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Synthesis of the First Resorcin[4]arene-Functionalized Triazolium Salts and Their Use in Suzuki–Miyaura Cross-Coupling Reactions

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Abstract: Two bulky triazolium salts, namely 1-{4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl}-4-phenyl-3-methyl-1*H*-1,2,3-triazolium tetrafluoro borate (**1**) and 1,4-bis{4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl resorcin[4]arene-5-yl}-3-methyl-1*H*-1,2,3-triazolium iodide (**2**), have been synthesized and assessed in the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl chlorides, with aryl boronic acids. As a general trend, the reaction rates obtained with **1** were significantly higher (up to 5 times) than those observed for **2**, this mainly reflected a sterically more accessible metal center in the catalytic intermediates formed with **1**. The presence of flexible pentyl chains in these intermediates, which might sterically interact with the metal center, when the latter adopts an exo-orientation with respect to the cavity, were likely responsible for the observed good performance.

Keywords: resorcinarene; triazolium salt; Suzuki–Miyaura cross-coupling

1. Introduction

In the last two decades *N*-heterocyclic carbenes (NHCs) have emerged as powerful ligands for the palladium-catalyzed Suzuki–Miyaura cross-coupling reactions [1,2]. Their performance mainly relies on their strong σ-donor properties, generally considered to be superior to that of phosphines, but also relies on the ease with which they can be made sterically bulky [3], this, generally being achieved by tethering appropriate substituents on their nitrogen atoms. These two features respectively promote the oxidative addition and the reductive elimination steps of the Suzuki–Miyaura catalytic cycle.

More recently, cyclic carbenes in which the carbene center is not flanked by two heteroatoms (N, S, O) have also attracted attention. Often referred to as abnormal (aNHCs) or mesoionic carbenes (MICs), such ligands typically display a stronger electron donating capacity, when compared to that of the classical NHCs. In this context, following the pioneering work of Albrecht [4] (who synthesized the first aNHC-transition metal complexes) and Bertrand [5] (who isolated the first free, non-conventional carbenes), 1,2,3-triazol-5-ylidenes (tzNHCs) have been studied extensively. Their precursors, namely 1,2,3-triazoles, are easily accessible through copper-catalyzed Huisgen [3 + 2] click-type cycloaddition of azides and alkynes (CuAAC) [6,7], followed by N3-quaternarization. The resulting 1,2,3-triazolium salts can then be converted to transition metal complexes that, *i.a.*, are suitable for Suzuki–Miyaura [8–18], Mizoroki-Heck [19,20], and Sonogashira coupling reactions [19,21], as well as for various reduction or oxidation reactions [22–27], and C-heteroatom bond forming reactions [28–32].

As an extension to our studies on the cavity-derived *N*-heterocyclic carbenes [33–38], here, we have described the synthesis of two sterically highly demanding triazolium salts (**1** and **2**, Figure 1) and their use as a ligand source in the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl chlorides with arylboronic acids. Very bulky NHCs are currently sought because of their ability to promote oxidative addition or reductive elimination in the Suzuki–Miyaura reactions [39–41]. Both salts have their triazole unit substituted by a bulky resorcinarenyl group attached to the N1 atom and a methyl group attached to the N3 atom. The ring carbon atom bonded to N3 in **1** is substituted by a phenyl group, that of **2** by a resorcinarene moiety.

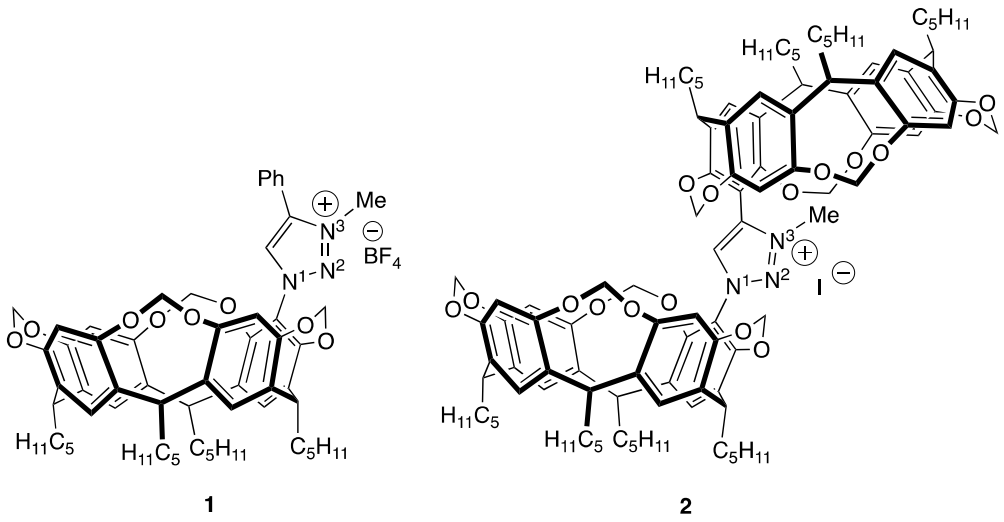


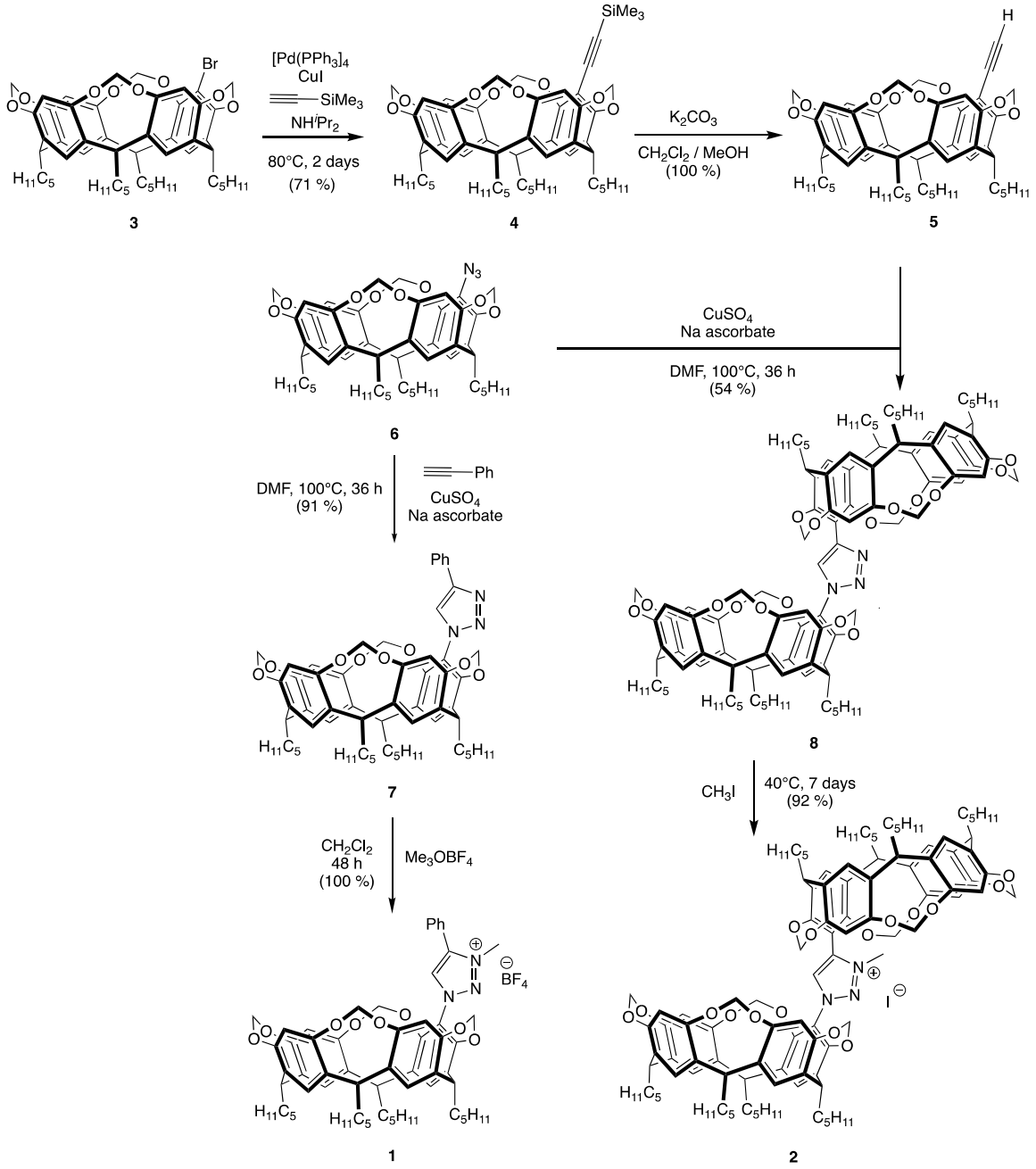
Figure 1. The resorcinarenyl-substituted triazolium salts used in this study.

