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Homogeneous Catalysis

Resorcinarene-Based *o*-Biarylphosphines in Palladium-Catalysed Suzuki–Miyaura Cross-Coupling Reactions of Bulky Substrates

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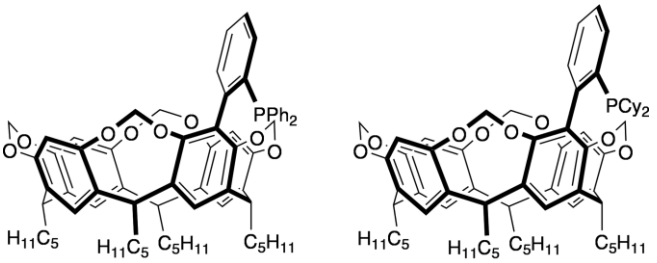
Abstract: Two *o*-biarylphosphines, in which the arene ring remote from the phosphorus atom is part of a resorcin[4]arene cavitand, have been synthesised, characterised by X-ray diffraction and assessed in the cross-coupling reactions of bulky aryl chlorides with sterically hindered arylboronic acids. Only atropisomers with externally located P atoms were obtained. The resorcinarene ligand with the *o*-$PCy_2C_6H_4$ substituent was found to be more efficient than the Buchwald analogue SPhos in catalysing coupling reactions, reacting around 1.4 times faster. Its superior performance has been attributed to the permanent *exo* positioning of the metal centre, which engenders steric interactions with two pentyl substituents and therefore facilitates the reductive elimination step.

Introduction

Known since 1979,[1] the Suzuki–Miyaura (SM) reaction, that is, the cross-coupling between organoboronic acids and aryl halides, has become one of the most valuable methods in modern organic chemistry for creating carbon–carbon bonds.[2] Over the years, SM catalysts have been improved so as to give access to more sophisticated coupling products. Thus, the formation of tri- or tetra-*ortho*-substituted biaryls starting from hindered aryl chlorides became possible with catalysts based on bulky and/or electron-rich phosphines[3] as well as N-heterocyclic carbenes.[4] In this regard, the Buchwald biarylphosphines are one of the most prominent families of ligands.[5] Their performance relies primarily on their ability to behave as hemilabile (*P,arene*) chelators involving a remote aryl ring. By forming chelate complexes, mono-phosphine palladium intermediates are favoured over bis-ligand complexes, the former increasing the rate of oxidative addition. Additionally, their intrinsic bulkiness is expected to facilitate the reductive elimination step.[6]

As an extension to our studies on calixarenyl- and resorcinarenyl-derived phosphines,[6c,7] we herein report the synthesis of the first resorcinarenes bearing Buchwald-type phosphine substituents (Figure 1) and their use in cross-coupling reactions between bulky aryl chlorides and sterically hindered arylboronic acids. Related biarylphosphines based on a calix[4]arene core, which is smaller in size than the resorcin[4]arene skeleton, have been reported recently.[7f]



1 2

Figure 1. Resorcinarenyl-phosphines synthesised and assessed in the present study.

Results and Discussion

Resorcinarenyl-phosphines **1** and **2** were each prepared in four steps from bromo-cavitand **3**,[8] as shown in Scheme 1. Their synthesis began with a halogen/lithium exchange followed by reaction with $B(OMe)_3$ and subsequent acidolysis leading to the expected boronic acid, which was isolated as the pinacol boronate derivative **4**. Palladium-catalysed Suzuki–Miyaura coupling of **4** with 2-bromoiodobenzene gave the atropisomers **5** (isolated yield 60 %) and **6** (isolated yield 5 %) with their bromine atom turned towards and away from the resorcinarene axis, respectively. The two atropisomers were separated chromatographically. It is worth noting that by carrying out such a reaction sequence with a tetrabrominated precursor instead of **3**, Sherburn and co-workers obtained a similar ratio of *inside*/*outside* atropisomers (*in*/*out*: 98:2).[9] The isolated *in*-bromo-cavitand **5** was treated with *n*BuLi, and the resulting organolithium derivative reacted in two separate experiments, with $ClPPh_2$ and $ClPCy_2$. To facilitate product separation the two phosphines formed (**1** and **2**) were isolated as their oxides (**7** and **8**, 65 and 60 % yields, respectively), which were obtained by addition of H_2O_2. Unlike the reaction leading to the bromo compounds **5** and **6**, compounds **7** and **8** were obtained as single products, as revealed by NMR spectroscopy. An X-ray

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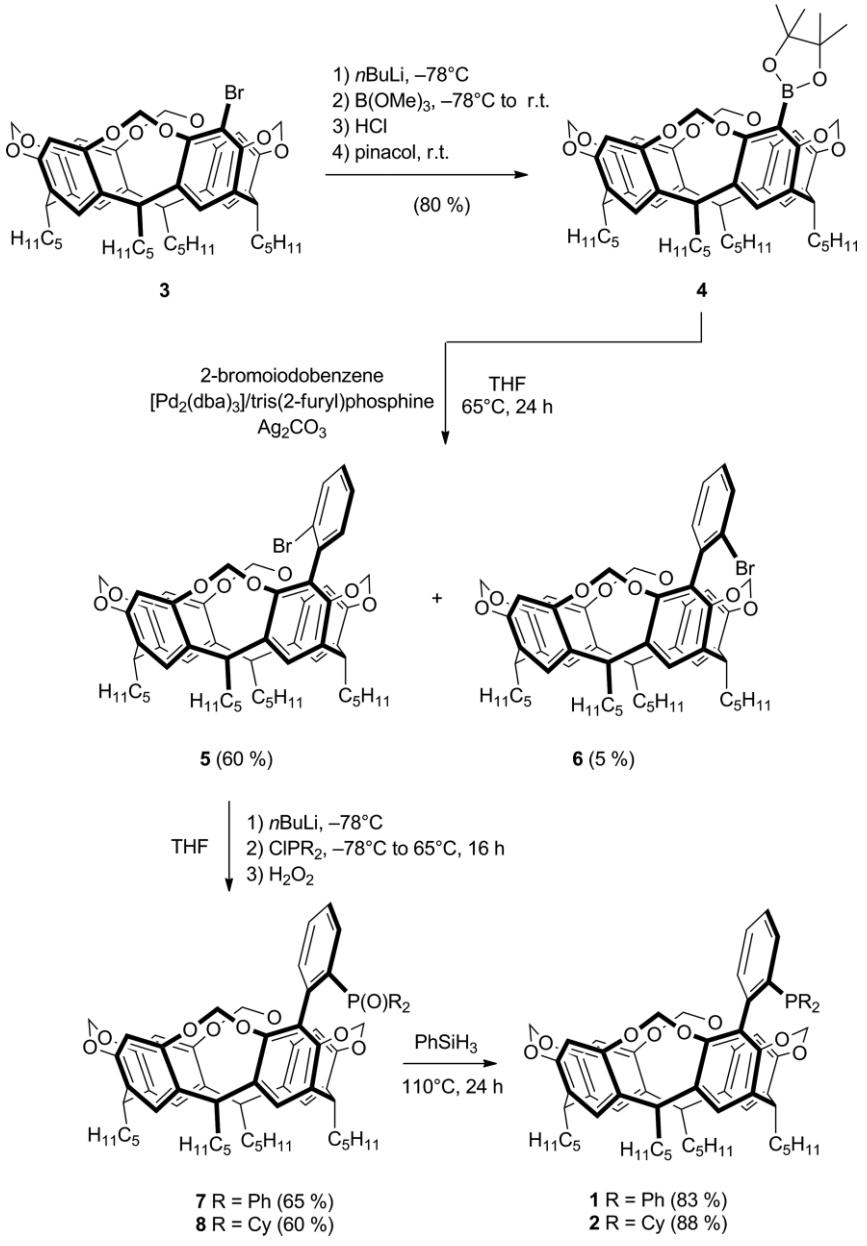


Scheme 1. Synthesis of phosphines **1** and **2**.

structure determination showed that the phosphoryl unit of **8** lies outside the cavity (Figure 2). The same is likely (see below) to apply to **7**, although this was not proven spectroscopically. A molecular mechanics calculation showed that the rotational barrier for *out*-**7**/*in*-**7** isomerisation is about 20 kcal mol^{-1}.

