Calix[4]arene-Supported *N*-Heterocyclic Carbene Ligands as Catalysts for Suzuki Cross-Coupling Reactions of Chlorotoluene

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Stable *N*-heterocyclic carbenes are generated starting from 5,17-(bis-imidazolium)-substituted calix[4]arenes. Addition of $Pd(OAc)_2$ to these carbenes leads to macrocyclic *cis*-palladium chelate complexes in which the distal bridging of the upper rim leads to a strong distortion of the calix[4]arene skeleton which was proven by X-ray crystal structure determination. Using an in-situ catalytic system consisting of a calixarene-imidazolium salt, Cs_2CO_3 as a base and a source of palladium, a species is formed which can be used to catalyse the Suzuki cross-coupling of 4-chloro toluene.

Introduction

Recently, imidazolium salts have gained a fair amount of interest in both organic syntheses and supramolecular chemistry. Such salts can be used as a recognition element in receptors for anions.[1] Appropriately substituted imidazolium salts find applications as ionic liquids which are novel tailor-made and "green" solvents for organic transformations.[2,3] Above all, imidazolium salts may serve as simple precursors for *N*-heterocyclic carbenes (NHC)[4−10], which are actually extensively used as ligands for transition metal complexes. Such NHCs can often replace phosphanes as ligands for catalysts, for example in metathesis,[10−12] and cross-coupling reactions.[10,13−18] Nucleophilic carbenes exhibit basically the same σ-donor and low π-acceptor ability as phosphanes[19,20] partly substituting the latter and supplementing the stock of organic ligands in transition metal catalysis. In dealing with chelating bis-NHC ligands, alkyl chains,[21−23] planar aromatics[24−28] or chiral binaphthyl[29] linkers are normally used. Macrocyclic compounds such as cyclophanes[30,31] have come into focus recently and may provide new and interesting applications.

Results and Discussion

During our previous studies of imidazole-substituted calix[4]arenes as simple enzyme mimics showing hydrolytic properties[32] our interest was focused on the use of imidazolium salts based on calixarenes as precursors for a new group of macrocyclic chelating NHC ligands. Based on thorough studies of calixarenes bearing phosphanes as ligands for transition metal complexes[33,34] the following basic building principle should be pursued: A calix[4]arene skeleton may serve as a platform to attach NHC ligands. Because of the typical geometry[35,36] of calix[4]arenes it is easy to identify different functional sites on the calixarene. The upper (wide) rim of the macrocycle may serve to place ligands at discrete positions. Variation of both the number and the relative geometry of the ligands can be easily adjusted to fit the needs imposed by the catalytic task. Functionalisation of the calix[4]arene at the lower (narrow) rim with propyl groups fixes the *cone* conformation and enhances the solubility in organic solvents.

A modular synthetic approach should be used to ensure fast and efficient access to imidazolium salts as precursors for NHC ligands. Two calixarenes **1**[37] and **3**[38] bearing chloromethyl groups at the upper rim and fixed in the *cone* conformation by propyl groups at the lower rim are central synthetic building blocks which can easily react with a plethora of substituted imidazoles to give the desired salts (Schemes 1 and 2).

Selective distal acylation of the *p*-*tert*-butylcalix[4]arene at the narrow rim[32,39] followed by removal of the *tert*-butyl groups located at the activated, unprotected phenol units leaves free positions at the wide rim that can be used for further functionalisation. NBS bromination, halogen metal exchange using *tert*-BuLi and quenching with carbon dioxide yields a bis-carboxylic acid.[40,41] Reduction and chlorination ($SOCl_2$) gives rise to the desired calixarene **1** bearing chloromethyl groups at the distal position at the upper rim (Scheme 1).

Direct chloromethylation of the de-*tert*-butylated calixarene intermediate is possible;[42,43] however, the yields we obtained were inferior to those obtained with the described multi-step protocol. Reaction with various substituted imidazoles results in calixarenes **2** bearing alternating *tert*-bu-

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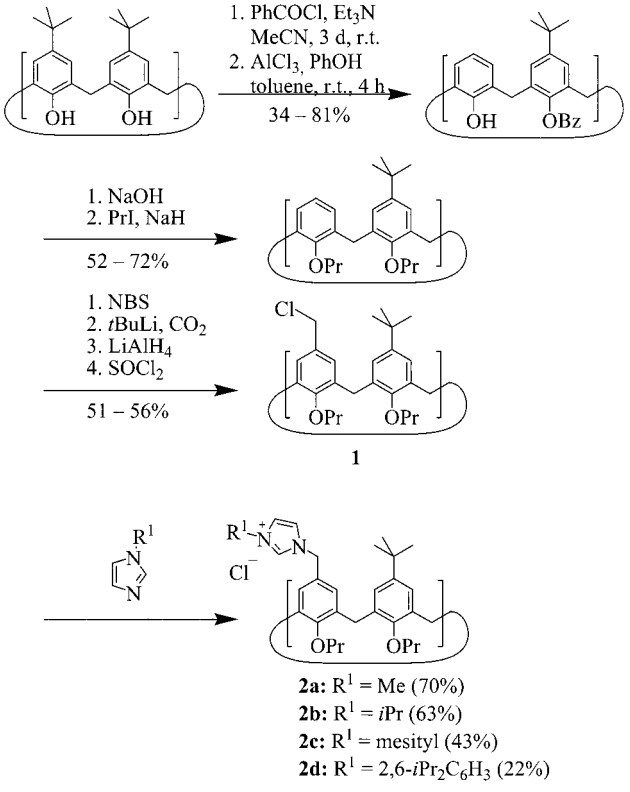
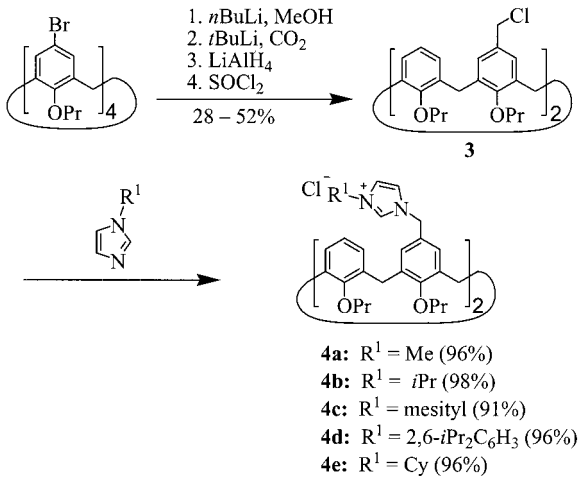
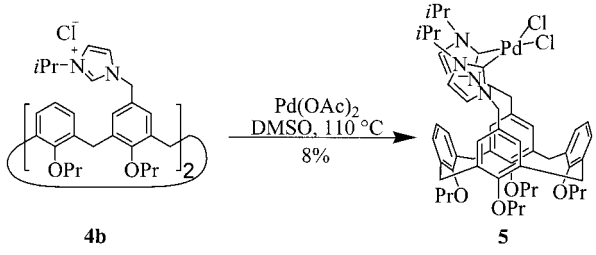


