Palladium(II) Complexes of a Sterically Bulky, Benzannulated N-Heterocyclic Carbene with Unusual Intramolecular C−H···Pd and $C_{carbene}$···Br Interactions and Their Catalytic Activities

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The sterically bulky carbene precursor 1,3-diisopropylbenzimidazolium bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$) (**A**) has been prepared by an improved method in 84% yield. Reaction of **A** with Pd(OAc)$_2$ and NaBr gave the dimeric Pd(II) benzimidazolin-2-ylidene complex [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ (**1**), which can be easily cleaved by CH$_3$CN, another equivalent of salt **A**, and triphenylphosphine to afford the novel benzannulated monocarbene complexes *trans*-[PdBr$_2$(CH$_3$CN)(^{i}Pr$_2$-bimy)] (**2**), (^{i}Pr$_2$-bimyH)[PdBr$_3$(^{i}Pr$_2$-bimy)] (**3**), *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Ph$_3$P)] (*trans*-**4**), and *cis*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Ph$_3$P)] (*cis*-**4**), respectively. All compounds have been fully characterized by multinuclei NMR spectroscopies and mass spectrometries (FAB, ESI). X-ray diffraction studies on single crystals of **1**−**3** and *cis*-**4** revealed a square planar geometry and a fixed orientation of the *N*-isopropyl substituents with the C−H group pointing to the metal center to maximize C−H···Pd interactions. The large downfield shift of the C−H protons in the ^{1}H NMR spectrum compared to the precursor **A** indicates that these C−H···Pd interactions are retained in solution and better described as weak hydrogen bonds, rather than as agostic interactions. Furthermore, the molecular structures of especially complexes **2** and **3** clearly show a bending of the bromo ligands toward the carbene carbon atom in order to maximize intramolecular $C_{carbene}$···Br interactions. The nature of these interactions can be attributed to a form of back-bonding to the formally vacant p-orbital of the $C_{carbene}$ atom with the electron density originating from the bromo ligands' lone pairs. A detailed study on the trans−cis isomerization of the mixed NHC−phosphine complexes **4** revealed that a cis arrangement in such complexes is thermodynamically favored. Furthermore, a preliminary catalytic study shows that complex **1** is highly active in the Suzuki−Miyaura coupling of aryl bromides and chlorides in pure water as environmentally benign solvent.

Introduction

N-Heterocyclic carbenes (NHC) and their transition-metal complexes have been the focus of intense research in organometallic chemistry and homogeneous catalysis for the past decade.[1] In particular, palladium(II) carbene complexes derived from imidazolium precursors have been successfully developed as highly active precatalysts for C−C coupling reactions such as Mizoroki−Heck and Suzuki−Miyaura couplings as well as CO-olefin copolymerization.[1] Some NHC complexes with hemilabile donor functions have also been reported to be highly active in norbornene and ethylene polymerization.[2] The majority of these precatalysts contain NHC as ancillary ligands that are derived from imidazolium salts. It is known that benzannulated carbenes derived from benzimidazolium precursors exhibit the topology of an unsaturated NHC, but show spectroscopic and structural properties and the reactivity of carbenes with a saturated N-heterocyclic ring.[3] However, complexes of benzannulated carbenes are much less established than their imidazole-derived counterparts, and only few studies on their catalytic activity have been reported.[4] Previously, a few examples of palladium(II) carbene complexes derived from benzimidazolium precursors with achiral[5] and chiral[6] alkyl groups or even the ferrocene moiety[7] adjacent to the nitrogen atoms have been described. The latter example is an exception, which can only be obtained by a multiple-step reaction sequence. To the best of our knowledge, all other benzimidazolin-2-ylidene complexes reported so far contain benzimidazole-nitrogen atoms that are bonded to a primary carbon. A secondary carbon attached to the nitrogen is desirable, since it increases the steric bulk of the resulting benzannulated carbene ligand and therefore extends

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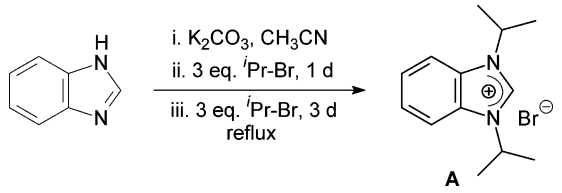
Scheme 1. Synthesis of 1,3-Diisopropylbenzimidazolium Bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$) (A)



the scope of its application in catalysis. In contrast to imidazolium salts, benzimidazolium salts are not available by condensation reactions of sterically bulky amines. On the other hand, sterically demanding benzimidazolin-2-ylidenes have been obtained in multiple steps from *o*-phenylenediamine.[3] However, this route is not feasible to introduce a secondary carbon on the nitrogen. Herein, we report the synthesis, structural characterization, and catalytic activities of palladium(II) complexes derived from a sterically bulky benzimidazolium salt with *N*-isopropyl substituents. The novel complexes exhibit unusual C−H···Pd and $C_{carbene}$···Br interactions, which have not been reported for Pd(II) NHC complexes yet.

Results and Discussion

Synthesis of 1,3-Diisopropylbenzimidazolium Bromide (A). In general, symmetrically 1,3-disubstituted benzimidazolium salts can be conveniently prepared from benzimidazole and suitable alkyl halides in the presence of a strong base. However, this methodology is limited to the use of primary alkyl halides, while secondary or tertiary alkyl halides would not react or provide only negligible yields of the desired salts. Recently, Komarova reported the synthesis of 1,3-diisopropylbenzimidazolium bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$, **A**) from alkylation of 1-isopropylbenzimidazole, which in turn was obtained by N-isopropylation of benzimidazole using KOH as a base, in an overall yield of only 24%.[8] The difficulty encountered in the N-alkylation of azoles using secondary or tertiary alkyl halides is due to the tendency of the latter two to undergo elimination reactions, which can be catalyzed by a strong base. We anticipated that a combination of a relatively weak base, large excess of alkylating agent, and prolonged reaction time should give the desired product **A** in high yield. Consequently, the reaction of benzimidazole with excess isopropyl bromide in the presence of K_2CO_3 as a relatively weak base was carried out for 4 days, which gave **A** as a white powder in an optimal yield of 84% (Scheme 1). Compound **A** is well soluble in halogenated solvents and alcohols as well as in CH_3CN, DMSO, water, and DMF.

