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Resorcin[4]arene-Derived Mono- and Diphosphines in Suzuki Cross-Coupling

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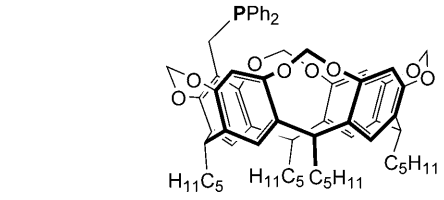
Abstract: Three resorcin[4]arene cavitands (**1**–**3**) having either one or two resorcinolic C-2 atoms substituted by a $-CH_2PPh_2$ podand arm were assessed in the Suzuki arylation of aryl bromides with phenylboronic acid. Using P:Pd ratios of 2:1 and operating in dioxane at 100 °C with a catalyst loading of 0.001 mol% resulted in highly efficient catalytic systems. For example, TOFs up to 34570 mol(converted ArBr)·mol(Pd)$^{-1}$·h^{-1} were obtained with the proximally-disubstituted cavitand **3** when using 4-bromotoluene as substrate. The performance was shown to vary in the following order: monophosphine **1** < diphosphine **2** < diphosphine **3** (where **2** is the distally disubstituted cavitand). A comparison of the catalytic properties of monophosphine-cavitand **1** with those of benzyldiphenylphosphine and *o*-anisylmethyldiphenyl phosphine suggests that **1** functions as a hemilabile phosphine, the oxygen atoms close to the phosphorus atom behaving as donors able to temporarily increase the electron density on the metal and/or favour the formation of mono-ligand Pd(0) species.

Keywords: cavitands; hemilabile ligands; palladium; phosphanes; resorcinarenes; Suzuki–Miyaura coupling

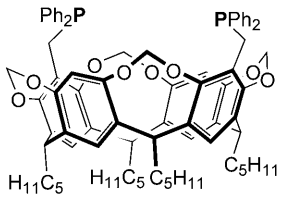
Introduction

Resorcinarenes provide valuable starting compounds for the preparation of cavitands, that is bowl-shaped molecules having a rigid structure.[1] In addition to their functioning as molecular receptors, cavitands also constitute ideal platforms for arranging a set of podand arms on a ring, thereby creating sophisticated ligand systems allowing, e.g., several metal ions to be maintained in close proximity. A number of investigations have recently illustrated the coordinative properties of cavitand-derived podands.[2,3] While ligands of this class have found numerous applications in separation science and sensing technology,[4–8] catalytic properties, surprisingly, have been little studied.[9,10] This is in stark contrast with podands obtained from the related calix[4]arene cavities,[11] in particular their phosphane derivatives,[11–20] which have already led to a rich transition metal chemistry.[2,21]

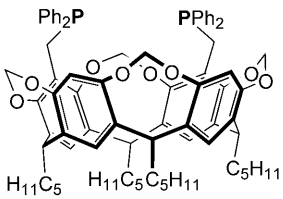
We have recently described the synthesis of the first mono- and diphosphines built on a resorcinarene cavitand (**1**–**3**, Scheme 1) and shown that these are suitable for complexation of transition metals, altering neither the cavity shape nor its receptor properties.[22]



1



2



3

Scheme 1. Resorcin[4]arene-derived podands used in this study.

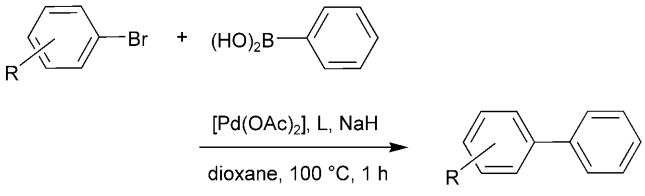
As an extension of our current investigations on cavity-shaped ligands, we now describe the catalytic properties of resorcinarenes **1**–**3** in Suzuki cross-coupling reactions.[23–25] The results are compared to those for other phosphines containing a benzyl subunit, notably Ph_2PCH_2Ph and Ph_2PCH_2(*o*-MeO-C_6H_4). It is worth mentioning that in the three cavitands assessed, the donor atoms are linked to the C-2 atoms of the resorcinol units, thus contrasting with the vast majority of cavitand-podands, in which the binding arms are directly connected to the oxygen atoms.[26–35]

Results and Discussion

The phosphines used in this study (**1**–**3**) were prepared according to the method reported previously.[22] We began the Suzuki cross-coupling tests (Scheme 2) using a catalytic system based on $[Pd(OAc)_2]$ and the mono-phosphinated cavitand **1**.

