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Resorcinarene-Functionalised Imidazolium Salts as Ligand Precursors for Palladium-Catalysed Suzuki–Miyaura Cross-Couplings

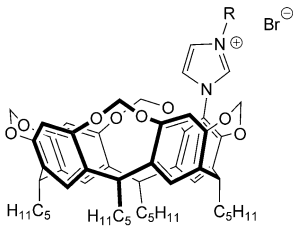
Neslihan Şahin,[a, c] David Sémeril,*[a] Eric Brenner,*[a] Dominique Matt,*[a] İsmail Özdemir,[b] Cemal Kaya,[c] and Loïc Toupet[d]

Three imidazolium salts based on a rigid resorcinarene platform (**1**–**3**) were synthesised and used as catalyst precursors in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid. In these pro-carbene ligands, the heterocyclic moiety has one N atom connected to a C2 atom of a resorcinolic ring, and the other is substituted by an alkyl group (R = *n*-propyl, *iso*-propyl, benzyl). The methinic C atoms of the macrocyclic core are all substituted by a pentyl group. The best catalytic performances were obtained by using an imidazolium/Pd ratio of 1:1. The catalytic systems displayed high activities, which increased in the order R = *n*-propyl (**1**) < *i*-propyl (**2**) < benzyl (**3**). For example, the use of **3** resulted in activities up to 30 100 mol(converted ArX) mol(Pd)$^{-1}$ h^{-1} in the arylation of bromotoluene at 100 °C in dioxane. Comparative studies showed that the performance of imidazolium salt **3** is significantly superior to that of related salts devoid of a cavity-shaped substituent. These experiments illustrate the role of the bulky resorcinarene unit, which facilitates the reductive elimination step. Modification of the cavitand structure by replacement of the pentyl substituents with phenyl groups further revealed that the catalytic outcome is influenced by the nature of the lower belt-substituents. The results strongly suggest that the Pd catalysts obtained from **1**–**3** have the metal centre preferentially located outside the cavity.

Introduction

Resorcinarenes are macrocyclic compounds that are formed in high yield by the reaction of resorcinol with an aldehyde under acidic conditions.[1] Their large backbone can be conveniently rigidified by linking the hydroxyl groups of neighbouring aryl rings with short bridges, thereby forming so-called resorcinarene cavitands (RCs).[2] These conical molecules have been extensively utilised for the design of sophisticated podands that exploit the presence of a rigid, pre-organised platform, a cavity-shaped structure suitable for substrate entrapment or both.[3–7] Functionalisation of a generic RC is typically achieved at the bridging C2 C atoms. In contrast to their calixarene analogues,[8–10] the number of RC-derived ligands that have been applied in homogeneous catalysis remains small.[11–14] Besides potential receptor properties, monodentate ligands that incorporate expanded resorcinarenyl units are expected to have steric interactions with the first coordination sphere of a complex rather than with the metal itself. It may also be anticipated that the resorcinarenyl substituent should provide very effective protection of the catalytic centre and possibly increase the catalyst's lifetime if it functions as a cavity able to embed metal–organic moieties.

As an extension to our studies on N-heterocyclic carbene (NHC) complexes,[14,15] we now describe the synthesis of the resorcinarenyl monoimidazolium salts **1**–**3** and their use in



1: R = *n*Pr
2: R = *i*Pr
3: R = Bn

[a] Dr. N. Şahin, Dr. D. Sémeril, Dr. E. Brenner, Dr. D. Matt
Université de Strasbourg
Laboratoire de Chimie Inorganique Moléculaire et Catalyse
UMR 7177 CNRS, 1 rue Blaise Pascal, 67008 Strasbourg Cedex (France)
E-mail: dsemeril@unistra.fr
brenner@unistra.fr
dmatt@unistra.fr

[b] Prof. İ. Özdemir
Department of Chemistry
Faculty of Science and Art
Inönü University
Malatya, TR 44280 (Turkey)

[c] Dr. N. Şahin, Prof. C. Kaya
Department of Chemistry
Faculty of Science
Cumhuriyet University
Sivas, TR 58140 (Turkey)

[d] L. Toupet
Institut de Physique, UMR 6251 CNRS
Université de Rennes 1
Campus de Beaulieu, 35042-Rennes Cedex (France)

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Suzuki–Miyaura cross-coupling reactions. These monodentate pro-ligands constitute the first examples of cavitands in which a resorcinarenic C2 atom is directly linked to the N atom of an imidazolium ring. The close proximity of the cavity and the pro-carbenic centre is expected to afford metal complexes with a highly crowded metal environment, which will consequently promote cross-coupling reactions. NHCs derived from imidazolium ions are now well-established ligands in organometallic catalysis.[16–22]

Results and Discussion

The imidazolium salts **1**–**3** were prepared according to Scheme 1. The first step consisted of an Ullmann coupling between the mono-brominated cavitand **4** and imidazole in the presence of CuI/*N*,*N*′-dimethylethylenediamine (DMEDA) in DMF with K_2CO_3 as a base,[15] which led to the imidazolyl resorcinarene **5** in 75% yield. Compound **5** was then alkylated with three alkylbromides (RBr; R = *n*-propyl, *iso*-propyl, benzyl), which resulted in the corresponding imidazolium salts **1**–**3** (yields: 95, 97 and 92%, respectively). Consistent with C_s symmetry, the ^{1}H NMR spectrum of each imidazolium salt displayed two AB patterns for the four OCH_2O groups and two methine triplets (intensity 2:2).

The solid-state structure of **3** was established by a single-crystal XRD study (Figure 1). The core of the molecule adopts the typical bowl-shaped structure found in numerous other resorcinarene cavitands, with separations between the opposed pairs of C2 atoms of 7.91 and 8.00 Å. The imidazolium ring is nearly perpendicular to the appended aromatic ring, and the NC–H bond is turned away from the cavity. A molecule of diisopropyl ether is poised above the larger cavity entrance, and the bromide anion sits on the opposite side.

NHC complexes derived from **1**–**3** were obtained straightforwardly by applying well-established procedures (Scheme 2). Thus, the reaction of [$PdCl_2$] with two equivalents of **2** in the presence of KBr and Cs_2CO_3 in dioxane at 80 °C afforded **6**. The *trans* stereochemistry of **6** was deduced from the ^{13}C NMR chemical shift of the carbenic C atom to 173.50 ppm, which lies in the expected range.[15]

The pre-catalytic Pd^{II} complex **7**, which, unlike **6**, contains only a single NHC ligand, was obtained in high yield by reacting **3** with [$PdCl_2$] in pyridine in the presence of KBr and K_2CO_3. The proceedure used for this synthesis is similar to that reported by Organ et al. for other Pd^{II}-NHC-pyridine complexes.[21] In the ^{13}C NMR spectrum, the carbenic C peak appears at 154.60 ppm. Similar values have been found for related mono-NHC complexes that have two *trans* bromido ligands.[15] The linear Br–Pd–Br arrangement was confirmed by an XRD study (Figure 2). In the solid state, the $PdBr_2$ unit is pushed towards the exterior of the cavity, and a molecule of diethyl ether sits in the upper part of the cavity. Interestingly, one of the pentyl chains attached to the ring that bears the NHC moiety approaches the pyridine moiety, and the shortest H···H separation is 2.30 Å. A ^{1}H-^{1}H ROESY NMR experiment clearly showed that a similar array persisted in solution. The question of whether in solution the $PdBr_2$–pyridine unit moves from a position outside to one inside the resorcinarene basket remains open, but molecular modelling indicates that there is a high rotational barrier about the N–$C_{resorcinarene}$ bond.

