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Complexes featuring N-heterocyclic carbenes with bowl-shaped wingtips.

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ABSTRACT

Three imidazolium salts having their two N-substituents equipped with remote calix[4]arenyl termini have been synthesised and converted into N-heterocyclic carbene (NHC) complexes of the type [PdCl₂(NHC)(pyridine)]. An X-ray diffraction study carried out for one of the complexes, namely *trans*-[1,3-bis(4-{25,26,27,28-tetrapropoxy-calix[4]aren-5-yl}phenyl)imidazol-2-ylidene](pyridine) palladium (II) dichloride, revealed that in the solid state the complex crystallises as a self-assembled dimer, its components being held together by dispersion forces involving the polyphenoxy units, the pyridine ligands and phenylene rings. This structure provides a new example of the diversity of interactions that may occur in NHC complexes of catalytic relevance, which are thus not limited to intramolecular ones. There was no spectroscopic indication that such interactions also occur in solution.

Keywords:

N-heterocyclic carbenes; calixarenes; Suzuki-Miyaura cross coupling; palladium

RESUME

Trois sels d'imidazolium ayant leurs atomes d'azote substitués par des groupes *arylcaxarényle* ont été préparés et utilisés pour la synthèse de complexes de type [PdCl₂(NHC)(pyridine)] (NHC = carbène N-hétérocyclique). L'analyse par diffraction des rayons X du complexe *trans*-[1,3-bis(4-{25,26,27,28-tétrapropoxy-calix[4]arèn-5-yl}phényl)imidazol-2-ylidène](pyridine) dichloropalladium(II) révèle, de manière inattendue, qu'à l'état solide ce composé s'auto-assemble, en formant un dimère dont les composantes sont maintenues ensemble par un jeu de forces faibles impliquant des unités phénoxy, les coordinats pyridine et les noyaux phénylène. Cette structure constitue un nouvel exemple de la complexité des phénomènes pouvant contribuer à influencer l'environnement stérique de complexes de carbènes N-hétérocycliques d'intérêt catalytique.

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1. Introduction

Steric effects play a central role in the chemistry of N-heterocyclic carbenes [1] (NHCs) and are largely controlled by the size and shape of the substituents of their nitrogen atoms [2-8]. Thus, bulky *N*-substituents provide kinetic stabilisation of free NHCs with respect to dimerisation [9, 10]; when bound to a metal, they may both increase complex stability and assist specific steps in catalytic reactions [11]. Typically, bulky NHCs such as IMes, IPr, IPent or IPr* (Fig. 1), display a hemi-ovoidal umbrella shape, thereby contrasting with the conical encumbrance brought about by bulky tertiary phosphines. The most useful parameter for the measure of their steric properties is the so-called “buried volume” ($\%V_{\text{Bur}}$), which expresses the percentage of volume occupied by the ligand within the first coordination sphere of the metal [12]. Actually, this parameter is only helpful for the rough prediction of steric effects, however it does not enable prediction of regioselectivities of catalytic reactions. These latter essentially depend on subtle interactions in the catalytic process between specific locations of the ligand and coordinated substrates. In this regard, it is useful to remind that a number of NHCs (notably the IBiox ligands, see Fig. 1) display in their complexes *flexible steric bulk* [13], a feature enabling these ligands to adapt to the steric requirements of intermediates of catalytic cycles and consequently improve the catalyst's performance. Thus, the value expressing the $\%V_{\text{Bur}}$ of a NHC may vary during a catalytic cycle. Finally, it should also be mentioned that the *buried volume* parameter does not integrate steric effects due to possible self-assembly phenomena.

"Figure 1 here"

Fig. 1. Conventional bulky NHCs

As part of a programme aimed at the development of NHCs displaying contours that delineate a sterically embracing environment, we have prepared the NHC precursors **1-3**, both characterised by the presence of cavity-shaped calixarene termini in their wingtips. We wondered whether in NHC-complexes derived from them, the two bowl-shaped units could influence ligands of the first coordination sphere. It is noteworthy that to date double calixarenes [14-16] having the macrocyclic units separated by an NHC spacer have not been documented.

"Figure 2 here"

Fig. 2. Imidazolium salts synthesised in the present study

2. Results and discussion

The imidazolium salts **1-3** were each prepared in a multi-step sequence (Scheme 1 and Scheme 2) starting from bromocalixarene **4**. Only the synthesis of **1** is discussed hereafter. Full description of the preparations of **2** and **3**, which are basically similar to that of **1**, are given in the experimental part. Thus, the preparation of **1** began with the synthesis of intermediate **5**, which was obtained from **4** by Br/Li exchange, followed by reaction with B(OMe)₃ and subsequent treatment with HCl (Scheme 1). The boronic acid **5**, which was used in its crude form, was then reacted with *tert*-butyl N-(4-bromo-2,6-dimethylphenyl)carbamate

under Suzuki-Miyaura coupling conditions, affording the N-protected aniline **6**. Deprotection of the latter with CF₃CO₂H in dichloromethane gave the primary amine **7**.

"Scheme 1 here"

Scheme 1. Stepwise synthesis of arylamine **7**

In the next step (Scheme 2), a solution of glyoxal, formaldehyde, acetic acid and ZnCl₂ was heated at 60°C for 5 min, then added to a mixture heated at 60°C of amine **7**, MgSO₄, and AcOH. After 0.5 h, dichloromethane was added to get an homogeneous solution. Treatment with HCl followed by addition of NH₄BF₄ in excess gave imidazolium salt **1**.

"Scheme 2 here"

Scheme 2. Multicomponent synthesis of imidazolium salt **1**

The ¹H NMR spectrum of each salt shows an imidazolium NCHN signal appearing in the usual range [17, 18], that of **1** being slightly less deshielded ($\delta = 8.46$) than that of the other two salts ($\delta = 9.26$ (**2**), $\delta = 9.26$ (**3**)). For all three compounds, the observed AB patterns (with *J* values ranging from 13.2 to 13.5 Hz) are characterised by a separation of the methylenic signals ($1.22 < \Delta\delta < 1.34$ ppm) typical of that of calix[4]arenes in the cone conformation [19, 20]. As expected, the BF₄ anions appear in the corresponding ¹⁹F NMR spectra as two broad peaks with relative intensities of 1:5 (separation *ca.* 0.05 ppm), this pattern being caused by the two boron isotopes, ¹⁰B and ¹¹B [21].

Compounds **1-3** were converted into the Pd-complexes **8-10** by their reaction with [PdCl₂] in pyridine in the presence of K₂CO₃ (Scheme 3). All three complexes were purified by column chromatography. The reaction leading to **8** was carried out at 80 °C, affording the product in 82% yield. Those resulting in **9** and **10** required to be done at room temperature in order to avoid product decomposition, this presumably due to facile cyclometallation. Under these conditions, **9** and **10** were obtained in respectively 60% and 68% yield.

"Scheme 3 here"

Scheme 3. Syntheses of complexes **8-10**

The ¹H and ¹³C{¹H} NMR spectra of the three carbene complexes present no anomalies. Thus, all ¹H NMR spectra show the presence of one NHC ring, one pyridine ligand and two equivalent calixarene units. The carbene carbons are observed at respectively 153.12 (**8**), 150.77 (**9**) and 151.53 (**10**) ppm in the ¹³C NMR spectra, these values being close to those observed for related [PdCl₂(NHC)(pyridine)] complexes based on a *imidazolylidene* [22].

The crystal structure of complex **9** was determined by a single crystal X-ray diffraction study (Fig. 3). Crystal and data collection are detailed in the experimental section. The unit cell consists of two pairs of self-assembled molecules of **9**, this considerably increasing crowding about the palladium atoms. The individual molecules of each dimer (denoted α and β) present similar structural features. Thus, in both molecules the palladium atom lies in a slightly distorted square planar ligand environment (non strictly linear Cl-Pd-Cl

arrangements, see Table 1) with Pd–C_{carb} (1.946(3) Å in α ; 1.954(3) in β), Pd–N (2.135(3) Å in α ; 2.099(3) in β), and Pd–Cl (2.312(1), 2.309(1) Å in α ; 2.310(1), 2.312(1) in β) bond lengths similar to those found in related molecules.

