DOI: 10.1002/chem.200903390

Cavity-Shaped Ligands: Calix[4]arene-Based Monophosphanes for Fast Suzuki–Miyaura Cross-Coupling

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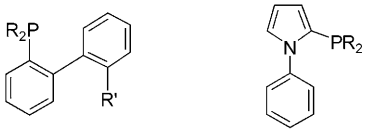
Abstract: Five conical calix[4]arenes that have a PPh_2 group as the sole functional group anchored at their upper rim were assessed in palladium-catalysed cross-coupling reactions of phenylboronic acid with aryl halides (dioxane, 100 °C, NaH). With arylbromides, remarkably high activities were obtained with the catalytic systems remaining stable for several days. The performance of the ligands is comparable to a Buchwald-type triarylphosphane, namely, (2′-methyl[1,1′-biphenyl]-2-yl)diphenylphosphane, which in contrast to the calixarenyl phosphanes tested may display chelating behaviour in solution. With the fastest ligand, 5-diphenylphosphanyl-25,26,27,28-tetra(*p*-methoxy)benzyloxy-calix[4]arene (**8**), the reaction turnover frequency for the arylation of 4-bromotoluene was 321000 versus 214000 mol(ArBr).mol(Pd)$^{-1}$.h^{-1} for the reference ligand. The calixarene ligands were also efficient in Suzuki cross-coupling reactions with aryl chlorides. Thus, by using 1 mol% of [$Pd(OAc)_2$] associated with one of the phosphanes, full conversion of the deactivated arenes 4-chloroanisole and 4-chlorotoluene was observed after 16 h. The high performance of the calixarenyl–phosphanes in Suzuki–Miyaura coupling of aryl bromides possibly relies on their ability to stabilise a monoligand [Pd^0L(ArBr)] species through supramolecular binding of the Pd-bound arene inside the calixarene cavity.

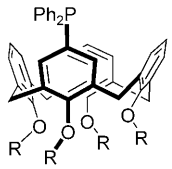
Keywords: bulky monophosphanes · calixarenes · cross-coupling · palladium · supramolecular catalysis

Introduction

Since the discovery by Suzuki and Miyaura in 1981 that [$Pd(PPh_3)_4$] catalyses the coupling of phenyl boronic acid with aryl halides,[1] many efforts have been spent to find variants of this catalyst based on ligands that accelerate the reaction and/or make the reaction proceed with less-reactive aryl chlorides or extremely hindered aryl halides.[2,3] Although it is now commonly accepted that strongly basic phosphanes promote the oxidative addition step,[4] the use of bulky phosphanes possibly serves to favour the formation of a monophosphane complex as the most active catalyst as well as to promote reductive elimination.[5,6] Buchwald has shown that high activities can be induced with phosphanes containing the sterically demanding 2,2′-biphenyl motif (Scheme 1).[7–9]



Buchwald-type phosphanes Zapf–Beller-type phosphanes



calix monophosphanes

6 R = $CH_2(CH_2)_4CH_3$
7 R = CH_2Ph
8 R = CH_2(*p*-$MeOC_6H_4$)
9 R = CH_2(*m*-$MeOC_6H_4$)
10 R = H

Scheme 1.

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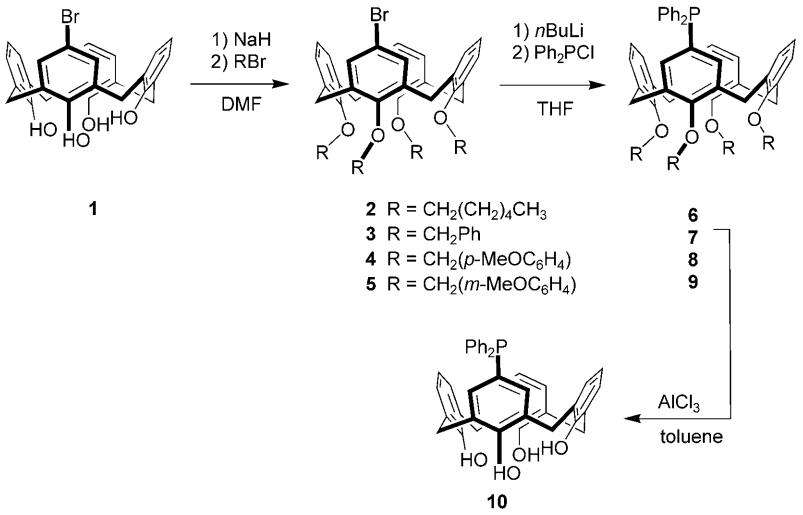
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903390.