The ^{1}H NMR spectrum of salt **A** in $CDCl_3$ shows a doublet at 1.88 ppm and a septet at 5.21 ppm characteristic for the isopropyl groups. In addition, a downfield signal at 11.45 ppm for the NCHN proton indicates the formation of an azolium salt. As expected, the positive mode ESI mass spectrum shows a base peak at $m/z = 203$ corresponding to the $[M - Br]^+$ cation. Furthermore, single crystals of the solvate **A**·H_2O were analyzed by X-ray diffraction for the purpose of comparison. A depiction of the molecular structure of salt **A** is shown in Figure 1.

Synthesis of Palladium(II) Complexes. A general method for the preparation of Pd(II) dicarbene complexes involves the reaction of $Pd(OAc)_2$ with 2 equiv of azolium salts under in-situ deprotonation of the latter to form the corresponding carbene ligand. Surprisingly, initial attempts to synthesize a Pd(II)

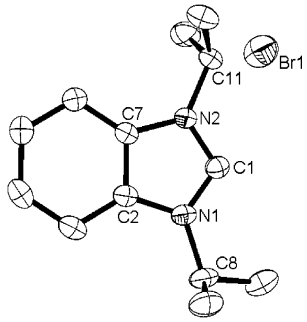


Figure 1. Molecular structure of ^{i}Pr$_2$-bimyH$^+$Br$^-$ (**A**) with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [deg]: C1−N1 1.328(2), C1−N2 1.326(2), N1−C2 1.389(2), N1−C8 1.4855(19), N2−C7 1.3948(19), N2−C11 1.4799(19), C2−C7 1.396(2); N1−C1−N2 110.90(14), C1−N1−C2 107.89(13), C1−N2−C7 108.24(12).

dicarbene complex by reacting $Pd(OAc)_2$ with salt **A** in various organic solvents (THF, CH_3CN, and DMSO) including NBu_4-Br as ionic liquid and under various reaction conditions (up to 120 °C) were unsuccessful and gave product mixtures with only negligible yield of the desired dicarbene complex. Even the Ag-carbene transfer method described by Lin et al.[9] showed similar results. Instead, the novel dimeric Pd(II) benzimidazolin-2-ylidene complex $[PdBr_2(^i$Pr$_2$-bimy$)]_2$ (**1**) was isolated as the main and kinetically controlled product in all cases. Although halo-bridged dimeric Pd(II)-carbene complexes of similar type derived from imidazole as well as imidazoline precursors are known,[10] it is noteworthy that complex **1** represents a novel example bearing benzannulated carbene ligands. The preference for the formation of **1** and thus its kinetic stability under these conditions was unexpected. Since complex **1** is a useful precursor for a range of monocarbene complexes, an optimized synthetic pathway for its preparation was sought. A synthetic protocol for dimeric carbene complexes by equimolar reaction of azolium salt with $Pd(OAc)_2$ in the presence of the base KO^t-Bu and excess NaI has been reported by Enders.[10a] This methodology proved successful for carbenes derived from imidazole and imidazoline. However, when this reaction was carried out with benzimidazolium salt **A** in THF or DMSO, we observed substantial deposition of palladium black, proving this method less suitable for the preparation of benzimidazolin-2-ylidene analogues. We anticipated that the formation of undesired palladium black was most likely due to the highly reactive base KO^{t}Bu. Therefore we omitted its use in further attempts. With this modification, the reaction proceeded much cleaner and a high yield of 93% for **1** was achieved by addition

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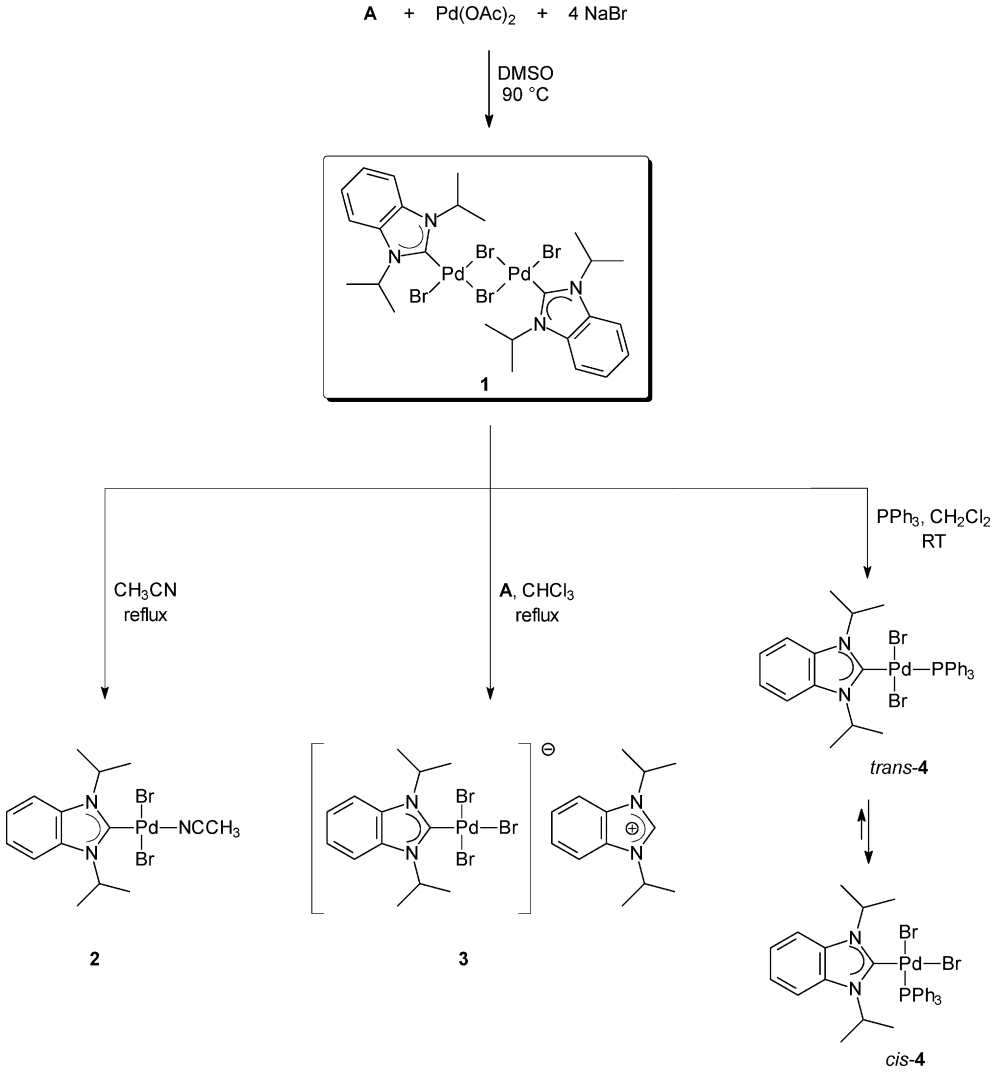
Scheme 2. Synthesis of Pd(II) Benzimidazolin-2-ylidene Complexes