2. Results

2.1. Synthesis of Triazolium Salts **1** *and* **2**

The resorcin[4]arene-derived triazolium salts **1** and **2** were synthesized, stepwise, according to the sequences shown in Scheme 1. The two key steps, namely those leading to intermediates **7** and **8**, each involved a copper-catalyzed alkyne-azide cycloaddition (CuAAC), between resorcinarene-azide **6** [38], and an alkyne (with phenyacetylene for the synthesis of triazole **7**; with ethynyl-resorcinarene **5** for the synthesis of **8**), in the presence of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate in DMF. Precursor **5** was obtained from bromo-resorcinarene **3** via a standard palladium-catalyzed Sonogashira cross-coupling with trimethylsilylacetylene. The final methylation steps were carried out with Me_3OBF_4 for **1** (quantitative yield), and with MeI for **2** (yield 92%).

The triazolium salts **1** and **2** were characterized by elemental analysis, ESI-TOF MS analysis, and ^1H and ^{13}C NMR spectroscopy (see experimental part). Consistent with a *Cs*-symmetrical compound, the ^1H NMR spectrum of salt **1** showed two AB patterns (intensity 4:4) for the four OCH_2O groups and two triplets (intensity 2:2) for the four methine atoms. That of **2** displayed four AB patterns for the eight -OCH_2O- bridges. The signals of the triazolium NCH and NCH_3 protons lay in the expected ranges (see experimental part).



Scheme 1. Synthesis of the resorcinarene-based triazolium salts **1** and **2**.

2.2. Crystal Structures of Triazole 8

Crystals of triazole **8** suitable for an X-ray diffraction study were obtained by slow diffusion of methanol into a dichloromethane solution of the product (Figure 2). Compound **8** crystallized in the monoclinic space group *C*2/*c*. The asymmetric unit contains two nearly identical molecules, A and B, but the B sites actually display a double occupancy (0.5:0.5) of the molecules of **8**, which are interchangeable through a plane perpendicular, which is perpendicular to the triazole ring and, which bisects the N–$C_{carbene}$–C angle. The two aromatic rings of the resorcinarenes connected to the triazole moiety are roughly perpendicular to the triazole plane (dihedral angles in A: 85.1° and 79.8°). This is in line with the observations made on conventional NHCs that have their N atoms substituted by bulky aryl groups [42]. Both cavitands of **8** adopt the typical bowl-shaped structures of resorcin[4]arene-derived cavitands equipped with -OCH_2O- linkers, with wide rim diameters [43–45] (i.e., the segments linking the C-2 aromatic carbon atoms of opposite resorcinols) of 7.80/8.07 Å and

7.89/8.01 Å in the two macrocycles of molecule A and of 7.91/8.00 Å (averaged), in the cavitands of molecule B. Interestingly, the lower rims of the two resorcinarene units of each molecule are facing each other, thereby creating a pseudo-capsular moiety.

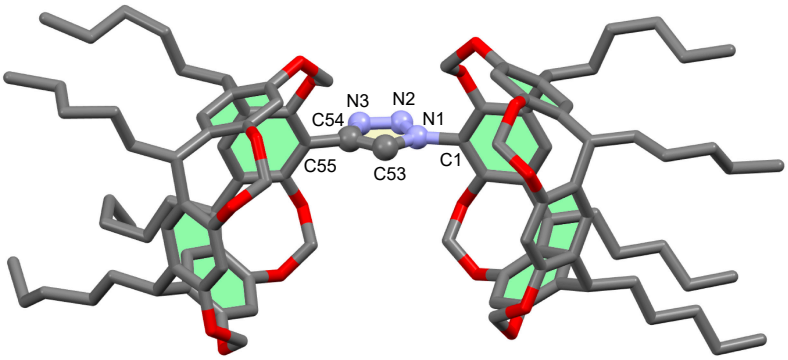
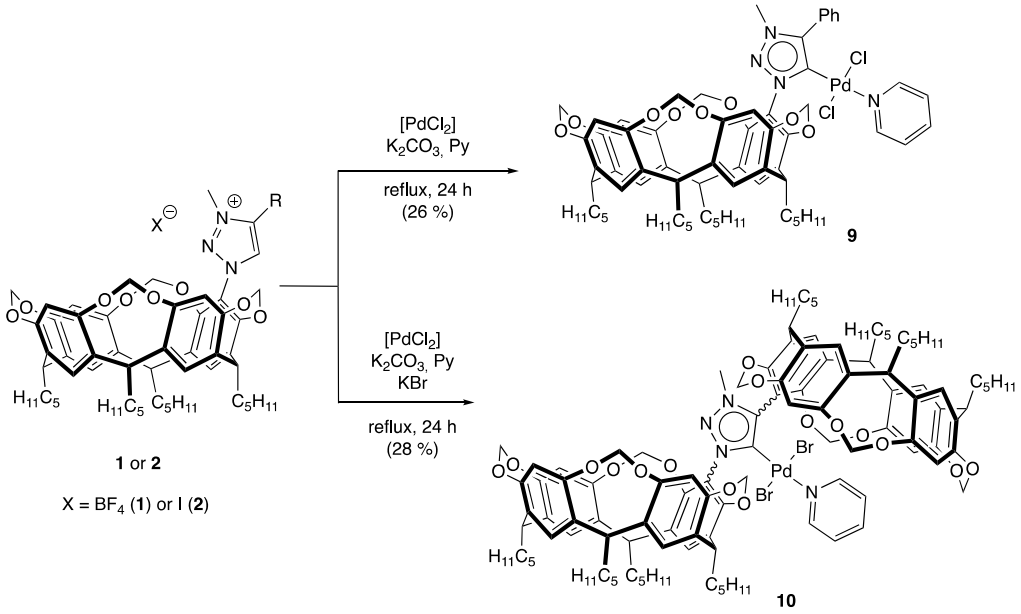


Figure 2. X-ray structure of triazole **8**. Only one of the two molecules present in the unit cell (molecule A) is shown. Selected bond lengths (Å): C1-N1 1.462(6); N1-N2 1.320(6); N2-N3 1.335(7); N3-C54 1.339(6); C54-C55 1.440(6); C53-C54 1.347(6); N1-C53 1.366(6).

