ChemPubSoc Europe

DOI: 10.1002/ejic.201501238

EurJIC European Journal of Inorganic Chemistry

Full Paper

C–C Coupling Catalysts

The Influence of Imidazolylidene Ligands with Bulky Resorcinarenyl Substituents on Catalysts for Suzuki–Miyaura Coupling

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Abstract: PEPPSI-type imidazolylidene palladium complexes having their carbenic ring *N*-substituted with an aryl ring and a cavity-shaped unit [25,26,27,28-tetrapropyloxycalix[4]aren-5-yl or 6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]aren-5-yl (TPR)] have been prepared and assessed in Suzuki–Miyaura cross-couplings. Remarkable efficiency in the coupling of aryl chlorides with sterically hindered arylboronic acids was observed for the carbene ligand having its N atoms (N1, N2) substituted by a mesityl and a TPR group, respectively. This good performance possibly arises from strong steric interactions between the pentyl-substituted cavitand unit and the catalytic centre, which favours reductive elimination. Two of the imidazolium salts used for complex synthesis were characterised by X-ray diffraction analysis.

Introduction

The discovery of the Suzuki–Miyaura cross-coupling (SMC) reaction in 1979 had a major impact on both academic and industrial organic chemistry.[1] Over the years, SMC has become the preferred method for preparing biaryl and substituted aromatic compounds. Such compounds constitute valuable synthons that give direct access to a wide range of natural products, pharmaceuticals, polymers, and ligands.[2] In the past few years, much effort has focused on the design and synthesis of new SMC catalysts that are suitable for the formation of tri- or tetra-*ortho*-substituted biaryls starting from hindered aryl chlorides because such coupling reactions are not possible with classical SMC catalysts. Catalysts meeting these criteria require the presence of ligands that display both strong donor properties and/or high steric crowding (phosphines[3] or N-heterocyclic carbenes[4]). Whereas strong donors typically facilitate the oxidative addition step, which is the rate-limiting step in the cross-coupling of aryl chlorides, bulky ligands play a double role: (a) they favour the formation of monoligated intermediates from which the oxidative addition step occurs more easily than from bis-ligand complexes;[5] (b) they efficiently promote the final reductive elimination step.[6]

As an extension to our studies on cavity-derived N-heterocyclic carbenes,[7] we now describe the synthesis of PEPPSI-type complexes **1**–**3** (Figure 1) (PEPPSI = pyridine-enhanced precatalyst preparation stabilisation and initiation[8]) and their use in coupling reactions of bulky aryl chlorides with *sterically hindered* arylboronic acids. The complexes tested have their carbenic ligand *N*-substituted with an aromatic ring (attached to N1) and a cavity-shaped unit (attached to N2), the latter being either a calixarenyl group or an extended resorcinarenyl (cavitand) moiety. In previous work focussed on calixarene derivatives, we have shown that analogues of **1** in which the N1 atom is substituted with an alkyl group instead of an aryl group, were only suitable for SMC between unencumbered aromatics.[9] This was recently confirmed in a study by Bonnamour et al.[10]

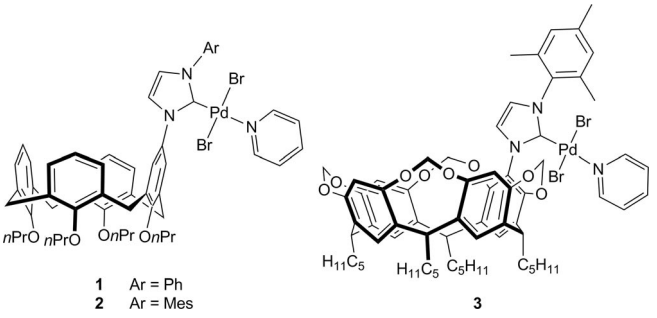

Figure 1. Imidazolylidene palladium complexes used in this study.

Results and Discussion

The synthesis of the Pd-PEPPSI complexes used in the present study based on a calixarene skeleton, namely **1** and **2**, required the preparation of imidazolium salts **6** and **7**, respectively (Scheme 1). These precursors were obtained in ca. 70 % yield