Scheme 1



Scheme 2

When imidazolium salts **2** and **4** are treated with $Pd(OAc)_2$ in DMSO at elevated temperatures the corresponding chelates $[Pd(L-L)Cl_2]$ can be isolated and purified by column chromatography (Scheme 3) emphasising the stability of such palladium complexes. The low yields of the palladium chelate complex may be partly due to the formation of oligomeric complexes.



Scheme 3

tyl groups and heterocycles at the upper rim. The yields of imidazolium salt decreases with increasing steric bulk of the substituent R^1 at the imidazole ring (**2a**−**d**, Scheme 1). This can be interpreted taking into account that in the minimum energy geometry of calixarene **1** the chlorine atoms are pointing outside the macrocyclic skeleton. Thus, backside attack by the imidazole must occur over the macrocycle, which may lead to steric interaction between the *tert*-butyl groups of the calixarene and the substituent of the attacking imidazole.

Calixarenes **4a**−**e** bearing no *tert*-butyl groups can be obtained in a way similar to the synthetic route shown in Scheme 1. Selective halogen metal exchange of 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxycalix[4]arene[44] using *n*BuLi and quenching with methanol removes two distal halogens (Scheme 2).[40,41] Starting from the remaining bromine substituents, the necessary chloromethyl groups can again be introduced in a multi-step process. Reaction of the chloromethyl compound **3** with substituted imidazoles now proceeds smoothly and in good yields because no sterically unfavourable interaction of the *tert*-butyl groups can interfere with the replacement reaction (yields of **4** > 90%, Scheme 2).

As a first example, imidazolium salt **4c** was treated with sodium hydride and potassium *tert*-butanolate in $[D_8]$THF as solvent. Deprotonation of the imidazolium salt to the carbene could be proven by a typical resonance of C-2 in the ^{13}C NMR spectra at $\delta = 214.5$ ppm[8] (Supporting Information, for Supporting Information see also the footnote on the first page of this article.)

The *cis* configuration of complex **5** derived from imidazolium salt **4b** could be proven by single-crystal structure determination (Figure 1). As expected, the metal−ligand fragment dominates the geometry: The distances Pd−C^2 (1.981−1.982 Å) and Pd−Cl (2.352−2.358 Å) are in the usual range; the bond angles around the palladium atom add up to 360.1° indicating square-planar coordination. The bond angle C^2−Pd−C^2 (96.6°) is a little larger than for similar structures reported in literature.[‡] This seems to be a compromise between the preconditions set up by the metal fragment and the conformationally strongly distorted calixarene scaffold. In the calixarene fragment of complex **5**, both unsubstituted phenol rings are bent outwards. The angles defined by these two phenol rings and the plane of the methylene bridges are 148.7 and 142.1°, respectively, and the angle between the two phenol rings is 112.8°. In contrast, the phenol rings bearing the NHC ligands are bent towards each other to allow the *cis* configuration around the palladium. The angles with the plane of the methylene bridges are 69.4 and 82.6°. The distortion of the

calixarene fragment also leads to buckling of the $C^{aryl}-CH_2(Im)$ bonds by 5.3 and 9.1°, respectively, against the neighbouring phenol ring. This shows, once again, that the calixarene skeleton can adjust very flexibly to steric preconditions.[33,45,46]

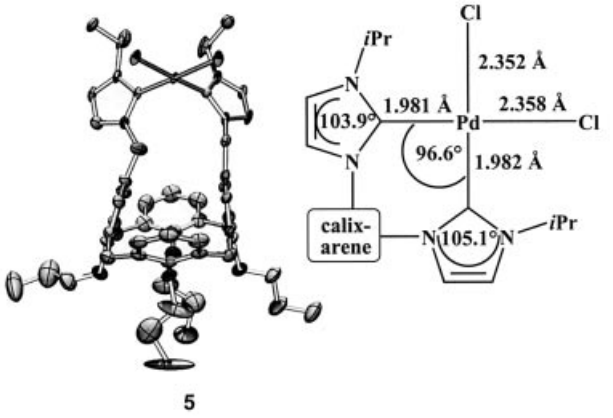


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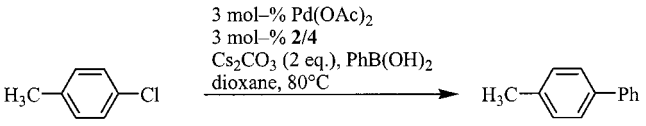
Figure 1. Solid-state structure of the palladium complex **5** (ORTEP-Plot, thermal ellipsoids are drawn at the 50% probability level)

