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PAPER

Calix[4]arenes with one and two *N*-linked imidazolium units as precursors of *N*-heterocyclic carbene complexes. Coordination chemistry and use in Suzuki–Miyaura cross-coupling†

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The calix[4]arene-imidazolium salts 5-(3-butyl-1-imidazolylium)-25,26,27,28-tetrabenzyloxy-calix[4]arene bromide (*cone*) (**2**), and 5,11-bis(3-alkyl-1-imidazolylium)-25,26,27,28-tetrabenzyloxycalix[4]arene diiodide (*cone*) (R = methyl, **3a**; R = *n*-butyl, **3b**) have been synthesised. Reaction of **2** in dioxane with $PdCl_2$ in the presence of $CsCO_3$ and KBr (80 °C, 24 h) gives the carbene complex *trans*-[$PdBr_2$(calix-monocarbene)$_2$] (**14**), containing two *N*-heterocyclic carbene ligands derived from **2** (yield: 63%). Repeating the reaction in pyridine instead of dioxane gives the mixed pyridine-carbene complex *trans*-[$PdBr_2$(calix-carbene)(pyridine)] (**15**) in 75% yield. Treatment of the bis-imidazolium salt **3a** with [$Pd(OAc)_2$] affords a chelate complex, *trans*-[PdI_2{calix-bis(carbene)}] (**16**), in which a metallo-(bis-carbene) fragment caps the upper rim of the calixarene basket. Complex **16**, as well as its analogue **17**, obtained from **3b**, display apparent C_s-symmetry in solution. This is not the case in the solid state, a single X-ray diffraction study carried out for **16** revealing a pinced *cone* structure for the calixarene skeleton, which reduces the symmetry to C_1. The chelate complex **17** shows poor activity in Suzuki–Miyaura cross-coupling of phenyl boronic acid and *p*-tolyl halides, an observation that suggests the presence of a strained metallocyclic unit preventing easy stereochemical rearrangement to an active species. Unlike **17**, complexes **14** and **15** show good activities in cross-coupling. A comparative study using the carbene precursor 1-butyl-3-(2,6-diisopropylphenyl)-imidazolium bromide (**18**), which is devoid of the receptor fragment, strongly suggests that the carbene ligands of **14** and **15** operate typically as bulky NHC-ligands.

Introduction

From the point of view of a coordination chemist, the use of the calix[4]arene skeleton has essentially two advantages. First, it constitutes an attractive platform for the construction of sophisticated coordination spheres by assembling a set of convergent podand arms on one of the two calixarene rims.[1–6] Ligands of this type often display unusual properties, most depending upon the particular features of the calixarene core, notably its flexibility,[7–9] shape,[10] and bulkiness[11,12] as well as its multifunctional character allowing, in particular, multiple metal binding.[13] Prominent examples of ligands of this type that have found applications in transition metal chemistry include those which are hemispherical,[14,15] hemilabile,[13] or chiral,[16] as well as highly strained bidentates.[17,18] The second valuable asset of the calix[4]arene backbone is its capacity to function as a molecular receptor, a property that is usually found only with calixarenes in the so-called *cone* conformation. By tethering functional groups suitable for transition metal binding on such receptors, ligands result that constitute potential candidates for supramolecular catalysis. To date, the only known ligands of this class are calixarene-monophosphines of type **1**, which, once associated with palladium salts, become very efficient Suzuki cross-coupling catalysts.[19] This property seemingly depends on the binding of metal–arene units within the cavity of the conical calixarene.

Wondering whether calixarenes equipped with podand arms other than a phosphino group would also be suitable for supramolecular catalysis, we decided to synthesise and investigate the properties of the calixarene-imidazolium salts **2** and **3a** and **3b**, which qualify as precursors for *N*-heterocylcic carbene (NHC) ligands.[20–25] In these derivatives, the NHC units are connected through one of the nitrogen atoms to the calixarene upper rim, without any linker, a feature which we expected would facilitate metal–cavity interactions. The only reported calixarene complexes having a NHC unit directly attached to the calixarene skeleton are Dinarès complexes **4a** and **4b**, which are active catalysts for the

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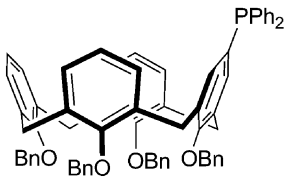
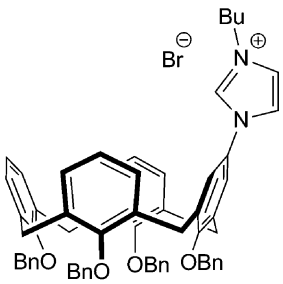
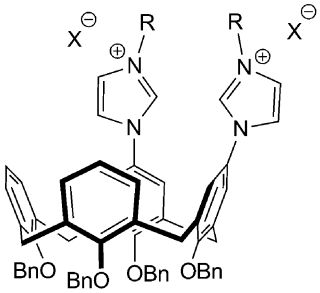
coupling between phenyboronic acid and aryl halides.[26] The study carried out with these complexes suggested that the catalytically active species had the palladium centre bonded to only one NHC ligand, although this was not certain. It is noteworthy that another, more flexible calixarenyl-NHC recently reported by Schatz *et al.* was also used in Suzuki cross coupling reactions.[27] Overall, despite their high catalytic potential, NHC-substituted calixarenes remain relatively unexplored.



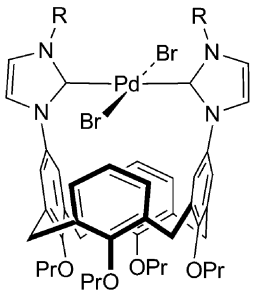
1 Bn = CH_2Ph



2



3a: R = Me, X = I
3b: R = *n*-Bu, X = Br



4a: R = *n*-Bu
4b: R = *i*-Pr

Results and discussion

Syntheses of mono- and bis-imidazolium salts

The mono-imidazolium derivative **2** was prepared in five steps according to Scheme 1. Its synthesis began with that of key intermediate **6**, which was obtained in 81% yield by tris-alkylation of **5** using benzyl bromide (BnBr) in the presence of $Ba(OH)_2 \cdot 8H_2O$. Note that the yield of this reaction significantly surpassed that of the tris-alkylation procedure previously reported by Shinkai *et al.*[28] Compound **6** was regioselectively iodinated with trichloroisocyanuric acid/sodium iodide (TCIA/NaI), leading to **7** in 69% yield.[29] We observed that **7** is moderately stable in air. Upon benzylation of **7** with BnBr/NaH in DMF, **8** formed quantitatively. Following the procedure described in a recent publication of Dinarès *et al.*[30] the imidazolyl group was then introduced efficiently *via* Ullmann coupling of **8** with imidazole in the presence of CuI/DMEDA and K_2CO_3 in DMF (yield 88%). The final step was the quantitative alkylation of the imidazolyl derivative **9** with *n*-BuBr in excess. All of the above calixarenes have their backbone in the *cone* conformation,[31,32] as could be unambiguously deduced from the corresponding ^{13}C NMR spectra, which showed Ar*C*H_2 signals lying in the range 31.5–30.0 ppm. In accord with C_s-symmetry, the ^1H NMR spectrum of each compound showed two AB patterns for the diastereotopic $ArCH_2$ protons. In these systems the A and B separations are typical for those found in calixarenes adopting a *cone* conformation ($\Delta\delta > 0.7$ ppm).[33]

The preparation of the bis-imidazolium salts **3a** and **3b** (Scheme 2) required the preparation of the proximally-dialkylated precursor **10**. The latter was obtained conveniently by treatment of **5** with BnBr in the presence of NaH (yield 66%) using a methodology described by Reinhoudt *et al.* for related dialkylated calixarenes.[34] The following steps were similar to those described above for the synthesis of the monoimidazolium salt: a) iodination of **10** with TCIA/KI giving **11** (91%); b) alkylation with BnBr/NaH of the two free hydroxyl groups of **11** leading to **12** in 88%; c) reaction of **12** with imidazole/CuI/DMEDA/K_2CO_3 to form the bis-imidazolyl compound **13** in 80% yield; d) alkylation of **13** with MeI or *n*-BuBr resulting quantitatively in **3a** and **3b**, respectively. Both these calixarenes, as well as their precursors, adopt a *cone* conformation.