of 4 equiv of NaBr, as depicted in Scheme 2. More importantly, the reaction can be carried out in wet DMSO and under aerobic conditions without notable loss of yield. Complex **1** can be isolated as a yellow solid soluble in halogenated solvents, sparingly soluble in diethyl ether, and insoluble in the nonpolar solvents hexane and toluene. Coordinating solvents (DMSO, THF, and CH_3CN) cleave the dimeric complex (vide infra). The formation of complex **1** was confirmed by ^{1}H NMR spectroscopy, which shows the absence of the NCHN proton. Furthermore, a significant downfield shift of the isopropyl CH resonance was observed upon coordination of the carbene ligand to the Pd(II) center from 5.21 ppm in the precursor salt **A** to 6.54 ppm in **1** ($\Delta\delta$H = 1.33 ppm), which indicates a possible intramolecular C−H···Pd interaction in the complex (vide infra) probably involving the filled d_{z^2}-orbital of the palladium atom.[11] The aromatic signals, on the other hand, shift to high field by ~0.2 ppm, whereas the methyl resonances remain relatively unaffected. Despite sufficient solubility, the signal for the carbenoid carbon was not resolved under the given conditions.

Single crystals of **1** suitable for X-ray diffraction analysis were grown from a saturated chloroform/toluene solution. The dimeric complex **1** crystallized as toluene solvate **1**·$C_6H_5CH_3$, and its molecular structure is shown in Figure 2.

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Each of the two Pd(II) centers is coordinated by one carbene, one terminal bromo, and two bridging μ-bromo ligands in an almost perfect square planar fashion (max. deviation of C1−Pd1−Br2 angle 87.5°). Due to a crystallographic inversion center, the carbene ligands are *anti*-oriented relative to each other. The carbene ring planes are almost perpendicular to the $Pd_2C_2Br_4$ coordination plane with a dihedral angle of 83.5°. The Pd−C bond lengths amount to 1.947(3) Å, which is in the same range observed for imidazolin-2-ylidene-derived analogues.[10g−i,l] There are three types of Pd−Br bonds in the complex, of which the Pd1−Br1 bond trans to the carbene ligand is significantly longer than the other two due to the strong trans influence of the NHC. Compared to the precursor salt **A**, the $C_{carbene}$−N1/N2 bond lengths have slightly increased, which is accompanied by a slight decrease of the N−C−N angle of 2.1°. Other bond parameters remain largely unchanged. More importantly, all isopropyl CH groups are orientated toward the metal center, giving rise to relatively short C−H···Pd distances of 2.6638(3) and 2.7182(3) Å.[12] The large downfield shift of these protons in the ^{1}H NMR spectrum indicates that the observed C−H···

(12) Conclusions derived from one isolated X-ray crystal structure can be uncertain in view of the difficulty of locating hydrogen atoms in X-ray molecular structures. In studying a larger number of similar structures, however, any broad patterns that appear are likely to be real. In all the structures reported here the located hydrogen positions are reasonable based on the well-determined heavy atom positions, which leave no doubt as to the hydrogen locations.[11]

Table 1. Comparison of Selected Structural and Spectroscopic Data for Complexes 1−4

complex	d(C−H···Pd) [Å]	δH ($\Delta\delta$H)[a] [ppm]	d($C_{carbene}$···Br) [Å]	θ($C_{carbene}$−Pd−Br) [deg]
1	2.6638(3), 2.7182(3)	6.54 (1.33)[b]	3.113(2), 3.038(4)	89.26(9), 87.50(9)
2	2.6942(2), 2.6955(2)	6.14 (0.93)[c]	3.050(2), 2.984(2)	87.89(6), 85.90(6)
3	2.6690(5), 2.6651(4)	6.60 (1.39)[b]	3.069(5), 2.983(5)	87.83(14), 85.11(14)
cis-**4**	2.7024(2), 2.7734(2)	5.84 (0.63)[b]	3.007(3)	84.13(8)
trans-**4**		6.03 (0.82)[b]		

[a] $\Delta\delta H = \delta H(\text{complex}) - \delta H(\text{salt } \mathbf{A})$. [b] Measured in $CDCl_3$. [c] Measured in CD_3CN.

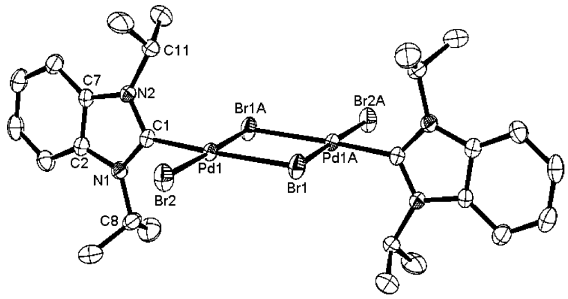

Figure 2. Molecular structure of the dimeric complex [$PdBr_2$-(^{i}Pr_2-bimy)]$_2$ (**1**) with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [deg]: C1−N1 1.341(4), C1−N2 1.338(4), N1−C2 1.398(4), N1−C8 1.482(4), N2−C7 1.399(4), N2−C11 1.483(4), C2−C7 1.398(4), Pd1−C1 1.947(3), Pd1−Br1 2.5281(4), Pd1−Br2 2.4182(4); N1−C1−N2 108.8(2), C1−N1−C2 109.4(2), C1−N2−C7 109.4(2), C1−Pd1−Br1 176.67(9), Br1A−Pd1−Br2 176.603(15), C1−Pd1−Br2 87.50(9), C1−Pd1−Br1A 89.26(9), Br1−Pd1−Br2 95.413(14), Br1−Pd1−Br1A 87.857(13), Pd1−Br1−Pd1A 92.143(13).