"Figure 3 here"

Fig. 3. Molecular structure of complex **9**. Solvent molecules have been omitted for clarity

Table 1

Selected distances (Å) and angles (°) in complex **9**

<i>Distances</i>			
<i>molecule α</i>			
C1-Pd1	1.946(3)	Pd1-Cl1	2.312(1)
Pd1-N3	2.135(3)	Pd1-Cl2	2.309(1)
<i>molecule β</i>			
C149-Pd2	1.954(3)	Pd2-Cl3	2.310(1)
Pd2-N6	2.099(3)	Pd2-Cl4	2.312(1)
<i>Angles</i>			
<i>molecule α</i>			
C49-Pd1-N3	179.13(11)	N3-Pd1-Cl2	93.38(9)
C49-Pd1-Cl2	86.37(10)	N3-Pd1-Cl1	94.40(9)
C49-Pd1-Cl1	85.84(10)	Cl2-Pd1-Cl1	172.20
<i>molecule β</i>			
C149-Pd2-N6	178.56(12)	N6-Pd2-Cl3	92.79(10)
C149-Pd2-Cl3	86.36(10)	N6-Pd2-Cl4	92.76(10)
C149-Pd2-Cl4	92.96(10)	Cl3-Pd2-Cl4	174.24(3)
<i>Interplanar angles</i>			
<i>molecule α</i>			
metal plane/pyridine plane	16.3(1)	metal plane/carbene ring	81.7(1)
carbene plane/N-aryl plane 1	36.2(1)	carbene plane/N-aryl plane 2	36.2(1)
<i>molecule β</i>			
metal plane/pyridine plane	32.9(1)	metal plane/carbene ring	32.9(1)
carbene plane/N-aryl plane 1	48.2(1)	carbene plane/N-aryl plane 2	39.2(1)

All calixarene units adopt a typical pinched cone conformation with interplanar angles between the facing phenoxy rings of 11.8°/79.1° and 23.4°/69.2° in α and 20.8°/72.6° and 22.0°/78.5° in β . It is interesting that the two phenoxy rings linked to the central NHC unit of each molecule are different in nature, one belonging to the pinched part of the corresponding calixarene moiety, the other to the flared part of the second calixarene end. Also noteworthy is the short separation between the *o*-phenylene protons and the metal centre (shortest separations 2.79(1) and 3.08(1) Å in α ; 2.73(1) and 2.84(1) Å in β), this suggesting that the phenylene units are prone to undergo cyclometallation (*vide supra*).

Examination of the solid state structure further reveals that the bulky calixarene moieties themselves are not responsible for the steric encumbrance created around the metal atoms, the observed crowding resulting in fact from the self-assembly phenomenon, which brings each pyridine ligand close to two calixarene phenoxy rings as well as to the pyridine moiety of the partner molecule. As could be inferred from the noncovalent interactions (NCI) analysis of the DFT-optimised structure, the two components of the dimer are held together by a network of attractive dispersion forces (Fig. 4). For example, each pyridine ligand is wrapped in a van der Waals surface involving interactions between the pyridine ligand (π stacking), a phenylene unit and a phenoxy(calix) ring of the partner molecule. Van der Waals interactions also exist between one phenoxy ring of each calixarene end and a specific phenylene-phenoxy fragment of the other molecule. However, these steric interactions could not be identified in solution (absence of crosspeaks in the corresponding ROESY spectrum).

"Figure 4 here"

Fig. 4. Non covalent interactions in complex **9-dimer** (optimised structure), with electrostatic interactions in blue, attractive dispersion forces in green, and steric repulsions in red.

Wondering whether the ability of Pd complexes of type **9** to self-assemble would influence their catalytic properties, we examined the behaviour of complex **8** in the cross coupling of phenyl boronic acid with 4-chlorotoluene at 80 °C (Scheme 4). Complexes **9** and **10** were not considered as appropriate for catalytic runs, as these readily underwent decomposition when heated. Catalysis was carried out in ethanol using 1 mol% of **8** in the presence of K_2CO_3 (1.5 equiv. per mol of 4-chlorotoluene). After 1h reaction time, 4-phenyltoluene was formed in 55% yield. Under identical conditions, the related complex

"Scheme 4 here"

Scheme 4. Suzuki-Miyaura cross coupling reaction with **8** and **11**

$[PdCl_2(IMEs)(pyridine)]$ (**11**) [23], an analogue which is devoid of calixarene ends, resulted in 77% yield. Since the carbene ligands of **8** and **11** possess quite similar electronic properties (δC_{carb}) = 153.1 (**8**); 152.9 (**11**) ppm), one would have expected that the bulkier carbene ligand of **8** would facilitate the reductive elimination step and thus result in a higher catalytic activity. As the reverse is the case, it appears likely that at least a fraction of the catalytic species self-assemble in a manner similar to that observed for **9** in the solid state, thereby rendering the metal more difficult of access. However, one has to be careful in interpreting our findings, as other phenomena may occur in a differentiated way for the two complexes, notably the formation of nanoparticles.

3. Conclusion

We have synthesised the first double calixarenes having their macrocyclic units linked through a symmetrically-substituted NHC spacer. The structural study of the $[PdCl_2(NHC)(pyridine)]$ complex **9** unexpectedly revealed how the presence of the calixarene termini may assist dimer formation in the solid state, thereby considerably increasing the

steric crowding about the metal centres. Consistent with a possible competitive aggregation phenomenon of this type in solution, the performance of **8** in a Suzuki cross coupling reaction was lower than that observed for a related, cavity-devoid analogue. Overall, the present study provides a new example of the difficulty in predicting steric effects in NHC complexes.

4. Experimental

Appendix A.

¹H and ¹³C NMR spectra of **1-3** and **8-10** and ¹⁹F NMR spectra of **1-3** can be found at <https://>

General procedures

The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ¹H and ¹³C{¹H} NMR spectra were recorded on FT Bruker Avance 500, 400 or 300 instruments at 25°C. ¹H NMR spectral data were referenced to residual protonated solvent (CHCl₃, δ 7.26; ¹³C chemical shifts are reported relative to deuterated solvent (CDCl₃, δ 77.16). The ¹⁹F NMR spectra of **1-3** were recorded on a FT Bruker Avance 300 apparatus (external reference CFC1₃). In the NMR data given hereafter, Cq denotes a quaternary carbon atom. The bridging CH₂ groups of the calixarene backbone are designated by the abbreviation ArCH₂Ar. 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. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (Unistra-CNRS), Strasbourg. X-ray diffraction analysis of complex **9** was performed by the Service de Radiocristallographie, Institut de Chimie de Strasbourg. *tert*-Butyl N-(4-bromo-2,6-dimethylphenyl)carbamate, *tert*-butyl N-(4-iodophenyl)carbamate and *tert*-butyl N-(3-bromophenyl)carbamate were obtained according to a procedure reported for a related compound [24] (*vide infra*). The procedure for the preparation of the *symmetrical* imidazolium salts **1-3** was inspired by that applied by Mauduit *et al.* for the synthesis of *unsymmetrically-substituted* imidazolium salts [25]. The structural formula of the N-protected compounds **6'** and **6''**, both related to calixarene **6**, and the amines **7'** and **7''**, analogues of **7**, are given in the supplementary data. 5-Bromo-25,26,27,28-tetrapropylcalix[4]arene **4** [26] and [PdCl₂(IMes)(pyridine)] (**11**) [23] were synthesised according to published methods. In the following the abbreviation "Py" stands for pyridine.

***tert*-Butyl N-(4-bromo-2,6-dimethylphenyl)carbamate.**

Boc₂O (4.40 g, 20.0 mmol) was added to a solution of 4-bromo-2,6-dimethylaniline (4.00 g, 20.0 mmol) in THF (20 mL). The resulting mixture was stirred for 18 h at 65°C. The solvent was removed in vacuo and the resulting residue was recrystallised from CH₂Cl₂/petroleum ether affording the arylcarbamate as a white solid (4.12 g, 69%). The product did not require further purification. ¹H NMR (400 MHz, CDCl₃), δ 7.19 (2H, s, ArH), 5.83 (1H, s, NH), 2.22 (6H, s, 2CH₃), 1.48 (9H, s, C(CH₃)₃). NMR spectroscopic data are consistent with those of the literature [27].

***tert*-Butyl N-(4-iodophenyl)carbamate.**

Boc₂O (5.00 g, 22.9 mmol) was added to a solution of 4-iodoaniline (5.00 g, 22.8 mmol) in THF (20 mL). The resulting mixture was stirred for 18 h at 65°C. Then the solvent was removed in vacuo and the resulting residue was recrystallised from CH₂Cl₂/petroleum ether

affording the arylcarbamate as a white solid (5.11 g, 70%). The product did not require further purification. ^1H NMR (500 MHz, CDCl_3), δ 7.55 (2H, d, $^3J = 8.5$ Hz, ArH), 7.14 (2H, d, $^3J = 8.5$ Hz, ArH), 6.62 (1H, s, NH), 1.49 (9H, s, CH_3). NMR spectroscopic data are consistent with those of the literature [28].