To test the catalytic activity of the calixarene-based palladium complexes the Suzuki cross-coupling of chlorotoluene and phenylboronic acid to yield 4-methylbiphenyl was chosen. The reaction conditions were set up exactly according to a published protocol[47] to enable easy comparison of the experimental results with the literature. For the catalysis an in-situ system was used,[16,47,48] in which the active catalytic species is formed prior to the cross-coupling by the reaction of the imidazolium salt, $Pd(OAc)_2$ as a source of palladium and a base in dioxane. Preparative runs using the calixarene-based in-situ system showed that it is possible to obtain 4-methylbiphenyl in 24 h in 95% yield with Cs_2CO_3 (5 runs, 92−99%) and in 80% yield with CsF (5 runs, 73−91%) as base.

In analytical runs the reactions were stopped after 2 h and the conversion was determined using ^{1}H NMR spectroscopy of the reaction mixture. In addition to the signals of the starting materials, only 4-methylbiphenyl could be identified. No by-products could be detected. The results of that approach are summarised in Table 1. The optimised system reported by Nolan et al.[47] uses simple symmetrically substituted imidazolium salts. Very good results (> 95%) were obtained for mesityl-substituted salts, whereas the yield dropped to 53% with 2,6-diisopropylphenyl substituents. With our sterically very demanding calixarene-based in-situ systems efficient catalysis of the Suzuki coupling of chloroaromatics is also possible. Yields well within the range of comparable systems are easily possible. The catalytic efficiency increases approximately with increasing steric bulk of the ligands. Calixarenes bearing distal substituents are usually superior to macrocycles without such substituents (see **2a/4a**, **2c/4d**).

Table 1. Suzuki-coupling catalysed by imidazolium salt **2** and **4** / $Pd(OAc)_2$



Ligand **2** or **4**[a]	R^1	R^2	Conversion after 2 h [%][b]
2a	Me	*t*Bu	19
2c	Mes	*t*Bu	60
2d	2,6-*i*Pr$_2$C$_6$H$_3$	*t*Bu	38
4a	Me	H	1
4b	*i*Pr	H	16
4c	Mes	H	50
4d	2,6-*i*Pr$_2$C$_6$H$_3$	H	40

[a] See formulas in Scheme 1 and 2. [b] The conversions were determined by integration of the raw ^{1}H NMR spectra after 2-h reaction time (average yields obtained from 3 independent runs, cf. text).

In principle, both series of catalytic experiments show parallel results. The observed yields of coupling product increase when changing from the methyl- to the mesityl-substituted imidazolium salt, the yields of the biphenyl go up from 19 (**2a**) to 60% (**2c**) and 1 (**4a**) to 50% (**4c**), respectively. When the steric bulk at the *ortho* positions is increased by replacing the mesityl group with a diisopropylphenyl substituent, the yields decreases slightly to 40 and 38% (**2d/4d**), respectively. As expected, without any imidazolium salt as a ligand precursor no coupling product can be identified by NMR spectroscopy. Therefore, ligand-free Suzuki coupling reactions[49] can be excluded.

Conclusion

In summary, the results presented clearly show that imidazolium salts based on calix[4]arenes are appealing macrocyclic precursors for chelating *N*-heterocyclic carbene ligands. Corresponding *cis*-[Pd(L−L)Cl$_2$] complexes could unambiguously characterised by single-crystal structure determination. Initial catalytic studies using a standard in-situ protocol for Suzuki cross-coupling reactions of non-activated chlorobenzenes show promising results and reasonable activity of the calixarene ligands.

Experimental Section

General Remarks: Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Bruker Vector 22 instrument from KBr pellets unless otherwise stated. Absorption [$\tilde{\nu}$] are given in wave numbers (cm^{-1}). NMR spectra were recorded with a Bruker DRX 400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C), or a Bruker AMX 500 (500.14 MHz for ^{1}H and 125.76 MHz for ^{13}C) instrument. Tetramethylsilane was used for the ^{1}H NMR spectra as internal

standard (δ = 0.00 ppm) and the solvent signals for the ^{13}C NMR spectra [δ ($CDCl_3$) = 77.0, δ ([D_6]DMSO) = 39.5, δ ([D_4]Methanol) = 49.3 ppm]. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. Assignments of ^{13}C chemical shifts are based on proton-coupled ^{13}C, (C,H) correlation, and DEPT-135 spectra. Mass spectra were obtained with Finnigan MAT TSQ7000 (FAB) or Bruker Daltonics Reflex III (MALDI-TOF spectra) spectrometers. Because of the known ability of calix[4]arenes to strongly include solvent molecules,[50] solvent molecules were included in the calculation for the microanalyses. Solvents used for these calculations are also observed by ^1H NMR spectroscopy and could not be totally removed even after prolonged heating. Solvents were dried by standard procedures. All reaction mixtures were stirred magnetically, unless otherwise noted.

General Procedure for the Reaction of Calixarenes 1 or 3 with Substituted 1-Alkylimidazoles: The corresponding 1-alkylimidazole (23.2 mmol) was added to a solution of calixarene **1** or **3** (5.80 mmol) in dry $CHCl_3$ (40 mL). After heating the solution for two to five days the solvent was removed under reduced pressure, diethyl ether (70 mL) was added and the mixture was heated for 2−3 h. After cooling the mixture the colourless hygroscopic precipitate was collected by filtration, washed with several portions of Et_2O and dried in a desiccator.

