Synthesis and Catalytic Activity of Pincer-Type Bis(benzimidazolin-2-ylidene) Palladium Complexes

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Reaction of the bridged bisbenzimidazolium salts 2,6-bis(N^1-alkyl-N^3-methylenebenzimidazolium)pyridine dibromide (**1**, alkyl = methyl; **2**, alkyl = ethyl; **3**, alkyl = *n*-propyl; **4**, alkyl = *n*-butyl) with palladium acetate yields the palladium pincer complexes of type [Pd(L)Br]Br, **5**−**8** (L = 2,6-bis(N^1-alkyl-N^3-methylenebenzimidazolin-2-ylidene)pyridine). Compounds **1**, **2**·0.5MeOH, **4**·CH_2Cl_2, and **6**·MeOH (L = 2,6-bis(N^1-ethyl-N^3-methylenebenzimidazolin-2-ylidene)pyridine) were characterized by X-ray diffraction. The molecular structure of **6** shows a distorted square-planar coordination geometry for the palladium atom. In situ generated pincer complexes **5**−**8** have been tested as catalysts in Heck-type coupling reactions of different aryl halides with styrene.

Introduction

The isolation of the first stable *N*-heterocyclic carbene (NHC) in 1991 by Arduengo et al.[1] caused a renewed interest in the chemistry of stable carbenes and carbene complexes.[2−5] Different types of NHCs derived from imidazole,[6] benzimidazole,[7] imidazolidine,[8] and triazole[9] have been reported during the last decade. In addition, a large number of NHC complexes, especially of the late transition metals, have been synthesized.[3,5] Such complexes with palladium as metal center (Figure 1) have found application in catalytic processes such as the Heck or Suzuki C−C coupling reaction.[10] Ruthenium complexes with NHCs are useful catalysts in various olefin metathesis reactions.[11] The advantage of the carbene complexes in comparison to the analogous phosphine complexes is found in the stronger interaction between the carbene donor function and the metal center. Donor-functionalized, bidentate carbene ligands have also been described. Palladium complexes with such mixed-donor ligands (carbene and P or N donor group) often show an increased catalytic activity.[12]

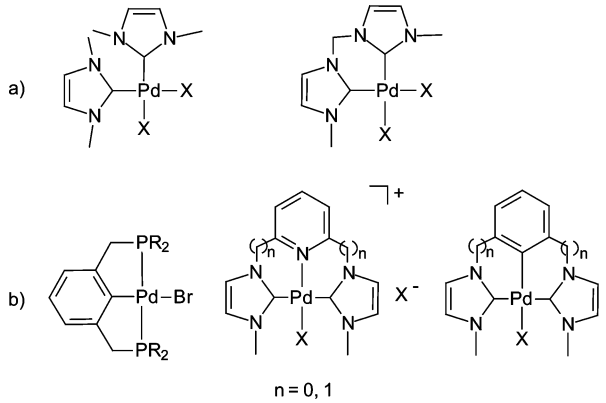

Figure 1. (a) Palladium carbene complexes for Heck- and Suzuki-type C−C couplings. (b) Pincer-type palladium complexes.

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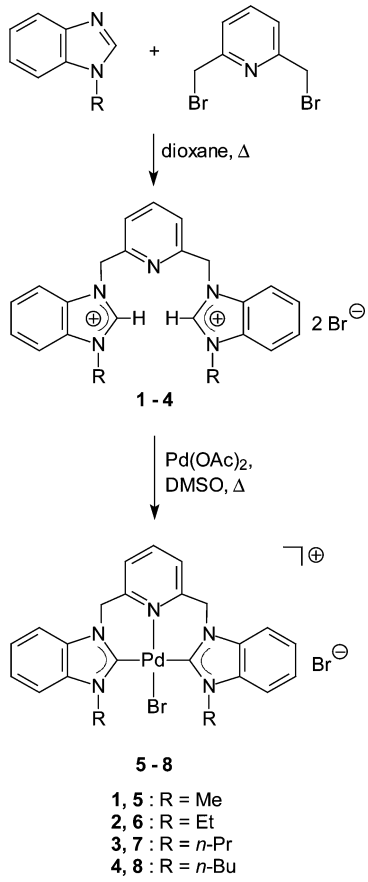
Recently the concept of donor-functionalized carbene ligands has been expanded to pincer-type[13] complexes (Figure 1), where the phosphine donors in the original P−C−P pincer ligands[14] have been substituted for NHCs. The combination of different donor functions in two metallacycles affords very stable and also highly active catalysts. Up to now a number of palladium pincer-type carbene complexes are known. The majority of these complexes possess imidazolin-2-ylidenes as carbenes bridged by a neutral pyridine[15,16] or a carbanionic function[15,16] (Figure 1). Similar complexes with C−N−C pincer ligands have been reported for ruthenium,[17] silver,[18] cobalt,[19] iron,[20] and chromium.[21]

Free benzimidazolin-2-ylidenes[7] behave differently compared to imidazolin-2-ylidenes. This could have consequences for the catalytic activity of pincer-type complexes with benzimidazolin-2-ylidene donor groups. We have prepared the lutidine-bridged bis(benzimidazolium) dibromides **1**−**4** and their palladium pincer complexes **5**−**8** (Scheme 1). Here we report the preparation of **1**−**8** and the molecular structure of the salts **1**, **2**, **4** and of complex **6** together with the catalytic activity of in situ generated complexes **5**−**8** in Heck coupling reactions.

