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Imidazolium−Calix[4]arene Molecular Frameworks: Bis(N-heterocyclic carbenes) as Bidentate Ligands[†]

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*Summary: The new palladium(II) bis(N-heterocyclic carbene) complexes **1a**,**b** were prepared efficiently from bis(imidazolium)-calix[4]arene salts **2a**,**b**. The Suzuki−Miyaura reaction was used to study their activity as catalysts when prepared in situ or from a well-defined complex.*

A broad array of imidazolium-based scaffolds have been rapidly developed with advances in both N-heterocyclic carbenes (NHCs)[2] and anion recognition chemistry,[3] as well as with room-temperature ionic liquids (RILs).[4] Complexes of N-heterocyclic carbenes (NHCs) have been of intense recent interest, due to their ease of synthesis, high stability, and excellent catalytic properties toward a variety of reactions.[5] On the other hand, generic calix[4]arenes provide exceptionally useful platforms for preparing multidentate ligands with convergent binding sites.[6] Despite the widespread applications of such multitopic ligands in supramolecular chemistry, the use of calixarenes in catalytic chemistry is only in its infancy.[7,8] Remarkably, only one example, reporteded by Shatz and co-workers,[8] includes NHCs in the calixarene scaffold. Two imidazolium moieties were incorporated in the upper rim of calix[4]arene using a methylene linker, and a *cis*-NHC−Pd−NHC complex was described, together with the excellent results in the Suzuki−

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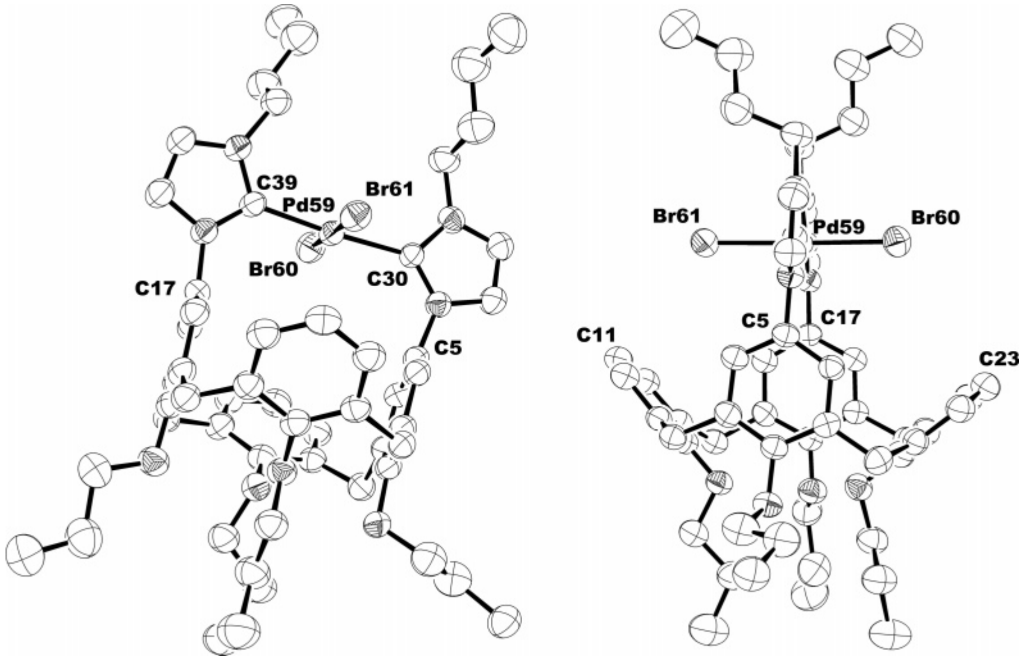
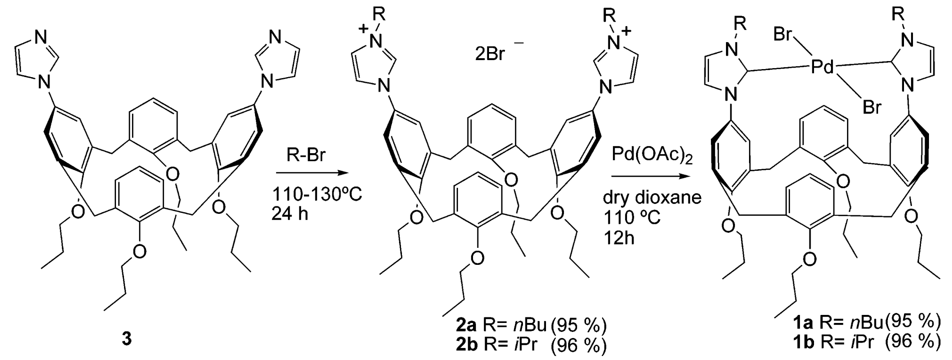