Palladium complexes derived from monoimidazolium salt 2 and bis-imidazolium salts 3a and 3b

NHC-complexes derived from the monoimidazolium salt **2** were obtained using conventional procedures.[35,36] Thus, reaction of calixarene **2** with $PdCl_2$ in dioxane at 80 °C in the presence of Cs_2CO_3 and KBr (in excess) afforded the bis-NHC complex **14** in 63% yield (Scheme 3). The *trans* stereochemistry of **14** was inferred from the corresponding $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), which showed a peak at 168.53 ppm for the carbenic carbon atoms. This value is close to that reported in the literature for other *trans*-$[PdX_2(NHC)_2]$ complexes (X = halide; NHC = imidazolylidene) (the $C_{carbene}$ of *cis* complexes typically appears near 160 ppm).[27,37,38] The coordination geometry of the complex was further confirmed by a single crystal X-ray diffraction study (Fig. 1). Applying conditions similar to those reported above for the synthesis of **14**, but carrying out the reaction in pyridine, gave the PEPPSI-type complex **15** in 75% yield. We were unable to assign with certainty a *trans* geometry to this complex, but this stereochemistry is the more likely in view of the chemical shift of the carbenic C atom (147.6 ppm), which is in keeping with that found in other PEPPSI complexes having a crystallographically-established *trans* configuration.[39] It is also worth mentioning here that the ^1H NMR ($CDCl_3$) spectra of complexes **14** and **15** revealed that the *p*-H atom of the phenolic ring opposite to the one bearing the heterocyclic ring appears as a doublet of doublets, so that in fact these molecules display a pseudo C_s-symmetry. This is

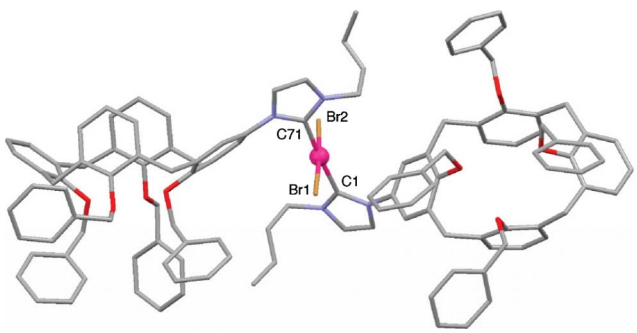
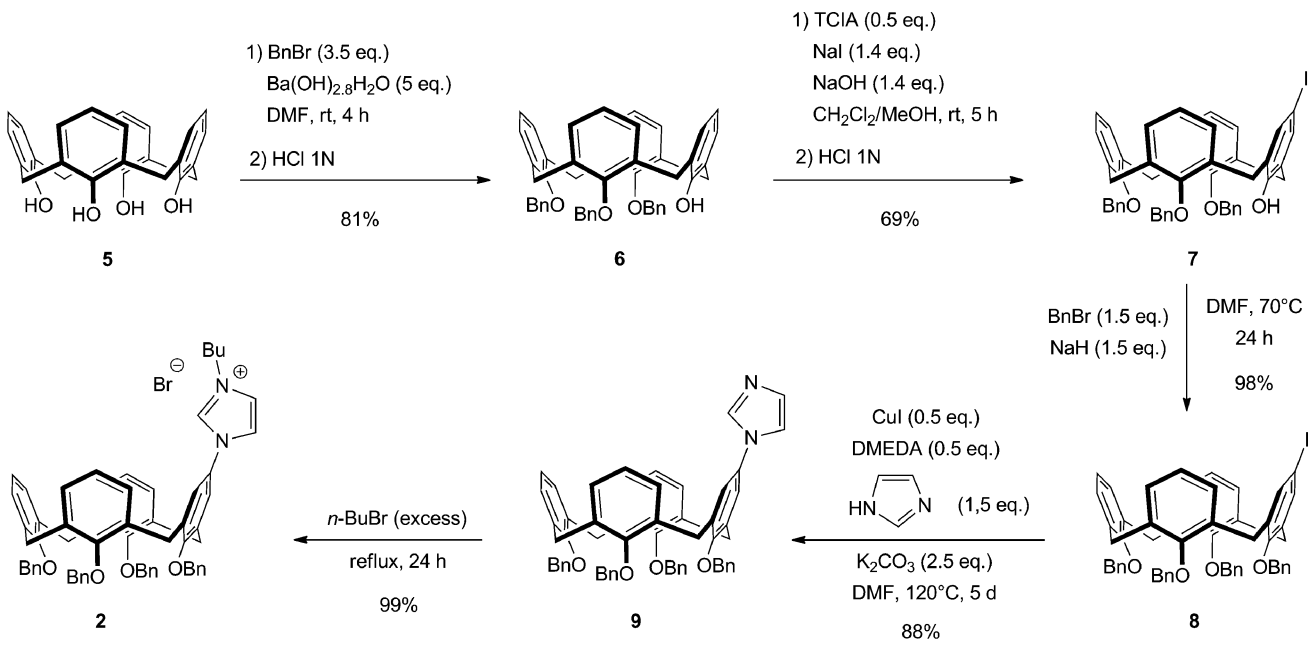
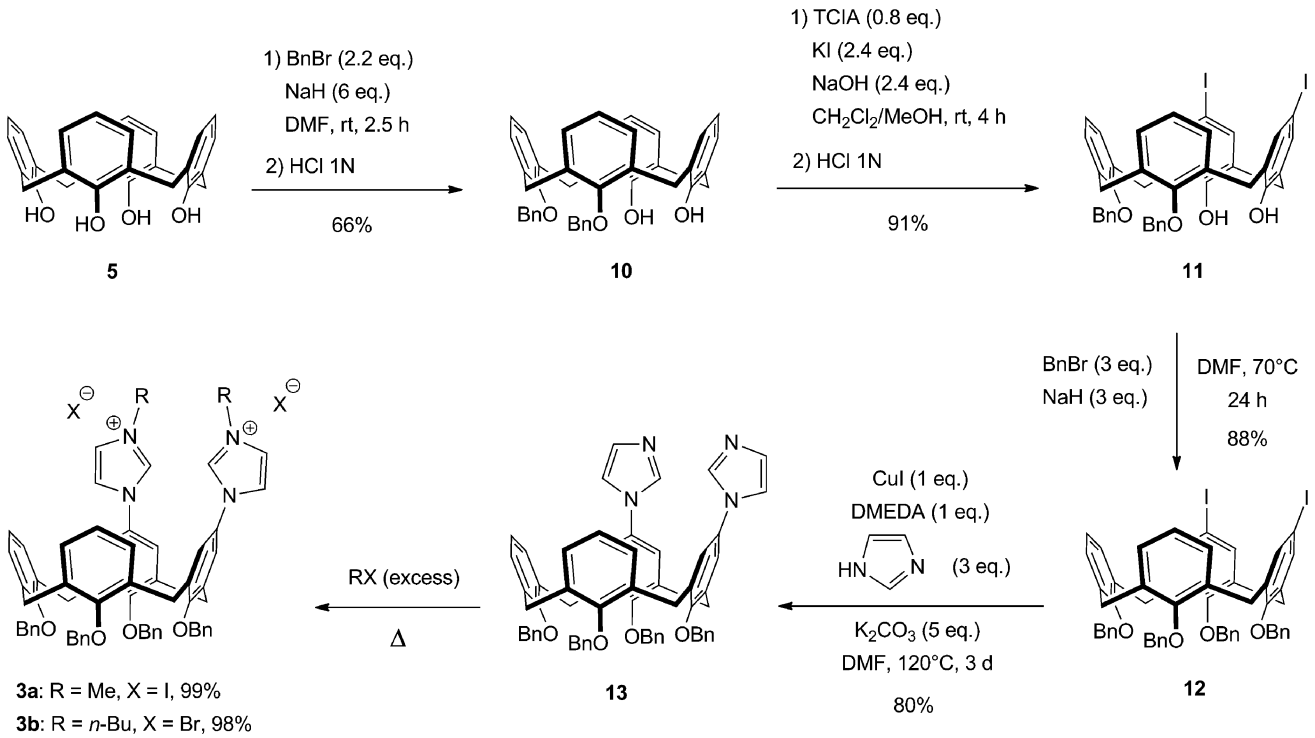


Fig. 1 The solid state structure of complex **14**. Important distances (Å) and angles (°): Pd–Br(1) 2.4280(4); Pd–Br(2) 2.4461(4); Pd–C(1) 2.016(3); Pd–C(71) 2.024(3); Br(1)–Pd–Br(2) 175.27(2); C(1)–Pd–C(71) 176.30(11).



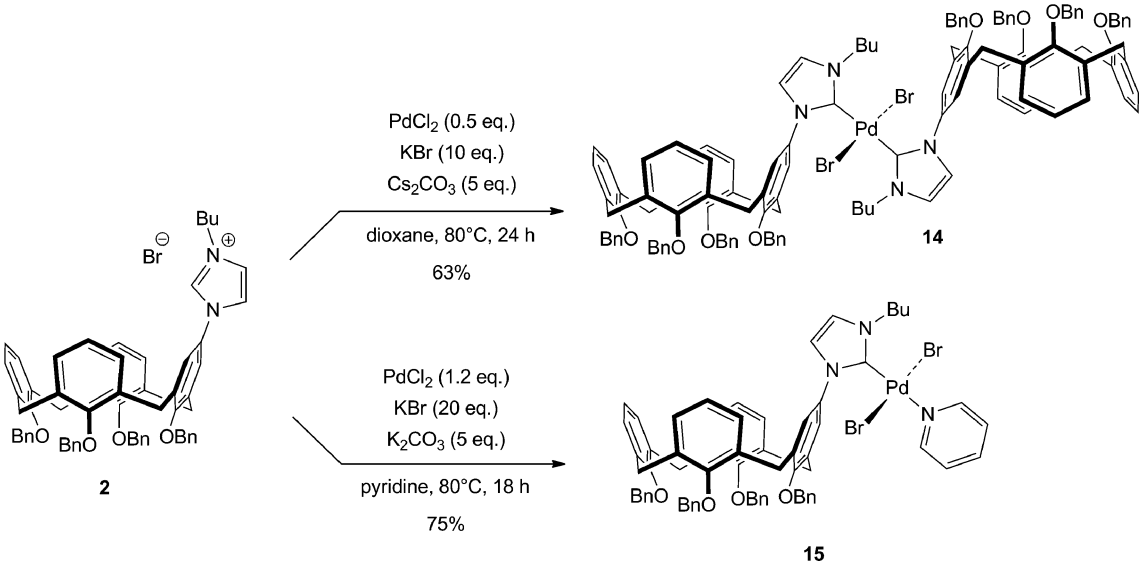
Scheme 1 Stepwise construction of imidazolium salt **2**.