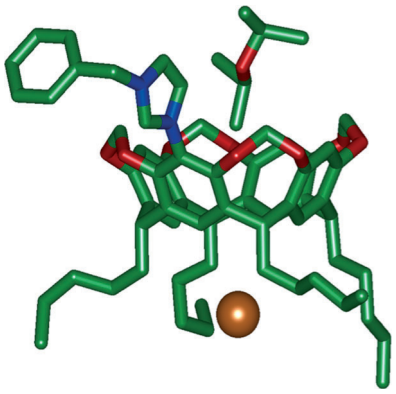
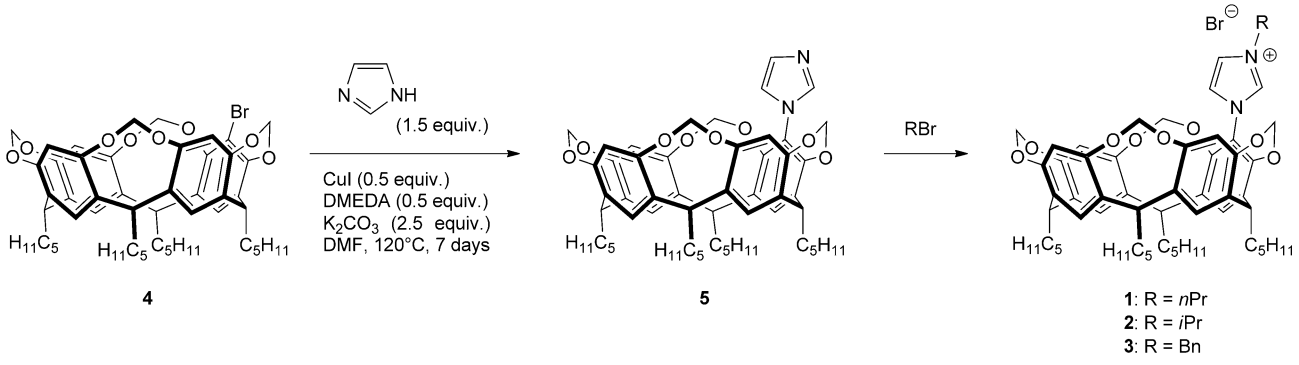
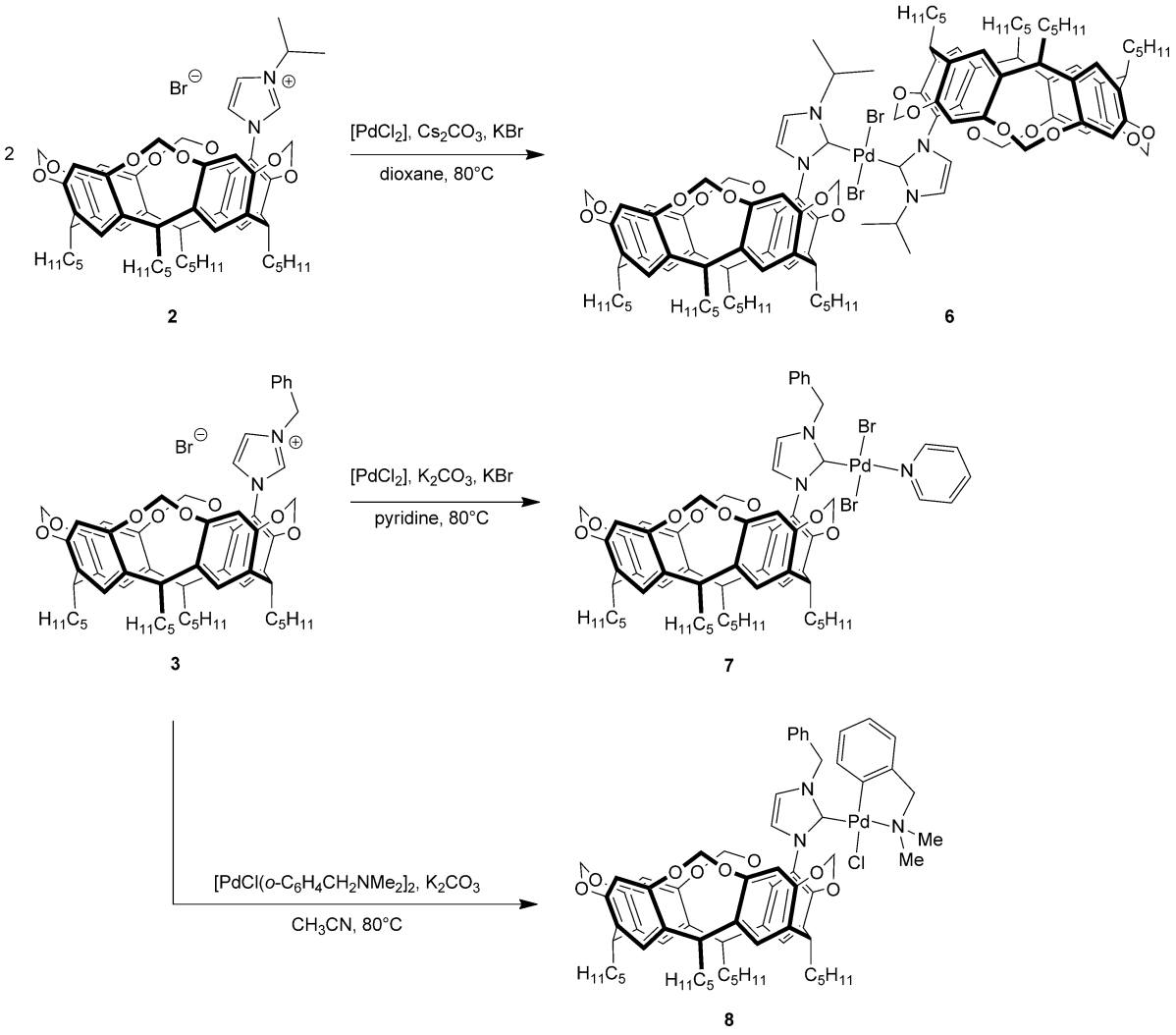


Figure 1. Molecular structure of **3**. For clarity, the molecule of dichloromethane located outside the cavity is not shown. Dihedral angle between the imidazolium ring and the connected resorcinol unit: 76.2°.

Treatment of **3** with [$PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$ in the presence of K_2CO_3 gave the expected Pd complex **8**. The ^{1}H NMR spectrum of **8** is consistent with a C_1-symmetric complex as it shows four AB patterns for the four OCH_2O groups, four methine triplets and an AB spectrum for the NCH_2 protons. The absence of any symmetry element in this complex likely reflects the hindered rotation of the $PdCl(o\text{-}C_6H_4CH_2NMe_2)$ unit



Scheme 1. Synthesis of imidazolium salts **1**–**3**.



Scheme 2. Synthesis of complexes **6**–**8**.

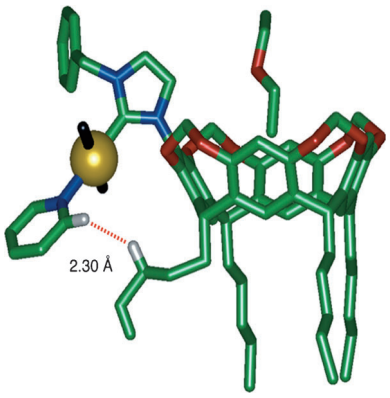


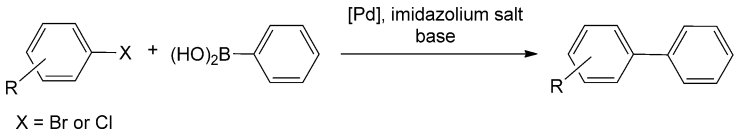
Figure 2. Molecular structure of **7**. A molecule of diethyl ether sits inside the cavity. For clarity, the solvent molecules located outside the cavity are not shown. Important distances [Å] and angles [°]: Pd–$C_{carbene}$ 1.968(6), Pd–N 2.082(6), Br1–Pd 2.423(1), Br2–Pd 2.416 (1), $C_{carbene}$–Pd–$N_{pyridine}$ 177.6(3), Br1–Pd–Br2 176.98(4).

around the $C_{carbene}$–Pd bond, which is a result of strong steric interactions between this moiety and the *N*-benzyl substituent.

Catalytic Suzuki–Miyaura cross-coupling—Optimisation of the catalytic conditions

The carbene precursors **1**–**3** were evaluated in the Suzuki–Miyaura cross-coupling between aryl bromides or aryl chlorides and phenylboronic acid in the presence of a base (Scheme 3). For the optimisation tests, the catalytic system was generated in situ from **2** and a Pd precursor. The runs were performed by using an aryl halide/Pd ratio of 10000. The conversions were determined after a reaction time of 1 h at 100 °C in 1,4-dioxane.

With 4-bromoanisole as substrate, we first investigated the influence of the Pd precursor (Table 1, entries 1–5). Five runs were carried out by using one equivalent of imidazolium salt per Pd. Under these conditions, the highest conversion was obtained with [Pd(OAc)$_2$] (conversion of 43.8%; Table 1, entry 5). Increasing the imidazolium salt/Pd ratio decreased the



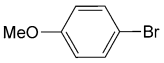
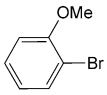
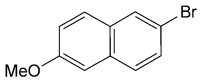
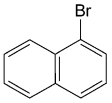
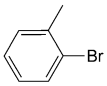
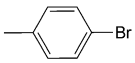
Scheme 3. Suzuki–Miyaura cross-coupling reaction.

Table 1. Suzuki–Miyaura cross-coupling of 4-bromoanisole with phenylboronic acid—the search for optimal conditions.[a]

Entry	Pd precursor	**2**/Pd	Base [mmol]	Conversion [%]
1	$[PdCl(\eta^3\text{-}C_3H_5)]$	1/1	NaH (1)	25.9
2	$[PdCl_2(PhCN)_2]$	1/1	NaH (1)	19.0
3	$[PdCl_2(cod)]$[b]	1/1	NaH (1)	30.1
4	$[Pd(dba)_2]$[c]	1/1	NaH (1)	28.5
5	$[Pd(OAc)_2]$	1/1	NaH (1)	43.8
6	$[Pd(OAc)_2]$	1.5/1	NaH (1)	36.5
7	$[Pd(OAc)_2]$	2/1	NaH (1)	22.9
8	$[Pd(OAc)_2]$	2.5/1	NaH (1)	19.8
9	$[Pd(OAc)_2]$	5/1	NaH (1)	20.8
10	$[Pd(OAc)_2]$	1/1	NaH (0.75)	47.3
11	$[Pd(OAc)_2]$	1/1	*t*BuOK (0.75)	17.7
12	$[Pd(OAc)_2]$	1/1	NaOH (0.75)	9.8
13	$[Pd(OAc)_2]$	1/1	K_3PO_4 (0.75)	19.6
14	$[Pd(OAc)_2]$	1/1	Cs_2CO_3 (0.75)	26.5

[a] Conditions: Pd precursor (5×10^{-5} mmol, 1×10^{-2} mol%), **2**, 4-bromoanisole (0.5 mmol), $PhB(OH)_2$ base (1 equiv.), dioxane (1.5 mL), decane (0.05 mL), 100 °C, 1 h. The conversions were determined by GC for which the calibrations were based on decane. [b] cod = 1,5-Cyclooctadiene. [c] dba = Dibenzylideneacetone.

