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Palladium-catalysed Suzuki–Miyaura cross-coupling with imidazolylidene ligands substituted by crowded resorcinarenyl and calixarenyl units

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Abstract: Two *N*-heterocyclic carbene (NHC) palladium complexes of formula [$PdBr_2$(NHC)(pyridine)] in which the carbenic ring is flanked by sterically crowded cavitand substituents were prepared from appropriate imidazolium salts bearing either two resorcinarene or a combination of resorcinarene and calixarene fragments. Both complexes displayed high stability and good activities in the cross-coupling of aryl bromides with phenyl boronic acid. One of the imidazolium salts was characterised by an X-ray diffraction study.

Key words: Resorcinarene, calixarene, cavitands, *N*-heterocyclic carbene, palladium, PEPPSI complexes, Suzuki–Miyaura coupling

1. Introduction

Over the last 20 years, *N*-heterocyclic carbenes have gained real practical importance in numerous catalytic processes,[1–12] the most prominent application for such ligands being their use in palladium-catalysed Suzuki–Miyaura cross coupling reactions. Current efforts in this latter area focus on the design of sophisticated NHCs able to exert high steric pressure on the catalytic centre, with the ligand displaying preferentially *variable steric bulk*, that is having adaptive steric properties ensuring both high catalyst efficiency and increased stability of certain catalytic intermediates. The concept of *variable bulk* was introduced by Glorius for NHCs in which the N atoms are part of a conformationally flexible ring that may alternately bend towards the metal centre, thereby favouring the reductive elimination step and stabilising reactive intermediates, and then move away from it so as to facilitate substrate approach.[13–16] A few other NHCs have been considered to show the same property,[17,18] notably NHCs in which the N atoms are connected to aryl or naphthyl groups with strongly shielding substituents (e.g., –$CHPh_2$),[8,9,19,20] and also alkylfluorenyl-substituted imidazolylidenes.[12]

We have recently reported the synthesis of the PEPPSI-type complex **1** (PEPPSI = Pyridine-Enhanced Precatalyst Preparation Stabilization and Initiation[21]), in which the carbenic ring bears a bulky, rotationally mobile resorcinarenyl substituent (Figure 1).[22] Complex **1** showed remarkable activity in Suzuki–Miyaura cross coupling between phenyl boronic acid and aryl bromides. The performance and stability of the catalytic system was attributed to the ability of two pentyl groups of the freely rotating resorcinarenyl substituent to temporarily

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interact with the metal's first coordination sphere, thereby providing side group assistance in the reductive elimination step.

Wondering whether the use of a NHC bearing an additional cavitand substituent tethered to the carbenic ring would improve the catalytic performance, we prepared and tested the unsymmetrical PEPPSI-type complex **2** containing two distinct substituents each based on a bulky resorcinarene cavitand skeleton. For comparison purposes, the related PEPPSI complex **3** was also prepared, this containing a sterically less encumbered calixarenyl substituent. While calixarene- and resorcinarene-derived ligands, notably phosphines, have been extensively studied in catalytic chemistry,[23−26] to the best of our knowledge there is no literature report on the use of NHCs with two cavitand substituents. The three ligands tested in this study all contain an imidazolylidene ring and therefore are of comparable donor strength.