2.3. *Synthesis of Palladium Complexes* **9** *and* **10**

The two triazolium salts were used as a ligand source for the synthesis of two pyridine-enhanced precatalyst preparation, stabilization and initiation (PEPPSI)-type complexes (**9** and **10**). Pd-PEPPSI complexes are currently considered to be very efficient catalysts for Suzuki–Miyaura coupling reactions [46]. These were obtained by the reactions of **1** or **2** with [$PdCl_2$] in refluxing pyridine, for 24 h in the presence of K_2CO_3 and a large excess of KBr in the case of salt **2** (Scheme 2). The observed yields (26% for **9** and 28% for **10**) were relatively low, but this was not unusual for reactions carried out with bulky NHC precursors [38,47]. Both complexes were characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. None of the mass spectra displayed the expected molecular peaks, but unambiguously revealed the formation of PdL species (L = carbene). Thus, the mass spectrum of complex **9** showed an intense peak at *m*/*z* = 1193.44, with the profile expected for the corresponding $[M - Cl]^+$ cation. Consistent with the proposed formula, the ^{1}H NMR of **9** showed two distinct AB systems for the methylenic OCH_2O atoms, two triplets for the four methine hydrogen atoms and a singlet at 4.05 ppm (3H), corresponding to the NCH_3 group. In the ^{13}C NMR spectrum, the carbenic C atom appeared as a singlet at 145.99 ppm. As could be inferred from the ^{1}H-^{1}H ROESY NMR spectrum, which revealed weak correlations between the pyridinic and pentyl H atoms, the C-Pd bond of **9** must, at least temporarily, be turned away from the cavity. This also means that during a catalytic process, the pentyl groups flanking the resorcinol moiety that bear the triazole unit, might interact with the metal first coordination sphere. Molecular models suggest that such a conformation which has an exo-oriented Pd atom is sterically favored over conformations that have the metal placed above the cavity entrance. However, there is no indication that endo-conformers exist in solution, unlike the observations recently made with the related complexes, based on the classical NHCs [33].

The mass spectrum of **10** showed a strong peak at 1937.79, corresponding to the [M − Br − pyridine + acetonitrile]$^+$ ions, which possibly formed in the spectrometer in the presence of adventitious acetonitrile. The ^{1}H NMR spectrum of **10** displayed four NCH_3 singlets, at 3.85, 3.78, 3.73 and 3.66 ppm (relative intensities: 26/57/11/6), thus revealing the presence of four distinct conformers (Figure 3). This observation suggests the existence of high rotational barriers about the N-C_{resorc} and $C_{triazole}$-C_{resorc} bonds. The reason why several stable conformers could be seen here (and not in the case of **9**), possibly arises from the difficulty of the "$PdBr_2$(pyridine)" moiety of **10** to adapt its orientation to the steric requirements imposed during the rotations of the resorcinarene moieties, respectively about the N-C_{resorc} and $C_{triazole}$-C_{resorc} bonds.



Scheme 2. Synthesis of the PEPPSI-type palladium complexes **9** and **10**.

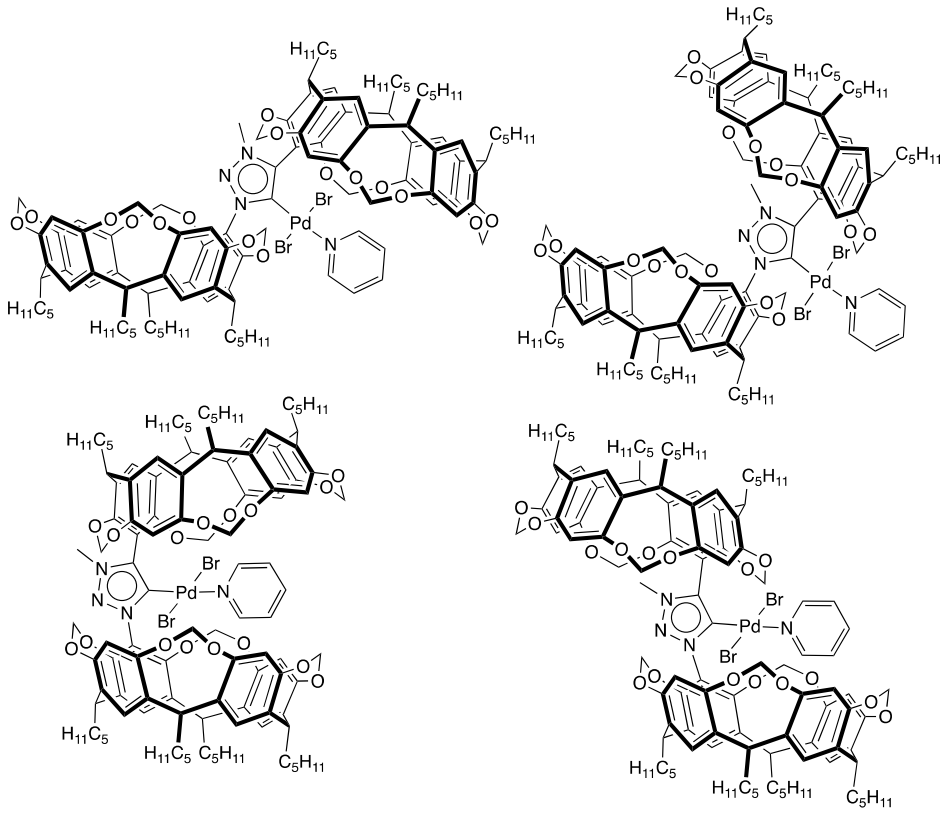
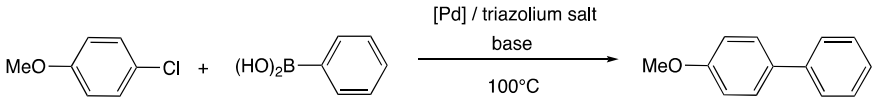


Figure 3. Rotational conformers of complex **10**.

2.4. Catalytic Suzuki–Miyaura Cross-Coupling Reactions with Triazolium Salts **1** *and* **2**

Triazolium salts **1** and **2** were first assessed in cross-coupling between the phenyl boronic acid and 4-chloroanisole (Scheme 3). To determine the best catalyst, reactions were carried out by using a palladium loading of 0.5 mol%. The conversions were determined after 2 h at 100 °C. In a first series of runs carried out in DMF using [$Pd(OAc)_2$], we determined the optimal base from Cs_2CO_3, K_2CO_3, NaH, K_3PO_4, and ^{t}BuOK. As can be deduced from Table 1, the most efficient base was ^{t}BuOK, which led to conversions of 30% and 25%, respectively, with **1** and **2** (Table 1, entries 9 and 11). In a second

series of tests, we investigated the influence on the reactivity of the palladium precursor. To this end, $[PdCl(\eta^3\text{-}C_3H_5)]_2$, $[PdCl_2(PhCN)_2]$, $[PdCl_2(cod)]$, and $[Pd_2(dba)_3]$ were considered for comparison with $[Pd(OAc)_2]$. The highest conversions were obtained with $[Pd(OAc)_2]$ and $[PdCl_2(PhCN)_2]$ in combination with the salts **1** (30%) and **2** (29%), respectively (Table 1, entries 9 and 15). Repeating the runs in 1,4-dioxane instead of DMF, increased the conversions up to 47% and 43%, respectively (Table 1, entries 10 and 16). Note that, when the cross-coupling of 4-chloroanisole (under optimized conditions) was achieved with complex **9**, the conversions were nearly the same as those obtained with the corresponding in-situ generated catalysts (Table 1, entries 10 and 22). Finally, we also verified that in the absence of triazolium salts, the production of coupling products dropped drastically (Table 1, entries 23 and 24).