***tert*-Butyl N-(3-bromophenyl)carbamate.**

Boc_2O (10.00 g, 58.1 mmol) was added to a solution of 3-bromoaniline (12.70 g, 58.1 mmol) in THF (40 mL). The resulting mixture was stirred for 18 h at 65°C . Then the solvent was removed in vacuo and the resulting residue was recrystallized from CH_2Cl_2 /petroleum ether affording the arylcarbamate as a white solid (10.30 g, 65%). The product did not require further purification. ^1H NMR (300 MHz, CDCl_3), δ 7.66 (1H, s, ArH), 7.23-7.08 (3H, m, ArH), 6.47 (1H, s, NH), 1.51 (9H, s, CH_3). NMR spectroscopic data are consistent with those of the literature [29].

5-(3,5-Dimethyl-4-*tert*-butyloxycarbonylaminophenyl)-25,26,27,28-tetrapropoxylix[4]arene (6).

A 1.5 M solution of *n*-BuLi in hexanes (3.1 mL, 4.90 mmol) was added dropwise to a solution of 5-bromo-25,26,27,28-tetrapropoxylix[4]arene (**4**) (3.00 g, 4.46 mmol) in THF (50 mL) at -78°C . After 40 min, $\text{B}(\text{OMe})_3$ (1.00 mL, 0.92 g, 8.95 mmol) was added dropwise to the solution. After stirring for 1 h at room temperature, the solution was quenched with aq. HCl (1 M, 100 mL) and the product extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried over MgSO_4 . The solvent was removed in vacuum yielding the crude boronic acid **5** as a white powder, which was used without further purification. *tert*-Butyl (4-bromo-2,6-dimethylphenyl)carbamate (1.34 g, 4.46 mmol), boronic acid **5**, K_2CO_3 (0.92 g, 6.69 mmol) and $[\text{PdCl}_2(\text{IMes})(\text{pyridine})]$ (0.125 g, 0.222 mmol) were introduced in a Schlenk flask containing absolute EtOH (50 mL). The mixture was stirred at 80°C for 24 h. After cooling to room temperature the mixture was passed through celite and the filtrate evaporated to dryness. The crude product was purified by flash chromatography (SiO_2 ; AcOEt/petroleum ether, 7 : 93; $R_f = 0.28$) to afford **6** as a white solid (2.18 g, 60%). ^1H NMR (CDCl_3 , 400 MHz), δ 6.98 (2H, s, ArH), 6.85-6.63 (8H, m, ArH), 6.56 (2H, d, $^3J = 7.3$ Hz, ArH), 6.40 (1H, t, $^3J = 7.3$ Hz, ArH), 5.92 (1H, br s, NH), 4.55 and 3.26 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.4$ Hz, Ar CH_2 Ar), 4.53 and 3.21 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.4$ Hz, Ar CH_2 Ar), 4.01-3.83 (8H, m, OCH_2), 2.32 (6H, s, *o*- CH_3), 2.07-1.92 (8H, m, CH_2CH_3), 1.56 (9H, br s, $\text{C}(\text{CH}_3)_3$), 1.13-1.01 (12H, m, CH_2CH_3) ppm. Due to the dynamic conformation of the carbamate group, some ^1H NMR peaks were very broad. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz), δ 156.83 (2 \times arom. Cq-O), 156.36 (arom. Cq-O), 156.06 (arom. Cq-O), 153.83 (NHCO), 140.42 (arom. Cq-N), 135.50 (arom. Cq), 135.35 (arom. Cq), 135.34 (arom. Cq), 134.95 (arom. Cq), 134.82 (arom. Cq), 132.33 (arom. Cq), 128.41 (2 \times arom. CH), 127.99 (arom. CH), 127.09 (arom. CH), 126.97 (arom. CH), 122.04 (2 \times arom. CH), 79.84 ($\text{C}(\text{CH}_3)_3$), 76.88 (OCH_2), 76.77 (3 \times OCH_2), 31.18 (Ar CH_2 Ar), 31.07 (Ar CH_2 Ar), 28.42 (CH_3)₃, 23.43 (CH_2CH_3), 23.40 (CH_2CH_3), 23.31 (2 \times CH_2CH_3), 18.61 (*o*- CH_3), 10.53 (CH_2CH_3), 10.37 (CH_2CH_3) ppm. Found C, 77.89; H, 8.05; N, 1.82. Calc. for $\text{C}_{53}\text{H}_{65}\text{NO}_6$ ($M_r = 811.48$): C, 78.38; H, 8.07; N, 1.73%. Despite several recrystallisations, elemental C-analyses remained unsatisfactory.

5-(4-*tert*-Butyloxycarbonylaminophenyl)-25,26,27,28-tetrapropoxylix[4]arene (6').

A 1.5 M solution of *n*-BuLi in hexanes (6.2 mL, 9.80 mmol) was added dropwise to a solution of 5-bromo-25,26,27,28-tetrapropoxylix[4]arene (**4**) (6.00 g, 8.93 mmol) in THF (120 mL) at -78°C . After 40 min, $\text{B}(\text{OMe})_3$ (2.00 mL, 1.84 g, 17.9 mmol) was added dropwise to the solution. After stirring for 1 h at room temperature, the solution was quenched with aq. HCl (1 M, 240 mL) and the product extracted with CH_2Cl_2 (3×100 mL). The combined

organic layers were dried over MgSO₄. The solvent was removed in vacuum yielding the crude boronic acid **5** as a white powder, which was used without further purification. *tert*-Butyl (4-iodophenyl)carbamate (2.85 g, 8.93 mmol), crude boronic acid **5**, K₂CO₃ (1.85 g, 13.39 mmol) and [PdCl₂(IMes)(pyridine)] (0.250 g, 0.445 mmol) were introduced in a Schlenk flask containing absolute EtOH (50 mL). The mixture was then stirred at 80°C for 24 h. After cooling to room temperature the solution was passed through Celite and the filtrate evaporated under reduced pressure. The residue was purified by flash chromatography (SiO₂; CH₂Cl₂/petroleum ether, 40 : 60; R_f = 0.33) to afford **6'** as a white solid (4.58 g, 65%). ¹H NMR (CDCl₃, 500 MHz), δ 7.39 (2H, d, ³J = 8.5 Hz, ArH), 7.25 (2H, d, ³J = 8.5 Hz, ArH), 6.93-6.83 (4H, m, ArH), 6.78 (2H, dd, ³J = ³J' = 7.4 Hz, ArH), 6.73 (2H, s, ArH), 6.64 (1H, s, NH), 6.50 (2H, d, ³J = 7.4 Hz, ArH), 6.33 (1H, t, ³J = 7.4 Hz, ArH), 4.59 and 3.29 (4H, d, AB spin system, ²J_{AB} = 13.5 Hz, ArCH₂Ar), 4.57 and 3.25 (4H, d, AB spin system, ²J_{AB} = 13.5 Hz, ArCH₂Ar), 4.07-3.98 (4H, m, OCH₂), 3.97-3.86 (4H, m, OCH₂), 2.13-1.95 (8H, m, CH₂CH₃), 1.62 (9H, s, C(CH₃)₃), 1.19-1.04 (12H, m, CH₂CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz), δ 157.07 (2 × arom. Cq-O), 156.17 (arom. Cq-O), 155.79 (arom. Cq-O), 152.91 (NHCO), 136.70 (arom. Cq-N), 136.45 (arom. Cq), 135.79 (arom. Cq), 135.60 (arom. Cq), 134.86 (arom. Cq), 134.56 (arom. Cq), 134.23 (arom. Cq), 128.51 (arom. CH), 128.49 (arom. CH), 127.83 (arom. CH), 127.34 (arom. CH), 126.42 (arom. CH), 122.10 (arom. CH), 121.99 (arom. CH), 118.57 (arom. CH), 80.46 (C(CH₃)₃), 76.86 (OCH₂), 76.73 (OCH₂), 76.71 (2 × OCH₂), 31.19 (ArCH₂Ar), 31.07 (ArCH₂Ar), 28.42 (C(CH₃)₃), 23.43 (CH₂CH₃), 23.26 (CH₂CH₃), 10.58 (CH₂CH₃), 10.28 (CH₂CH₃) ppm. Found C, 77.97; H, 7.99; N, 1.66. Calc. for C₅₁H₆₁NO₆ (M_r = 784.05): C, 78.13; H, 7.84; N, 1.79%.