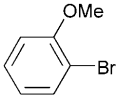
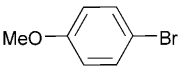
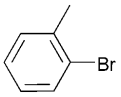
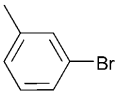
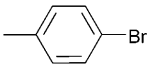
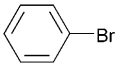
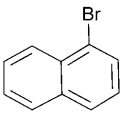
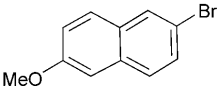
Catalytic testing was carried out in 1 h runs at 100 °C in the presence of NaH and with 1,4-dioxane as solvent. We noted that when operating with Cs_2CO_3/DMF at 130 °C, which corresponds to classical conditions for this kind of catalysis, significantly lower activities were observed. The best conversion, determined by using 4-bromoanisole as substrate, was observed when a ratio of two phosphorus atoms per palladium was applied. This led to a conversion of 100% *vs.* 80.7% when a phosphine to palladium ratio of 1 was applied (Table 1, entries 3 and 4). Performing the runs at only 0.001 mol% of metal (ArBr/catalyst ratio = 1×10^5) led to TOFs of *ca.* 27000 mol(converted ArBr)·mol(Pd)$^{-1}$·h^{-1} for 4-bromoanisole, 4-bromotoluene and 2-bromo-6-methoxynaphthalene (Table 1, entries 5, 11 and 17). In comparaison, carrying out the arylation of 4-bromotoluene with 2 equivalents of PPh_3 as ligand (substrate/Pd = 10000), resulted in a TOF of 5210 mol(converted ArBr)·mol(Pd)$^{-1}$·h^{-1} (*vs.* 27120 for **1**). It is worth noting that in all runs, the amount of homocoupling product was lower than 5%.

In order to evaluate the contribution of the cavity scaffold on the performance of this ligand, the Suzuki coupling of 4-bromoanisole with phenylboronic acid was repeated with 2 equivalents of benzyldiphenylphosphine (**4**), applying the conditions displayed in entry 4, Table 1. In this case the conversion dropped



Scheme 2. Suzuki cross-coupling reaction.

Table 1. Suzuki reaction catalyzed by the $[Pd(OAc)_2]$/**1** system.[a]

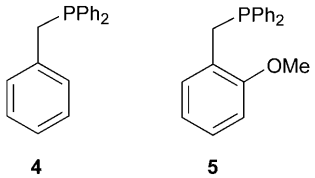
Entry	ArBr	Substrate/Pd	Conversion [%][b]	TOF [mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}]
1		1×10^4	40.6	4060
2		1×10^5	6.4	6380
3[c]		1×10^4	80.7	8070
4		1×10^4	100	10000
5		1×10^5	26.7	26680
6		1×10^4	34.4	3440
7		1×10^5	4.4	4380
8		1×10^4	72.8	7280
9		1×10^5	12.4	12360
10		1×10^4	97.8	9780
11		1×10^5	27.1	27120
12		1×10^4	61.0	6100
13		1×10^5	20.7	20670
14		1×10^4	47.9	4790
15		1×10^5	16.7	16690
16		1×10^4	100	10000
17		1×10^5	27.0	27030

[a] $[Pd(OAc)_2]$, **1** (2 equiv./Pd), aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (0.044 g, 1.0 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C, 1 h.

[b] Determined by GC, calibration based on decane.

[c] $[Pd(OAc)_2]$ (0.011 mg, 0.05 μmol), **1** (0.051 mg, 0.05 μmol, 1 equiv./Pd).

by *ca.* 50% compared to that obtained for **1** (conversion: 45.9% against 100%). In view of the fact that the two oxygen atoms of **1**, which are separated from the phosphorus centre by four bonds, might coordinate the metal centre during catalysis, we then decided to compare this ligand with the methoxy-substitut-



4 **5**

ed benzyldiphenylphosphine **5**. This ligand was prepared in 93% overall yield in a two-step sequence (not shown): (*i*) phosphorylation of bromomethyl-*o*-anisyl with ethyl diphenylphosphinite at 140 °C; (*ii*) reduction of the phosphine oxide thus produced with