Results and Discussion

Synthesis of Bis(benzimidazolium) Dibromides and Pincer Complexes. The synthesis of the lutidine-bridged bis(benzimidazolium) dibromides **1**−**4** (Scheme 1) starts from N^1-alkylated benzimidazole.[22] Reaction of N^1-alkylated benzimidazole with 2,6-bis(bromomethyl)pyridine in dioxane gives the bisbenzimidazolium salts **1**−**4** in good yields between 77 and 95%. The molecular structures of the salts **1**, **2**, and **4** were determined by X-ray diffraction (see Supporting Information). The ^{1}H NMR spectra (in DMSO-d_6) exhibit the signal for the N−CH−N protons in the range between δ 9.91 and 10.09 ppm. These values are typical for the N−CH−N protons in benzimidazolium salts.[23] Apparently, no interaction between the N−CH−N protons and the pyridine nitrogen atoms exists. The resonances for the methylene protons of the bridge fall in a narrow range between δ 5.84 and 5.89 ppm and are observed as singlets. The isolation of the free biscarbenes or their dibenzotetraazafulvalene dimers by deprotonation of the C2-carbon atom of the benzimidazolium ring with NaH failed. The acidity of the methylene protons of the bridge leads to undesired side reactions during the C2-deprotonation with strong bases.

Scheme 1. Preparation of Bis(benzimidazolium) Dibromides 1−4 and of the Pincer Complexes 5−8



The palladium complexes **5**−**8** with a C−N−C pincer ligand are synthesized by the reaction of salts **1**−**4** with palladium acetate in DMSO (Scheme 1). The yellow complexes were obtained after recrystallization (dichloromethane/diethyl ether) in yields of 75% and higher. An alternative synthetic protocol employing silver carbene complexes[15d,18] in a transmetalation reaction gives lower yields of the palladium complexes (10%). Both the reaction mixture and the palladium complexes are not sensitive to air or moisture in the solid state and in solution.

NMR Spectroscopy. The ^{1}H NMR spectra of complexes **5**−**8** exhibit at ambient temperature a broad resonance at $\delta \approx 6.1$ ppm for the bridging methylene groups (Figure 2 for complex **7**). This resonance is also

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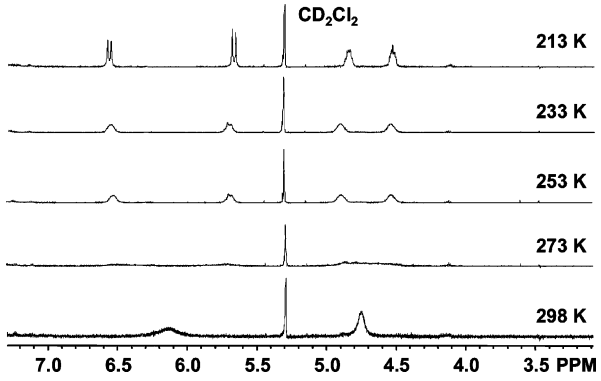

Figure 2. Variable-temperature ^{1}H NMR spectra (in CD_2Cl_2) of complex **7**.