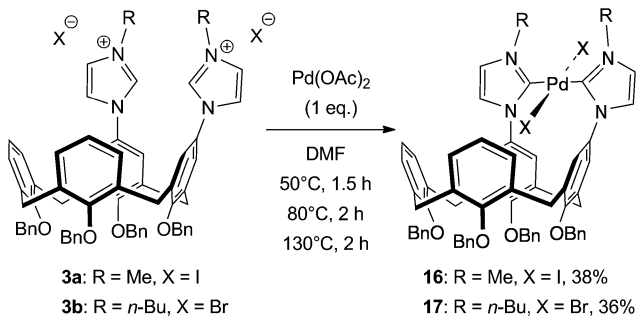
Scheme 2 Synthesis of imidazolium salts **3a** and **3b**.

likely to arise from the unsymmetrical structure of the heterocycle which adopts a sideways orientation enabling its conjugation with the phenolic ring to which it is connected.[40] Unsurprisingly, the spectra of **2** and **9** showed the same feature.

The carbenes derived from salts **3a** and **3b** turned out to be suitable for forming chelate complexes, but the yields were moderate. Thus, reaction of **3a** and **3b** with $[Pd(OAc)_2]$ (Scheme 4) in DMF gave complexes **16** and **17**, respectively, in *ca.* 37% yield. Chromatographic separation revealed the formation, beside that of **16** or **17**, of coloured by-products, possibly oligomeric complexes, which were not identified. The monomeric nature of the complexes was deduced from the corresponding mass spectra (see experimental section). The *trans* configuration of the complexes was again inferred from the corresponding $^{13}C\{^1H\}$ NMR spectra (carbene peaks at 167.0 (**16**) and 168.24 (**17**) ppm). As expected for C_s-symmetrical complexes, both ^1H NMR spectra showed three AB systems (intensity 1 : 2 : 1) for the bridging methylene units. One of the two H atoms of the NHC-substituted phenolic rings



Scheme 3 Synthesis of palladium complexes **14** and **15**.



Scheme 4 Synthesis of palladium complexes **16** and **17**.

of both complexes is considerably low-field shifted with respect to the other one (*ca.* 2 ppm), reflecting hydrogen bond interactions with one of the palladium-bonded halogen atoms.

This was confirmed by an X-ray diffraction study of **16** (H(6)–I(2): 3.179 Å; H(9)–I(2) 3.334 Å) (Fig. 2). This further revealed that the calixarene adopts a pinced *cone* structure which therefore renders the NHC units inequivalent. Note that in the NMR spectra of **16** the two heterocycles appear equivalent over the range –80 to 25 °C, showing that the formation of a metallo-bridge does not prevent "breathing" of the calixarene backbone.[6]

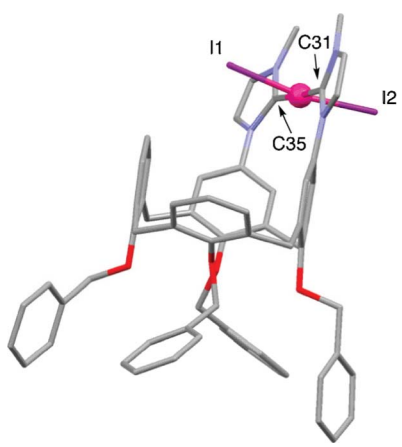
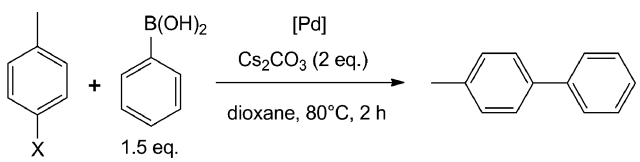


Fig. 2 The solid state structure of complex **16**. Important distances (Å) and angles (°): Pd–I(1) 2.5984(3); Pd–I(2) 2.6297(2); Pd–C(35) 2.015(2); Pd–C(31) 2.035(2); I(1)–Pd–I(2) 169.28(1); C(31)–Pd–C(35) 176.1(1).

Suzuki–Miyaura cross-coupling

For the catalytic tests, phenyl boronic acid was reacted with either *p*-tolyl bromide or *p*-tolyl chloride. The runs were carried out with the complexes **14**, **15** and **17**. The conditions applied were those used by Dinarès *et al.* for the study of **4a** and **4b** (dioxane, 80 °C, 2 h, Cs_2CO_3). The results are summarised in Table 1.

Table 1 Suzuki–Miyaura cross-coupling of phenyl boronic acid with *p*-tolyl halides[a]



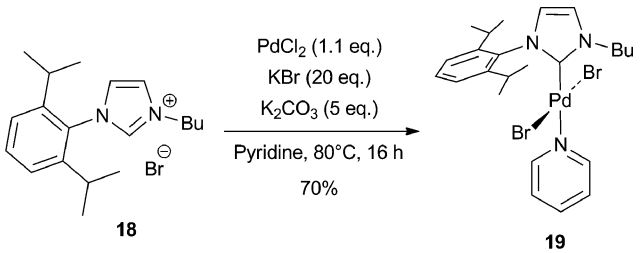
Entry	Complex	X	[Pd] (mol%)	yield (%)[b]
1	**14**	Br	0.1	100
2	**14**	Br	0.05	92
3	**14**	Br	0.01	1
4	**14**	Cl	1	67
5	**15**	Br	0.1	100
6	**15**	Br	0.05	84
7	**15**	Br	0.01	2
8	**15**	Cl	1	45
9	**17**	Br	0.1	100[c]
10	**17**	Br	0.1	4
11	**19**	Br	0.05	61
12	**19**	Cl	1	64

[a] Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 mL). [b] Yields determined by ^{1}H NMR using 1,4-dimethoxybenzene as internal standard. Averaged over two runs. [c] After 24 h of reaction.

The mono-NHC calixarene complexes **14** and **15** showed good activities in the coupling with the *p*-tolyl halides, the reactivity towards the bromide being, as expected, higher than that towards the chloride (Table 1, entries 1–8). Interestingly, the association of two calixarene ligands with the palladium centre (as in complex **14**) does not significantly improve the reaction rate with respect to the reactions where only one equivalent of NHC is present (see entries 2 and 6).

The activities observed with the chelate complex **17** were disappointingly low when compared with the performances of **14** and **15** (compare entries 9 and 10 with entries 1 and 5, respectively). This may reflect the high stability of the chelate complex which does not favour dissociation of a carbenic ligand with concomitant formation of a mono-NHC complex similar to those obtained with **14** or **15**. This behaviour markedly contrasts with that of the Dinarès complexes **4a** and **4b**, which displayed 10–20 times higher activities than **17**.[26] It is likely that complexes **4a** and **4b** undergo easy stereochemical rearrangements facilitating either the formation of mono-NHC intermediates, or that of a *cis*-chelate complex, both types of complexes having intrinsically higher activities than the *trans* complexes **4**. The fact that the reactions rates obtained with **14** and **15** were of the same order of magnitude as those of **4a** (in fact their activity is roughly twice that of **4a**), suggests that with the latter the active species is a mono-NHC-ligand complex.

One question that arises is whether the mono-NHC ligand of complex **15** operates in a supramolecular manner like the previously reported phosphine ligand **1** when used in Suzuki–Miyaura cross-coupling. To answer this question, complex **19** was prepared, which is structurally close to **15**, but which lacks a receptor unit. The synthesis of **19** was similar to that of **15** (Scheme 5).



Scheme 5 Synthesis of palladium complex **19**.

In fact, the catalytic runs performed with **19** revealed catalytic activities similar to those observed with **15** (Table 1, entries 11 and 12; compare with entries 6 and 8). These findings suggest that the NHC of **15** simply operates as a bulky ligand and not as a receptor unit able to enhance the catalytic activity.

Conclusion

In summary, we have described the first calix[4]arenes substituted by a single imidazolylium moiety, as well as the first calix[4]arenes proximally-substituted by two such units. N-heterocyclic carbene complexes were conveniently obtained from both types of salts using conventional procedures. Chelate palladium complexes of *trans* stereochemistry could be obtained from the calixarenes with the proximal substitution pattern, thereby leading to metallo-capped calix[4]arenes, the backbone of which retains, in solution, the usual breathing motion observed for conical calix[4]arenes. The chelate complex **17** showed poor activity in the cross-coupling of phenylboronic acid and *p*-tolyl halides, suggesting that the generation of an active species is made difficult by the presence of a rather rigid *trans*-spanning bis-carbene ligand. In contrast, the palladium complexes obtained from the mono-imidazolium salts displayed good activities in Suzuki cross-coupling. Comparison of their activity with a related calixarene complex lacking a receptor moiety shows that no supramolecular effect is involved in the catalysis with complexes **14** and **15**.