$PhSiH_3$ (for a full characterization, see Experimental Section). Surprisingly, the cross-coupling reaction of 4-bromoanisole with phenylboronic acid using **5** (same conditions as in entry 5, Table 1) led to a TOF comparable to that observed with **1** [TOF = 26400 mol(converted ArBr)·mol(Pd)$^{-1}$·h^{-1}]. Similar observations were made for the following substrates: 2-bromo-6-methoxynaphthalene, 4-bromotoluene, and 1-bromonaphthalene (see Supporting Information). These results illustrate the beneficial role of an alkoxy substituent located at the *ortho*-carbon atom of the arylmethyl fragment bearing the phosphorus atom, and suggest that cavitand phosphine **1** behaves as a hemilabile ligand[36] during the catalytic process. It is worth mentioning here that some ether-phosphines able to form 6-membered palladacycles have already been shown to efficiently catalyze the Suzuki arylation. In the corresponding reports, the efficiency was assigned to the ability of such phosphines to form *P,O*-chelated monophosphine intermediates.[37] According to more recent investigations on Suzuki cross-coupling reactions, the formation of a Pd(0)-monophosphine complex appears to be a key step that precedes the oxidative addition step of aryl bromides.[38–42] On the other hand, the transient binding of an oxygen atom is expected to increase the electronic density of the metal centre, thereby favouring the oxidation addition step, irrespective of whether the active species is a bis- or a mono-phosphine complex.[43] Note that the presence during the catalytic process of zerovalent Pd intermediates bearing two phosphine ligands cannot be excluded, since we found that the use of two equivalents of phosphine gave significantly better results than when using one. Possibly, oxygen binding within such an intermediate would not only increase the electron density at the metal, but also increase the steric encumbrance about the metal centre and incidentally lower the energy barrier for the reductive elimination step.

The ability of **1** to bind palladium was formally only shown in the case of Pd(II). Thus, its reaction with 0.5 equiv. of $[PdCl_2(PhCN)_2]$ in CH_2Cl_2 gave quantitatively *cis*-$[PdCl_2{\cdot}\mathbf{1}_2]$ (**6**). The stereochemistry of this complex was deduced from the corresponding ^{31}P NMR spectrum, which shows a single peak at 30.6 ppm, a value which is very close that found in *cis*-$[PdCl_2(Ph_2PCH_2C_6H_5)_2]$ ($\delta_{cis} = 30.2$ ppm; *cf.* 20.1 ppm for the corresponding *trans* complex).[44,45] Attempts to determine the solid state structure of **6** failed, but single crystals suitable for such a study could be obtained for the related complex *cis*-$[PtCl_2{\cdot}\mathbf{1}_2]$ (**7**). In the solid state (Figure 1), the latter adopts C_2 symmetry. The structure reveals that oxygen atom O-1, which is separated by four bonds from the corresponding P atom, comes close to the metal centre. Although the distance of O-1 to the platinum atom (3.65 Å) rules out any bonding interaction, it is obvious from this study that there is no steric hindrance precluding a small rotation about the P–CH_2 axis so as to permit a Pt···O contact, in other terms to allow the phosphine to behave as a chelating system.

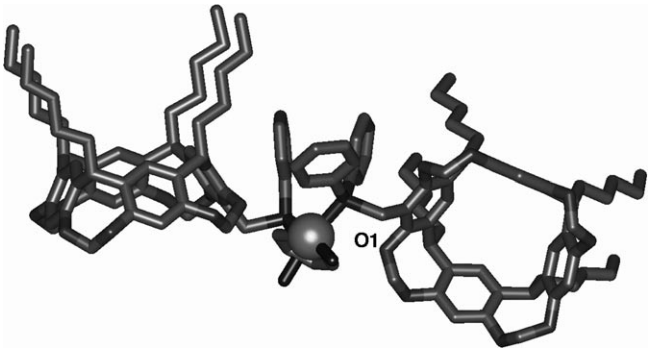
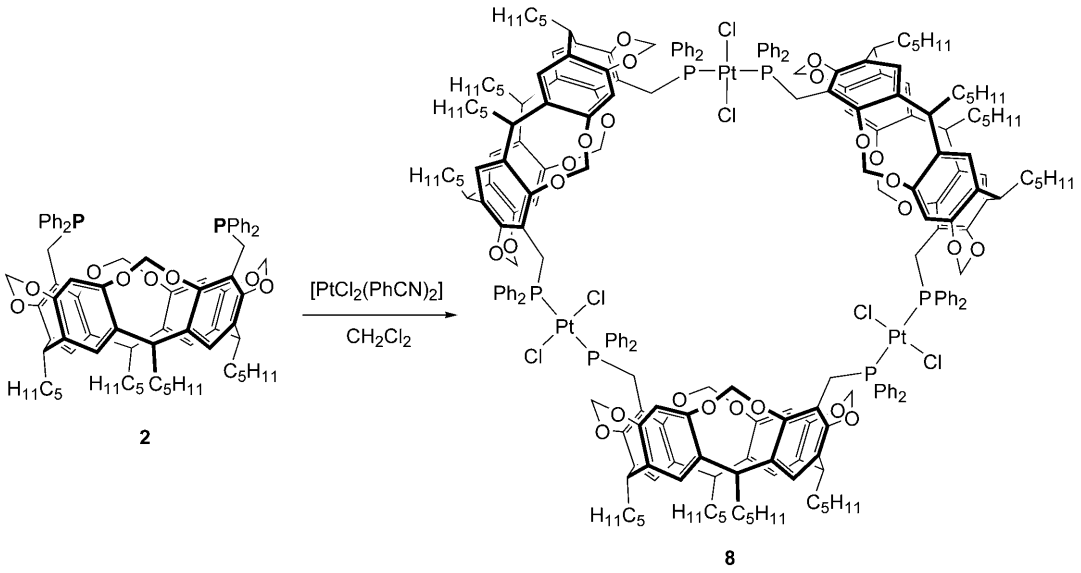