5-(3-*tert*-Butyloxycarbonylaminophenyl)-25,26,27,28-tetrapropylloxycalix[4]arene (**6''**).

A 1.5 M solution of *n*-BuLi in hexanes (6.2 mL, 9.80 mmol) was added dropwise to a solution of 5-bromo-25,26,27,28-tetrapropylloxycalix[4]arene (**4**) (6.00 g, 8.93 mmol) in THF (120 mL) at -78 °C. After 40 min, B(OMe)₃ (2.00 mL, 1.84 g, 17.9 mmol) was added dropwise to the solution. After stirring for 1 h at room temperature, the solution was quenched with aq. HCl (1 M, 240 mL) and the product extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over MgSO₄. The solvent was removed in vacuum yielding the crude boronic acid **5** as a white powder, which was used without further purification. *tert*-Butyl (3-bromophenyl)carbamate (2.43 g, 8.93 mmol), boronic acid **5**, K₂CO₃ (1.850 g, 13.39 mmol) and [PdCl₂(IMes)(pyridine)] (0.250 g, 0.445 mmol) were introduced in a Schlenk flask containing absolute EtOH (50 mL). The mixture was stirred at 80°C for 24 h. After cooling to room temperature the mixture was passed through celite and the filtrate evaporated to dryness. The crude product was purified by flash chromatography (SiO₂; CH₂Cl₂/petroleum ether, 40 : 60; R_f = 0.27) to afford **6''** as a white solid (4.55 g, 65%). ¹H NMR (CDCl₃, 500 MHz), δ 7.38-7.30 (1H, m, ArH), 7.27 (1H, dd, ³J = ³J' = 7.6 Hz, ArH), 7.23 (1H, s, ArH), 6.94 (2H, d, ³J = 7.6 Hz, ArH), 6.77 (2H, s, ArH), 6.74- 6.67 (4H, m, ArH), 6.64 (2H, dd, ³J = ³J' = 7.5 Hz, ArH), 6.53 (2H, d, ³J = 7.5 Hz, ArH), 6.50 (1H, s, NH), 6.37 (1H, t, ³J = 7.5 Hz, ArH), 4.51 and 3.22 (4H, d, AB spin system, ²J_{AB} = 13.3 Hz, ArCH₂Ar), 4.48 and 3.17 (4H, d, AB spin system, ²J_{AB} = 13.3 Hz, ArCH₂Ar), 3.95-3.81 (8H, m, OCH₂), 2.03-1.88 (8H, m, CH₂CH₃), 1.55 (9H, s, C(CH₃)₃), 1.08-0.97 (12H, m, CH₂CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz), δ 156.82 (2 × arom. Cq-O), 156.49 (arom. Cq-O), 156.45 (arom. Cq-O), 152.83 (NHCO), 142.55 (arom. Cq-N), 138.42 (arom. Cq), 135.49 (arom. Cq), 135.26 (arom. Cq), 135.23 (arom. Cq), 135.01 (arom. Cq), 134.48 (arom. Cq), 129.01 (arom. CH), 128.43 (arom. CH), 128.39 (arom. CH), 128.07 (arom. CH), 126.94 (arom. CH), 122.08 (2 × arom. CH), 121.92 (arom. CH), 117.21 (arom. CH), 116.58 (arom. CH), 80.53 (C(CH₃)₃), 76.89 (OCH₂), 76.80 (3 × OCH₂), 31.28 (ArCH₂Ar), 31.10 (ArCH₂Ar), 28.49 ((CH₃)₃), 23.44 (CH₂CH₃),

23.41 (CH_2CH_3), 23.35 ($2 \times \text{CH}_2\text{CH}_3$), 10.54 (CH_2CH_3), 10.42 (CH_2CH_3) ppm. Found C, 77.92; H, 7.82; N, 1.98. Calc. for $\text{C}_{51}\text{H}_{61}\text{NO}_6$ ($M_r = 784.05$): C, 78.13; H, 7.84; N, 1.79%.

5-(4-Amino-3,5-dimethylphenyl)-25,26,27,28-tetrapropoxy-calix[4]arene (7).

Trifluoroacetic acid (1.82 g, 15.9 mmol) was added dropwise to a stirred solution of calix[4]arene **6** (1.00 g, 1.23 mmol) in CH_2Cl_2 (12 mL) cooled at 0°C . After 15 min, the reaction mixture was allowed to reach room temperature and stirred for a further 2 h. The mixture was washed with an aqueous solution of K_2CO_3 (20%, 150 mL) and the two phases were separated. The aqueous phase was treated with dichloromethane (2×100 mL) and the organic phases were then combined. The solvent was removed under reduced pressure to afford **7** as a beige solid (0.816 g, 93%), which did not need further purification. ^1H NMR (CDCl_3 , 500 MHz), δ 6.98 (2H, s, ArH), 6.84 (2H, s, ArH), 6.67 (4H, d, $^3J = 7.4$ Hz, ArH), 6.63-6.55 (4H, m, ArH), 6.53 (1H, t, $^3J = 7.4$ Hz, ArH), 4.53 and 3.24 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.3$ Hz, ArCH_2Ar), 4.51 and 3.20 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.3$ Hz, ArCH_2Ar), 3.98-3.85 (8H, m, OCH_2), 3.50 (2H, br s, NH_2), 2.26 (6H, s, $o\text{-CH}_3$), 2.06-1.92 (8H, m, CH_2CH_3), 1.11-0.99 (12H, m, CH_2CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz), δ 156.76 (arom. Cq-O), 156.54 ($2 \times$ arom. Cq-O), 155.69 (arom. Cq-O), 141.41 (arom. Cq-N), 135.38 (arom. Cq), 135.27 (arom. Cq), 135.03 ($3 \times$ arom. Cq), 131.89 (arom. Cq), 128.30 (arom. CH), 128.21 (arom. CH), 128.13 (arom. CH), 127.12 (arom. CH), 126.62 (arom. CH), 122.00 ($2 \times$ arom. CH), 121.76 (arom. Cq), 76.81 ($3 \times$ OCH_2), 76.72 (OCH_2), 31.22 (ArCH_2Ar), 31.10 (ArCH_2Ar), 23.39 ($3 \times \text{CH}_2\text{CH}_3$), 23.35 (CH_2CH_3), 17.92 ($o\text{-CH}_3$), 10.51 ($2 \times \text{CH}_2\text{CH}_3$), 10.44 (CH_2CH_3), 10.43 (CH_2CH_3) ppm. Found C, 80.69; H, 8.11; N, 2.09. Calc. for $\text{C}_{48}\text{H}_{57}\text{NO}_4$ ($M_r = 711.99$): C, 80.97; H, 8.07; N, 1.97%.

5-(4-Aminophenyl)-25,26,27,28-tetrapropoxy-calix[4]arene (7').