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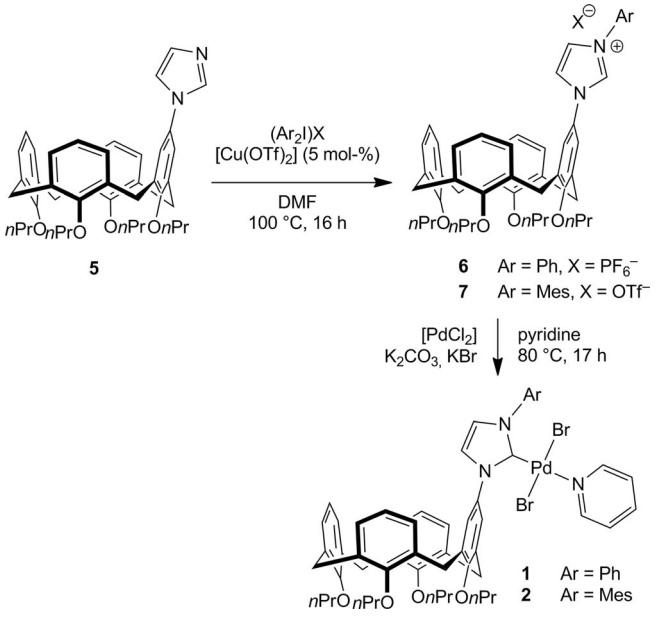
through copper-catalysed arylation of imidazole **5** (DMF, 100 °C, 16 h) by using appropriate aryliodonium salts.[11] Their structures were confirmed by single X-ray diffraction studies, which revealed that for each compound, in the solid state at least, the procarbenic C–H bond is turned slightly towards the cavity axis (Figure 2). These salts were converted into **1** and **2** in pyridine by applying a procedure developed by Organ[8] (Scheme 1). Consistent with C_s symmetry of the molecules, the ^{1}H NMR spectrum of each complex displays two AB patterns for the four $ArCH_2Ar$ groups of the calixarene skeleton. The same is true for the corresponding imidazolium precursors.



Scheme 1. Synthesis of palladium complexes **1** and **2**.

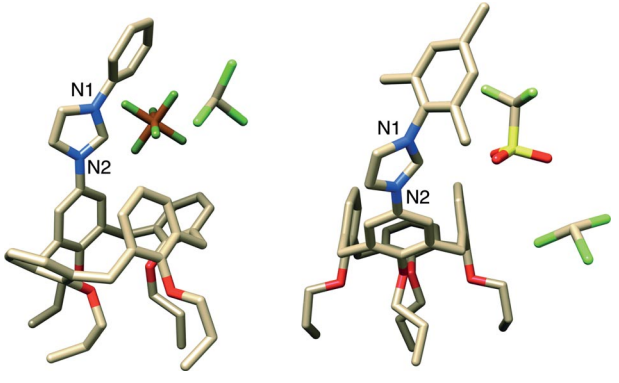
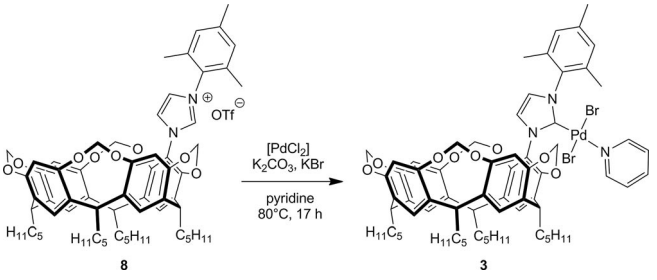


Figure 2. Molecular structures of imidazolium salts **6** (left) and **7** (right). Both salts crystallise with a chloroform molecule. Interplanar angles between opposite phenolic rings: 29.7° and 67.9° in **6**, and 13.7° and 74.6° in **7**. Dihedral angles between the N1–Ar plane and the carbenic ring: 22.0° in **6** and 33.3° in **7**.

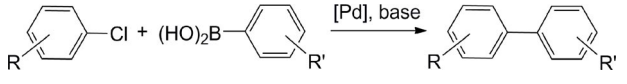
The related resorcinarenyl complex **3** was prepared in a similar manner (Scheme 2), starting from the previously reported mesitylimidazolium salt **8**.[12] As expected, the ^{1}H NMR spectrum of **3** shows two AB patterns for the four OCH_2O groups. For comparative purposes, an analogue **4** of this complex, in which the mesityl group was replaced with a propyl group, was also prepared (see experimental part).



Scheme 2. Synthesis of PEPPSI complex **3**.

Suzuki–Miyaura Cross-Coupling Reactions with Aryl Chlorides

The above palladium complexes were first assessed in cross-coupling between phenylboronic acid and the three aryl chlorides 4-chloroanisole and 2- and 4-chlorotoluene, using NaH as the base (Scheme 3). To identify the most active catalyst, reactions were carried out at 100 °C in 1,4-dioxane with a palladium loading of 0.1 mol-%, and the products were analysed after 1 h (Table 1). The activity of the complexes increased in the order **1** < **2** << **4** < **3**, with that of the two resorcinarene derivatives being significantly higher than for those in which the NCH contains a calixarenyl substituent. Thus, for example, 4-chlorotoluene was converted into 4-methyl-biphenyl in yields of only 4.1 and 9.9 % with complexes **1** and **2**, respectively, vs. 39.2 and 50.1 % when using the palladium complexes **4** and **3**, respectively (Table 1, entry 3). Similar differences in the catalytic behaviour of calixarene- and resorcinarene-based Pd-PEPPSI complexes have been observed in a previous study (concerning cross-coupling reactions involving aryl *bromides*) and are in keeping with steric effects that impact on the reductive elimination step.[7a,9] Also related to sterics is the observation that mesityl complex **3** gave slightly better results (activity increase of 5 to 10 %) than its *n*-propyl analogue **4**. Note that the catalytic activity of **3** is roughly five times greater than that of the previ-