Figure 1. Molecular structure of *cis*-$[PtCl_2{\cdot}\mathbf{1}_2]$ (**7**) (the molecule possesses a C_2 axis). For clarity, the molecule of hexane located inside each cavitand is not shown. Important distances (Å) and angles (°): Pt–P 2.250(1), Pt–Cl 2.339(1), Pt···O1 3.65, P1–Pt–P2 102.9(1), Cl1–Pt–Cl2 86.6(1).

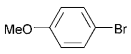
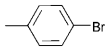
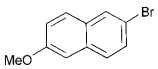
As our next investigation, we studied the catalytic properties of ligand **2**, which contains two remote phosphine subunits. Molecular models unambiguously show that diphosphine **2** is not suited for forming *P,P*-chelate complexes. The propensity of **2** to form straightforward oligomeric complexes was revealed by studying the reaction of $[PtCl_2(PhCN)_2]$ with a stoichiometric amount of **2**. This reaction gave in high yield a complex of the formula $[PtCl_2(\mathbf{2})]_n$ (**8**) (Scheme 3), to which we tentatively assign a cyclic, trimeric structure on the basis of both its ESI-TOF spectrum and its ^{31}P NMR spectrum. The mass spectrum shows a strong peak at $m/z = 4401$, with the profile expected for the corresponding $[M-Cl]^+$ cation. The ^{31}P NMR spectrum of the complex shows a single, sharp peak at 13.2 ppm flanked by two platinum satellites. The J(P,Pt) coupling constant, 2581 Hz, is in keeping with the platinum centres adopting a trans configuration.

The catalytic runs carried out with **2** were again all done in dioxane at 100 °C in the presence of NaH. The highest conversions were observed for a ligand/Pd ratio of 1:1 (Table 2, entries 2 and 3), a finding which suggests that again two phosphorus centres are coordinated to the Pd ion during catalysis. As can be inferred from Table 2, the general trend is that diphosphine **2** results in higher conversions than monophosphine **1**, the efficiency increase reaching *ca.* 70% in the case of 1-bromonaphthalene. Only with 2- and 4-bromoanisole did the conversion slightly drop, but we have no rational explanation for this observation. The highest activity was for 4-bromotoluene [Table 2, entry 10: TOF = 29500 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}]. Since the two phosphorus atoms of **2** can only bind in-



Scheme 3. Synthesis of the trimeric complex **8**.

Table 2. Suzuki reaction catalyzed by the $[Pd(OAc)_2]$/**2** system.[a]

Entry	ArBr	Substrate/Pd	Conversion [%][b]	TOF [mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}]
1		1×10^4	25.5	2550
2[c]		1×10^4	72.2	7220
3		1×10^4	91.1	9110
4		1×10^5	25.0	25030
5		1×10^4	45.6	4560
6		1×10^5	13.6	13620
7		1×10^4	91.0	9100
8		1×10^5	20.4	20420
9		1×10^4	98.9	9890
10		1×10^5	29.5	29500
11		1×10^4	62.8	6280
12		1×10^5	21.8	21800
13		1×10^4	94.5	9450
14		1×10^5	28.8	28780
15		1×10^4	97.7	9770
16		1×10^5	29.4	29360

[a] $[Pd(OAc)_2]$, **2** (1 equiv./Pd), aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (0.040 g, 1.0 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C, 1 h.

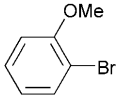
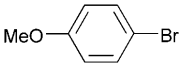
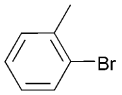
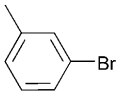
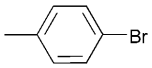
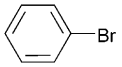
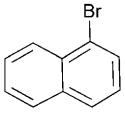
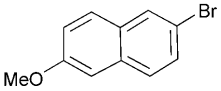
[b] Determined by GC, calibration based on decane.