Figure 1. ORTEP representation of the structure of **1a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(30)−Pd(59) = 2.025(2), C(39)−Pd(59) = 2.026(3), Pd(59)−Br(60) = 2.4490(9), Pd(59)−Br(61) = 2.4411(9); C(30)−Pd(59)−C(39) = 175.69(9), Br(60)−Pd(59)−Br(61) = 178.911(13), C(30)−Pd(59)−Br(60) = 89.39(7), C(30)−Pd(59)−Br(61) = 90.31(7), C(39)−Pd(59)−Br(60) = 90.70(8), C(39)−Pd(59)−Br(61) = 89.52(8).

Scheme 1



Miyaura reaction with the catalytic system generated in situ either in dioxane[8a] or in dioxane−water.[8b]

As part of our ongoing research into imidazolium-based frameworks,[1] herein we report the synthesis of the new bidentate palladium(II) complexes **1a**,**b** from the bis(imidazolium)-calixarene salts **2a**,**b**. The Suzuki−Miyaura reaction was used to study their activity as catalysts, when they were prepared either in situ or from a well-defined complex.

Initially, the bis(imidazolium)calix[4]arene salts **2a**,**b** were prepared, in good yields, by quaternization of imidazole units of the calixarene **3** using 1-bromobutane or 2-bromopropane as the reactant and solvent (see Scheme 1, and the Supporting Information).

In situ deprotonation of an azolium salt to produce the desired NHC is advantageous, as the carbene does not have to be isolated, thus simplifying the reaction workups when the aim is to prepare the metal complex. This avoids the handling of the free NHCs, which are usually air- and moisture-sensitive.[9] In this context, the NHC precursors can be deprotonated by basic ligands on the metal complexes. The use of Pd(II) diacetate has become a method which is often used to prepare imida-

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[10] Palladium(II) diacetate (0.037 g, 0.164 mmol) was added to a solution of bis(3-butyl-1-imidazolium)calix[4]arene dibromide (**2a**; 0.151 g, 0.151 mmol) in anhydrous dioxane (10 mL) under an argon atmosphere. The mixture was heated to 50 °C for 1 h, followed by 110 °C for 12 h. The resulting solution was evaporated to dryness, and the remaining black solid was dissolved in dichloromethane and filtered through a Celite pad. The solvent was eliminated, yielding the bis(*N*-butylcarbene) palladium(II) complex **1a** as a yellow solid (0.180 g, 95%). Anal. Calcd for $C_{54}H_{68}Br_2N_4O_4Pd\cdot 2CH_2Cl_2\cdot H_2O$: C, 52.09; H, 5.78; N, 4.34. Found: C, 51.86; H, 5.89, N, 3.97. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.939−1.000 (m, 9H, $H_{37,46}$ and $H_{52,58}$), 1.120 (t, 6H), 1.399−1.493 (m, 4H), 1.917−2.045 (m, 8H), 2.135−2.233 (m, 4H), 3.169 (d, 4H), 3.700 (t, 4H), 4.110 (t, 4H), 4.511 (d, 4H), 4.567 (t, 4H), 6.512 (d, 2H), 6.514 (s, 4H), 6.571 (d, 2H), 6.901 (t, 2H), 7.087 (d, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.8, 10.7, 13.9, 20.3, 22.9, 23.5, 30.8, 32.5, 50.6, 76.5, 77.7, 119.2, 123.7, 123.9, 127.9, 129.0, 133.3, 134.0, 135.2, 154.9, 156.9, 169.7. MS (ESI$^+$): *m/z* 1064.2 ($[C_{54}H_{68}BrN_4O_4{}^{106}Pd]^+CNCH_3$ requires 1064.5), 1023.1 ($C_{54}H_{68}BrN_4O_4{}^{106}Pd]^+$ requires 1022.9). Crystals suitable for X-ray crystallographic studies were grown in dichloromethane.