The reduction of **7** and **8** with $PhSiH_3$ gave the targeted phosphines **1** and **2** in high yields. Compounds **1** and **2** each show a singlet peak in their ^{31}P NMR spectrum [δ = –10.5 (**1**) and –8.7 ppm (**2**)]. The corresponding ^{1}H NMR spectra are in keeping with C_s-symmetrical molecules, as revealed by the presence in each of two AB patterns (intensity 4:4) for the four OCH_2O groups and two triplets (intensity 2:2) for the methine groups. ^{1}H-^{1}H ROESY NMR experiments carried out on **2** showed spatial correlations between hydrogen atoms of the PCy_2 unit and the two pentyl groups, which means that the

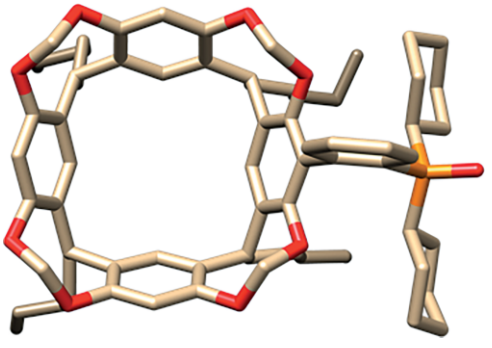


Figure 2. Molecular structure of **8**. For clarity, the molecule of MeOH located outside the cavity is not shown. Biaryl dihedral angle: 85.85°. Separation between the centroids of the distal aromatic rings: 6.67 and 6.57 Å.

phosphino group lies on the outer face of the cavitand. The external position of the P atoms in **1** and **2** was confirmed by two single-crystal X-ray structure determinations (Figure 3 and Figure 4). To estimate the cone angle of **2**, we assumed that the *out*-PCy_2 group freely rotates around the corresponding P–phenylene bond, this resulting in a cone angle varying within the range 158–165°.

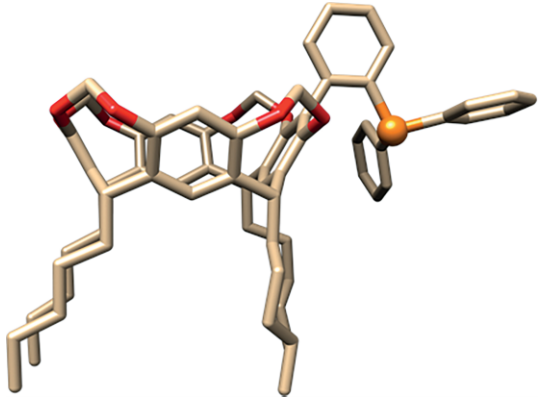


Figure 3. Molecular structure of **1**. Biaryl dihedral angle: 84.55°. Separation between the centroids of distal aromatic rings: 6.65 and 6.56 Å.

Phosphine **1** readily formed complexes with palladium(II). Thus, by using a Pd/L stoichiometry of 1:1, the reaction of **1** with $[PdCl_2(PhCN)_2]$ and $[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$ in CH_2Cl_2 gave complexes **9** and **10**, respectively (Scheme 2). Again, the ^1H NMR spectra are in keeping with C_s-symmetrical cavitand cores. Their ^{31}P NMR spectra each consist of a singlet (δ = 33.3 ppm for **9** and 43.3 ppm for **10**). Note that the significant variation in the ^{31}P chemical shift ($\Delta\delta$ = 43.8 ppm) observed on going from phosphine **1** to complex **9** is per se a clear indication of the formation of a $[PdCl(phosphine)(\mu\text{-}Cl)]_2$ complex rather than

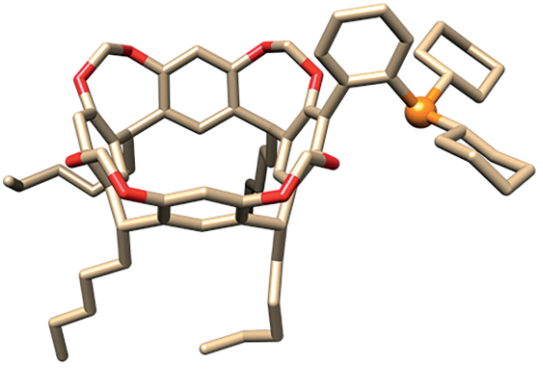


Figure 4. Molecular structure of **2**. Biaryl dihedral angle: 88.54°. Separation between the centroids of distal aromatic rings: 6.61 and 6.59 Å.

a $[PdCl_2(phosphine)_2]$ complex.[10] The formation of the dimer was confirmed by a single-crystal X-ray structure determination (Figure 5).

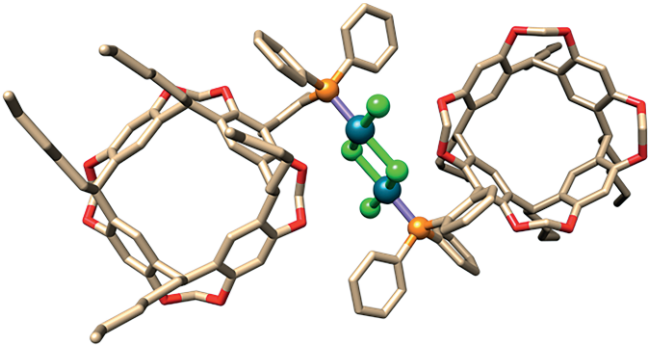
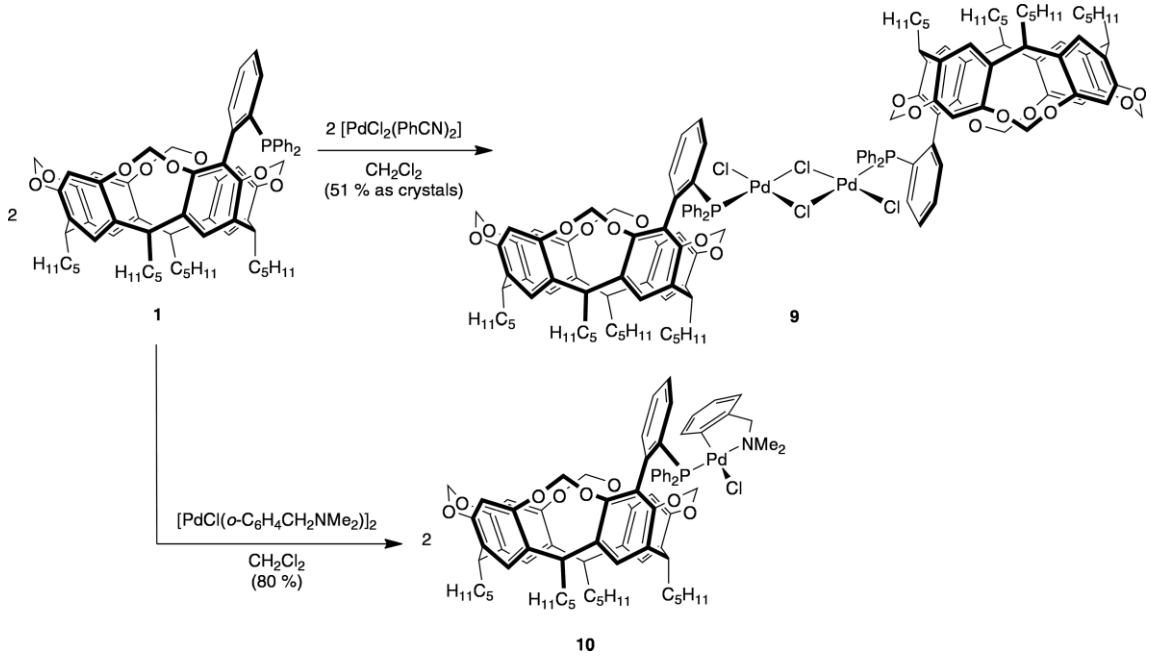


