, 0.5 mmol) was stirred in CH_2Cl_2 at ambient temperature in the dark for 14 h. The suspension was then filtered over Celite, and the residue was washed with CH_2Cl_2 (3 × 1 mL). The solvent of the filtrate was evaporated to obtain the crude product, which was then purified by silica gel chromatography using CH_2Cl_2 as eluent. The product was obtained as a pale yellow powder containing the rotamers *trans-anti*-**1a** and *trans-syn*-**1a** (353 mg, 0.4 mmol, 80%). Data for *trans-anti*-**1a** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.14 (s, 1 H, NCHN), 7.07 (s, 2 H, Ar-H), 4.84 (t, 2 H, NCH_2), 3.23 (t, 2 H, CH_2Br), 2.39 (m, 2 H, $CH_2CH_2CH_2$), 2.37 (s, 3 H, *p*-CH_3), 2.17 (s, 6 H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ 172.76 ($C_{carbene}$), 145.5 (NCH_2N), 140.9, 137.2, 132.9, 130.1 (Ar-C), 52.5 (NCH_2), 33.6 (CH_2Br), 30.9 ($CH_2CH_2CH_2$), 21.2 (*o*-CH_3), 19.8 (*p*-CH_3). Data for *trans-syn*-**1a** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.08 (s, 1 H, NCHN), 6.92 (s, 2 H, Ar-H), 4.85 (t, 2 H, NCH_2), 3.60 (t, 2 H, CH_2Br), 2.72 (m, 2 H, $CH_2CH_2CH_2$), 2.46 (s, 3 H, *p*-CH_3), 1.87 (s, 6 H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): 172.8 ($C_{carbene}$), 145.6 (NCH_2N), 140.2, 136.5, 132.5, 130.1 (Ar-C), 52.4 (NCH_2), 33.9 (CH_2Br), 31.5 ($CH_2CH_2CH_2$), 21.3 (*o*-CH_3), 19.5 (*p*-CH_3). Anal. Calcd for $C_{28}H_{36}Br_4N_6Pd$: C, 38.10; H, 4.11; N, 9.52. Found: C, 38.15; H, 4.15; N, 9.61. MS (ESI): calcd for $[M - Br]^+$, $C_{28}H_{36}Br_3N_6Pd$, m/z 803;[23] found, m/z 803.

***trans*-[$PdBr_2$(B)$_2$] (1b).** Complex **1b** was synthesized in analogy to **1a**, from **B**·HBr (431 mg, 1 mmol), Ag_2O (128 mg, 0.55 mmol), and $PdBr_2$ (133 mg, 0.5 mmol). The product was obtained as a yellow solid containing a mixture of rotamers *trans-anti*-**1b** and *trans-syn*-**1b** (425 mg, 0.44 mmol, 88%). Data for *trans-anti*-**1b** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.29 (s, 1 H, NCHN), 7.57 (t, ^3J(H−H) = 7.8 Hz, 1 H, *p*-Ar-H), 7.40 (d, 2 H, *m*-Ar-H), 4.47 (t, 2 H, NCH_2CH_2), 3.15 (t, 2 H, CH_2Br), 2.73−2.84 (m, 2 H, $CH(CH_3)_2$), 2.33 (m, 2 H, $CH_2CH_2CH_2$), 1.30 (d, 6 H, $CH(CH_3)_2$), 0.95 (d, 6 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 173.6 ($C_{carbene}$), 147.3, 144.3, 131.0, 130.6, 128.9 (Ar-C), 51.9 (NCH_2), 32.3, 30.2, 28.7, 26.6, 22.9. Data for *trans-syn*-**1b** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.19 (s, 1 H, NCHN), 7.44 (t, ^3J(H−H) = 7.8 Hz, 1 H, *p*-Ar-H), 7.14 (d, ^3J(H−H) = 7.8 Hz, 2 H, *m*-Ar-H), 4.98 (t, 2 H, NCH_2), 3.67 (t, 2 H, CH_2Br), 2.72−2.84 (2 H, $CH(CH_3)_2$), 2.53 (m, 2 H, $CH_2CH_2CH_2$), 0.87 (d, 6 H, $CH(CH_3)_2$), 0.86 (d, 6 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 173.2 ($C_{carbene}$), 146.6, 144.5, 131.5, 131.0, 124.2, 52.3, 32.6, 30.6, 28.3, 26.3, 22.8. Anal. Calcd for $C_{34}H_{48}Br_4N_6Pd$: C, 42.24; H, 5.00; N, 8.69. Found: C, 42.23; H, 4.82; N, 8.95. MS (ESI): calcd for $[M - Br]^+$, $C_{34}H_{48}Br_3N_6Pd$, m/z 887;[23] found, m/z 887.