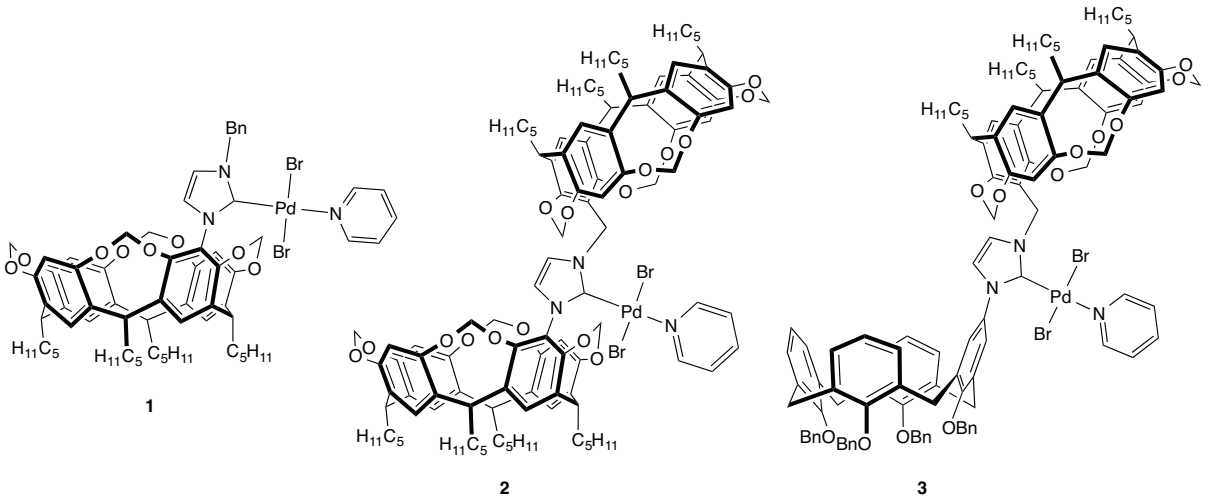


Figure 1. PEPPSI-type palladium complexes tested in the present study.

2. Results and discussion

2.1. Synthesis of two palladium complexes containing cavitand-substituted NHCs

Complex **2**, which contains a resorcinarenyl and a resorcinarenylmethyl substituent, was prepared according to Scheme 1. The first step consisted of alkylating imidazolyl-cavitand **4** with the bromomethyl derivative **5** in refluxing chloroform, this giving imidazolium salt **6** in 96% yield. The structure of **6** was confirmed by a single-crystal X-ray diffraction study (Figure 2), which revealed that in the solid state the two resorcinarene bowls adopt a head-to-tail arrangement, while the length of the molecule approaches 30 Å. Imidazolium salt **6** was then converted into the PEPPSI-complex **2** (53%) by reaction with $[PdCl_2]$ in refluxing pyridine in the presence of K_2CO_3 and a large excess of KBr. The related calixarene-resorcinarene complex **3** was prepared in a similar manner, starting from imidazolyl-calixarene **7** (with an overall yield of 39%) (Scheme 2). Both complexes as well as their imidazolium precursors, **6** and **8**, respectively, were unambiguously characterised by ^{1}H and ^{13}C NMR and elemental analyses (see Experimental section). Note that in the ^{1}H NMR spectrum of complex **3**, as well as in that of its imidazolium precursor **8**, the ArCH_2 signals, which appear as two AB systems with a large AB separation ($>$1 ppm), are consistent with a cone conformation of the calixarene unit (see Experimental section).[27]