Similar observations were made by Beller and Zapf with closely related ligands, the so-called N-aryl-phosphanylpyrroles (Scheme 1).[10] The way that the Buchwald ligands operate is still not fully understood, but it was suggested that coordination of the *ipso* carbon atom of the remote aryl ring is likely to play a key role, that is, the ligands may display hemilability during catalysis.[11–13] Interestingly, the increased activity of such ligands in Suzuki–Miyaura arylations was shown to arise for tertiary phosphanes of both types, $P(alkyl)_2(2,2'\text{-}C_6H_4Ar)$ and $PPh_2(2,2'\text{-}C_6H_4Ar)$, but the air-sensitive dialkyl-substituted ligands are the better ones for the reactions with aryl chlorides.[14] Wondering whether high productivity might also be observed with triarylphosphanes that cannot function as hemilabile/chelating ligands, we decided to assess a series of encumbered monodentate arylphosphanes, namely, ligands **6**–**10** (Scheme 1), which are all based on a conical calix[4]arene backbone. These phosphanes must, of course, be regarded as ligands of medium basicity. It is worth mentioning that bowl-shaped triarylphosphanes with no auxiliary binding group in which the phosphorus atom sits deep in a molecular pocket[15] were recently shown to catalyse the Suzuki–Miyaura coupling of unactivated aryl chlorides at low temperatures efficiently.[16] Bulky, dendritic triarylphosphanes that display high efficiency in Suzuki cross-coupling were also reported, but the latter may all potentially behave as hemilabile ligands so that their efficiency possibly relies on secondary ligating groups.[17,18] Note that the coordination chemistry of calixarenyl monophosphanes related to those described in this paper has recently been studied thoroughly. A striking feature of these ligands concerns their ability to behave as supramolecular chelators towards metal–arene moieties.[19,20]



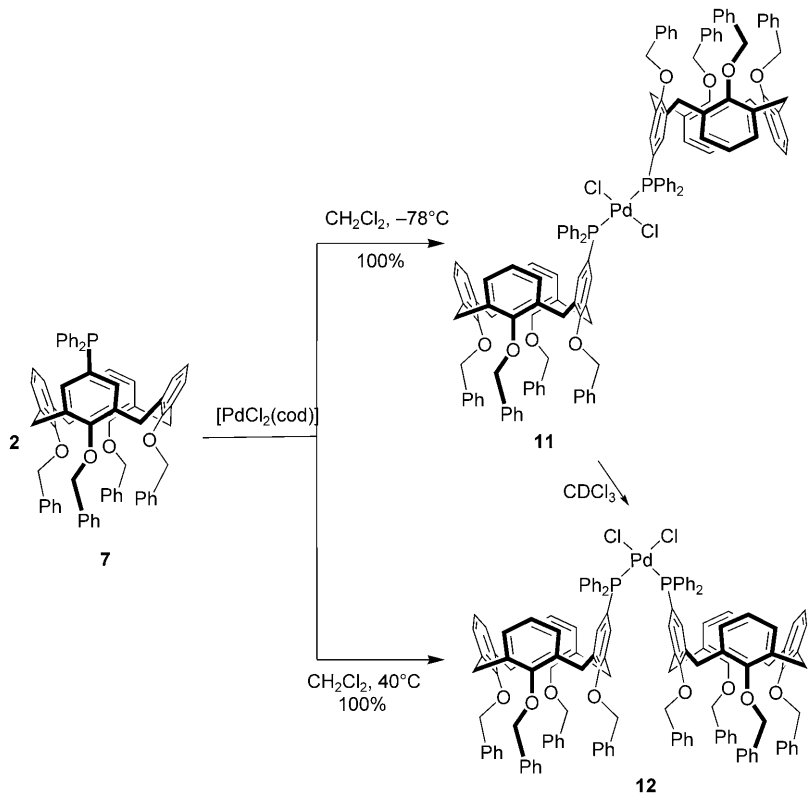
Scheme 2. Synthesis of monophosphanes **6**–**10**.