Table 2. Suzuki–Miyaura cross-coupling of aryl bromides catalysed by $[Pd(OAc)_2]$/imidazolium salts.

Entry	ArBr	Conversion [%]		
		1	**2**	**3**
1[a]		44.0	47.3	59.0
2[a]		12.1	27.8	35.1
3[a] 4[b]		33.2	41.6	68.8 14.0
5[a]		28.8	27.8	50.9
6[a]		14.1	9.0	58.9
7[a] 8[b]		43.5	52.7	74.6 30.1

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), imidazolium salt (5×10^{-5} mmol, 1×10^{-2} mol%), ArBr (0.5 mmol), $PhB(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil, 0.030 g, 0.75 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C, 1 h. The conversions were determined by GC for which the calibrations were based on decane. [b] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol%), **3** (5×10^{-6} mmol, 1×10^{-3} mol%).

conversion, which dropped to 20% for an imidazolium/Pd ratio of 2 (Table 1, entries 5–9). This observation strongly suggests that the active species of the catalytic reaction contains only one carbene ligand per Pd. Notably, by performing the arylation of 4-bromoanisole with complex **6** under the conditions of Table 1, entry 7, a conversion similar to that obtained by mixing $[Pd(OAc)_2]$ with two equivalents of imidazolium salt **2** was observed (Table S7, entries 1 and 2). Finally, we found that by using 1.5 equivalents of NaH instead of two per 4-bromoanisole resulted in slightly better conversions (47.3 vs. 43.8%; Table 1, entries 5 and 10). Other bases led to lower conversions (Table 1, entries 10–14). In the following experiments, we therefore used only 1.5 equivalents of NaH per mole of aryl halide.

Catalytic Suzuki–Miyaura cross-coupling of aryl bromides

For all tests, we applied the optimal conditions defined above ($[Pd(OAc)_2]$, 1.5 equivalents of NaH/ArBr, dioxane, 100 °C). As a general trend, we observed an increase of reactivity with increasing bulkiness of the R group (**1** < **2** < **3**; Table 2). For example, in the arylation of 4-bromotoluene, conversions up to 74.6% were observed after 1 h by using the most crowded salt **3** (Table 2, entry 7). *Ortho*-substituted aryl bromides could also be converted into biaryls, and conversions of 35.1 and 58.9% were observed with imidazolium salt **3** in the arylation of 2-bromoanisole and 2-bromotoluene, respectively (Table 2, entries 2 and 6). As expected, higher conversions were obtained when the reaction time was increased. Thus, 2-bromo-6-methoxynaphthalene and 4-bromotoluene were converted in 85.4 and 92.8% yield, respectively, when the reaction was performed for 2 h instead of 1 h (Table S6, entries 3 and 6). If the catalyst loading was reduced by an order of magnitude, the conversion still reached 14% after 1 h in the arylation of 2-bromo-6-methoxynaphthalene and 30.1% for the arylation of 4-bromotoluene (turnover frequency (TOF) = 14000 and 30100 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}, respectively; Table 2, entries 4 and 8). Notably, under these conditions the catalyst was still active after 4 h after which the conversion reached 100%. This conversion corresponds to a turnover number (TON) of 100000 (Table 3). Repeating the cross-coupling of 4-bromoanisole with complex **7** gave a conversion slightly higher than that obtained with the corresponding in-situ-generated catalyst (Table S7, entry 4 and Table 2, entry 1). Finally, the catalytic system based on **3** is 30 times more active than those derived from more flexible analogues in which the imidazolium ring is attached to the resorcinarene unit by a methylene linker.[14]

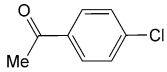
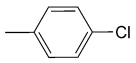
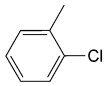
Less reactive aryl chlorides could also be converted efficiently into biaryls if 1 mol% of Pd at 100 °C was used. After 1 h, 4-chlorobenzaldehyde, 4-chorotoluene and 2-chlorotoluene were converted into biaryls in 84.2, 81.3 and 85.7% yield, respectively (Table 4, entries 2, 6 and 9). In the cross-coupling of aryl

Table 3. Suzuki–Miyaura cross-coupling of 4-bromotoluene catalysed by $[Pd(OAc)_2]$/**3**.[a]

Entry	*t* [h]	Conversion [%]	TON [mol(ArBr) mol(Pd)$^{-1}$]	TOF [mol(ArBr) mol(Pd)$^{-1}$ h^{-1}]
1	1	30.1	30100	30100
2	2	55.7	55700	27850
3	4	96.9	96900	24225
4	6	100	100000	16700

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol%), **3** (5×10^{-6} mmol, 1×10^{-3} mol%), ArBr (0.5 mmol), $PhB(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil, 0.030 g, 0.75 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C. The conversions were determined by GC for which the calibrations were based on decane.

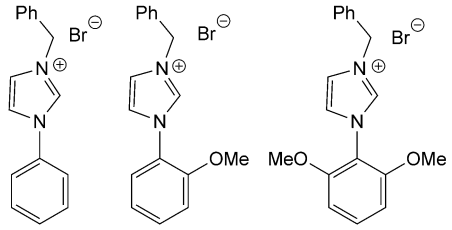
Table 4. Suzuki–Miyaura cross-coupling of aryl chlorides catalysed by $[Pd(OAc)_2]$/**3**.[a]

Entry	ArCl	$[Pd(OAc)_2]$ [mol%]	*T* [°C]	*t* [h]	Conv. [%]	Product distribution [%] Ar–Ph	Ar–H
1		0.1	100	3	43.0	40.1	2.9
2		1	100	1	87.4	84.2	3.2
3		1	50	24	84.7	61.3	23.4
4		1	25	24	0	–	–
5		0.1	100	5	38.7	21.9	16.8
6		1	100	1	100	81.3	18.7
7		1	50	24	100	70.6	29.4
8		0.1	100	16	73.6	69.5	4.1
9		1	100	1	88.7	85.7	3.0
10		1	50	24	16.8	16.3	0.5

[a] $[Pd(OAc)_2]$, **3** (1 equiv. relative to Pd), ArCl (0.25 mmol), $PhB(OH)_2$ (0.045 g, 0.37 mmol), dioxane (0.75 mL), NaH (60% dispersion in mineral oil, 0.015 g, 0.37 mmol), decane (0.025 mL). The conversions were determined by GC for which the calibrations were based on decane.

chlorides, the formation of significant amounts of dehalogenated products (ArH) was frequently observed. Furthermore, we found that the catalysis was effective at 50 °C, but longer reaction times were then needed (24 h). Under these conditions, unhindered substrates were converted in good yields (61.3 and 70.6% for 4-chlorobenzaldehyde and 4-chlorotoluene, respectively; Table 4, entries 3 and 7). Interestingly, the proportion of by-products increased when the rate of the cross-coupling reaction decreased, which suggests that transmetallation becomes more difficult at 50 °C. Notably, no reaction took place within 1 day at room temperature (Table 4, entries 3 and 4).

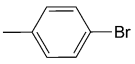
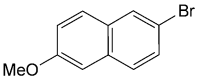
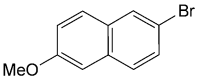
To evaluate the influence of the resorcinarene moiety on the catalytic outcome, three resorcinarene-free imidazolium salts related to **3** (**9**–**11**) were studied (Figure 3). In these heterocycles, the aryl substituent borne by one of the N atoms contained no (**9**), one (**10**) or two (**11**) *o*-methoxy substituents. The tests revealed that the higher the number of methoxy substituents, the higher the conversion. However, the conversions remained significantly lower than those obtained with the resorcinarenyl imidazolium salt **3** (Table 5). For example, with 4-bromotoluene, the imidazolium salts **9**, **10**, **11** and **3** led to conversions of 16.6, 26.3, 43.8 and 74.6%, respectively (Table 5, entry 1). The higher conversions observed for **11** compared to those of **9** and **10** possibly arise from its greater bulk (the presence of two methoxy substituents in *ortho* positions), which possibly promotes the elimination step during the catalytic process. Oxidative addition may also be favoured through hemilabile binding of the ether groups of **10** and **11**, but this effect is probably marginal as the oxidative addition of aryl halide is known to be very facile with the strong NHC donors. The high efficiency of the catalytic system derived from **3** likely relies on steric effects, either from the orientation of the $C_{carbene}$–Pd vector of the PdArAr′L intermediates towards the RC axis or if it is turned towards the exterior of the cavity. Should the former situation occur, then the whole cavity may exert a strong steric pressure on the two aryl moieties that undergo the coupling reaction (Figure 4a). If the $C_{carbene}$–Pd vector is oriented outwards, steric pressure may arise from the two pentyl groups (Figure 4b), which is suggested by the structural study of **7** (see above). To confirm the possible influence of the pentyl groups, we prepared imidazolium salt **14** with downwardly oriented phenyl groups attached to each methyne C atom. This carbene precursor was prepared in two steps from tetrabromocavitand **12**[23] via intermediate **13** (Scheme 4 and Experimental Section). Molecular models showed that in hypothetical Pd–carbene complexes derived from this ligand, no steric interactions between the downward-



9 **10** **11**

Figure 3. Salts used to rank the resorcinarenyl imidazolium salts.