Trifluoroacetic acid (4.20 g, 36.8 mmol) was added dropwise to a stirred solution of calix[4]arene **6'** (2.17 g, 2.77 mmol) in CH_2Cl_2 (20 mL) cooled at 0°C . After 15 min, the reaction mixture was allowed to reach room temperature and stirred for a further 2 h. The mixture was washed with an aqueous solution of K_2CO_3 (20%, 100 mL) and the two phases were separated. The aqueous phase was treated with dichloromethane (2×100 mL) and the organic phases were then combined. The solvent was removed under reduced pressure to afford **7'** as a white solid (1.66 g, 88%), which did not need further purification. ^1H NMR (CDCl_3 , 500 MHz), δ 7.16 (2H, d, $^3J = 8.3$ Hz, ArH), 6.80 (2H, d, $^3J = 7.5$ Hz, ArH), 6.76 (2H, s, ArH), 6.75 (2H, d, $^3J = 8.3$ Hz, ArH), 6.72-6.66 (4H, m, ArH), 6.55 (2H, d, $^3J = 7.5$ Hz, ArH), 6.41 (1H, t, $^3J = 7.5$ Hz, ArH), 4.55 and 3.26 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.4$ Hz, ArCH_2Ar), 4.54 and 3.22 (4H, d, AB spin system, $^2J_{\text{AB}} = 13.4$ Hz, ArCH_2Ar), 3.96 (4H, t, $^3J = 7.6$ Hz, OCH_2), 3.93-3.87 (4H, m, OCH_2), 3.63 (2H, br s, NH_2), 2.06-1.94 (8H, m, CH_2CH_3), 1.14-1.01 (12H, m, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz), δ 156.87 ($2 \times$ arom. Cq-O), 156.41 (arom. Cq-O), 155.51 (arom. Cq-O), 144.94 (arom. Cq-N), 135.50 (arom. Cq), 135.40 (arom. Cq), 134.98 (arom. Cq), 134.92 (arom. Cq), 134.78 (arom. Cq), 132.20 (arom. Cq), 128.40 (arom. CH), 128.35 (arom. CH), 127.99 (arom. CH), 127.81 (arom. CH), 126.20 (arom. CH), 122.06 (arom. CH), 121.97 (arom. CH), 115.17 (arom. CH), 76.86 (OCH_2), 76.75 ($3 \times \text{OCH}_2$), 31.21 (ArCH_2Ar), 31.08 (ArCH_2Ar), 23.43 (CH_2CH_3), 23.39 (CH_2CH_3), 23.32 ($2 \times \text{CH}_2\text{CH}_3$), 10.53 (CH_3), 10.38 (CH_3) ppm. Found C, 80.67; H, 7.82; N, 2.06. Calc. for $\text{C}_{46}\text{H}_{53}\text{NO}_4$ ($M_r = 683.93$): C, 80.78; H, 7.81; N, 2.05%.

5-(3-Aminophenyl)-25,26,27,28-tetrapropoxy-calix[4]arene (7'').

Trifluoroacetic acid (7.56 g, 66.3 mmol) was added dropwise to a stirred solution of calix[4]arene **6''** (4.00 g, 5.10 mmol) in CH_2Cl_2 (20 mL) cooled at 0°C . After 15 min, the reaction mixture was allowed to reach room temperature and stirred for a further 2 h. The

mixture was washed with an aqueous solution of K_2CO_3 (20%, 150 mL) and the two phases were separated. The aqueous phase was treated with dichloromethane (2×100 mL) and the organic phases were then combined. The solvent was removed under reduced pressure to afford **7'** as a white solid (3.43 g, 97%), which did not need further purification. 1H NMR ($CDCl_3$, 500 MHz), δ 7.14 (1H, dd, $^3J = ^3J' = 7.7$ Hz, ArH), 6.77-6.68 (7H, m, ArH), 6.66-6.60 (3H, m, ArH), 6.59 (1H, dd, $^3J = 7.7$ Hz, $^4J = 1.9$ Hz, ArH), 6.51 (2H, d, $^3J = 7.4$ Hz, ArH), 6.38 (1H, t, $^3J = 7.4$ Hz, ArH), 4.51 and 3.21 (4H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 4.48 and 3.17 (4H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 3.94-3.81 (8H, m, OCH₂), 3.65 (2H, br s, NH₂), 2.02-1.89 (8H, m, CH₂CH₃), 1.09-0.96 (12H, m, CH₃), ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 156.88 (2 \times arom. Cq-O), 156.44 (arom. Cq-O), 156.24 (arom. Cq-O), 146.26 (arom. Cq-N), 142.87 (arom. Cq), 135.56 (arom. Cq), 135.34 (arom. Cq), 135.06 (arom. Cq), 134.95 (arom. Cq), 134.93 (arom. Cq), 129.28 (arom. CH), 128.42 (2 \times arom. CH), 128.03 (arom. CH), 126.87 (arom. CH), 122.08 (arom. CH), 122.05 (arom. CH), 117.78 (arom. CH), 114.03 (arom. CH), 113.30 (arom. CH), 76.92 (OCH₂), 76.79 (3 \times OCH₂), 31.23 (ArCH₂Ar), 31.11 (ArCH₂Ar), 23.46 (CH₂CH₃), 23.42 (CH₂CH₃), 23.34 (2 \times CH₂CH₃), 10.55 (CH₃), 10.40 (CH₃) ppm. Found C, 80.57; H, 7.76; N, 2.09. Calc. for C₄₆H₅₃NO₄ ($M_r = 683.93$): C, 80.78; H, 7.81; N, 2.05%.

1,3-Bis[2,6-dimethyl-4-(25,26,27,28-tetrapropoxyxycalix[4]aren-5-yl)phenyl]imidazolium tetrafluoroborate (**1**).

A mixture of 5-(4-amino-3,5-dimethylphenyl)-25,26,27,28-tetrapropoxyxycalix[4]arene (**7**) (1.71 g, 2.41 mmol) and acetic acid (0.310 mL, 0.325 g, 5.42 mmol) was heated at 60°C for 5 min and MgSO₄ (0.290 g, 2.41 mmol) was added (mixture A). In another flask, a mixture of glyoxal (0.137 mL, 0.174 g, 1.20 mmol, 40 wt % in water), formaldehyde (0.090 mL, 0.097 g, 1.20 mmol, 37 wt % in water) and acetic acid (0.310 mL, 0.325 g, 5.42 mmol) was heated at 60°C for 5 min and ZnCl₂ (0.196 g, 1.44 mmol) was added (mixture B). At 60°C mixture B was added to mixture A, the resulting mixture was stirred at 60°C for 25 min and then cooled to room temperature. CH₂Cl₂ (30 mL) and a 3 M aqueous solution of HCl (50 mL) were added and the resulting mixture was stirred for 1 h at room temperature. The organic layer was separated. Water (20 mL) and ammonium tetrafluoroborate (0.313 g, 2.99 mmol) were added, and the mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO₂; EtOAc/petroleum ether, 50 : 50, R_f = 0-0.47) to afford **1** as a tan solid (1.33 g, 71%). 1H NMR ($CDCl_3$, 500 MHz), δ 8.45 (1H, s, NCHN), 7.67 (2H, s, NCH), 7.14 (4H, s, ArH), 6.81 (4H, s, ArH), 6.73 (4H, d, $^3J = 7.4$ Hz, ArH), 6.69-6.61 (8H, m, ArH), 6.57 (4H, d, $^3J = 7.4$ Hz, ArH), 6.40 (2H, t, $^3J = 7.4$ Hz, ArH), 4.54 and 3.23 (8H, d, AB spin system, $^2J_{AB} = 13.5$ Hz, ArCH₂Ar), 4.50 and 3.16 (8H, d, AB spin system, $^2J_{AB} = 13.4$ Hz, ArCH₂Ar), 3.99-3.82 (16H, m, OCH₂), 2.18 (12H, s, *o*-CH₃), 2.05-1.91 (16H, m, CH₂CH₃), 1.13-0.97 (24H, m, CH₂CH₃) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 157.12 (arom. Cq-O), 156.65 (2 \times arom. Cq-O), 156.53, (arom. Cq-O), 144.63 (arom. Cq-N), 136.54 (NCHN), 135.67 (arom. Cq), 135.33 (arom. Cq), 135.05 (arom. Cq), 134.91 (arom. Cq), 134.23 (arom. Cq), 132.98 (arom. Cq), 131.10 (arom. Cq), 128.43 (arom. CH), 128.36 (arom. CH), 127.99 (arom. CH), 127.79 (arom. CH), 127.12 (arom. CH), 125.52 (arom. CH), 122.15 (arom. CH), 121.85 (arom. CH), 76.91 (OCH₂), 76.80 (2 \times OCH₂), 76.77 (OCH₂), 31.12 (ArCH₂Ar), 31.00 (ArCH₂Ar), 23.39 (CH₂CH₃), 23.34 (CH₂CH₃), 23.30 (2 \times CH₂CH₃), 17.57 (*o*-CH₃), 10.45 (CH₂CH₃), 10.37 (CH₂CH₃) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), -152.32 (br s, ^{19}F - ^{10}B), -152.37 to -152.39 (m, ^{19}F - ^{11}B) ppm. Found C, 76.55; H, 7.40; N, 1.75. Calc. for C₉₉H₁₁₃BF₄N₂O₈ ($M_r = 1545.80$): C, 76.92; H, 7.37; N, 1.81%

1,3-Bis[4-(25,26,27,28-tetrapropylloxycalix[4]aren-5-yl)phenyl]imidazolium tetrafluoroborate (2).