Results and Discussion

The phosphanes presented in this study all contain a phosphorus atom that has three aryl substituents, one of which is a bulky calixarenyl unit. Our choice to focus on medium-basic phosphane ligands rather than strongly basic ones was made to isolate steric effects from electronic ones in Suzuki–Miyaura cross-couplings because phosphanes with alkyl substituents are known to accelerate these reactions drastically.[4,8,21] Note that calixarene monophosphanes have only been sparingly used in homogeneous catalysis.[22–26]

Monophosphanes **6**–**9** were synthesised readily in two steps from monobromo calixarene **1** according to Scheme 2. In the first step precursor **1** was alkylated in DMF with the appropriate alkylbromide by using NaH as base. The phosphanyl group was then introduced by halogen–lithium exchange followed by reaction with PPh_2Cl. The deprotected calixarene **10** was obtained quantitatively from the tetrabenzylated derivative **7** upon treatment with $AlCl_3$ in toluene. Each phosphane is characterised by a singlet near −5.5 ppm in its ^{31}P NMR spectrum (see also $\delta = -4.5$ ppm for PPh_3). The corresponding ^1H NMR spectra are in keeping with C_s-symmetrical ligands, each of them showing the presence of two distinct AB patterns for the diastereotopic $ArCH_2Ar$ protons. For each ligand, the $ArCH_2Ar$ signals appear near 31.5 ppm in the corresponding ^{13}C NMR spectrum, a value which is typical for calixarenes that adopt a cone conformation.[25]

To gain insight into the coordinative properties of these phosphanes, we investigated the reaction of **7** with $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) in CH_2Cl_2 at −78 °C (Scheme 3). This reaction led to *trans*-$[PdCl_2(\mathbf{7})_2]$ (**11**), the stereochemistry of which was determined by an X-ray diffraction study (Figure 1). In the ^{31}P NMR spectrum of **11**, the phosphorus signal is seen at 22.7 ppm, a value that, according to the Bartik and Himmler scale, indicates that the electronic properties of **7** should be close to those of P(*o*-tolyl)$_3$ (see also the ^{31}P chemical shift of *trans*-$[PdCl_2\{P(o\text{-tolyl})_3\}_2]$: $\delta = 22.2$ ppm).[27] Repeating the above reaction at 40 °C instead of −78 °C afforded the corresponding *cis* isomer **12**, which also formed when a $CDCl_3$ solution of the *trans* complex was allowed to stand for several days. These findings unambiguously demonstrate the ability of a palladium centre to coordinate two bulky calixarene monophosphanes. The X-ray structural study carried out for *trans*-$[PdCl_2(\mathbf{7})_2]$ further revealed that in the solid state the palladium atom sits on the centre of symmetry of a molecule that has a length of approximately 28 Å. The calixarene skeletons adopt a typically flattened cone conformation. Within each calixarene fragment, the distances between the cent-



Scheme 3. Synthesis of *trans*-**11** and *cis*-**12**.