Experimental section

General procedures

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25 °C. ^{1}H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26; DMSO, δ 2.50), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16; DMSO-d_6, δ 39.52). For column chromatography Geduran SI (E. Merck, 0.040–0.063 mm) silica was used. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Mass spectra were recorded either with a Bruker MicroTOF spectrometer (ESI-TOF) using CH_2Cl_2 or CH_3CN as solvent, or with a Bruker MaldiTOF spectrometer (MALDI-TOF) using dithranol as matrix. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Tetrahydroxycalix[4]arene (**5**)[41] and 1-butyl-3-(2,6-diisopropylphenyl)imidazolium bromide (**18**)[42] were prepared as described in the literature. In the NMR data given hereafter, the bridging CH_2 groups of the calixarene backbone are designated by the abbreviation "ArCH_2Ar". Cq denotes a quaternary carbon atom.

Syntheses

25,26,27-Tribenzyloxy-28-hydroxycalix[4]arene (*cone*) (6). To a stirred mixture of calix[4]arene **5** (5.00 g, 11.8 mmol) and benzyl bromide (7.06 g, 41.3 mmol) in DMF (80 mL), at room temperature, was added portionwise $Ba(OH)_2{\cdot}8H_2O$ (18.6 g, 59.0 mmol). The reaction mixture was stirred for 4 h at room temperature before cooling with an ice bath. Aqueous HCl (1 N, 100 mL) was then slowly added to the mixture, followed by $CHCl_3$ (150 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2 × 100 mL). The extracts were combined and washed with water (3 × 100 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 (SiO_2, CH_2Cl_2/petroleum ether, 25 : 75, v/v) to afford **6** as a white solid (R_f 0.47, SiO_2, CH_2Cl_2/petroleum ether, 40 : 60, v/v). Yield: 6.66 g, 81%; mp 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.22 (13H, m, ArH), 7.20–7.05 (6H, m, ArH), 6.94 (1H, t, ^{3}J = 7.4 Hz, ArH), 6.80 (1H, t, ^{3}J = 7.4 Hz, ArH),

6.55–6.42 (6H, m, ArH), 5.35 (1H, s, OH), 5.11 (2H, s, OCH_2), 4.80 and 4.75 (4H, AB spin system, $^2J_{AB}$ = 11.7 Hz, OCH_2), 4.39 and 3.20 (4H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar), 4.17 and 3.02 (4H, AB spin system, $^2J_{AB}$ = 13.2 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.34 (s, arom. Cq–O), 153.91 (s, 2x, arom. Cq–O), 153.49 (s, arom. Cq–O), 137.54, 137.33, 133.76, 133.07 and 131.07 (5 s, arom. Cq), 130.45, 129.09, 128.71, 128.54, 128.47, 128.21, 128.09, 128.02, 127.67, 123.61, 123.16 and 119.43 (12 s, arom. CH), 77.65 (s, 2x, OCH_2), 75.69 (s, OCH_2), 31.42 and 31.17 (2 s, ArCH_2Ar). Found: C, 84.80; H, 6.33. Calc. for $C_{49}H_{42}O_4$ (M_r = 694.86): C, 84.70; H, 6.09%.

5-Iodo-25,26,27-tribenzyloxy-28-hydroxycalix[4]arene (*cone*) (7). A stirred mixture of calix[4]arene **6** (1.70 g, 2.45 mmol), NaOH (0.137 g, 3.43 mmol) and NaI (0.514 g, 3.43 mmol) in MeOH/CH_2Cl_2 (30 mL, 1 : 1, v/v) was cooled at 0 °C and protected from light. Trichloroisocyanuric acid (TCIA, 0.265 g, 1.14 mmol) in MeOH (3 mL) was added dropwise to the mixture which was then allowed to reach room temperature. After 5 h, CH_2Cl_2 (100 mL), water (50 mL) and aqueous HCl (1 N, 15 mL) were successively added to the mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The extracts were combined and washed with aqueous $Na_2S_2O_3$ (5%, 100 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 (SiO_2, CH_2Cl_2/petroleum ether, 30 : 70, v/v) to afford **7** as a white solid (R_f 0.37, SiO_2, CH_2Cl_2/petroleum ether, 30 : 70, v/v). Yield: 1.39 g, 69%; mp 174–175 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.64 (1H, s, OH), 7.41 (2H, s, ArH), 7.39–7.30 (12H, m, ArH), 7.29–7.22 (3H, m, ArH), 7.17 (2H, d, ^3J = 7.6 Hz), 6.90 (2H, dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, ArH), 6.85–6.76 (3H, m, ArH), 6.65 (2H, dd, ^3J = $^3J'$ = 7.6 Hz, ArH), 4.86 (2H, s, OCH_2), 4.73 and 4.68 (4H, AB spin system, $^2J_{AB}$ = 11.7 Hz, OCH_2), 4.13 and 3.11 (4H, AB spin system, $^2J_{AB}$ = 12.4 Hz, ArCH_2Ar), 3.92 and 3.18 (4H, AB spin system, $^2J_{AB}$ = 13.1 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, DMSO-d_6): δ 154.52 (s, arom. Cq–O), 153.10 (s, 2x, arom. Cq–O), 152.95 (s, arom. Cq–O), 137.57 and 136.75 (2 s, arom. Cq), 136.36 (s, arom. CH), 135.82, 134.52, 132.46 and 131.43 (4 s, arom. Cq), 128.84, 128.75, 128.71, 128.62, 128.41, 128.33, 128.15, 127.76, 127.54, 124.05 and 123.58 (11 s, arom. CH), 81.32 (s, arom. Cq–I), 77.42 (s, 2x, OCH_2), 75.44 (s, OCH_2), 30.26 and 30.08 (2 s, ArCH_2Ar). Found: C, 71.47; H, 5.08. Calc. for $C_{49}H_{41}IO_4$ (M_r = 820.75): C, 71.71; H, 5.04%.

5-Iodo-25,26,27,28-tetrabenzyloxycalix[4]arene (*cone*) (8). To a stirred mixture of calix[4]arene **7** (1.65 g, 2.01 mmol) and benzyl bromide (0.514 g, 3.02 mmol) in DMF (10 mL), at room temperature, was added portionwise NaH (0.121 g of a 60% dispersion in paraffin, 3.02 mmol). After stirring for 1 h at room temperature, the reaction mixture was heated at 70 °C for 24 h. After cooling to room temperature, aqueous HCl (0.5 N, 20 mL) was added followed by $CHCl_3$ (80 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2 × 50 mL). The extracts were combined and washed with water (4 × 80 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 (SiO_2, CH_2Cl_2/petroleum ether, 24 : 76, v/v) to afford **8** as a white solid (R_f 0.46, SiO_2, CH_2Cl_2/petroleum ether, 30 : 70, v/v). Yield: 1.80 g, 98%; mp 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.14 (21H, m, ArH), 6.74–6.62 (8H, m, ArH), 6.45 (2H, d, ^3J = 7.5 Hz, ArH), 5.03 and 4.98 (4H, AB spin system, $^2J_{AB}$ = 11.8 Hz, OCH_2), 4.90 (2H, s, OCH_2), 4.85 (2H, s, OCH_2), 4.27 and 3.02 (4H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 4.10 and 2.84 (4H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.52 (s, 2x, arom. Cq–O), 155.39 (s, arom. Cq–O), 155.33 (s, arom. Cq–O), 137.88, 137.74, 137.66 and 137.32 (4 s, arom. Cq), 136.80 (s, arom. CH), 136.12, 135.25 and 134.79 (3 s, arom. Cq), 129.93, 129.56, 129.37, 128.94, 128.36, 128.31, 128.14, 128.09, 128.05, 127.95, 122.81 and 122.54 (12 s, arom. CH), 86.43 (s, arom. Cq–I), 76.79 and 76.73 (2 s, OCH_2), 76.26 (s, 2x, OCH_2), 31.46 and 31.12 (2 s, ArCH_2Ar). Found: C, 74.18; H, 5.48. Calc. for $C_{56}H_{47}IO_4$ (M_r = 910.87): C, 73.84; H, 5.20%.

