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PAPER

Resorcin[4]arene-derived mono-, bis- and tetra-imidazolium salts as ligand precursors for Suzuki–Miyaura cross-coupling†‡

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Eleven resorcinarene cavitands bearing either one, two or four (3-R-1-imidazolylium)-methyl substituents (R = ^{n}Bu, Ph, Mes, $^{i}Pr_2C_6H_3$) anchored at resorcinolic "*ortho*" positions have been synthesised from the appropriate bromomethylated precursor. Combining the imidazolium salts with palladium acetate and Cs_2CO_3 gave active Suzuki–Miyaura cross coupling catalysts. The highest activities were observed with the doubly functionalised cavitands, which all have the imidazolylium groups attached to proximal resorcinol units.

Introduction

The palladium catalysed Suzuki–Miyaura cross-coupling of organoboron compounds has been established as one of the most selective palladium-catalysed cross-coupling reactions, thereby leading to many important developments in modern organic chemistry.[1–4] While this reaction is usually performed in the presence of tertiary phosphines, recent studies have shown that high catalytic efficiency can also be obtained with *N*-heterocyclic carbenes (NHCs), ligands of this type being conveniently generated from imidazolium salts.[5,6] To date research in this area has mainly focused on mono-NHC ligands, although some palladium complexes containing *bis*[7–13] or *tetrakis*[14]-NHC ligands are known.

The present work concerns the use of NHC ligands supported on a rigidified calixarene of the cavitand type. The term "cavitand" applies specifically to the sub-family of calixarenes termed "resorcinarenes" where linking of the hydroxyl substituents on the macrocycles has been used to reinforce their structure, creating a well-defined cavity, usually of fourfold symmetry.[15,16] In calix[4]arene analogues, even those where phenolic-*O* alkylation has been used to block conformational inversion, a degree of conformational flexibility is retained, as is well illustrated by the fact that a *cone* calix[4]arene distally substituted with imidazolylium-methyl groups is able, after deprotonation, to form a *trans* chelate NHC (*N*-heterocyclic carbene) complex with, for example, Pd(II), in which the substituent-bearing phenyl groups are tilted in towards the cavity of the calixarene.[12] In unrestricted *cone* calix[4]arenes, this tilting is usually outwards. An interesting aspect of the structure of this particular Pd(II) complex is that the metal ion is poised above the cavity, though it seems that the phenyl ring tilting may restrict access to the cavity, since neither of the additional ligands on the metal are contained within it, a situation unlike that observed with some related complexes where phosphorus ligating sites are present. Further, although the Pd calixaryl(NHC)$_2$ complex can be used as a catalyst precursor for the Suzuki–Miyaura reaction, it appears that chelation is not retained in the catalytically active species and, more significantly, there is no evidence of a "cavity effect" which might arise from substrate inclusion by the calixarene. Given our interest in such determinants of catalyst activity, we have sought to clarify the situation concerning NHC functionalities grafted to a calix[4]arene scaffold by examining the properties of rigidified resorcinarenes bearing either a single substituent or multiple substituents in which chelation by proximal groups might be possible. For the species bearing multiple substituents, it may be noted that the possibility of binding through a single site would leave charged imidazolylium groups in the vicinity of the catalytic centre, providing another factor that might be used to influence the catalyst properties.

Thus, we describe herein the synthesis of cavitands bearing one, two and four imidazolium units (Scheme 1). These imidazolium salts, which in fact are procarbenes, were assessed in Suzuki–Miyaura cross-coupling between phenyl boronic acid and several aryl bromides. A literature survey indicates that only three imidazolium salts built on a resorcinarene skeleton have been reported to date, their use being restricted to molecular recognition studies.[17–19] This is in marked contrast with the chemistry of the related calix[4]arene analogues, which have already found numerous applications in homogeneous catalysis.[8,10–12,20] The present report constitutes an extension of our previous work on functionalised cavitands.[21–23]

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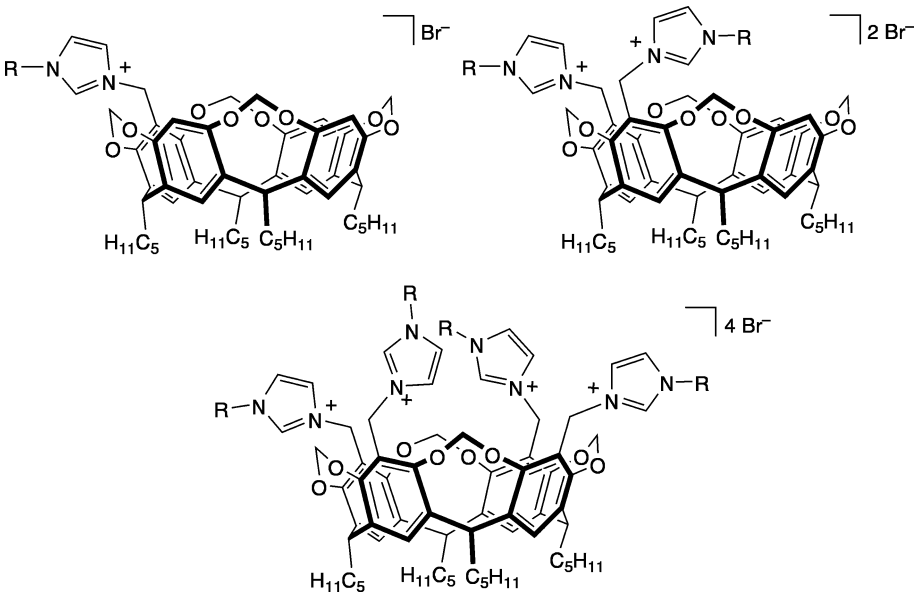
‡ Dedicated to Professor Christian Bruneau (CNRS – University of Rennes) on the occasion of his 60th Birthday.



Scheme 1 The three types of imidazolium salt synthesised in this study.

Results and discussion

Synthesis of resorcinarenyl-imidazolium salts

Eleven resorcinarene-derived imidazolium salts were synthesised, all in high yields, according to the routes outlined in Scheme 2. The general synthetic strategy consisted in reacting a mono- or multi-bromomethylated resorcinarene with *N*-substituted imidazoles in refluxing chloroform. All compounds were unambiguously characterized by ^{1}H and ^{13}C NMR, elemental analysis and mass spectrometry.

The ^{1}H NMR spectra of mono-imidazolium salts **2–4** are in keeping with C_s-symmetrical cavitands, each of them showing the presence of two distinct AB patterns for the diastereotopic OCH_2O protons, and that of two methine triplets. The bis-imidazolium salts **6–9** display C_s symmetry as well. Consistent with the presence of a symmetry plane that bisects the two substituted resorcinol rings, the ^{1}H spectra of these latter compounds show three AB patterns of intensity 1 : 2 : 1 for the four OCH_2O groups and three distinct methine triplets. An X-ray diffraction study was carried out for one of the bis-imidazolium salts, namely **8** (Fig. 1), which confirmed the presence of the two imidazolium moieties on adjacent resorcinol rings. In the solid state, the two imidazolium arms are bent towards the exterior of the cavity. The cavitand core hosts a molecule of $CHCl_3$, while two other molecules of $CHCl_3$ were found remote from the cavity. Significantly, the bromide counter anions are all remote from the cavity, although anion inclusion in resorcinarene cavitands has already been observed.[24]

The tetra-imidazolium resorcinarenes **11–14** have C_{4v} symmetry and, accordingly, their ^{1}H NMR spectra show a single AB pattern for the four OCH_2O groups. On going from the imidazole precursors to the corresponding imidazolium salts the NCHN protons undergo a deshielding of about 2 ppm (the imidazolium NCHN signals appearing in the range 9.61–10.13 ppm). Consistent with this apparent increase in acidity, the imidazolium-resorcinarenes could easily be converted into coordinated NHC ligands under basic conditions. For example, treatment of compound **7** with

