Synthesis of Pincer-Type Bis(benzimidazolin-2-ylidene) Palladium Complexes and Their Application in C−C Coupling Reactions

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Reaction of the xylene-bridged bisbenzimidazolium salts 2,6-bis(*N*-alkyl-*N*′-methylenebenzimidazolium)-1-bromophenylene dibromide (**1**, alkyl = ethyl; **2**, alkyl = *n*-propyl; **3**, alkyl = *n*-butyl) with $[Pd_2(dba)_3]$ yields the palladium pincer complexes of type [Pd(L)Br], **4**−**6** (L = 2,6-bis(*N*-alkyl-*N*′-methylenebenzimidazolin-2-ylidene)phenylene). Pincer complexes **4**−**6** have been tested as precatalysts in Heck and Suzuki coupling reactions of various aryl bromides with styrene and phenylboronic acid, respectively.

Introduction

For the last 15 years the preparation of stable N-heterocyclic carbenes (NHCs) and their metal complexes has been an area of intensive research,[1] initiated by the isolation of the first stable N-heterocyclic carbene by Arduengo et al. in 1991.[2] Meanwhile a large number of NHCs derived from imidazole,[3] imidazolidine,[4] triazole,[5] and benzimidazole[6] have been synthesized. Even heterocyclic carbenes with P,P[1a,7] and N,C[1a,8] stabilized carbene centers are known.

Carbene complexes of the late transition metals have been recognized as catalysts for selected transformations such as the ruthenium-catalyzed olefin metathesis[9] and the rhodium-catalyzed hydrosilylation.[10] Among the most widespread application of carbene complexes are the palladium-catalyzed C−C coupling reactions.[1b] On the basis of their superior metal-binding properties[11] carbene ligands have replaced the more expensive phosphines in many metal-catalyzed processes. In general carbene ligands behave as better σ-donors than the best phosphines with the exception of the sterically most demanding derivatives.[12,13] In addition, M→C π-backbonding can most likely be neglected,[13] although its presence in selected metal complexes is still the subject of discussion.[14] The highly stable metal−carbon bond leads to a high stability of carbene complexes against heat and moisture. Computational methods have demonstrated that the strong σ-bond in carbene complexes also causes a stabilization of the metal center in catalytic C−C coupling reactions.[15]

Apart from mono-, bi-,[6b,11,16] tri-,[14b,17] and tetradentate[18] carbene ligands a large number of complexes with donor-functionalized carbenes have been prepared and tested as homogeneous catalysts, often exhibiting an increased catalytic activity.[19] An extension of the concept of donor-functionalized carbene ligands has been the introduction of complexes with pincer-type carbene ligands.[20] Pincer complexes such as **A**

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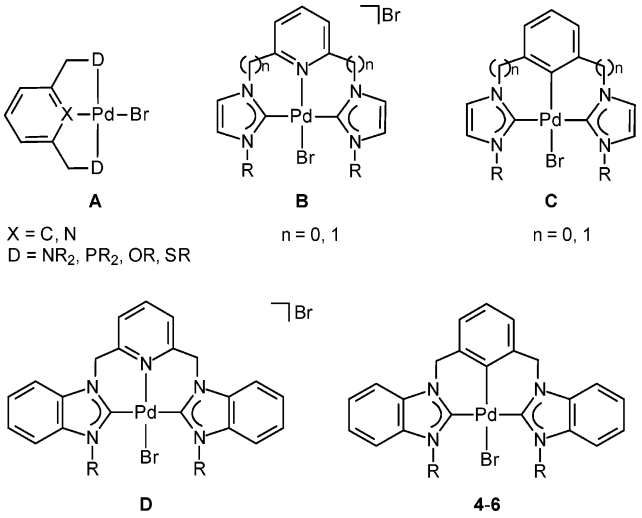
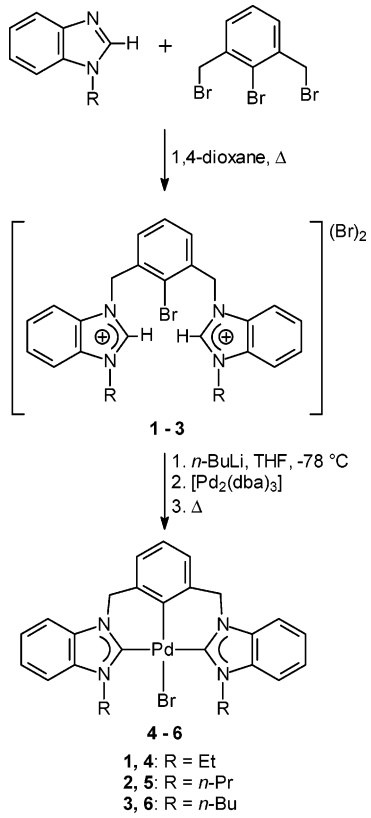
possess a tridentate ligand, which coordinates to the metal center under formation of two metallacycles. Such complexes have found widespread application as homogeneous catalysts.[21] Substitution of two donor functions in **A** with NHCs affords tridentate pincer-type carbene complexes **B**, which have been shown to be very stable and active catalysts for C−C coupling reactions. Several palladium complexes of type **B** have been prepared. The majority of these complexes have been derived from imidazolin-2-ylidene as carbene source and pyridine or lutidine as bridging unit between the carbene donors.[22] Some related ruthenium, iron, chromium, and cobalt complexes have also been described.[23] Only a few examples of pincer complexes of type **C** with xylene-bridged imidazolin-2-ylidene ligands are known.[24]