Table 5. Comparison of imidazolium salts in the Suzuki–Miyaura cross-coupling of aryl bromides.[a]

Entry	ArBr	Conversion [%] **9**	**10**	**11**	**14**	**3**
1		16.5	26.3	43.8	44.9	74.6
2		7.0	22.4	35.2	37.9	68.8
3		6.6	13.1	23.6	28.7	50.9

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), imidazolium salt (5×10^{-5} mmol, 1×10^{-2} mol%), ArBr (0.5 mmol), $PhB(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil, 0.030 g, 0.75 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C, 1 h. The conversions were determined by GC for which the calibrations were based on decane.

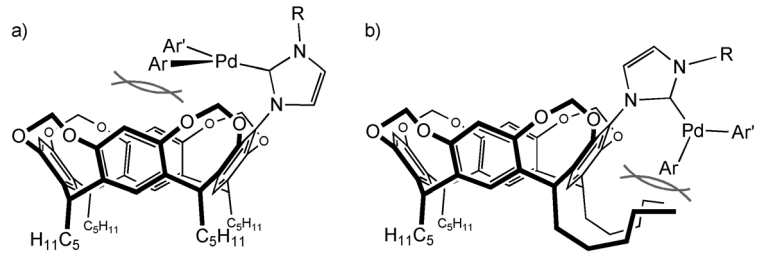
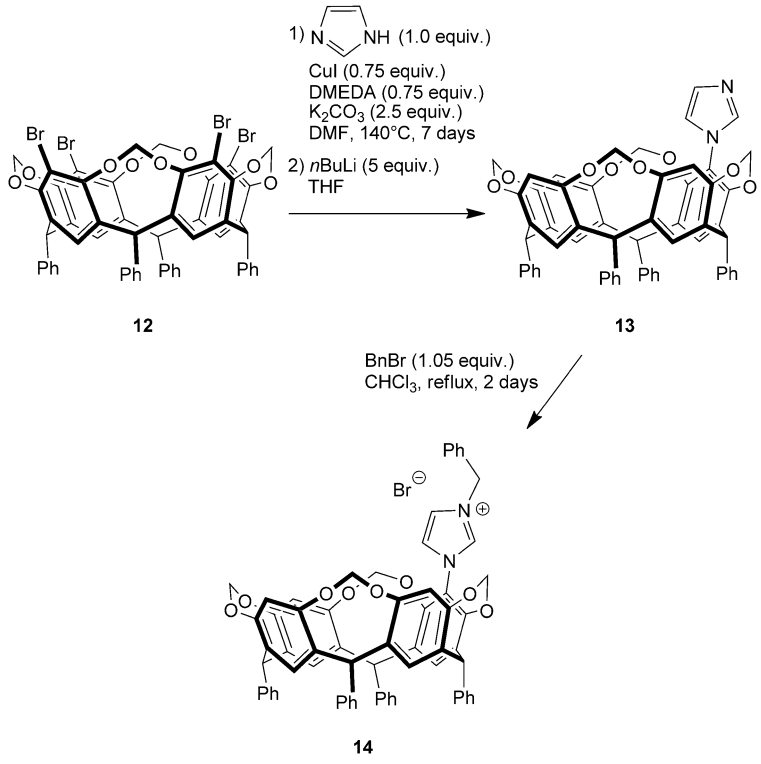


Figure 4. Possible steric interactions in catalytic intermediates derived from **1**–**3**.



Scheme 4. Synthesis of cavitand **14**.

ly oriented phenyl groups and the catalytic centre would occur.

Cross-coupling experiments performed with **14** showed that the performance of this salt compares with that of resorcinarene-free **11** as both compounds result in catalytic activities that lie significantly below that of **3** (Table 5). These findings strongly suggest that in the catalysts derived from **1**–**3**, the metal centre sits predominantly outside the cavity, if not permanently, so as to undergo steric interactions with the pentyl chains.

Conclusions

We have described the synthesis of three imidazolium-substituted resorcin[4]arene cavitands in which the heterocyclic ring is attached to a resorcinolic C2 atom by one of its N atoms. The imidazolium salts were straightforwardly converted into mono- and bis-carbene Pd complexes by using standard procedures. The solid-state structure of a NHC-Pd^{II} complex was determined by an XRD study, which showed that the carbenic unit is oriented away from the cavity. Combined with $[Pd(OAc)_2]$ and NaH, all three salts resulted in highly efficient Suzuki–Miyaura catalysts for the coupling of aryl halides with phenylboronic acid, the activity of which increased with increasing ligand size. TOFs up to 30100 mol(ArBr) mol(Pd)$^{-1}$ h^{-1} were obtained in the case of bromotoluene. A comparison of the performance of **3** with those of three analogues devoid of a cavity confirmed that the high activity observed for **3** arises from the presence of a bulky resorcinarenyl substituent, which possibly favours the reductive elimination step. Furthermore, the influence of the pentyl groups in **3** on the catalytic outcome was clearly demonstrated by the investigation of an analogue in which the pentyl groups had been replaced by substituents that cannot interact sterically with a Pd centre. The results of these investigations suggest that the Pd catalysts obtained from **1**–**3** have the metal centre preferentially located outside the cavity.

Experimental Section

General

All syntheses were performed in Schlenk-type flasks under dry N_2. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded by using Bruker AVANCE 300 or AVANCE 400 spectrometers. ^{1}H NMR spectra were referenced to residual protic solvents (7.26 ppm for $CDCl_3$) and ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$). Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177, Université de Strasbourg. The catalytic solutions were analysed by using a Varian 3900 GC equipped with a WCOT fused-silica column (25 m×0.25 mm). 5-Bromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**4**),[6] 5,11,17,23-tretrabromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetraphenylresorcin[4]arene (**12**),[23] 1-phenyl-1H-imidazole[24] and 1-(2-methoxyphenyl)-1H-imidazole[24] were prepared according to literature procedures.

Syntheses

5-*N*-Imidazolyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**5**): A mixture of monobromocavitand **4** (1.000 g, 1.12 mmol), imidazole (0.114 g, 1.67 mmol), K_2CO_3 (0.385 g, 2.79 mmol), DMEDA (0.074 g, 0.84 mmol) and CuI (0.159 g, 0.84 mmol) was dissolved in DMF (20 mL). The reaction mixture was stirred at 140 °C for a week. After cooling to room temperature, water (50 mL) and $CHCl_3$ (50 mL) were added to the mixture. The organic layer was separated and the aqueous phase extracted with $CHCl_3$ (2×50 mL). The combined organic layers were washed with aqueous disodium ethylenediaminetetraacetic acid (Na_4EDTA, 0.2 N, 3×50 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure.

The crude product was purified by flash chromatography (MeOH/CH_2Cl_2 4:96 v/v) to afford **5** in 75% yield (0.742 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (s br, 1H, NCHN), 7.23 (s br, 1H, NC*H*CHN), 7.16 (s, 1H, Ar CH), 7.14 (s, 3H, Ar CH), 6.81 (s br, 1H, NCHC*H*N), 6.50 (s, 1H, Ar CH), 6.49 (s, 2H, Ar CH), 5.77 and 4.40 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.51 and 4.37 (AB spin system, 4H, OCH_2O, ^2J = 6.9 Hz), 4.75 (t, 4H, $CHCH_2$, ^3J = 8.1 Hz), 2.29–2.20 (m, 8H, $CHCH_2$), 1.48–1.30 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.93 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.92 ppm (t, 6H, CH_2CH_3, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.03, 154.90, 154.60, 150.15 (4 s, Ar $C_{quat.}$), 137.88 (1 s, NCHN), 139.32, 138.90, 138.64, 137.80 (4 s, Ar $C_{quat.}$), 128.94, 124.57 (2 s, NCHCHN), 120.84, 120.57, 120.42, 116.78, 116.13 (5 s, Ar CH), 99.66 (s, OCH_2O), 36.72 (s, $CHCH_2$), 36.40 (s, $CHCH_2$), 32.01 (s, $CH_2CH_2CH_3$), 29.83 (s, $CHCH_2$), 27.55 (s, $CHCH_2CH_2$), 22.70 (s, CH_2CH_3), 14.11 ppm (s, CH_2CH_3); MS (ESI-TOF): *m/z*: 883.49 [M+H$^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{55}H_{66}N_2O_8$ (883.12): C 74.80, H 7.53, N 3.17; found: C 74.85, H 7.48, N 3.09.

General procedure for the preparation of the imidazolium salts **1** and **2**: A mixture of imidazolyl resorcinarene **5** (0.500 g, 0.57 mmol) and the corresponding alkyl bromide (≈6 mL) was heated under reflux for 1 day. After cooling to room temperature, the solution was evaporated to dryness. The residue was washed with petroleum ether and dried under vacuum. The product was used without further purification.