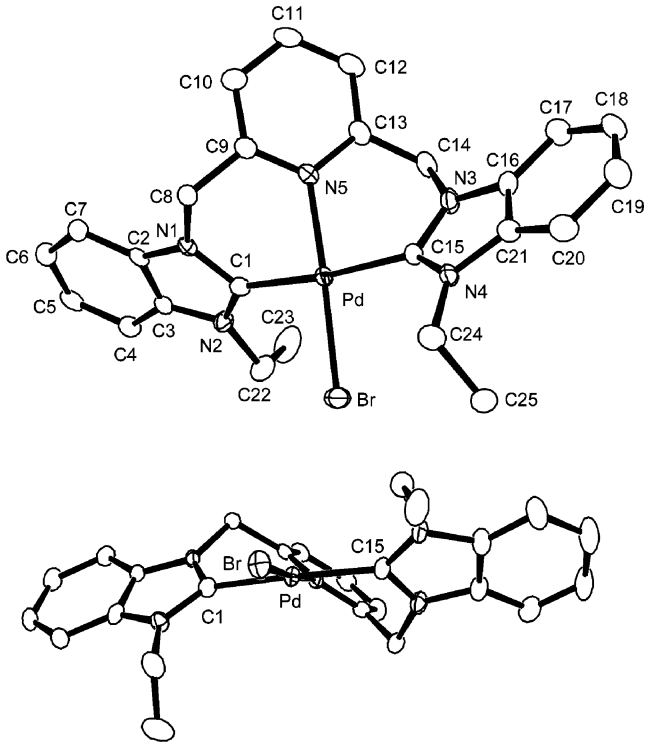

Figure 3. Two views of the molecular structure of complex **6**. Hydrogen atoms and the noncoordinating bromide anion are not shown. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Pd−Br = 2.4193(5), Pd−N5 = 2.072(3), Pd−C1 = 2.025(3), Pd−C15 = 2.040(3), N1−C1 = 1.360(4), N2−C1 = 1.347(4), N3−C15 = 1.353(4), N4−C15 = 1.344(4); Br−Pd−N5 176.29(8), Br−Pd−C1 92.83(10), Br−Pd−C15 93.48(10), N5−Pd−C1 86.58(12), N5−Pd−C15 87.21(12), C1−Pd−C15 173.54(14), N1−C1−N2 105.8(3), N3−C15−N4 106.2(3).

shifted downfield compared to the bisbenzimidazolium dibromides **1**−**4** ($\delta \approx 5.9$ ppm). The broadening of the resonance for the methylene protons indicates that these upon complex formation become involved in a dynamic process. A similar behavior has been observed and discussed in detail for palladium complexes with C−N−C and C−C−C pincer ligands that possess imidazolin-2-ylidene donor units.[16a,b] As discussed there, complexes **5**−**8** adopt a twisted conformation (Figure 3, bottom) and the dynamic process involves the interconversion between the two possible conformations. An average structure which has C_{2v} symmetry with equivalent methylene protons of the bridging group is observed at 298 K. Decoalescence of the broad signal is observed at 273 K. At 213 K two sharp doublets at δ 6.58 and 5.68 ppm (AB pattern) are observed. The coupling constant ($^2J_{H,H}$ = 15.3 Hz) is typical for a geminal coupling of diastereotopic protons.[16b]

A line shape analysis[16b,24] of the temperature-dependent NMR spectra of **7** provides thermodynamic parameters for the atropisomerization process. As described previously,[16] we assume that $\Delta S^{\ddagger}$ is close to zero for this intramolecular process. A value of $\Delta H^{\ddagger}$ = 50.5 kJ/mol was calculated, which is in good agreement with the values obtained for palladium complexes with similar pincer ligands.[16b]

Interconversion of the two geometrical isomers of **7** at room temperature leads also to a broad signal for the *N*-methylene protons of the propyl substituents (δ 4.78 ppm, in CD_2Cl_2). Decoalescence occurs at lower temperature (273 K), and the singlet resonance is split into two multiplets (Figure 2).

The ^{13}C NMR spectra of the complexes **5**−**8** show the resonance of the carbene carbon atom around δ 175 ppm. Compared to the free benzimidazolin-2-ylidene ($\delta \approx 230$ ppm),[7] this represents an upfield shift of about 55 ppm upon coordination to palladium. Slightly smaller upfield shifts for the ^{13}C resonance of the carbene carbon atom have been observed upon coordination of imidazolin-2-ylidene ligands to palladium(II) (free ligands $\delta \approx 212$ ppm,[1,6a] palladium complex $\delta \approx 170$ ppm[15,16]).

Molecular Structures. Crystals of the salts **1**, **2**·0.5MeOH, and **4**·CH_2Cl_2 were obtained by recrystallization from dichloromethane/methanol (**1**, **2**·0.5MeOH) or dichloromethane/diethyl ether (**4**·CH_2Cl_2). Crystals of complex **6**·MeOH were obtained by recrystallization from dichloromethane/methanol. The molecular structures of the salts **1**, **2**, and **4** are described in the Supporting Information. Two views of the cation in **6**·MeOH are depicted in Figure 3.

The Pd−$C_{carbene}$ bond distances in **6** (2.025(3) and 2.040(3) Å) fall in the range observed previously for neutral complexes of type *trans*-[$PdBr_2$(benzimidazolin-2-ylidene)$_2$].[23b] They are also very similar to the Pd−$C_{carbene}$ bond distances found for similar pincer complexes with two *trans*-positioned imidazolin-2-ylidene donor groups.[15d,16a] The *cis* orientation of the carbene ligands in complexes of type *cis*-[PdI_2(NHC)$_2$] appears, however, to cause a slight shortening of the Pd−$C_{carbene}$ distance for both NHC = imidazolin-2-ylidene (1.990(3) and 1.997(3) Å)[10a] and NHC = benzimidazolin-2-ylidene (1.987(4) and 1.989(4) Å).[23a] The palladium atom in **6** is surrounded by a slightly distorted square-planar arrangement of the ligands with the angle C1−Pd−C15 (173.54(14)°) showing the greatest deviation from a perfect square-planar arrangement. This is due to the steric constraints caused by the bridge between the carbene donor units. The N−C−C bond angles at the bridging methylene carbon atoms (C8, C14), however, are close to tetrahedral. The N−C−N angle at the carbene center in **6** (≈106°) is, as expected, significantly smaller than the equivalent angle in the benzimidazolium salts **1**, **2**, and **4** (≈111°) but not as small as in the free benzimidazolin-2-ylidene (≈104°).[7a]