11,23-Di-*tert*-butyl-5,17-bis[(3-methylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (2a): Yield 1.69 g (1.75 mmol, 70%). M.p. 237−240 °C. IR (KBr): ṽ = 3074 (w) (Ar−H), 2960 (s), 2873 (m) (C−H), 1942 (w) (−C=N−), 1607 (w), 1571 (m), 1480 (s) (C=C), 1465 (s) (C−H), 1385 (m), 1362 (m) [−C(CH_3)$_3$], 1309 (m), 1280 (m) (C−H), 1220 (m), 1200 (m), 1162 (s), 1136 (m), 1008 (s) (Ar−O−C), 877 (w), 754 (m) (Ar−H) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.87 and 1.10 (t, *J* = 7.3 Hz and *J* = 7.3 Hz, 2 × 6 H, CH_2CH_3), 1.36 [s, 18 H, C(CH_3)$_3$], 1.84−2.01 (m, 8 H, CH_2CH_3), 3.13 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 3.67 (t, *J* = 6.7 Hz, 4 H, OCH_2), 3.99 (s, 6 H, NCH_3), 4.01 (t, *J* = 8.3 Hz, 4 H, OCH_2), 4.45 (d, *J* = 13.3 Hz, 4 H, ArCH_2Ar), 4.89 (s, 4 H, ArCH_2Im), 6.18 (s, 4 H, Ar−*H*), 6.57 (m, 2 H, Im), 7.11 (s, 4 H, Ar−*H*), 7.63 (m, 2 H, Im), 9.78 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.65 and 10.72 (CH_2CH_3), 22.75 and 23.41 (CH_2CH_3), 31.26 (ArCH_2Ar), 31.74 [C(CH_3)$_3$], 34.15 [$C(CH_3)_3$], 36.44 (NCH_3), 52.91 (ArCH_2Im), 76.24 and 77.20 (OCH_2), 120.70, 123.54 (Im), 125.52, 125.92, 128.16, 134.87, 135.38 (Ar−*C*), 136.81(Im), 145.10, 155.00, 156.44 (Ar−*C*) ppm. MS: (pos. FAB), calcd. for $C_{58}H_{78}N_4ClO_4$: 929.6; found *m*/*z* = 929.6 [M − Cl]$^+$. $C_{58}H_{78}O_4N_4Cl_2 \cdot 3.3H_2O$ (1025.63): calcd. C 67.92, H 8.31, N 5.46; found C 67.80, H 8.24, N 5.55.

11,23-Di-*tert*-butyl-5,17-bis[(3-isopropylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (2b): Yield 2.42 g (2.37 mmol, 63%). M.p. 186−188 °C. IR (KBr): ṽ = 2961 (s), 2874 (s) (C−H), 1607 (w), 1558 (m) (C=C), 1465 (s) (C−H), 1385 (m), 1362 (m) [−C(CH_3)$_3$ and C(CH_3)$_2$], 1307 (m), 1277 (m) (C−H), 1220 (s), 1200 (s), 1178 (s), 1150 (s), 1008 (s) (Ar−O−C), 876 (m), 819 (w), 753 (m) (Ar−H) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.87 and 1.11 (t, *J* = 7.5 Hz and *J* = 7.5 Hz, 2 × 6 H, CH_2CH_3), 1.37 [s, 18 H, C(CH_3)$_3$], 1.59 (d, *J* = 6.7 Hz, 12 H, CH(CH_3)$_2$], 1.84−1.98 (m, 8 H, CH_2CH_3), 3.14 (d, *J* = 13.3 Hz, 4 H, ArCH_2Ar), 3.69 and 4.00 (t, *J* = 6.8 Hz and *J* = 8.3 Hz, 2 × 4 H, OCH_2), 4.46 (d, *J* = 13.3 Hz, 4 H, ArCH_2Ar), 4.74 [sept, *J* = 7.0 Hz, 2 H, C*H*(CH_3)$_2$], 4.88 (s, 4 H, ArCH_2-Im), 6.12 (s, 4 H, Ar−*H*), 6.52 (t, *J* = 1.6 Hz, 2 H, Im), 7.11 (s, 4 H, Ar−*H*), 7.87 (t, *J* = 1.7 Hz, 2 H, Im), 10.46 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.66 and 10.59 (CH_2CH_3), 22.77 (CH_2CH_3), 22.99 ($CHCH_3$), 23.34 (CH_2CH_3), 30.75 (ArCH_2Ar), 52.74 ($CHCH_3$), 53.10 (ArCH_2Im), 76.40 and 77.20 (OCH_2), 120.59, 120.85, 122.55, 125.31, 128.51, 129.14, 134.86, 135.26, 136.18, 156.51, 157.29 (Ar−*C* and Im) ppm. MS: (MALDI-TOF), calcd. for $C_{62}H_{86}N_4ClO_4$: 985.6; found *m*/*z* = 985.9 [M − Cl]$^+$. $C_{62}H_{86}Cl_2O_4N_4 \cdot 3.5H_2O$ (1085.34): calcd. C 68.61, H 8.64, N 5.16; found C 68.48, H 8.51, N 5.31.