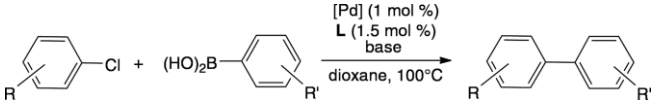
Figure 5. Molecular structure of centrosymmetric **9**. Biaryl dihedral angle in the cavitand subunits: 78.9°. Separation between the centroids of distal aromatic rings in each cavitand: 6.58 and 6.63 Å. Selected bond lengths [Å] and angles [°]: Pd–μ-Cl 2.3462(7) and 2.3951(7), Pd–Cl 2.2827(8), Pd–P 2.2421(7), Pd–μ-Cl–Pd 95.68(2), μ-Cl–Pd–Cl 90.78(3), Cl–Pd–P 91.29(3), P–Pd–μ-Cl 93.14(3), μ-Cl–Pd–μ-Cl 84.31(2).



Scheme 2. Synthesis of palladium complexes **9** and **10**.

Catalytic Suzuki–Miyaura Cross-Coupling Reactions with Phosphines 1 and 2

Both phosphines were assessed in the palladium-catalysed Suzuki–Miyaura cross-coupling reactions of aryl chlorides (Scheme 3). The catalysts were generated in situ by mixing a suitable palladium precursor with 1.5 equiv. of phosphine per palladium.



Scheme 3. Suzuki–Miyaura cross-coupling reactions of aryl chlorides with arylboronic acids.

To determine the optimal catalytic conditions, a series of cross-coupling reactions between 4-chloroanisole and phenylboronic acid were investigated with the following bases: Cs_2CO_3, NaH, KOH and *t*BuOK. These test reactions were performed with ligand **2** and $[Pd(OAc)_2]$ at 100 °C in 1,4-dioxane and by applying a palladium loading of 1 mol-%. The conversions were determined after 1 hour. As can be inferred from Table 1, entries 1–4, *t*BuOK led to the highest conversion (90.6 %). As expected,[6] a lower conversion (52.1 %) was obtained with the less basic and less encumbered phosphine **1** (Table 1, entry 6). The use of $[Pd_2(dba)_3]$ as palladium precursor in combination with phosphine **2** gave a slightly lower conversion than that achieved with $[Pd(OAc)_2]$ (Table 1, entry 5). We further found that for reactions performed at room temperature it was best to use $K_3PO_4{\cdot}H_2O$ as a base in THF (see below).

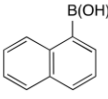
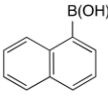
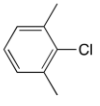
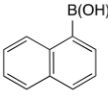
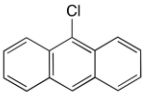
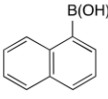
Table 1. Suzuki–Miyaura cross-coupling reaction of 4-chloroanisole with phenylboronic acid: a search for optimal catalytic conditions.[a]

Entry	[Pd]	Phosphine	Base	Conversion [%]
1	$[Pd(OAc)_2]$	**2**	Cs_2CO_3	traces
2	$[Pd(OAc)_2]$	**2**	NaH	18.8
3	$[Pd(OAc)_2]$	**2**	KOH	76.9
4	$[Pd(OAc)_2]$	**2**	*t*BuOK	90.6
5	$[Pd_2(dba)_3]$	**2**	*t*BuOK	74.7
6	$[Pd(OAc)_2]$	**1**	*t*BuOK	52.1

[a] Reagents and conditions: [Pd] (1.0 mol-%), phosphine (1.5 mol-%), 4-$MeOC_6H_4Cl$ (0.25 mmol), $PhB(OH)_2$ (0.37 mmol), base (0.37 mmol), decane (0.025 mL), dioxane (0.75 mL), 100 °C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

Applying these optimised conditions ($[Pd(OAc)_2]$, *t*BuOK, ligand **2**), four sterically hindered aryl chlorides, namely 2-chlorotoluene, 2-chloroanisole, 2,6-dimethylchlorobenzene and 9-chloroanthracene, were used in cross-coupling reactions with four arylboronic acids (Table 2). 2-Chlorotoluene and 2-chloroanisole were both converted into heterobiaryls with high conversions (82.6–86.0 %) when treated with phenylboronic acid (2 h) and naphthalene-1-boronic acid (8 h, Table 2, entries 1, 2, 5 and 6). With the bulky *ortho* boronic derivatives 2-methylphenylboronic acid and 2-methoxyphenylboronic acid, as expected, somewhat lower conversions (52.3–75.0 % after 16 h) were obtained with these chlorides (Table 2, entries 3, 4, 7 and 8). Longer reaction times were also required with the di-*ortho*-substituted arene 2,6-dimethylchlorobenzene (Table 2, entries 9–12). As frequently observed in SM coupling reactions, 9-chloroanthracene gave rather high conversions. Thus, for example, conversions higher than 90 % were observed after 16 h when this substrate was treated with 2-methylphenylboronic

Table 2. Suzuki–Miyaura cross-coupling reactions of aryl chlorides catalysed by using $[Pd(OAc)_2]$/phosphine **2**.[a]

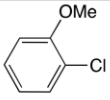
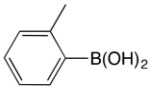
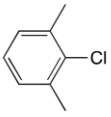
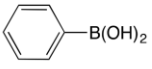
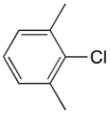
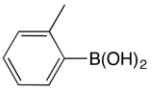
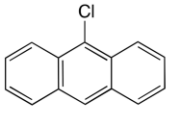
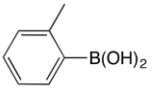
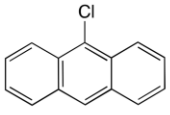
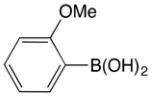
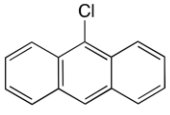
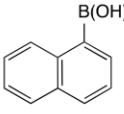
Entry	ArCl	$Ar'B(OH)_2$	Time [h]	Conversion [%]
1			2	84.3
2			8	82.6
3			16	67.9
4			16	52.3
5			2	86.0
6			8	84.4
7			16	75.0
8			16	69.7
9			8	83.6
10			16	79.5
11			24	54.5
12			24	79.1
13			5	99.4
14			8	95.8
15			16	99.8
16			16	92.6

[a] Reagents and conditions: $[Pd(OAc)_2]$ (1.0 mol-%), phosphine **2** (1.5 mol-%), ArCl (0.25 mmol), $ArB(OH)_2$ (0.37 mmol), *t*BuOK (0.37 mmol), decane (0.025 mL), dioxane (0.75 mL), 100 °C. The conversions were determined by GC, the calibrations being based on decane.

acid (99.8 %) or 2-methoxyphenylboronic acid (92.6 %) (Table 2, entries 15 and 16).