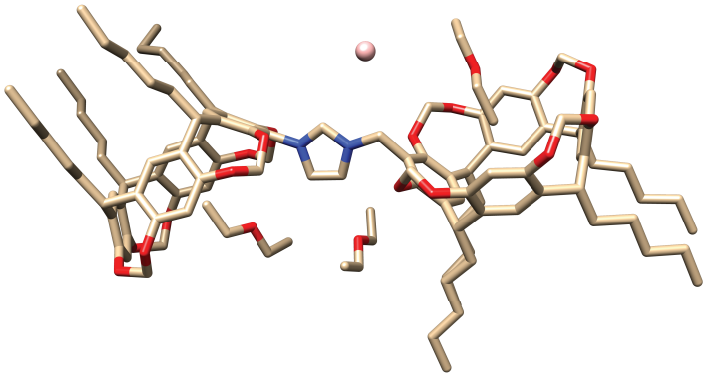
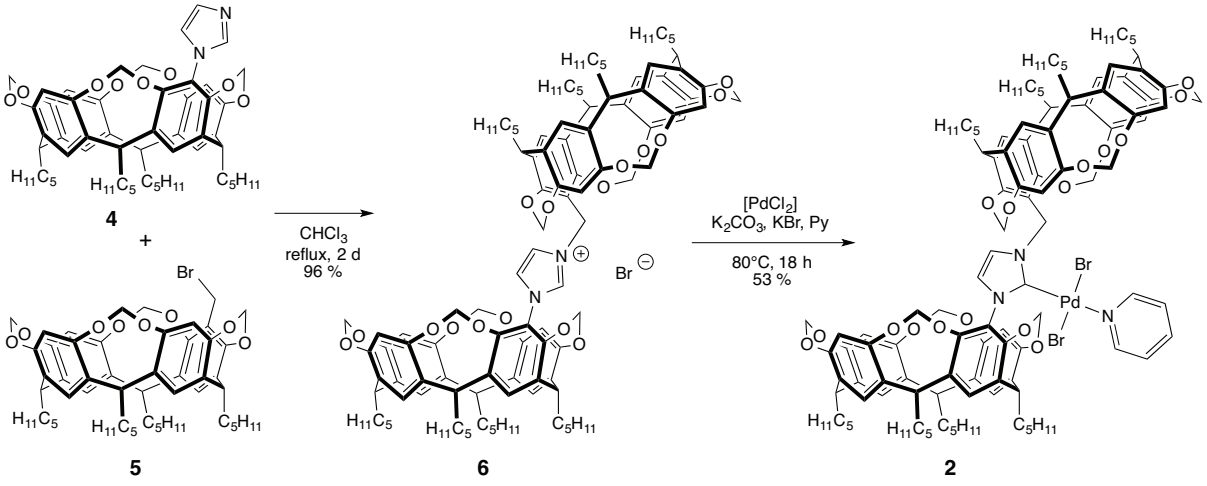
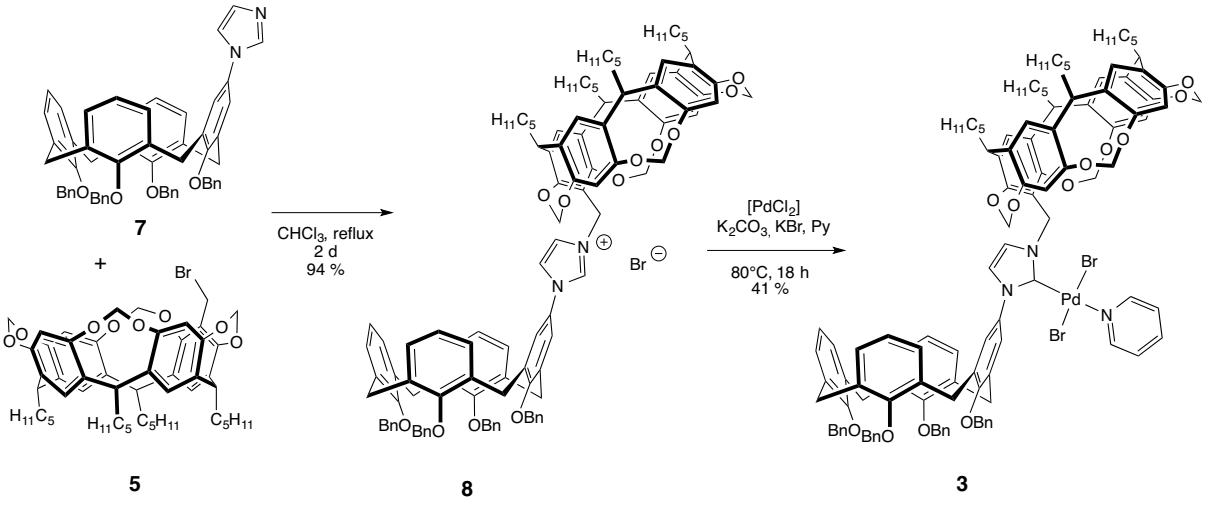


Figure 2. Molecular structure of salt **6**.3(Et_2O).0.5(CH_2Cl_2). Only the ether molecules are shown.



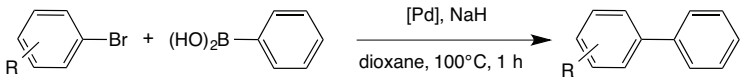
Scheme 1. Synthesis of palladium complex **2**.



Scheme 2. Synthesis of palladium complex **3**.

2.2. Catalytic Suzuki–Miyaura cross-coupling of aryl bromides

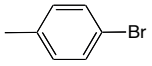
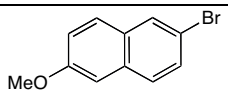
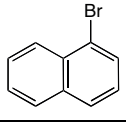
The new palladium complexes **2** and **3** were evaluated as catalysts for Suzuki–Miyaura cross-coupling between three aryl bromides and phenylboronic acid. The runs were performed using an aryl halide/Pd ratio of 10,000:1 with NaH as the base. The conversions were determined after 1 h reaction time at 100 °C in 1,4-dioxane (Scheme 3). In order to get a better insight into the role played by the substituents, notably for that of the methylresorcinarenyl group, catalytic runs were also carried out under similar conditions with the reference complex **1**.