[c] $[Pd(OAc)_2]$ (0.011 mg, 0.05 μmol), **2** (0.030 mg, 0.025 μmol, 0.5 equiv./Pd).

dependent metal centres, the better activities observed with **2** *vs.* **1** probably reflect a first coordination sphere that is considerably different from the one found in the catalytic intermediates derived from **1**. This could notably arise by formation of small cyclic oligomers, in which the PMP angles would, owing to steric congestion within the metallomacrocyclic structure, be larger than in monomeric complexes. It is now commonly accepted that an increase of the PMP angle in $[Pd(phosphine)_2XY]$ complexes favours the reductive elimination step in C–C coupling reactions.[46–48] Formation of such species do, of course, not prevent from forming *P,O*-chelated intermediates.

The third series of tests was achieved with the proximally-substituted cavitand **3**. The reaction conditions were as for **2**. With the exception of 1-bromonaphthalene, all substrates resulted in conversions significantly higher than those obtained with **1** and **2** (Table 3). For example, with 4-bromotoluene, the TOFs were 27120, 29500, and 34570 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1} using **1**, **2**, and **3**, respectively. It is interesting to note that with congested aryl bromides the best results were also obtained with diphosphine **3**. Thus, the latter gave TOFs of 8450, 15650 and 22770 mol(converted ArBr)·mol(Pd)$^{-1}$·h^{-1} (Table 3, entries 2, 6 and 14) with 2-bromoanisole, 2-bromotoluene and 1-bromonaphthalene, respectively. The increased performance of **3** *vs.* that of **2** possibly arises from its partial conversion into *P,P*-chelate complexes in which the ligand displays a large bite angle,[49] this latter feature being known, as already mentioned above, to promote reductive elimination in cross-coupling reactions.[46–48] Molecular mechanics calculations (SPARTAN) indeed show that in hypothetical $[PdX_2(\mathbf{3})]$ chelate complexes (X = halide, aryl), be they square planar or tetrahedral, the corresponding PMP angles are significantly larger than in conventional ML_2X_2 complexes. Here the resulting strain generated within

Table 3. Suzuki reaction catalyzed by the $[Pd(OAc)_2]$/**3** system.[a]

Entry	ArBr	Substrate/Pd	Conversion [%][b]	TOF [mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}]
1		1×10^4	52.6	5260
2		1×10^5	8.5	8450
3		1×10^4	100	10000
4		1×10^5	28.7	28740
5		1×10^4	85.9	8590
6		1×10^5	15.7	15650
7		1×10^4	98.1	9810
8		1×10^5	23.7	23710
9		1×10^4	100	10000
10		1×10^5	34.6	34570
11		1×10^4	68.6	6860
12		1×10^5	24.8	24780
13		1×10^4	57.3	5730
14		1×10^5	22.8	22770
15		1×10^4	100	10000
16		1×10^5	32.1	32130

[a] $[Pd(OAc)_2]$, **3** (1 equiv./Pd), aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (0.040 g, 1.0 mmol), decane (0.05 mL), dioxane (1.5 mL), 100 °C, 1 h.

[b] Determined by GC, calibration based on decane.

the corresponding metallomacrocycle intensifies the steric interactions between two of the PPh rings (those having an upward orientation) and the X substituents (Figure 2).

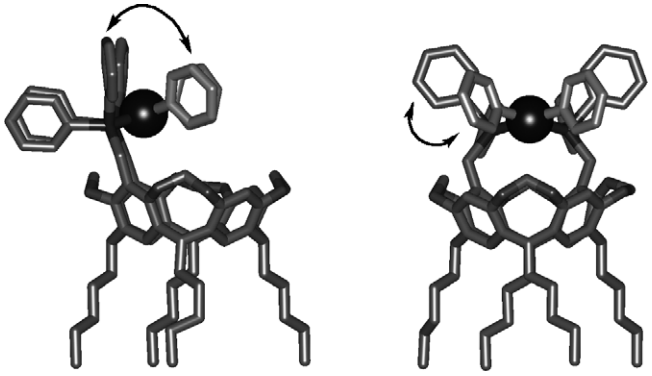


Figure 2. SPARTAN-generated, hypothetical $[Pd(C_6H_5)_2$·**3**] complex showing the spatial proximity of upwards-oriented PPh rings and the palladium-coordinated phenyl groups.

Conclusions

In summary, the combination of $[Pd(OAc)_2]$ with the phosphinated resorcin[4]arenes **1**–**3** efficiently catalyzes Suzuki cross-coupling reactions. The best performing of these ligands, namely the proximally substituted cavitand **3**, resulted in remarkable TOFs [up to 34570 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1} when starting from 4-bromotoluene] using catalyst loadings as low as 0.001 mol%. Overall, the reaction rates for the three phosphines were 5–7 times higher than those observed for PPh_3. At least two effects may be invoked to explain the high performances observed with these ligands in Suzuki arylations: (*i*) the possibility of forming, in the case of monophosphine **1**, transient *P,O*-chelate complexes involving the oxygen atoms of the resorcinolic unit bearing the P atom(s). Oxygen binding may assist the formation of monophosphine palladium(0) species believed to play a key role in substrate activation. It may further increase the electron density of the metal centre so as to facilitate oxidative addition of the aryl bromide; (*ii*) the ability of two **2** and **3** to generate intermediates displaying increased PMP angles, the latter being induced either by steric repulsions occurring in cyclic oligomers (possibly with ligand **2**) or arising from the formation a strained chelate complex (case of **3**).