Recently we described the preparation and catalytic properties of the first palladium pincer complex **D** containing two lutidine-bridged benzimidazolin-2-ylidene carbene units.[24] It was hoped that the unique behavior[6] and donor properties[6a] of the benzimidazolin-2-ylidene carbene units would lead to novel pincer complexes with interesting catalytic properties. In an extension of this study we report here on the preparation and catalytic properties of the neutral xylene-bridged pincer complexes **4**−**6**, which contain two benzimidazolin-2-ylidene donor groups.

Scheme 1. Preparation of the Dibenzimidazolium Salts 1−3 and the Dicarbene Palladium Complexes 4−6



Results and Discussion

The xylene-bridged dibenzimidazolium salts **1**−**3** (Scheme 1) were synthesized by reaction of *N*-alkylated benzimidazole derivatives with 1,3-di(bromomethyl)-2-bromophenylene in 1,4-dioxane. After purification the dibenzimidazolium salts **1**−**3** were obtained in good yields of 79−95%.

The ^{1}H NMR spectra of the dibenzimidazolium salts **1**−**3** exhibit a singlet for the resonance of the NCHN group at δ 10.1 ppm. This value falls in the range observed for related benzimidazolium salts.[25−27] The resonances for the methylene protons of the xylene bridge were observed as broad singlets at δ 5.9 ppm for all three salts. As reported earlier for similar compounds the preparation of the free dicarbenes or their dibenzotetraazafulvalene dimers by deprotonation with a strong base failed owing to the acidity of the methylene protons of the bridge[25] and the known rearrangement reactions of *N*-benzyl- or *N*-allyl-substituted benzimidazolium salts upon C2 depro-

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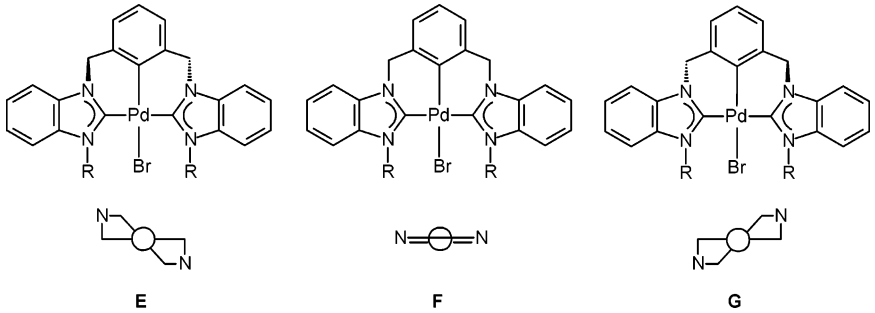
Scheme 2. Limiting Structures E and G and the Average Structure F for Complexes 4−6



tonation.[28] The molecular structure of **2**·MeOH has been determined and is described in the Supporting Information.

The dibenzimidazolium salts **1**−**3** were initially deprotonated in THF with *n*-butyllithium at −78 °C. Very likely the free dicarbenes were obtained at this temperature, and these reacted at −78 °C with $[Pd_2(dba)_3]$, giving red solutions presumably containing the palladium dicarbene complexes. Heating of these red THF solutions under reflux for 12 h led to oxidative addition of the C−Br bond to the palladium(0) center, which resulted in a color change of the solution from red to yellow. After purification by recrystallization the palladium complexes **4**−**6** were obtained as air- and moisture-stable, bright yellow solids.