11,23-Di-*tert*-butyl-5,17-bis[3-(mesitylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (2c): Yield 1.57 g (1.34 mmol, 43%). M.p. >255 °C (dec.). ^1H NMR ($CDCl_3$): δ = 0.86 and 1.10 (t, *J* = 7.3 Hz and *J* = 7.5 Hz, 2 × 6 H, CH_2CH_3), 1.36 [s, 18 H, C(CH_3)$_3$], 1.83−1.96 (m, 8 H, CH_2CH_3), 2.00 (s, 12 H, Ar−CH_3), 2.28 (s, 6 H, Ar−CH_3), 3.12 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 3.69 and 4.00 (t, *J* = 6.7 Hz and *J* = 8.2 Hz, 2 × 4 H, OCH_2), 4.46 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 5.10 (s, 4 H, ArCH_2Im), 6.09 (s, 4 H, Ar−*H*), 6.91 (s, 4 H, Ar−*H*), 7.10 (s, 4 H, Ar−*H*), 7.12 and 7.57 (t, *J* = 1.5 Hz and *J* = 1.7 Hz, 2 × 2 H, Im), 10.33 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.60 and 10.68 (CH_2CH_3), 17.46 and 20.90 (ArCH_3), 22.72 and 23.40 (CH_2CH_3), 31.22 (ArCH_2Ar), 31.62 [C(CH_3)$_3$], 34.07 [$C(CH_3)_3$], 53.27 (ArCH_2Im), 76.25 and 77.12 (OCH_2), 121.91, 124.23, 125.01, 125.84, 128.04, 129.59, 130.73, 133.96, 135.07, 135.38, 137.26, 140.75, 145.02, 155.10, 156.58 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{74}H_{94}N_4ClO_4$: 1137.7; found *m*/*z* = 1138.0 [M − Cl]$^+$. $C_{74}H_{94}O_4N_4Cl_2 \cdot 2.9H_2O$ (1226.73): calcd. C 72.45, H 8.20, N 4.57; found C 72.46, H 8.11, N 4.67.

11,23-Di-*tert*-butyl-5,17-Bis[3-(2,6-diisopropylphenylimidazolium)-methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (2d): Yield 860 mg (0.68 mmol, 22%). M.p. 235−238 °C. IR (KBr): ṽ = 3158 (w) (Ar−H), 2964 (s), 2873 (s) (C−H), 1636 (w), 1606 (w), 1548 (m) (C=C and C=N), 1465 (s) (C−H), 1386 (m), 1365 (m) [−C(CH_3)$_3$ and C(CH_3)$_2$], 1309 (m), 1279 (w) (C−H), 1202 (s), 1132 (m), 1109 (w), 1009 (s) (Ar−O−C), 872 (w), 804 (w), 754 (m) (Ar−H) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 6 H, CH_2CH_3), 1.10−1.14 [m, 18 H, CH(CH_3)$_2$ and CH_2CH_3], 1.18 [d, *J* = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.39 [s, 18 H, C(CH_3)$_3$], 1.85−1.98 (m, 8 H, CH_2CH_3), 2.19−2.26 [m, 4 H, C*H*(CH_3)$_2$], 3.14 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 3.71 and 4.01 (t, *J* = 6.7 Hz and *J* = 8.3 Hz, 2 × 4 H, AroCH_2), 4.49 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 5.23 (s, 4 H, ArCH_2Im), 6.15 (s, 4 H, Ar−*H*), 7.13 (s, 4 H, Ar−*H*), 7.24 (d, *J* = 7.8 Hz, 4 H, Ar−*H*), 7.37 (s, 2 H, Im), 7.45−7.49 (m, 4 H, Ar−*H* and Im), 10.28 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.66 and 10.78 (CH_2CH_3), 22.79 and 23.50 (CH_2CH_3), 23.89 and 24.56 [CH(CH_3)$_2$], 28.59 [C*H*(CH_3)$_2$], 31.35 (ArCH_2Ar), 31.74 [C(CH_3)$_3$], 34.17 [$C(CH_3)_3$], 53.49 (ArCH_2Im), 76.32 and 77.17 (OCH_2), 122.49, 124.44, 124.93, 125.46, 125.98, 128.28, 130.41, 131.56, 135.22, 135.47, 137.51, 145.15, 145.25, 155.19, 156.73 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{80}H_{106}N_4O_4$: 1186.8; found *m*/*z* = 1186.2 [M − 2Cl]$^+$. $C_{80}H_{106}Cl_2O_4N_4 \cdot 1.3\ CHCl_3$ (1413.84): calcd. C 69.07, H 7.65, N 3.96; found C 69.20, H 7.85, N 4.04.

5,17-Bis[(3-methylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (4a): Yield 4.73 g (5.53 mmol, 95%). M.p. > 280 °C (dec.). IR (KBr): ṽ = 3069 (m) (Ar−H), 2961 (s), 2927 (s), 2874 (s) (C−H), 1725 (w) (C=N), 1607 (m), 1571 (m) (C=C), 1464 (s), 1385 (m), 1281 (m) (C−H), 1256 (m), 1219 (s), 1162 (s), 1129 (m), 1009 (m) (Ar−O−C), 889 (w), 836 (w), 775 (m), 756 (m) (Ar−H) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90 and 1.09 (t, *J* = 7.5 Hz and *J* = 7.4 Hz, 2 × 6 H, CH_2CH_3), 1.84−2.02 (m, C8 H, H_2CH_3), 3.17 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 3.69 (t, *J* = 6.9 Hz, 4 H, AroCH_2), 3.99 (s, 6 H, NCH_3), 4.02 (t, *J* = 8.2 Hz, 4 H, AroCH_2), 4.45 (d, *J* = 13.1 Hz, 4 H, ArCH_2Ar), 4.94 (s, 4 H, ArCH_2Im), 6.28 (s, 4 H, Ar−*H*), 6.72 (m, 2 H, Im), 6.92 (t, *J* = 7.5 Hz, 2 H, Ar−*H*), 7.12 (d, *J* = 7.5 Hz, 4 H, Ar−*H*), 7.69 (m, 2 H, Im), 10.10

(s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.70 and 10.59 (CH_2CH_3), 22.80 and 23.35 (CH_2CH_3), 30.76 (ArCH_2Ar), 36.40 (NCH_3), 52.83 (ArCH_2Im), 76.43 and 77.27 (OCH_2), 120.93, 122.64, 123.58, 125.56, 128.40, 129.17, 134.91, 136.12, 136.92, 156.48, 157.22 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{50}H_{62}N_4ClO_4$: 817.4; found *m*/*z* = 817.5 [M − Cl]$^+$. $C_{50}H_{62}Cl_2N_4O_4·2.2H_2O$ (893.60): calcd. C 67.21, H 7.49, N 6.27; found C 67.21, H 7.55, N 6.13.