Scheme 3. Suzuki–Miyaura cross-coupling of 4-chloroanisole with phenylboronic acid.

Table 1. Suzuki–Miyaura cross-coupling reaction of 4-chloroanisole with phenylboronic acid—a search for optimal catalytic conditions.

Entry	Triazolium Salt	[Pd]	Base	Solvent	Conversion (%)
1	**1**	$[Pd(OAc)_2]$	Cs_2CO_3	DMF	3
2	**2**				8
3	**1**	$[Pd(OAc)_2]$	K_2CO_3	DMF	traces
4	**2**				traces
5	**1**	$[Pd(OAc)_2]$	NaH	DMF	1
6	**2**				18
7	**1**	$[Pd(OAc)_2]$	K_3PO_4	DMF	traces
8	**2**				traces
9	**1**	$[Pd(OAc)_2]$	^{t}BuOK	DMF	30
10	**1**			dioxane	47
11	**2**			DMF	25
12	**1**	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	^{t}BuOK	DMF	traces
13	**2**				19
14	**1**	$[PdCl_2(PhCN)_2]$	^{t}BuOK	DMF	28
15	**2**			DMF	29
16	**2**			dioxane	43
17	**1**	$[PdCl_2(cod)]$	^{t}BuOK	DMF	31
18	**1**			dioxane	36
19	**2**			DMF	23
20	**1**	$[Pd_2(dba)_3]$	^{t}BuOK	DMF	9
21	**2**				17
22	/	Complex **9**	^{t}BuOK	dioxane	46
23	/	$[Pd(OAc)_2]$	^{t}BuOK	dioxane	8
24	/	$[PdCl_2(PhCN)_2]$	^{t}BuOK	dioxane	6

Reagents and conditions: [Pd] (0.5 mol %), triazolium salt (0.5 mol %), 4-$MeOC_6H_4Cl$ (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), base (0.75 mmol), decane (0.025 mL), solvent (2.00 mL), 100°C, 2 h. The conversions were determined by GC, the calibrations being based on decane.

The above optimized conditions (^{t}BuOK/$[Pd(OAc)_2]$/salt **1**; ^{t}BuOK/$[PdCl_2(PhCN)_2]$/salt **2**; dioxane at 100 °C) were then applied to the coupling reactions between four aryl chlorides, namely 4-chloroanisole, 4-chlorotoluene, 2-chlorotoluene, and 9-chloroanthracene, and four boronic acids—phenylboronic acid, 2-methylphenylboronic acid, 2-methoxyphenylboronic acid, and

naphthalene-1-boronic acid (Table 2). High conversions (80%–100%) were observed after 5 h with both triazolium salts in the reactions involving 4-chloroanisole or 4-chlorotoluene, with any arylboronic acid. Unsurprisingly, the sterically more encumbered 2-chlorotoluene and 9-chloroanthracene substrates resulted in activities that were five-times lower (Table 2, entries 9–12).

Table 2. Suzuki–Miyaura cross-coupling of aryl chlorides using triazolium salts **1** or **2**.

Entry	ArCl	Triazolium Salt - Conditions		$B(OH)_2$	$B(OH)_2$	MeO $B(OH)_2$	$B(OH)_2$
1	MeO–Cl	**1** - A (5 h)	conv. (%)	100	98	100	98
2		**2** - B (5 h)	conv. (%)	96	81	80	78
3		**11** - A (5 h)	conv. (%)		31	41	
4		**11** - B (5 h)	conv. (%)		18	19	
5	Cl	**1** - A (5 h)	conv. (%)	95	77	80	99
6		**2** - B (5 h)	conv. (%)	100	85	83	100
7		**11** - A (5 h)	conv. (%)		15	16	
8		**11** - B (5 h)	conv. (%)		5	6	
9	Cl	**1** - A (24 h)	conv. (%)	100	100	63	97
10		**2** - B (24 h)	conv. (%)	83	65	52	76
11	Cl	**1** - A (24 h)	conv. (%)	100	99	95	100
12		**2** - B (24 h)	conv. (%)	98	99	83	99

Reagents and conditions—conditions A [$Pd(OAc)_2$] (0.5 mol %), triazolium salt (0.5 mol %) ArCl (0.5 mmol), Ar′$B(OH)_2$ (0.75 mmol), ^{t}BuOK (0.75 mmol), decane (0.025 mL), dioxane (2.00 mL), 100 °C; conditions B [$PdCl_2(PhCN)_2$] (0.5 mol %), triazolium salt (0.5 mol %), ArCl (0.5 mmol), Ar′$B(OH)_2$ (0.75 mmol), ^{t}BuOK (0.75 mmol), decane (0.025 mL), dioxane (2.00 mL), 100 °C; reaction time—5 h (for entries 1–8); 24 h (for entries 9–12). The conversions were determined by GC, the calibrations being based on decane.

To highlight the influence of the resorcinarenyl substituent on the catalytic outcome, we prepared the triazolium salt **11** devoid of the macrocyclic moiety (Figure 4). The activity of the corresponding catalytic system turned out to be lower than that observed for **1** or **2** (Table 2, entries 3, 4, 7 and 8). On the basis of the latter results, as well as recent studies on the use of Suzuki–Miyaura couplings of conventional NHCs substituted by a resorcinarenyl moiety [33,35,36], we assigned the high efficiency of triazolium salt **1** in the above reactions, to the presence of two flexible pentyl chains that are able to sterically interact with the metal center (vide supra) in those complexes where the palladium displayed an exo orientation with respect to the cavity (Figure 5), which then facilitated the reductive elimination step. The observation that salt **2** led to lower conversions than salt **1** was merely due to the high steric encumbrance created about the palladium in the complexes formed from the bulky **2**, which impeded the approach of the substrates.

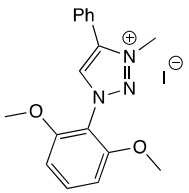


Figure 4. Cavity-free **11** used to rank the triazolium salts **1** and **2**.

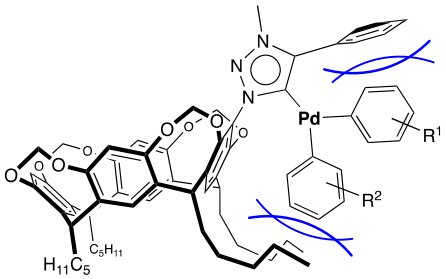


Figure 5. Catalysis with derivatives of **1**. Possible steric interactions during the catalytic cycle between the pentyl groups and the metal center.