5-*N*-(3-Propyl-1-imidazolylium)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene bromide (**1**): Yield 95% (0.545 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.44 (s, 1H, NCHN), 7.33 (s br, 1H, NC*H*CHN), 7.30 (s, 1H, Ar CH), 7.19 (s br, 1H, NCHC*H*N), 7.10 (s, 3H, Ar CH), 6.60 (s, 2H, Ar CH), 6.49 (s, 1H, Ar CH), 5.70 and 4.60 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.60 and 4.74 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 4.72 (t, 2H, NCH_2, ^3J = 7.5 Hz), 4.70 (t, 4H, $CHCH_2$, ^3J = 8.7 Hz), 2.32–2.14 (m, 8H, $CHCH_2$), 1.95 (hex, 2H, NCH_2CH_2, ^3J = 7.2 Hz), 1.44–1.28 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.94 (t, 3H, $NCH_2CH_2CH_3$, ^3J = 7.2 Hz), 0.90 (t, 6H, $CH_2CH_2CH_2CH_3$, ^3J = 7.2 Hz), 0.89 ppm (t, 6H, $CH_2CH_2CH_2CH_3$, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.66, 154.72, 154.30, 148.80, 139.85, 139.26, 137.90 (7 s, Ar C_{quat}), 137.72 (s, NCHN), 136.47 (s, Ar C_{quat}), 124.84, 123.10 (2 s, NCHCHN), 121.31 (s, Ar CH), 120.99 (s, Ar C_{quat}), 120.05, 117.68, 117.19 (3 s, Ar CH), 101.11 (s, OCH_2O), 99.46 (s, OCH_2O), 51.58 (s, NCH_2), 36.70 (s, $CHCH_2$), 36.37 (s, $CHCH_2$), 32.03 (s, $CH_2CH_2CH_3$), 31.92 (s, $CH_2CH_2CH_3$), 30.01 (s, $CHCH_2$), 29.76 (s, $CHCH_2$), 27.55 (s, $CHCH_2CH_2$), 23.87 (s, NCH_2CH_2), 22.68 (s, $CH_2CH_2CH_2CH_3$), 14.08 (s, $CH_2CH_2CH_2CH_3$), 10.26 ppm (s, $NCH_2CH_2CH_3$); MS (ESI-TOF): *m/z*: 925.52 [M−Br$^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{58}H_{73}N_2O_8Br$ (1006.11): C 69.24, H 7.31, N 2.78; found: C 69.31, H 7.45, N 2.87.

5-*N*-(3-*iso*-Propyl-1-imidazolylium)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene bromide (**2**): Yield 97% (0.556 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.36 (s, 1H, NCHN), 7.36 (s br, 1H, NC*H*CHN), 7.33 (s, 1H, Ar CH), 7.22 (s br, 1H, NCHC*H*N), 7.10 (s, 3H, Ar CH), 6.61 (s, 2H, Ar CH), 6.50 (s, 1H, Ar CH), 5.72 (hept, 1H, $NCH(CH_3)_2$, ^3J = 6.6 Hz), 5.70 and 4.60 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.61 and 4.76 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 4.70 (t, 4H, $CHCH_2$, ^3J = 8.4 Hz), 2.31–2.16 (m, 8H, $CHCH_2$), 1.60 (d, 6H, $NCH(CH_3)_2$, ^3J = 6.6 Hz), 1.44–1.28 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 0.89 ppm (t, 6H, CH_2CH_3, ^3J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.68, 154.75, 154.33, 148.97, 139.84, 139.27, 137.99 (7 s, Ar C_{quat}), 136.843 (1 s, NCHN), 136.48 (s, Ar C_{quat}), 124.98, 123.07 (2 s, NCHCHN), 120,07, 117.78, 117.67, 117.21 (4 s, Ar CH), 101.16 (s, OCH_2O), 99.50 (s, OCH_2O), 53.24 (s, $NCH(CH_3)_2$), 36.70 (s, $CHCH_2$), 36.38 (s, $CHCH_2$), 32.04 (s, $CH_2CH_2CH_3$), 31.93 (s, $CH_2CH_2CH_3$), 30.02 (s, $CHCH_2$), 29.77 (s, $CHCH_2$), 27.58 (s, $CHCH_2CH_2$), 27.54 (s, $CHCH_2CH_2$), 23.24 (s, $NCH(CH_3)_2$), 22.68 (s, CH_2CH_3), 14.09 ppm (s, CH_2CH_3); MS (ESI-TOF): *m/z*: 925.52 [M−Br$^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{58}H_{73}N_2O_8Br$ (1006.11): C 69.24, H 7.31, N 2.78; found: C 69.35, H 7.43, N 2.73.

5-*N*-(3-Benzyl-1-imidazolylium)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene bromide (**3**):

Imidazolyl resorcinarene **5** (0.500 g, 0.57 mmol) and benzylbromide (0.101 g, 0.59 mmol) were dissolved in $CHCl_3$ (15 mL). The reaction mixture was then heated to reflux for 2 d. After cooling to room temperature, the solvent was removed under vacuum. The solid was washed with pentane and recrystallised from CH_2Cl_2/isopropyl ether to afford the imidazolium salt **3**. Yield 92% (0.552 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.37 (s, 1H, NCHN), 7.51–7.48 (m, 2H, Ar CH of benzyl), 7.39–7.37 (m, 3H, Ar CH of benzyl), 7.32 (s, 1H, Ar CH of resorcinarene), 7.27 (s br, 1H, NC*H*CHN), 7.14 (s br, 1H, NCHC*H*N), 7.10 (s, 3H, Ar CH of resorcinarene), 6.60 (s, 2H, Ar CH of resorcinarene), 6.50 (s, 1H, Ar CH of resorcinarene), 5.91 (s, 2H, CH_2Ph), 5.71 and 4.61 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.53 and 4.70 (AB spin system, 4H, OCH_2O, ^2J = 7.5 Hz), 4.73 (t, 2H, $CHCH_2$, ^3J = 8.1 Hz), 4.68 (t, 2H, $CHCH_2$, ^3J = 8.1), 2.03–2.13 (m, 8H, $CHCH_2$), 1.45–1.27 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.90 (t, 6H, CH_2CH_3, ^3J = 7.1 Hz), 0.89 ppm (t, 6H, CH_2CH_3, ^3J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.66, 154.73, 154.30, 148.94, 139.85, 139.28, 138.01 (7 s, Ar C_{quat}), 137.38 (s, NCHN), 136.50, 133.31 (2 s, Ar C_{quat}), 129.64, 129.51, 128.92 (3 s, Ar CH of benzyl), 124.69, 123.08 (2 s, NCHCHN), 121.15, 120.07, 117.66, 117.17, (4 s, Ar CH of resorcinarene), 101.11 (s, OCH_2O), 99.45 (s, OCH_2O), 53.66 (s, CH_2Ph), 36.69 (s, $CHCH_2$), 36.37 (s, $CHCH_2$), 32.03 (s, $CH_2CH_2CH_3$), 31.91 (s, $CH_2CH_2CH_3$), 30.01 (s, $CHCH_2$), 29.75 (s, $CHCH_2$), 27.56 (s, $CHCH_2CH_2$), 27.52 (s, $CHCH_2CH_2$), 22.67 (s, CH_2CH_3), 14.09 ppm (s, CH_2CH_3); MS (ESI-TOF): *m/z*: 973.55 [M−Br$^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{62}H_{73}N_2O_8Br$ (1054.16): C 70.64, H 6.98, N 2.66; found: C 70.71, H 7.06, N 2.59.

trans-Dibromo-bis[5-(3-*iso*-propylimidazol-2-yliden-1-yl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene] palladium(II) (**6**): To a stirred suspension of Cs_2CO_3 (0.324 g, 1.00 mmol) in dioxane (10 mL) was added [$PdCl_2$] (0.018 g, 0.10 mmol), **2** (0.200 g, 0.20 mmol) and KBr (0.237 g, 2.00 mmol). The reaction mixture was heated to reflux for 24 h. After cooling to room temperature, the mixture was filtered through Celite. The filtrate was evaporated to dryness, and the resulting residue purified by flash chromatography (EtOAc/petroleum ether 20:80 v/v). The yellow complex **6** was obtained in 70% yield (0.148 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (s, 2H, Ar CH), 7.12 (s, 2H, Ar CH), 6.90 (s br, 1H, NC*H*CHN), 6.51 (s br, H, NCHC*H*N), 6.46 (s, 1H, Ar CH), 6.43 (s, 2H, Ar CH), 5.84 (hept, 1H, $NCH(CH_3)_2$, ^3J = 6.3 Hz), 5.75 and 4.35 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.64 and 4.31 (AB spin system, 4H, OCH_2O, ^2J = 6.9 Hz), 4.83–4.74 (m, 2H, $CHCH_2$), 4.72 (t, 2H, $CHCH_2$, ^3J = 7.9), 2.48–2.35 (m, 2H, $CHCH_2$), 2.29–2.14 (m, 4H, $CHCH_2$), 2.09–1.98 (m, 2H, $CHCH_2$), 1.51–1.30 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.46 (d, 6H, $NCH(CH_3)_2$, ^3J = 6.3 Hz), 0.90 ppm (t, 12H, CH_2CH_3, ^3J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.50 (s, NCN), 155.26, 154.82, 150.68, 139.23, 138.89, 138.19, 137.87, 127.60 (8 s, Ar C_{quat}), 122.52, 121.04 (2 s, NCHCHN), 120.48, 119.89, 116.76, 115.98, 115.72 (5 s, Ar CH), 99.76 (s, OCH_2O), 99.20 (s, OCH_2O), 72.09 (s, $NCH(CH_3)_2$), 36.72 (s, $CHCH_2$), 36.41 (s, $CHCH_2$), 32.09 (s, $CH_2CH_2CH_3$), 29.92 (s, $CHCH_2$), 27.63 (s, $CHCH_2CH_2$), 27.54 (s, $CHCH_2CH_2$), 23.36 (s, $NCH(CH_3)_2$), 22.74 (s, CH_2CH_3), 22.67 (s, CH_2CH_3), 14.15 (s, CH_2CH_3), 14.11 ppm (s, CH_2CH_3); MS (ESI-TOF): *m/z* = 2155.75 [M+K$^+$], 2139.78 [M+Na$^+$], 2076.90 [M−Br+CH_3CN^+]

and 2035.87 [$M-Br^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{116}H_{144}O_{16}N_4Br_2Pd$ (2116.63): C 65.82, H 6.86, N 2.65; found: C 65.87, H 6.71, N 2.97.