5,17-Bis[(3-isopropylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (4b): Yield quantitative, 5.80 g (7.25 mmol, 100%). M.p. 182−184 °C. IR (KBr): ṽ = 3058 (m) (Ar−H), 2963 (s), 2933 (s), 2874 (s) (C−H), 1743 (w) (C=N), 1608 (m), 1586 (m), 1559 (m) (C=C), 1464 (s), 1383 (m), 1281 (m) (C−H), 1220 (s), 1177 (m), 1153 (m), 1132 (m), 1008 (s) (Ar−O−C), 889 (m), 837 (w), 757 (m) (Ar−H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.89 and 1.10 (t, *J* = 7.5 Hz and *J* = 7.4 Hz, 2 × 6 H, CH_2CH_3), 1.60 (d, *J* = 6.7 Hz, 12 H, $CHCH_3$), 1.84−2.01 (m, 8 H, CH_2CH_3), 3.17 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 3.69 and 4.02 (t, *J* = 6.9 Hz and *J* = 8.2 Hz, 2 × 4 H, ArOCH_2), 4.46 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar) 4.74 (sept, *J* = 6.7 Hz, 2 H, $CHCH_3$), 4.94 (s, 4 H, ArCH_2Im), 6.25 (s, 4 H, Ar−*H*), 6.72 (t, *J* = 1.7 Hz, 2 H, Im), 6.93 (t, *J* = 7.5 Hz, 2 H, Ar−*H*), 7.12 (d, *J* = 7.5 Hz, 4 H, Ar−*H*), 7.79 (t, *J* = 1.8 Hz, 2 H, Im), 10.42 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.66 and 10.59 (CH_2CH_3), 22.77 (CH_2CH_3), 22.99 ($CHCH_3$), 23.34 (CH_2CH_3), 30.75 (ArCH_2Ar), 52.74 ($CHCH_3$), 53.10 (ArCH_2Im), 76.40 and 77.20 (OCH_2), 120.59, 120.85, 122.55, 125.31, 128.51, 129.14, 134.86, 135.26, 136.18, 156.51, 157.29 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{54}H_{70}N_4O_4$: 838.5; found *m*/*z* = 838.4 [M − 2Cl]$^+$. $C_{54}H_{70}Cl_2N_4O_4·2.9H_2O$ (962.32): calcd. C 67.40, H 7.94, N 5.82; found C 67.56, H 7.91, N 5.75.

5,17-Bis[(3-mesitylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (4c): Yield 5.59 g (5.26 mmol, 91%). M.p. 212−214 °C. IR (KBr): ṽ = 3021 (m) (Ar−H), 2961 (s), 2921 (s), 2875 (s) (C−H), 1608 (m), 1546 (m) (C=C), 1460 (s), 1381 (m), 1282 (m) (C−H), 1215 (s), 1161 (m), 1130 (m), 1066 (m), 1039 (m), 1008 (s) (Ar−O−C), 857 (m), 754 (s) (Ar−H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.90 and 1.11 (t, *J* = 7.5 Hz and *J* = 7.4 Hz, 2 × 6 H, CH_2CH_3), 1.85−1.99 (m, 8 H, CH_2CH_3), 2.04 (s, 12 H, Ar−CH_3), 2.30 (s, 6 H, Ar−CH_3), 3.17 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 3.71 and 4.48 (t, *J* = 6.8 Hz and *J* = 8.2 Hz, 2 × 4 H, ArOCH_2), 4.48 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 5.23 (s, 4 H, ArCH_2Im), 6.27 (s, 4 H, Ar−*H*), 6.94 (s, 4 H, Ar−*H*), 6.96 (t, *J* = 7.3 Hz, 2 H, Ar−*H*), 7.11 (d, *J* = 7.5 Hz, 4 H, Ar−*H*), 7.24 and 7.44 (s, 2 × 2 H, Im), 10.23 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.73 and 10.66 (CH_2CH_3), 17.60 and 20.97 (ArCH_3), 22.84 and 23.43 (CH_2CH_3), 30.88 (ArCH_2Ar), 53.25 (ArCH_2Im), 76.49 and 77.16 (OCH_2), 122.08, 122.71, 123.78, 125.54, 128.45, 129.19, 129.65, 130.79, 134.11, 135.05, 136.19, 137.27, 140.85, 156.61, 157.38 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{66}H_{78}N_4ClO_4$: 1025.6; found *m*/*z* = 1025.7 [M − Cl]$^+$. $C_{66}H_{78}Cl_2N_4O_4·2.8H_2O$ (1112.71): calcd. C 71.24, H 7.57, N 5.04; found C 71.34, H 7.53, N 4.96.