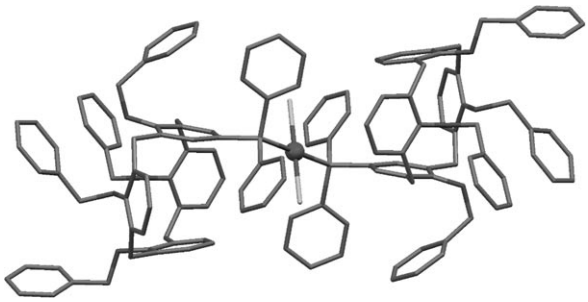
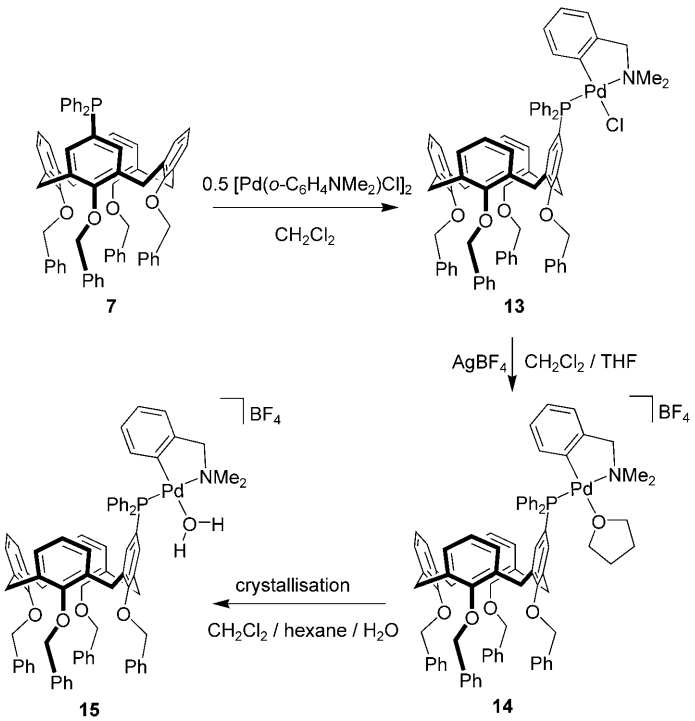


Figure 1. Molecular structure of *trans*-[$PdCl_2$·**7**$_2$] (**11**). Important bond lengths [Å] and angles [°]: Pd–P 2.3285(5), Pd–Cl 2.3028(5); Cl(1)-Pd-P(1) 89.72(2), P(1)-Pd-Cl(2) 90.28(2).

roids of distal phenol rings are 4.83 and 7.75 Å, respectively. The P–M vectors are nearly tangentially oriented with respect to the cone delineated by the corresponding calixarene moiety, but with the metal atom still lying inside the cone. Note that it is not appropriate to attempt to determine a cone-angle value for **7**. Indeed, given that the PPh_2 moiety can freely rotate about the P–C_{calix} axis (see below), the cone-angle value does considerably change by varying the orientation of the phosphorus lone pair. The cone angle clearly reaches its highest value when the P lone pair points towards the calixarene axis, that is, when a coordinated metal ion sits exactly above the cavity entrance.

Reaction of **7** with [Pd(*o*-$C_6H_4NMe_2$)Cl]$_2$ quantitatively gave the monophosphane complex **13** (see the Experimental Section; Scheme 4). Coordination of the phosphorus atom was unambiguously deduced from the corresponding ^{1}H NMR spectrum, which shows a doublet for the NMe_2 protons (^4J(P,H) = 2 Hz). Treatment of **13** with $AgBF_4$ in THF gave the cationic complex **14**. The ^{1}H NMR spectrum of **14** is, as for **13**, consistent with a C_s-symmetrical molecule. During recristallisation of **14** from a dichlorohexane solution, an aquo complex **15** formed owing to the presence of trace amounts of water. Interestingly, two types of crystals, **15a** and **15b**, were obtained for this complex, which were both studied by X-ray diffraction. The main difference between the corresponding solid-state structures concerns the positioning of the Pd atom, which is located near the receptor entrance in **15a**, and is pushed away from the cavity in **15b** (Figure 2). A rough determination of the



Scheme 4. Synthesis of complexes **13**–**15**.