5-(*N*-imidazolyl)-25,26,27,28-tetrabenzyloxycalix[4]-arene (*cone*) (9). To a mixture of iodocalix[4]arene **8** (1.50 g, 1.65 mmol), imidazole (0.168 g, 2.47 mmol), K_2CO_3 (0.569 g, 4.12 mmol) and DMEDA (0.073 g, 0.828 mmol) was added 10 mL of degassed DMF. CuI (0.156 g, 0.820 mmol) was added and the reaction mixture was stirred under exclusion of light at 120 °C for 5 days. After cooling to room temperature, water (50 mL) was added followed by $CHCl_3$ (50 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$ (2 × 50 mL). The extracts were combined and washed with aqueous Na_4EDTA 0.2 N by vigorous stirring of the biphasic mixture over 1 h (3 × 80 mL). The organic layer was dried over Na_2SO_4, then the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, MeOH/CH_2Cl_2, 1 : 99, v/v) to afford **9** as a white solid (R_f 0.34, SiO_2, MeOH/CH_2Cl_2, 2 : 98, v/v). Yield: 1.23 g, 88%; mp 177–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.24 (17H, m, ArH and NCHN), 7.22–7.12 (4H, m, ArH), 7.07 (1H, s, NCHC), 7.01 (2H, dd, ^3J = 7.0 Hz, ^4J = 2.1 Hz, ArH), 6.96–6.84 (4H, m, ArH), 6.80 (1H, s, NCHC), 6.24 (2H, d, ^3J = 7.5 Hz, ArH), 6.19 (2H, s, ArH), 6.12 (1H, dd, ^3J = 8.2 Hz, $^3J'$ = 6.7 Hz, *p*-H of Ar opposite to Ar–N), 5.22 and 5.15 (4H, AB spin system, $^2J_{AB}$ = 11.9 Hz, OCH_2), 4.82 (2 × 2H, s, OCH_2), 4.33 and 3.06 (4H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar), 4.24 and 2.95 (4H, AB spin system, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.67 (s, 2x, arom. Cq–O), 155.10 and 154.29 (2 s, arom. Cq–O), 137.68, 137.51, 137.17, 137.09, 136.31 and 135.91 (6 s, arom. Cq), 135.51 (s, arom. CH), 133.84 and 131.70 (2 s, arom. Cq), 129.42, 129.36, 129.21, 129.02, 128.61, 128.45, 128.43, 128.25, 128.06, 127.92, 127.87, 127.61, 122.57, 122.40, 120.51 and 118.16 (16 s, arom. CH), 77.28 and 75.83 (2 s, 2x, OCH_2), 31.47 and 31.39 (2 s, ArCH_2Ar). Found: C, 82.80; H, 6.05; N, 3.01. Calc. for $C_{59}H_{50}N_2O_4 \cdot 0.4\ H_2O$ (M_r = 851.04 + 7.21): C, 82.57; H, 5.97; N, 3.26%.

5-(3-Butyl-1-imidazolylium)-25,26,27,28-tetrabenzyl-oxycalix[4]-arene bromide (*cone*) (2). A stirred solution of **9** (0.775 g, 0.910 mmol) in *n*-butyl bromide (6 mL), was heated under reflux for 24 h. The precipitate formed was collected by filtration and washed with petroleum ether. The white solid (**2**) was dried under vacuum and used without further purification. Yield: 0.896 g, 99%; mp 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.15 (1H, s, NCHN), 7.69 (1H, s, NCHC), 7.43–7.09 (20H, m, ArH), 6.97–6.69 (7H, m, ArH and NCHC), 6.45 (2H, s, ArH), 6.28 (2H, d, ^3J = 7.5 Hz, ArH), 6.12 (1H, dd, ^3J = 7.8 Hz, $^3J'$ = 7.0 Hz, *p*-H of Ar opposite to Ar–N), 5.08 and 5.01 (4H, AB spin

system, $^2J_{AB}$ = 11.8 Hz, OCH_2), 4.79 (4H, s, OCH_2), 4.53 (2H, t, ^3J = 7.4 Hz, NCH_2), 4.23 and 2.96 (4H, AB spin system, $^2J_{AB}$ = 13.4 Hz, ArCH_2Ar), 4.11 and 2.92 (4H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 1.89 (2H, tt, $^3J = {}^3J'$ = 7.4 Hz, NCH_2CH_2), 1.37 (2H, tq, $^3J = {}^3J'$ = 7.4 Hz, CH_2CH_3), 0.92 (3H, t, ^3J = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 156.55 and 155.35 (2 s, arom. Cq–O), 155.31 (s, 2x, arom. Cq–O), 137.45, 137.34, 137.20, 136.54, 136.40 and 135.45 (6 s, arom. Cq), 134.89 (s, arom. CH), 134.49 (s, arom. Cq), 130.08, 129,38, 129.19, 129.16 and 128.71 (5 s, arom. CH), 128.58 (s, arom. Cq), 128.39, 128.29, 128.04, 127.98, 127.90, 127.56, 122.82, 122.68, 121.60, 121,13 and 120.51 (11 s, arom. CH), 77.16 and 75.99 (2 s, 2x, OCH_2), 50.03 (s, NCH_2), 32.28 (s, NCH_2CH_2), 31.28 (s, 4x, ArCH_2Ar), 19.43 (s, CH_2CH_3), 13.52 (s, CH_3). Found: C, 76.12; H, 6.01; N, 2.66. Calc. for $C_{63}H_{59}BrN_2O_4 \cdot 0.3\ H_2O$ (M_r = 988.06 + 5.40): C, 76.17; H, 6.05; N, 2.82%.

25,26-Dibenzyloxy-27,28-dihydroxycalix[4]arene (*cone*) (10). To a stirred mixture of calix[4]arene **5** (5.00 g, 11.8 mmol) and benzyl bromide (4.43 g, 25.9 mmol) in DMF (125 mL), was added portionwise NaH (2.83 g of a 60% dispersion in paraffin, 70.7 mmol). The reaction mixture was stirred for 2.5 h at room temperature before cooling with an ice bath. Aqueous HCl (1 N, 100 mL) was then slowly added to the mixture, upon which the precipitate formed was collected on a Büchner funnel and washed with water (*ca.* 100 mL). The white solid was dissolved in CH_2Cl_2 (*ca.* 60 mL), and the resulting solution was dried with Na_2SO_4, then evaporated to dryness. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 35 : 65, v/v) to afford **10** as a white solid (R_f 0.44, SiO_2, CH_2Cl_2/petroleum ether, 50 : 50, v/v). Yield: 4.69 g, 66%; mp 224–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.97 (2H, s, OH), 7.52–7.46 (4H, m, ArH), 7.39–7.28 (6H, m, ArH), 7.06 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, ArH), 6.98–6.89 (6H, m, ArH), 6.78 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 6.57 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 5.05 and 4.86 (4H, AB spin system, $^2J_{AB}$ = 11.3 Hz, OCH_2), 4.47 and 3.32 (2H, AB spin system, $^2J_{AB}$ = 12.7 Hz, ArCH_2Ar), 4.23 and 3.30 (2H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar), 4.11 and 3.21 (4H, AB spin system, $^2J_{AB}$ = 13.0 Hz). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 153.28 and 151.17 (2 s, arom. Cq–O), 136.64, 134.74 and 134.48 (3 s, arom. Cq), 129.27 (s, 2x, arom. Cq and arom. CH), 129.03, 128.97, 128.80 and 128.70 (4 s, arom. CH), 128.64 (s, arom. Cq), 128.57, 128.12, 125.00 and 120.53 (4 s, arom. CH), 78.51 (s, OCH_2), 31.95 (s, 3x, ArCH_2Ar), 30.63 (s, ArCH_2Ar). The spectroscopic data are in full agreement with the literature.[43] Found: C, 83.15; H, 6.07. Calc. for $C_{42}H_{36}O_4$ (M_r = 604.73): C, 83.42; H, 6.00%.

5,11-Diiodo-25,26-dibenzyloxy-27,28-dihydroxycalix-[4]arene (*cone*) (11). A stirred mixture of calix[4]arene **10** (1.83 g, 3.03 mmol), NaOH (0.291 g, 7.27 mmol) and KI (1.21 g, 7.27 mmol) in MeOH/CH_2Cl_2 (40 mL, 1 : 1, v/v) was cooled at 0 °C and protected from light. Trichloroisocyanuric acid (TCIA, 0.561 g, 2.42 mmol) in MeOH (4 mL) was added dropwise to the mixture, which was then allowed to reach room temperature. After 4 h, CH_2Cl_2 (100 mL), water (50 mL) and aqueous HCl (1 N, 20 mL) were successively added to the mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The extracts were combined and washed with aqueous $Na_2S_2O_3$ (5%, 100 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 (SiO_2, CH_2Cl_2/petroleum ether, 30 : 70, v/v) to afford **11** as a white solid (R_f 0.61, SiO_2, CH_2Cl_2/petroleum ether, 50 : 50, v/v). Yield: 2.37 g, 91%; mp 245–248 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.98 (2H, s, OH), 7.52–7.45 (4H, m, ArH), 7.44–7.36 (6H, m, ArH), 7.27 (2H, d, ^4J = 2.2 Hz, ArH), 7.20 (2H, d, ^4J = 2.2 Hz, ArH), 7.13 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, ArH), 6.97 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, ArH), 6.86 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 5.06 and 4.86 (4H, AB spin system, $^2J_{AB}$ = 11.3 Hz, OCH_2), 4.46 and 3.36 (2H, AB spin system, $^2J_{AB}$ = 12.6 Hz, ArCH_2Ar), 4.11 and 3.18 (2H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar), 4.01 and 3.17 (4H, AB spin system, $^2J_{AB}$ = 13.0 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 153.11 and 151.29 (2 s, arom. Cq–O), 137.17 and 136.80 (2 s, arom. CH), 136.35, 134.73, 133.51, 132.03 and 130.50 (5 s, arom. Cq), 129.38, 129.30 and 129.05 (3 s, arom. CH), 128.78 and 128.75 (2 s, arom. CH), 125.32 (s, arom. CH), 82.65 (s, arom. Cq–I), 78.68 (s, OCH_2), 31.60 (s, 2x, ArCH_2Ar), 31.10 and 30.56 (2 s, ArCH_2Ar). Found: C, 59.14; H, 4.09. Calc. for $C_{42}H_{34}I_2O_4$ (M_r = 856.53): C, 58.89; H, 4.00%.