Experimental Section

General Procedure

All manipulations involving phosphorus derivatives 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, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with Bruker FT instruments (AC-300). ^1H NMR spectra were referenced to residual protiated solvents (7.26 ppm for $CDCl_3$), ^{13}C NMR chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Gas chromatographic analyses were performed on a Varian 3900 gas chromatograph using a WCOT fused silica column (25 m, 0.32 mm, inside diameter, 0.25 mm film thickness). The complex $[PtCl_2(PhCN)_2]$[50] and phosphines **1**–**3**[22] were prepared according to the literature procedures. A high-yield synthesis of monophosphine **5**, starting from (2-methoxy)benzyl alcohol, is reported below. The previously reported procedure gave a yield of only 30%.[51]

(2-Methoxybenzyl) Bromide

To a solution of 2-methoxybenzyl alcohol (0.500 g, *ca.* 0.48 mL, 3.62 mmol) in CH_2Cl_2 (40 mL) was added PBr_3 (0.490 g, *ca.* 0.17 mL, 1.81 mmol). After stirring for 1 h, the

reaction mixture was washed with brine (3×30 mL), and the organic layer was separated. The latter was dried over Na_2SO_4 and then evaporated under vacuum to afford the product as a colourless liquid; yield: 0.650 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38–7.30 (2H, arom. CH), 6.97 (dd, 1H, arom. CH, ^3J = 7.3 Hz, ^3J = 7.5 Hz), 6.90 (d, 1H, arom. CH, ^3J = 8.2 Hz), 4.62 (s, 2H, CH_2Br), 3.98 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.56 (s, arom. C_{quat}), 131.01 (s, arom. CH), 130.34 (s, arom. CH), 126.18 (s, arom. C_{quat}), 120.78 (s, arom. CH), 111.08 (s, arom. CH), 55.65 (s, OCH_3), 29.21 (s, CH_2Br).

(2-Methoxybenzyl)diphenylphosphine Oxide

A solution of (2-methoxybenzyl) bromide (0.300 g, 1.49 mmol) in ethyl diphenylphosphinite (0.343 g, *ca.* 0.32 mL, 1.49 mmol) was stirred for 12 h at 140 °C. After cooling to room temperature, the product was precipitated with diisopropyl ether (5 mL); yield: 0.460 g (95%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.73–7.66 (m, 4H, CH of PPh_2), 7.49–7.34 (7H, CH of PPh_2 and benzyl), 7.14 (pseudo t, 1H, CH of benzyl), 6.86 (dd, 1H, CH of benzyl, ^3J = 7.5 Hz, ^3J = 7.3 Hz), 6.65 (d, 1H, CH of benzyl, ^3J = 8.2 Hz), 3.74 (d, 2H, CH_2P, ^3J = 14.2 Hz), 3.44 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 156.77, 132.85, 119.81 (3 arom. Cq), 131.66, 131.50, 131.17, 128.16, 128.13, 120.56, 110.16 (7 arom. CH), 54.84 (s, OCH_3), 31.08 (d, CH_2P, $^1J_{P,C}$ = 67.9 Hz). The J(P,C_{arom}) coupling constants are not given. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 30 (s, CH_2P).

(2-Methoxybenzyl)diphenylphosphine (5)

A suspension of (2-methoxybenzyl) diphenylphosphine oxide (0.200 g, 0.62 mmol) in $PhSiH_3$ (0.134 g, *ca.* 0.15 cm^3, 1.24 mmol) was stirred for 8 h at 110 °C. The reaction mixture was cooled to room temperature and $PhSiH_3$ in excess was removed under vacuum. The residue was washed with diisopropyl ether (2×10 mL) to afford the product as a pure white solid; yield: 0.186 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): 7.76–7.69 (m, 1H, CH of benzyl), 7.47–7.40 (m, 4H, PPh_2), 7.34–7.31 (m, 6H, PPh_2), 7.17–7.11 (m, 1H, CH of benzyl), 6.91–6.66 (m, 2H, CH of benzyl), 3.72 (s, 3H, OCH_3), 3.46 (s, 2H, CH_2P); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.22, 138.91, 131.23 (3 arom. Cq), 133.03, 130.58, 128.32, 128.25, 128.18, 120.16, 110.34 (7 arom. CH), 55.29 (s, OCH_3), 29.52 (d, CH_2P, $^1J_{P,C}$ = 15.5 Hz). The J-(P,C_{arom}) coupling constants are not given. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = −11.8 (s, CH_2P).