The ^{13}C NMR spectra of the complexes **4**−**6** exhibit the resonance of the carbene carbon atom around δ 189 ppm downfield from the resonances for the benzimidazolium salts **1**−**3** (δ 143 ppm), indicative for a metalation of the benzimidazolium salts. Surprisingly, the downfield shift upon metalation is more pronounced for the neutral palladium pincer complexes **4**−**6** with the xylene-bridged bis(benzimidazolin-2-ylidene) ligands than observed for cationic pincer complexes with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands (type **D**, δ 175 ppm).[25] On the basis of the overall charge of the complexes one would expect to find the more pronounced downfield resonances for the cationic complexes with the lutidine-bridged ligands. However, a similar, yet to be explained behavior has been observed for the neutral palladium pincer complexes with xylene-bridged bis(imidazolin-2-ylidene) ligands **C** ($\delta_{carbene}$ 177.5−180.9 ppm) and the cationic derivatives **B** with the lutidine-bridged dicarbene ligands ($\delta_{carbene}$ 164−168 ppm).[22f,24b] The resonance for the carbene carbon atoms in complexes **4**−**6** is significantly shifted upfield compared to the free benzimidazolin-2-ylidene ligand (δ 230 ppm).[6a,b]

The ^{1}H NMR spectra (200 MHz, ambient temperature) of complexes **4**−**6** exhibit two doublets at δ 5.5 ppm and 5.2 ppm for the resonances of the protons of the bridging methylene groups. The resonances are shifted upfield relative to the corresponding benzimdazolium salts **1**−**3** (δ 5.94 ppm). A ^2J coupling constant of 13.8 Hz was observed, which is typical for geminal coupling of diastereotopic protons. The diastereotopic behavior of the benzylic protons in **4**−**6** at room temperature differs from the behavior of the protons for the methylene bridges in the palladium complexes **D** with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands reported by us previously,[25] where the resonances for the methylene protons of the bridge appear as broad singlets at ambient temperature. We have attributed this behavior to an atropisomerization process (Scheme 2).

In the case of the palladium complexes **4**−**6** with xylene-bridged dicarbene ligands this atropisomerization process is apparently hindered by a higher energy barrier for the interconversion between the two possible limiting twisted conformations **E** and **G** (Scheme 2). Coalescence of the resonances signals at δ 5.5 and 5.2 ppm in ^{1}H NMR spectrum (400 MHz) (Figure 1) of **6** was achieved at 380 K, and above 420 K the protons of the bridging methylene groups appear as a broad singlet at δ 5.4 ppm, indicating a fast interconversion resulting in an average structure **F** (Scheme 2) with C_{2v} symmetry and equivalent methylene protons.

The thermodynamic parameters of the atropisomerization process have been calculated by line shape analysis[24b,c,29] of the variable-temperature NMR spectra of **6**. Because the dynamic process is of an intramolecular nature, $\Delta S^{\#}$ is assumed to be close to zero. The value of $\Delta H^{\#}$ has been determined to be 73.8 kJ/mol. This value is higher than observed for the analogous palladium complexes with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands ($\Delta H^{\#} = 50.5$ kJ/mol),[25] which explains the different spectroscopic behavior of the of the methylene protons in palladium complexes with lutidine- and xylene-bridged bis(benzimidazolin-2-ylidene) ligands. The calculated values for the atropisomerization are in good agreement with those found for similar pincer complexes with two imidazolin-2-ylidene donor groups.[24b,c]

The resonance for the *N*-methylene protons of the *n*-butyl substituents in **6** is also split into two multiplets at room temperature (δ 5.42−3.30 and 4.51−4.35 ppm, in DMSO-d_6). An increase of the temperature leads to coalescence of the two multiplets at 380 K. At higher temperature a very broad signal is observed at δ 4.90 ppm.