5,11-Diiodo-25,26,27,28-tetrabenzyloxycalix[4]arene (*cone*) (12). To a stirred mixture of calix[4]arene **11** (1.65 g, 1.93 mmol) and benzyl bromide (0.990 g, 5.79 mmol) in DMF (15 mL) was added portionwise NaH (0.232 g of a 60% dispersion in paraffin, 5.79 mmol). After stirring for 1 h at room temperature, the reaction mixture was heated at 70 °C for 24 h. After cooling to room temperature, aqueous HCl (1 N, 20 mL) was added followed by AcOEt (50 mL). The organic layer was separated and the aqueous phase was extracted with AcOEt (2 × 50 mL). The extracts were combined and washed with water (4 × 50 mL). The organic layer was dried over Na_2SO_4, then the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 25 : 75, v/v) to afford **12** as a white solid (R_f 0.44, SiO_2, CH_2Cl_2/petroleum ether, 30 : 70, v/v). Yield: 1.75 g, 88%; mp 182–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.20 (20H, m, ArH), 6.87 (2H, d, ^4J = 2.2 Hz, ArH), 6.80 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 6.80 (2H, d, ^4J = 2.2 Hz, ArH), 6.61 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, ArH), 6.55 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, ArH), 5.01–4.84 (8H, m, OCH_2), 4.29 and 3.05 (2H, AB spin system, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar), 4.13 and 2.89 (4H, AB spin system, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar), 3.96 and 2.70 (2H, AB spin system, $^2J_{AB}$ = 13.9 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.41 (s, 4x, arom. Cq–O), 138.34, 137.62 and 137.48 (3 s, arom. Cq), 137.35 (s, arom. CH), 137.08 (s, arom. Cq), 136.66 (s, arom. CH), 135.43 and 134.58 (2 s, arom. Cq), 129.79, 129.61, 128.71, 128.21, 128.05 and 122.94 (6 s, arom. CH), 86.43 (s, arom. Cq–I), 76.68 and 76.47 (2 s, OCH_2), 31.41 (s, ArCH_2Ar), 31.11 (s, 2x, ArCH_2Ar), 30.74 (s, ArCH_2Ar). Found: C, 65.03; H, 4.53. Calc. for $C_{56}H_{46}I_2O_4$ (M_r = 1036.77): C, 64.87; H, 4.47%.

5,11-Bis(*N*-imidazolyl)-25,26,27,28-tetrabenzyloxy-calix[4]-arene (*cone*) (13). To a mixture of diiodocalix[4]arene **12** (2.00 g, 1.93 mmol), imidazole (0.394 g, 5.79 mmol), K_2CO_3 (1.33 g, 9.65 mmol) and DMEDA (0.170 g, 1.93 mmol) was added 15 mL of degassed DMF. CuI (0.367 g, 1.93 mmol) was added and the reaction mixture was stirred under exclusion of light at 120 °C for 3 days. After cooling to room temperature, water (50 mL) was added followed by $CHCl_3$ (50 mL). The organic layer was separated and the aqueous phase was extracted with $CHCl_3$

(2 × 50 mL). The extracts were combined and washed with aqueous Na_4EDTA 0.2 N by vigorous stirring of the biphasic mixture over 1 h (3 × 80 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 (SiO_2, $MeOH/CH_2Cl_2$, 5 : 95, v/v) to afford **13** as a white solid (R_f 0.39, SiO_2, $MeOH/CH_2Cl_2$, 6 : 94, v/v). Yield: 1.41 g, 80%; mp 171–174 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56 (2H, s, NCHN), 7.36–7.21 (20H, m, ArH), 7.11 (2H, s, NCHC), 6.98 (2H, s, NCHC), 6.66–6.42 (10H, m, ArH), 5.05–4.87 (8H, m, OCH_2), 4.29 and 3.04 (2H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar), 4.22 and 2.94 (4H, AB spin system, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar), 4.16 and 2.85 (2H, AB spin system, $^2J_{AB}$ = 14.0 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.48 and 154.54 (2 s, arom. Cq–O), 137.54, 137.42, 136.90 and 136.56 (4 s, arom. Cq), 135.60 (s, arom. CH), 135.55 and 134.63 (2 s, arom. Cq), 131.84 (s, arom. Cq–N), 129.89, 129.71, 128.78, 128.34, 128.27, 128.18 and 128.04 (7 s, arom. CH), 76.90 and 76.60 (2 s, OCH_2), 31.62 (s, ArCH$_2$Ar), 31.50 (s, 2x, ArCH$_2$Ar), 31.35 (s, ArCH$_2$Ar). Found: C, 81.04; H, 5.75; N, 5.97. Calc. for $C_{62}H_{52}N_4O_4$ (M_r = 917.10): C, 81.20; H, 5.72; N, 6.11%.

5,11-Bis(3-methyl-1-imidazolylium)-25,26,27,28-tetra-benzyloxycalix[4]arene diiodide (*cone*) (3a). A stirred mixture of **13** (0.300 g, 0.33 mmol) and methyl iodide (65 µL, 1.04 mmol) in $CHCl_3$ (8 mL) was heated at 40 °C for 24 h. The reaction mixture was then evaporated to dryness to afford a yellow-brown solid, which was collected by filtration and washed with petroleum ether. The solid (**3a**) was dried under vacuum and used without further purification. Yield: 0.393 g, 99%; mp 152–154 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 10.23 (2H, s, NCHN), 7.80 (2H, s, NCHC), 7.43 (2H, s, NCHC), 7.37–7.23 (20H, m, ArH), 7.20 (2H, d, ^4J = 2.6 Hz, ArH), 6.84 (2H, d, ^4J = 2.6 Hz, ArH), 6.69–6.62 (4H, m, ArH), 6.51 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 5.04–4.86 (8H, m, OCH_2), 4.29 and 3.17 (2H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 4.22 and 3.02 (4H, AB spin system, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar), 4.17 (6H, s, CH_3), 4.15 and 3.04 (2H, AB spin system, $^2J_{AB}$ = 13.6 Hz, ArCH_2Ar). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 156.31 and 155.08 (2 s, arom. Cq–O), 138.08, 136.86, 136.11 and 135.27 (4 s, arom. Cq), 135.05 (s, arom. CH), 134.03 (s, arom. Cq), 129.54 and 129.45 (2 s, arom. CH), 128.64 (s, arom. Cq), 128.44, 128.29, 128.21, 128.14, 128.00, 124.28, 122.34, 121.64, 121.43 and 120.68 (10 s, arom. CH), 76.65 and 76.61 (2 s, OCH_2), 37.11 (s, CH_3), 31.04 (s, 3x, ArCH$_2$Ar), 30.83 (s, ArCH$_2$Ar). Found: C, 63.70; H, 5.13; N, 4.47. Calc. for $C_{64}H_{58}I_2N_4O_4$ (M_r = 1200.98): C, 64.00; H, 4.87; N, 4.67%.

5,11-Bis(3-butyl-1-imidazolylium)-25,26,27,28-tetra-benzyloxycalix[4]arene dibromide (*cone*) (3b). A stirred solution of **13** (0.400 g, 0.436 mmol) in *n*-butyl bromide (8 mL), was heated at reflux for 24 h. The precipitate formed was collected by filtration and washed with petroleum ether. The white solid (**3b**) was dried under vacuum and used without further purification. Yield: 0.514 g, 98%; mp 158–160 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 10.65 (2H, s, NCHN), 7.81 (2H, s, NCHC), 7.48 (2H, s, NCHC), 7.34–7.06 (22H, m, ArH), 6.73 (2H, d, ^4J = 2.3 Hz, ArH), 6.58 (2H, d, ^3J = 7.5 Hz, ArH), 6.51 (2H, d, ^3J = 7.5 Hz, ArH), 6.39 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 5.00–4.78 (8H, m, OCH_2), 4.51–4.30 (4H, ABX$_2$ spin system, NCH_2), 4.24 and 3.04 (2H, AB spin sytem, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 4.15 and 2.91 (4H, AB spin sytem, $^2J_{AB}$ = 13.8 Hz, ArCH_2Ar), 4.04 and 2.99 (2H, AB spin sytem, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 1.91 (4H, tt, $^3J = {}^3J'$ = 7.4 Hz, NCH_2CH_2), 1.35 (4H, tq, $^3J = {}^3J'$ = 7.4 Hz, CH_2CH_3), 0.90 (6H, t, ^3J = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 156.31 and 155.33 (2 s, arom. Cq–O), 138.11, 137.12, 137.03, 136.27 and 135.49 (5 s, arom. Cq), 135.18 (s, arom. CH), 134.33 (s, arom. Cq), 129.75 and 129.62 (2 s, arom. CH), 128.83 (s, arom. Cq), 128.60, 128.45, 128.28, 128.18, 123.14, 122.36, 121.71, 121.22 and 120.84 (9 s, arom. CH), 76.84 and 76.73 (2 s, OCH_2), 49.99 (s, NCH_2), 32.14 (s, NCH_2CH_2), 31.29 (s, 2x, ArCH$_2$Ar), 31.18 (s, ArCH$_2$Ar), 31.11 (s, ArCH$_2$Ar), 19.42 (s, CH_2CH_3), 13.46 (s, CH_3). Found: C, 69.29; H, 6.04; N, 4.49. Calc. for $C_{70}H_{70}Br_2N_4O_4 \cdot H_2O$ (M_r = 1191.14 + 18.02): C, 69.53; H, 6.00; N, 4.63%.