zolylidene and benzimidazolylidene complexes of Pd.[9b,c] Bidentate palladium(II) complexes **1a**,**b** were synthesized by treating the bis(imidazolium)calixarene salts **2a**,**b** with Pd(II) diacetate, using dry dioxane as a solvent.[10,11] A sealed tube was required for complex **1b**.[11] In both cases, the NHC−Pd^{II}−NHC complex was easily isolated as the only compound formed, with excellent yield. Furthermore, the bidentate palladium(II) complexes **1a**,**b** showed great stability in air and in chromatography or crystallization processes.

All compounds were characterized by ^{1}H and ^{13}C NMR studies. Chemical shifts of the cationic systems **2a**,**b** correlated with both imidazolium salt and substituted calixarene architecture. H_{axial} and $H_{equatorial}$ δ values of the interannular $-CH_2-$ bridge indicated a cone conformation.[6b] ^{1}H NMR data for the NHC−Pd^{II}−NHC complexes **1a**,**b** showed large shielding of H bonded to C_4 and C_5 of the heterocyclic ring, whereas H−C_2 had disappeared. In the ^{13}C NMR spectra, deshielding of C_2 to 170 ppm was observed in the carbene ring, in accordance with the literature.[9c,13c] On the other hand, palladium complexes **1a**,**b** were characterized by ESI-MS in the positive mode. In both compounds, the most intense peak corresponded to the cation obtained by monodebromination, with a molecule of solvent ($CNCH_3$) (see refs 10 and 11 and the Supporting Information).

The structure of compound **1a** was confirmed by single-crystal X-ray crystallography and is consistent with the spectroscopic data[12] (see Figure 1, and the Supporting Information).

As expected, the Pd adopts a square-planar coordination geometry, with the bidentate ligand occupying two trans positions. A small heterocyclic N−C−N bond angle (103.5(2)°) was characteristic of a singlet carbene. The planes of the two NHC rings adopt an almost coplanar conformation, which is slightly tilted (7.63(17)°), and are nearly perpendicular (average value 81.2°) to the aromatic ring plane of calixarene that they are bound to (Figure 1). The Pd−C_{NHC} bond distances are 2.025(2) and 2.026(3) Å, and the C_{NHC}−Pd−C_{NHC} angle is 175.68(10)°, which is in accordance with data described in the literature.[8a,13]

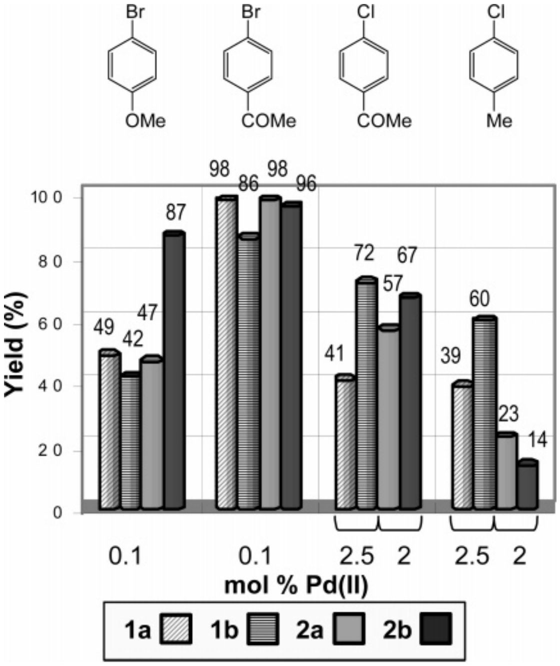

Figure 2. Graphical representation of isolated yields obtained in the Suzuki−Miyaura reaction, after chromatographic purification. Reaction conditions: 1 mmol of aryl halide, 1.5 mmol of phenylboronic acid, 2 mmol of Cs_2CO_3, catalyst (ligand precursor/$Pd(OAc)_2$ or bis(NHC)−Pd(II) complex), 3 mL of dioxane, 80 °C, 2 h.