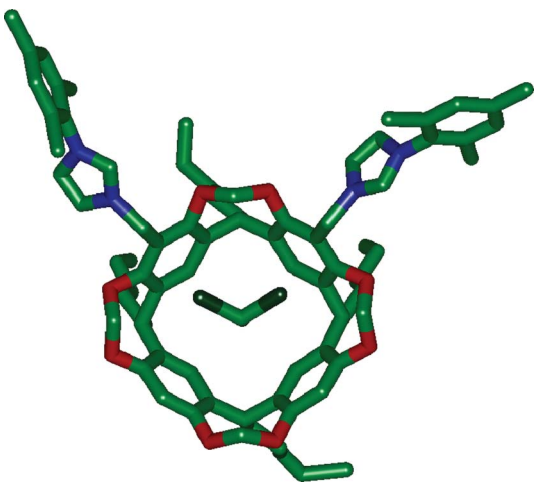
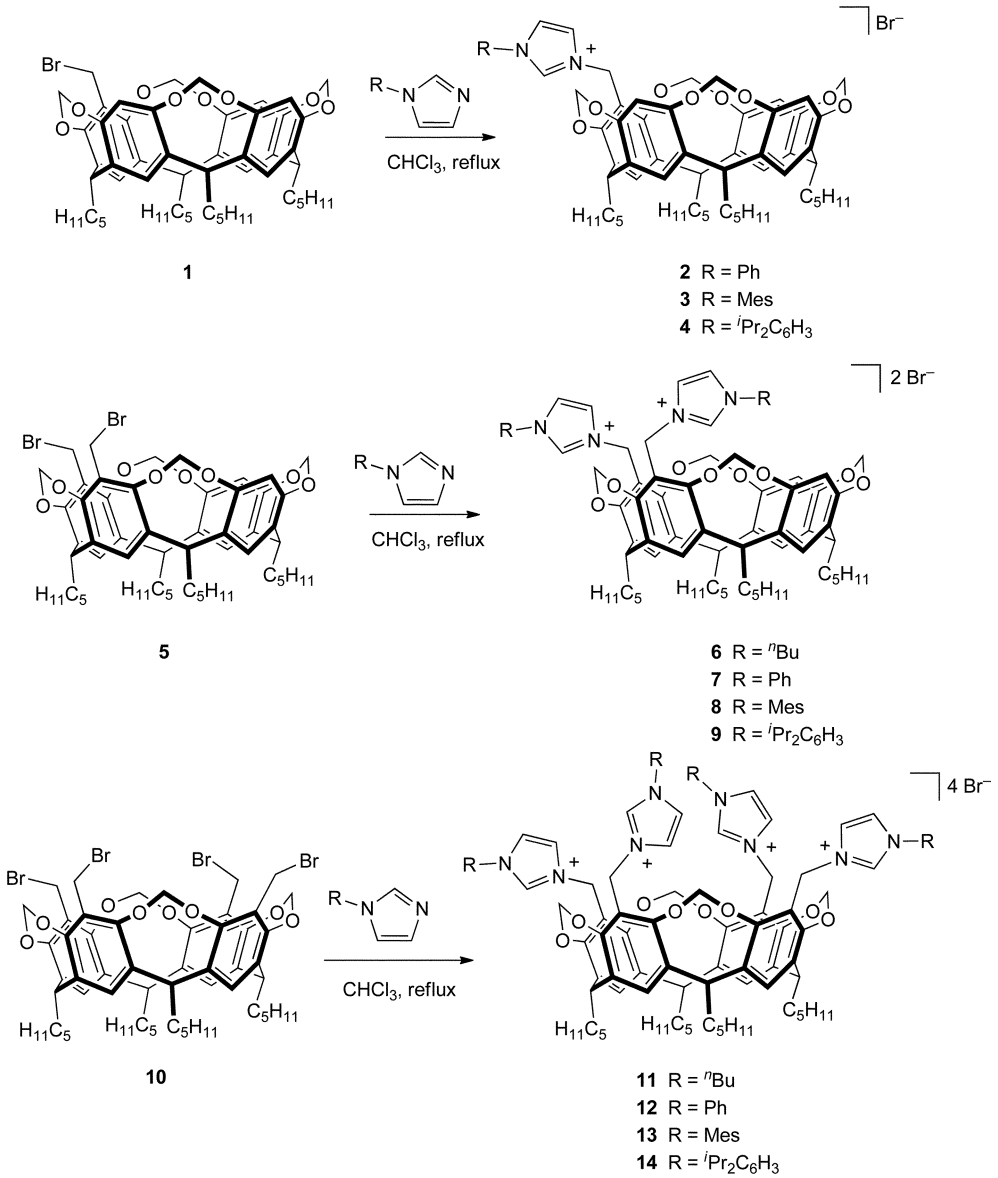


Fig. 1 Molecular structure of resorcinarene **8** (hosting a molecule of $CHCl_3$). For clarity, the two $CHCl_3$ molecules lying out of the cavity and two the Br^- anions are not shown.

1 equivalent of Ag_2O in acetonitrile led to the white silver (I) complex $[(AgBr)_2L]$ (**15**), in which L represents the bis-carbene ligand derived from **7**. The mass spectrum of **15** displayed a strong peak at 1385.28, corresponding to the $[M - Br]^+$ cation. In keeping with carbene formation, the ^{1}H NMR spectrum no longer revealed the presence of a NC*H*N signal. The coordination of silver was inferred from the ^{13}C NMR spectrum, in which the carbenic carbon atom appears at 181.47 ppm, which is a value typical for coordinated NHCs. However, no Ag–C coupling was seen, as is often the case, this finding probably reflecting the fluxional nature of the complex.[25]

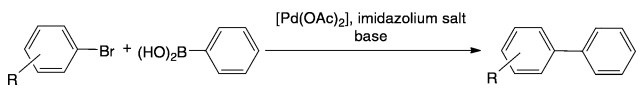
Utilisation of the resorcinarene-imidazolium salts in Suzuki–Miyaura cross-coupling

Being potential precursors of carbenes, that is of strong 2-electron donors, the above compounds were evaluated in Suzuki–Miyaura



Scheme 2 Synthesis of the resorcinarene-imidazolium salts used in this study.

cross-coupling between phenylboronic acid and aryl bromides in the presence of a base (Scheme 3). For each test, the catalytic system was generated *in situ* by mixing the imidazolium salt and $[Pd(OAc)_2]$, a palladium complex which is routinely used for generating carbene complexes.[8,26] The runs were carried out using an ArBr/Pd ratio of 10 000 and the conversions were determined after one hour.



Scheme 3 Suzuki–Miyaura cross-coupling reaction.

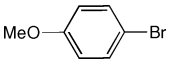
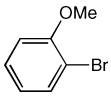
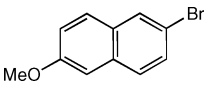
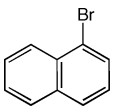
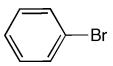
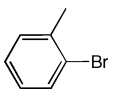
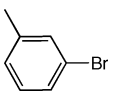
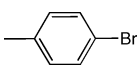
The first series of runs were aimed at optimisation of the catalytic conditions with respect to solvent and base. Four tests were carried out with the tetra-imidazolium salt **13** either in dimethylformamide (DMF) or in dioxane and either with Cs_2CO_3 or NaH (Table 1). The highest conversion of 4-bromoanisole into Ph–(*p*-OMe-C_6H_4) (26.1%) was observed when carrying out the reaction in DMF at 130 °C in the presence of Cs_2CO_3 (Table 1, entry 4). It is likely that under these conditions the solubility of the imidazolylium salt as well as that of Cs_2CO_3 is better in DMF than

Table 1 Suzuki–Miyaura cross-coupling of 4-bromoanisole with phenylboronic acid using **13** - the search for optimal catalytic conditions[a]

Entry	Solvent	Base	*T*/°C	Conversion (%)
1	Dioxane	NaH	100	19.3
2	Dioxane	Cs_2CO_3	100	22.3
3	DMF	NaH	130	0.4
4	DMF	Cs_2CO_3	130	26.1

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), imidazolium salt **13** (5×10^{-5} mmol, 1 equiv./Pd), 4-bromoanisole (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), base (1.0 mmol), solvent (1.5 mL), decane (0.05 mL), 1 h. The conversions were determined by GC, the calibrations being based on decane.

Table 2 Suzuki–Miyaura cross-coupling of aryl bromides catalysed by [Pd(OAc)$_2$]/mono-imidazolium salts using 10^{-2} mol% palladium[a]

Entry	ArBr		Mono-imidazolium salt			
			Equiv./Pd	**2**	**3**	**4**
1		Conv. (%) TOF	1		10.0 1000	
2		Conv. (%) TOF	2	5.7 570	10.5 1050	13.4 1340
3		Conv. (%) TOF	2	7.9 790	12.4 1240	14.8 1480
4		Conv. (%) TOF	2	50.2 5020	38.1 3810	51.7 5170
5		Conv. (%) TOF	2	39.1 3910	45.3 4530	53.4 5340
6		Conv. (%) TOF	2	6.5 650	13.0 1300	9.1 910
7		Conv. (%) TOF	2	10.6 1060	8.2 820	5.2 520
8		Conv. (%) TOF	2	4.4 440	7.0 700	4.8 480
9		Conv. (%) TOF	2	7.5 750	7.9 790	11.2 1120

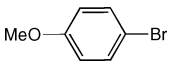
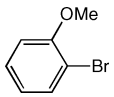
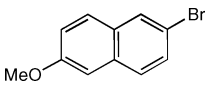
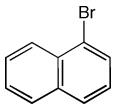
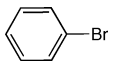
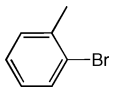
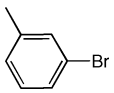
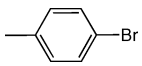
[a] Conditions: [Pd(OAc)$_2$] (5×10^{-5} mmol, 1×10^{-2} mol%), mono-imidazolium salt, ArBr (0.5 mmol), PhB(OH)$_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC, the calibrations being based on decane. The TOFs are expressed in mol(ArBr) mol(Pd)$^{-1}$ h^{-1}.

in dioxane. In none of the tests did the amount of homocoupling product (Ph–Ph) exceed 9% of the products formed (see ESI†).