Crystals of **6** have been obtained from a concentrated dichloromethane solution. The molecular structure of **6** is depicted in Figure 2. Bond distances and angles in **6** are similar to the values found for the palladium complex with a lutidine-bridged dicarbene ligand (type **D**).[25]

The Pd−$C_{carbene}$ bond distances in **6** (2.047(4) and 2.036(4) Å) fall in the range observed previously for neutral[27] and cationic

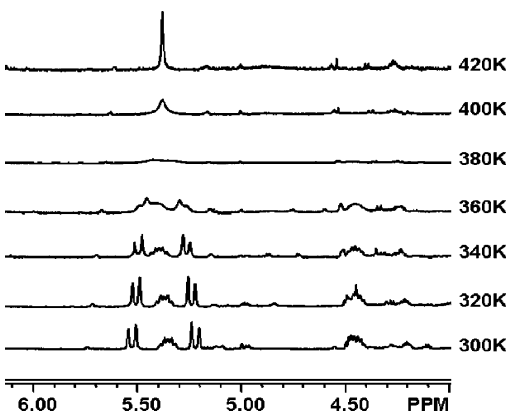


Figure 1. Variable-temperature ^{1}H NMR spectra (400 MHz, DMSO-d_6) of complex **6**.

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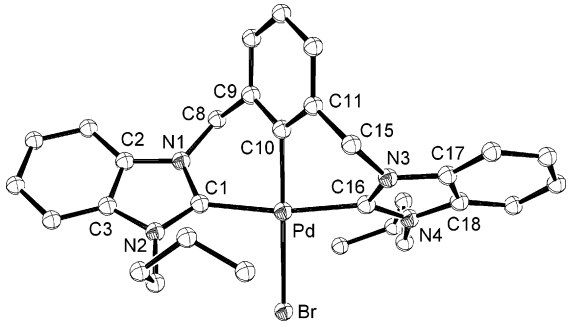

Figure 2. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−Br 2.5567(6), Pd−C1 2.047(4), Pd−C10 2.025(5), Pd−C16 2.036(4), N1−C1 1.354(6), N2−C1 1.341(6), N3−C16 1.352(6), N4−C16 1.353(6); Br−Pd−C1 94.00(13), Br−Pd−C10 177.85(14), Br−Pd−C16 96.45(14), C1−Pd−C10 85.4(2), C1−Pd−C16 169.5(2), C10−Pd−C16 84.2(2), N1−C1−N2 106.8(4), N3−C16−N4 106.1(4), N1−C8−C9 110.0(4), N3−C15−C11 109.4(4), C9−C10−C11 119.4(5).

pincer-type[25] *trans*-bis(benzimidazolin-2-ylidene) palladium complexes. However, they are longer than those found in palladium complexes of the type *cis*-[PdI_2(benzimidazolin-2-ylidene)$_2$], which exhibit Pd−$C_{carbene}$ distances in the range 1.972(3) to 1.991(7) Å.[16f−h] In addition, the Pd−$C_{carbene}$ bond distances in **6** are similar to the equivalent parameters in palladium pincer complexes with two imidazolin-2-ylidene donor groups.[22f,24b] The Pd−C_{phenyl} bond length (2.025(5) Å) is almost identical to the Pd−$C_{carbene}$ bond lengths, an observation made previously with similar palladium pincer complexes with two imidazolin-2-ylidene donor groups.[22f,24b]

The palladium atom in **6** is surrounded by a distorted square-planar arrangement by the four donor groups. The greatest deviation from a perfect square-planar arrangement is found for the C1−Pd−C16 angle (169.5(2)°). This angle is significantly smaller than found in the corresponding palladium pincer complexes with a lutidine-bridged bis(benzimidazolin-2-ylidene) ligand (173.54(14)°).[25] We attribute this observation to the shorter Pd−C10 bond distance in **6** compared to the longer Pd−N distance (2.072(3) Å)[25] in the pincer complex with the lutidine-bridged bis(benzimidazolin-2-ylidene) ligand. Coordination of the ligand in **6** appears to be strain-free, as judged from the almost perfect tetrahedral angles at the bridging methylene groups.

The N1−C1−N2 and N3−C16−N4 angles at the carbene carbon atom in **6** (106.8(4)° and 106.1(4)°) are smaller than the equivalent angle in the benzimidazolium salt **2** (110.6(4)°), but they are larger than in the free benzimidazolin-2-ylidene ligand (103.49(13)° and 104.26(14)°).[6a]

Catalysis. The palladium complexes **4**−**6** have been tested as precatalysts in Heck-type coupling reactions of different aryl bromides with styrene. The complexes are thermally stable and inert toward air and moisture in the solid state. These properties allowed for catalytic experiments under aerobic conditions. Differently *para*-functionalized aryl bromides were used in the catalytic experiments (see Supporting Information).