A mixture of 5-(4-aminophenyl)-25,26,27,28-tetrapropylloxycalix[4]arene (**7'**) (6.65 g, 9.72 mmol) and acetic acid (1.25 mL, 1.31 g, 21.9 mmol) was heated at 60°C for 5 min and MgSO₄ (1.17 g, 9.72 mmol) was added (mixture A). In another flask, a mixture of glyoxal (0.555 mL, 0.705 g, 4.86 mmol, 40 wt % in water), formaldehyde (0.361 mL, 0.394 g, 4.86 mmol, 37 wt % in water) and acetic acid (1.25 mL, 1.31 g, 21.9 mmol) was heated at 60°C for 5 min and ZnCl₂ (0.794 g, 5.83 mmol) was added (mixture B). At 60°C mixture B was added to mixture A, the resulting mixture was stirred at 60°C for 25 min and then cooled to room temperature. CH₂Cl₂ (70 mL) and a 3 M aqueous solution of HCl (100 mL) were added and the resulting mixture was stirred for 1 h at room temperature. The organic layer was separated. Water (40 mL) and ammonium tetrafluoroborate (1.02 g, 9.72 mmol) were added, and the mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO₂; EtOAc/petroleum ether, 50 : 50, R_f = 0-0.51) to afford **2** as a tan solid (4.40 g, 61%). ¹H NMR (CDCl₃, 500 MHz), δ 9.26 (1H, s, NCHN), 7.73 (2H, s, NCH), 7.64 (4H, d, ³J = 7.7 Hz, ArH), 7.39 (4H, d, ³J = 7.7 Hz, ArH), 6.80 (4H, d, ³J = 7.4 Hz, ArH), 6.77 (4H, d, ³J = 7.4 Hz, ArH), 6.70 (4H, dd, ³J = ³J' = 7.4 Hz), 6.65 (4H, s, ArH), 6.36 (4H, d, ³J = 7.4 Hz, ArH), 6.16 (2H, t, ³J = 7.4 Hz, ArH), 4.50 and 3.19 (8H, d, AB spin system, ²J_{AB} = 13.4 Hz, ArCH₂Ar), 4.45 and 3.12 (8H, d, AB spin system, ²J_{AB} = 13.4 Hz, ArCH₂Ar), 3.97-3.88 (8H, m, OCH₂), 3.85 (4H, t, ³J = 7.2 Hz, OCH₂), 3.77 (4H, t, ³J = 7.2 Hz, OCH₂), 2.01-1.85 (16H, m, CH₂CH₃), 1.07 (6H, t, ³J = 7.4 Hz, CH₃), 1.04 (6H, t, ³J = 7.4 Hz, CH₃), 0.98 (12H, t, ³J = 7.4 Hz, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz), δ 157.03 (2 × arom. Cq-O), 157.00 (arom. Cq-O), 156.20 (arom. Cq-O), 144.02 (arom. Cq-N), 135.89 (arom. Cq), 135.48 (arom. Cq), 135.37 (arom. Cq), 134.60 (arom. Cq), 132.35 (arom. Cq), 131.95 (NCHN), 128.73 (arom. CH), 128.71 (arom. CH), 128.51 (arom. CH), 127.79 (arom. CH), 126.76 (arom. CH), 122.39 (arom. CH), 122.24 (arom. CH), 122.16 (arom. CH), 121.89 (arom. CH), 77.00 (OCH₂), 76.85 (OCH₂), 76.75 (2 × OCH₂), 31.17 (ArCH₂Ar), 31.04 (ArCH₂Ar), 23.50 (CH₂CH₃), 23.45 (CH₂CH₃), 23.26 (2 × CH₂CH₃), 10.63 (CH₃), 10.27 (CH₃) ppm. ¹⁹F NMR (CDCl₃, 282 MHz), -151.00 (br s, ¹⁹F-¹⁰B), -151.05 (br s, ¹⁹F-¹¹B) ppm. Found C, 76.23; H, 7.22; N, 2.10. Calc. for C₉₅H₁₀₅BF₄N₂O₈ (M_r = 1489.69): C, 76.60; H, 7.10; N, 1.88%.

1,3-Bis[3-(25,26,27,28-tetrapropylloxycalix[4]aren-5-yl)phenyl]imidazolium tetrafluoroborate (3).

A mixture of 5-(3-aminophenyl)-25,26,27,28-tetrapropylloxycalix[4]arene (**7''**) (2.04 g, 2.99 mmol) and acetic acid (0.384 mL, 0.404 g, 6.73 mmol) was heated at 60°C for 5 min and MgSO₄ (0.359 g, 2.99 mmol) was added (mixture A). In another flask, a mixture of glyoxal (0.170 mL, 0.216 g, 1.49 mmol, 40 wt % in water), formaldehyde (0.111 mL, 0.121 g, 1.49 mmol, 37 wt % in water) and acetic acid (0.384 mL, 0.404 g, 6.73 mmol) was heated at 60°C for 5 min and ZnCl₂ (0.244 g, 1.79 mmol) was added (mixture B). At 60°C mixture B was added to mixture A, the resulting mixture was stirred at 60°C for 25 min and then cooled to room temperature. CH₂Cl₂ (30 mL) and a 3 M aqueous solution of HCl (50 mL) were added and the resulting mixture was stirred for 1 h at room temperature. The organic layer was separated. Water (20 mL) and ammonium tetrafluoroborate (0.313 g, 2.99 mmol) were added, and the mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO₂; EtOAc/petroleum ether, 50 : 50, R_f = 0-0.5) to afford **3** as a tan solid (0.508 g, 23%). ¹H NMR (CDCl₃, 500 MHz), δ 9.26 (1H, s, NCHN), 7.74 (2H, s, NCH), 7.63-7.42 (4H, m, ArH), 7.40-7.20 (4H, m, ArH), 6.93-6.75 (8H,

m, ArH), 6.71 (4H, d, $^3J = 7.3$ Hz, ArH), 6.66 (4H, dd, $^3J = ^3J' = 7.3$ Hz), 6.49 (4H, d, $^3J = 7.3$ Hz, ArH), 6.26 (2H, t, $^3J = 7.3$ Hz, ArH), 4.51 and 3.29 (8H, d, AB spin system, $^2J_{AB} = 13.2$ Hz, ArCH₂Ar), 4.48 and 3.16 (8H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 3.97-3.85 (12H, m, OCH₂), 3.83 (4H, t, $^3J = 7.4$ Hz, OCH₂), 2.03-1.88 (16H, m, CH₂CH₃), 1.10-0.96 (24H, m, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 125 MHz), δ 157.25 (arom. Cq-O), 156.85 (2 \times arom. Cq-O), 156.45 (arom. Cq-O), 144.06 (arom. Cq-N), 135.80 (arom. Cq), 135.53 (arom. Cq), 135.25 (arom. Cq), 134.96 (arom. Cq), 134.44 (arom. Cq), 132.37 (NCHN), 132.19 (arom. Cq), 130.76 (arom. CH), 128.86 (arom. CH), 128.56 (arom. CH), 128.47 (arom. CH), 127.88 (arom. CH), 126.98 (arom. CH), 122.72 (arom. CH), 122.14 (arom. CH), 121.77 (arom. CH), 120.27 (arom. CH), 120.10 (arom. CH), 76.96 (OCH₂), 76.85 (OCH₂), 76.77 (2 \times OCH₂), 31.10 (ArCH₂Ar), 31.05 (ArCH₂Ar), 23.43 (CH₂CH₃), 23.39 (CH₂CH₃), 23.29 (2 \times CH₂CH₃), 10.52 (CH₃), 10.34 (CH₃) ppm. ^{19}F NMR (CDCl₃, 282 MHz), -150.31 (br s, ^{19}F - ^{10}B), -150.36 (br s, ^{19}F - ^{11}B) ppm. Found C, 72.97; H, 6.92; N, 1.73. Calc. for C₉₅H₁₀₅BF₄N₂O₈·CH₂Cl₂ ($M_r = 1489.69 + 84.93$): C, 73.23; H, 6.85; N, 1.78%.