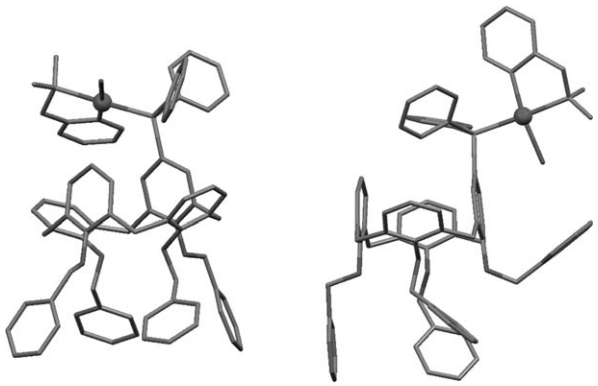
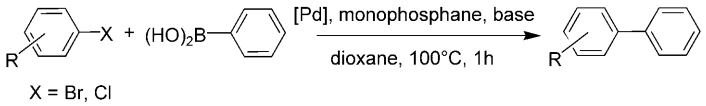


Figure 2. Molecular structures of the cationic complexes **15a** and **15b**. For clarity, the BF_4 anions and the CH_2Cl_2 solvate molecule of **15a** are not shown. Important bond lengths [Å] and angles [°]: **15a**: Pd–P 2.2659(7), Pd–O 2.171(2), P–2.151(2); N-Pd-O 91.41(7), N-Pd-P 177.55(7), O-Pd-P 89.88 (5); **15b**: Pd–P 2.264(1), Pd–O 2.186(2), P–N 2.158(3); N-Pd-O 89.1(1), N-Pd-P 174.99(9), O-Pd-P 93.32 (7).

ligand encumbrance according to Tolman's definition[28] shows that when the phosphorus is oriented as in **15a**, the corresponding cone angle is larger than that determined from **15b** by approximately 35°. Note that within the temperature range +25 to −80 °C the ^{1}H NMR (CD_2Cl_2) spectrum of **14** (that has coordinated THF instead of H_2O) remained sharp, revealing the presence of only one species in solution. Thus, it was not possible to freeze-out the possible rotation of the {$Ph_2PPd(Me_2NCH_2C_6H_4)$} unit about the P–C(calixarene) bond.

Catalytic Suzuki–Miyaura cross-coupling—Optimising the reaction conditions: Monophosphanes **6–10** were assessed in the palladium-catalysed Suzuki–Miyaura cross-coupling reactions (Scheme 5). The catalysts were generated in situ by



Scheme 5. Suzuki–Miyaura cross-coupling.

mixing the palladium precursor with two equivalents of monophosphane per palladium. We noted that, as expected for bulky phosphines, higher phosphine/Pd ratios did not significantly modify the catalytic outcome (see the Supporting Information).

Determination of the optimal catalytic system was carried out with ligand **6** by studying the cross-coupling reaction between 4-bromoanisole and phenylboronic acid at 100 °C in 1,4-dioxane. In a first series of runs we investigated the influence on the reactivity of the following palladium precursors: [Pd(η^3-C_3H_5)Cl]$_2$, [Pd(dba)$_2$], [$PdCl_2$(cod)] and [Pd(OAc)$_2$]. The highest conversion was obtained with [Pd(OAc)$_2$], which led to a conversion of 94.9 % versus 48.7–86.5 % for the other salts (Table 1). This complex was used in all following tests.

Table 1. Influence of the palladium precursor on Suzuki–Miyaura cross-coupling by using monophosphane **6**.[a]

Entry	Palladium precursor	Conversion [%]
1	[Pd(η^3-C_3H_5)Cl]$_2$	86.5
2	[Pd(dba)$_2$]	78.2
3	[$PdCl_2$(cod)]	48.7
4	[Pd(OAc)$_2$]	94.9

[a] [Pd] (5×10^{-5} mmol, 1×10^{-2} mol %, ArBr/Pd = 10000), **6** (1×10^{-4} mmol, 2 equiv/Pd), 4-bromoanisole (0.094 g, 0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (60 % dispersion in mineral oil, 0.040 g, 1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane.