***trans*-[$PdBr_2$(C)$_2$]Br_2 (2a).** A Schlenk tube was charged with **1a** (310 mg, 0.35 mmol), triethylamine (480 μL, 3.5 mmol), and CH_3CN (5 mL). The mixture was then heated at 70 °C for 5 h, and then another portion of triethylamine (480 μL, 3.5 mmol) was added. The reaction was further stirred at 70 °C for 10 h. The volatiles were then removed under reduced pressure to give a white solid, which was washed with tetrahydrofuran (3 × 5 mL) and dichloromethane (3 × 1 mL) to give **2a** (360 mg, 0.33 mmol, 95%). Data for *trans-anti*-**2a** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.32 (s, 1 H, NCHN), 7.13 (s, 2 H, Ar-H), 4.56 (t, 2 H, NCH_2CH_2), 3.52 (m, 6 H, CH_2CH_3), 3.26 (m, 2 H, CH_2Br), 2.99 (m, 2 H, $CH_2CH_2CH_2$), 2.38 (s, 3 H, *p*-CH_3), 2.20 (s, 6 H, *o*-CH_3), 1.14 (t, 9 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 173.2 ($C_{carbene}$), 146.4 (NCH_2N), 141.0, 137.3, 132.9, 130.2, 55.1, 54.0, 50.6, 22.8, 21.4, 19.9, 8.0. Data for *trans-syn*-**2a** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.22 (s, 1 H, NCHN), 6.91 (s, 2 H, Ar-H), 4.89 (t, 2 H, NCH_2), 3.25 (m, 6 H, CH_2CH_3), 3.10 (m, 2 H, CH_2Br), 2.61 (m, 2 H, $CH_2CH_2CH_2$), 2.47 (s, 3 H, *p*-CH_3), 1.87 (s, 6 H, *o*-CH_3), 1.22 (t, 9 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 173.2 ($C_{carbene}$), 146.4 (NCH_2N), 140.4, 136.4, 132.3, 130.2, 55.7, 54.3, 51.0, 23.1, 21.4, 19.5, 8.2. Anal. Calcd for $C_{40}H_{66}Br_4N_8Pd$: C, 44.28; H, 6.13; N, 10.33. Found: C, 44.35; H, 6.21; N, 10.40. MS (ESI): calcd

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for $[M - Br]^+$, $C_{40}H_{66}Br_3N_8Pd$, m/z 1005;[23] found, m/z 1005; calcd for $[M - 2Br]^{2+}$, $C_{40}H_{66}Br_2N_8Pd$, m/z 462; found, m/z 462.

***trans*-[PdBr$_2$(C)$_2$](PF$_6$)$_2$ (2a′).** A solution of **2a** (200 mg, 0.18 mmol) in 2 mL of methanol was added dropwise to a solution of KPF_6 (680 mg, 3.7 mmol) in 100 mL of water. The white precipitate that formed was filtered through a plug of Celite. The solid was washed with water (3 × 0.5 mL) and collected using methanol. Removal of the volatile solvent gave the product as white solids (210 mg, 0.17 mmol, 94%). ^{1}H NMR (400 MHz, CD_3CN, anti:syn = 0.7:1): *trans-anti*-**2a′**, δ 8.24 (s, 1 H, NCHN), 7.12 (s, 2 H, Ar-H), 4.53 (t, 2 H, NCH_2), 3.06 (q, ^3J(H−H) = 7.1 Hz, 6 H, NCH_2CH_3), 2.93−2.89 (m, 2 H, CH_2Br), 2.37 (s, 3 H, *p*-CH_3), 2.15−2.25 (2 H, $CH_2CH_2CH_2$), 2.19 (s, 6 H, *o*-CH_3), 1.12 (t, ^3J(H−H) = 7.1 Hz, 9 H, NCH_2CH_3); *trans-syn*-**2a′**, δ 8.19 (s, 1 H, NCHN), 6.92 (s, 2 H, Ar-H), 4.84 (t, 2 H, NCH_2), 3.23−3.03 (m, 2 H, CH_2Br), 3.22 (q, ^3J(H−H) = 7.1 Hz, 6 H, NCH_2CH_3), 2.43−2.52 (2 H, $CH_2CH_2CH_2$), 2.19 (s, 3 H, *p*-CH_3), 1.87 (s, 6 H, *o*-CH_3), 1.12 (t, ^3J(H−H) = 7.1 Hz, 9 H, NCH_2CH_3). ^{19}F{^{1}H} NMR (376.29 MHz, CD_3CN): δ −72.8 (d, ^1J(P−F) = 707 Hz, PF_6^-). ^{31}P{^{1}H} NMR (161.92 MHz, CD_3CN): δ −144.6 (sep, ^1J(P−F) = 707 Hz, PF_6^-). Anal. Calcd for $C_{40}H_{66}Br_2F_{12}N_8P_2Pd$: C, 39.54; H, 5.47; N, 9.22. Found: C, 39.71; H, 5.51; N, 9.32.