Furthermore, to accommodate the complex, calixarene adopts a pinched-cone conformation with the distance between C(5) and C(17) of 5.460(4) Å and between C(11) and C(23) of 9.503(4) Å.

The cross-coupling reaction between aryl halides and arylboronic acids (the Suzuki−Miyaura reaction) is the most versatile method for synthesizing substituted biaryls. It is frequently utilized to show the efficiency of palladium(II) catalysts, and efforts are currently being directed toward obtaining improved results with deactivated substrates such as aryl chlorides at very low catalyst loadings.[14] Accordingly, the Suzuki−Miyaura reaction was selected to explore the catalytic efficiency of the new bidentate palladium(II) complexes **1a**,**b** as well as palladium(II) catalyst systems generated in situ from ligand precursors **2a**,**b**. In this case, catalytic species were formed prior to the cross-coupling reaction by treating equimolecular amounts of the bis(imidazolium) salt and Pd$(OAc)_2$ (as a source of palladium and as a base) in dioxane for 2 h at 80 °C.[15] All experiments were stopped after 2 h, and the reaction mixture was treated to isolate the coupling product.

Initially, we examined the coupling of 4-bromoanisole (a deactivated bromoarene) and phenylboronic acid, using 1 or 0.1 mol % of the bis(imidazolium) salts **2a**,**b** and palladium(II) diacetate (Figure 2, and Table S1 in the Supporting Information). The results with 0.1 mol % showed a good yield (87%) for the ligand precursor **2b** and a moderate yield for dication **2a**. The results obtained from the catalyst prepared either in situ from the bis(*N*-butylimidazolium) dibromide **2a** or from the well-defined NHC−Pd^{II}−NHC complex **1a** were comparable. Nev-

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(11) Palladium(II) diacetate (23.12 mg, 0.103 mmol) was added to a solution of bis[3-(2-propyl)butyl-1-imidazolium]calix[4]arene dibromide (**2b**; 0.099 g, 0.102 mmol) in anhydrous dioxane (10 mL) under an argon atmosphere in an oven-dried resealable tube, sealed with a Teflon valve. The mixture was heated to 50 °C for 1 h, followed by 110 °C for 12 h. The resulting solution was evaporated to dryness, and the remaining black solid was dissolved in dichloromethane and filtered through a Celite pad. The solvent was eliminated, yielding the bis(carbene) palladium(II) complex **1b** as a yellow solid (0.120 g, 96%). Anal. Calcd for $C_{52}H_{64}Br_2N_4O_4Pd$: C, 58.08; H, 6.00; N, 5.21. Found C, 58.25; H, 6.10; N, 5.06. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.939 (t, 6H), 1.101 (t, 6H), 1.517 (d, 12H), 1.899−1.990 (m, 4H), 2.117−2.215 (m, 4H), 3.154 (d, 4H), 3.683 (t, 4H), 4.096 (t, 4H), 4.496 (d, 4H), 5.881−5.984 (m, 2H), 6.526 (d, 2H), 6.564 (s, 4H), 6.795 (d, 2H), 6.887 (t, 2H), 7.081 (d, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.8, 10.7, 22.9, 23.0, 23.5, 30.9, 51.9, 76.5, 77.7, 115.1, 123.7, 124.0, 127.9, 129.0, 133.2, 134.0, 135.2, 154.9, 156.9, 169.1. MS (ESI$^+$): m/z 1036.2 ($[C_{52}H_{64}BrN_4O_4{}^{106}Pd]^+CNCH_3$ requires 1036.47), 995.0 ($[C_{52}H_{64}BrN_4O_4{}^{106}Pd]^+$ requires 994.92).