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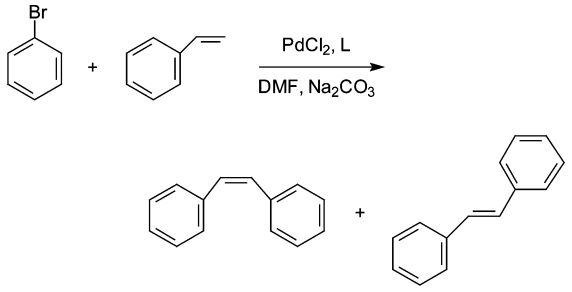
Table 1. Catalytic Heck Reactions of Phenylbromide with Styrene[a]



L	*cis*-stilbene	*trans*-stilbene	conversion (%)
1	5.11	48.21	53.32
2	4.54	67.76	72.3
3	3.93	70.8	74.73
4	4.68	78.69	83.37

[a] Reaction conditions: DMF (5 mL), phenyl bromide (2.5 mmol), sodium carbonate (3.75 mmol), $PdCl_2$ (0.0125 mmol, 2.2 mg), L (0.0075 mmol), and styrene (3.25 mmol). Temperature 115 °C, reaction time 24 h.

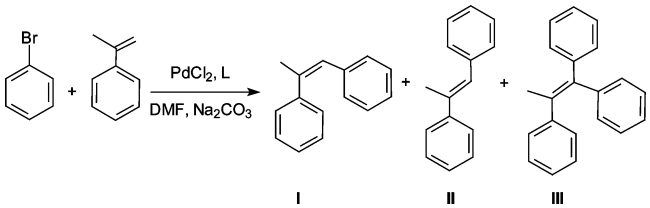
Catalysis. The high thermal and air stability of the pincer carbene complexes both in the solid state and in solution permitted the catalytic reactions to be carried out completely aerobically. Preliminary experiments showed that the performance of the catalyst was enhanced by the use of inorganic bases such as Na_2CO_3, whereas in the case of organic bases (amines) the yields were considerably reduced and the regioselectivity minimized. This may be due in part to steric effects exerted by competitive coordination of the amine to the palladium center. Conditions were found where temperature, reaction time, and amount of catalyst are optimal. Using these optimized reaction conditions experiments with the isolated carbene complexes **5**−**8** were performed. The catalytic activity of these complexes for the Heck reaction was probed through studies of the reactions of styrene with iodo- and bromobenzene. Quantitative conversion to the corresponding olefins was achieved under the conditions used (24 h, 180 °C). The observed catalytic behavior, in regard to both yield and turnover numbers (TON), is similar to that obtained by Crabtree et al. for their bis(imidazolin-2-ylidene)palladium pincer complex.[15a]

The fact that the identity of the catalytic precursor is known prompted us to explore the possibility to further simplify our experimental procedure, such that we could avoid the isolation of the monometallic catalytic precursor. The substituents attached to the benzimidazole moiety allow us also to study the steric effects of these substituents. In a common experiment $PdCl_2$ and a benzimidazolium salt were mixed in DMF and the reactions were allowed to proceed for 24 h. Chromatographic analysis of the samples after the prescribed reaction time showed good conversions in all examined cases (Table 1).

Using the new ligands and palladium dichloride with the hindered substrate α-methylstyrene for the synthesis of trisubstituted olefins was also successful. The effect of the substituent on the reactivity of this substrate was examined at 115 °C, affording good yields and showing a trend in the reactivity (Table 2).

In both cases the best yields were obtained with the catalytic system employing ligand **4**, which contains the

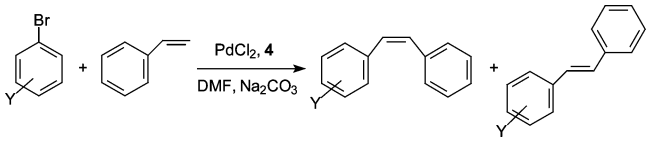
Table 2. Catalytic Heck Reactions of Phenylbromide with α-Methylstyrene[a]



L	**I** (%)	**II** (%)	**III** (%)	conversion (%)
1	23.6	20.3	7.14	51.04
2	22.19	35.07	13.01	70.27
3	23.9	33.42	9.33	66.65
4	20.45	40.16	11.49	72.1

[a] Reaction conditions: DMF (5 mL), phenylbromide (2.5 mmol), sodium carbonate (3.75 mmol), $PdCl_2$ (0.0125 mmol, 2.2 mg), L (0.0075 mmol), and α-methylstyrene (3.25 mmol). Temperature 115 °C, reaction time 24 h.