***trans*-[PdBr$_2$(D)$_2$]Br$_2$ (2b).** Complex **2b** was synthesized in analogy to **2a** using **1b** (386 mg, 0.4 mmol) and triethylamine (2 × 560 μL, 2 × 4 mmol). The product was obtained as a white powder, which was hygroscopic (400 mg, 0.34 mmol, 86%). Data for *trans-anti*-**2b** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.51 (s, 1 H, NCHN), 7.66 (t, 1 H, *p*-Ar-H), 7.46−7.52 (2 H, *m*-Ar-H), 4.63 (t, 2 H, NCH_2CH_2), 3.05 (q, ^3J(H−H) = 7.2 Hz, 6 H, NCH_2CH_3), 2.87 (m, 2 H, CH_2N), 2.81 (m, 2 H, $CH(CH_3)_2$), 2.11 (m, 2 H, $CH_2CH_2CH_2$), 1.34 (d, 6 H, $CH(CH_3)_2$), 1.12 (t, ^3J(H−H) = 7.2 Hz, 9 H, CH_2CH_3), 0.99 (d, 6 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ 171.9 ($C_{carbene}$), 146.7, 145.5, 131.0, 130.5, 123.9, 53.0, 52.2, 49.1, 28.3, 25.8, 22.4, 21.5, 7.1. Data for *trans-syn*-**2b** are as follows. ^{1}H NMR (400 MHz, CD_3CN): δ 8.36 (s, 1 H, NCHN), 7.46−7.52 (1 H, *p*−Ar-H), 7.18 (d, 2 H, *m*-Ar-H), 5.01 (t, 2 H, NCH_2CH_2), 3.57 (m, 2 H, CH_2N), 3.36 (q, ^3J(H−H) = 7.2 Hz, 6 H, NCH_2CH_3), 2.74 (m, 2 H, $CH(CH_3)_2$), 2.51 (m, 2 H, $CH_2CH_2CH_2$), 1.26 (t, ^3J(H−H) = 7.2 Hz, 9 H, CH_2CH_3), 0.88−0.91 (12 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ 171.9 ($C_{carbene}$), 146.4, 145.5, 131.3, 130.6, 123.8, 53.8, 52.4, 49.7, 27.8, 25.5, 22.4, 21.7, 7.2. Anal. Calcd for $C_{46}H_{78}Br_4N_8Pd$: C, 47.25; H, 6.72; N, 9.58. Found: C, 44.35; H, 6.21; N, 10.40.[22] MS (ESI): calcd for $[M - Br]^+$, $C_{46}H_{78}Br_3N_8Pd$, m/z 1089;[23] found, m/z 1089; calcd for $[M - 2Br]^{2+}$, $C_{46}H_{78}Br_2N_8Pd$, m/z 504; found, m/z 504.