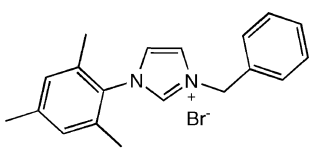
The three mono-imidazolium salts **2–4** were used in Suzuki–Miyaura coupling of several aryl bromides. Under the optimal conditions defined above, the mono-imidazolium salt **3** led to slightly better conversions when using an imidazolium : Pd ratio of 2 : 1 instead of 1 : 1 (Table 2, entries 1 and 2). All subsequent runs were therefore carried out with two equivalents of imidazolium per Pd. It appears that the activity of the systems depends on both the substrate and the mono-imidazolium employed. For example, the crowded salt **4** was the more efficient proligand for the arylation of 2-, and 4-bromoanisole, 2-bromo-6-methoxynaphthalene, 1-bromonaphthalene and 4-bromotoluene (Table 2, entries 2–5 and 9). Whatever the mono-imidazolium employed, the reaction with 4-bromoanisole was relatively slow in comparison with that of the sterically hindered 2-bromoanisole (Table 2, entries 2 and 3). The activities observed for 2-bromo-6-methoxynaphthalene were 4–8 times higher than for 4-bromoanisole (Table 2, entries 2 and 4), this being rather surprising as these two substrates usually show comparable reaction rates in Suzuki cross-coupling. Bromobenzene and 3-bromotoluene reacted faster when mono-imidazolium **3** was used (Table 2, entries 6 and 8). The highest activity observed, 5340 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}, was found in the arylation of 1-bromonaphthalene with mono-imidazolium **4** (Table 2, entry 5). Unsurprisingly, for the whole series of substrates nearly complete conversions could be obtained by increasing either the catalyst loading or the reaction time (Table 3). For example, 2-bromo-6-methoxynaphthalene was nearly fully converted in 3 h using 0.01 mol% of palladium or in 1 h with a palladium loading of 0.1 mol% (Table 3, entries 5 and 6).

To test for any cavitand contribution, we investigated imidazolium **16** having a mesityl and a benzyl group as N-substituents (Fig. 2). Using this salt and applying the conditions of Table 2 led to slightly higher activities than those observed with mono-imidazolium **3** (Table S3†). For example, the activity of **16** was 5160 mol(ArBr) mol(Pd)$^{-1}$ h^{-1} in the arylation of 1-bromonaphthalene *vs.* 4530 mol(ArBr) mol(Pd)$^{-1}$ h^{-1} using **3** (Table S3†, entry 3). These findings strongly suggest that should **3** act as a receptor during catalysis, then this would not have a beneficial role on the catalyst performance. It also suggests that **3** does not function as a hemilabile[23] ligand *via* the oxygen atoms of the functionalised resorcinol ring.

Table 3 Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and a mono-imidazolium salt – increasing the palladium loading or the reaction time[a]

Entry	ArBr	Imidazolium salt	$[Pd(OAc)_2]$ (mol%)	Time (h)	Conversion (%)
1		**4**	0.1	2	92.8
2		**4**	0.01	16	94.9
3		**4**	0.1	2	89.3
4		**4**	0.01	16	95.7
5		**4**	0.1	1	98.6
6		**4**	0.01	3	98.5
7		**4**	0.1	1	99.1
8		**4**	0.01	3	97.6
9		**3**	0.1	2	93.7
10		**3**	0.01	16	94.8
11		**2**	0.1	2	87.9
12		**2**	0.01	16	91.6
13		**3**	0.1	2	81.6
14		**3**	0.01	16	76.7
15		**4**	0.1	2	90.3
16		**4**	0.01	16	89.1

[a] Conditions: $[Pd(OAc)_2]$, mono-imidazolium salt (2 equiv./Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130 °C. The conversions were determined by GC, the calibrations being based on decane.



16

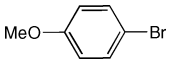
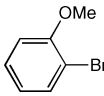
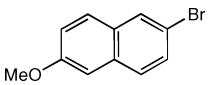
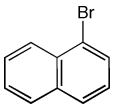
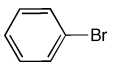
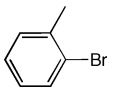
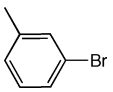
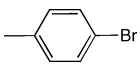
Fig. 2 Imidazolium salt **16** used as reference.

The bis-imidazolium salts **6–9** were tested towards the same aryl bromides as those used above (Table 4). The catalytic runs were carried out in DMF at 130 °C using Cs_2CO_3 as base and with an optimised bis-imidazolium/Pd ratio of 1 : 1 (Table 4, entries 9–11). Under these conditions, the bis-imidazolium salts led to higher activities than those obtained with the mono-imidazolium salts **2–4** (salt/Pd ratio = 2 : 1). As observed in those cases, the four bis-carbene precursors **6–9** showed low activity in the arylation of 4-bromoanisole. In fact, this reaction was about four times slower than that with 2-bromo-6-methoxynaphthalene (Table 4, entries 1 and 3). The bis-imidazolium salts **7** and **9** showed also relatively low activities in the transformation of 3-bromotoluene, this reagent displaying usually a reactivity lying between that of 2- and 4-bromotoluene (Table 4, entries 7, 8 and 10).

Unlike the observations usually made with NHCs, the *n*-butyl-substituted **6** led to higher conversions than the more crowded imidazoliums **7–9** in the arylation of 4-bromoanisole (14.7%) and 2-bromo-6-methoxynaphthalene (76.9%) (Table 4, entries 1 and 3). The highest activity (TOF = 9660 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}) was found in the cross-coupling of 1-bromonaphthalene with bis-imidazolium **8** (substituted by two mesityl groups) (Table 4, entry 4). Reduction of the palladium loading to 0.001 mol% resulted with 1-bromonaphthalene in a TOF of 41600 mol(ArBr) mol(Pd)$^{-1}$ h^{-1} (Table 4, entry 5). It is interesting to mention here that the activities observed with the bis-imidazolium salts **6–9** were in general lower than those previously reported for analogous cavitands bearing two $-CH_2PPh_2$ groups instead of (3-R-1-imidazolylium)-methyl substituents.[23]

In contrast to the results obtained with the mono- and bis-imidazolium salts described above, the tetra-carbene precursors **11–14** led to higher conversions when applying a tetraimidazolium/Pd ratio of 1 : 1 (*i.e.* a procarbene/Pd ratio of 4 : 1) (Table 5, entries 1–3). The bromotoluenes turned out to be converted faster into coupling products when the bulky imidazolium **14** was employed (Table 5, entries 8–10). The highest activity was obtained in the arylation of 1-bromonaphthalene using the mesityl-substituted resorcinarene **13** (TOF = 7710 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}; Table 5, entry 6). Overall, the four tetra-imidazolium salts were less efficient than the disubstituted derivates, but their activities were significantly higher than those of the corresponding mono-imidazoliums.

Table 4 Suzuki–Miyaura cross-coupling of aryl bromides catalysed by [Pd(OAc)$_2$]/bis-imidazolium salts[a]

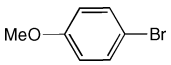
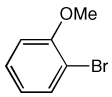
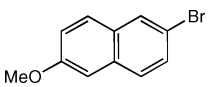
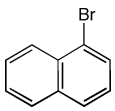
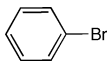
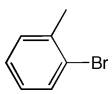
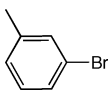
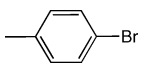
Entry	ArBr		Bis-imidazolium salt Equiv./Pd	**6**	**7**	**8**	**9**
1		Conv. (%) TOF	1	14.7 1470	10.9 1090	12.5 1250	11.6 1160
2		Conv. (%) TOF	1	4.2 420	12.0 1200	17.5 1750	13.5 1350
3		Conv. (%) TOF	1	76.9 7690	51.5 5150	61.1 6110	40.5 4050
4		Conv. (%) TOF	1	52.4 5240	91.3 9130	96.6 9660	41.9 4190
5[b]		Conv. (%) TOF	1		37.2 37200	41.6 41600	
6		Conv. (%) TOF	1	7.9 790	26.6 2660	43.3 4330	32.6 3260
7		Conv. (%) TOF	1	6.1 610	29.6 2960	22.4 2240	14.1 1410
8		Conv. (%) TOF	1	7.9 790	6.1 610	17.9 1790	22.9 2290
9		Conv. (%) TOF	0.5			6.1 610	
10		Conv. (%) TOF	1	15.9 1590	39.6 3960	54.4 5440	57.3 5730
11		Conv. (%) TOF	2			53.2 5320	