Phosphine **2** also gave very good results in reactions carried out at room temperature (Table 3). These were performed with an ArBr/Pd ratio of 200 (0.5 mol-%) and in the presence of $K_3PO_4{\cdot}H_2O$, a base that was found to be superior to *t*BuOK at room temperature (see above). After 24 h, conversions of between 58 and 100 % were obtained, the catalyst performance depending again on the degree of encumbrance in the aromatic reagents. Thus, the coupling of *o*-chloroanisole with *o*-tolylboronic acid produced the corresponding *ortho*,*ortho*'-disubstituted biphenyl in 65.4 % yield (Table 3, entry 1), full conversion was observed in the cross-coupling of 2,6-dimethylchlorobenzene with phenylboronic acid (Table 3, entry 2) and good-to-excellent conversions were further obtained in coupling reactions involving 9-chloroanthracene (Table 3, entries 4–6).

Table 3. Suzuki–Miyaura cross-coupling reactions of aryl chlorides catalysed by using $[Pd(OAc)_2]$/phosphine **2** at room temperature.[a]

Entry	ArCl	Ar'B(OH)$_2$	Conversion [%]
1			65.4
2			99.9
3			58.1
4			95.5
5			89.3
6			92.7

[a] Reagents and conditions: $[Pd(OAc)_2]$ (0.5 mol-%), phosphine **2** (0.75 mol-%), ArCl (0.5 mmol), ArB(OH)$_2$ (1.5 mmol), $K_3PO_4{\cdot}H_2O$ (0.75 mmol), decane (0.025 mL), THF (0.50 mL), room temp., 24 h. The conversions were determined by GC, the calibrations being based on decane.

To evaluate the influence of the resorcinarene subunit on the catalytic activity at room temperature, the reactions shown in entries 1 and 3 of Table 3 were repeated with the Buchwald ligand SPhos (**11**, Figure 6; same conditions: 0.5 mol-% of $[Pd(OAc)_2]$, $K_3PO_4{\cdot}H_2O$, room temperature for 24 h). SPhos is a biarylphosphine in which the remote aryl ring bears, exactly as in **2**, oxygen atoms at the two *ortho* positions. The two reactions considered here revealed the conversions obtained with **2** (65.4 and 58.1 %, respectively) to be around 40 % higher than those observed with SPhos (47.7 and 42.3 %, respectively). Bearing in mind that complexes of **2** bear an *exo*-positioned metal centre, the superiority of **2** in SM coupling reactions is best explained by considering the steric influence of the two pentyl chains flanking the biaryl unit. These may indeed bend towards the catalytic centre and thus sterically interact with the transiently formed Pd–Ar bonds, this facilitating the reductive elimination step (Figure 7). Similar side-group effects have already been observed in SM reactions with related cavitands equipped with N-heterocyclic carbene units.[4g,4h]

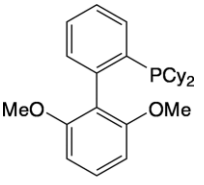


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Figure 6. SPhos ligand, used to assess the efficacy of the arylresorcinarenyl phosphine ligand **2**.

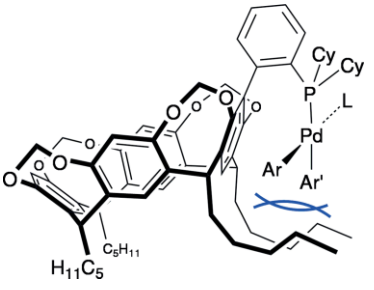

Figure 7. Possible steric interactions in catalytic intermediates formed with **2**.

Conclusions

The introduction of a 2-(dicyclohexylphosphino)phenyl or 2-(diphenylphosphino)phenyl unit as a substituent directly attached to a resorcinarene cavitand has been found to provide two useful *o*-biarylphosphines for the palladium-catalysed Suzuki–Miyaura cross-coupling reactions of bulky aryl chlorides with sterically hindered arylboronic acids. A significant aspect of the ligand structures revealed by X-ray structure determinations of both the free ligands and their Pd^{II} complexes is that they exist exclusively as the *outside* atropisomer. The resorcinarene bearing the *o*-$(PCy_2)C_6H_4$ group displayed activities that were around 40 % higher than those of a related Buchwald ligand devoid of a cavity, and its better performance has been attributed to the permanent *exo*-positioning of the metal during catalysis, which enables steric interactions of two pentyl substituents with the second coordination sphere of the metal, this impacting on the reductive elimination step. Further studies are aimed at exploiting the steric properties of expanded biarylphosphines in carbon–carbon bond-forming reactions.

Experimental Section

General Experimental Methods: All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were purified by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed through a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$NMR spectra were recorded with Bruker FT instruments (AVANCE 400 and 500). The chemical shifts in the ^1H NMR spectra are referenced to the residual protiated solvent (δ = 7.26 ppm for $CHCl_3$ and 7.16 ppm for C_6D_5H). The chemical shifts of the ^{13}C NMR spectra are reported relative to the deuteriated solvents (δ = 77.16 ppm for $CDCl_3$ and 128.06 ppm for C_6D_6). The chemical shifts of the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and Hz, respectively. C_q denotes a quaternary carbon atom. The catalytic solutions were analysed by using a Varian 3900 GC equipped with a WCOT fused-silica column (25 m × 0.25 mm). Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. 5-Bromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**3**) was prepared according to a literature procedure.[8]

5-(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-yl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (4): *n*BuLi (1.6 M in hexane, 3.64 mL, 5.82 mmol) was slowly added to a solution of 5-bromo-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**3**; 5.000 g, 5.58 mmol) in THF (90 mL) at –78 °C. After stirring for 0.5 h, $B(OMe)_3$ (1.79 mL, 16.00 mmol) was added and the resulting mixture was stirred at room temperature for a further 5 h. After hydrolysis with a HCl solution (1 M, 100 mL), the product was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were then dried with Na_2SO_4. After filtration, the solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (90 mL). Pinacol (0.945 g, 8.00 mmol) and $MgSO_4$ (5.000 g) were then added and the resulting mixture was stirred overnight at room temperature. After filtration, the solvent was removed under vacuum. The crude product was purified by flash chromatography (CH_2Cl_2/petroleum ether, 6:4, v/v) to afford compound **4** as a white solid (4.210 g, 80 % yield). R_f = 0.15 (EtOAc/petroleum ether, 1:9, v/v). ^1H NMR (400 MHz, C_6D_6): δ = 7.52 (s, 1 H, arom. CH), 7.51 (s, 1 H, arom. CH), 7.50 (s, 2 H, arom. CH), 6.61 (s, 1 H, arom. CH), 6.53 (s, 2 H, arom. CH), 5.76 and 4.57 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.59 and 4.37 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.16 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 5.15 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 2.35–2.23 (m, 8 H, $CHCH_2$), 1.40–1.27 (m, 16 H, $CH_2CH_2CH_2CH_3$), 1.25–1.20 (m, 8 H, CH_2CH_3), 1.07 [s, 12 H, $C(CH_3)_2$], 0.81 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 0.80 (t, ^3J = 6.8 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 158.69 (s, arom. C_qO), 155.74 (s, arom. C_qO), 155.60 (s, arom. C_qO), 155.53 (s, arom. C_qO), 139.26–117.14 (arom. Cs), 99.92 (s, OCH_2O), 99.50 (s, OCH_2O), 83.73 [s, $C(CH_3)_2$], 36.99 (s, $CHCH_2$), 36.94 (s, $CHCH_2$), 32.32 (s, $CH_2CH_2CH_3$), 30.47 (s, $CHCH_2$), 30.40 (s, $CHCH_2$), 28.01 (s, $CHCH_2CH_2$), 27.96 (s, $CHCH_2CH_2$), 24.76 [s, $C(CH_3)_2$], 23.05 (s, CH_2CH_3), 14.27 (s, CH_2CH_3) ppm. MS (ESI-TOF): m/z = 981.51 $[M + K]^+$; expected isotopic profiles. $C_{58}H_{75}BO_{10}$ (943.02): calcd. C 73.87, H 8.02; found C 74.02, H 8.13.