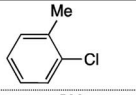
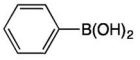
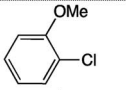
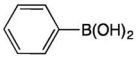
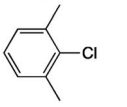
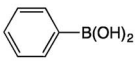
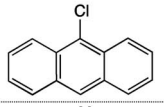
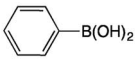
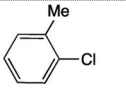
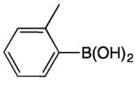
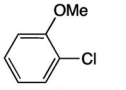
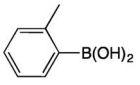
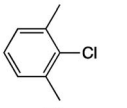
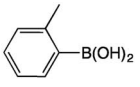
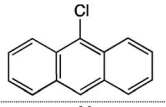
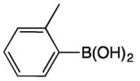
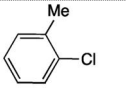
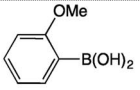
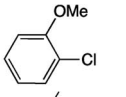
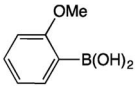
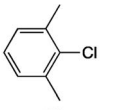
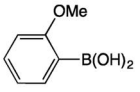
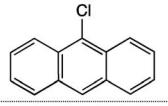
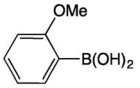
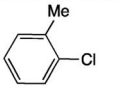
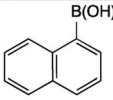
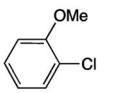
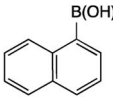
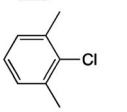
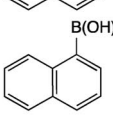
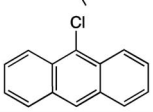
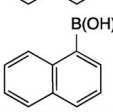
Scheme 3. Suzuki–Miyaura cross-coupling of aryl chlorides with arylboronic acids.

Table 1. Suzuki–Miyaura cross-coupling of aryl chlorides catalysed by complexes **1**–**4**.[a]

Entry	ArCl		Palladium complex 1	2	3	4
1	MeO–Cl	conv. (%)	2.5	5.6	47.4	41.9
2	Me, Cl	conv. (%)	1.2	7.7	40.8	34.1
3	Me–Cl	conv. (%)	4.1	9.9	50.1	39.2

[a] Reaction conditions: $[PdBr_2(NHC)Py]$ (2.5×10^{-4} mmol, 0.1 mol-%), ArCl (0.25 mmol), $PhB(OH)_2$ (0.045 g, 0.37 mmol), NaH (60 % dispersion in mineral oil; 0.015 g, 0.37 mmol), decane (0.025 mL), dioxane (0.75 mL), 100 °C, 1 h. Conversions determined by GC analysis with decane as internal standard.

Table 2. Suzuki–Miyaura cross-coupling of aryl chlorides catalysed by complex **3**.[a]

Entry	ArCl	Ar'B(OH)$_2$	T (°C)	Time (h)	Conv. (%)
1			100	1	98.6
2			75	1	84.9
3			50	5	72.4
4			25	16	4.8
5			75	1	73.9
6			75	5	78.7
7			75	3	97.4
8			75	8	77.3
9			75	8	74.8
10			75	16	67.6
11			75	8	40.2
12			75	8	100
13			75	8	60.3
14			75	16	29.1
15			75	8	89.7
16			75	5	76.7
17			75	5	80.6
18			75	8	50.5
19			75	5	78.5

[a] Reaction conditions: **3** (2.5×10^{-4} mmol, 1 mol-%), ArCl (0.25 mmol), ArB(OH)$_2$ (0.045 g, 0.37 mmol), NaH (60 % dispersion in mineral oil; 0.015 g, 0.37 mmol), decane (0.025 mL), dioxane (0.75 mL). The conversions were determined by GC analysis with decane as internal standard.

ously reported complex [PdCl$_2$(IMes)(pyridine)] (IMes = 1,3-dimesitylimidazolylidene).[13]

Unsurprisingly, almost full conversion (98.6 %) was achieved for 2-chlorotoluene when the catalyst loading of **3** was increased from the initial 0.1 to 1 % (Table 2, entry 1). The reaction rates were quite temperature sensitive: 2-chlorotoluene, for example, was converted approximately five times faster at 75 than at 50 °C (Table 2, entries 2 and 3). Low conversion was measured for runs performed at room temperature (Table 2, entry 4). Based on these observations, the following tests were carried out at 75 °C with a catalyst loading of 1 mol-%.