Complexes **4**−**6** have shown good catalytic activity over 24 h at elevated temperature with activated substrate such as 4-bromobenzaldehyde and 4-bromoacetophenone (see Supporting Information). A shorter reaction time of only 2 h gave still reasonable yields of 55−84% for 4-bromobenzaldehyde as substrate. Much lower activity was observed with the deactivated 4-bromoanisole. The coupling of bromobenzene proceeded also with low yield. The catalytic activity of the neutral complexes **4**−**6** is generally lower than found for the analogous cationic pincer complexes with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands.[25] Similar behavior has been described for neutral and cationic palladium pincer complexes with xylene- or lutidine-bridged bis(imidazolin-2-ylidene) ligands.[24b]

Complexes **5** and **6** have also been tested in Suzuki coupling reactions. Without any optimization of the reaction conditions the coupling of several aryl bromides with phenylboronic acid and potassium carbonate as base in boiling toluene was investigated (see Supporting Information). The catalytic coupling reaction of bromobenzene with phenylboronic acid gave the biphenyl over 24 h in up to 80% yield using 0.1 mol % catalyst **6**. Smaller catalyst loadings (0.01 mol %) led to approximately 65% conversion over 24 h. The Suzuki coupling reaction using activated aryl bromides as substrates led to 100% conversion after 24 h. Reduction of the reaction time to only 2 h resulted in a significant lower conversion rate of about 50%. No homocoupling products were obtained from *para*-functionalized aryl bromides and phenylboronic acid under the reaction conditions described.

Complexes **4**−**6** have been obtained by deprotonation of the benzimidazolium salts, presumably leading to the free dicarbene species, which then coordinates to palladium(0). The subsequent oxidative addition of the C−Br bond to the palladium center gave the neutral palladium complexes with pincer topology bearing two carbene and one carbanionic donor function. The ^{1}H NMR spectra of complexes **4**−**6** exhibit resonances for nonequivalent geminal coupled methylene protons at room temperature caused by a high barrier for the interconversion of the two atropisomers ($\Delta H^{\#} = 73.8$ kJ/mol). Complexes **4**−**6** are stable toward moisture and air and tolerate high temperatures. They have been demonstrated to catalyze Heck and Suzuki coupling reactions with *para*-functionalized aryl bromides. Their high stability might make them suitable for C−C coupling reactions using the less reactive aryl halides.

Experimental Section

General Methods. All preparations were carried out in an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried with standard methods and freshly distilled prior to use. 2,6-Bis(bromomethyl)-1-bromophenylene[30] and the *N*-alkylated benzimidazole derivatives[25−29] were prepared using published procedures. The detailed description of the preparation and analytical data for **1**−**3** have been deposited as Supporting Information. A description of the catalytic experiments can also be found in the Supporting Information. Tris(dibenzylideneacetone)-palladium(0) was purchased from Aldrich. Nuclear magnetic resonance spectra were recorded at ambient temperature (except for the variable-temperature experiments with complex **6**). Mass spectra were measured on a Varian MAT 212 instrument. Elemental analyses (C, H, N) were obtained for all compounds using an Elementar Vario EL III elemental analyzer at the WWU Münster.

General Procedure for the Synthesis of [2,6-Bis-(*N*-alkyl-*N*-methylenebenzimidazolin-2-ylidene)phenylene]bromopalladium(II) (4−6). One of the dibenzimidazolium salts **1**−**3** (0.3 mmol) was suspended in THF (60 mL). To this was added dropwise at −78 °C *n*-butyllithium (0.66 mmol). The reaction mixture was stirred for 30 min, and then [Pd_2(dba)$_3$] (0.15 mmol) was added. The reaction mixture was allowed to slowly warm to ambient temperature. Subsequently the obtained red solution was heated under reflux for 12 h. During this period the color changed to dark

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yellow. The solvent was removed in vacuo, and the resulting residue was dissolved in 2 mL of dichloromethane. This solution was added dropwise to 100 mL of *n*-hexane. The formed precipitate was collected by filtration and dried in vacuo.