[a] Conditions: [Pd(OAc)$_2$] (5×10^{-5} mmol, 1×10^{-2} mol%), bis-imidazolium salt, ArBr (0.5 mmol), PhB(OH)$_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC, the calibrations being based on decane. The TOFs are expressed in mol(ArBr) mol(Pd)$^{-1}$ h^{-1}. [b] [Pd(OAc)$_2$] (5×10^{-6} mmol, 1×10^{-3} mol%)

An appealing rationalisation of the greater activity of catalysts derived from tetrakis- and bis- rather than mono-imidazolium salts is that the former may give rise to chelate species as the active catalyst. Molecular modelling (Spartan) of the imidazolylium-methyl-substituted resorcinarene cavitands **2–4**, **6–9** and **11–14** shows that, as might be expected due to repulsions between the cationic centres, the substituents are oriented away from the rigidified cavity (and this is as observed in the crystal structure of **8** as its dibromide, where the cavity is occupied by a chloroform molecule and note NOT the anion). Modelling of the Pd(II) complexes which might be formed by deprotonation of the NHC-precursor sites shows, nonetheless, that for the poly-imidazolylium derivatives the carbene-C sites can be brought into an orientation such that *cis* chelation by proximal sites is possible. It is worth mentioning here that Schatz *et al.* have recently reported a structurally-related chelate complex derived from a bis-imidazolium salt based on the more flexible calix[4]arene platform.[8] There, the metal atom adopts a *cis* coordination geometry. However, in the present cases, chelation as modelled involves either an *endo*-cavity orientation where the metal is inserted rather deeply into the cavity and where there would be no room for additional ligands on the metal, or an *exo*-cavity orientation where there would be extreme clashes between the (desirable) bulky substituents on the NHC units. Thus, the expectation would be that ligands such as **2–4**, **6–9** and **11–14** would most likely function as single-site NHC sources, albeit ones with very large substituents and (except for **2–4**) positive charges adjacent to the active centre. Hence, aside from statistical factors associated with the number of substituents and any possible influence of charge, all three ligands might be anticipated to show similar properties as catalyst precursors for the Suzuki–Miyaura reaction.

Indeed, the results presently reported are consistent with all the substituted cavitands giving rise to catalysts of similar activity, TOF values under identical conditions varying by little more than a factor of two, clearly corresponding to rather minor activation energy differences which might well be ascribed to differences in solvation associated with the charge differences. If there is no chelation by the carbene species, then the catalysts derived from

Table 5 Suzuki–Miyaura cross-coupling of aryl bromides catalysed by $[Pd(OAc)_2]$/tetra-imidazolium salts[a]

Entry	ArBr		Tetra-imidazolium salt				
			Equiv./Pd	**11**	**12**	**13**	**14**
1		Conv. (%)	0.5			13.4	
		TOF				1340	
2		Conv. (%)	1	14.1	11.3	26.1	23.8
		TOF		1410	1130	2610	2380
3		Conv. (%)	2			11.0	
		TOF				1100	
4		Conv. (%)	1	8.8	2.1	20.8	23.4
		TOF		880	210	2080	2340
5		Conv. (%)	1	32.3	30.9	61.9	35.1
		TOF		3230	3090	6190	3510
6		Conv. (%)	1	50.4	58.4	77.1	57.7
		TOF		5040	5840	7710	5770
7		Conv. (%)	1	25.8	26.9	30.7	28.9
		TOF		2580	2690	3070	2890
8		Conv. (%)	1	6.6	5.4	12.6	23.5
		TOF		660	540	1260	2350
9		Conv. (%)	1	8.5	5.3	15.1	31.1
		TOF		850	530	1510	3110
10		Conv. (%)	1	11.2	21.9	21.7	32.0
		TOF		1120	2190	2170	3200

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), tetra-imidazolium salt, ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130 °C, 1 h. The conversions were determined by GC, the calibrations being based on decane. The TOFs are expressed in mol(ArBr) mol(Pd)$^{-1}$ h^{-1}.

6–9 and **11–14** would have residual cationic centres close to the metal and it is conceivable that this could have some influence on the binding of anionic boronate substrates. This may be a partial explanation of the greater effectiveness of the bis- and tetrakis-imidazolylium derivatives, though again it appears that any such effect must be small. Attempts to isolate a well-defined species by treatment of **9** with $[Pd(OAc)_2]$ failed, this reaction leading to a mixture of compounds that could not be separated. Analysis of the corresponding mass spectra revealed the presence of an intense peak at m/z 1563.54, which could not be assigned unequivocally, this peak corresponding either to the species $[PdBr_2(\text{bis-carbene})_2 + H^+]$ or its isomer $[PdBr_2(\text{monocarbene-monoimidazolium})]^+$ (see ESI†).

In summary, we have described the synthesis of eleven resorcin[4]arenes substituted either by one, two, or four imidazolium units. In combination with $[Pd(OAc)_2]$ and a base, these salts resulted in efficient Suzuki–Miyaura catalysts for the cross-coupling of aryl bromides with phenylboronic acid. The highest activity (TOF = 41 600 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}) was observed in the arylation of 1-bromonaphthalene using the proximally-disubstituted cavitand **8**. The relatively small differences in activity observed within the three series of imidazolium salts suggest that they all behave as single-site NHC sources.

Experimental

General remarks

All manipulations involving imidazolium derivatives were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried 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 and $^{13}C\{^1H\}$ spectra were recorded with a Bruker FT instrument (AC-300). ^1H spectra were referenced to residual protiated solvents (7.26 ppm for $CDCl_3$, 2.50 ppm for

DMSO-d_6, 2.05 ppm for acetone-d_6), ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$, 39.52 ppm for DMSO-d_6, 29.84 ppm for acetone-d_6). Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm, inside diameter, 0.25 mm film thickness). Bromomethylated cavitands **1**, **5** and **10**,[22] *N*-substituted imidazoles (R′ = Ph,[27] R′ = mesityl,[28] R′ = 2,6-diisopropylphenyl[28]), and imidazolium salt **16**[29] were prepared according to procedures described in the literature. NMR spectral data of the resulting 4-methoxybiphenyl,[30] biphenyl,[30] 4-methylbiphenyl,[30] 2-methoxybiphenyl,[31] 1-phenylnaphthalene,[31] 2-methylbiphenyl,[31] 3-methylbiphenyl[31] and 2-methoxy-6-phenylnaphthalene[32] were in agreement with those reported in the literature.

General procedure for the synthesis of imidazolium salts

A chloroform solution of the appropriate bromomethylated resorcinarene and imidazole (1 equiv. of imidazole per –CH_2Br unit) was refluxed for 5 days. The reaction mixture was evaporated to dryness and the solid residue was washed with Et_2O (2 × 15 mL) to afford the imidazolium-resorcinarene as a white solid.

5-(3-Phenyl-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene bromide (2). Yield: 0.562 g, 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.90 (s, 1H, NCHN), 7.71–7.68 (m, 2H, arom. CH of NPh), 7.59–7.52 (m, 3H, arom. CH of NPh), 7.49 (s br, 1H, NC*H*CHN), 7.36 (s br, 1H, NCHC*H*N), 7.20 (s, 1H, arom. CH of resorcinarene), 7.09 (s, 1H, arom. CH of resorcinarene), 7.08 (s, 2H, arom. CH of resorcinarene), 6.55 (s, 2H, arom. CH of resorcinarene), 6.48 (s, 1H, arom. CH of resorcinarene), 6.18 and 4.55 (AB spin system, 4H, OCH_2O, ^2J = 7.4 Hz), 5.77 (s br., 2H, $ArCH_2N$), 5.73 and 4.45 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 4.72 (t, 2H, C*H*CH_2, ^3J = 7.9 Hz), 4.70 (t, 2H, C*H*CH_2, ^3J = 7.7 Hz), 2.32–2.11 (m, 8H, CHC*H*$_2$), 1.38–1.30 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.90 (t, 6H, CH_2CH_3, ^3J = 6.2 Hz), 0.89 (t, 6H, CH_2CH_3, ^3J = 6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.27–137.37 (arom. C_{quat}), 136.24 (s, NCHN), 134.43 (arom. C_{quat}), 130.70 (s, arom. CH of NPh), 130.42, 122.71 (2 s, NCHCHN), 122.25, 121,88 (2 s, arom. CH of NPh), 120.38, 120.29, 120.13 (3 s, arom. CH of resorcinarene), 119.71 (s, arom. C_{quat}), 116.79, 116.67 (2 s, arom. CH of resorcinarene), 100.43 (s, OCH_2O), 99.59 (s, OCH_2O), 44.08 (s, $ArCH_2N$), 36.65 (s, *C*HCH_2), 36.33 (s, *C*HCH_2), 32.02 (s, *C*H_2CH_2CH_3), 31.99 (s, *C*H_2CH_2CH_3), 29.90 (s, CH*C*H_2), 29.81 (s, CH*C*H_2), 27.56 (s, CHCH_2*C*H_2), 22.68 (s, *C*H_2CH_3), 22.65 (s, *C*H_2CH_3), 14.09 (s, CH_2*C*H_3). Anal. calcd. for $C_{62}H_{73}O_8N_2Br$ (M_r = 1054.16): C 70.64, H 6.98, N 2.66%; found: C 70.56, H 7.07, N 2.47%. MS (ESI-TOF): m/z = 973.50 [M – Br]$^+$ expected isotopic profiles.