Scheme 3. Suzuki–Miyaura cross-coupling reaction.

As a general trend, the conversions increased with increasing ligand size, that is in the order **1** < **3** < **2** (Table). For example, starting from 2-bromo-6-methoxynaphthalene resulted in the corresponding coupling product in yields of 59.4%, 63.9%, and 67.1% using complexes **1**, **3**, and **2**, respectively (Table, entry 2). The only side-product in these reactions was the homocoupling product (Ph–Ph), the yield of which did not exceed 3%. The highest conversion, 76.5%, was observed for the arylation of 4-bromotoluene with complex **2** (Table, entry 1; TOF = 7650 mol(ArBr) mol(Pd)$^{-1}$ h^{-1}). Thus, replacement of the benzyl group of **1** by a bulkier resorcinarenylmethyl moiety improved the catalytic outcome. This effect, although moderate, reflects the ability of the resorcinarenylmethyl group of **2** to sterically interact during catalysis with the palladium first coordination sphere in a better way than does a N-*benzyl* group. Molecular modelling (SPARTAN)[28] revealed that such interactions, when occurring (that is when the metal points away from the cavity), involve either one of the two methylenic O*CH*$_2$O or one of the two *pentyl* groups attached to the NCH$_2$*Ar* ring (Figure 3). Note that for the other N-*substituent* of **2**, namely the resorcinarenyl fragment, only two pentyl groups may come in contact with the metal centre. The fact that the resorcinarenylmethyl fragment of **2** may freely rotate about the corresponding N–CH$_2$(resorc) bond, and thus exert a variable steric pressure on the metal centre, may explain why the activity increase observed on going from **1** to **2** remains limited to ca. 15%. For complex **3**, the activity increase was less pronounced, this as a result of a sterically less demanding calixarenyl substituent.

Table. Comparison of palladium complexes in the Suzuki–Miyaura cross-coupling of aryl bromides.

Entry	ArBr		Complexes		
			1	**2**	**3**
1		Conversion (%)	66.5	76.5	72.6
2		Conversion (%)	59.4	67.1	63.9
3		Conversion (%)	61.1	66.5	66.2

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

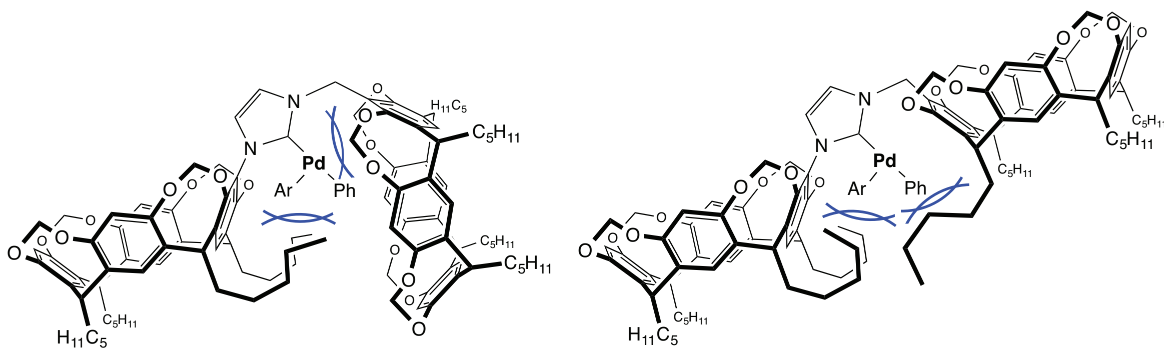


Figure 3. Steric interactions (involving pentyl and/or OCH_2O fragments) that may occur in catalytic intermediates derived from **2**.