***trans*-[1,3-Bis-{2,6-dimethyl-4-(25,26,27,28-tetrapropoxy-calix[4]aren-5-yl)phenyl}imidazol-2-ylidene](pyridine)palladium(II) dichloride (8).**

A suspension of imidazolium salt **1** (0.200 g, 0.133 mmol), finely crushed K₂CO₃ (0.092 g, 0.665 mmol) and PdCl₂ (0.028 g, 0.159 mmol) in pyridine (4 mL) was heated at 80°C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the collected solid washed with CH₂Cl₂ (ca. 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; CH₂Cl₂/petroleum ether, 60 : 40; R_f = 0.68) to afford **8** as a yellow solid (0.187 g, 82%). ^1H NMR (CDCl₃, 500 MHz), δ 8.51-8.47 (2H, m, *o*-NC₅H₅), 7.54 (1H, tt, $^3J = 7.6$ Hz, $^4J = 1.7$ Hz, *p*-NC₅H₅), 7.19 (4H, s, ArH), 7.13 (2H, s, NCH), 7.10-7.05 (2H, m, *m*-NC₅H₅), 6.93 (4H, s, ArH), 6.73-6.66 (4H, m, ArH), 6.64-6.57 (12H, m, ArH), 6.48 (2H, t, $^3J = 7.5$ Hz, ArH), 4.53 and 3.25 (8H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 4.48 and 3.17 (8H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 3.93 (4H, t, $^3J = 7.4$ Hz, OCH₂), 3.90-3.84 (12H, m, OCH₂), 2.43 (12H, s, *o*-CH₃), 2.02-1.88 (16H, m, CH₂CH₃), 1.06-0.98 (24H, m, CH₂CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 125 MHz), δ 156.81 (arom. Cq-O), 156.72 (arom. Cq-O), 156.65 (2 \times arom. Cq-O), 153.12 (NCN), 151.67 (arom. CH *o*-Py), 142.39 (arom. Cq-N), 137.52 (arom. CH *p*-Py), 136.67 (arom. Cq), 136.01 (arom. Cq), 135.62 (arom. Cq), 135.33 (arom. Cq), 135.23 (arom. Cq), 135.00 (arom. Cq), 134.05 (arom. Cq), 128.47 (arom. CH), 128.33 (arom. CH), 128.17 (arom. CH), 127.20 (arom. CH), 127.18 (arom. CH), 124.34 (arom. CH), 124.05 (arom. CH), 122.22 (arom. CH), 122.13 (arom. CH), 76.91 (OCH₂), 76.87 (2 \times OCH₂), 76.79 (OCH₂), 31.29 (ArCH₂Ar), 31.16 (ArCH₂Ar), 23.46 (CH₂CH₃), 23.41 (3 \times CH₂CH₃), 19.52 (*o*-CH₃), 10.50 (CH₂CH₃), 10.48 (CH₂CH₃) ppm. Found C, 72.64; H, 6.97; N, 2.53. Calc. for C₁₀₄H₁₁₇Cl₂N₃O₈Pd ($M_r = 1714.41$): C, 72.86; H, 6.88; N, 2.45%.

***trans*-[1,3-Bis{4-(25,26,27,28-tetrapropoxy-calix[4]aren-5-yl)phenyl}imidazol-2-ylidene](pyridine) palladium(II) dichloride (9).**

A suspension of imidazolium salt **2** (0.429 g, 0.298 mmol), finely crushed K₂CO₃ (0.206 g, 1.49 mmol) and PdCl₂ (0.063 g, 0.357 mmol) in pyridine (6 mL) was stirred at room temperature for 18 h. The mixture was filtered through Celite and the filtered solid washed with CH₂Cl₂ (ca. 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; CH₂Cl₂/petroleum ether, 50 : 50; R_f = 0.59) leading to **9** as a yellow solid (0.296 g, 60%). ^1H NMR (CDCl₃, 500 MHz), δ 8.69 (2H, d, $^3J = 5.2$ Hz, *o*-NC₅H₅), 8.10 (4H, d, $^3J = 8.2$ Hz, ArH), 7.66 (1H, t, $^3J = 7.7$ Hz, *p*-NC₅H₅), 7.47 (4H, d, $^3J = 8.2$ Hz, ArH), 7.33 (2H, s, NCH), 7.22 (2H, dd, $^3J = 7.7$ Hz, $^3J' = 5.2$ Hz, *m*-NC₅H₅), 6.90

(4H, d, $^3J = 7.4$ Hz, ArH), 6.85 (4H, d, $^3J = 7.4$ Hz, ArH), 6.82-6.74 (7H, m, ArH), 6.45 (4H, d, $^3J = 7.4$ Hz, ArH), 6.30 (2H, t, $^3J = 7.4$ Hz, ArH), 4.58 and 3.29 (8H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 4.52 and 3.21 (8H, d, AB spin system, $^2J_{AB} = 13.3$ Hz, ArCH₂Ar), 3.99 (8H, dd, $^3J = ^3J' = 7.1$ Hz, OCH₂), 3.91 (4H, t, $^3J = 7.1$ Hz, OCH₂), 3.85 (8H, t, $^3J = 7.1$ Hz, OCH₂), 2.12-1.91 (16H, m, CH₂CH₃), 1.12 (6H, t, $^3J = 7.3$ Hz, CH₃), 1.09 (6H, t, $^3J = 7.3$ Hz, CH₃), 1.03 (12H, t, $^3J = 7.3$ Hz, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz), δ 157.07 (2 \times arom. Cq-O), 156.43 (arom. Cq-O), 156.14 (arom. Cq-O), 151.25 (arom. CH *o*-Py), 150.77 (NCN), 142.05 (arom. Cq-N), 137.77 (arom. CH *p*-Py), 137.64 (arom. Cq), 135.89 (arom. Cq), 135.51 (arom. Cq), 135.11 (arom. Cq), 134.53 (arom. Cq), 133.47 (arom. Cq), 128.67 (arom. CH), 128.52 (arom. CH), 127.85 (arom. CH), 127.61 (arom. CH), 126.81 (arom. CH), 125.94 (arom. CH), 124.36 (arom. CH), 123.56 (arom. CH), 122.18 (arom. CH), 122.04 (arom. CH), 76.94 (OCH₂), 76.78 (OCH₂), 76.72 (2 \times OCH₂), 31.21 (ArCH₂Ar), 31.07 (ArCH₂Ar), 23.47 (CH₂CH₃), 23.43 (CH₂CH₃), 23.25 (2 \times CH₂CH₃), 10.61 (CH₃), 10.26 (CH₃) ppm. Found C, 72.22; H, 6.71; N, 2.45. Calc. for C₁₀₀H₁₀₉Cl₂N₃O₈Pd ($M_r = 1658.31$): C, 72.43; H, 6.63; N, 2.53%.

***trans*-[1,3-Bis-{3-(25,26,27,28-tetrapropoxy)calix[4]aren-5-yl}phenyl]imidazol-2-ylidene(pyridine) palladium(II) dichloride (10).**

A suspension of imidazolium salt **3** (0.200 g, 0.139 mmol), finely crushed K₂CO₃ (0.096 g, 0.695 mmol) and PdCl₂ (0.029 g, 0.166 mmol) in pyridine (4 mL) was stirred at room temperature for 18 h. The mixture was filtered through Celite and the collected solid washed with CH₂Cl₂ (ca. 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO₂; CH₂Cl₂/petroleum ether, 60 : 40; R_f = 0.56) to afford **10** as a yellow solid (0.157 g, 68%). ¹H NMR (CDCl₃, 500 MHz), δ 8.68 (2H, d, $^3J = 5.2$ Hz, *o*-NC₅H₅), 8.32 (2H, s, ArH), 8.14 (2H, d, $^3J = 7.5$ Hz, ArH), 7.65-7.55 (4H, m, ArH), 7.53 (1H, t, $^3J = 7.3$ Hz, *p*-NC₅H₅), 7.42 (2H, s, NCH), 7.18 (4H, s, ArH), 7.06 (2H, dd, $^3J = 7.3$ Hz, $^3J' = 5.2$ Hz, *m*-NC₅H₅), 6.76 (4H, d, $^3J = 7.5$ Hz, ArH), 6.60 (2H, t, $^3J = 7.4$ Hz, ArH), 6.57-6.53 (4H, m, ArH), 6.41-6.43 (8H, m, ArH), 4.51 and 3.21 (8H, d, AB spin system, $^2J_{AB} = 13.2$ Hz, ArCH₂Ar), 4.49 and 3.17 (8H, d, AB spin system, $^2J_{AB} = 13.2$ Hz, ArCH₂Ar), 3.97 (4H, t, $^3J = 7.4$ Hz, OCH₂), 3.93 (4H, t, $^3J = 7.4$ Hz, OCH₂), 3.83 (8H, t, $^3J = 7.4$ Hz, OCH₂), 2.02-1.87 (16H, m, CH₂CH₃), 1.06 (12H, t, $^3J = 7.4$ Hz, CH₃), 1.01 (6H, t, $^3J = 7.4$ Hz, CH₃), 0.99 (6H, t, $^3J = 7.4$ Hz, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz), δ 157.37 (arom. Cq-O), 157.07 (arom. Cq-O), 156.21 (2 \times arom. Cq-O), 151.53 (NCN), 151.29 (arom. CH *o*-Py), 142.71 (arom. Cq-N), 139.73 (arom. Cq), 137.65 (arom. CH *p*-Py), 136.27 (arom. Cq), 135.82 (arom. Cq), 134.62 (arom. Cq), 134.34 (arom. Cq), 133.31 (arom. Cq), 129.51 (arom. CH), 128.39 (arom. CH), 128.24 (arom. CH), 128.07 (arom. CH), 127.27 (arom. CH), 127.18 (arom. CH), 124.42 (arom. CH), 123.77 (arom. CH), 123.48 (arom. CH), 122.19 (arom. CH), 122.00 (arom. CH), 76.92 (2 \times OCH₂), 76.81 (OCH₂), 76.70 (OCH₂), 31.24 (ArCH₂Ar), 31.10 (ArCH₂Ar), 23.45 (2 \times CH₂CH₃), 23.33 (CH₂CH₃), 23.29 (CH₂CH₃), 10.61 (CH₃), 10.32 (CH₃) ppm. Found C, 71.84; H, 6.69; N, 2.43. Calc. for C₁₀₀H₁₀₉Cl₂N₃O₈Pd \cdot 0.25 CH₂Cl₂ ($M_r = 1658.31 + 21.23$): C, 71.69; H, 6.52; N, 2.50%.