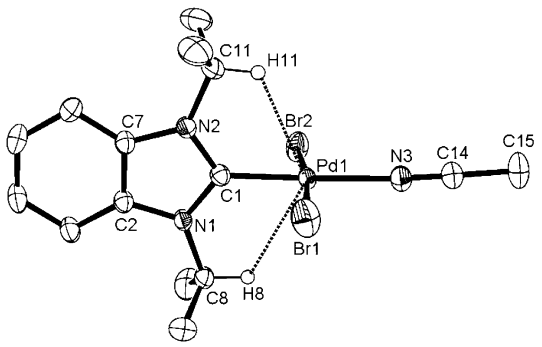

Figure 3. Molecular structure of the complex *trans*-[$PdBr_2$(CH_3-CN)(^{i}Pr_2-bimy)] (**2**) with the crystallographic numbering scheme; hydrogen atoms, except for H8 and H11, are omitted for clarity; selected bond lengths [Å] and angles [deg]: C1−N1 1.348(2), C1−N2 1.349(2), N1−C2 1.398(2), N1−C8 1.475(2), N2−C7 1.392-(2), N2−C11 1.481(2), C2−C7 1.397(3), Pd1−C1 1.9359(19), Pd1−Br1 2.4143(3), Pd1−Br2 2.4287(3), Pd1−N3 2.0814(17), C14−N3 1.130(3), C14−C15 1.457(3); N1−C1−N2 108.25(16), C1−N1−C2 109.38(15), C1−N2−C7 109.55(15), C1−Pd1−N3 177.20(7), Br1−Pd1−Br2 173.329(10), C1−Pd1−Br1 85.90(6), C1−Pd1−Br2 87.89(6), N3−Pd1−Br1 92.76(5), N3−Pd1−Br2 93.55(5), Pd1−N3−C14 175.35(18), N3−C14−C15 179.3(3).

Pd interactions are retained in solution and better described as weak hydrogen bonds, rather than as agostic interactions.[11] Such an interaction has recently been observed for a Rh(I) complex of a six-membered ring NHC ligand.[13] A comparison of structural and spectroscopic data supporting these interactions for all complexes discussed here is shown in Table 1.

Cleavage of 1 with Acetonitrile. Dimeric carbene complexes of type **1** can be readily cleaved by various ligands and are therefore excellent precursors for a range of monocarbene complexes. Not surprisingly, the neutral complex *trans*-[$PdBr_2$(CH_3CN)(^{i}Pr_2-bimy)] (**2**) forms when **1** is dissolved and heated in the coordinating solvent CH_3CN. Upon slow evaporation of a concentrated CH_3CN solution, complex **2** can be obtained as air-stable yellow crystals in good yield. The ^{1}H NMR spectrum of the product in CD_3CN shows that complex **2** has formed as the sole product. The signal for the isopropyl CH groups at 6.13 ppm is still significantly downfield compared to the ligand precursor **A**, indicating that the C−H···Pd interactions are maintained upon cleavage of **1** and subsequent coordination of the CH_3CN ligand. The ^{1}H NMR spectrum of the same product in $CDCl_3$, on the other hand, shows two sets of signals corresponding to **1** and **2**. Comparison of the integrals reveals that the two complexes are in equilibrium in a dimer/monomer ratio of approximately 1:1. The formation of **2** is therefore reversible and only preferred in an excess of CH_3CN. The solid-state structure of complex **2** was determined by single-crystal X-ray diffraction, and Figure 3 depicts the molecular structure. The coordination geometry around the palladium center is essentially square planar with a weakly bonded acetonitrile ligand in trans position to the NHC (Pd−N 2.0814-(17) Å). The Pd−C bond has shortened compared to the parent dimer **1**, suggesting a more Lewis acidic metal center. Here too, the isopropyl CH groups are pointing to the palladium center, resulting in short C−H···Pd distances of 2.6942(2) and 2.6955(2) Å, respectively. The two bromo ligands cis to the NHC lie almost perpendicular to the NHC plane and are surprisingly bent toward this ligand (C1−Pd1−Br1 85.90(6)° and C1−Pd1−Br2 87.89(6)°) rather than toward the nonbulky CH_3CN ligand. The distances of these bromo ligands, Br1 and Br2, to the $C_{carbene}$ atom amount to 2.984(2) and 3.050(2) Å, respectively, and are well within the sum of the van der Waals radii for carbon and bromine (3.55 Å), suggesting weak intramolecular interactions between the bromo ligands and the $C_{carbene}$. To the best of our knowledge, such a phenomenon has not been reported for group 10 metals. However, Abernethy and Cowley recently reported a similar but more pronounced behavior of chloro ligands in the high-oxidation-state transition-metal complexes [V(O)Cl_3(NHC)][14] and [Ti(NMe_2)$_2$$Cl_2$(NHC)][15] (NHC = 1,3-dimesitylimidazolin-2-ylidene). The nature of this halo−carbene interaction was attributed to a form of back-bonding to the formally vacant p-orbital of the $C_{carbene}$ atom with the electron density originating from the halo ligands' lone pairs rather than the metal.

Cleavage of 1 with Benzimidazolium Salt A. Quaternary ammonium salts are often used as ionic liquids, phase-transfer catalysts, or additives in a wide range of reactions including C−C couplings of the Heck type.[4c,16] It is often believed that these salts stabilize active species by coordination or formation of ion pairs.[16e] Respectively, we were interested in studying the cleavage of **1** with azolium salts to investigate the formation of

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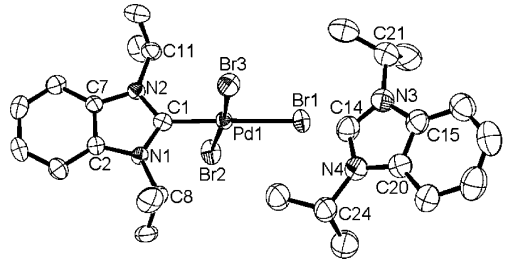

Figure 4. Molecular structure of the complex (^{i}Pr$_2$-bimyH)[PdBr$_3$(^{i}Pr$_2$-bimy)] (**3**) with the crystallographic numbering scheme; four chloroform molecules and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [deg]: C1−N1 1.340(6), C1−N2 1.340(7), N1−C2 1.403(6), N1−C8 1.473(7), N2−C7 1.400(6), N2−C11 1.471(7), C2−C7 1.397(7), Pd1−C1 1.951(5), Pd1−Br1 2.5042(7), Pd1−Br2 2.4284(7), Pd(1)−Br3 2.4441(7), C14−N3 1.321(8), C14−N4 1.337(8), N3−C15 1.383(8), N3−C21 1.487(9), N4−C20 1.386(8), N4−C24 1.495(8), C15−C20 1.390(8); N1−C1−N2 108.7(4), C1−N1−C2 109.2(4), C1−N2−C7 109.8(4), C1−Pd1−Br1 178.02(15), Br2−Pd1−Br3 172.92(3), C1−Pd1−Br2 85.11(14), C1−Pd1−Br3 87.83(14), Br1−Pd1−Br2 93.06(3), Br1−Pd1−Br3 94.01(2), N3−C14−N4 111.3(6), C14−N3−C15 108.2(6), C14−N4−C20 106.8(5).