Table 3. Catalytic Heck Reactions of Aryl Halides with Styrene[a]



Y	Hammett parameter	unsubstituted stilbene[b]	*cis*-stilbene	*trans*-stilbene	conversion (%)
CHO	0.42	15.03	8.5	76.47	100
Cl	0.23		9.12	81.39	90.51
H	0.0		4.68	78.69	83.37
Me	−0.17		3.95	71.78	75.73
OMe	−0.27		7.08	54.24	61.32

[a] Reaction conditions: DMF (5 mL), aryl halide (2.5 mmol), sodium carbonate (3.75 mmol), $PdCl_2$ (0.0125 mmol, 2.2 mg), L = **4** (0.0075 mmol), and styrene (3.25 mmol). Temperature 115 °C, reaction time 24 h. [b]This product being the result of a decarbonylation process of the starting material.

n-butyl substituent attached to one nitrogen atom. Thus, the reactivities of various aryl bromides were also examined under the optimized conditions with the most reactive catalytic system **4** and uniformly showed good selectivity for the *trans*-configured product (Table 3). It is noteworthy that the reaction of the catalytic system with *para*-bromobenzaldehyde also afforded a substantial amount of unsubstituted stilbene, a product probably generated from a decarbonylative process of the aldehyde by the palladium species. Efforts aimed to shed some light regarding this particular process are currently under way in our laboratories.

The precise mechanism of the catalytic reaction remains to be elucidated. There has been considerable debate in the literature about the oxidation states of the species involved in the cycle with Pd(IV)/Pd(II) and Pd(II)/Pd(0) both being suggested at various times. As is the case in other examples of Heck catalyst employing pincer type ligands,[14a,15a,25] we favor the Pd(IV)/Pd(II) mechanism, although participation of species Pd(0)/Pd(II) cannot be ruled out.

Conclusion

In summary the carbene-pincer/palladium systems are efficient catalysts for the olefinic coupling of aryl

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bromides and iodides with both styrene and the sterically hindered α-methylstyrene. The catalytic systems afford good yields even with less-active bromobenzenes, and in the particular case of the *para*-bromobenzaldehyde a decarbonylation process seems to be taking place. Most significantly, the present systems are very versatile since they can be modified by changing the *N*-substituents in the benzimidazole moiety, thus tuning either the sterics and/or the electronics and hence the activity and selectivity in a given reaction. It is also noteworthy that the attractive features of this catalytic system—good yields and air and water stability—approach those required for commercial viability and open future possibilities for its use in other palladium-catalyzed reactions, which are currently under investigation.

Experimental Section

General Procedures. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk techniques. 2,6-Bis(bromomethyl)pyridine and palladium acetate were purchased from Aldrich and Fluka. The *N*-alkylated benzimidazole derivatives were prepared using published procedures.[22,23] Nuclear magnetic resonance spectra were recorded at ambient temperature (except the temperature-dependent measurements). Elemental analyses (C, H, N) were performed on a Vario EL elemental analyzer at the Department of Chemistry, WWU Münster.

General Procedure for the Synthesis of 2,6-Bis(*N*^{1}-alkyl-*N*^{3}-methylenebenzimidazolium)pyridine Dibromides. A solution of 1 equiv of 2,6-bis(bromomethyl)pyridine and 2.2 equiv of *N*-alkylbenzimidazole in 1,4-dioxane (60 mL) was heated under reflux for 16 h. Then the solvent was removed and the solid residue was washed twice with THF (5 mL). The white solid obtained was dried in a vacuum. Crystals of **1**−**4** were obtained by recrystallization from dichloromethane/methanol or dichloromethane/diethyl ether at room temperature. Correct elemental analyses for the hygroscopic benzimidaziolium salts were difficult to obtain. DMSO was used as a solvent for the preparation of complexes **5**−**8**. This was difficult to remove during workup, which had an effect on the elemental analyses of the pincer complexes. Normally only five of the six required resonances for the aromatic carbon atoms of the benzimidazol-2-ylidene moiety could be resolved in the ^{13}C NMR spectra of **1**−**8**.

2,6-Bis(*N*^{1}-methyl-*N*^{3}-methylenebenzimidazolium)pyridine Dibromide (1). Yield: 76.5%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 9.91 (s, 2H, NCHN), 8.01 (t, 1H, ^3J = 7.8 Hz, pyridine-H$_\gamma$), 7.97 (d, 2H, ^3J = 8.1 Hz, Ar-H), 7.70 (d, 2H, ^3J = 7.8 Hz, pyridine-H$_\beta$), 7.64−7.59 (m, 4H, Ar−H), 7.42 (dt, 2H, ^3J = 8.1 Hz, ^4J = 0.8 Hz, Ar-H), 5.84 (s, 4H, N-CH$_2$-pyridine), 4.08 (s, 6H, N-CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 153.5 (pyridine-C$_\alpha$), 143.4 (NCN), 139.1 (pyridine-C$_\gamma$), 131.7, 131.2, 126.7 (Ar-C), 122.9 (pyridine-C$_\beta$), 113.9, 113.7 (Ar-C), 50.7 (N-CH$_2$-pyridine), 33.9 (N-CH$_3$). MS (MALDI): *m/z* 448 ([M − Br]$^+$), 369 (M + H − 2Br]$^+$). Anal. Calcd for $C_{23}H_{23}N_5Br_2$ (529.27): C, 52.19; H, 4.38; N, 13.23. Found: C, 50.54; H, 3.91; N, 12.57.