The resorcinarenyl-palladium complex **3** was further assessed in the cross-coupling of phenylboronic acid with four sterically hindered aryl chlorides; namely, 2-chlorotoluene, 2-chloroanisole, 2,6-dimethylchlorobenzene and 9-chloroanthracene. 2-Chlorotoluene and 2-chloroanisole were both rapidly converted into biaryls (conversions of 84.9 and 73.9 % after 1 h, respectively) (Table 2, entries 2 and 5). As anticipated, somewhat lower activities were found with the two di-*ortho*-substituted chlorobenzenes 2,6-dimethylchlorobenzene (78.7 % conversion in 5 h) and 9-chloroanthracene (97.4 % in 3 h) (Table 2, entries 6 and 7). A similar trend was observed when phenylboronic acid was replaced with the bulkier substrates 2-methyphenylboronic acid, (2-methoxyphenyl)boronic acid and naphthalene-1-boronic acid. For example, 2-chlorotoluene gave conversions after 8 h of 77.3 and 100 %, respectively, when reacted with (2-methylphenyl)boronic acid and (2-methoxyphenyl)boronic acid (Table 2, entries 8 and 12). Finally, we found that complex **3** catalyses the formation of *ortho*-trisubstituted biphenyls in moderate to good yields. Thus, reaction of naphthalene-1-boronic acid with 2,6-dimethylchlorobenzene and 9-chloroanthracene gave conversions of 50.5 and 78.5 %, respectively, after 8 and 5 h with this complex (Table 2, entries 18 and 19).

The above results are in line with our earlier studies involving unencumbered aryl bromides, and they confirm the superiority in SMC of PEPPSI complexes based on a 2,8,14,20-tetrapentylresorcin[4]arene cavitand unit over those built on a tetrapropyloxycalix[4]arene unit.

As proposed earlier,[7a,7c] the efficiency of the cavitand moiety over the calixarenyl group can reasonably be assigned to the presence of two pentyl chains in **3** and **4** that are able to sterically interact with the metal centre so as to facilitate the reductive elimination step (Figure 3). The finding that **3** gave

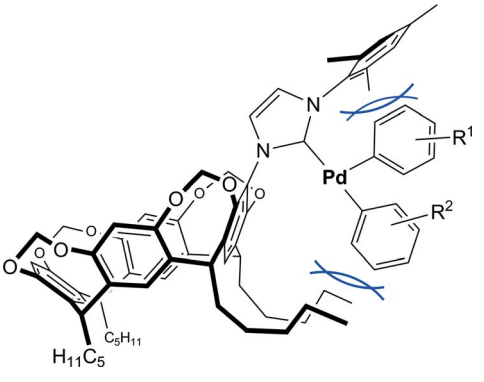


Figure 3. Steric interactions involving pentyl and mesityl substituents, which may occur in catalytic intermediates derived from the palladium complex **3**.

slightly better results than **4** is a further indication that sterics play a key role in these reactions.

Conclusions

In this study, we prepared four new Pd-PEPPSI complexes in which a nitrogen atom of the N-heterocyclic carbene ligand is substituted by a cavity-shaped unit, either a calixarene-5-yl or a 25,26,27,28-tetrabenzyloxycalix[4]aren-5-yl group. The complexes were all found to be suitable for Suzuki–Miyaura cross-coupling between encumbered aryl chlorides and arylboronic acids, but those substituted with the resorcinarene moiety showed significantly higher activities. This result reflects both the greater steric bulk of the macrocycle and the presence of two pendent pentyl groups, which may transiently interact with the second coordination sphere of the metal so as to facilitate reductive elimination. Our findings confirm previous studies carried out on complexes related to **1**–**4** but which were limited to SMC between unencumbered aromatic reagents.

Experimental Section

General Methods: All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were purified by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with Bruker FT instruments (AVANCE 500). ^1H NMR spectra are referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuteriated solvents (δ = 77.16 ppm for $CDCl_3$), and the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. The catalytic solutions were analysed with a Varian 3900 GC equipped with a WCOT fused-silica column (25 m × 0.25 mm). Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg, France. 5-*N*-Imidazolyl-25,26,27,28-tetrapropyloxycalix[4]arene[9] (**5**), 2-*N*-[2,4,6-trimethylphenyl]-5-*N*-[4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]aren-5-yl]imidazolinium triflate[12] (**8**) and 2-*N*-propyl-5-*N*-[4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]aren-5-yl]imidazolinium bromide[7a] were prepared according to reported procedures.

General Procedure for the Preparation of Imidazolium Salts 6 and 7: A mixture of calixarenylimidazole **5** (0.500 g), diarylidonium salt (1.5 equiv.) and $[Cu(OTf)_2]$ (5 mol-%) in DMF (3 mL) was stirred at 100 °C for 16 h. The solvent was then removed under reduced pressure and the solid residue was purified by flash chromatography to afford the corresponding white imidazolium salt.