Palladium complexes

***trans*-Bis[5-(3-butylimidazol-2-yliden-1-yl)-25,26,27,28-tetra-benzyloxycalix[4]arene] palladium(II) dibromide (*cone*) (14).** A mixture of bromide **2** (0.412 g, 0.416 mmol), $PdCl_2$ (0.037 g, 0.208 mmol), Cs_2CO_3 (0.677 g, 2.08 mmol) and KBr (0.495 g, 4.16 mmol) in dioxane (5 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 70 : 30, v/v) to afford **14** as a yellow solid (R_f 0.43, SiO_2, CH_2Cl_2/petroleum ether, 70 : 30, v/v). Yield: 0.272 g, 63%; mp 134–136 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.41 (4H, m, ArH), 7.39–7.25 (28H, m, ArH), 7.24–7.16 (8H, m, ArH and NCHC), 7.07 (4H, s, ArH), 6.86–6.78 (6H, m, ArH), 6.77–6.67 (8H, m, ArH), 6.53–6.48 (2H, m, ArH), 6.48–6.41 (4H, m, ArH), 6.38 (2H, dd, ^3J = 8.7 Hz, $^3J'$ = 6.0 Hz, *p*-H of Ar opposite to Ar–N), 5.08 (8H, s, OCH_2), 4.95 (4H, s, OCH_2), 4.88 (4H, s, OCH_2), 4.42 (4H, t, ^3J = 6.6 Hz, NCH_2), 4.33 and 3.10 (8H, AB spin system, $^2J_{AB}$ = 13.5 Hz, ArCH_2Ar), 4.25 and 2.97 (8H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 1.82 (4H, tt, ^3J = 7.4 Hz $^3J'$ = 6.6 Hz, NCH_2CH_2), 1.30 (4H, tq, $^3J = {}^3J'$ = 7.4 Hz, CH_2CH_3), 0.84 (6H, t, ^3J = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 168.53 (s, NCN), 155.35 (s, arom. Cq–O), 155.30 (s, 2x, arom. Cq–O), 155.06 (s, arom. Cq–O), 137.75, 137.39, 135.98, 135.43, 135.20, 135.00 and 134.82 (7 s, arom. Cq), 130.01, 129.51, 129.35, 129.04, 128.79, 128.54, 128.26, 128.12, 128.01, 127.95, 127.90, 125.46, 122.77, 122.54, 122.22 and 120.04 (16 s, arom. CH), 77.24 and 76.93 (2 s, OCH_2), 76.11 (s, 2x, OCH_2), 50.42 (s, NCH_2), 32.20 (s, NCH_2CH_2), 31.50 (s, 4x, ArCH$_2$Ar), 20.19 (s, CH_2CH_3), 14.15 (s, CH_3). Found: C, 72.71; H, 5.68; N, 2.56. Calc. for $C_{126}H_{116}Br_2N_4O_8Pd$ (M_r = 2080.52): C, 72.74; H, 5.62; N, 2.69%.

***trans*-[5-(3-Butylimidazol-2-iden-1-yl)-25,26,27,28-tetrabenzyl-oxycalix[4]arene](pyridine) palladium(II) dibromide (*cone*) (15).** A mixture of bromide **2** (0.205 g, 0.207 mmol), $PdCl_2$ (0.044 g, 0.248 mmol), K_2CO_3 (0.143 g, 1.04 mmol) and KBr (0.492 g, 4.14 mmol) in pyridine (2 mL), was stirred at 80 °C for 18 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 60 : 40, v/v) to afford **15** as a yellow solid (R_f 0.32, SiO_2, CH_2Cl_2/petroleum ether, 60 : 40, v/v). Yield: 0.194 g, 75%; mp 105–108 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.91–8.85 (2H, m, *o*-NC_5H_5), 7.66 (1H, tt, ^3J = 7.6 Hz ^4J = 1.7 Hz, *p*-NC_5H_5), 7.40–7.13 (22H, m, ArH), 7.12–7.05 (2H, m, *m*-NC_5H_5), 6.96 (1H, d,

^3J = 2.0 Hz, NCHC), 6.83 (1H, d, ^3J = 2.0 Hz, NCHC), 6.72–6.62 (4H, m, ArH), 6.57 (1H, dd, ^3J = 8.3 Hz, $^3J'$ = 6.4 Hz, *p*-H of Ar opposite to Ar–N), 6.42–6.30 (4H, m, ArH), 5.04 (2H, s, OCH_2), 4.99 (2H, s, OCH_2), 4.91 and 4.85 (4H, AB spin system, $^2J_{AB}$ = 11.6 Hz, OCH_2), 4.57 (2H, t, ^3J = 7.5 Hz, NCH_2), 4.23 and 2.96 (4H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 4.18 and 2.95 (4H, AB spin system, $^2J_{AB}$ = 13.7 Hz, ArCH_2Ar), 2.11 (2H, tt, ^3J = $^3J'$ = 7.5 Hz, NCH_2CH_2), 1.52 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, CH_2CH_3), 1.04 (3H, t, ^3J = 7.5 Hz, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 155.70 and 155.41 (2 s, arom. Cq–O), 155.08 (s, 2x, arom. Cq–O), 152.65 (*o*-NC_5H_5), 147.61 (s, NCN), 137.77 (s, arom. Cq), 137.63 (*p*-NC_5H_5), 137.17, 136.81, 136.02, 134.60, 134.23 and 133.74 (6 s, arom. Cq), 130.17, 129.83, 129.52, 128.80, 128.42, 128.22, 128.07, 128.05, 127.97, 127.93, 127.90, 126.13, 124.42, 123.11, 122.73, 122.08 and 121.50 (17 s, arom. CH), 76.73 (s, 2x, OCH_2), 76.37 and 76.31 (2 s, OCH_2), 51.30 (s, NCH_2), 32.14 (s, NCH_2CH_2), 31.42 (s, 4x, ArCH_2Ar), 20.12 (s, CH_2CH_3), 13.93 (s, CH_3). Found: C, 65.48; H, 5.37; N, 3.21. Calc. for $C_{68}H_{63}Br_2N_3O_4Pd$ (M_r = 1252.47): C, 65.21; H, 5.07; N, 3.35%.

***trans*-[5,11-Bis(3-methylimidazol-2-yliden-1-yl)-25,26,27,28-tetrabenzyloxycalix[4]arene] palladium(II) diiodide (*cone*) (16).** A solution of diiodide **3a** (0.250 g, 0.208 mmol) and $Pd(OAc)_2$ (0.047 g, 0.208 mmol) in DMF (50 mL), was stirred at 50 °C for 1.5 h, then at 80 °C for 2 h and finally at 130 °C for 2 h. The mixture was cooled at room temperature and evaporated to dryness to afford a brown solid. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 90 : 10, v/v) to afford **16** as a yellow solid (R_f 0.38, SiO_2, CH_2Cl_2). Yield: 0.104 g, 38%; mp > 200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.87 (2H, d, ^4J = 2.6 Hz, *m*-ArH), 7.47–7.02 (20H, m, ArH), 7.15 (2H, d, ^3J = 1.8 Hz, NCHC), 6.97 (2H, d, ^3J = 1.8 Hz, NCHC), 6.90 (2H, dd, ^3J = 6.5 Hz, ^4J = 2.6 Hz, ArH), 6.74 (2H, d, ^4J = 2.6 Hz, ArH), 6.69–6.58 (4H, m, ArH), 5.06 and 4.92 (4H, AB spin system, $^2J_{AB}$ = 11.7 Hz, OCH_2), 4.99 (2H, s, OCH_2), 4.95 (2H, s, OCH_2), 4.38 and 3.30 (2H, AB spin system, $^2J_{AB}$ = 12.5 Hz, ArCH_2Ar), 4.28 and 2.91 (4H, AB spin system, $^2J_{AB}$ = 13.0 Hz, ArCH_2Ar), 4.14 and 2.94 (2H, AB spin system, $^2J_{AB}$ = 13.2 Hz, ArCH_2Ar), 4.08 (6H, s, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 167.00 (s, NCN), 154.77 and 154.34 (2 s, arom. Cq–O), 137.79, 137.46, 136.05, 135.12, 134.92, 134.51 and 133.41 (7 s, arom. Cq), 129.98, 129.62, 129.37, 128.79, 128.35, 128.18, 127.97, 127.82, 125.44, 123.57, 122.82, 122.32 and 121.31 (13 s, arom. CH), 77.82 and 76.01 (2 s, OCH_2), 39.28 (s, CH_3), 31.66 (s, ArCH_2Ar), 31.18 (s, 2x, ArCH_2Ar), 30.26 (s, ArCH_2Ar). ESI-TOF mass spectrum: *m*/*z* (%) 1343.11 (18) $[M + K]^+$, 1327.15 (16) $[M + Na]^+$, 1177.25 (100) $[M - I]^+$. Found: C, 58.24; H, 4.64; N, 4.13. Calc. for $C_{64}H_{56}I_2N_4O_4Pd{\cdot}0.6\ H_2O$ (M_r = 1305.38 + 10.81): C, 58.40; H, 4.38; N, 4.26%.