General procedure for palladium-catalysed Suzuki-Miyaura cross-coupling reactions: A mixture of the palladium complex (0.01 mmol), phenylboronic acid (0.146 g, 1.20 mmol) and K₂CO₃ (0.207 g, 1.50 mmol) was suspended in absolute ethanol (3 mL). After addition of *p*-tolyl chloride (0.126 g, 1 mmol), the mixture was vigorously stirred at 80 °C for 1 h. The hot mixture was filtered through Celite. 1,4-Dimethoxybenzene (0.069 g, 0.5 mmol), used as internal standard, was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ¹H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ (Me) = 2.41 ppm]

with that of the internal reference [$\delta(\text{Me}) = 3.78$ ppm]. The isolated yield (concerning experiments with chromatographic product separation) turned out to be very close to that determined by using the internal reference (deviation less than 5%).

Crystal data for complex 9. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a chloroform solution of the complex. Crystal data: $\text{C}_{100}\text{H}_{109}\text{Cl}_2\text{N}_3\text{O}_8\text{Pd}\cdot\text{CHCl}_3$, $M_r = 1777.56$ g mol⁻¹, triclinic, space group $P\bar{1}$, $a = 13.7011(5)$ Å, $b = 22.8400(8)$ Å, $c = 35.5075(13)$ Å, $\alpha = 73.332(2)^\circ$, $\beta = 83.700(2)^\circ$, $\gamma = 79.678(2)^\circ$, $V = 10452.3(7)$ Å³, $Z = 4$, $D = 1.130$ g cm⁻³, $\mu = 3.004$ mm⁻¹, $F(000) = 3728$, $T = 173(2)$ K. The sample was studied on a Kappa APEX II diffractometer (graphite monochromated Cu-K α radiation, $\lambda = 1.54178$ Å). The data collection ($2\theta_{\text{max}} = 133.7^\circ$, omega scan frames by using 2° omega rotation and 10 s per frame, range hkl : $h -16,16$ $k -27,23$ $l -42,40$) gave 204167 reflections. The structure was solved using SHELXS-2013 [30], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all hydrogen atoms were found using a Fourier difference map. The structure was refined using SHELXL-2013 [31] by the full-matrix least-squares technique (use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N and Pd atoms; x, y, z in riding mode for H atoms); 2138 variables and 27946 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.1202P)^2 + 1.2609P]$ where $P = (F_o^2 + 2F_c^2)/3$, with the resulting $R = 0.0601$, $R_w = 0.1837$ and $S_w = 1.081$, $\Delta\rho < 1.149$ e Å⁻³. CCDC 1882970.

Computational details

All calculations were performed with the Gaussian 09 program [32], using the functional PBEPBE [33]. Dispersion corrections were included [34]. All atoms were described using the def2-SVP basis set [35] and associated pseudopotential for the palladium atom. To get an optimised structure, the geometry was simplified by replacing the propoxy groups of the calixarenes by methoxy groups. The structure was fully optimised and the wavefunction saved. The non-covalent interactions analysis [36] was performed on this geometry. All calculations were performed in gas phase.

Acknowledgements

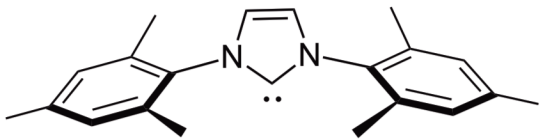
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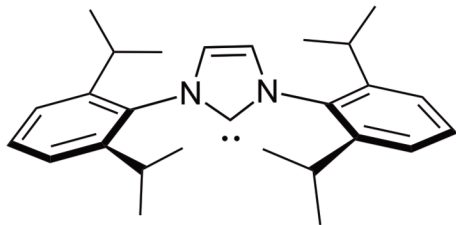
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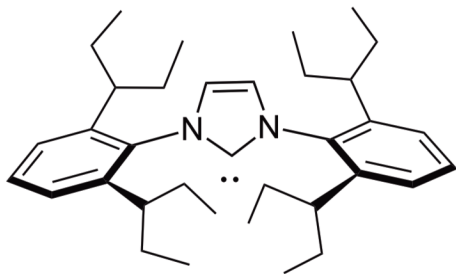
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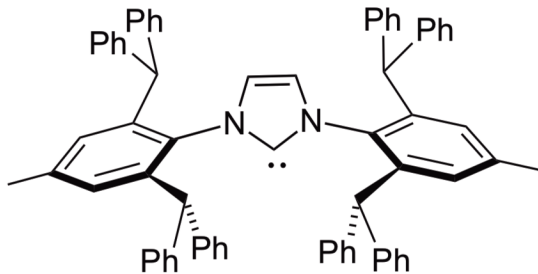
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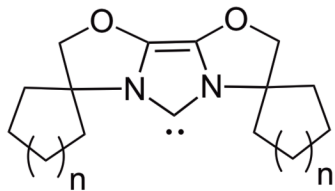
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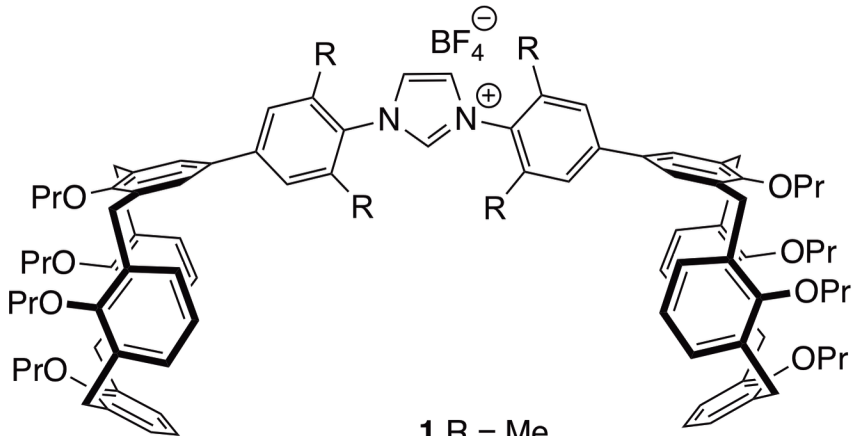
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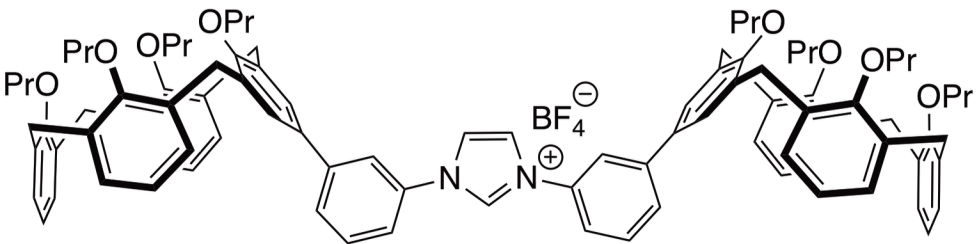
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IBiox



1 R = Me
2 R = H



3