***trans*-[PdBr$_2$(D)$_2$](PF$_6$)$_2$ (2b′).** **2b′** was synthesized in a manner similar to that for **2a′**, using 150 mg of **2b** (0.13 mmol) and 480 mg (2.6 mmol) of KPF_6. The product was obtained as white solids (140 mg, 0.11 mmol, 85%). ^{1}H NMR (400 MHz, CD_3CN, anti:syn = 1.2:1): *trans-anti*-**2b′**, δ 8.42 (s, 1 H, NCHN), 7.62 (t, 1 H, Ar-H), 7.45 (d, 2 H, Ar-H), 4.59 (t, 2 H, NCH_2), 2.99 (q, ^3J(H−H) = 7.2 Hz, 6 H, NCH_2CH_3), 2.83−2.86 (m, 2 H, CH_2Br), 2.79 (m, 2 H, $CH(CH_3)_2$), 2.03−2.11 (2 H, $CH_2CH_2CH_2$), 1.30 (d, 6 H, $CH(CH_3)_2$), 1.08 (t, ^3J(H−H) = 7.2 Hz, 9 H, NCH_2CH_3), 0.96 (d, 6 H, $CH(CH_3)_2$); *trans-syn*-**2b′**, δ 8.31 (s, 1 H, NCHN), 7.48 (t, 1 H, Ar-H), 7.16 (d, 2 H, Ar-H), 4.95 (t, 2 H, NCH_2), 3.31−3.35 (m, 2 H, CH_2Br), 3.25 (q, ^3J(H−H) = 7.2 Hz, 6 H, NCH_2CH_3), 2.52−2.61 (m, 2 H, $CH_2CH_2CH_2$), 2.47 (m, 2 H, $CH(CH_3)_2$), 1.21 (t, ^3J(H−H) = 7.2 Hz, 9 H, NCH_2CH_3), 1.21 (d, 6 H, $CH(CH_3)_2$), 0.86−0.90 (m, 6 H, $CH(CH_3)_2$). ^{19}F{^{1}H} NMR (376.29 MHz, CD_3CN): δ −72.9 (d, ^1J(P−F) = 707 Hz, PF_6^-). ^{31}P{^{1}H} NMR (161.92 MHz, CD_3CN): δ −146.8 (sep, ^1J(P−F) = 707 Hz, PF_6^-). Anal. Calcd for $C_{46}H_{78}Br_2F_{12}N_8P_2Pd$: C, 42.52; H, 6.05; N, 8.62. Found: C, 42.73; H, 5.49; N, 8.85.[22]

Suzuki−Miyaura Catalysis. In a typical run, a pressure tube was charged with a mixture of aryl halide (8 mmol), arylboronic acid (10 mmol), potassium carbonate (16 mmol), an appropriate amount of the catalyst, isopropyl alcohol (24 mL), and H_2O (24 mL). The mixture was stirred at the appropriate temperature for the required time. The product was then extracted with ethyl acetate (3 × 40 mL). The combined extracts were dried over $MgSO_4$, and volatile solvent was removed using a rotary evaporator. The residue was subjected to column chromatography (SiO_2) using a hexane/ethyl acetate (4/1 v/v) mixture as eluent.

Mizoroki−Heck Catalysis. A 25 mL pressure tube was charged with aryl halide (1.0 mmol), alkene (1.2 mmol), an appropriate amount of the catalyst, base (2.0 mmol), and solvents (3 mL of isopropyl alcohol and 3 mL of H_2O). The mixture was then allowed to react with stirring for an appropriate amount of time. After the mixture was cooled, the product was extracted with ethyl acetate (3 × 5 mL). The combined organic extract was dried over $MgSO_4$, and the volatile solvent was then removed using a rotary evaporator. The expected product was isolated by column chromatography (SiO_2) using a hexane/ethyl acetate (4/1 v/v) mixture as eluent.

X-ray Crystallography. Single-crystal X-ray diffraction was carried out on a Bruker AXS SMART APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The software used was as follows: SMART for collecting frames of data, indexing reflections, and determining lattice parameters;[24] SAINT for integration of intensity of reflections and scaling;[25] SADABS for empirical absorption correction;[26] SHELXTL for space group determination, structure solution, and least-squares refinements on $|F|^2$.[27] Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions.

Computational Details. Gas-phase structures of all complexes were optimized by the DFT method using the B3PW91 hybrid functional.[28] The 6-31G(d) basis set was used for H, C, and N;[29] 6-311G(d) was used for Br.[30] The heavy Pd atoms were described by a Stuttgart−Dresden (SDD) relativistic effective core potential and associated basis sets.[31] The solvent effect CPCM model[32] was utilized for single-point calculations for **1a** in solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00329.

DFT-optimized geometries for rotamers of **1a** and ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{31}P{^{1}H} NMR spectra of the salts and complexes (PDF)

Accession Codes

CCDC 1548181−1548182 and 1548184−1548185 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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