ion pairs. Thus, the reaction of **1** with 2 equiv of azolium salt **A** in $CHCl_3$ afforded the complex (^{i}Pr$_2$-bimyH)[PdBr$_3$(^{i}Pr$_2$-bimy)] (**3**) in good yield. Complex **3** contains a NHC-stabilized tribromo complex-anion, the charge of which is compensated by the corresponding benzimidazolium cation (^{i}Pr$_2$-bimyH)$^+$. In that respect, complex **3** can be regarded as a model compound possibly occurring in a catalytic cycle, in which an azolium salt stabilizes a coordinatively unsaturated metal center. A closely related triiodo complex derived from a diimidazolium salt has been reported by Herrmann et al.[17] The formation of complex **3** is supported by negative mode ESI spectrometry, which shows an isotopic envelope centered at $m/z = 549$ corresponding to the complex-anion [PdBr$_3$(^{i}Pr$_2$-bimy)]$^-$. ^{1}H NMR spectroscopy performed on crystals of **3** in $CDCl_3$ shows not only the presence of **3** but also signals of the parent compound **1**, indicating that the association of salt **A** and thus the formation of **3** is reversible. It is worth mentioning that such a reversible behavior is undoubtedly desirable, especially in catalysis, since it offers the possibility of both stabilization of unsaturated intermediates and substrate binding. As observed for the complexes **1** and **2**, X-ray diffraction studies and ^{1}H NMR spectroscopy support the presence of weak C−H···Pd bonds only in the complex-anion. In the countercation on the other hand, the orientation of the *N*-isopropyl groups is random. The molecular structure of complex **3** depicted in Figure 4 also reveals intramolecular $C_{carbene}$···Br interactions with distances of 3.069(5) and 2.983(5) Å, respectively.

Cleavage of 1 with Triphenylphosphine. Neutral and mixed NHC−phosphine complexes of palladium(II) derived from imidazole,[10c,f,m,18] imidazoline,[10j,19] and even pyrazole[20] have been reported to be active catalyst precursors for C−C couplings and amide α-arylations. Although both cis and trans isomers of such complexes have been characterized independently, their isomerism has never been studied in detail. Surprisingly, derivatives incorporating benzannulated NHCs are also unknown so far. Hence, we investigated the cleavage of parent complex **1** with triphenylphosphine in CH_2Cl_2. The reaction is rapid, affording *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Ph$_3$P)] (*trans*-**4**) as the kinetically controlled and initial major product, which slowly isomerizes to *cis*-**4** (vide infra). The ^{1}H NMR spectrum of *trans*-**4** in $CDCl_3$ shows a characteristic multiplet at 6.03 ppm for the C−H proton and a doublet at 1.76 ppm for the Me groups of the *N*-isopropyl substituents. The C−H proton of the cis isomer, on the other hand, resonates at higher field with a chemical shift of 5.84 ppm. Furthermore, two doublets of equal intensity are found at 1.66 and 0.87 ppm, indicating two inequivalent Me groups. This observation is in agreement with a sterically hindered rotation of the Pd−$C_{carbene}$ and the N−CH(CH$_3$)$_2$ bond in *cis*-**4**. Due to these distinct differences, the relatively slow trans−cis isomerization can be easily monitored by ^{1}H NMR spectroscopy. Figure 5 depicts the time-dependent ^{1}H NMR spectra in the range of 5.75−6.20 ppm (C−H group) recorded in CD_2Cl_2. The predominant species after 5 min (∼0.08 h) is *trans*-**4** (6.03 ppm), which slowly isomerizes to *cis*-**4** (5.84 ppm) with a ∼50% conversion after 16 h. After 46 h most of the *trans*-**4** has transformed into *cis*-**4**. The same isomerization is much faster when monitored in CD_3CN, revealing that the rate of conversion is solvent-dependent.

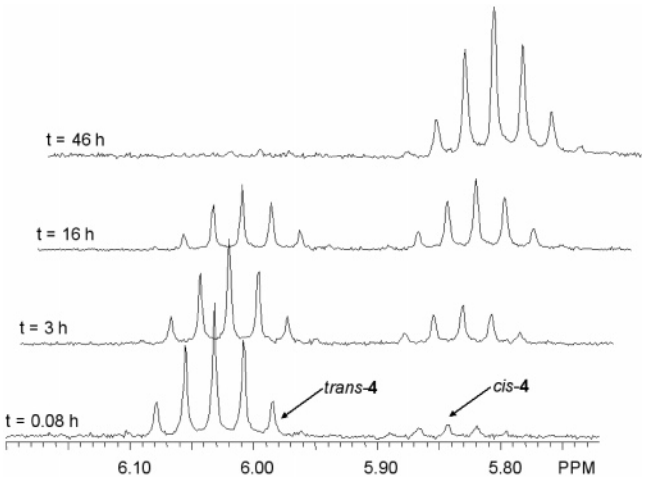

Figure 5. Time-dependent ^{1}H NMR spectra showing the trans−cis isomerization of a mixed NHC−phosphine complex.

Complete conversion to *cis*-**4** in a lab-scale experiment can be achieved by refluxing the reaction mixture in CH_2Cl_2 overnight. Single crystals of *cis*-**4** suitable for X-ray diffraction were obtained by slow evaporation of a concentrated CH_2Cl_2 solution at ambient temperature. The molecular structure of *cis*-**4**, depicted in Figure 6, shows the expected square planar arrangement with the NHC and the phosphine cis to each other. The Pd−C and Pd−P bond lengths amount to 1.978(3) and 2.2624(8) Å, respectively, and are in the expected range. However, the Pd−C bond is significant longer than found in the parent dimer **1** (1.947(3) Å), which may be due to both steric repulsion and a less Lewis acidic metal center induced by the coordination of the phosphine ligand. This also explains the weaker C−H···Pd interactions with distances of 2.7024(2) and 2.7734(2) Å. Furthermore, the Pd−Br2 bond trans to the

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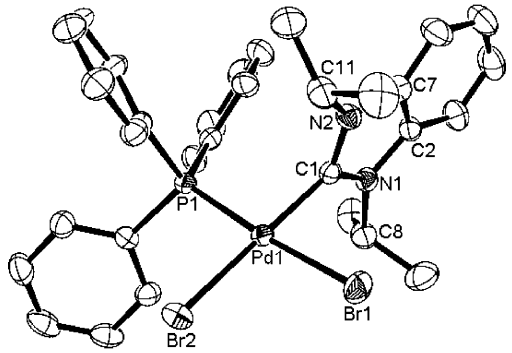
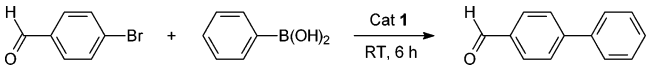


Figure 6. Molecular structure of the complex *cis*-[PdBr$_2$(^{i}Pr$_2$-bimy)(Ph$_3$P)] (*cis*-**4**) with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [deg]: C1−N1 1.342(4), C1−N2 1.343(4), N1−C2 1.396(4), N1−C8 1.489(4), N2−C7 1.406(4), N2−C11 1.486(4), C2−C7 1.393(4), Pd1−C1 1.978(3), Pd1−P1 2.2624(8) Pd1−Br1 2.4761(4), Pd1−Br2 2.4815(4); N1−C1−N2 108.4(3), C1−N1−C2 109.8(2), C1−N2−C7 109.2(2), C1−Pd1−Br2 175.15(9), P1−Pd1−Br1 175.28(2), C1−Pd1−Br1 84.13(8), C1−Pd1−P1 91.61-(9), Br1−Pd1−Br2 92.626(14), P1−Pd1−Br2 91.50(2).