5-(2-Bromophenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arenes (Atropisomers 5 and 6): A 100 mL Schlenk tube was filled with the boronic ester **4** (3.000 g; 3.18 mmol), 2-bromoiodobenzene (1.30 mL, 10.15 mmol), Ag_2CO_3 (1.754 g, 6.36 mmol), $[Pd_2(dba)_3]$ (0.348 g, 0.38 mmol) and tri(2-furyl)phosphine (0.369 g, 1.59 mmol). THF (50 mL) was added and the resulting mixture was heated at 65 °C for 24 h. The reaction mixture was then filtered through a short plug of Celite and the filtered solution washed with CH_2Cl_2 (3 × 20 mL). The solvent was removed under vacuum to afford the crude product, which was purified by flash chromatography (EtOAc/petroleum ether, 1:9, v/v) to give the atropisomers **5** and **6**.

***Inside* Atropisomer 5:** Yield: 1.852 g, 60 %. R_f = 0.27 (EtOAc/petroleum ether, 1:9, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, ^3J = 8.0, ^4J = 0.8 Hz, 1 H, arom. CH, C_6H_4), 7.34 (td, ^3J = 7.4, ^4J = 1.2 Hz, 1 H, arom. CH, C_6H_4), 7.24–7.20 (m, 1 H, arom. CH, C_6H_4), 7.22 (s, 2 H, arom. CH, resorcin.), 7.19 (s, 2 H, arom. CH, resorcin.), 7.06 (dd, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, arom. CH, C_6H_4), 6.51 (s, 1 H, arom. CH, resorcin.), 6.46 (s, 2 H, arom. CH, resorcin.), 5.77 and 4.42 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.41 and 4.71 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.77 (t, ^3J = 8.4 Hz, 2 H, $CHCH_2$), 4.74 (t, ^3J = 8.4 Hz, 2 H, $CHCH_2$), 2.34–2.20 (m, 8 H, $CHCH_2$), 1.46–1.33 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.93 (t, ^3J = 7.2 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.23 (s, arom. C_qO), 155.09 (s, arom. C_qO), 154.95 (s, arom. C_qO), 152.46 (s, arom. C_qO), 138.76–116.10 (arom. Cs), 100.07 (s, OCH_2O), 99.71 (s, OCH_2O), 36.78 (s, $CHCH_2$), 36.56 (s, $CHCH_2$), 32.19 (s, $CH_2CH_2CH_3$), 32.17 (s, $CH_2CH_2CH_3$), 30.28 (s, $CHCH_2$), 30.04 (s, $CHCH_2$), 27.74 (s, $CHCH_2CH_2$), 22.83 (s, CH_2CH_3), 14.24 (s, CH_2CH_3) ppm. MS (ESI-TOF): m/z = 1009.36 $[M + K]^+$; expected isotopic profiles. $C_{58}H_{67}BrO_8$ (970.40): calcd. C 71.66, H 6.95; found C 71.70, H 7.02.

***Outside* Atropisomer 6:** Yield: 0.154 g, 5 %. R_f = 0.10 (EtOAc/petroleum ether, 1:9, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dd, ^3J = 7.6, ^4J = 1.2 Hz, 1 H, arom. CH, C_6H_4), 7.24–7.19 (m, 2 H, arom. CH, C_6H_4), 7.21 (s, 1 H, arom. CH, resorcin.), 7.20 (s, 1 H, arom. CH, resorcin.), 7.18 (s, 2 H, arom. CH, resorcin.), 6.87 (dd, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, arom. CH, C_6H_4), 6.51 (s, 1 H, arom. CH, resorcin.), 6.45 (s, 2 H, arom. CH, resorcin.), 5.79 and 4.22 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.35 and 4.36 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.80 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.77 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 2.38–2.21 (m, 8 H, $CHCH_2$), 1.48–1.33 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.93 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 0.92 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.06 (s, arom. C_qO), 154.99 (s, arom. C_qO), 154.79 (s, arom. C_qO), 152.22 (s, arom. C_qO), 138.89–115.97 (arom. Cs), 99.82 (s, OCH_2O), 99.41 (s, OCH_2O), 36.65 (s, $CHCH_2$), 36.54 (s, $CHCH_2$), 32.16 (s, $CH_2CH_2CH_3$), 32.06 (s, $CH_2CH_2CH_3$), 29.98 (s, $CHCH_2$), 29.96 (s, $CHCH_2$), 27.71 (s, $CHCH_2CH_2$), 27.61 (s, $CHCH_2CH_2$), 22.83 (s, CH_2CH_3), 14.21 (s, CH_2CH_3) ppm. MS (ESI-TOF): m/z = 1009.36 $[M + K]^+$; expected isotopic profiles. $C_{58}H_{67}BrO_8$ (970.40): calcd. C 71.66, H 6.95; found C 71.75, H 7.11.

General Procedure for the Preparation of the Phosphine Oxides 7 and 8: *n*BuLi (1.6 M in hexane, 0.72 mL, 1.16 mmol) was slowly added to a solution of 5-(2-bromophenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (**5**; 1.000 g, 1.03 mmol) in THF (50 mL) at –78 °C. After 1 h, $ClPR_2$ (1.16 mmol) was added slowly and the resulting mixture was stirred at 65 °C for 16 h. The reaction mixture was cooled to room temperature, then H_2O_2 (30 % in H_2O, 20 mL, 25 mmol) was added. After stirring for 1 h, the organic product was extracted with CH_2Cl_2 (2 × 10 mL), the organic phases were combined and washed with water (2 × 20 mL), after drying with Na_2SO_4 and filtration, the solution was evaporated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/Et_2O, 85:15, v/v) to afford the corresponding phosphine oxide as a white solid.

5-(2-Diphenylphosphinoylphenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (7): Yield: 0.722 g, 65 %. R_F = 0.36 (CH_2Cl_2/Et_2O, 85:15, v/v). ^1H NMR (500 MHz, C_6D_6): δ = 7.81 (s, 1 H, arom. CH, resorcin.), 7.67 (s, 2 H,