3. Materials and Methods

3.1. Experimental Section

All manipulations involving sensitive derivatives were carried out in Schlenk-type flasks under dry argon. Solvents were dried by conventional methods and were distilled immediately before use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen, over molecular sieves (4 Å). Routine ^1H and $^{13}C\{^1H\}$ spectra were recorded with Bruker FT instruments (AC 300, 400, and 500). ^1H NMR spectra were referenced to the residual protiated solvents (δ = 7.26 ppm for $CDCl_3$). ^{13}C NMR chemical shifts were reported, relative to the deuterated solvents (δ = 77.16 ppm for $CDCl_3$). Chemical shifts and coupling constants were reported in ppm and Hz, respectively. Infrared spectra were recorded with a Bruker FTIR Alpha-P spectrometer. Elemental analyses were carried out by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. The catalytic solutions were analyzed with a Varian 3900 gas chromatograph, fitted with a WCOT-fused silica column (25 m × 0.25 mm, 0.25 μm film thickness). 5-bromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**3**) [48], 5-azido-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**6**) [38], tosyl azide [49], and 2-azido-1,3-dimethoxybenzene [50] were prepared as per the standard procedures found in the literature.

*3.2. Synthesis of 5-(Trimethylsilyl)ethynyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra pentylresorcin[4]arene (**4**)*

To a solution of bromo-cavitand **3** (2.000 g, 2.23 mmol), $[Pd(PPh_3)_4]$ (0.265 g, 0.23 mmol) and CuI (0.023 g, 0.12 mmol) in NH^iPr_2 (100 mL) was added to trimethylsilylacetylene (3.1 mL, 22.30 mmol). The mixture turned rapidly from yellow to black. The resulting suspension was stirred for 48 h at 80 °C, then cooled to room temperature. The solution was evaporated to dryness and the resulting residue was dissolved in CH_2Cl_2 (200 mL). The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure, and the crude product was purified by column chromatography (Et_2O/petroleum ether, 10:90; *Rf* = 0.36) to give **4** (1.453 g, 71%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 4H, arom. CH, resorcinarene), 6.50 (s, 3H, arom. CH, resorcinarene), 5.81 and 4.46 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.74 and 4.44 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 4.76 (t, 2H, $CHCH_2$, ^3J = 8.2 Hz), 4.72 (t, 2H, $CHCH_2$, ^3J = 8.2 Hz), 2.25–2.16 (m, 8H, $CHCH_2$), 1.45–1.31 (m, 24H $CH_2CH_2CH_2CH_3$), 0.91 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz), 0.19 (s, 9H, $Si(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.86–96.93 (arom. Cs), 112.74 (s, $C{\equiv}CSiMe_3$), 103.58 (s, $C{\equiv}CSiMe_3$), 99.63 (s, OCH_2O), 98.89 (s, OCH_2O), 36.51 (s, $CHCH_2$), 36.50 (s, $CHCH_2$), 32.17 (s, $CH_2CH_2CH_3$), 32.06 (s, $CH_2CH_2CH_3$), 29.98 (s, $CHCH_2$), 29.74 (s, $CHCH_2$), 27.70 (s, $CHCH_2CH_2$), 27.63 (s, $CHCH_2CH_2$), 22.84 (s, CH_2CH_3), 14.24 (s, CH_2CH_3), 0.05 (s, $Si(CH_3)_3$) ppm. Elemental analysis calcd. (%) for $C_{57}H_{72}O_8Si$ (913.26): C 74.96, H 7.95; found C 75.25, H 8.18.

*3.3. Synthesis of 5-Ethynyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4] arene (***5***)*

A solution of **4** (1.000 g, 2.90 mmol) and K_2CO_3 (1.508 g, 10.91 mmol) in CH_2Cl_2/MeOH (50 mL; 25:75 *v*/*v*) was stirred at room temperature for 16 h. The reaction mixture was evaporated to dryness and the residue was treated with a mixture of CH_2Cl_2/H_2O (500 mL; 1:1 *v*/*v*). The aqueous layer was washed with CH_2Cl_2 (2 × 100 mL), then the combined organic layers were dried with $MgSO_4$. After filtration, the solvent was evaporated off, under reduced pressure, to afford **5** as a white solid (0.918 g, yield 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11 (s, 1H, arom. CH, resorcinarene), 7.09 (s, 3H, arom. CH, resorcinarene), 6.51 (s, 2H, arom. CH, resorcinarene), 6.50 (s, 1H, arom. CH, resorcinarene), 5.84 and 4.46 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.75 and 4.44 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 4.76 (t, 2H, C*H*CH_2, ^3J = 8.0 Hz), 4.72 (t, 4H, C*H*CH_2, ^3J = 8.0 Hz), 3.30 (s, 1H, C≡CH), 2.25–2.17 (m, 8H, CHC*H*$_2$), 1.45–1.31 (m, 24H, *CH*$_2$*CH*$_2$*CH*$_2$$CH_3$), 0.91 (t, 12 H, CH_2CH_3, ^3J = 7.0 Hz) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 156.18–111.71 (arom. Cs), 99.62 (s, OCH_2O), 99.11 (s, OCH_2O), 85.27 (s, *C*≡CH), 75.81 (s, C≡*C*H), 36.53 (s, *C*HCH$_2$), 36.48 (s, *C*HCH$_2$), 32.16 (s, *C*H$_2$CH$_2$CH$_3$), 32.10 (s, *C*H$_2$CH$_2$CH$_3$), 29.95 (s, CH*C*H$_2$), 29.78 (s, CH*C*H$_2$), 27.70 (s, CHCH$_2$*C*H$_2$), 27.64 (s, CHCH$_2$*C*H$_2$), 22.84 (s, *C*H$_2$CH$_3$), 14.26 (s, CH$_2$*C*H$_3$) ppm. Elemental analysis calcd. (%) for $C_{54}H_{64}O_8$ (841.08): C 77.11, H 7.67; found C 77.26, H 7.89.

*3.4. Synthesis of 1-{4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl-4-phenyl-1H-1,2,3-triazole (***7***)*

Phenylacetylene (0.06 mL, 0.58 mmol) was added to a solution of azido-cavitand **6** (0.500 g, 0.58 mmol), $CuSO_4{\cdot}5H_2O$ (0.014 g, 0.06 mmol), and sodium ascorbate (0.012 g, 0.06 mmol) in DMF (50 mL). The mixture was stirred for 36 h at 100 °C, then cooled to room temperature. The solution was evaporated to dryness and the resulting residue was dissolved in CH_2Cl_2 (200 mL). The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer were dried over $MgSO_4$, filtered, and evaporated, under reduced pressure, and the crude product was purified by column chromatography (Et_2O/petroleum ether, 20:80; *R*f = 0.39) to give **7** (0.510 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (s, 1H, CH, triazole), 7.87 (d, 2H, arom. CH, Ph, ^3J = 7.5 Hz), 7.46 (t, 2H, arom. CH, Ph, ^3J = 7.5 Hz), 7.37 (t, 1H, arom. CH, Ph, ^3J = 7.5 Hz), 7.34 (s, 1H, arom. CH, resorcinarene), 7.12 (s, 2H, arom. CH, resorcinarene), 7.12 (s, 1H, arom. CH, resorcinarene), 6.59 (s, 1H, arom. CH, resorcinarene), 6.47 (s, 2H, arom. CH, resorcinarene), 5.74 and 4.60 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.42 and 4.36 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 4.79 (t, 2H, C*H*CH_2, ^3J = 8.2 Hz), 4.74 (t, 2H, C*H*CH_2, ^3J = 8.0 Hz), 2.31–2.21 (m, 8H, CHC*H*$_2$), 1.48–1.33 (m, 24H *CH*$_2$*CH*$_2$*CH*$_2$$CH_3$), 0.94 (t, 6H, CH_2CH_3, ^3J = 7.5 Hz), 0.92 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 155.33–116.79 (arom. Cs), 122.90 (s, CH, triazole), 99.83 (s, OCH_2O), 99.52 (s, OCH_2O), 36.79 (s, *C*HCH$_2$), 36.51 (s, *C*HCH$_2$), 32.17 (s, *C*H$_2$CH$_2$CH$_3$), 32.11 (s, *C*H$_2$CH$_2$CH$_3$), 30.08 (s, CHCH$_2$), 29.80 (s, CHCH$_2$), 27.71 (s, CHCH$_2$CH$_2$), 22.83 (s, *C*H$_2$CH$_3$), 14.23 (s, CH$_2$*C*H$_3$) ppm. MS (ESI-TOF): *m*/*z* = 960.52 $[M + H]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{60}H_{69}N_3O_8$ (960.21): C 75.05, H 7.24, N 4.38; found C 74.86, H 7.02, N 4.23.