2-*N*-Phenyl-5-*N*-[25,26,27,28-tetrapropyloxycalix[4]aren-5-yl]-imidazolinium Hexafluorophosphate (6): Flash chromatography (EtOAc), yield 75 % (0.408 g). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.64 (s, 1 H, NCHN), 7.64 (br. s, 1 H, NC*H*CHN), 7.57 (d, ^3J = 7.5 Hz, 2 H, Ar CH), 7.51–7.44 (m, 3 H, Ar CH), 7.08 (d, ^3J = 7.5 Hz, 2 H, Ar CH), 7.02 (br. s, 1 H, NCHC*H*N), 7.01 (d, ^3J = 8.5 Hz, 2 H, Ar CH), 6.86 (t, ^3J = 7.2 Hz, 2 H, Ar CH), 6.45 (s, 2 H, Ar CH), 6.27 (d, ^3J = 7.5 Hz, 2 H, Ar CH), 6.10 (t, ^3J = 7.5 Hz, 1 H, Ar CH), 4.50 and 3.28 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.45 and 3.16 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.05–4.00 (m, 2 H, OCH_2), 3.98–3.92 (m, 2 H, OCH_2), 3.79 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 3.71 (t, ^3J = 7.0 Hz, 2 H, OCH_2), 2.00–1.86 (m, 8 H, CH_2CH_3), 1.09 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.07 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 0.92 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.88 (s, Ar CqO), 157.40 (s, Ar CqO), 156.09 (s, Ar CqO), 137.45–121.23 (Ar C's), 77.50 (s, OCH_2), 77.20 (s, OCH_2), 76.81 (s, OCH_2), 31.06 (s, $ArCH_2Ar$), 31.03 (s, $ArCH_2Ar$), 23.57 (s, CH_2CH_3), 23.52 (s, CH_2CH_3), 23.14 (s, CH_2CH_3), 10.81 (s, CH_2CH_3), 10.73 (s, CH_2CH_3), 10.05 (s, CH_2CH_3) ppm. ^{31}P NMR (201 MHz, $CDCl_3$): δ = –144.01 (sept, $J_{P,F}$ = 709.9 Hz, PF_6) ppm. MS (ESI-TOF): *m/z* = 735.42 $[M - PF_6]^+$ expected isotopic profiles. $C_{49}H_{55}F_6N_2O_4P$ (880.93): calcd. C 66.81, H 6.29, N 3.18; found C 66.72, H 6.34, N 3.15.

2-*N*-[2,4,6-Trimethylphenyl]-5-*N*-[25,26,27,28-tetrapropyloxycalix[4]aren-5-yl]imidazolinium Triflate (7): Flash chromatography (acetone/EtOAc, 10:90 v/v), yield 71 % (0.501 g). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.00 (s, 1 H, NCHN), 7.36 (br. s, 1 H, NC*H*CHN), 7.29 (br. s, 1 H, NCHC*H*N), 7.02 (d, ^3J = 7.0 Hz, 2 H, Ar CH, calix.), 7.01 (s, 2 H, Ar CH, mesityl), 6.94 (d, ^3J = 7.0 Hz, 2 H, Ar CH, calix.), 6.82 (t, ^3J = 7.0 Hz, 2 H, Ar CH, calix.), 6.49 (s, 2 H, Ar CH, calix.), 6.28 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.06 (t, ^3J = 7.5 Hz, 1 H, Ar CH, calix.), 4.50 and 3.29 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.46 and 3.16 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.02–3.97 (m, 2 H, OCH_2), 3.95–3.90 (m, 2 H, OCH_2), 3.81 (t, ^3J = 7.0 Hz, 2 H, OCH_2), 3.73 (t, ^3J = 7.2 Hz, 2 H, OCH_2), 2.33 (s, 3 H, *p*-CH_3-mesityl), 2.03 (s, 6 H, *o*-CH_3-mesityl), 1.97–1.88 (m, 8 H, CH_2CH_3), 1.08 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.06 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 0.93 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.91 (s, Ar CqO), 157.31 (s, Ar CqO), 156.29 (s, Ar CqO), 141.58–121.07 (Ar C's), 120.75 (q, J_{CF} = 320.4 Hz, CF_3), 77.28 (s, OCH_2), 77.07 (s, OCH_2), 76.75 (s, OCH_2), 31.06 (s, $ArCH_2Ar$), 23.53 (s, CH_2CH_3), 23.49 (s, CH_2CH_3), 23.17 (s, CH_2CH_3), 21.24 (s, *p*-CH_3-mesityl), 17.47 (s, *o*-CH_3-mesityl), 10.73 (s, CH_2CH_3), 10.66 (s, CH_2CH_3), 10.09 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m/z* = 777.45 $[M - TfO]^+$ expected isotopic profiles. $C_{53}H_{61}F_3N_2O_7S$ (927.12): calcd. C 68.66, H 6.63, N 3.02; found C 68.55, H 6.74, N 2.89.