5,17-Bis[(3-(2,6-diisopropylphenyl)imidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (4d): Yield 4.80 g (4.19 mmol, 96%). M.p. 206−209 °C. IR (KBr): ṽ = 2964 (s), 2931 (s), 2873 (s) (C−H), 1626 (w), 1590 (w), 1543 (m) (C=C), 1459 (s) (C−H), 1385 (m), 1369 (m) [$C(CH_3)_2$], 1307 (m) (C−H), 1247 (m), 1223 (m), 1194 (s), 1007 (s) (Ar−O−C), 890 (w), 806 (m), 758 (s) (Ar−H) ppm. ^{1}H NMR ([D$_4$][D$_4$]Methanol): δ = 0.90 (t, *J* = 7.5 Hz, 6 H, CH_2CH_3), 1.09−1.14 [m, 18 H, $CH(CH_3)_2$ and CH_2CH_3], 1.20 [d, *J* = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.85−2.00 (m, 8 H, CH_2CH_3), 2.19−2.27 [m, 4 H, $CH(CH_3)_2$], 3.17 (d, *J* = 13.6 Hz, 4 H, ArCH_2Ar), 3.72 and 4.03 (t, *J* = 6.7 Hz and *J* = 8.2 Hz, 2 × 4 H, ArOCH_2), 4.48 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 5.33 (s, 4 H, ArCH_2Im), 6.31 (s, 4 H, Ar−*H*), 6.98 (t, *J* = 7.5 Hz, 2 H, Ar−*H*), 7.12 (d, *J* = 7.5 Hz, 4 H, Ar−*H*), 7.25 (d, *J* = 7.7 Hz, 4 H, Ar−*H*), 7.35 (s, 2 H, Im), 7.46−7.50 (m, 4 H, Ar−*H* and Im), 10.18 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ([D$_4$]Methanol): δ = 10.86 and 11.34 (CH_2CH_3), 24.53 [$CH(CH_3)_2$], 24.66 (CH_2CH_3), 24.80 [$CH(CH_3)_2$], 24.81 (CH_2CH_3), 30.26 [$CH(CH_3)_2$], 32.22 (ArCH_2Ar), 54.87 (ArCH_2Im), 78.35 and 78.45 (OCH_2), 123.65, 124.73, 126.10, 127.23, 129.11, 129.44, 130.15, 132.24, 133.33, 135.35, 138.86, 139.29, 147.02, 157.59, 159.75 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{72}H_{90}ClN_4O_4$: 1109.7; found *m*/*z* = 1110.0 [M − Cl]$^+$. $C_{72}H_{90}N_4O_4Cl_2·3.5H_2O$ (1209.48): calcd. C 71.50, H 8.08, N 4.63; found C 71.55, H 7.78, N 4.52.

5,17-Bis[(3-cyclohexylimidazolium)methyl]-25,26,27,28-tetrapropoxycalix[4]arene (4e): Yield 7.00 g (7.07 mmol, 96%). M.p. 166−169 °C. IR (KBr): ṽ = 2932 (s), 2872 (s) (C−H), 1607 (w), 1586 (w), 1557 (m) (C=C), 1461 (s), 1384 (m), 1281 (m) (C−H), 1220 (s), 1158 (s), 1133 (s), 1082 (m), 1040 (m), 1007 (s) (Ar−O−C), 891 (m), 837 (w), 758 (s) (Ar−H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.89 and 1.10 (t, *J* = 7.5 Hz and *J* = 7.5 Hz, 2 × 6 H, CH_2CH_3), 1.25−1.33 (m, 2 H, *CyHex*), 1.38−1.49 (m, 4 H, CyHex), 1.69−1.80 (m, 6 H, CyHex), 1.85−1.99 (m, 12 H, CyHex and CH_2CH_3), 2.18−2.21 (m, 4 H, CyHex), 3.16 (d, *J* = 13.5 Hz, 4 H, ArCH_2Ar), 3.69 and 4.02 (t, *J* = 6.8 Hz and *J* = 8.3 Hz, 2 × 4 H, ArOCH_2), 4.74 (tt, *J* = 11.9 Hz and *J* = 3.9 Hz, 2 H, $CHCH_2$), 4.45 (d, *J* = 13.4 Hz, 4 H, ArCH_2Ar), 4.96 (s, 4 H, ArCH_2Im), 6.23 (s, 4 H, Ar−*H*), 6.72 (s, 2 H, Im), 6.94 (t, *J* = 7.3 Hz, 2 H, Ar−*H*), 7.12 (d, *J* = 7.5 Hz, 4 H, Ar−*H*), 7.73 (s, 2 H, Im), 10.34 (s, 2 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.65 and 10.60 (CH_2CH_3), 22.77 (CyHex), 23.35 (CH_2CH_3), 24.45 (CyHex), 24.81 (CH_2CH_3), 30.76 (ArCH_2Ar), 33.32 (CyHex), 52.77 (ArCH_2Im), 59.83 ($CHCH_2$), 76.40 and 77.20 (OCH_2), 120.70, 122.57, 125.29, 128.53, 129.14, 129.77, 134.86, 135.67, 136.19, 156.50, 157.30 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{60}H_{78}N_4O_4Cl$: 953.6; found *m*/*z* = 953.5 [M − Cl]$^+$. $C_{60}H_{78}Cl_2N_4O_4·2.8H_2O$ (1040.65): calcd. C 69.25, H 8.10, N 5.38; found C 69.35, H 7.95, N 5.62.

General Procedure for the Reaction of Imidazolium Salts 2 and 4 with Pd(OAc)$_2$: $Pd(OAc)_2$ (1.1 equiv.) was added to a solution of imidazolium salt **2** or **4** (1.0 equiv.) in dry DMSO (20 mL for 2.50−3.00 mmol of imidazolium salt) under an inert atmosphere. The resulting mixture was heated at 50 °C for 1 h followed by 110 °C for 3 h. After removal of the solvent under reduced pressure the remaining greenish solid was dissolved in dry CH_2Cl_2 and filtered to remove any elemental Pd formed during the reaction. The remaining product was purified by column chromatography on silica using acetone/CH_2Cl_2 (1:7) as eluent.