[2,6-Bis(*N*-ethyl-*N*-methylenebenzimidazolin-2-ylidene)phenylene]bromopalladium(II) (4). Yield: 63.2%. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 7.48−7.35 (m, 3H, Ar−H), 7.34−7.26 (m, 5H, Ar−H), 7.10−7.04 (m, 2H, Ph−H), 6.90−6.78 (m, 1H, Ph−H), 5.49 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 5.31−5.11 (m, 2H, NCH_2CH_3), 5.15 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 4.76−4.56 (m, 2H, NCH_2CH_3), 1.51 (t, 6H, NCH_2CH_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 189.2 (NCN), 151.9, 141.3 (Ph−C), 134.4 (Ar−C), 125.3, 123.2 (Ph−C), 123.1, 123.0, 111.3, 110.4 (Ar−C), 54.6 (NCH_2Ph), 43.5 (NCH_2CH_3), 16.0 (NCH_2CH_3). MS (MALDI): *m*/*z* 499 ([M − Br]$^+$). Anal. Calcd for $C_{26}H_{25}N_4Br_1Pd_1$ (579.8): C, 53.86; H, 4.35; N, 9.66. Found: C, 53.56; H, 4.27; N, 9.34.

[2,6-Bis(*N*-propyl-*N*-methylenebenzimidazolin-2-ylidene)phenylene]bromopalladium(II) (5). Yield: 65.2%. ^{1}H NMR (200.1 MHz, DMSO-d_6): δ 7.46−7.35 (m, 2H, Ar−H), 7.34−7.26 (m, 6H, Ar−H), 7.10−7.01 (m, 2H, Ph−H), 6.90−6.78 (m, 1H, Ph−H), 5.47 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 5.40−5.24 (m, 2H, $NCH_2CH_2CH_3$), 5.16 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 4.56−4.28 (m, 2H, $NCH_2CH_2CH_3$), 1.94 (m, 4H, $NCH_2CH_2CH_3$), 0.91 (t, 6H, $NCH_2CH_2CH_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 189.5 (NCN), 151.9, 141.3 (Ph−C), 133.8, 133.7 (Ar−C), 125.3, 123.4 (Ph−C), 123.3, 123.2, 111.6, 110.6 (Ar−C), 54.9 (NCH_2Ph), 49.3 ($NCH_2CH_2CH_3$), 23.0 ($NCH_2CH_2CH_3$), 11.8 ($NCH_2CH_2CH_3$). MS (MALDI): *m*/*z* 527 ([M − Br]$^+$). Anal. Calcd for $C_{28}H_{29}N_4Br_1Pd_1$ (607.9): C, 55.33; H, 4.81; N, 9.22. Found: C, 54.97; H, 4.64; N, 9.02.

[2,6-Bis(*N*-butyl-*N*-methylenebenzimidazolin-2-ylidene)phenylene]bromopalladium(II) (6). Yield: 71.3%. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 7.46−7.35 (m, 3H, Ar−H), 7.34−7.26 (m, 5H, Ar−H), 7.10−7.03 (m, 2H, Ph−H), 6.90−6.80 (m, 1H, Ph−H), 5.53 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 5.42−5.30 (m, 2H, $NCH_2CH_2CH_2CH_3$), 5.23 (d, ^{gem}J = 13.8 Hz, 2H, NCH_2Ph), 4.51−4.35 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.91 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.94 (t, 6H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (100.1 MHz, CD_2Cl_2): δ 189.3 (NCN), 151.8, 141.0 (Ph−C), 133.8, 133.7 (Ar−C), 125.1, 122.9 (Ph−C), 122.8, 122.7, 111.1, 110.2 (Ar−C), 54.4 (NCH_2Ph), 47.5 ($NCH_2CH_2CH_2CH_3$), 32.1 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 13.8 ($NCH_2CH_2CH_2CH_3$). MS (MALDI): *m*/*z* 556 ([M − Br]$^+$). Anal. Calcd for $C_{30}H_{33}N_4Br_1Pd_1$ (635.9): C, 56.66; H, 5.23; N, 8.81. Found: C, 56.21; H, 4.97; N, 8.64.

X-ray Diffraction Studies. A summary of the crystal data, collection, and refinement for compounds **2**·MeOH and **6** is given in the Supporting Information.

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Supporting Information Available: Descriptions of the preparation of **1**−**3**, the molecular structure of **2**·MeOH, and the X-ray diffraction and catalysis experiments are available as Supporting Information. Full crystallographic data for compounds **2**·MeOH and **6** are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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