***trans*-[5,11-Bis(3-butylimidazol-2-yliden-1-yl)-25,26,27,28-tetrabenzyloxycalix[4]arene] palladium(II) dibromide (*cone*) (17).** A solution of dibromide **3b** (0.337 g, 0.282 mmol) and $Pd(OAc)_2$ (0.063 g, 0.282 mmol) in DMF (70 mL), was stirred at 50 °C for 1.5 h, then at 80 °C for 2 h and finally at 130 °C for 2 h. The mixture was cooled at room temperature and evaporated to dryness to afford a brown solid. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2) to afford **17** as a yellow solid (R_f 0.35, SiO_2, CH_2Cl_2). Yield: 0.131 g, 36%; mp > 240 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.92 (2H, d, ^4J = 2.4 Hz, *m*-ArH), 7.44–7.17 (20H, m, ArH), 7.08 (2H, d, ^3J = 1.5 Hz, NCHC), 6.93 (2H, d, ^3J = 1.5 Hz, NCHC), 6.81 (2H, dd, ^3J = 6.6 Hz, ^4J = 2.2 Hz, ArH), 6.69 (2H, d, ^4J = 2.4 Hz, ArH), 6.64–6.54 (4H, m, ArH), 5.01 and 4.92 (4H, AB spin system, $^2J_{AB}$ = 11.6 Hz, OCH_2), 4.93 and 4.88 (4H, AB spin system, $^2J_{AB}$ = 11.3 Hz, OCH_2), 4.78–4.51 (4H, ABX_2 spin system, NCH_2), 4.39 and 3.32 (2H, AB spin system, $^2J_{AB}$ = 12.4 Hz, ArCH_2Ar), 4.23 and 2.85 (4H, AB spin system, $^2J_{AB}$ = 13.0 Hz, ArCH_2Ar), 4.12 and 2.91 (2H, AB spin system, $^2J_{AB}$ = 13.3 Hz, ArCH_2Ar), 2.11 (4H, tt, ^3J = $^3J'$ = 7.4 Hz, NCH_2CH_2), 1.52 (4H, tq, ^3J = $^3J'$ = 7.4 Hz, CH_2CH_3), 1.04 (6H, t, ^3J = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 168.24 (s, NCN), 154.80 and 154.41 (2 s, arom. Cq–O), 137.91, 137.58, 135.97, 135.37, 134.95, 134.65 and 133.48 (7 s, arom. Cq), 130.05, 129.70, 129.32, 128.89, 128.38, 128.18, 128.01, 127.85, 125.85, 123.43, 122.57, 121.12 and 120.94 (13 s, arom. CH), 77.89 and 76.02 (2 s, OCH_2), 51.50 (s, NCH_2), 32.58 (s, NCH_2CH_2), 31.80 (s, ArCH_2Ar), 31.09 (s, 2x, ArCH_2Ar), 30.46 (s, ArCH_2Ar), 20.47 (s, CH_2CH_3), 14.03 (s, CH_3). MALDI-TOF mass spectrum: *m*/*z* (%) 1295.28 (44) $[M + H]^+$, 1134.42 (100) $[M - 2Br]^{2+}$, 1216.35 (37) $[M - Br + H]^{2+}$. Found: C, 65.19; H, 5.45; N, 4.14. Calc. for $C_{70}H_{68}Br_2N_4O_4Pd$ (M_r = 1295.54): C, 64.90; H, 5.29; N, 4.32%.

***trans*-[1-Butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]-(pyridine) palladium(II) dibromide (19).** A mixture of bromide **18** (0.502 g, 1.37 mmol), $PdCl_2$ (0.268 g, 1.51 mmol), K_2CO_3 (0.949 g, 6.87 mmol) and KBr (3.27 g, 27.5 mmol) in pyridine (7 mL), was stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate evaporated to dryness. The crude mixture was purified by flash chromatography (SiO_2, CH_2Cl_2/petroleum ether, 60 : 40, v/v) to afford **19** as a yellow solid (R_f 0.39, SiO_2, CH_2Cl_2/petroleum ether, 70 : 30, v/v). Yield: 0.603 g, 70%; mp 179–180 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.81–8.75 (2H, m, *o*-NC_5H_5), 7.64 (1H, tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.49 (1H, t, ^3J = 7.8 Hz, ArH), 7.33 (2H, d, ^3J = 7.8 Hz, ArH), 7.24–7.17 (2H, m, *m*-NC_5H_5), 7.12 (1H, d, ^3J = 2.0 Hz, NCHC), 6.96 (1H, d, ^3J = 2.0 Hz, NCHC), 4.79 (2H, t, ^3J = 7.9 Hz, NCH_2), 3.01 (2H, qq, ^3J = $^3J'$ = 6.7 Hz, $CHMe_2$), 2.19 (2H, tt, ^3J = 7.9 Hz $^3J'$ = 7.5 Hz, NCH_2CH_2), 1.58 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, CH_2CH_3), 1.41 (6H, d, 1.04, ^3J = 6.7 Hz, CH_3 of ^{i}Pr), 1.10 (3H, t, ^3J = 7.5 Hz, CH_2CH_3), 1.04 (6H, d, 1.04, ^3J = 6.7 Hz, CH_3 of ^{i}Pr). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 152.65 (*o*-NC_5H_5), 150.26 (NCN), 147.21 (s, arom. Cq), 137.60 (*p*-NC_5H_5), 134.69 (s, arom. Cq–N), 130.37 and 126.26 (2 s, arom. CH), 124.35 and 124.13 (2 s, NCH), 120.73 (s, arom. CH), 52.14 (s, NCH_2), 32.30 (s, NCH_2CH_2), 28.67 (s, $CHMe_2$), 26.66 ($CHCH_3$), 23.48 ($CHCH_3$), 20.20 (s, CH_2CH_3), 14.01 (s, CH_2CH_3). Found: C, 45.34; H, 5.32; N, 6.43. Calc. for $C_{24}H_{33}Br_2N_3Pd$ (M_r = 629.77): C, 45.77; H, 5.28; N, 6.67%.

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

In a Schlenk tube under nitrogen were introduced phenylboronic acid (0.183 g, 1.50 mmol), Cs_2CO_3 (0.652 g, 2 mmol) and a solution of the palladium complex in CH_2Cl_2. The solvent was removed under vacuum and 3 mL of dioxane were added. The stirred mixture was degassed by nitrogen bubbling (2 min), upon which the halide (1 mmol) was added and the mixture vigorously stirred at 80 °C for 2 h. The hot mixture was filtered through Celite. Then 1,4-dimethoxybenzene (0.069 g, 0.5 mmol; internal standard) was added to the filtrate. The solvent was removed under

reduced pressure and the crude mixture analysed by ^{1}H NMR. The yields were determined by comparing the intensity of methyl signal of the product (δ(Me) = 2.41 ppm) with that of the internal reference (δ(Me) = 3.78 ppm). In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than 5%) to that determined using the internal reference.

X-Ray crystallography

Crystal data for **14**: crystals suitable for X-ray diffraction were obtained by slow diffusion of cyclohexane into a thf solution of the complex: $C_{127.50}H_{119}Br_2N_4O_8Pd$, M = 2101.49, monoclinic, space group $P2_1/a$, a = 21.6895(4), b = 21.7815(3), c = 23.3319(4) Å, β = 106.156(2), V = 10587.4(3) Å^3, Z = 4, μ = 0.991 mm^{-1}, F(000) = 4368. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 140 K. 80046 reflections were collected ($2.55 < \theta < 27.00°$), 22899 were found to be unique and 11333 were observed (merging R = 0.0537). The structure was solved with SHELXS-97.[44] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.1037, 0.0383, 0.0863, 0.0783, 0.799. Residual electron density minimum/maximum = –0.601/0.606 e Å^{-3}. Important bond lengths and angles are given in Fig. 1. CCDC 821364.†

Crystal data for **16**: crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of the complex: $C_{66}H_{60}Cl_4I_2N_4O_4Pd$, M = 1475.18, triclinic, space group $P\bar{1}$, a = 13.2867(2), b = 13.6636(2), c = 19.0656(3) Å, α = 98.340(1), β = 94.964(1), γ = 117.181(1), V = 3000.2(1) Å^3, Z = 2, μ = 1.569 mm^{-1}, F(000) = 1472. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 150 K. 59591 reflections were collected ($2.56 < \theta < 27.00°$), 12097 were found to be unique and 9678 were observed (merging R = 0.0291). The structure was solved with SHELXS-97.[44] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0369, 0.0266, 0.0689, 0.0671, 0.952. Residual electron density minimum/maximum = –0.718/1.110 e Å^{-3}. Important bond lengths and angles are given in Fig. 2. CCDC 748587.†

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