2,6-Bis(*N*^{1}-ethyl-*N*^{3}-methylenebenzimidazolium)pyridine Dibromide (2). Yield: 95.1%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 10.06 (s, 2H, NCHN), 8.05 (d, 2H, ^3J = 8.2 Hz, Ar-H), 8.00 (t, 1H, ^3J = 7.7 Hz, pyridine-H$_\gamma$), 7.71 (d, 2H, ^3J = 7.7 Hz, pyridine-H$_\beta$), 7.62 (m, 4H, Ar−H), 7.42 (m, 2H, Ar-H), 5.88 (s, 4H, N-CH$_2$-pyridine), 4.52 (q, 4H, ^3J = 7.3 Hz, N-CH$_2$), 1.51 (t, 6H, ^3J = 7.3 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 153.5 (pyridine-C$_\alpha$), 142.7 (NCN), 139.2 (pyridine-C$_\gamma$), 131.5, 130.9, 126.7 (Ar-C), 122.9 (pyridine-C$_\beta$), 114.0, 113.9 (Ar-C), 50.9 (N-CH$_2$-pyridine), 42.6 (N-CH$_2$), 14.6 (CH$_3$). MS (MALDI): *m/z* 478 ([M − Br]$^+$), 397 ([M + H − 2Br]$^+$). Anal. Calcd for $C_{25}H_{27}N_5Br_2$ (557.33): C, 53.88; H, 4.88; N, 12.57. Found: C, 53.42; H, 4.72; N, 12.50.

2,6-Bis(*N*^{1}-*n*-propyl-*N*^{3}-methylenebenzimidazolium)pyridine Dibromide (3). Yield: 85.1%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 10.09 (s, 2H, NCHN), 8.09 (d, 2H, ^3J = 8.3 Hz, Ar-H), 8.01 (t, 1H, ^3J = 7.7 Hz, pyridine-H$_\gamma$), 7.71 (d, 2H, ^3J = 7.7 Hz, pyridine-H$_\beta$), 7.62 (m, 4H, Ar-H), 7.43 (t, 2H, ^3J = 8.3 Hz, Ar-H), 5.89 (s, 4H, N-CH$_2$-pyridine), 4.49 (t, 4H, ^3J = 7.2 Hz, N-CH$_2$), 1.89 (sext, 4H, ^3J = 7.2 Hz, N-CH$_2$-C*H*$_2$-CH$_3$), 0.91 (t, 6H, ^3J = 7.2 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 153.6 (pyridine-C$_\alpha$), 143.0 (NCN), 139.2 (pyridine-C$_\gamma$), 131.4, 131.1, 126.8 (Ar-C), 123.0 (pyridine-C$_\beta$), 114.1, 113.9 (Ar−C), 51.0 (N−CH$_2$-pyridine), 48.5 (N-CH$_2$), 22.5 (N-CH$_2$-*C*H$_2$-CH$_3$), 11.0 (CH$_3$). MS (MALDI): *m/z* 504 ([M − Br]$^+$), 424 ([M + H − 2Br]$^+$). Anal. Calcd for $C_{27}H_{31}N_5Br_2$ (585.38): C, 55.40; H, 5.34; N, 11.96. Found: C, 54.95; H, 5.17; N, 11.77.

2,6-Bis(*N*^{1}-*n*-butyl-*N*^{3}-methylenebenzimidazolium)pyridine Dibromide (4). Yield: 84.4%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 10.06 (s, 2H, NCHN), 8.07 (d, 2H, ^3J = 8.3 Hz, Ar-H), 8.01 (t, 1H, ^3J = 7.7 Hz, pyridine-H$_\gamma$), 7.69 (d, 2H, ^3J = 7.7 Hz, pyridine-H$_\beta$), 7.63 (m, 2H, Ar-H), 7.45 (m, 4H, Ar-H), 5.86 (s, 4H, N-CH$_2$-pyridine), 4.50 (t, 4H, ^3J = 7.5 Hz, NCH$_2$), 1.86 (quint, 4H, ^3J = 7.5 Hz, N-CH$_2$-C*H*$_2$), 1.35 (sext, 4H, ^3J = 7.5 Hz, N-CH$_2$-CH$_2$-C*H*$_2$-CH$_3$), 0.92 (t, 6H, ^3J = 7.5 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 153.6 (pyridine-C$_\alpha$), 143.0 (NCN), 139.2 (pyridine-C$_\gamma$), 131.4, 131.1, 126.8 (Ar-C), 123.0 (pyridine-C$_\beta$), 114.1, 113.9 (Ar-C), 51.0 (N-CH$_2$-pyridine), 46.9 (N-CH$_2$), 31.0 (N-CH$_2$-*C*H$_2$-*C*H$_2$), 19.4 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 13.8 (CH$_3$). MS (MALDI): *m/z* 532 ([M − Br]$^+$), 453 ([M + H − 2Br]$^+$). Anal. Calcd for $C_{29}H_{33}N_5Br_2$ (613.43): C, 56.78; H, 5.75; N, 11.42. Found: C, 54.62; H, 5.69; N, 11.19.