*3.5. Synthesis of 1,4-bis{4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl}-1H-1,2,3-triazole (***8***)*

A solution of ethynyl-cavitand **5** (0.490 g, 0.58 mmol), azido-cavitand **6** (0.500 g, 0.58 mmol), $CuSO_4{\cdot}5H_2O$ (0.014 g, 0.06 mmol), and sodium ascorbate (0.012 g, 0.06 mmol) in DMF (50 mL) was stirred for 36 h at 100 °C. Afterwards, the mixture was cooled to room temperature and evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2 (200 mL). The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer were dried over $MgSO_4$, filtered, and evaporated under reduced pressure, and the crude product was purified by column chromatography (Et_2O/petroleum ether, 20:80; *R*f = 0.28) to give **8** (0.535 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (s, 1H, CH, triazole), 7.34 (s, 1H, arom. CH,

resorcinarene), 7.23 (s, 1H, arom. CH, resorcinarene), 7.12 (s, 2H, arom. CH, resorcinarene), 7.12 (s, 3H, arom. CH, resorcinarene), 7.11 (s, 1H, arom. CH, resorcinarene), 6.58 (s, 1H, arom. CH, resorcinarene), 6.54 (s, 1H, arom. CH, resorcinarene), 6.48 (s, 2H, arom. CH, resorcinarene), 6.46 (s, 2H, arom. CH, resorcinarene), 5.74 and 4.56 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.73 and 4.51 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.57 and 4.41 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.32 and 4.29 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 4.83 (t, 2H, C*H*CH_2, ^3J = 8.0 Hz), 4.77 (t, 2H, C*H*CH_2, ^3J = 8.0 Hz), 4.74 (t, 2H, C*H*CH_2, ^3J = 7.5 Hz), 4.72 (t, 2H, C*H*CH_2, ^3J = 7.5 Hz), 2.30–2.21 (m, 16H, CHCH_2), 1.48–1.33 (m, 48H $CH_2CH_2CH_2CH_3$), 0.94 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.93 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.92 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.33–116.74 (arom. Cs), 127.33 (s, CH, triazole), 99.77 (s, OCH_2O), 99.65 (s, OCH_2O), 99.58 (s, OCH_2O), 99.52 (s, OCH_2O), 36.79 (s, *C*HCH_2), 36.51 (s, *C*HCH_2), 32.19 (s, $CH_2CH_2CH_3$), 32.14 (s, $CH_2CH_2CH_3$), 30.08 (s, $CHCH_2$), 29.96 (s, $CHCH_2$), 29.81 (s, $CHCH_2$), 27.78 (s, $CHCH_2CH_2$), 27.72 (s, $CHCH_2CH_2$), 22.85 (s, CH_2CH_3), 14.27 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m*/*z* = 1698.93 $[M + H]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{106}H_{127}N_3O_{16}$ (1697.16): C 74.93, H 7.53, N 2.47; found C 74.68, H 7.47, N 2.39.

*3.6. Synthesis of 1-{4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl}-3-methyl-4-phenyl-1H-1,2,3-triazolium tetrafluoroborate (**1**)*

Triazole-cavitand **7** (0.500 g, 0.52 mmol) and Me_3OBF_4 (0.115 g, 0.78 mmol) were dissolved in CH_2Cl_2 (20 mL) and the resulting solution was stirred for 2 days at room temperature. The organic solution was washed with brine (3 × 100 mL) and the aqueous layers were extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was dissolved in the minimum amount of CH_2Cl_2 and salt **1** was precipitated by addition of hexane (200 mL), the solid was filtered and dried under vacuum (0.550 g, 100%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.21 (s, 1H, CH, triazolium), 7.70 (d, 2H, arom. CH, phenyl, ^3J = 7.0 Hz) 7.66–7.59 (m, 3H, arom. CH, phenyl), 7.43 (s, 1H, arom. CH, resorcinarene), 7.12 (s, 1H, arom. CH, resorcinarene), 7.12 (s, 2H, arom. CH, resorcinarene), 6.59 (s, 2H, arom. CH, resorcinarene), 6.54 (s, 1H, arom. CH, resorcinarene), 5.73 and 4.59 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.66 and 4.60 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 4.79 (t, 2H, C*H*CH_2, ^3J = 8.2 Hz), 4.75 (t, 2H, C*H*CH_2, ^3J = 8.2 Hz), 4.35 (s, 3H, triazolium-CH_3), 2.30–2.18 (m, 8H, CHCH_2), 1.60–1.33 (m, 24H $CH_2CH_2CH_2CH_3$), 0.93 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.92 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.77–117.32 (arom. Cs), 129.60 (s, CH, triazolium), 101.04 (s, OCH_2O), 99.60 (s, OCH_2O), 39.17 (s, triazolium-CH_3), 36.77 (s, *C*HCH_2), 36.49 (s, *C*HCH_2), 32.18 (s, $CH_2CH_2CH_3$), 32.07 (s, $CH_2CH_2CH_3$), 30.11 (s, $CHCH_2$), 29.77 (s, $CHCH_2$), 27.69 (s, $CHCH_2CH_2$), 22.84 (s, CH_2CH_3), 14.26 (s, CH_2CH_3), 14.25 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m*/*z* = 974.53 $[M - BF_4]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{61}H_{72}N_3O_8BF_4$ (1062.05): C 68.98, H 6.83, N 3.96; found C 69.16, H 6.72, N 3.82.

*3.7. Synthesis of 1,4-bis{4(24),6(10),12(16),18(22)-Tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl}-3-methyl-1H-1,2,3-triazolium iodide (**2**)*

A mixture of triazole-bis-cavitand **8** (0.100 g, 0.06 mmol) and MeI (2.00 mL, 32.13 mmol) was heated at 40 °C for 7 days. After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was washed with hexane (20 mL), the solid was filtered and dried under vacuum (0.099 g, 92%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.47 (s br, 1H, CH, triazolium), 7.64 (s, 2H, arom. CH, resorcinarene), 7.11 (s, 4H, arom. CH, resorcinarene), 7.09 (s, 1H, arom. CH, resorcinarene), 7.08 (s, 1H, arom. CH, resorcinarene), 6.58 (s, 2H, arom. CH, resorcinarene), 6.57 (s, 2H, arom. CH, resorcinarene), 6.54 (s, 1H, arom. CH, resorcinarene), 6.52 (s, 1H, arom. CH, resorcinarene), 5.66 and 4.65 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.64 and 4.70 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.47 and 4.72 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.31 and 5.05 (AB spin system, 4H, OCH_2O, ^2J = 6.5 Hz), 4.75–4.70 (m, 8H, C*H*CH_2), 4.20 (s, 3H, triazolium-CH_3), 2.36–2.19 (m, 16H, CHCH_2), 1.47–1.32