cis-P,P-Dichloro-bis{5-diphenylphosphinomethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}palladium(II) (6)

To a solution of **1** (0.080 g, 0.079 mmol) in CH_2Cl_2 (5 mL) was added a solution of $[PdCl_2(PhCN)_2]$ (0.015 g, 0.039 mmol) in CH_2Cl_2 (5 mL). After stirring for 0.5 h, the reaction mixture was concentrated to *ca.* 1 mL, whereupon *n*-hexane (20 mL) was added. The yellow precipitate was recovered by filtration and dried under vacuum; yield: 0.081 g (95%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.83–7.77 (4H, PPh_2), 7.68–7.42 (m, 16H, PPh_2), 7.06 (s, 2H, arom. CH of resorcinarene), 7.01 7.06 (s, 4H, arom. CH of resorcinarene), 6.94 (d, 2H, arom. CH of resorcinarene, ^6J = 1.8 Hz), 6.54 (s, 4H, arom. CH of resorcinarene), 6.45 (s, 2H, arom. CH of resorcinarene), 5.94 and 4.43 (AB spin system, 8H, OCH_2O, ^2J = 7.2 Hz), 5.70 and 4.52 (AB spin system, 8H, OCH_2O, ^2J = 7.2 Hz), 4.70 (t, 4H, $CHCH_2CH_2$, ^3J = 8.1 Hz), 4.47–4.39 (m, 8H, $CHCH_2CH_2$ and CH_2P, overlapping signals), 2.25–2.02 (m, 16H, $CHCH_2CH_2$), 1.42–1.14 (m, 48H, $CH_2CH_2CH_2CH_3$), 0.94 (t, 12H, CH_2CH_3, ^3J = 6.6 Hz), 0.90 (t, 12H, CH_2CH_3, ^3J = 6.9 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 30.6 (s, PPh_2). Anal. calcd for $C_{130}H_{150}O_{16}P_2PdCl_2$ (M_r = 2207.84): C 70.72, H 6.85%; found: C 70.65, H 6.93.

cis-P,P-Dichloro-bis{5-diphenylphosphinomethyl-4(24),6(10),12(16),18(22)-tetramethylenedioxy-2,8,14,20-tetrapentylresorcin[4]arene}platinum(II) (7)

To a solution of **1** (0.090 g, 0.089 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[PtCl_2(PhCN)_2]$ (0.021 g, 0.044 mmol) in CH_2Cl_2 (10 mL). After stirring for 12 h, the reaction mixture was concentrated to *ca.* 2 mL, whereupon *n*-hexane (50 mL) was added. The white precipitate was recovered by filtration and dried under vacuum; yield: 0.086 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.43 (8H, PPh_2), 7.10 (t, 4H, PPh_2, ^3J = 7.2 Hz), 7.04 (s, 2H, arom. CH of resorcinarene), 7.00 (s, 4H, arom. CH of resorcinarene), 6.93–6.88 (m, 8H, PPh_2), 6.80 (s, 2H, arom. CH of resorcinarene), 6.46 (s, 4H, arom. CH of resorcinarene), 6.45 (s, 2H, arom. CH of resorcinarene), 6.02 and 4.28 (AB spin system, 8H, OCH_2O, ^2J = 7.1 Hz), 5.71 and 4.38 (AB spin system, 8H, OCH_2O, ^2J = 7.0 Hz), 4.69 (t, 4H, $CHCH_2CH_2$, ^3J = 8.0 Hz), 4.55–4.50 (m, 4H, $CHCH_2CH_2$), 4.26–4.22 (m, 4H, CH_2P), 2.22–2.10 (m, 12H, $CHCH_2CH_2$), 2.05–1.94 (m, 4H, $CHCH_2CH_2$), 1.44–1.27 (m, 36H, $CH_2CH_2CH_2CH_3$), 1.23–1.13 (m, 12H, $CH_2CH_2CH_2CH_3$), 0.94 (t, 12H, CH_2CH_3, ^3J = 6.8 Hz), 0.90 (t, 12H, CH_2CH_3, ^3J = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.87–137.40 (arom. C_{quat}), 134.24 (s br, arom. CH of PPh_2), 130.18 (s, arom. CH of PPh_2), 127.51–127.27 (arom. CH of PPh_2), 120.54, 120.40, 118.18, 116.62, 116.34 (5 s, arom. CH of resorcinarene), 99.53 (s, OCH_2O), 99.01 (s, OCH_2O), 36.62 (s, $CHCH_2$), 36.30 (s, $CHCH_2$), 32.16 (s, $CH_2CH_2CH_3$), 31.98 (s, $CH_2CH_2CH_3$), 29.85 (s, $CHCH_2$), 29.79 (s, $CHCH_2$), 27.93 (s, $CHCH_2CH_2$), 27.49 (s, $CHCH_2CH_2$), 22.86 (s, CH_2CH_3), 22.66 (s, CH_2CH_3), 14.15 (s, CH_2CH_3), 14.08 (s, CH_2CH_3). The PCH_2 signal, which is usually weak, was not detected. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 9.6 (s with Pt satellites, PPh_2, J_{PPt} = 3810 Hz); anal. calcd. for $C_{130}H_{150}O_{16}P_2PtCl_2{\cdot}CH_2Cl_2$ (M_r = 2296.50 + 84.93): C 66.07, H 6.43%; found: C 66.19, H 6.37. MS (ESI-TOF): m/z = 2258.95 $[M-Cl]^+$, expected isotope profiles.