trans-Dibromo-[5-(3-benzylimidazol-2-yliden-1-yl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene]pyridine palladium(II) (**7**): To a stirred suspension of K_2CO_3 (0.069 g, 0.50 mmol) in pyridine (3.5 mL) was added [$PdCl_2$] (0.027 g, 0.15 mmol), **3** (0.105 g, 0.10 mmol) and KBr (0.237 g, 2 mmol). The reaction mixture was heated at 80 °C for 17 h. After cooling to room temperature, the mixture was filtered through Celite. The filtrate was evaporated under vacuum, and the solid residue purified by flash chromatography (EtOAc/petroleum ether 50:50 v/v) to afford the yellow complex **7** in 75% yield (0.094 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.83–8.80 (m, 2H, Ar CH of Py), 7.65 (tt, 1H, Ar CH of Py, ^3J = 7.6 Hz, ^4J = 1.6 Hz), 7.54–7.51 (m, 2H, Ar CH of benzyl), 7.42–7.33 (m, 3H, Ar CH of benzyl), 7.29 (s, 1H, Ar CH of resorcinarene), 7.24–7.14 (m, 5H, Ar CH of Py and resorcinarene), 6.75 (d, 1H, NC*H*CHN, ^3J = 2.1 Hz), 6.63 (d, 1H, NC*H*CHN, ^3J = 2.1 Hz), 6.47 (s, 1H, Ar CH of resorcinarene), 6.45 (s, 2H, Ar CH of resorcinarene.), 5.92 (s, 2H, $CH_2C_6H_5$), 5.75 and 4.34 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.67 and 4.37 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 4.90 (t, 2H, $CHCH_2$, ^3J = 7.9 Hz), 4.73 (t, 2H, $CHCH_2$, ^3J = 8.0 Hz), 2.34–2.19 (m, 8H, $CHCH_2$), 1.48–1.28 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 6H, CH_2CH_3, ^3J = 7.2 Hz), 0.88 ppm (t, 6H, CH_2CH_3, ^3J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.82 (s, Ar C_{quat}), 154.60 (s, NCN), 152.56 (Ar CH of Py), 150.98, 139.07, 138.73, 138.58, 138.34 (5 s, Ar C_{quat}), 137.49 (s, Ar CH of Py), 135.18 (s, Ar C_{quat}), 129.17, 129.00, 128.49 (3 s, Ar CH of CH_2Ph), 126.63 (s, Ar C_{quat}), 124.21 (s, Ar CH of Py), 123.84 (s, NCHCHN), 120.94 (s, Ar CH of resorcinarene), 120.87 (s, NCHCHN), 120.58, 116.63, 115.91 (3 s, Ar CH of resorcinarene), 99.71 (s, OCH_2O), 99.23 (s, OCH_2O), 55.97 (s, $CH_2C_6H_5$), 36.74 (s, $CHCH_2$), 36.40 (s, $CHCH_2$), 32.01 (s, $CH_2CH_2CH_3$), 29.90 (s, $CHCH_2$), 29.80 (s, $CHCH_2$), 27.56 (s, $CHCH_2CH_2$), 27.51 (s, $CHCH_2CH_2$), 22.71 (s, CH_2CH_3), 14.11 ppm (s, CH_2CH_3); elemental analysis calcd (%) for $C_{67}H_{77}O_8N_3Br_2Pd$ (1318.57): C 61.03, H 5.89, N 3.19; found: C 60.89, H 6.02, N 3.11.

Chloro-(*o*-dimethylaminomethylphenyl-*C*,*N*)-[5-(3-benzylimidazol-2-yliden-1-yl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene] palladium(II) (**8**): To a stirred suspension of K_2CO_3 (0.035 g, 0.25 mmol) in acetonitrile (10 mL) was added [$PdCl(o\text{-}C_6H_4CH_2NMe_2]_2$ (0.055 g, 0.10 mmol) and **3** (0.211 g, 0.20 mmol). The reaction mixture was heated at 80 °C for 16 h. After cooling to room temperature, the grey solution was filtered through Celite. The filtrate was evaporated to dryness, and the resulting residue purified by flash chromatography (EtOAc/petroleum ether 40:60 v/v). The yellow complex **8** was obtained in 79% yield (0.197 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, 2H, Ar CH, ^3J = 6.8 Hz), 7.33–7.24 (m, 3H, Ar CH), 7.10 (s, 1H, Ar CH of resorcinarene), 7.06 (s, 1H, Ar CH of resorcinarene), 7.04 (s, 1H, Ar CH of resorcinarene), 6.99 (s, 1H, Ar CH of resorcinarene), 6.81 (d, 1H, NC*H*CHN, ^3J = 2.0 Hz), 6.78–6.65 (m, 3H, Ar CH), 6.67 (d, 1H, NCHC*H*N, ^3J = 2.0 Hz), 6.45 (s, 1H, Ar CH of resorcinarene), 6.43 (s, 1H, Ar CH of resorcinarene), 6.42 (s, 1H, Ar CH of resorcinarene), 6.17 (d, 1H, Ar CH, ^3J = 8.0 Hz), 6.03 and 5.53 (AB spin system, 2H, CH_2Ph, ^2J = 6.8 Hz), 5.78 and 4.23 (AB spin system 2H, OCH_2O, ^2J = 6.8 Hz), 5.72 and 4.32 (AB spin system, 2H, OCH_2O, ^2J = 7.2 Hz), 5.72 and 4.31 (AB spin system, 2H, OCH_2O, ^2J = 7.2 Hz), 5.53 and 4.40 (AB spin system, 2H, OCH_2O, ^2J = 7.2 Hz), 4.88 (dd, 1H, $CHCH_2$, ^3J = 9.1 Hz, ^3J = 6.9 Hz), 4.70 (t, 1H, $CHCH_2$, ^3J = 8.0), 4.70 (t, 1H, $CHCH_2$, ^3J = 8.0 Hz), 4.35 (t, 1H, $CHCH_2$, ^3J = 5.6 Hz), 3.75 and 3.54 (AB spin system, 2H, $CH_2N(CH_3)_2$, ^2J = 14.1 Hz), 2.80 (s, 3H, NCH_3), 2.66 (s, 3H, NCH_3), 2.25–2.10 (m, 6H, $CHCH_2$), 2.05–1.90 (m, 2H, $CHCH_2$), 1.44–1.26 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.92 (t, 3H, CH_2CH_3, ^3J = 7.3 Hz), 0.90 (t, 3H, CH_2CH_3, ^3J = 6.8 Hz), 0.89 (t, 3H, CH_2CH_3, ^3J = 6.2 Hz), 0.88 ppm (t, 3H, CH_2CH_3, ^3J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.75 (s, NCN), 154.90, 154.87, 154.79, 154.69, 154.53 151.30, 150.21, 147.05, 138.87, 138.77, 138.67, 138.61, 138.45, 138.35, 138.24, 137.78 (16 s, Ar C_{quat}), 136.97 (s, Ar CH), 135.94 (s, Ar C_{quat}), 129.23, 128.81, 128.20 (3 s, Ar CH), 127.40 (s, Ar C_{quat}), 124.67, 123.25 (2 s, Ar CH), 122.52, (s, NCHCHN), 121.13, 120.79, 120.63, 120.40, 119.91 (5 s, Ar CH), 119.63 (s, NCHCHN), 116.64, 116.34, 116.07 (3 s, Ar CH), 99.66 (s, OCH_2O), 99.80 (s, OCH_2O), 71.99 (s, $CH_2N(CH_3)_2$), 56.34 (s, CH_2Ph), 51.66 (s, NCH_3), 50.11 (s, NCH_3), 36.81 (s, $CHCH_2$), 36.67 (s, $CHCH_2$), 36.37 (s, 2 X $CHCH_2$), 32.25 (s, $CH_2CH_2CH_3$), 31.98 (s, $CH_2CH_2CH_3$), 30.06 (s, $CHCH_2$), 30.00 (s, $CHCH_2$), 29.81 (s, $CHCH_2$), 29.69 (s, $CHCH_2$), 27.93 (s, $CHCH_2CH_2$), 27.50 (s, $CHCH_2CH_2$), 22.85 (s, CH_2CH_3), 22.66 (s, CH_2CH_3), 14.19 (s, CH_2CH_3), 14.09 ppm (s, CH_2CH_3); elemental analysis calcd (%) for $C_{71}H_{84}N_3O_8PdCl$ (1249.31): C 68.26, H 6.78, N 3.36; found: C 68.35, H 6.87, N 3.22.