(m, 48H $CH_2CH_2CH_2CH_3$), 0.93 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz), 0.91 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.64–109.45 (arom. Cs), 117.36 (s, CH, triazolium), 99.56 (s, OCH_2O), 99.27 (s, OCH_2O), 99.15 (s, OCH_2O), 98.91 (s, OCH_2O), 39.23 (s, triazolium-CH_3), 36.68 (s, $CHCH_2$), 36.64 (s, $CHCH_2$), 36.45 (s, $CHCH_2$), 32.15 (s, $CH_2CH_2CH_3$), 32.02 (s, $CH_2CH_2CH_3$), 30.16 (s, $CHCH_2$), 30.11 (s, $CHCH_2$), 29.92 (s, $CHCH_2$), 29.80 (s, $CHCH_2$), 27.68 (s, $CHCH_2CH_2$), 27.63 (s, $CHCH_2CH_2$), 22.78 (s, CH_2CH_3), 22.76 (s, CH_2CH_3), 14.20 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m*/*z* = 1712.95 $[M - I]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{107}H_{130}N_3O_{16}I$ (1839.10): C 69.80, H 7.12, N 2.28; found C 69.93, H 7.10, N 2.06.

*3.8. Synthesis of Trans-dichloro-{1-[4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl resorcin[4]arene-5-yl]-3-methyl-4-phenyl-1H-1,2,3-triazol-5-yliden}pyridine palladium(II) (**9**)*

A mixture of K_2CO_3 (0.155 g, 1.12 mmol), pyridine (5 mL), $[PdCl_2]$ (0.040 g, 0.23 mmol) and triazolium salt **1** (0.200 g, 0.19 mmol) was heated at 80 °C for 24 h. The reaction mixture was filtered through Celite, the filtrate was evaporated under vacuum, and the solid residue was purified by column chromatography (AcOEt/CH_2Cl_2, 10:90; *R*f = 0.54) to afford complex **9** (0.060 g, 26%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.74 (dd, 2H, arom. CH, pyridine, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 8.11 (dd, 2H, arom. CH, phenyl, ^3J = 8.5 Hz, ^4J = 1.5 Hz), 7.65–7.54 (m, 4H, arom. CH, pyridine and phenyl), 7.43 (s, 1H, arom. CH, resorcinarene), 7.20–7.19 (m, 2H, arom. CH, pyridine), 7.17 (s, 2H, arom. CH, resorcinarene), 7.15 (s, 1H, arom. CH, resorcinarene), 6.55 (s, 1H, arom. CH, resorcinarene), 6.48 (s, 2H, arom. CH, resorcinarene), 5.76 and 4.52 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.69 and 4.42 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 4.94 (t, 2H, $CHCH_2$, ^3J = 8.0 Hz), 4.75 (t, 2H, $CHCH_2$, ^3J = 8.2 Hz), 4.05 (s, 3H, triazolyliden-CH_3), 2.38–2.21 (m, 8H, $CHCH_2$), 1.46–1.34 (m, 24H $CH_2CH_2CH_2CH_3$), 0.93 (t, 6H, CH_2CH_3, ^3J = 7.2 Hz), 0.92 (t, 6H, CH_2CH_3, ^3J = 7.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.13–116.61 (arom. Cs), 145.99 (s, C_q-Pd), 99.81 (s, OCH_2O), 99.55 (s, OCH_2O), 37.76 (s, triazolyliden-CH_3), 36.78 (s, $CHCH_2$), 36.54 (s, $CHCH_2$), 32.19 (s, $CH_2CH_2CH_3$), 32.09 (s, $CH_2CH_2CH_3$), 30.06 (s, $CHCH_2$), 29.81 (s, $CHCH_2$), 27.74 (s, $CHCH_2CH_2$), 27.58 (s, $CHCH_2CH_2$), 22.86 (s, CH_2CH_3), 14.26 (s, CH_2CH_3) ppm. MS (ESI-TOF): *m*/*z* = 1193.44 $[M - Cl]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{66}H_{76}N_4O_8PdCl_2$ (1230.65): C 64.41, H 6.22, N 4.55; found C 64.18, H 6.03, N 4.42.

*3.9. Synthesis of Trans-dibromo-{1,4-bis[4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl resorcin[4]arene-5-yl]-3-methyl-1H-1,2,3-triazol-5-yliden}pyridine palladium(II) (**10**)*

A mixture of K_2CO_3 (0.081 g, 0.59 mmol), pyridine (5 mL), $[PdCl_2]$ (0.021 g, 0.12 mmol), KBr (0.233 g, 1.96 mmol), and triazolium salt **2** (0.180 g, 0.10 mmol) was heated at 80 °C for 24 h. The reaction mixture was filtered through Celite, the filtrate was evaporated under vacuum, and the solid residue was purified by column chromatography (pure CH_2Cl_2; *R*f = 0.62) to afford complex **10** (0.056 g, 28%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.93–8.87 (m, 0.6H, arom. CH, pyridine), 8.65–8.59 (m, 2H, arom. CH, pyridine), 7.79–7.65 (m, 1.4H, arom. CH, pyridine), 7.38–7.31 (m, 2H, arom. CH, pyridine and resorcinarene), 7.19–7.14 (m, 7H, arom. CH, resorcinarene), 4.54–6.33 (m, 6H, arom. CH, resorcinarene), 5.95 and 5.82 (AB spin system, 4H, OCH_2O, ^2J = 9.0 Hz), 5.77–5.62 and 4.50–4.24 (AB spin systems, 12H, OCH_2O), 4.92–4.68 (m, 8H, $CHCH_2$), 3.85–3.66 (m, 3H, triazolyliden-CH_3), 2.37–2.21 (m, 16H, $CHCH_2$), 1.50–1.31 (m, 48H $CH_2CH_2CH_2CH_3$), 0.96–0.86 (m, 24H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.32–115.41 (arom. Cs), 150.03 (s, C_q-Pd), 149.96 (s, C_q-Pd), 100.61 (s, OCH_2O), 100.12 (s, OCH_2O), 99.83 (s, OCH_2O), 99.68 (s, OCH_2O), 99.56(s, OCH_2O), 99.36 (s, OCH_2O), 99.26 (s, OCH_2O), 38.13 (s, triazolyliden-CH_3), 37.82 (s, triazolyliden-CH_3), 37.62 (s, triazolyliden-CH_3), 36.74 (s, $CHCH_2$), 36.52 (s, $CHCH_2$), 32.22 (s, $CH_2CH_2CH_3$), 32.19 (s, $CH_2CH_2CH_3$), 32.14 (s, $CH_2CH_2CH_3$), (s, $CH_2CH_2CH_3$), 32.10 (s, $CH_2CH_2CH_3$), 31.99 (s, $CH_2CH_2CH_3$), 30.19 (s, $CHCH_2$), 30.10 (s, $CHCH_2$), 30.03 (s, $CHCH_2$), 29.97 (s, $CHCH_2$), 29.85 (s, $CHCH_2$), 29.82 (s, $CHCH_2$), 29.76 (s, $CHCH_2$), 27.83 (s, $CHCH_2CH_2$), 27.76 (s, $CHCH_2CH_2$), 27.72 (s, $CHCH_2CH_2$), 27.60 (s, $CHCH_2CH_2$), 22.86 (s, CH_2CH_3), 22.83 (s, CH_2CH_3), 22.72 (s, CH_2CH_3), 14.28 (s, CH_2CH_3), 14.24 (s, CH_2CH_3) ppm. MS (ESI-TOF):

m/*z* = 1937.79 $[M - Br - Py + NCCH_3]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{112}H_{134}N_4O_{16}PdBr_2$ (2058.51): C 65.35, H 6.56, N 2.72; found C 65.24, H 6.45, N 2.67.