3. Experimental

All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H and $^{13}C\{^1H\}$ spectra were recorded with Bruker FT instruments (AVANCE 300 and 400). ^1H spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$) and ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$). Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. *trans*-Dibromo-[2-{4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]aren-5-yl}-5-benzyl-imidazol-2-yliden] pyridine palladium(II) (**1**),[22] 5-*N*-imidazolyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene (**4**),[22] 5-bromomethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene (**5**),[29] and 5-*N*-imidazolyl-25,26,27,28-tetrabenzyloxycalix[4]arene (**7**)[30] were prepared according to literature procedures.

3.1. General procedure for the preparation of the imidazolium salts 6 and 8

N-Aryl-imidazole (0.25 mmol) and 5-bromomethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**5**) (0.25 mmol) were dissolved in $CHCl_3$ (10 mL). The reaction mixture was heated to reflux for 2 days. After cooling to room temperature, the solvent was removed under vacuum. The solid was washed with pentane and recrystallised from CH_2Cl_2/isopropyl ether to afford the corresponding imidazolium salt.

3.1.1. 2-*N*-[(4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resor cin[4]arene-5-methyl]-5-*N*-[4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene-5-yl]imidazolinium bromide (6)

Yield, 0.429 g, 96%; ^1H NMR (400 MHz, $CDCl_3$): δ = 10.36 (s, 1H, NCHN), 7.35 (s, 1H, arom. CH), 7.22 (s, 1H, arom. CH), 7.20 (s br, 1H, NCHCHN), 7.13 (s, 3H, arom. CH), 7.09 (s, 3H, arom. CH), 7.02 (s br, 1H, NCHCHN), 6.66 (s, 2H, arom. CH), 6.55 (s, 1H, arom. CH), 6.53 (s, 2H, arom. CH), 6.47 (s, 1H, arom. CH), 6.13 and 4.48 (AB spin system, 4H, OCH_2O, ^2J = 7.4 Hz), 5.80 (s, 2H, NCH_2), 5.74 and 4.41 (AB spin system, 4H, OCH_2O, ^2J = 7.2 Hz), 5.73 and 4.67 (AB spin system, 4H, OCH_2O, ^2J = 7.4 Hz), 5.63 and 4.70 (AB spin

system, 4H, OCH_2O, ^2J= 7.6 Hz), 4.78–4.66 (m, 8H, $CHCH_2$), 2.32–2.14 (m, 16H, $CHCH_2$), 1.46–1.32 (m, 48H, $CH_2CH_2CH_2CH_3$), 0.92 (t, 12H, CH_2CH_3, ^3J= 7.2 Hz), 0.91 (t, 12H, CH_2CH_3, ^3J= 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 155.70–116.68 (arom. C's), 137.74 (s, NCHN), 121.36 (s, $NCHCHN$), 117.80 (s, $NCHCHN$), 100.02 (s, OCH_2O), 100.54 (s, OCH_2O), 99.71 (s, OCH_2O), 99.52 (s, OCH_2O), 43.84 (s, NCH_2), 36.77 (s, $CHCH_2$), 36.48 (s, $CHCH_2$), 32.16 (s, $CH_2CH_2CH_3$), 32.09 (s, $CH_2CH_2CH_3$), 32.01 (s, $CH_2CH_2CH_3$), 30.10 (s, $CHCH_2$), 30.00 (s, $CHCH_2$), 29.90 (s, $CHCH_2$), 27.68 (s, $CHCH_2CH_2$), 22.81 (s, CH_2CH_3), 22.78 (s, CH_2CH_3), 14.22 (s, CH_2CH_3); MS (ESI-TOF): m/z: 1712.93 $[M - Br]^+$ expected isotopic profiles; elemental analysis calcd (%) for $C_{108}H_{131}N_2O_{16}Br$ (M_r = 1793.10): C 72.34, H 7.36, N 1.56; found: C 72.39, H 7.43, N 1.67.