5-(3-(2,4,6-Trimethylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene bromide (3). Yield: 0.580 g, 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (s, 1H, NCHN), 7.31 (s, 1H, NC*H*CHN), 7.20 (s, 1H, NCHC*H*N), 7.09 (s, 1H, arom. CH of resorcinarene), 7.08 (s, 2H, arom. CH of resorcinarene), 7.05 (s, 1H, arom. CH of resorcinarene), 6.99 (s, 2H, arom. CH of mes), 6.54 (s, 2H, arom. CH of resorcinarene), 6.47 (s, 1H, arom. CH of resorcinarene), 6.00 and 4.56 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 5.99 (s br, 2H, $ArCH_2N$), 5.71 and 4.46 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 4.74 (t, 2H, C*H*CH_2, ^3J = 7.9 Hz), 4.66 (t, 2H, C*H*CH_2, ^3J = 8.0 Hz), 2.32 (s, 3H, CH_3 *para* of Mes), 2.27–2.10 (m, 8H, CHC*H*$_2$), 2.05 (s, 6H, CH_3 *ortho* of Mes), 1.39–1.29 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.89 (t, 12H, CH_2CH_3, ^3J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.27–153.46 (arom. C_{quat}), 141.45 (s, NCHN), 138.99–130.56 (arom. C_{quat}), 129.89 (s, arom. CH of Mes), 122.82 (s, arom. CH of resorcinarene), 122.26, 122.11 (2 s, NCHCHN), 120.33, 120.25 (2 s, arom. CH of resorcinarene), 119.84 (s, arom. C_{quat}), 116.85, 116.67 (2 s, arom. CH of resorcinarene), 100.55 (s, OCH_2O), 99.56 (s, OCH_2O), 44.17 (s, $ArCH_2N$), 36.52 (s, *C*HCH_2), 36.33 (s, *C*HCH_2), 32.03 (s, *C*H_2CH_2CH_3), 31.92 (s, *C*H_2CH_2CH_3), 29.92 (s, CH*C*H_2), 29.77 (s, CH*C*H_2), 27.56 (s, CHCH_2*C*H_2), 27.51 (s, CHCH_2*C*H_2), 22.68 (s, *C*H_2CH_3), 22.64 (s, *C*H_2CH_3), 21.07 (s, CH_3 *para* of Mes), 17.46 (s, CH_3 *ortho* of Mes), 14.09 (s, CH_2*C*H_3). Anal. calcd. for $C_{65}H_{79}O_8N_2Br$ (M_r = 1096.23): C 71.22, H 7.26, N 2.55%; found: C 71.05, H 7.38, N 2.37%. MS (ESI-TOF): m/z = 1015.56 [M – Br]$^+$ expected isotopic profiles.

5-(3-(2,6-Diisopropylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene bromide (4). Yield: 0.607 g, 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.25 (s, 1H, NCHN), 7.54 (t, 1H, arom. CH of ^{i}Pr$_2$C$_6$H$_3$, ^3J = 7.7 Hz), 7.35 (s br, 1H, NC*H*CHN), 7.30 (d, 2H, arom. CH of ^{i}Pr$_2$C$_6$H$_3$, ^3J = 7.7 Hz), 7.21 (s, 1H, arom. CH of resorcinarene), 7.10 (s, 1H, arom. CH of resorcinarene), 7.08 (s, 2H, arom. CH of resorcinarene), 7.06–7.05 (m, 1H, NCHC*H*N), 6.55 (s, 2H, arom. CH of resorcinarene), 6.48 (s, 1H, arom. CH of resorcinarene), 6.09 (s, 2H, $ArCH_2N$), 6.00 and 4.57 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 5.72 and 4.47 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 4.72 (t, 2H, C*H*CH_2, ^3J = 7.9 Hz), 4.70 (t, 2H, C*H*CH_2, ^3J = 7.7 Hz), 2.36–2.11 (m, 10H, CHC*H*$_2$ and C*H*$(CH_3)_2$), 1.40–1.30 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.20 (d, 6H, $CH(CH_3)_2$, ^3J = 6.9 Hz), 1.14 (d, 6 H, $CH(CH_3)_2$, ^3J = 6.8 Hz), 0.90 (t, 12H, CH_2CH_3, ^3J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.30–138.78 (arom. C_{quat}), 138.61 (s, NCHN), 138.05, 137.23 (arom. C_{quat}), 131.99 (s, arom. CH of ^{i}Pr$_2$C$_6$H$_3$), 130.03 (arom. C_{quat}), 124.74 (s, arom. CH of ^{i}Pr$_2$C$_6$H$_3$), 123.70, 122.20 (2 s, NCHCHN), 122.06, 120.32, 120.22 (3 s, arom. CH of resorcinarene), 120.00 (s, arom. C_{quat}), 116.88, 116.76 (2 s, arom. CH of resorcinarene), 100.65 (s, OCH_2O), 99.56 (s, OCH_2O), 44.22 (s, $ArCH_2N$), 36.49 (s, *C*HCH_2), 36.33 (s, *C*HCH_2), 32.04 (s, *C*H_2CH_2CH_3), 31.89 (s, *C*H_2CH_2CH_3), 29.93 (s, CH*C*H_2), 29.77 (s, CH*C*H_2), 28.69 (s, *C*H$(CH_3)_2$), 27.56 (s, CHCH_2*C*H_2), 27.52 (s, CHCH_2*C*H_2), 24.46 (s, CH(*C*$H_3)_2$), 24.10 (s, CH(*C*$H_3)_2$), 22.68 (s, *C*H_2CH_3), 22.65 (s, *C*H_2CH_3), 14.09 (s, CH_2*C*H_3). Anal. calcd. for $C_{68}H_{85}O_8N_2Br$ (M_r = 1138.31): C 71.75, H 7.53, N 2.46%; found: C 71.79, H 7.55, N 2.33%. MS (ESI-TOF): m/z = 1057.61 [M – Br]$^+$ expected isotopic profiles.

5,11-Bis(3-butyl-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetramethylene-dioxy-2,8,14,20-tetrapentylresorcin[4]arene dibromide (6). Yield: 0.510 g, 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.95 (s, 2H, NCHN), 7.46 (s br, 2H, NC*H*CHN), 7.27 (s br, 2H, NCHC*H*N), 7.13 (s, 2H, arom. CH of resorcinarene), 7.05 (s, 2H, arom. CH of resorcinarene), 6.61 and 4.56 (AB spin system,

2H, OCH_2O, ^2J = 7.5 Hz), 6.54 (s, 2H, arom. CH of resorcinarene), 6.12 and 4.54 (AB spin system, 4H, OCH_2O, ^2J = 7.4 Hz), 5.69 and 4.48 (AB spin system, 2H, OCH_2O, ^2J = 7.3 Hz), 5.54 and 5.45 (AB spin system, 4H, $ArCH_2N$, ^2J = 14.3 Hz), 4.71 (t, 1H, $CHCH_2$, ^3J = 5.3 Hz), 4.68 (t, 2H, $CHCH_2$, ^3J = 5.5 Hz), 4.66 (t, 1H, $CHCH_2$, ^3J = 5.5 Hz), 4.31 (t, 4H, NCH_2CH_2, ^3J = 7.3 Hz), 2.30–2.03 (m, 8H, $CHCH_2$), 1.86 (quint, 4H, NCH_2CH_2, ^3J = 7.4 Hz), 1.42–1.25 (m, 28H, $CH_2CH_2CH_2CH_3$ and CH_2CH_3 of N^{n}Bu), 0.90 (t, 12H, CH_2CH_3 of resorcinarene, ^3J = 7.1 Hz), 0.87 (t, 6H, CH_2CH_3 of N^{n}Bu, ^3J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 155.12–137.35 (arom. C_{quat}), 136.70 (s, NCHN), 122.21, 122.10 (2 s, NCHCHN), 121.82 (s, arom. CH of resorcinarene), 120.31 (s, arom. C_{quat}), 120.08, 116.95 (2 s, arom. CH of resorcinarene), 100.69 (s, OCH_2O), 100.40 (s, OCH_2O), 99.60 (s, OCH_2O), 49.88 (s, NCH_2CH_2), 43.66 (s, $ArCH_2N$), 36.77 (s, $CHCH_2$), 36.61 (s, $CHCH_2$), 36.33 (s, $CHCH_2$), 32.12 (s, NCH_2CH_2), 31.98 (s, $CH_2CH_2CH_3$ of resorcinarene), 29.92 (s, $CHCH_2$), 29.68 (s, $CHCH_2$), 27.53 (s, $CHCH_2CH_2$), 27.52 (s, $CHCH_2CH_2$), 27.51 (s, $CHCH_2CH_2$), 22.68 (s, CH_2CH_3 of resorcinarene), 22.63 (s, CH_2CH_3 of resorcinarene), 22.58 (s, CH_2CH_3 of resorcinarene), 19.45 (s, CH_2CH_3 of N^{n}Bu), 14.08 (s, CH_2CH_3 of resorcinarene), 13.42 (s, CH_2CH_3 of N^{n}Bu). Anal. calcd. for $C_{68}H_{90}O_8N_4Br_2$ (M_r = 1251.27): C 65.27, H 7.25, N 4.48%; found: C 65.03, H 7.44, N 4.16%. MS (ESI-TOF): m/z = 1171.60 $[M - Br]^+$ and 545.35 $[M - Br_2]^{2+}$ expected isotopic profiles.