*3.10. Synthesis of 1-(2,6-Dimethoxyphenyl)-3-methyl-4-phenyl-1H-1,2,3-triazolium iodide (**11**)*

3.10.1. Step 1: Synthesis of 1-(2,6-Dimethoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole

To a solution of 2-azido-1,3-dimethoxybenzene (0.480 g, 2.68 mmol), $CuSO_4{\cdot}5H_2O$ (0.067 g, 0.27 mmol), and sodium ascorbate (0.053 g, 0.27 mmol) in DMF (10 mL) phenylacetylene was added (0.29 mL, 2.68 mmol). The mixture was stirred for 36 h at 100 °C, then cooled to room temperature. The solution was evaporated to dryness and the resulting residue was dissolved in AcOEt (100 mL). The organic solution was washed with brine (3 × 50 mL) and the aqueous layers were extracted with AcOEt (2 × 50 mL). The combined organic layer were dried over $MgSO_4$, filtered, and evaporated under reduced pressure, and the crude product was purified by column chromatography (CH_2Cl_2/MeOH, 95:5; *R*f = 0.60) to give 1-(2,6-dimethoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (0.621 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (dd, 2H, arom. CH, Ph, ^3J = 8.4 Hz, ^4J = 1.5 Hz), 7.86 (s, 1H, CH, triazole), 7.46–7.39 (m, 3H, arom. CH, Ph and dimethoxybenzene), 7.33 (tt, 1H, arom.CH, Ph, ^3J = 7.4 Hz, ^4J = 1.4 Hz), 6.69 (d, 2H, arom. CH, dimethoxybenzene, ^3J = 8.7 Hz), 3.78 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 156.08 (s, arom. Cq, CO), 146.92 (s, Cq, triazole), 131.52 (s, arom. CH, dimethoxybenzene), 131.00 (s, arom. Cq, Ph), 128.88 (s, arom. CH, Ph), 128.02 (s, arom. CH, Ph), 125.90 (s, arom. CH, Ph), 123.24 (s, CH, triazole), 115.44 (s, arom. Cq, dimethoxybenzene), 104.41 (s, arom. CH, dimethoxybenzene), 56.33 (s, OCH_3) ppm. Elemental analysis calcd. (%) for $C_{16}H_{15}N_3O_2$ (281.31): C 68.31, H 5.37, N 14.94; found C 68.15, H 5.34, N 14.83.

3.10.2. Step 2: Synthesis of 1-(2,6-Dimethoxyphenyl)-3-methyl-4-phenyl-1*H*-1,2,3-triazolium iodide (**11**)

A mixture of 1-(2,6-dimethoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (0.200 g, 0.71 mmol) and MeI (1.00 mL, 16.06 mmol) was heated at 40 °C for 7 days. After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was washed with hexane (20 mL), the solid was filtered and dried under vacuum (0.282 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.84 (s, 1H, CH, triazolium), 7.95–7.91 (m, 2H, arom. CH, Ph), 7.64–7.62 (m, 3H, arom. CH, Ph), 7.56 (t, 1H, arom. CH, dimethoxybenzene, ^3J = 8.7 Hz), 6.75 (d, 2H, arom. CH, dimethoxybenzene, ^3J = 8.7 Hz), 4.57 (s, 3H, triazolium-CH_3), 3.89 (s, 6H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.20 (s, arom. Cq, CO), 143.35 (s, Cq, triazole), 134.37 (s, arom. CH, Ph), 132.25 (s, arom. CH, dimethoxybenzene), 131.41 (s, CH, triazolium), 130.10 (s, arom. CH, Ph), 130.03 (s, arom. CH, Ph), 121.34 (s, arom. Cq, Ph), 112.33 (s, arom. Cq, dimethoxybenzene), 104.69 (s, arom. CH, dimethoxybenzene), 56.96 (s, OCH_3), 40.64 (s, triazolium-CH_3) ppm. MS (ESI-TOF): *m*/*z* = 296.13 $[M - I]^+$, expected isotopic profile. Elemental analysis calcd. (%) for $C_{17}H_{18}N_3O_2I$ (423.25): C 48.24, H 4.29, N 9.93; found C 48.01, H 4.21, N 9.85.

3.11. Typical Procedure for the Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions

A 10 mL-Schlenk tube was filled with the palladium precursor (0.5 mol %), triazolium salt (0.5 mol %), aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), ^{t}BuOK (0.75 mmol), and decane (0.025 mL, internal reference). Dioxane (2 mL) was then added. The reaction mixture was stirred at 100 °C during the desired time. An aliquot (0.3 mL) of the resulting solution was then passed through a Millipore filter and analyzed by GC.

*3.12. X-ray Crystal Structure Analysis of Triazole **8***

Single crystals of **8** suitable for X-ray analysis were obtained by slow diffusion of methanol into a CH_2Cl_2 solution of the triazole. Crystal data: $C_{106}H_{127}N_3O_{16}$, *M*r = 1699.10 g mol^{-1}, monoclinic, space group *C* 2/c, *a* = 52.4158(14) Å, *b* = 10.5297(3) Å, *c* = 56.6335(14) Å, β = 103.308(2)°, *V* = 30417.9(14) Å^3, *Z* = 12, *D* = 1.113 g cm^{-3}, μ = 0.592 mm^{-1}, *F*(000) = 10944, *T* = 173(2) K. The sample was studied on a

Bruker APEX II CCD (graphite monochromated Cu-$K\alpha$ radiation, λ = 1.54178 Å). The data collection (2θmax = 66.9°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: *h* -61,61 *k* -6,12 *l* -57,67) gave 128,330 reflections. The structure was solved with SHELXS-2013 [51], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found with a Fourier difference map. The structure was refined with SHELXL-2013 [51] by the full-matrix least-square techniques (use of *F* square magnitude; *x*, *y*, *z*, ij for C, N, and O atoms; *x*, *y*, *z* in riding mode for H atoms); 1,677 variables and 11,315 observations with $I > 2.0\ \sigma(I)$; calcd. $w = 1/[\sigma^2(Fo^2) + (0.1312P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$, with the resulting $R = 0.0921$, $R_W = 0.2703$ and $S_W = 0.964$, $\Delta\rho < 0.599$ eÅ^{-3}. CCDC entry 1848246 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

4. Conclusions

In summary, we have described the first triazolium salts substituted by resorcinarene units (**1** and **2**). These were assessed in the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl chlorides with aryl boronic acids. Significantly higher reaction rates were observed with the sterically less hindered triazolium salt **1**, which bore a single resorcinarene substituent. Its better performance, compared to that of **2**, likely reflected a higher substrate accessibility in the resulting catalytic intermediates, as well as the presence of flexible pentyl groups that might interact with the metal center, so as to facilitate the reductive elimination step. Further studies will be aimed at exploiting the steric as well as the receptor properties of the resorcinarene-derived triazolium salts in carbon-carbon bond forming reactions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/4/388/s1, characterizing data of compounds **1**, **2**, **4**, **5**, **7–11** and 1-(2,6-dimethoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole, typical procedure for the Suzuki–Miyaura cross-coupling reactions, Table S1: Comparison of imidazolium salts.

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