Single crystals of **6** · 3 Et_2O · 0.5 CH_2Cl_2 suitable for a single crystal X-ray diffraction study were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the imidazolium salt. Mr = 2057.88, monoclinic, space group $P2_1/n$, a = 18.0840(10), b = 22.4160(10), c = 28.819(2) Å, β = 104.932(5), V = 11287.9(11) Å^3, Z = 4, D_x = 1.211 mg m^{-3}, λ(Mo$_{Ka}$) = 0.71073 Å, μ = 0.454 mm^{-1}, $F(000)$ = 4412, T = 120(2) K. The sample (0.408 × 0.309 × 0.182 mm) was studied on an Oxford Diffraction Xcalibur Sapphire 3 diffractometer (graphite monochromated MoK_a radiation, λ = 0.71073 Å). The data collection ($2\theta_{max} = 27°$, omega scan frames via 0.7° omega rotation and 30 s per frame, range *HKL*: *H* –22.23 *K* –28.28 *L* –35.36) gave 83,816 reflections. The data led to 24,049 independent reflections with $I > 2.0\sigma(I)$ observed. The structure was solved with SIR-97,[31] which revealed the nonhydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found with a Fourier difference. The whole structure was refined with SHELXL97[32] by the full matrix least-square techniques (use of F square magnitude; x, y, z, βij for C, Br, Cl, N, and O atoms, x, y, z in riding mode for H atoms; 1316 variables and 24,049 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.849P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R= 0.0850, R_W = 0.2017, and S_W = 0.849, $\Delta\rho$ <0.514 eÅ^{-3}. The major difficulty in the structure determination arose from the tendency of the crystal to desolvate rapidly. Disorder was found for one of the pentyl groups. Owing to the difficulties caused by this disorder, it was necessary to use DFIX and DANG instructions, this explaining the level A alerts.

Supplementary crystallographic data CCDC 842333 can be obtained free of charge from The Cambridge Crystallographic Data Centre under www.ccdc.cam.ac.uk/data_request/cif.

3.1.2. 2-*N*-[(4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene-5-methyl]-5-*N*-[25,26,27,28-tetrabenzyloxy-calix[4]arene-5-yl]imidazolinium bromide (8)

Yield, 0.414 g, 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (s, 1H, NCHN), 7.40–7.33 (m, 8H, arom. CH), 7.30–7.24 (m, 6H, arom. CH and $NCHCHN$), 7.19–7.02 (m, 14H, arom. CH), 6.98 (d, 2H, arom. CH, calixarene, ^3J= 7.4 Hz), 6.92 (t, 2H, arom. CH, calixarene, ^3J= 7.4 Hz), 6.67 (s br, 1H, $NCHCHN$), 6.58 (s, 2H, arom. CH, resorcinarene), 6.50 (s, 1H, arom. CH, resorcinarene), 6.15 (s, 2H, NCH_2), 6.14 (s, 2H, arom. CH), 6.02 and 4.57 (AB spin system, 4H, OCH_2O, ^2J= 7.2 Hz), 5.74 and 4.49 (AB spin system, 4H, OCH_2O, ^2J= 7.2 Hz), 5.71–5.67 (m, 2H, arom. CH), 5.17 and 5.06 (AB spin system, 4H, $CH_2C_6H_5$, ^2J = 12.0 Hz), 4.76–4.71 (m, 2H, $CHCH_2$), 4.73 (s, 2H, $CH_2C_6H_5$), 4.72 (s, 2H, $CH_2C_6H_5$), 4.68 (t, 2H, $CHCH_2$, ^3J = 8.0 Hz), 4.27 and 3.00 (AB spin system, 4H, $ArCH_2Ar$, ^2J= 13.6 Hz), 4.07 and 2.85 (AB spin system, 4H, $ArCH_2Ar$, ^2J= 14.0 Hz), 2.30–2.17 (m, 6H, $CHCH_2$), 2.10–2.00 (m, 2H, $CHCH_2$), 1.43–1.23 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 6H, CH_2CH_3,^3J= 7.0 Hz), 0.88 (t, 6H, CH_2CH_3, ^3J= 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$):