General Procedure for the Preparation of the PEPPSI Type Complexes 1–4: A mixture of K_2CO_3 (0.138 g, 1.00 mmol), pyridine (7 mL), $[PdCl_2]$ (0.054 g, 0.30 mmol), imidazolium salt (0.20 mmol) and KBr (0.474 g, 4.00 mmol) was heated at 80 °C for 17 h. The reaction mixture was then filtered through Celite, the filtrate was evaporated under vacuum, and the solid residue was purified by flash chromatography (EtOAc) to afford the corresponding palladium complex.

***trans*-Dibromo-[5-(3-phenylimidazol-2-yliden-1-yl)-25,26,27,28-tetrapropyloxycalix[4]arene]pyridinepalladium(II) (1):** Yield 46 % (0.100 g). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.70 (d, ^3J = 5.0 Hz, 2 H, Ar CH, Py), 8.13 (d, ^3J = 7.5 Hz, 2 H, Ar CH, Ph), 7.62–7.57 (m, 3 H, Ar CH, 2 H Py and 1 H Ph), 7.49 (t, ^3J = 7.2 Hz, 1 H, Ar CH, Ph), 7.42 (s, 2 H, Ar CH, calix.), 7.22 (d, ^3J = 2.0 Hz, 1 H, Ar CH, NC*H*CHN), 7.15–7.13 (m, 2 H Ar CH, 1 H Py and 1 H Ph), 6.96 (d, ^3J = 2.0 Hz, 1 H, Ar CH, NCHC*H*N), 6.84 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.78 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.64 (t, ^3J = 7.5 Hz, 1 H, Ar CH, calix.), 6.48 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.37 (t, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 4.53 and 3.30 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.47 and 3.17 (AB spin system, ^2J = 13.0 Hz, 4 H, $ArCH_2Ar$), 4.01 (t, ^3J = 7.2 Hz, 2 H, OCH_2), 3.90 (t, ^3J = 7.7 Hz, 2 H, OCH_2), 3.85–3.81 (m, 4 H, OCH_2), 2.03–1.91 (m, 8 H, CH_2CH_3), 1.04 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3), 1.03 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 0.99 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.44 (s, Ar CqO), 157.11 (s, Ar CqO), 156.12 (s, Ar CqO), 152.58–121.78 (Ar C's), 77.01 (s, OCH_2), 76.85 (s, OCH_2), 76.77 (s, OCH_2), 31.04 (s, $ArCH_2Ar$), 31.02 (s, $ArCH_2Ar$), 23.42 (s, CH_2CH_3), 23.32 (s, CH_2CH_3), 10.57 (s, CH_2CH_3), 10.39 (s, CH_2CH_3), 10.35 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m/z* =

1078.20 [M + H]$^+$ expected isotopic profiles. $C_{54}H_{59}Br_2N_2N_3O_4Pd$ (1080.29): calcd. C 60.04, H 5.50, N 3.89; found C 60.18, H 6.08, N 3.71.

***trans*-Dibromo-{5-[3-(2,4,6-trimethylphenyl)-imidazol-2-yliden-1-yl]-25,26,27,28-tetrapropyloxycalix[4]arene}pyridine-palladium(II) (2):** Yield 31 % (0.070 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, ^3J = 4.5 Hz, 2 H, Ar CH, Py), 7.61 (s, 2 H, Ar CH, mesityl), 7.56 (t, ^3J = 7.7 Hz, 1 H, Ar CH, Py), 7.12 (d, ^3J = 1.5 Hz, 1 H, Ar CH, NC*H*CHN), 7.10–7.08 (m, 2 H, Ar CH, Py), 7.04 (s, 2 H, Ar CH, calix.), 6.95 (d, ^3J = 1.5 Hz, 1 H, Ar CH, NCHC*H*N), 6.87 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.77 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.71 (t, ^3J = 7.5 Hz, 1 H, Ar CH, calix.), 6.32 (d, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 6.27 (t, ^3J = 7.5 Hz, 2 H, Ar CH, calix.), 4.52 and 3.31 (AB spin system, ^2J = 13.5 Hz, 4 H, $ArCH_2Ar$), 4.46 and 3.16 (AB spin system, ^2J = 13.0 Hz, 4 H, $ArCH_2Ar$), 4.04 (t, ^3J = 7.7 Hz, 2 H, OCH_2), 3.94 (t, ^3J = 7.7 Hz, 2 H, OCH_2), 3.79–3.76 (m, 4 H, OCH_2), 2.38 (s, 6 H, *o*-CH_3-mesityl), 2.38 (s, 3 H, *p*-CH_3-mesityl), 2.03–1.90 (m, 8 H, CH_2CH_3), 1.06 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3), 0.99 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 0.95 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.70 (s, Ar CqO), 157.53 (s, Ar CqO), 155.81 (s, Ar CqO), 152.79–121.80 (Ar C's), 76.86 (s, OCH_2), 76.85 (s, OCH_2), 76.66 (s, OCH_2), 31.12 (s, $ArCH_2Ar$), 31.11 (s, $ArCH_2Ar$), 23.54 (s, CH_2CH_3), 23.35 (s, CH_2CH_3), 23.28 (s, CH_2CH_3), 21.33 (s, *p*-CH_3-mesityl), 20.18 (s, *o*-CH_3-mesityl), 10.74 (s, CH_2CH_3), 10.31 (s, CH_2CH_3), 10.25 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m/z* = 1120.24 [M + H]$^+$ expected isotopic profiles. $C_{57}H_{65}Br_2N_2N_3O_4Pd$ (1122.37): calcd. C 61.00, H 5.84, N 3.74; found C 61.14, H 5.91, N 3.54.