arom. CH, resorcin.), 7.56 (s, 1 H, arom. CH, resorcin.), 7.27–7.23 (m, 4 H, arom. CH, PPh_2), 7.02–6.94 (m, 3 H, arom. CH, C_6H_4 and PPh_2), 6.89 (t, ^3J = 6.5 Hz, 4 H, arom. CH, PPh_2), 6.80 (s, 2 H, arom. CH, resorcin.), 6.80–6.78 (m, 2 H, arom. CH, C_6H_4), 6.16 (s, 1 H, arom. CH, resorcin.), 5.60 and 4.42 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 4.16 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 5.12–5.09 (m, 2 H, $CHCH_2$), 5.01 and 4.24 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 4.87–4.84 (m, 1 H, arom. CH, C_6H_4), 2.86–2.79 (m, 2 H, $CHCH_2$), 2.68–2.60 (m, 2 H, $CHCH_2$), 2.42–2.34 (m, 2 H, $CHCH_2$), 2.29–2.23 (m, 2 H, $CHCH_2$), 1.60–1.19 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.90 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.82 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 155.88 (s, arom. C_qO), 155.56 (s, arom. C_qO), 155.40 (s, arom. C_qO), 152.20 (s, arom. C_qO), 140.25–116.83 (arom. Cs), 99.34 (s, OCH_2O), 99.59 (s, OCH_2O), 37.38 (s, $CHCH_2$), 37.05 (s, $CHCH_2$), 32.46 (s, $CH_2CH_2CH_3$), 32.33 (s, $CH_2CH_2CH_3$), 30.45 (s, $CHCH_2$), 30.06 (s, $CHCH_2$), 28.12 (s, $CHCH_2CH_2$), 28.05 (s, $CHCH_2CH_2$), 23.23 (s, CH_2CH_3), 23.09 (s, CH_2CH_3), 14.49 (s, CH_2CH_3), 14.31 (s, CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 24.4 [s, P(O)Ph_2] ppm. MS (ESI-TOF): m/z = 1093.53 $[M + H]^+$; expected isotopic profiles. $C_{70}H_{77}O_9P$ (1093.33): calcd. C 76.90, H 7.10; found C 77.02, H 7.22.

5-(2-Dicyclohexylphosphinoylphenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (8): Yield: 0.683 g, 60 %. R_f = 0.32 (CH_2Cl_2/Et_2O, 9:1, v/v). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.28–8.24 (m, 1 H, arom. CH, C_6H_4), 7.45 (t, ^3J = 7.5 Hz, 1 H, C_6H_4), 7.36 (t, ^3J = 7.2 Hz, 1 H, C_6H_4), 7.23 (s, 1 H, arom. CH, resorcin.), 7.19 (s, 1 H, arom. CH, resorcin.), 7.16 (s, 2 H, arom. CH, resorcin.), 6.79–6.77 (m, 1 H, arom. CH, C_6H_4), 6.52 (s, 1 H, arom. CH, resorcin.), 6.45 (s, 2 H, arom. CH, resorcin.), 5.79 and 4.40 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 5.22 and 4.34 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 4.76 (t, ^3J = 8.5 Hz, 2 H, $CHCH_2$), 4.74 (t, ^3J = 8.5 Hz, 2 H, $CHCH_2$), 2.35–2.20 (m, 8 H, $CHCH_2$), 1.94–1.81 (m, 2 H, PCy_2), 1.75–1.73 (m, 4 H, PCy_2), 1.69–1.65 (m, 2 H, PCy_2), 1.60–1.52 (m, 4 H, PCy_2), 1.48–1.34 (m, 26 H, $CH_2CH_2CH_2CH_3$ and PCy_2), 1.29–1.15 (m, 6 H, PCy_2), 1.10–1.03 (m, 2 H, PCy_2), 0.93 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 0.93 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.03 (s, arom. C_qO), 154.87 (s, arom. C_qO), 154.83 (s, arom. C_qO), 153.05 (s, arom. C_qO), 138.82–116.01 (arom. Cs), 99.85 (s, OCH_2O), 99.20 (s, OCH_2O), 38.02 (d, $^1J_{PC}$ = 65.8 Hz, PCH), 36.76 (s, $CHCH_2$), 36.54 (s, $CHCH_2$), 32.16 (s, $CH_2CH_2CH_3$), 32.06 (s, $CH_2CH_2CH_3$), 30.23 (s, $CHCH_2$), 29.90 (s, $CHCH_2$), 27.90 (s, $CHCH_2CH_2$), 27.70 (s, $CHCH_2CH_2$), 27.01 (d, $^2J_{PC}$ = 12.6 Hz, $PCHCH_2$), 26.61 (d, $^3J_{PC}$ = 26.6 Hz, $PCHCH_2CH_2$), 25.86 (s, $PCHCH_2CH_2CH_2$), 22.84 (s, CH_2CH_3), 22.82 (s, CH_2CH_3), 14.27 (s, CH_2CH_3), 14.21 (s, CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 47.7 [s, P(O)Cy_2] ppm. $C_{70}H_{89}O_9P$ (1105.43): calcd. C 76.06, H 8.11; found C 76.21, H 8.19.

General Procedure for the Preparation of Phosphines 1 and 2: A suspension of phosphine **7** or **8** oxide in $PhSiH_3$ (10 equiv./phosphine oxide) was stirred for 24 h at 110 °C. The reaction mixture was cooled to room temperature and then the solution was evaporated to dryness. The residue was washed with MeOH (3 × 10 mL) to afford the phosphine as a white solid.

5-(2-Diphenylphosphinophenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (1): Yield: 0.409 g, 83 %. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 12 H, arom. CH, PPh_2 and C_6H_4), 7.21 (s, 1 H, arom. CH, resorcin.), 7.16 (s, 2 H, arom. CH, resorcin.), 7.14–7.12 (m, 1 H, arom. CH, C_6H_4), 7.08 (s, 1 H, arom. CH, resorcin.), 6.83–6.80 (m, 1 H, arom. CH, C_6H_4), 6.53 (s, 1 H, arom. CH, resorcin.), 6.47 (s, 2 H, arom. CH, resorcin.), 5.81 and 4.45 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 5.31 and 4.36 (AB spin system, ^2J = 7.0 Hz, 4 H, OCH_2O), 4.78 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.60 (t, ^3J = 7.7 Hz, 2 H, $CHCH_2$), 2.30–2.17 (m, 8 H, $CHCH_2$), 1.48–1.37 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.98 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.96 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.07 (s, arom. C_qO), 154.93 (s, arom. C_qO), 154.64 (s, arom. C_qO), 152.49 (s, arom. C_qO), 140.84–116.01 (arom. Cs), 99.81 (s, OCH_2O), 99.30 (s, OCH_2O), 36.62 (s, $CHCH_2$), 36.52 (s, $CHCH_2$), 32.24 (s, $CH_2CH_2CH_3$), 32.20 (s, $CH_2CH_2CH_3$), 30.09 (s, $CHCH_2$), 29.94 (s, $CHCH_2$), 27.74 (s, $CHCH_2CH_2$), 22.93 (s, CH_2CH_3), 22.86 (s, CH_2CH_3), 14.33 (s, CH_2CH_3), 14.27 (s, CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = –10.5 (s, PPh_2) ppm. $C_{70}H_{77}O_8P$ (1077.33): calcd. C 78.04, H 7.20; found C 78.09, H 7.25.

5-(2-Dicyclohexylphosphinophenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene (2): Yield: 1.388 g, 88 %. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, ^3J = 7.6 Hz, 1 H, arom. CH, C_6H_4), 7.30 (t, ^3J = 7.2 Hz, 1 H, arom. CH, C_6H_4), 7.24 (t, ^3J = 7.2 Hz, 1 H, arom. CH, C_6H_4), 7.21 (s, 1 H, arom. CH, resorcin.), 7.19 (s, 2 H, arom. CH, resorcin.), 7.15 (s, 1 H, arom. CH, resorcin.), 6.77 (dd, ^3J = 6.4, ^4J = 2.0 Hz, 1 H, C_6H_4), 6.52 (s, 1 H, arom. CH, resorcin.), 6.45 (s, 2 H, arom. CH, resorcin.), 5.79 and 4.45 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.25 and 4.34 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.77 (t, ^3J = 7.6 Hz, 2 H, $CHCH_2$), 4.76 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 2.37–2.25 (m, 8 H, $CHCH_2$), 1.80–1.62 (m, 10 H, PCy_2), 1.51–1.36 (m, 26 H, $CH_2CH_2CH_2CH_3$ and PCy_2), 1.27–1.11 (m, 10 H, PCy_2), 0.94 (t, ^3J = 7.0 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.13 (s, arom. C_qO), 155.00 (s, arom. C_qO), 154.67 (s, arom. C_qO), 152.54 (s, arom. C_qO), 138.90–116.22 (arom. Cs), 99.84 (s, OCH_2O), 99.30 (s, OCH_2O), 36.58 (s, $CHCH_2$), 34.46 (d, $^1J_{PC}$ = 15.1 Hz, PCH), 32.21 (s, $CH_2CH_2CH_3$), 32.00 (s, $CH_2CH_2CH_3$), 30.31 (d, $^2J_{PC}$ = 17.4 Hz, $PCHCH_2$), 30.04 (s, $CHCH_2$), 30.01 (s, $CHCH_2$), 29.47 (d, $^3J_{PC}$ = 9.7 Hz, $PCHCH_2CH_2$), 27.75 (s, $CHCH_2CH_2$), 27.61 (s, $CHCH_2CH_2$), 26.65 (s, $PCHCH_2CH_2CH_2$), 22.87 (s, CH_2CH_3), 22.85 (s, CH_2CH_3), 14.24 (s, CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = –8.7 (s, PCy_2) ppm. $C_{70}H_{89}O_8P$ (1089.43): calcd. C 77.17, H 8.23; found C 77.15, H 8.21.

Bis{chlorido(μ-chlorido)[5-(2-diphenylphosphinophenyl)-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene]palladium(II)} (9): A solution of $[PdCl_2(PhCN)_2]$ (0.037 g, 0.09 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **1** (0.050 g, 0.05 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5 h, the reaction mixture was concentrated to about 1 mL and MeOH (20 mL) was added. The yellow precipitate was separated by filtration and dried under vacuum. Slow diffusion of MeOH (10 mL) into a solution of the crude product in $CHCl_3$ (3 mL) led to the formation of orange crystals, which were separated by filtration and dried under vacuum to afford complex **9** (0.030 g, 51 % yield, based on the amount of isolated crystals). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 8 H, arom. CH, PPh_2), 7.81–7.76 (m, 2 H, arom. CH, C_6H_4), 7.33–7.28 (m, 8 H, arom. CH, PPh_2 and C_6H_4), 7.20 (t, ^3J = 6.7 Hz, 8 H, arom. CH, PPh_2), 7.14 (s, 2 H, arom. CH, resorcin.), 7.05 (s, 4 H, arom. CH, resorcin.), 6.81 (s, 2 H, arom. CH, resorcin.), 6.69–6.66 (m, 2 H, arom. CH, C_6H_4), 6.49 (s, 2 H, arom. CH, resorcin.), 6.41 (s, 4 H, arom. CH, resorcin.), 5.76 and 4.37 (AB spin system, ^2J = 7.5 Hz, 8 H, OCH_2O), 5.47 and 4.23 (AB spin system, ^2J = 7.0 Hz, 8 H, OCH_2O), 4.72 (t, ^3J = 8.0 Hz, 4 H, $CHCH_2$), 4.56–4.53 (m, 4 H, $CHCH_2$), 2.35–2.17 (m, 12 H, $CHCH_2$), 1.95–1.88 (m, 4 H, $CHCH_2$), 1.48–1.33 (m, 48 H, $CH_2CH_2CH_2CH_3$), 0.95 (t, ^3J = 7.0 Hz, 12 H, CH_2CH_3), 0.92 (t, ^3J = 7.5 Hz, 12 H, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.37 (s, arom. C_qO), 154.94 (s, arom. C_qO), 154.72 (s, arom. C_qO), 151.52 (s, arom. C_qO), 139.00–115.75 (arom. Cs), 99.87 (s, OCH_2O), 99.03 (s, OCH_2O), 36.51 (s, $CHCH_2$), 32.39 (s, $CH_2CH_2CH_3$), 32.23 (s, $CH_2CH_2CH_3$), 30.20 (s, $CHCH_2$), 30.00 (s, $CHCH_2$), 29.86 (s, $CHCH_2$), 27.87 (s, $CHCH_2CH_2$), 27.78 (s, $CHCH_2CH_2$), 22.95 (s, CH_2CH_3), 22.89 (s, CH_2CH_3), 14.40 (s, CH_2CH_3), 14.28 (s, CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ =

33.3 (s, PPh_2) ppm. MS (ESI-TOF): m/z = 2469.80 [M – Cl]$^+$; expected isotopic profiles. $C_{140}H_{154}Cl_4O_{16}P_2Pd_2$ (2509.31): calcd. C 67.01, H 6.19; found C 66.77, H 6.10.

Chlorido(*o*-dimethylaminomethylphenyl-*C*,*N*)[5-(2-diphenylphosphinophenyl)-4(24),6 (10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene]palladium(II) (10): A solution of [PdCl(*o*-$C_6H_4CH_2NMe_2$)]$_2$ (0.013 g, 0.02 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **1** (0.050 g, 0.05 mmol) in CH_2Cl_2 (10 mL). After stirring at room temperature for 0.5 h, the reaction mixture was concentrated to about 1 mL and then MeOH (20 mL) was added. The yellow precipitate was separated by filtration and dried under vacuum to give compound **10** (0.050 g, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 4 H, arom. CH, PPh_2), 7.51–7.46 (m, 1 H, arom. CH, C_6H_4P), 7.31–7.25 (m, 2 H, arom. CH, C_6H_4P), 7.23–7.18 (m, 6 H, arom. CH, PPh_2), 7.13 (s, 1 H, arom. CH, resorcin.), 7.05 (s, 2 H, arom. CH, resorcin.), 6.98 (d, ^3J = 7.2 Hz, 1 H, arom. CH, ArPd), 6.80 (s, 1 H, arom. CH, resorcin.), 6.80–6.77 (m, 1 H, arom. CH, ArPd), 6.64–6.61 (m, 1 H, arom. CH, C_6H_4P), 6.48 (s, 1 H, arom. CH, resorcin.), 6.40 (s, 2 H, arom. CH, resorcin.), 6.30 (t, ^3J = 7.2 Hz, 1 H, arom. CH, ArPd), 6.06 (t, ^3J = 7.2 Hz, 1 H, arom. CH, ArPd), 5.75 and 4.37 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 5.54 and 4.19 (AB spin system, ^2J = 7.2 Hz, 4 H, OCH_2O), 4.72 (t, ^3J = 8.0 Hz, 2 H, $CHCH_2$), 4.45 (t, ^3J = 7.8 Hz, 2 H, $CHCH_2$), 4.12 (br. s, 2 H, CH_2N), 2.91 [s, 6 H, $N(CH_3)_2$], 2.26–2.17 (m, 6 H, $CHCH_2$), 1.98–1.89 (m, 2 H, $CHCH_2$), 1.44–1.28 (m, 24 H, $CH_2CH_2CH_2CH_3$), 0.92 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.92 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.23 (s, arom. C_qO), 154.90 (s, arom. C_qO), 154.74 (s, arom. C_qO), 152.11 (s, arom. C_qO), 150.05–115.91 (arom. Cs), 99.82 (s, OCH_2O), 98.94 (s, OCH_2O), 73.76 (s, CH_2N), 50.32 [s, $N(CH_3)_2$], 36.82 (s, $CHCH_2$), 36.45 (s, $CHCH_2$), 32.30 (s, $CH_2CH_2CH_3$), 32.16 (s, $CH_2CH_2CH_3$), 30.20 (s, $CHCH_2$), 29.91 (s, $CHCH_2$), 28.03 (s, $CHCH_2CH_2$), 27.69 (s, $CHCH_2CH_2$), 22.85 (s, CH_2CH_3), 14.31 (s, CH_2CH_3), 14.25 (s, CH_2CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 43.3 (s, PPh_2) ppm. MS (ESI-TOF): m/z = 1352.51 [M + H]$^+$; expected isotopic profiles. $C_{79}H_{89}ClNO_8PPd$ (1353.40): calcd. C 70.11, H 6.63; found C 69.95, H 6.51.