Complex 5: Yield 180 mg (0.18 mmol, 8%). M.p. > 295 °C (dec.). IR (KBr): ṽ = 3155 (w), 3132 (w), 3093 (m) (Ar−H), 2962 (s), 2929 (s), 2874 (s) (C−H), 1690 (w), 1635 (w), 1586 (w) (C=C and C=N), 1463 (s), 1425 (m), 1373 (m) (C−H), 1280 (m), 1215 (s), 1130 (m), 1073 (m), 1007 (m) (Ar−O−C), 887 (w), 834 (w), 764 (m) (Ar−H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.86, 0.87 and 1.11 (t, *J* = 7.5, *J* = 7.3 Hz and *J* = 7.3 Hz, 2 × 3 H and 6 H, CH_2CH_3), 1.31 and 1.58 [d, *J* = 6.8 Hz and *J* = 6.6 Hz, 2 × 6 H, $NCH(CH_3)_2$], 1.83−1.93 (m, 8 H, CH_2CH_3), 3.09 and 3.19 (d, *J* = 13.8 Hz and *J* = 13.8 Hz, 2 × 2 H, ArCH_2Ar), 3.63−3.73 (m, 4 H, ArOCH_2), 3.98 and 3.98 (t, 2 × *J* = 8.2 Hz, 2 × 2 H, ArOCH_2), 4.43 and 4.46 (d, *J* = 13.1 Hz and *J* = 13.5 Hz, 2 × 2 H, ArCH_2Ar), 4.77 and 5.09 (d, *J* = 15.8 Hz and *J* = 15.8 Hz, 2 × 2 H, ArCH_2Im), 5.42 (sept., *J* = 6.8 Hz, 2 H, $NCH(CH_3)_2$], 5.69 and 6.11 (d, *J* =

2.0 Hz and J = 2.2 Hz, 2 × 2 H, Ar−*H*), 6.72 (t, J = 7.5 Hz, 1 H, Ar−*H*), 6.77 and 6.89 (d, J = 2.0 Hz and J = 2.2 Hz, 2 × 2 H, Im), 6.99 (d, J = 7.5 Hz, 2 H, Ar−*H*), 7.08 (dd, J = 7.0 Hz and J = 7.9 Hz, 1 H, Ar−*H*), 7.20 (d, J = 7.3 Hz, 2 H, Ar−*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.79 and 10.80 (CH_2CH_3), 22.90 (CH_2CH_3), 23.01 [$NCH(CH_3)_2$], 23.53 (CH_2CH_3), 24.09 [$NCH(CH_3)_2$], 31.11 and 31.24 ($ArCH_2Ar$), 53.00 [$NCH(CH_3)_2$], 54.68 ($ArCH_2Im$), 76.36, 76.40 and 76.97 (OCH_2), 116.40, 121.27, 122.02, 123.23, 125.41, 126.78, 127.97, 128.96, 129.71, 134.01, 134.87, 136.61, 136.91, 155.45, 157.63, 158.26, 158.91 (Ar−*C* and Im-*C*) ppm. MS: (MALDI-TOF), calcd. for $C_{54}H_{68}N_4ClO_4Pd$: 977.4; found m/z = 977.4 $[M - Cl]^+$. $C_{54}H_{68}Cl_2N_4O_4Pd \cdot 1.5(CH_3)_2CO$ (1101.60): calcd. C 63.78, H 7.50, N 5.09; found C 63.66, H 7.05, N 5.14.

Suzuki Cross-coupling Reactions: The Suzuki cross-coupling reactions were performed following a published protocol.[47] The yields given in Table 1 are the average yields obtained in 2−3 independent runs.

X-ray Crystallographic Study: Crystals of complex **5** suitable for single-crystal structure determination were obtained by slow evaporation of a solution of complex **5** in *p*-xylene and CH_2Cl_2 at room temperature. During the crystallisation process solvent molecules were incorporated in the crystal lattice. Complex **5**·*p*-xylene·CH_2Cl_2, $C_{54}H_{68}N_4Cl_2O_4Pd \cdot C_8H_{10} \cdot CH_2Cl_2$: M_r 1205.51, space group $P2_1/c$, a = 21.890(6), b = 15.517(3), c = 18.353(4) Å, α = 90, β = 99.09(3), γ = 90°. V = 6156(3) Å^3, Z = 4, ρ(calcd.) = 1.301 Mg·m^{-3}, μ(Mo-K_α) = 0.523 mm^{-1}, crystal size 0.15 × 0.31 × 0.38 mm. The data collection was done on a STOE IPDS imaging plate instrument using Mo-K_α irradiation (λ = 0.71073 Å) at T = 193(2) K; 39435 reflections were collected in a range 2.30° ≤ θ ≤ 24.11°, 9780 independent reflections (R_{int} = 0.0921, $-25 \le h \le 25$, $-17 \le k \le 17$, $-21 \le l \le 20$) were collected. The structure was solved using the program package SHELX-97[51] and refined to final R values $R1$ = 0.0784 [$I > 2\sigma(I)$] and $wR2$ = 0.2391 (all data).

The crystal contains one dichloromethane and one *p*-xylene molecule in the asymmetric unit. Owing to dynamic and/or positional disorder, several restraints were imposed on these solvate molecules. The dichloromethane molecule is disordered over to closely positioned sites (site occupation factors fixed at 0.67 and 0.33). The xylene molecule was refined as a rigid body (idealized benzene ring, methyl carbon atoms in calculated positions and riding on their bond neighbours) with isotropic thermal displacement factors.

CCDC-210528 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: Comparison of structural data of various bis-NHC−Pd complexes [$Pd(NHC)_2X_2$] deposited with the Cambridge Crystallographic Database (CCSD) and ^{13}C NMR spectra of imidazolium salt **4c** and the carbene derived from it.

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