***trans*-Dibromo-{5-[3-(2,4,6-trimethylphenyl)-imidazol-2-yliden-1-yl]-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}pyridinepalladium (II) (3):** Yield 43 % (0.126 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60–8.58 (m, 2 H, Ar CH, Py), 7.59–7.54 (m, 1 H, Ar CH, Py), 7.33 (s, 1 H, Ar CH, resorcinarene), 7.20 (s, 1 H, Ar CH, resorcinarene), 7.19 (s, 2 H, Ar CH, resorcinarene), 7.12–7.08 (m, 2 H, Ar CH, Py), 7.02 (s, 2 H, Ar CH, mesityl), 6.83 (br. s, 1 H, Ar CH, NC*H*CHN), 6.83 (br. s, 1 H, Ar CH, NC*H*CHN), 6.51 (s, 1 H, Ar CH, resorcinarene), 6.49 (s, 2 H, Ar CH, resorcinarene), 5.79 and 4.40 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.74 and 4.47 (AB spin system, ^2J = 6.8 Hz, 4 H, OCH_2O), 4.94 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.77 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 2.38 (s, 6 H, *o*-CH_3-mesityl), 2.37 (s, 3 H, *p*-CH_3-mesityl), 2.33–2.22 (m, 8 H, $CHCH_2$), 1.46–1.31 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.93 (t, ^3J = 6.8 Hz, 6 H, CH_2CH_3), 0.89 (t, ^3J = 6.8 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.03–116.09 (Ar C's), 99.88 (s, OCH_2O), 99.29 (s, OCH_2O), 36.96 (s, $CHCH_2$), 36.58 (s, $CHCH_2$), 32.19 (s, $CH_2CH_2CH_3$), 32.17 (s, $CH_2CH_2CH_3$), 30.13 (s, $CHCH_2$), 29.96 (s, $CHCH_2$), 27.71 (s, $CHCH_2CH_2$), 22.85 (s, CH_2CH_3), 21.35 (s, *p*-CH_3-mesityl), 20.38 (s, *o*-CH_3-mesityl), 14.24 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m/z* = 1268.44 [M – Py]$^+$, 1228.43 [M – Br – Py + MeCN]$^+$ expected isotopic profiles. $C_{69}H_{81}Br_2N_3O_8Pd$ (1346.62): calcd. C 61.54, H 6.06, N 3.12; found C 61.66, H 6.19, N 2.98.

***trans*-Dibromo-[5-(3-propylimidazol-2-yliden-1-yl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene]pyridinepalladium(II) (4):** Yield 51 % (0.130 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.85–8.82 (m, 2 H, Ar CH, Py), 7.67 (tt, ^3J = 7.5, ^4J = 1.5 Hz, 1 H, Ar CH, Py), 7.30 (s, 1 H, Ar CH, resorcinarene), 7.25–7.20 (m, 2 H, Ar CH, Py), 7.19 (s, 1 H, Ar CH, resorcinarene), 7.17 (s, 2 H, Ar CH, resorcinarene), 7.01 (d, ^3J = 1.5 Hz, 1 H, Ar CH, NC*H*CHN), 6.68 (d, ^3J = 1.5 Hz, 1 H, Ar CH, NCHC*H*N), 6.49 (s, 1 H, Ar CH, resorcinarene), 6.48 (s, 2 H, Ar CH, resorcinarene), 5.78 and 4.38 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.70 and 4.38 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 4.90 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.75 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.63 (t, ^3J = 7.5 Hz, 2 H, NCH_2), 2.33–2.12 (m, 10 H, $CHCH_2$ and NCH_2CH_2), 1.46–1.31 (m, 24 H, $CH_2CH_2CH_2CH_3$), 1.09 (t, ^3J = 7.5 Hz, 3 H, $NCH_2CH_2CH_3$), 0.93 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.89 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.97–116.07 (Ar C's), 99.87 (s, OCH_2O), 99.40 (s, OCH_2O), 53.96 (s, NCH_2), 36.87 (s, $CHCH_2$), 36.56 (s, $CHCH_2$), 32.16 (s, $CH_2CH_2CH_3$), 30.05 (s, $CHCH_2$), 29.96 (s, $CHCH_2$), 27.71 (s, $CHCH_2CH_2$), 27.64 (s, $CHCH_2CH_2$), 23.93 (s, NCH_2CH_2), 22.85 (s, CH_2CH_3), 14.25 (s, CH_2CH_3), 11.59 (s, $NCH_2CH_2CH_3$) ppm. $C_{63}H_{77}Br_2N_3O_8Pd$ (1270.53): calcd. C 59.56, H 6.11, N 3.31; found C 59.47, H 5.98, N 3.17.