General Procedure for the Synthesis of [Bis(*N*^{1}-alkyl-*N*^{3}-methylenebenzimidazolin-2-ylidene)pyridine]bromopalladium(II)(1+) Bromide. A solution containing 1 equiv of palladium acetate and 1 equiv of one of the salts **1**−**4** in DMSO (10 mL) was stirred at ambient temperature for 2 h. The solution had turned orange after this time. Then the temperature was raised to 50 °C for 12 h, and finally the solution was stirred for 3 h at 125 °C. The solvent was removed in a vacuum, and the residue was dissolved in dichloromethane (2 mL). This solution was added dropwise to ice cold diethyl ether (200 mL). A bright yellow precipitate formed. The solvent was decanted, and the solid was isolated and washed with twice with diethyl ether (5 mL each). The solid residue was dried under vacuum.

[Bis(*N*^{1}-methyl-*N*^{3}-methylenebenzimidazolin-2-ylidene)pyridine]bromopalladium(II)(1+) Bromide (5). Yield: 81.2%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 8.24 (t, 1H, ^3J = 7.7 Hz, pyridine-H$_\gamma$), 8.17−8.09 (m, 4H, Ar-H), 7.81−7.76 (m, 2H, pyridine-H$_\beta$), 7.54−7.46 (m, 4H, Ar-H), 6.13 (s, 4H, N-CH$_2$-pyridine), 4.24 (s, 6H, CH$_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 175.0 (NCN), 155.1 (pyridine-C$_\alpha$), 142.0 (pyridine-C$_\gamma$), 134.2, 132.5, 125.6 (Ar-C), 124.1 (pyridine-C$_\beta$), 111.3 (Ar-C), 51.1 (N-CH$_2$-pyridine), 35.4 (CH$_3$). MS (MALDI): *m/z* 554 ([M − Br]$^+$). Anal. Calcd for $C_{23}H_{21}N_5Br_2Pd$·DMSO (711.8): C, 42.18; H, 3.82; N, 9.84. Found: C, 41.23; H, 3.66; N, 9.47.

[Bis(*N*^{1}-ethyl-*N*^{3}-methylenebenzimidazolin-2-ylidene)pyridine]bromopalladium(II)(1+) Bromide (6). Yield: 85.3%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 8.25−8.08 (m, 5H, pyridine-H$_\gamma$ and Ar-H), 7.82 (m, 2H, pyridine-H$_\beta$), 7.47 (m, 4H, Ar-H), 6.12 (s, 4H, N-CH$_2$-pyridine), 4.85 (q, 4H, ^3J = 7.1 Hz, N-CH$_2$), 1.54 (t, 6H, ^3J = 7.1 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 175.3 (NCN), 155.4 (pyridine-C$_\alpha$), 142.1 (pyridine-C$_\gamma$), 133.3, 133.1, 125.5 (Ar-C), 124.3 (pyridine-C$_\beta$), 112.2, 111.8 (Ar-C), 51.5 (N-CH$_2$-pyridine), 43.1 (N-CH$_2$), 15.9 (CH$_3$). MS (MALDI): *m/z* 582 ([M − Br]$^+$). Anal. Calcd for $C_{25}H_{25}N_5Br_2Pd$·DMSO (739.9): C, 43.83; H, 4.22; N, 9.47. Found: C, 42.74; H, 4.11; N, 9.04.