(12) Crystal/refinement data for $\mathbf{1a}\cdot CH_2Cl_2$ ($\equiv C_{56}H_{72}Br_2Cl_4N_4O_4Pd$): $M_r = 1273.20$, size 0.2 × 0.1 × 0.1 mm, triclinic, space group $P\bar{1}$, $a = 11.615(6)$ Å, $b = 11.840(5)$ Å, $c = 23.718(10)$ Å, $\alpha = 103.00(3)°$, $\beta = 92.74(3)°$, $\gamma = 112.08(2)°$, $F(000) = 1304$, $V = 2913(2)$ Å^3, $T = 293(2)$ K, $D_c(Z = 2) = 1.451$ Mg/m^3, $\mu = 1.920$ mm^{-1}, refinement method full-matrix least squares on F^2, R1 = 0.0492 (observed data with $I > 2\sigma(I)$), wR2 = 0.1225, GOF = 1.241.

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ertheless, yields obtained using the palladium(II) complex **1b** were smaller than for the corresponding catalytic system formed from the bis(*N*-isopropylimidazolium) dibromide **2b** (see Figure 2, and Table S1 in the Supporting Information). This result indicates that when the palladium(II) catalysts were generated in situ the exact amount and chemical composition of the catalyst remained unknown. Therefore, special care must be taken when postulating the nature of active species for in situ generated NHC−Pd systems.

Better results were obtained when the reaction was carried out with an activated bromoarene such as 4-bromoacetophenone. When using 0.1 mol % of the bis(imidazolium) salt **2a**,**b** and palladium(II) diacetate, the coupling reaction produced similarly satisfactory isolated yields (≥95%) (see Figure 2, and Table S1 in the Supporting Information). This confirms the catalytic efficiency of the in situ palladium(II)/bis(N-heterocyclic carbene) system, even at low concentrations. Furthermore, bidentate palladium complexes **1a**,**b** had similar catalytic activities.

Bearing in mind that the Suzuki−Miyaura reaction involving chloroarenes requires higher catalyst loading (2.5−3 mol %),[14] we examined cross-coupling with 4-chloroacetophenone using 2.5 mol % of either **2a** or **2b** and palladium(II) diacetate. This produced moderate yields for the diaryl product, while yields decreased below 25% with 4-chlorotoluene (see Figure 2, and Table S1 in the Supporting Information). Nevertheless, catalysis using 2 mol % of the bis(*N*-butylcarbene) palladium complex **1a** gave nearly the same yield with both chloroarenes.

Notably, catalysis using 2 mol % of the bis(*N*-isopropylcarbene) palladium complex **1b** showed that coupling with either 4-chlorotoluene or the activated 4-chloroacetophenone resulted in similar isolated, good yields for the diaryl product in comparison to yields obtained with the ligand precursor bis(*N*-isopropylimidazolium) dibromide **2b** (see Figure 2, and Table S1 in the Supporting Information).

In summary, the new bidentate palladium(II) complexes **1a**,**b** were prepared efficiently from the bis(imidazolium)calix[4]arene salts **2a**,**b**. The Suzuki−Miyaura reaction was used to study their activity as catalysts when prepared either in situ or from a well-defined complex. *N*-Butyl compounds **1a** and **2a** produced similar yields in the coupling reaction of phenylboronic acid with bromoarenes. The bis(*N*-butylcarbene) palladium complex **1a** was more efficient than **2a** in coupling with 4-chlorotoluene. Remarkably, the palladium(II) catalyst system produced in situ from the bis(*N*-isopropylimidazolium) dibromide **2b** with palladium(II) dicetate demonstrated its efficiency with bromoarenes when using low catalyst system loading. The corresponding bis(*N*-isopropylcarbene) palladium(II) complex **1b** produced its highest yields with chloroarenes. These results show that when palladium(II) catalysts were generated in situ, the exact amount and chemical composition of the catalyst remained unknown. Therefore, special care must be taken when postulating the nature of active species for in situ generated NHC−Pd systems.

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Supporting Information Available: Text, figures, and tables giving full experimental details of the synthesis and characterization of compounds **1a**,**b** and **2a**,**b** and crystallographic studies of **1a**; crystal data are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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