Table 2. Effect of the Solvent on the Suzuki−Miyaura Cross-Coupling Reactions catalyzed by 1[a]



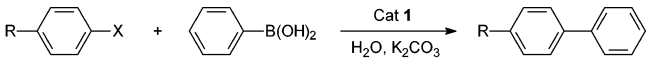
entry	solvent	yield [%][b]
1	H_2O	100[c]
2	CH_3CN/H_2O (1:1 in volume)	100[c]
3	toluene	98[c]
4	CH_3CN	39[c]
5	H_2O	96[d]
6	CH_3CN/H_2O (1:1 in volume)	76[d]

[a] Reaction conditions: 1 mmol of 4-bromobenzaldehyde; 1.2 mmol of phenylboronic acid; 3 mL of solvent; 1.5 equiv of K_2CO_3; 0.5 mol % of **1**. [b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c] Reactions were carried out under nitrogen atmosphere. [d] Reactions were carried out under air.

NHC (2.4815(4) Å) is slightly longer than the Pd−Br1 bond trans to the phosphine (2.4761(4) Å), confirming a slightly stronger trans influence of the NHC. However, a more pronounced effect was observed in an imidazole-derived analogue.[18a]

Catalysis. In a preliminary study, the dimeric complex **1** was tested for its catalytic activity in the Suzuki−Miyaura reaction. The coupling of activated (electron-poor) 4-bromobenzaldehyde with phenylboronic acid with 0.5 mol % catalyst loading (1 mol % Pd) and a reaction time of 6 h at ambient temperature was chosen as a standard test reaction to study the effect of various solvents. The results summarized in Table 2 indicate an excellent catalytic activity of **1** in toluene, in an acetonitrile/water mixture, and even in pure water as "green" solvent (entries 1−3), giving virtually quantitative yields of cross-coupling products. This finding is especially remarkable, since efficient coupling reactions in aqueous media usually require higher temperatures,[21] microwave heating,[22] or higher catalysts loading.[23] On the other hand, the use of pure acetonitrile resulted in only poor yield (entry 4), suggesting that CH_3CN is a poor solvent, and thus complex **2** is probably a less suitable catalyst precursor for this reaction. Furthermore, we observed a drop of yield when the coupling was carried out under air as compared to under nitrogen. Again, the involvement of acetonitrile led to a lower yield (entry 6).

Table 3. Air-Free Suzuki−Miyaura Cross-Coupling Reactions Catalyzed by 1 in Aqueous Media[a]



X = Br, Cl
R = $COCH_3$, CHO, OCH_3, CH_3

entry	aryl halide	*t* [h]	temp [°C]	yield [%][b]
1	4-bromoacetophenone	6	RT	89
2	4-bromotoluene	12	85	55
3	4-bromotoluene	12	85	100[c]
4	4-bromoanisole	12	85	28
5	4-bromoanisole	12	85	100[c]
6	4-chlorobenzaldehyde	12	85	18[c]
7	4-chloroacetophenone	12	85	66[c]

[a] Reaction conditions: 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 3 mL of water; 1.5 equiv of K_2CO_3; 0.5 mol % of **1**. [b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c] With addition of 1.5 equiv of [N(*n*-C_4H_9)$_4$]Br.

Encouraged by these results, we focused on the coupling of other substrates with phenylboronic acid in pure water (Table 3). Similar to 4-bromobenzaldehyde, the coupling of 4-bromoacetophenone occurs already at ambient temperature, giving a good yield of 89% (entry 1). The reaction of nonactivated 4-bromotoluene and 4-bromoanisole, on the other hand, proceeds only at elevated temperature (85 °C), however with low yields of 55% (entry 2) and 28% (entry 4), respectively. Noteworthy is that the addition of [N(*n*-C_4H_9)$_4$]Br (TBAB) leads to a substantial improvement and the latter two substrates can be coupled in quantitative yield (entries 3/5).[21a] These results suggest that a tribromo complex similar to **3** is probably a better catalyst precursor. With the addition of TBAB, 4-chloroacetophenone and 4-chlorobenzaldehyde can also be coupled, affording yields of 66% and 18% (entries 6/7), respectively. However, it is still unclear why the yields for the coupling of the two activated aryl chlorides are so different. We are currently optimizing the reaction conditions for the coupling of aryl chlorides in general in order to answer this question.

Conclusion

The dimeric Pd(II) benzimidazolin-2-ylidene complex **1** has been prepared by the reaction of Pd(OAc)$_2$ with the sterically bulky 1,3-diisopropylbenzimidazolium bromide precursor **A**. Cleavage of complex **1** with CH_3CN, salt **A**, and triphenylphosphine afforded the novel benzannulated monocarbene complexes **2**, **3**, *trans*-**4**, and *cis*-**4**, respectively. The trans−cis isomerization of the mixed NHC−phosphine complexes **4** monitored by ^{1}H NMR spectroscopy demonstrates that a cis arrangement in such complexes is thermodynamically favored. Furthermore, X-ray single-crystal diffraction analyses of complexes **1**−**3** and *cis*-**4** revealed that the orientation of the *N*-isopropyl substituents is locked with the C−H group pointing to the metal center to maximize C−H···Pd interactions. The large downfield shift of these protons in the ^{1}H NMR spectrum indicates that these C−H···Pd interactions are retained in solution and better described as weak hydrogen bonds, rather than as agostic interactions. In addition, the molecular structures of especially complexes **2** and **3** clearly show a bending of the bromo ligands toward the carbene carbon atom in order to maximize intramolecular $C_{carbene}$···Br interactions. The nature of these interactions can be attributed to a form of back-bonding to the formally vacant p-orbital of the $C_{carbene}$ atom with the electron