δ= 156.50–116.90 (arom. C's), 134.58 (s, NCHN), 122.45 (s, N*C*HCHN), 122.15 (s, NCH*C*HN), 100.57 (s, OCH_2O), 99.71 (s, OCH_2O), 77.36 ($CH_2C_6H_5$), 75.94 ($CH_2C_6H_5$), 44.32 (s, NCH_2), 36.78 (s, $CHCH_2$), 36.47 (s, $CHCH_2$), 32.18 (s, $CH_2CH_2CH_3$), 32.13 (s, $CH_2CH_2CH_3$), 31.49 (ArCH_2Ar), 31.47 (ArCH_2Ar), 30.07 (s, $CHCH_2$), 29.93 (s, $CHCH_2$), 27.70 (s, $CHCH_2CH_2$), 22.83 (s, CH_2CH_3), 22.79 (s, CH_2CH_3), 14.23 (s, CH_2CH_3); MS (ESI-TOF): m/z: 1680.86 $[M - Br]^+$ expected isotopic profiles; elemental analysis calcd (%) for $C_{112}H_{115}N_2O_{12}Br$ (M_r = 1761.02): C 76.39, H 6.58, N 1.59; found: C 76.44, H 7.61, N 1.47.

3.2. General procedure for the preparation of the PEPPSI-type complexes 2 and 3

A mixture of K_2CO_3 (0.069 g, 0.50 mmol), pyridine (3.5 mL), $[PdCl_2]$ (0.027 g, 0.15 mmol), imidazolium salt (0.10 mmol), and KBr (0.237 g, 2.00 mmol) was heated at 80 °C for 17 h. The reaction mixture was then filtered through Celite. The filtrate was evaporated under vacuum, and the solid residue purified by flash chromatography (EtOAc/petroleum ether 50:50 v/v) to afford the corresponding palladium complex.

3.2.1. *trans*-Dibromo-[2-{4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]aren-5-yl}-5-{(4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetra pentylresorcin[4]arene-5-methyl}-imidazol-2-yliden] pyridine palladium(II) (2)

Yield, 0.116 g, 53%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (dd, 2H, arom. CH, Py, ^3J= 6.3 Hz, ^4J= 1.5 Hz), 7.80 (tt, 1H, arom. CH, Py, ^3J= 7.6 Hz, ^4J= 1.5 Hz), 7.41 (s, 1H, arom. CH of resorcinarene), 7.38 (s, 2H, arom. CH, resorcinarene), 7.37–7.34 (m, 2H, arom. CH, Py), 7.31 (s, 2H, arom. CH, resorcinarene), 7.29 (s, 3H, arom. CH, resorcinarene), 6.92 (d, 1H, NC*H*CHN, ^3J= 1.8 Hz), 6.72 (d, 1H, NCHC*H*N, ^3J= 1.8 Hz), 6.64 (s, 2H, arom. CH, resorcinarene), 6.61 (s, 1H, arom. CH, resorcinarene), 6.66 (s, 1H, arom. CH, resorcinarene), 6.59 (s, 2H, arom. CH, resorcinarene), 6.27 and 4.64 (AB spin system, 4H, OCH_2O, ^2J= 7.2 Hz), 5.89 and 4.50 (AB spin system, 4H, OCH_2O, ^2J= 7.2 Hz), 5.88 and 4.49 (AB spin system, 4H, OCH_2O, ^2J= 7.2 Hz), 5.81 and 4.53 (AB spin system, 4H, OCH_2O, ^2J= 7.1 Hz), 5.72 (s, 2H, NCH_2), 5.02 (t, 2H, C*H*CH_2, ^3J= 8.1 Hz), 4.96–4.83 (m, 6H, C*H*CH_2), 2.48–2.26 (m, 16H, CHC*H*$_2$), 1.61–1.32 (m, 48H, C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 1.04 (t, 18H, CH_2CH_3, ^3J= 7.2 Hz), 1.01 (t, 6H, CH_2CH_3, ^3J= 7.2 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.04–115.93 (arom. C), 99.69 (s, OCH_2O), 99.63 (s, OCH_2O), 99.50 (s, OCH_2O), 99.21 (s, OCH_2O), 46.80 (s, NCH_2), 36.66 (s, $CHCH_2$), 36.37 (s, $CHCH_2$), 32.04 (s, $CH_2CH_2CH_3$), 31.96 (s, $CH_2CH_2CH_3$), 29.86 (s, $CHCH_2$), 29.79 (s, $CHCH_2$), 29.69 (s, $CHCH_2$), 27.56 (s, $CHCH_2CH_2$), 27.48 (s, $CHCH_2CH_2$), 22.69 (s, CH_2CH_3), 14.10 (s, CH_2CH_3) ppm; elemental analysis calcd (%) for $C_{113}H_{135}N_3O_{16}Br_2Pd$ (Mr = 2057.52): C 65.96, H 6.61, N 2.04; found: C 66.07, H 6.66, N 1.98.