1-(2,6-Dimethoxyphenyl)-1H-imidazole: This reaction was performed in air. A mixture of 2,6-dimethoxyphenylboronic acid (1.000 g, 5.49 mmol), imidazole (0.449 g, 6.59 mmol) and CuI (0.052 g, 0.27 mmol) was dissolved in methanol (40 mL). The reaction mixture was heated to reflux overnight. After cooling to room temperature, the solvent was removed under vacuum. The residual solid was dissolved in dichloromethane, filtered through Celite and dried. The crude product was purified by flash chromatography (EtOAc) to afford the aryl imidazole in 25% yield (0.280 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (s br, 1H, NCHN), 7.32 (t, 1H, Ar CH, ^3J = 8.4 Hz), 7.17 (s br, 1H, NC*H*CHN), 7.02 (s br, 1H, NCHC*H*N), 6.66 (d, 2H, Ar CH, ^3J = 8.4 Hz), 3.77 ppm (s, 6H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$): 155.21 (s, CH_3OC_{quat}), 138.74 (s, NCHN), 129.58 (s, Ar CH), 127.44, 121.25 (2 s, NCHCHN), 115.16 (s, NC_{quat}), 104.36 (s, Ar CH), 56.05 ppm (s, CH_3O); elemental analysis calcd (%) for $C_{11}H_{12}O_2N_2$ (204.22): C 64.69, H 5.92, N 13.72; found: C 64.73, H 5.87, N 13.68.

General procedure for the preparation of imidazolium salts **9**–**11**: 1-Aryl imidazole (3.00 mmol) and benzyl bromide (3.10 mmol) were dissolved in $CHCl_3$ (15 mL). The reaction mixture was heated to reflux for 2 days. After cooling to room temperature, the solvent was removed under vacuum. The solid was washed with diethyl ether to afford the desired imidazolium salts **9**–**11**.

1-Benzyl-3-phenylimidazolium bromide (**9**): Yield 78% (0.737 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.11 (t, 1H, NCHN, ^4J = 1.5 Hz), 7.72 (dt, 2H, Ar CH, ^3J = 7.2 Hz, ^4J = 1.9 Hz), 7.63–7.58 (m, 3H, Ar CH), 7.55 (s br, 1H, NC*H*CHN), 7.53–7.42 (m, 3H, Ar CH), 7.37–7.32 (m, 3H, NCHC*H*N and Ar CH), 5.81 ppm (s, 2H, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$): 135.85 (s, NCHN), 134.37, 132.93 (2 s, Ar C_{quat}), 130.59, 130.30, 129.55, 129.41 (4 s, Ar CH), 122.73 (s, NCHCHN), 121.79 (s, Ar CH), 120.50 (s, NCHCHN), 53.58 ppm (s, CH_2Ph); elemental analysis calcd (%) for $C_{16}H_{15}N_2Br$ (315.21): C 60.97, H 4.80, N 8.89; found: C 61.08, H 4.85, N 8.76.

1-Benzyl-3-(2-methoxyphenyl)imidazolium bromide (**10**): Yield 83% (0.860 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.52 (s, 1H, NCHN), 7.61–7.55 (m, 4H, Ar CH), 7.45–7.40 (m, 2H, Ar CH), 7.36–7.30 (m, 3H, NC*H*CHN and Ar CH), 7.06 (s br, 1H, NCHC*H*N), 7.04–7.01 (m, 1H, Ar CH), 5.85 (s, 2H, CH_2Ph), 3.86 ppm (s, 3H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.86 (s, CH_3OC_{quat}), 137.12 (s, NCHN), 133.20 (s, CH_2C_{quat}), 131.77, 129.35, 129.28, 129,01 (4 s, Ar CH), 125.60 (s, Ar CH), 123.15 (s, NC_{quat}), 123.02 (s, NCHCHN), 121.59 (s, Ar CH), 112.62 (s, NCHCHN), 56.29 (s, CH_3O), 53.35 ppm (s, CH_2Ph); elemental analysis calcd (%) for $C_{17}H_{17}ON_2Br$ (345.23): C 59.14, H 4.96, N 8.11; found: C 59.25, H 5.02, N 8.08.

1-Benzyl-3-(2,6-dimethoxyphenyl)imidazolium bromide (**11**): Yield 87% (0.978 g); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.25$ (s br, 1H, NCHN), 7.57–7.54 (m, 2H, Ar CH), 7.51 (dd, 1H, NCHC*H*N, $^3J =$ 1.6 Hz, $^4J = 1.6$ Hz), 7.40–7.33 (m, 4H, Ar CH), 7.16 (dd, 1H, NCHC*H*N, $^3J = 1.6$ Hz, $^4J = 1.6$ Hz), 6.63 (s, 2H, Ar CH, $^3J = 8.7$ Hz), 5.88 (s, 2H, CH_2Ph), 3.79 ppm (s, 6H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.66$ (s, CH_3OC_{quat}), 139.11 (s, NCHN), 133.90 (s, CH_2C_{quat}), 132.52, 129.68 (2 s, Ar CH), 124.68, 121.34 (2 s, NCHCHN), 112.47 (s, NC_{quat}), 104.93 (s, Ar CH), 56.94 (s, CH_3O), 53.71 ppm (s, CH_2Ph); elemental analysis calcd (%) for $C_{18}H_{19}O_2N_2Br$ (375.26): C 57.61, H 5.10, N 7.47; found: C 57.65, H 5.01, N 7.54.

N-Imidazolyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetraphenylresorcin[4]arene (**13**): A mixture of tetrabromocavitand **12** (1.000 g, 0.86 mmol), imidazole (0.059 g, 0.86 mmol), K_2CO_3 (0.299 g, 2.16 mmol), DMEDA (0.057 g, 0.65 mmol) and CuI (0.123 g, 0.65 mmol) was dissolved in DMF (20 mL). The reaction mixture was stirred at 140 °C for a week. After cooling to room temperature, water (50 mL) and $CHCl_3$ (50 mL) were added. The organic layer was separated, and the aqueous phase extracted with $CHCl_3$ (2×50 mL). The combined organic layers were washed with aqueous Na_4EDTA 0.2 N (3×50 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (MeOH/CH_2Cl_2 2:98 v/v) to afford 0.065 g of a mixture of mono-, di- and tri-brominated imidazole cavitands (R_f in the range 0.78–0.67 MeOH/CH_2Cl_2 4:96 v/v). *n*-Butyllithium (0.30 mmol) was then slowly added to a solution of the brominated compounds (0.065 g, ca. 0.06 mmol) in THF (10 mL) at −78 °C. After 0.5 h, the reaction was quenched with methanol (0.5 mL) and water (10 mL). The aqueous phase was washed with CH_2Cl_2 (2× 10 mL). The combined organic phases were dried over Na_2SO_4 and evaporated under reduced pressure to afford 0.052 g of **13** (global yield 7%). $R_f = 0.45$ MeOH/CH_2Cl_2 2:98 v/v); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (s br, 1H, NCHN), 7.34–7.26 (m, 16H, C_6H_5), 7.22 (s br, 1H, NC*H*CHN), 7.18 (t, 4H, C_6H_5, $^3J = 6.8$ Hz), 7.09 (s, 1H, Ar CH of resorcinarene), 7.03 (s, 1H, Ar CH of resorcinarene), 7.01 (s, 2H, Ar CH of resorcinarene), 6.95 (s br, 1H, NCHC*H*N), 6.72 (s, 1H, Ar CH of resorcinarene), 6.70 (s, 2H, Ar CH of resorcinarene), 6.42 (s, 4H, C*H*Ph), 5.89 and 4.53 (AB spin system, 4H, OCH_2O, $^2J = 7.2$ Hz), 5.63 and 4.57 ppm (AB spin system, 4H, OCH_2O, $^2J = 7.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 156.13$, 156.01, 155.71, 151.23, 139.21, 138.68, 138.15, 137.98 (8 s, Ar $C_{quat.}$), 137.96 (1 s, NCHN), 137.16 (s, Ar $C_{quat.}$), 129.32 (s, NCHCHN), 128.63, 128.57, 128.19, 128.08, 127.00, 126.84, 126.77, 126.57 (8 s, Ar CH), 124.84 (s, NCHCHN), 116.93, 116.29 (2 s, Ar CH), 99.80 (s, OCH_2O), 41.89 (s, *C*HPh), 41.60 ppm (s, *C*HPh); elemental analysis calcd (%) for $C_{59}H_{42}O_8N_2$ (906.97): C 78.13, H 4.67, N 3.09; found: C 77.92, H 4.53, N 2.98.