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Table 4. Selected X-ray Crystallographic Data for Salt A, Complexes 1−3, and *cis*-4

	A·H_2O	**1**·$C_6H_5CH_3$	**2**	**3**·4$CHCl_3$	*cis*-**4**
formula	$C_{13}H_{19}BrN_2$·H_2O	$C_{26}H_{36}Br_4N_4Pd_2$·$C_6H_5CH_3$	$C_{15}H_{21}Br_2N_3Pd$	$C_{26}H_{37}Br_3N_4Pd$·4$CHCl_3$	$C_{31}H_{33}Br_2N_2PPd$
fw	301.23	1029.16	509.57	1229.20	730.78
color, habit	colorless, block	yellow, thin plate	orange, block	orange, block	yellow, block
cryst size [mm]	0.60 × 0.60 × 0.30	0.28 × 0.20 × 0.10	0.40 × 0.40 × 0.38	0.36 × 0.20 × 0.18	0.46 × 0.30 × 0.20
temperature [K]	223(2)	223(2)	223(2)	223(2)	223(2)
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	8.9656(5)	8.6931(6)	8.6495(4)	15.7290(7)	10.5155(5)
b [Å]	9.1636(5)	9.2111(6)	9.7830(4)	8.9604(4)	17.5035(7)
c [Å]	9.7359(5)	12.6637(8)	12.3440(5)	33.5536(16)	16.4655(7)
α [deg]	77.3460(10)	102.5090(10)	103.1770(10)	90	90
β [deg]	66.4200(10)	96.3810(10)	99.5350(10)	93.0060(10)	94.7220(10)
γ [deg]	83.5500(10)	110.5480(10)	109.9120(10)	90	90
V [Å^3]	715.01(7)	907.33(10)	921.84(7)	4722.5(4)	3020.3(2)
Z	2	1	2	4	4
D_c [g cm^{-3}]	1.399	1.884	1.836	1.729	1.607
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	2.863	5.423	5.338	3.637	3.336
θ range [deg]	2.28−27.50	1.68−27.50	2.33−27.49	1.22−27.50	1.70−27.50
no. of unique data	9106	11 885	12 169	32 676	23 338
max., min. transmn	0.4805, 0.2785	0.6131, 0.3120	0.2362, 0.2240	0.5605, 0.3543	0.5551, 0.3091
final *R* indices	$R_1 = 0.0258$	$R_1 = 0.0312$	$R_1 = 0.0215$	$R_1 = 0.0591$	$R_1 = 0.0283$
[$I > 2\sigma(I)$]	$wR_2 = 0.0668$	$wR_2 = 0.0682$	$wR_2 = 0.0556$	$wR_2 = 0.1297$	$wR_2 = 0.0552$
R indices (all data)	$R_1 = 0.0285$	$R_1 = 0.0446$	$R_1 = 0.0243$	$R_1 = 0.1116$	$R_1 = 0.0407$
	$wR_2 = 0.0682$	$wR_2 = 0.0733$	$wR_2 = 0.0566$	$wR_2 = 0.1483$	$wR_2 = 0.0565$
goodness-of-fit on F^2	1.060	1.010	1.059	0.996	0.845
peak/hole [e Å^{-3}]	0.399/−0.383	0.894/−0.398	0.288/−0.786	1.037/−0.691	0.368/−0.283

density originating from the bromo ligands' lone pairs. A preliminary catalytic study revealed that complex **1** is active in the Suzuki−Miyaura coupling of aryl bromides and chlorides in pure water as environmentally benign solvent.

Experimental Section

General Considerations. Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. All solvents were used as received. $Pd(OAc)_2$ was purchased from Alfa Aesar. Benzimidazole, isopropyl bromide, and triphenylphosphine were obtained from Fluka. All chemicals were used as received without any further treatment if not noted otherwise. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ACF 300 spectrometer, and the chemical shifts (*δ*) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C) or externally to 85% H_3PO_4 (^{31}P). Mass spectra were measured using a Finnigan MAT LCQ (ESI) and Finnigan/MAT 95XL-T (FAB) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

1,3-Diisopropylbenzimidazolium Bromide (A). A mixture of benzimidazole (591 mg, 5 mmol) and K_2CO_3 (760 mg, 5.5 mmol) was suspended in CH_3CN (3 mL) and stirred at ambient temperature for 1 h. To the suspension was added isopropyl bromide (1.40 mL, 15 mmol). The reaction mixture was stirred under reflux conditions for 24 h followed by a second addition of isopropyl bromide (1.40 mL, 15 mmol). Stirring under reflux continued for an additional 72 h. After removing the volatiles in vacuo, CH_2Cl_2 (50 mL) was added to the residue and the resulting suspension was filtered over Celite. The remaining solid was washed with CH_2Cl_2 (5 × 20 mL), and the solvent of the filtrate was removed in vacuo to give a spongy solid, which upon washing with ethyl acetate afforded the product as a white powder (1190 mg, 4.2 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 11.45 (s, 1 H, NCHN), 7.80 (dd, 2 H, Ar−H), 7.65 (dd, 2 H, Ar−H), 5.21 (m, ^3J(H,H) = 6.7 Hz, 2 H, NC*H*$(CH_3)_2$), 1.88 (d, ^3J(H,H) = 6.7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 140.7 (s, NCHN), 131.0, 127.0, 114.0 (s, Ar−C), 52.5 (s, N*C*H$(CH_3)_2$), 22.3 (s, CH_3). Anal. Calc for $C_{13}H_{19}BrN_2$·H_2O: C, 51.84; H, 7.03; N, 9.30. Found: C, 51.98; H, 7.00; N, 9.38. MS (ESI): *m*/*z* = 203 [M − Br]$^+$.

Di-*μ*-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromodipalladium(II) (1). A mixture of salt **A** (85 mg, 0.3 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), and NaBr (124 mg, 1.2 mmol) in DMSO (7 mL) was stirred at 90 °C for 24 h. The reaction mixture was filtered over Celite, and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was suspended in CH_2Cl_2 (30 mL) and then extracted with H_2O (4 × 20 mL). Drying of the organic phase over $MgSO_4$ followed by removal of the solvent in vacuo afforded the product as an orange solid (131 mg, 0.14 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.61 (dd, 4 H, Ar−H), 7.26 (dd, 4 H, Ar−H), 6.54 (m, ^3J(H,H) = 7.1 Hz, 4 H, NC*H*$(CH_3)_2$), 1.82 (d, ^3J(H,H) = 7.1 Hz, 24 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 133.5, 123.0, 113.0 (s, Ar−C), 55.0 (s, N*C*H$(CH_3)_2$), 21.0 (s, CH_3), carbene signal not detected. Anal. Calc for $C_{26}H_{36}Br_4N_4Pd_2$: C, 33.33; H, 3.87; N, 5.98. Found: C, 33.04; H, 4.11; N, 6.23. MS (FAB): *m*/*z* = 505 [M/2 + K]$^+$.