3.2.2. *trans*-Dibromo-[2-{25,26,27,28-tetrabenzyloxycalix[4]arene-5-yl}-5-{(4(24),6(10), 12(16), 18(22)-tetramethylenedioxy-2,8,14,20-tetrapentyl-resorcin[4]arene-5-methyl}-imidazol-2-yliden] pyridine palladium(II) (3)

Yield, 0.101 g, 41%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90–8.86 (m, 2H, arom. CH, Py), 7.72–7.65 (m, 1H, arom. CH, Py), 7.33–7.06 (m, 28H, arom. CH), 6.71–6.53 (m, 7H, arom. CH and NC*H*CHN), 6.50 (s, 2H, arom. CH, resorcinarene), 6.47 (s, 1H, arom. CH, resorcinarene), 6.43–6.34 (m, 4H, arom. CH and NCHC*H*N), 6.09 and 4.46 (AB spin system, 4H, OCH_2O, ^2J= 7.5 Hz), 5.74 and 4.40 (AB spin system, 4H, OCH_2O, ^2J= 7.5 Hz), 5.46 (s, 2H, NCH_2), 5.01 (s, 2H, C*H*$_2$C$_6$H$_5$), 4.97 (s, 2H, C*H*$_2$C$_6$H$_5$), 4.91 and 4.86 (AB spin system,

4H, $CH_2C_6H_5$, ^2J= 10.5 Hz), 4.80 (t, 2H, $CHCH_2$, ^3J= 7.9 Hz), 4.73 (t, 2H, $CHCH_2$, ^3J= 7.8 Hz), 4.22 and 2.94 (AB spin system, 4H, $ArCH_2Ar$, ^2J= 13.8 Hz), 4.17 and 2.94 (AB spin system, 4H, $ArCH_2Ar$, ^2J= 14.1 Hz), 2.33–2.14 (m, 8H, $CHCH_2$), 1.46–1.31 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.91 (t, 6H, CH_2CH_3, ^3J= 6.9 Hz), 0.91 (t, 6H, CH_2CH_3, ^3J =6.9 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.80–116.59 (arom. C), 99.85 (s, OCH_2O), 99.73 (s, OCH_2O), 76.81 (s, $CH_2C_6H_5$), 76.61 (s, $CH_2C_6H_5$), 76.50 (s, $CH_2C_6H_5$), 45.83 (s, NCH_2), 36.87 (s, $CHCH_2$), 36.59 (s, $CHCH_2$), 32.24 (s, $CH_2CH_2CH_3$), 31.56 ($ArCH_2Ar$), 30.09 (s, $CHCH_2$), 29.91 ($ArCH_2Ar$), 27.78 (s, $CHCH_2CH_2$), 22.90 (s, CH_2CH_3), 14.33 (s, CH_2CH_3) ppm; elemental analysis calcd (%) for $C_{117}H_{119}N_3O_{12}Br_2Pd$ (Mr = 2025.44): C 69.38, H 5.92, N 2.07; found: C 69.47, H 6.01, N 1.98.

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

A mixture of [$PdBr_2$(NHC)(pyridine)] (5×10^{-5} mmol, 1×10^{-2} mol %), ArBr (0.5 mmol), $PhB(OH)_2$ (0.091 g, 0.75 mmol), NaH (60% dispersion in mineral oil; 0.030 g, 0.75 mmol) dioxane (1.5 mL), and decane (0.05 mL, internal reference) was heated for 1 h at 100 °C. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analysed by GC. All products were unambiguously identified by NMR after their isolation. The NMR spectra were compared to those reported in the literature.

4. Conclusion

We have described the first PEPPSI-type palladium complex in which a carbene ligand is N-substituted by two bulky, freely rotating cavitand subunits. The beneficial role of the resorcinarenylmethyl fragment over that of a benzyl one was shown in Suzuki–Miyaura cross coupling experiments involving aryl bromides (activity increase of ca. 15%). The activity increase would probably be enhanced by limiting the degree of rotational freedom of the resorcinarenylmethyl group, for example by expanding the flat carbenic heterocycle.

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