Reaction of 2 with $[PtCl_2(PhCN)_2]$

To a solution of **2** (0.095 g, 0.078 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of $[PtCl_2(PhCN)_2]$ (0.037 g, 0.078 mmol) in CH_2Cl_2 (10 mL). After stirring for 48 h, the reaction mixture was concentrated to *ca.* 2 mL, whereupon *n*-hexane (50 mL) was added. The yellow precipitate (**8**) was recovered by filtration and dried under vacuum; yield: 0.100 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.87–

7.72 (m, 24H, PPh_2), 7.30 (m, 36H, PPh_2), 6.93 (s br, 6H, arom. CH of resorcinarene), 6.74 (s br, 6H, arom. CH of resorcinarene), 6.35 (s br, 6H, arom. CH of resorcinarene), 5.85 and 4.21 (br AB spin system, 24H, OCH_2O), 4.62–4.45 (m, 12H, $CHCH_2$), 3.97 (br d with Pt satellites, 12H, CH_2P, $^2J(PH) = 13$ Hz, $^3J(PtH) = 42$ Hz), 2.22–2.09 (m, 12H, $CHCH_2$), 2.02–1.90 (m, 12H, $CHCH_2$), 1.46–1.31 (m, 48H, $CH_2CH_2CH_2CH_3$), 1.29–1.17 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.00–0.90 (m, 36H, CH_2CH_3); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 13.2$ (s with Pt satellites, PPh_2, $J_{PPt} = 2581$ Hz); anal. calcd. for $C_{234}H_{258}O_{24}P_6Pt_3Cl_6$ ($M_r = 4438.33$): C 63.32, H 5.86%; found: C 63.21, H 5.73; MS (ESI-TOF): $m/z = 4401.48$ $[(PtCl_2 \cdot \mathbf{2})_3 - Cl]^+$, expected isotope profile.

Crystallography

Single crystals of **7**·2 C_6H_{14} suitable for diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. $M_r = 2468.77$, monoclinic, space group $C2/c$, $a = 43.811(5)$, $b = 14.546(1)$, $c = 29.621(3)$ Å, $\beta = 131.24(1)°$, $V = 14194(2)$ Å^3, $Z = 4$, $D_x = 1.155$ mg.m^{-3}, $\lambda(\text{MoK}<\iota\nu\phi>\alpha<\iota\nu\phi>) = 0.71073$ Å, $\mu = 11.06$ cm^{-1}, $F(000) = 5200$, $T = 150(2)$ K. Data were collected on a Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite MoK_a radiation, $\lambda = 0.71073$ Å). The structure was solved with SIR-97,[52] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97[53] and full-matrix least-square techniques (use of F^2; x, y, z, b_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms; 754 variables and 9498 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[s^2(F_0^2) + (0.0886P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1 = 0.047$, $wR2 = 0.153$, $S_w = 1.062$, $\Delta\rho < 2.7$eÅ^{-3}. The A level alerts observed in the checkcif are mainly due to a disordered pentyl group (C38···C42). The observed voids are classical in this family of compounds. CCDC 722727 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Suzuki Cross-Coupling Reactions

A solution of $[Pd(OAc)_2]$ in dioxane (0.5 mL) was mixed with a solution of phosphine in dioxane (0.5 mL) in a Schlenk tube. NaH (60% in mineral oil, 0.044 g, 1.00 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), aryl bromide (0.5 mmol), and dioxane (0.5 mL) were then added successively. The reaction mixture was heated at 100 °C for 1 hour. After cooling, decane (0.05 mL) was added as internal reference. A sample of 0.5 mL was taken and filtered over Celite for GC analysis.

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