Typical Procedure for Palladium-Catalysed Suzuki–Miyaura Cross-coupling: A 10 mL-Schlenk tube was filled with palladium complex (2.5×10^{-4} mmol, 1 mol-%), aryl chloride (0.25 mmol), arylboronic acid (0.37 mmol), NaH (60 % dispersion in mineral oil; 0.015 g, 0.37 mmol) and decane (0.025 mL, internal reference). 1,4-Dioxane (0.75 mL) was then added. The reaction mixture was heated at 75 °C. After cooling to room temperature, an aliquot (0.5 mL) of the resulting solution was passed through a Millipore filter and analysed by GC.

X-ray Crystallographoc Data: Single crystals of **6**·$CHCl_3$ suitable for X-ray analysis were obtained by slow diffusion of hexane into a chloroform solution of the imidazolium salt. M_r = 1000.31; orthorhombic; space group *Pbca*; *a* = 16.6926(3), *b* = 17.8582(2), *c* = 30.7047(5) Å; *V* = 9749.3(3) Å^3; *Z* = 8; D_x = 1.363 mg m^{-3}; λ(Cu-K_α) = 1.54184 Å; μ = 2.600 mm^{-1}; *F*(000) = 4176; *T* = 100(2) K. The sample ($0.197 \times 0.188 \times 0.058$ mm) was studied with an Oxford Diffraction SuperNova EOS2 diffractometer. The data collection ($2\theta_{max}$ = 67.7°, omega scan frames via 0.7° omega rotation and 30 s per frame, range *hkl*: *h* –20, 20 *k* –21, 21 *l* –40,39) gave 9463 reflections. The structure was solved with SIR-97,[14] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found with a Fourier Difference. The structure was refined with SHELXL-2014[15] by the full-matrix least-square techniques [use of *F* square magnitude; *x*, *y*, *z*, β_{ij} for C, Cl, F, N, O and P atoms, *x*, *y*, *z* in riding mode for H atoms; 595 variables and 7906 observations with $I > 2.0\sigma(I)$]; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0818P)^2 + 4.4884P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.0533, R_W = 0.1419 and S_W = 1.051, $\Delta\varrho$ < 0.757 e Å^{-3}.

Single crystals of **7**·$CHCl_3$ suitable for X-ray analysis were obtained by slow diffusion of hexane into a chloroform solution of the imidazolium salt. M_r = 1046.50; monoclinic; space group $P2_1$; *a* = 9.43380(10), *b* = 18.6628(2), *c* = 15.1485(2) Å, β = 100.221(1)°; *V* = 2624.75(5) Å^3; *Z* = 2; D_x = 1.324 mg m^{-3}; λ(Cu-K_α) = 1.54184 Å; μ = 2.480 mm^{-1}; *F*(000) = 1100; *T* = 150(2) K. The sample ($0.312 \times 0.304 \times 0.053$ mm) was studied with an Oxford Diffraction SuperNova EOS2 diffractometer. The data collection ($2\theta_{max}$ = 71.337°, omega scan frames via 0.7° omega rotation and 30 s per frame, range *hkl*: *h* –11, 11 *k* –22, 19 *l* –18,18) gave 9342 reflections. The structure was solved with SIR-97,[14] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL-2014[15] by the full-matrix least-square techniques [use of *F* square magnitude; *x*, *y*, *z*, β_{ij} for C, Cl, F, N, O and S atoms, *x*, *y*, *z* in riding mode for H atoms; 634 variables and 9134 observations with $I > 2.0\sigma(I)$]; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0799P)^2 + 0.8441P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.043, R_W = 0.1209 and S_W = 1.036, $\Delta\varrho$ < 0.565 e Å^{-3}.

CCDC 1058184 (for **6**) and 1057661 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for compounds **1**–**7** and procedure for the catalytic runs.

Acknowledgments

The authors thank the Scientific and Technological Research of Turkey (TÜBITAK-BIDEB), International Research Fellowship Programme, for a grant to M. K. and the French Agence Nationale de la Recherche (ANR) (ANR-12-BS07-0001-01-RESICAT) for financial support.

Keywords: Calixarenes · Cavitands · N-Heterocyclic carbenes · Palladium · Cross-coupling

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Received: October 28, 2015
Published Online: January 29, 2016