Typical Procedure for the Palladium-Catalysed Suzuki–Miyaura Cross-Coupling Reactions: A 10 mL-Schlenk tube was filled with [Pd(OAc)$_2$], phosphine (1.5 equiv.), aryl chloride, arylboronic acid, base and decane (0.025 mL, internal reference). Solvent was then added. The reaction mixture was stirred at the desired temperature. An aliquot (0.3 mL) of the resulting solution was then passed through a Millipore filter and analysed by GC.

X-ray Crystal Structure Determination of 1: Colourless single crystals of **1** suitable for X-ray diffraction were obtained by the slow diffusion of MeOH into a $CHCl_3$ solution of **1** at room temperature. The sample (0.400 × 0.300 × 0.120 mm) was analysed with a Bruker APEX-II CCD diffractometer with graphite-monochromatised Mo-K_α radiation. Formula of the crystals: $C_{70}H_{77}O_8P$, M_r = 1077.33, monoclinic, space group $P2_1/c$, a = 26.4361(14), b = 10.5173(6), c = 22.6688(12) Å, β = 91.644(1)°, V = 6300.2(6) Å^3, Z = 4, D = 1.136 mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 0.097 mm^{-1}, F(000) = 2304, T = 173(2) K. Data collection ($2\theta_{max}$ = 28.085°, ω scan frames with 0.7° ω rotation and 30 s per frame, range *hkl*: h –33 to 34, k –13 to 13, l –21 to 29) gave 73709 reflections. The data revealed 15259 independent reflections of which 10012 were observed with $I > 2.0\sigma(I)$. The structure was solved by using SHELXS-2013,[11] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. The whole structure was refined with SHELXL[12] by using the full-matrix least-squares technique {use of F^2; x, y, z, β_{ij} for C, O and P atoms, x, y, z in the riding mode for hydrogen atoms; 716 variables and 10012 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 3.0616P]$ in which $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.0671, R_w = 0.1515, S_w = 1.033 and $\Delta\varrho$ < 0.353 e Å^{-3}.

X-ray Crystal Structure Determination of 2: Colourless single crystals of **2** suitable for X-ray diffraction were obtained by the slow diffusion of MeOH into a $CHCl_3$ solution of **2** at room temperature. The sample (0.200 × 0.180 × 0.160 mm) was analysed with a Bruker APEX-II CCD diffractometer with graphite-monochromatised Mo-K_α radiation. Formula of the crystals: $C_{70}H_{88}O_8P$, M_r = 1088.42, monoclinic, space group $P2_1/c$, a = 10.5450(11), b = 39.596(4), c = 15.0845(15) Å, β = 96.850(2)°, V = 6253.4(11) Å^3, Z = 4, D = 1.156 mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 0.098 mm^{-1}, F(000) = 2348, T = 173(2) K. Data collection ($2\theta_{max}$ = 28.072°, ω scan frames with 0.7° ω rotation and 30 s per frame, range *hkl*: h –13 to 13, k –52 to 51, l –19 to 19) gave 77586 reflections. The data revealed 15132 independent reflections of which 10047 were observed with $I > 2.0\sigma(I)$. The structure was solved by using SHELXS-2013,[11] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. The whole structure was refined with SHELXL[12] by using the full-matrix least-squares technique {use of F^2; x, y, z, β_{ij} for C, O and P atoms, x, y, z in the riding mode for hydrogen atoms; 758 variables and 10047 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 5.7537P]$ in which $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.0706, R_w = 0.1547, S_w = 1.031 and $\Delta\varrho$ < 0.407 e Å^{-3}.

X-ray Crystal Structure Determination of 8·CH$_3$OH: Colourless single crystals of **8** suitable for X-ray diffraction were obtained by the slow diffusion of MeOH into a $CHCl_3$ solution of **8** at room temperature. The sample (0.220 × 0.200 × 0.160 mm) was analysed with a Bruker APEX-II CCD diffractometer with graphite-monochromatised Mo-K_α radiation. Formula of the crystals: $C_{70}H_{89}Cl_2O_9P{\cdot}CH_4O$, M_r = 1137.47, monoclinic, space group $P2_1/c$, a = 11.3479(6), b = 30.8843(18), c = 19.4521(9) Å, β = 108.131(3)°, V = 6478.9(6) Å^3, Z = 4, D = 1.166 mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 0.099 mm^{-1}, F(000) = 2456, T = 296(2) K. Data collection ($2\theta_{max}$ = 28.015°, ω scan frames with 0.7° ω rotation and 30 s per frame, range *hkl*: h –9 to 14, k –37 to 40, l –25 to 24) gave 93455 reflections. The data revealed 15634 independent reflections of which 7967 were observed with $I > 2.0\sigma(I)$. The structure was solved by using SHELXS-2013,[11] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. The whole structure was refined with SHELXL[12] by using the full-matrix least-squares technique {use of F^2; x, y, z, β_{ij} for C, O and P atoms, x, y, z in the riding mode for hydrogen atoms; 716 variables and 7967 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.1577P)^2 + 4.6299P]$ in which $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.0881, R_w = 0.3111, S_w = 1.026 and $\Delta\varrho$ < 0.864 e Å^{-3}.

X-ray Crystal Structure Determination of 9: Orange single crystals of **9** suitable for X-ray diffraction were obtained by the slow diffusion of MeOH into a $CHCl_3$ solution of **9** at room temperature. The sample (0.500 × 0.150 × 0.120 mm) was analysed with a Bruker APEX-II CCD diffractometer with graphite-monochromatised Mo-K_α radiation. Formula of the crystals: $C_{140}H_{154}Cl_4O_{16}P_2Pd_2{\cdot}2CHCl_3$, M_r = 2748.06, triclinic, space group $P\bar{1}$, a = 13.3339(5), b = 13.7721(5), c = 22.0637(8) Å, α = 101.534(1), β = 99.705(1), γ = 112.025(1)°, V = 3545.4(2) Å^3, Z = 1, D = 1.287 mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 0.524 mm^{-1}, F(000) = 1428, T = 173(2) K. Data collection ($2\theta_{max}$ = 30.065°, ω scan frames with 0.7° ω rotation and 30 s per frame, range *hkl*: h –18 to 18, k –19 to 19, l –30 to 31) gave 97148 reflections. The data revealed 20622 independent reflections of which 15130 were observed with $I > 2.0\sigma(I)$. The structure was solved by

using SHELXS-2013,[11] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. The whole structure was refined with SHELXL[12] by using the full-matrix least-squares technique {use of F^2; x, y, z, β_{ij} for C, Cl, O, P and Pd atoms, x, y, z in the riding mode for hydrogen atoms; 792 variables and 15130 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.0863P)^2 + 3.6987P]$ in which $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.0625$, $R_w = 0.1739$, $S_w = 1.101$ and $\Delta\rho < 1.984$ e Å^{-3}.

CCDC 1508357 (for **1**), 1508355 (for **2**), 1508354 (for **8**) and 1508356 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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