5,11-Bis(3-phenyl-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetramethylene-dioxy-2,8,14,20-tetrapentylresorcin[4]-arene dibromide (7). Yield: 0.527 g, 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.57 (s, 2H, NCHN), 7.87 (s br, 2H, NC*H*CHN), 7.80 (d, 4H, arom. CH *ortho* of NPh, ^3J = 7.4 Hz), 7.56 (s br, 2H, NCHC*H*N), 7.53 (t, 4H, arom. CH *meta* of NPh, ^3J = 7.5 Hz), 7.49 (t, 2H, arom. CH *para* of NPh, ^3J = 7.4 Hz), 7.16 (s, 2H, arom. CH of resorcinarene), 7.06 (s, 2H, arom. CH of resorcinarene), 6.84 and 4.64 (AB spin system, 2H, OCH_2O, ^2J = 7.0 Hz), 6.55 (s, 2H, arom. CH of resorcinarene), 6.30 and 4.58 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 5.75 and 5.58 (AB spin system, 4H, $ArCH_2N$, ^2J = 14.1 Hz), 5.69 and 4.45 (AB spin system, 2H, OCH_2O, ^2J = 7.4 Hz), 4.73 (t, 1H, $CHCH_2$, ^3J = 8.2 Hz), 4.71 (t, 2H, $CHCH_2$, ^3J = 8.0 Hz), 4.70 (t, 1H, $CHCH_2$, ^3J = 7.9 Hz), 2.31–2.06 (m, 8H, $CHCH_2$), 1.41–1.25 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.89 (t, 3H, CH_2CH_3, ^3J = 6.8 Hz), 0.88 (t, 9H, CH_2CH_3, ^3J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.13–137.34 (arom. C_{quat}), 135.30 (s, NCHN), 134.51 (arom. C_{quat}), 130.50 (s, arom. CH of NPh), 130.05, 123.49 (2 s, NCHCHN), 121.93 (s, arom. CH of NPh), 121.88 (s, arom. CH of NPh), 120.82 (s, arom. CH of resorcinarene), 120.31 (arom. C_{quat}), 120.06, 116.98 (2 s, arom. CH of resorcinarene), 100.89 (s, OCH_2O), 100.53 (s, OCH_2O), 99.56 (s, OCH_2O), 44.05 (s, $ArCH_2N$), 36.89 (s, $CHCH_2$), 36.66 (s, $CHCH_2$), 36.33 (s, $CHCH_2$), 32.00 (s, $CH_2CH_2CH_3$), 29.92 (s, $CHCH_2$), 29.69 (s, $CHCH_2$), 27.55 (s, $CHCH_2CH_2$), 22.68 (s, CH_2CH_3), 22.63 (s, CH_2CH_3), 22.58 (s, CH_2CH_3), 14.08 (s, CH_2CH_3). Anal. calcd. for $C_{72}H_{82}O_8N_4Br_2$ (M_r = 1291.25): C 66.97, H 6.40, N 4.34%; found: C 67.03, H 6.35, N 4.29%. MS (ESI-TOF): m/z = 565.31 $[M - Br_2]^{2+}$ expected isotopic profiles.

5,11-Bis(3-(2,4,6-trimethylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetra-pentylresorcin[4]arene dibromide (8). Yield: 0.570 g, 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.94 (s, 2H, NCHN), 7.52 (s, 2H, NC*H*CHN), 7.29 (s, 2H, NCHC*H*N), 7.17 (s, 2H, arom. CH of resorcinarene), 7.06 (s, 2H, arom. CH of resorcinarene), 6.96 (s, 4H, arom. CH of Mes), 6.58 and 4.61 (AB spin system, 2H, OCH_2O, ^2J = 7.4 Hz), 6.53 (s, 2H, arom. CH of resorcinarene), 6.14 and 4.57 (AB spin system, 4H, OCH_2O, ^2J = 7.3 Hz), 5.88 and 5.68 (AB spin system, 4H, $ArCH_2N$, ^2J = 14.0 Hz), 5.67 and 4.45 (AB spin system, 2H, OCH_2O, ^2J = 7.2 Hz), 4.71 (t, 1H, $CHCH_2$, ^3J = 7.9 Hz), 4.70 (t, 2H, $CHCH_2$, ^3J = 7.9 Hz), 4.68 (t, 1H, $CHCH_2$, ^3J = 7.9 Hz), 2.31 (s, 6H, CH_3 *para* of Mes), 2.25–2.11 (m, 8H, $CHCH_2$), 2.03 (s, 12H, CH_3 *ortho* of Mes), 1.41–1.26 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.88 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.13–138.16 (arom. C_{quat}), 137.59 (s, NCHN), 137.26–130.72 (arom. C_{quat}), 129.79 (s, arom. CH of Mes), 123.55, 122.94 (2 s, NCHCHN), 121.97 (s, arom. CH of resorcinarene), 120.36 (arom. C_{quat}), 120.05, 116.94 (2 s, arom. CH of resorcinarene), 100.87 (s, OCH_2O), 100.68 (s, OCH_2O), 99.64 (s, OCH_2O), 43.96 (s, $ArCH_2N$), 36.73 (s, $CHCH_2$), 36.52 (s, $CHCH_2$), 36.31 (s, $CHCH_2$), 32.02 (s, $CH_2CH_2CH_3$), 31.91 (s, $CH_2CH_2CH_3$), 31.79 (s, $CH_2CH_2CH_3$), 29.95 (s, $CHCH_2$), 29.84 (s, $CHCH_2$), 29.54 (s, $CHCH_2$), 27.57 (s, $CHCH_2CH_2$), 27.48 (s, $CHCH_2CH_2$), 27.40 (s, $CHCH_2CH_2$), 22.68 (s, CH_2CH_3), 22.62 (s, CH_2CH_3), 22.58 (s, CH_2CH_3), 21.07 (s, CH_3 *para* of Mes), 17.60 (s, CH_3 *ortho* of Mes), 14.08 (s, CH_2CH_3). Anal. calcd. for $C_{78}H_{92}O_8N_4Br_2$ (M_r = 1373.39): C 68.21, H 6.75, N 4.08%; found: C 68.25, H 6.84, N 4.18%. MS (ESI-TOF): m/z = 607.36 $[M - Br_2]^{2+}$ expected isotopic profiles.