[Bis(N^1-*n*-propyl-N^3-methylenebenzimidazolin-2-ylidene)pyridine]bromopalladium(II)(1+) Bromide (7). Yield: 93.2%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 8.21−8.11 (m, 5H, pyridine-H$_\gamma$ and Ar-H), 7.85 (m, 2H, pyridine-H$_\beta$), 7.48 (m, 4H, Ar-H), 6.09 (s, 4H, N-CH$_2$-pyridine), 4.77 (t, 4H, ^3J = 7.2 Hz, N-CH$_2$), 1.97 (sext, 4H, ^3J = 7.2 Hz, N-CH$_2$-C*H*$_2$), 0.92 (t, 6H, ^3J = 7.2 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 175.4 (NCN), 155.3 (pyridine-C$_\alpha$), 142.3 (pyridine-C$_\gamma$), 133.6, 133.0, 125.6 (Ar-C), 124.3 (pyridine-C$_\beta$), 112.4, 111.7 (Ar-C), 51.5 (N-CH$_2$-pyridine), 49.0 (N-CH$_2$), 23.3 (N-CH$_2$-*C*H$_2$), 11.1 (CH$_3$). MS (MALDI): *m/z* 610 ([M − Br]$^+$). Anal. Calcd for $C_{27}H_{29}N_5Br_2Pd$·DMSO (767.9): C, 45.36; H, 4.59; N, 9.12. Found: C, 43.98; H, 4.59; N, 8.77.

Correct microanalytical data for the complexes **5**−**7** were difficult to obtain due to varying amounts of DMSO present in the solids.

[Bis(N^1-*n*-butyl-N^3-methylenebenzimidazolin-2-ylidene)-pyridine]bromopalladium(II)(1+) Bromide (8). Yield: 76.5%. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 8.25−8.08 (m, 5H, pyridine-H$_\gamma$ and Ar-H), 7.83 (m, 2H, pyridine-H$_\beta$), 7.47 (m, 4H, Ar-H), 6.10 (s, 4H, N-CH$_2$-pyridine), 4.82 (t, 4H, ^3J = 7.2 Hz, N-CH$_2$), 1.92 (quint, 4H, ^3J = 7.2 Hz, N-CH$_2$-C*H*$_2$-CH$_2$), 1.35 (sext, 4H, ^3J = 7.2 Hz, N-CH$_2$-CH$_2$-C*H*$_2$-CH$_3$), 0.91 (t, 6H, ^3J = 7.2 Hz, CH$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 175.3 (NCN), 155.2 (pyridine-C$_\alpha$), 142.3 (pyridine-C$_\gamma$),133.6, 133.0, 125.7 (Ar-C), 124.3 (pyridine-C$_\beta$), 112.3, 111.8 (Ar-C), 51.5 (N-CH$_2$-pyridine), 47.3 (N-CH$_2$), 31.8 (N-CH$_2$-*C*H$_2$), 19.5 (N-CH$_2$-CH$_2$-*C*H$_2$), 13.7 (CH$_3$). MS (MALDI): *m/z* 638 ([M − Br]$^+$). Anal. Calcd for $C_{29}H_{33}N_5Br_2Pd$ (717.8): C, 48.52; H, 4.63; N, 9.76. Found: C, 47.66; H, 4.53; N, 9.63.

X-ray Diffraction Studies. Diffraction data for **1**, **2**·0.5MeOH, **4**·CH_2Cl_2, and **6**·MeOH were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 123(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the full sphere and were corrrected for absorption (no absorption correction was applied to the data for **4**·CH_2Cl_2). Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2 with SHELXL-97[26] by using first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms.

The asymmetric unit of **1** contains half of the molecule bisected by a 2-fold axis. The asymmetric unit of **2**·0.5MeOH contains two molecules of **2** and one molecule of methanol, and the asymmetric unit of **4**·CH_2Cl_2 contains one formula unit. Crystallographic data for **1**, **2**·0.5MeOH, **4**·CH_2Cl_2, and **6**·MeOH (in CIF format) have been deposited as Supporting Information. Crystal data for **6**·MeOH: $C_{26}H_{29}N_5Br_2OPd$, M = 693.76, yellow plate (0.10 × 0.06 × 0.03 mm^3), monoclinic, space group $P2_1/c$ (no. 14), a = 10.3800(12) Å, b = 25.802(3) Å, c = 9.8561(11) Å, β = 99.366(3)°, V = 2604.5(5) Å^3, Z = 4, D_c = 1.769 g cm^{-3}, μ(Mo Kα) = 3.810 mm^{-1}, 30 120 intensities collected, unique reflections = 7584, reflections ($I \geq 2\sigma(I)$) = 5593, R_1 = 0.0452, wR_2 = 0.0923, GOF = 1.012.

General Method for the Heck Reactions. A dimethylformamide (5 mL) solution of $PdCl_2$ (0.0125 mmol, 2.2 mg) and L (0.0075 mmol) was mixed and heated at 100 °C for 15 min. After this time the solution was cooled, and the aryl halide (2.5 mmol) and styrene (3.25 mmol) were added followed by addition of sodium carbonate (3.75 mmol). The resulting solution was then heated to 115 °C under stirring for 24 h. After that time, the mixture was allowed to cool to room temperature and the organic phase subjected to a quantitative GC analysis by GC-MS in a Varian Saturn 3 with a DB-5 capillary column (30.0 m).

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Supporting Information Available: X-ray crystallographic file for the complexes **1**, **2**·0.5MeOH, **4**·CH_2Cl_2, and **6**·MeOH in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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