5-*N*-(3-Benzyl-1-imidazolylium)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetraphenylresorcin[4]arene bromide (**14**): Imidazolyl resorcinarene **13** (0.052 g, 0.06 mmol) and benzylbromide (0.012 g, 0.07 mmol) were dissolved in $CHCl_3$ (3 mL). The reaction mixture was heated to reflux for 2 days. After cooling to room temperature, the solvent was removed under vacuum. The solid was washed with pentane and recrystallised from CH_2Cl_2/isopropyl ether to afford the imidazolium salt. Yield 95% (0.059 g); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.60$ (s, 1H, NCHN), 7.60–7.57 (m, 2H, Ar CH of benzyl), 7.47–7.44 (m, 3H, Ar CH of benzyl), 7.43–7.27 (m, 16H, Ar CH of Ph), 7.24 (s br, 1H, NC*H*CHN), 7.22 (s, 1H, Ar CH of resorcinarene), 7.22–7.18 (m, 4H, Ar CH of Ph), 7.15 (7.15 (s br, 1H, NCHC*H*N), 6.99 (s, 3H, Ar CH of resorcinarene), 6.86 (s, 2H, Ar CH of resorcinarene), 6.75 (s, 1H, Ar CH of resorcinarene), 6.44 (s, 4H, C*H*Ph), 6.38 (s, 4H, C*H*Ph), 5.99 (s, 2H, CH_2Ph), 5.86 and 4.83 (AB spin system, 4H, OCH_2O, $^2J = 7.2$ Hz), 5.69 and 4.94 ppm (AB spin system, 4H, OCH_2O, $^2J = 7.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 156.70, 155.79, 155.37, 150.03, 139.58, 139.18, 138.49, 138.25 (8 s, Ar C_{quat}), 137.73, (s, NCHN), 137.34, 137.25, 135.89, 133.25 (4 s, Ar C_{quat}), 129.66, 129.52, 128.98, 128.74, 128.62, 128.41, 128.37, 128.22, 127.94 126.85, 126.34 (11 s, Ar CH), 126.26, 124.80 (2 s, NC*H*CHN), 121.56, 117.78, 117.30 (3 s, Ar CH), 101.26 (s, OCH_2O), 99.53 (s, OCH_2O), 53.66 (s, CH_2Ph), 41.74 (s, *C*HPh), 41.57 ppm (s, *C*HPh); MS (ESI-TOF): *m/z*: 997.34 [$M-Br^+$] expected isotopic profile; elemental analysis calcd (%) for $C_{66}H_{49}N_2O_8Br$ (1078.01): C 73.53, H 4.58, N 2.60; found: C 73.44, H 4.65, N 2.48.

General procedure for Pd-catalysed Suzuki–Miyaura cross-coupling reactions: A solution of [$Pd(OAc)_2$] in dioxane, a solution of the imidazolium salt in dioxane, aryl halide (0.5 mmol), phenylboronic acid (0.122 g, 1.0 mmol), base (1.0 mmol), decane (0.05 mL, internal reference) and a complementary amount of dioxane (so that the total reaction volume was 1.5 mL) were mixed in a Schlenk tube. The reaction mixture was heated for 1 h at 100 °C. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analysed by GC. All products were unambiguously identified by NMR after their isolation. The NMR spectra were compared to those reported in the literature.

X-ray Crystallographic data

Single crystals of **3**·$C_6H_{14}O$·0.5 CH_2Cl_2 suitable for study by XRD were obtained by the slow diffusion of diisopropyl ether into a dichloromethane solution of the imidazolium salt. $M_r = 1198.80$, triclinic, space group $P\bar{1}$, $a = 13.5809(3)$, $b = 15.7798(4)$, $c =$ 16.3060(4) Å, $\alpha = 83.082(2)$, $\beta = 71.709(2)$, $\gamma = 79.299(2)°$, $V =$ 3252.94(14) Å^3, $Z = 2$, $D_x = 1.224$ mg m^{-3}, $\lambda(MoK_\alpha) = 0.71073$ Å, $\mu =$ 0.729 mm^{-1}, $F(000) = 1274$, $T = 293(2)$ K. Data were collected by using an Oxford Diffraction Xcalibur Sapphire 3 diffractometer (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å). The structure was solved by using SIR-97,[25] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by Fourier difference analysis. The whole structure was refined by using SHELX-97[26] and full-matrix least-square techniques (use of F^2; *x*, *y*, *z*, b_{ij} for C, Br, Cl, N and O atoms, *x*, *y*, *z* in riding mode for H atoms; 748 variables and 7341 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.1006P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1 = 0.0662$, $wR2 = 0.1823$, $S_w = 0.994$, $\Delta\rho <$ 2.596 e Å^{-3}.

Single crystals of **7**·1.25 $C_4H_{10}O$·0.25 CH_2Cl_2 suitable for study by XRD were obtained by the slow diffusion of diethyl ether into a dichloromethane solution of the complex. $M_r = 1432.46$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 12.0065(5)$, $b = 13.4108(7)$, $c =$ 22.4332(9) Å, $\alpha = 96.609(4)$, $\beta = 91.436(4)$, $\gamma = 107.581(4)°$, $V =$ 3413.7(3) Å^3, $Z = 2$, $D_x = 1.388$ mg m^{-3}, $\lambda(MoK_\alpha) = 0.71073$ Å, $\mu =$ 1.520 mm^{-1}, $F(000) = 1477$, $T = 120(2)$ K. Data were collected by using an Oxford Diffraction Xcalibur Sapphire 3 diffractometer (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å). The structure was solved by using SIR-97,[25] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found by Fourier difference analysis. The whole structure was refined by using SHELX-97[26] and full-matrix least-square techniques (use of F^2; *x*, *y*, *z*, b_{ij} for C, Br, Cl, N, Pd and O atoms, *x*, *y*, *z* in riding mode for H atoms; 805 variables and 5030 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.0868P)^2]$, in which $P = (F_o^2 + 2F_c^2)/3$. $R1 = 0.0549$, $wR2 = 0.1200$, $S_w = 0.648$, $\Delta\rho <$ 1.035 e Å^{-3}. The crystal used was very small and poorly diffracting,

which explains the B level alerts. Disorder was found for of one of the C_5H_{11} chains. Large thermal motion of the diisopropyl ether molecule inside the cavity and the presence of a site partially occupied by dichloromethane and diisopropyl ether molecules explain the A level alerts. Owing to the difficulties caused by disorder, it was necessary to use DFIX and DANG instructions.

Supplementary crystallographic data for compounds **3** (CCDC 815329) and **7** (CCDC 828859) can be obtained free of charge from The Cambridge Crystallographic Data Centre under www.ccdc.cam.ac.uk/data_request/cif.

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[1] V. K. Jain, P. H. Kanaiya, *Russ. Chem. Rev.* **2011**, *80*, 75 – 102.
[2] H. Boerrigter, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 7148 – 7155.
[3] D. Eisler, W. Hong, M. C. Jennings, R. J. Puddephatt, *Organometallics* **2002**, *21*, 3955 – 3960.
[4] D. J. Eisler, R. J. Puddephatt, *Inorg. Chem.* **2003**, *42*, 6352 – 6365.
[5] D. J. Eisler, R. J. Puddephatt, *Inorg. Chem.* **2005**, *44*, 4666 – 4678.
[6] H. El Moll, D. Sémeril, D. Matt, L. Toupet, *Eur. J. Org. Chem.* **2010**, 1158 – 1168.
[7] H. El Moll, D. Sémeril, D. Matt, L. Charbonnière, L. Toupet, *Dalton Trans.* **2011**, *40*, 4391 – 4393.
[8] D. Sémeril, C. Jeunesse, D. Matt, L. Toupet, *Angew. Chem.* **2006**, *118*, 5942 – 5946; *Angew. Chem. Int. Ed.* **2006**, *45*, 5810 – 5814.
[9] D. M. Homden, C. Redshaw, *Chem. Rev.* **2008**, *108*, 5086 – 5130.
[10] L. Monnereau, D. Sémeril, D. Matt, L. Toupet, *Chem. Eur. J.* **2010**, *16*, 9237 – 9247.
[11] C. Gibson, J. Rebek, *Org. Lett.* **2002**, *4*, 1887 – 1890.
[12] H. El Moll, D. Semeril, D. Matt, M. T. Youinou, L. Toupet, *Org. Biomol. Chem.* **2009**, *7*, 495 – 501.
[13] H. El Moll, D. Sémeril, D. Matt, L. Toupet, *Adv. Synth. Catal.* **2010**, *352*, 901 – 908.
[14] H. El Moll, D. Sémeril, D. Matt, L. Toupet, J.-J. Harrowfield, *Org. Biomol. Chem.* **2012**, *10*, 372 – 382.
[15] E. Brenner, D. Matt, M. Henrion, M. Teci, L. Toupet, *Dalton Trans.* **2011**, *40*, 9889 – 9898.
[16] Ö. Doğan, S. Demir, İ. Özdemir, B. Çetinkaya, *Appl. Organomet. Chem.* **2011**, *25*, 163 – 167.
[17] F.-X. Legrand, M. Ménand, M. Sollogoub, S. Tilloy, E. Monflier, *New J. Chem.* **2011**, *35*, 2061 – 2065.
[18] İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, C. Bruneau, *Eur. J. Inorg. Chem.* **2010**, 1798 – 1805.
[19] J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O'Brien, A. Lough, M. G. Organ, *Chem. Eur. J.* **2010**, *16*, 10844 – 10853.
[20] Ö. Doğan, N. Gürbüz, İ. Özdemir, B. Çetinkaya, O. Şahin, O. Büyükgüngör, *Dalton Trans.* **2009**, 7087 – 7093.
[21] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824 – 2870; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768 – 2813.
[22] N. Marion, O. Navarro, J. G. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101 – 4111.
[23] J. A. Tucker, C. B. Knobler, K. N. Trueblood, D. J. Cram, *J. Am. Chem. Soc.* **1989**, *111*, 3688 – 3699.
[24] D.-F. Hu, C.-M. Weng, F.-E. Hong, *Organometallics* **2011**, *30*, 1139 – 1147.
[25] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74 – 77.
[26] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Univ. of Göttingen, Germany, **1997**.

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