5,11-Bis(3-(2,6-diisopropylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetra-pentylresorcin[4]arene dibromide (9). Yield: 0.810 g, 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 2H, NCHN), 7.55 (s br, 2H, NC*H*CHN), 7.51 (t, 2H, arom. CH of ^{i}Pr$_2$C$_6$H$_3$, ^3J = 7.7 Hz), 7.29 (s br, 2H, NCHC*H*N), 7.27 (d, 4H, arom. CH of ^{i}Pr$_2$C$_6$H$_3$, ^3J = 7.7 Hz), 7.19 (s, 2H, arom. CH of resorcinarene), 7.07 (s, 2H, arom. CH of resorcinarene), 6.58 and 4.60 (AB spin system, 2H, OCH_2O, ^2J = 7.2 Hz), 6.54 (s, 2H, arom. CH of resorcinarene), 6.14 and 4.60 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 6.01 and 5.72 (AB spin system, 4H, $ArCH_2N$, ^2J = 14.1 Hz), 5.68 and 4.44 (AB spin system, 2H, OCH_2O, ^2J = 7.0 Hz), 4.74 (t, 1H, $CHCH_2$, ^3J = 8.2 Hz), 4.68 (t, 2H, $CHCH_2$, ^3J = 8.4 Hz), 4.66 (t, 1H, $CHCH_2$, ^3J = 8.4 Hz), 2.32–2.09 (m, 12H, $CHCH_2$ and $CH(CH_3)_2$), 1.42–1.29 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.20 (d, 3H, $CH(CH_3)_2$, ^3J = 6.7 Hz), 1.19 (d, 6H, $CH(CH_3)_2$, ^3J = 6.7 Hz), 1.18 (d, 3H, $CH(CH_3)_2$, ^3J = 6.8 Hz), 1.13 (d, 6H, $CH(CH_3)_2$, ^3J = 6.6 Hz), 1.12 (d, 6H, $CH(CH_3)_2$, ^3J = 6.6 Hz), 0.90 (t, 3H, CH_2CH_3, ^3J = 6.8 Hz), 0.89 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.88 (t, 3H, CH_2CH_3, ^3J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.20–138.50 (arom. C_{quat}), 138.28 (s, NCHN), 138.14, 137.19 (arom. C_{quat}), 131.81 (s, arom. CH of ^{i}Pr$_2$C$_6$H$_3$), 130.21 (arom. C_{quat}), 124.63 (s, arom. CH of ^{i}Pr$_2$C$_6$H$_3$), 124.38, 122.86 (2 s, NCHCHN), 121.92 (s, arom. CH of resorcinarene), 120.59 (arom. C_{quat}), 120.44, 116.93 (2 s, arom. CH of resorcinarene), 100.95 (s, OCH_2O), 100.93 (s, OCH_2O), 99.70 (s, OCH_2O), 43.95 (s, $ArCH_2N$), 36.85 (s, $CHCH_2$), 36.51 (s, $CHCH_2$), 36.31 (s, $CHCH_2$), 32.02 (s, $CH_2CH_2CH_3$), 31.91 (s, $CH_2CH_2CH_3$), 31.88 (s, $CH_2CH_2CH_3$), 29.93 (s, $CHCH_2$), 29.87 (s, $CHCH_2$), 29.61 (s, $CHCH_2$), 28.62 (s, $CH(CH_3)_2$), 27.58 (s, $CHCH_2CH_2$), 27.56 (s, $CHCH_2CH_2$), 27.52 (s, $CHCH_2CH_2$), 24.62 (s, $CH(CH_3)_2$), 24.57 (s, $CH(CH_3)_2$), 23.92 (s, $CH(CH_3)_2$), 23.90 (s, $CH(CH_3)_2$), 22.68 (s, CH_2CH_3), 22.63 (s,

CH_2CH_3), 14.09 (s, CH_2CH_3), 14.08 (s, CH_2CH_3). Anal. calcd. for $C_{84}H_{106}O_8N_4Br_2{\cdot}CHCl_3$ (M_r = 1459.57 + 119.38): C 64.66, H 6.83, N 3.55%; found: C 64.78, H 6.62, N 3.37%. MS (ESI-TOF): m/z = 649.91 $[M - Br_2]^{2+}$ expected isotopic profile.

5,11,17,23-Tetra(3-butyl-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin-[4]arene tetrabromide (11). Yield: 0.652 g, 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (s, 4H, NCHN), 7.54 (s, 4H, NC*H*CHN), 7.26 (s, 4H, NCHC*H*N), 7.10 (s, 4H, arom. CH of resorcinarene), 6.58 and 4.58 (AB spin system, 8H, OCH_2O, ^2J = 6.2 Hz), 5.45 (s, 8H, $ArCH_2N$), 4.67 (t, 4H, C*H*CH_2, ^3J = 7.7 Hz), 4.33 (t, 8H, NC*H*$_2$$CH_2$, ^3J = 6.9 Hz), 2.18–2.10 (m, 8H, CHC*H*$_2$), 1.87 (quint, 8H, NCH_2CH_2, J = 6.9 Hz), 1.40–1.24 (m, 32H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$ of resorcinarene and C*H*$_2$$CH_3$ of N^{n}Bu), 0.91 (t, 12H, CH_2CH_3 of resorcinarene, ^3J = 7.3 Hz), 0.84 (t, 12H, CH_2CH_3 of N^{n}Bu, ^3J = 7.0 Hz);^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.58, 138.51 (arom. C_{quat}), 136.54 (s, NCHN), 122.34, 122.23 (2 s, NCHCHN), 121.59 (s, arom. CH of resorcinarene), 120.68 (arom. C_{quat}), 100.76 (s, OCH_2O), 49.89 (s, NCH_2CH_2), 43.40 (s, $ArCH_2N$), 36.84 (s, *C*HCH_2), 32.11 (s, NCH_2CH_2), 31.95 (s, *C*$H_2CH_2CH_3$ of resorcinarene), 29.80 (s, CH*C*H_2), 27.46 (s, $CHCH_2CH_2$), 22.55 (s, *C*H_2CH_3 of resorcinarene), 19.46 (s, *C*H_2CH_3 of N^{n}Bu), 14.09 (s, CH_2CH_3 of resorcinarene), 13.51 (s, CH_2CH_3 of N^{n}Bu). Anal. calcd. for $C_{84}H_{116}O_8N_8Br_4{\cdot}CHCl_3$ (M_r = 1685.48 + 119.38): C 56.56, H 6.53, N 6.20%; found: C 56.48, H 6.32, N 6.27%. MS (ESI-TOF): m/z = 481.94 $[M - Br_3]^{3+}$ and 341.23 $[M - Br_4]^{4+}$ expected isotopic profiles.

5,11,17,23-Tetra-(3-phenyl-1-imidazolylium)-methyl-4(24),6(10),12(16),18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene tetrabromide (12). Yield: 0.723 g, 97%. ^{1}H NMR (300 MHz, DMSO): δ = 10.13 (s, 4H, NCHN), 8.38 (s, 4H, NC*H*CHN), 7.89 (s, 4H, NCHC*H*N), 7.87–7.84 (m, 12H, arom. CH of NPh), 7.71–7.59 (m, 12H, arom. CH of resorcinarene and NPh), 6.47 and 4.54 (AB spin system, 8H, OCH_2O, ^2J = 7.7 Hz), 5.42 (s, 8H, $ArCH_2N$), 4.67 (t, 4H, C*H*CH, ^3J = 7.7 Hz), 2.48–2.42 (m, 8H, CHC*H*$_2$), 1.38–1.24 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 0.82 (t, 12H, CH_2CH_3, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, DMSO): δ = 155.40, 139.06 (arom. C_{quat}), 135.85 (s, NCHN), 135.04 (arom. C_{quat}), 130.59, 130.34 (2 s, arom. CH of NPh), 124.61 (s, arom. CH of resorcinarene), 123.77 (s, N*C*HCHN), 122.55 (s, arom. CH of NPh), 122.13 (s, NCH*C*HN), 120.81 (arom. C_{quat}), 100.36 (s, OCH_2O), 43.37 (s, $ArCH_2N$), 37.61 (s, *C*HCH_2), 31.82 (s, *C*$H_2CH_2CH_3$), 29.63 (s, CH*C*H_2), 27.72 (s, $CHCH_2CH_2$), 22.64 (s, *C*H_2CH_3), 14.37 (s, CH_2CH_3). Anal. calcd. for $C_{92}H_{100}O_8N_8Br_4$ (M_r = 1765.44): C 62.59, H 5.71, N 6.35%; found: C 6.43, H 5.75, N 6.12%. MS (ESI-TOF): m/z = 1685.59 $[M - Br]^+$ expected isotopic profiles.

5,11,17,23-Tetra(3-(2,4,6-trimethylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16), 18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene tetrabromide (13). Yield: 0.773 g, 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.61 (s, 4H, NCHN), 7.51 (s, 4H, NC*H*CHN), 7.39 (s, 4H, NCHC*H*N), 7.21 (s, 4H, arom. CH of resorcinarene), 6.91 (s, 8H, arom. CH of Mes), 6.51 and 4.63 (AB spin system, 8H, OCH_2O, ^2J = 7.3 Hz), 5.67 (s br, 8H, $ArCH_2N$), 4.69 (t, 4H, C*H*CH_2, ^3J = 7.7 Hz), 2.29 (s, 12H, CH_3 *para* of Mes), 2.25–2.13 (m, 8H, CHC*H*$_2$), 1.98 (s, 24H, CH_3 *ortho* of Mes), 1.36–1.25 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 0.84 (t, 12H, CH_2CH_3, ^3J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.55, 140.92, 138.62 (3 s, arom. C_{quat}), 137.22 (s, NCHN), 134.33, 130.77 (2 s, arom. C_{quat}), 129.71 (s, arom. CH of Mes), 124.08, 123.15 (2 s, NCHCHN), 122.09 (s, arom. CH of resorcinarene), 120.62 (arom. C_{quat}), 101.05 (s, OCH_2O), 43.86 (s, $ArCH_2N$), 36.77 (s, *C*HCH_2), 31.72 (s, *C*$H_2CH_2CH_3$), 29.65 (s, CH*C*H_2), 27.35 (s, $CHCH_2CH_2$), 22.56 (s, *C*H_2CH_3), 21.09 (s, CH_3 *para* of Mes), 17.65 (s, CH_3 *ortho* of Mes), 14.09 (s, CH_2CH_3). Anal. calcd. for $C_{104}H_{124}O_8N_8Br_4{\cdot}CHCl_3$ (M_r = 1933.76 + 119.38): C 61.42, H 6.14, N 5.46%; found: C 61.39, H 6.34, N 5.57%. MS (ESI-TOF): m/z = 403.09 $[M - Br_4]^{4+}$ expected isotopic profiles.