***trans*-Dibromo(acetonitrile)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (2).** A suspension of complex **1** (47 mg, 0.05 mmol) in CH_3CN (5 mL) was stirred at ambient temperature for 6 h and then refluxed for 2 h. The reaction mixture was filtered over Celite. Removal of the solvent in vacuo afforded the product as a yellow powder (44 mg, 0.09 mmol, 90%). ^{1}H NMR (300 MHz, CD_3CN): *δ* 7.73 (dd, 2 H, Ar−H), 7.29 (dd, 2 H, Ar−H), 6.14 (m, ^3J(H,H) = 7.1 Hz, 2 H, NC*H*$(CH_3)_2$), 1.96 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent), 1.70 (d, ^3J(H,H) = 7.1 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): 158.4 (s, NCN), 133.8, 123.9 (s, Ar−C), 118.3 (s, CN), 113.9 (s, Ar−C), 55.8 (s, N*C*H$(CH_3)_2$), 20.5 (s, CH_3), 1.32 (m, *C*H_3CN, assignment is tentative due to overlap with solvent signals). Anal. Calc for $C_{15}H_{21}Br_2N_3Pd$: C, 35.36; H, 4.15; N, 8.25. Found: C, 35.64; H, 4.08; N, 8.06. MS (ESI): *m*/*z* = 471 [M − Br + CH_3CN]$^+$.

1,3-Diisopropylbenzimidazoliumtribromo(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (3). A mixture of complex **1** (94 mg, 0.1 mmol) and salt **A** (57 mg, 0.2 mmol) was stirred in refluxing $CHCl_3$ (6 mL) for 2 h. The reaction mixture was filtered over Celite. Slow evaporation of $CHCl_3$ afforded the product as orange crystalline plates (143 mg, 0.19 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$, signals arising from the countercation are indicated with an asterisk*): *δ* 11.04 (s, 1 H, NCH*N), 7.77 (dd, 2 H, Ar−H*), 7.61 (dd, 2 H, Ar−H*), 7.54 (dd, 2 H, Ar−H), 7.16 (dd, 2 H,

Ar−H), 6.60 (m, ^3J(H,H) = 7.1 Hz, 2 H, NC*H*$(CH_3)_2$), 5.28 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H**$(CH_3)_2$), 1.90 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH*$_3$), 1.75 (d, ^3J(H,H) = 7.1 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): 165.1 (s, NCN), 141.3 (s, NC*HN), 133.8, 121.9, 112.6 (s, Ar−C), 131.0, 126.7, 114.2 (s, Ar−C*), 54.2 (s, N*C*H$(CH_3)_2$), 52.7 (s, N*C**H$(CH_3)_2$), 22.3 (s, C*H_3), 20.7 (s, CH_3). Anal. Calc for $C_{26}H_{37}Br_3N_4Pd$: C, 41.54; H, 4.96; N, 7.45. Found: C, 41.42; H, 4.98; N, 7.38. MS (ESI): 498 [M − $C_{13}H_{19}BrN_2$ + CH_3O]$^-$, 549 [M − $C_{13}H_{19}N_2$]$^-$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)-(triphenylphosphine)palladium(II) (*trans*-4).** A mixture of complex **1** (140 mg, 0.15 mmol) and triphenylphosphine (81 mg, 0.31 mmol) in CH_2Cl_2 (8 mL) was stirred at ambient temperature for 10 min. Removal of the solvent in vacuo afforded the product as a spectroscopically pure orange powder in quantitative yield. Further purification proved difficult due to trans−cis isomerization. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (m, 6 H, Ar−H), 7.56 (dd, 2 H, Ar−H), 7.43 (br, 9 H, Ar−H), 7.20 (dd, 2 H, Ar−H), 6.03 (m, ^3J(H,H) = 7.0 Hz, 2 H, NC*H*$(CH_3)_2$), 1.76 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): 18.0 (s, PPh_3). No ^{13}C NMR data are reported, because *trans*-**4** converts to *cis*-**4** during the measurement.

***cis*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(triphenylphosphine)palladium(II) (*cis*-4).** A mixture of complex **1** (234 mg, 0.25 mmol) and triphenylphosphine (144 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) was stirred under reflux conditions overnight. Slow evaporation of a dichloromethane/toluene mixture afforded the product as yellow crystals (333 mg, 0.46 mmol, 92%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, 2 H, Ar−H), 7.40 (br, 15 H, Ar−H), 7.22 (dd, 2 H, Ar−H), 5.84 (m, ^3J(H,H) = 7.1 Hz, 2 H, NC*H*$(CH_3)_2$), 1.66 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH_3), 0.87 (d, ^3J(H,H) = 7.1 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): 134.5 (br, Ar−C), 133.8 (s, Ar−C), 131.3 (br, Ar−C), 128.8, 128.6, 122.9, 113.0 (s, Ar−C), 54.9 (s, N*C*H$(CH_3)_2$), 21.1, 19.4 (s, CH_3), carbene signal not detected. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): 26.6 (s, PPh_3). Anal. Calc for $C_{31}H3_3Br_2N_2PPd$: C, 50.95; H, 4.55; N, 3.83. Found: C, 50.82; H, 4.70; N, 4.12. MS (FAB): m/z = 651 [M − Br]$^+$.

General Procedure for the Suzuki−Miyaura Cross-Coupling Reaction. In a typical run, a Schlenk tube was charged with a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (1.5 mmol), $[PdBr_2(^iPr_2\text{-bimy})]_2$ (**1**) (0.005 mmol), and $[N(n\text{-}C_4H_9)_4]Br$ (1.5 mmol) (for entries 3, 5, 6, 7 in the Table 3). The reaction vessel was degassed under vacuum and filled with nitrogen. Degassed solvent (3 mL) was then added to the mixture using a syringe. The reaction mixture was vigorously stirred at the appropriate temperature. After the desired reaction time, the solution was allowed to cool. Then 10 mL of dichloromethane was added to the reaction mixture, and the organic phase was extracted with water (6 × 5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^1H NMR spectroscopy.

X-ray Diffraction Studies. Diffraction data for **A**, **1**−**3**, and *cis*-**4** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97[24] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 4.

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Supporting Information Available: Crystallographic data for **A**, **1**−**3**, and *cis*-**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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