5,11,17,23-Tetra(3-(2,6-diisopropylphenyl)-1-imidazolylium)-methyl-4(24),6(10),12(16), 18(22)-tetra-methylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene tetrabromide (14). Yield: 0.813 g, 92%. ^{1}H NMR (300 MHz, acetone-d_6): δ = 10.12 (s, 4H, NCHN), 8.44 (s, 4H, NC*H*CHN), 7.78 (s, 4H, NCHC*H*N), 7.78 (s, 4H, arom. CH of resorcinarene), 7.67 (t, 4H, arom. CH of $^iPr_2C_6H_3$, ^3J = 7.8 Hz), 7.40 (d, 8H, arom. $^iPr_2C_6H_3$, ^3J = 7.8 Hz), 6.70 and 4.68 (AB spin system, 8H, OCH_2O, ^2J = 7.9 Hz), 5.88 (s, 8H, $ArCH_2N$), 4.82 (t, 4H, C*H*CH_2, ^3J = 8.1 Hz), 2.85–2.77 (m, 8H, CHC*H*$_2$), 2.44 (hept, 8H, C*H*$(CH_3)_2$, ^3J = 6.6 Hz), 1.48–1.30 (m, 24H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 1.12 (d, 48H, CH(C*H*$_3$)$_2$, ^3J = 6.6 Hz), 0.89 (t, 12H, CH_2CH_3, ^3J = 6.8 Hz); ^{13}C NMR (75 MHz, acetone-d_6): δ = 153.42, 145.63, 139.40 (3 s, arom. C_{quat}), 138.84 (s, NCHN), 131.52 (s, arom. CH of $^iPr_2C_6H_3$), 130.72 (arom. C_{quat}), 126.01, 124.61 (2 s, NCHCHN), 124.47 (s, arom. CH of $^iPr_2C_6H_3$), 122.93 (s, arom. CH of resorcinarene), 120.65 (arom. C_{quat}), 101.60 (s, OCH_2O), 43.94 (s, $ArCH_2N$), 37.86 (s, *C*HCH_2), 31.46 (s, *C*$H_2CH_2CH_3$), 29.93 (s, CH*C*H_2), 28.29 (s, *C*H$(CH_3)_2$), 27.77 (s, $CHCH_2CH_2$), 24.04 (s, CH(*C*H_3)$_2$), 23.16 (s, CH(*C*H_3)$_2$), 22.58 (s, *C*H_2CH_3), 13.58 (s, CH_2CH_3). Anal. calcd. for $C_{116}H_{148}O_8N_8Br_4{\cdot}CHCl_3$ (M_r = 2102.08 + 119.38): C 63.26, H 6.76, N 5.04%; found: C 63.01, H 6.51, N 4.87%. MS (ESI-TOF): m/z = 620.70 $[M - Br_3]^{3+}$ and 445.54 $[M - Br_4]^{4+}$ expected isotopic profiles.

Dibromido-5,11-bis{(3-diisopropyl-1-imidazol-2-idenyl-1-yl)-methyl}-4(24),6(10),12(16),18(22)-tetramethylene-dioxy-2,8,14,20-tetrapentylresorcin[4]arene disilver(I) (15). To a stirred solution of **9** (0.150 g, 0.12 mmol) in acetonitrile (30 mL) was added Ag_2O (0.028 g, 0.12 mmol). The solution was refluxed for 12 h. The reaction mixture was allowed to reach room temperature and was then filtered through a pad of Celite. The solvent was removed under vacuum. The residue was washed with hexane (2 × 10 mL) to afford **15** as a white solid (0.161 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (s, 2H, CH of resorcinarene), 7.13 (d, 2H, NC*H*CHN, ^3J = 1.6 Hz), 7.11 (s, 2H, CH of resorcinarene), 6.90 (d, 2H, NCHC*H*N, ^3J = 1.6 Hz), 6.53 (s, 2H, CH of resorcinarene), 6.52 and 4.57 (AB spin system, 2H, OCH_2O, ^2J = 6.8 Hz), 6.05 and 4.46 (AB spin system, 4H, OCH_2O, ^2J = 7.0 Hz), 5.76 and 4.43 (AB spin system, 2H, OCH_2O, ^2J = 7.1 Hz), 5.17 and 5.05 (AB spin system, 4H, $ArCH_2N$, ^2J = 13.8 Hz), 4.73 (2 overlapping t, 3H, C*H*CH_2, ^3J = 7.9 Hz), 4.71 (t, 1H, C*H*CH_2, ^3J = 7.7 Hz), 4.16–4.00 (m, 4H, NC*H*$_2$$CH_2$), 2.30–2.10 (m, 8H, CHC*H*$_2$), 1.77 (quint, 4H, NCH_2CH_2, ^3J = 7.5 Hz), 1.43–1.28 (m, 28H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$ of resorcinarene and C*H*$_2$$CH_3$ of N^{n}Bu), 0.93 (t, 12H, CH_2CH_3 of resorcinarene, ^3J = 7.3 Hz), 0.90 (t, 6H, CH_2CH_3 of N^{n}Bu, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.42 (s, NCN), 155.10–121.84 (arom.

C_{quat}), 121.37, 121.17 (2 s, NCHCHN), 120.87, 120.43, 116.62 (3 s, arom. CH of resorcinarene), 99.54 (s, OCH_2O), 99.52 (s, OCH_2O), 99.50 (s, OCH_2O), 51.77 (s, NCH_2CH_2), 45.62 (s, $ArCH_2N$), 36.92 (s, $CHCH_2$), 36.73 (s, $CHCH_2$), 36.40 (s, $CHCH_2$), 33.50 (s, NCH_2CH_2), 32.06 (s, $CH_2CH_2CH_3$ of resorcinarene), 32.03 (s, $CH_2CH_2CH_3$ of resorcinarene), 32.01 (s, $CH_2CH_2CH_3$ of resorcinarene), 29.99 (s, $CHCH_2$), 29.92 (s, $CHCH_2$), 29.87 (s, $CHCH_2$), 27.60 (s, $CHCH_2CH_2$), 27.55 (s, $CHCH_2CH_2$), 27.52 (s, $CHCH_2CH_2$), 22.72 (s, CH_2CH_3 of resorcinarene), 22.68 (s, CH_2CH_3 of resorcinarene), 22.64 (s, CH_2CH_3 of resorcinarene), 19.78 (s, CH_2CH_3 of N^{n}Bu), 14.11 (s, CH_2CH_3 of resorcinarene), 13.70 (s, CH_2CH_3 of N^{n}Bu). Anal. calcd. for $C_{68}H_{88}Ag_2O_8N_4Br_2$ (M_r = 1465.00) C 55.75, H 6.05, N 3.82%; found: C 55.62, H 5.87, N 4.08%. MS (MALDI-TOF): m/z = 1385.28 $[M - Br]^+$ expected isotopic profile.

Crystallography

Single crystals of **8·3 $CHCl_3$·^{i}Pr_2O** suitable for diffraction study were obtained by slow diffusion of diisopropyl ether into a chloroform solution of **8**. Mr = 1833.70, monoclinic, space group $P2_1/c$, a = 15.9979(3), b = 29.8312(5), c = 20.5629(5) Å, β = 105.044(3)°, V = 9477.0(3) Å^3, Z = 4, D_x = 1.275 mg m^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 1.161 mm^{-1}, F(000) = 3788, T = 110(2)K. Data were collected on an Oxford Diffraction CCD Sapphire 3 Xcalibur diffractometer (graphite MoK_a radiation, λ = 0.71073 Å). The structure was solved with SHELX-97[33] and full-matrix least-square techniques (use of F^2; x, y, z, b_{ij} for C, N, O, Cl and Br atoms, x, y, z in riding mode for H atoms; 1004 variables and 6327 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.1725P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. R_1 = 0.095, wR_2 = 0.307, S_w = 0.873, $\Delta\rho$ < 1.313eÅ^{-3}. The level A alerts in the checkcif file mainly reflect the presence of two strongly disordered diisopropyl ether molecules. The use of the SQUEEZE option in PLATON did not improve resolution. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre under deposition number 737674. This data is given in the ESI†.

General procedure for palladium-catalysed Suzuki–Miyaura cross-coupling reactions

In a Schlenk tube under an inert atmosphere a solution of $[Pd(OAc)_2]$ in DMF, a solution of the ligand in DMF, aryl bromide (0.5 mmol), phenylboronic acid (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL, internal reference) and an additional amount of DMF (so that the total reaction volume was 1.5 mL) were introduced. The reaction mixture was then heated for 1 h at 100 °C. Thus, the 1 h reaction period included the period of time needed for generating the active species. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analyzed by GC.

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