In a second series of runs, we determined the optimal base from Cs_2CO_3, K_2CO_3, CsF, CsCl, NaH, NaOH, KOH and NEt_3. As can be inferred from Table 2, the most efficient base was NaH, which led to a conversion of 94.9 % (Table 2, entry 5).

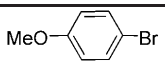
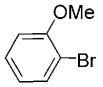
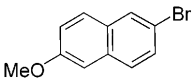
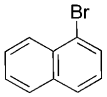
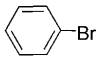
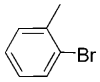
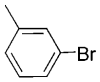
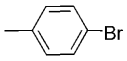
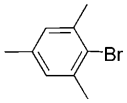
Table 2. Research of the optimal base for the Suzuki–Miyaura cross-coupling catalysed by [Pd(OAc)$_2$]/calix[4]arene monophosphane **6**.[a]

Entry	Base	Conversion [%]
1	Cs_2CO_3	75.5
2	K_2CO_3	86.9
3	CsF	64.7
4	CsCl	28.7
5	NaH	94.9
6	NaOH	57.7
7	KOH	93.6
8	NEt_3	35.3

[a] [Pd(OAc)$_2$] (5×10^{-5} mmol, 1×10^{-2} mol %, ArBr/Pd = 10000), **6** (1×10^{-4} mmol, 2 equiv/Pd), 4-bromoanisole (0.094 g, 0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), base (1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane.

Suzuki–Miyaura cross-coupling of arylbromides: By using the above optimised reaction parameters (dioxane, 100 °C, [Pd(OAc)$_2$] and NaH; 1 h reaction time), the runs were carried out applying an ArBr/Pd ratio of 100000:1 (which corresponds to a palladium loading of 10^{-3} mol %). As found by other authors,[14] no significant differences in activity were observed when using either 1 or 2 equivalents of phosphane per palladium. This suggests that the active species of the reaction is an intermediate containing only one monophosphane per palladium. Nevertheless, to increase the catalyst lifetime and also to allow comparison with published work, a L/Pd ratio of 2:1 was used in all catalytic tests. For each substrate, except for mesitylbromide, at least one of the ligands tested was found to be suitable for a conversion higher than 80 % after 1 h reaction time (Table 3, entries 1–8). For the less-reactive mesitylbromide, all phosphanes were of comparable efficiency (Table 3, entry 9).

Table 3. Palladium-catalysed Suzuki–Miyaura cross-coupling of arylbromides by using monophosphanes **6–10** and by applying an ArBr/Pd ratio of 100 000:1.[a]

Entry	ArBr		Calix[4]arene monophosphane				
			6	**7**	**8**	**9**	**10**
1		conv. [%]	99.7	95.4	49.8	89.4	94.4
		TOF	99700	95400	49800	89400	94400
2		conv. [%]	80.3	27.1	40.0	42.0	76.1
		TOF	80300	27100	40000	42000	76100
3		conv. [%]	95.0	94.7	47.6	99.3	98.8
		TOF	95000	94700	47600	99300	98800
4		conv. [%]	100	48.7	91.4	96.2	100
		TOF	100000	48700	91400	96200	100000
5		conv. [%]	46.1	38.0	88.0	51.9	83.2
		TOF	46100	38000	88000	51900	83200
6		conv. [%]	49.1	26.7	99.2	58.5	26.4
		TOF	49100	26700	99200	58500	26400
7		conv. [%]	92.9	64.1	99.0	93.1	77.6
		TOF	92900	64100	99000	93100	77600
8		conv. [%]	97.9	100	99.2	100	92.0
		TOF	97900	100000	99200	100000	92000
9[b]		conv. [%]	47.0	38.1	52.7	42.0	36.1
		TOF	4700	3810	5270	4200	3610

[a] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol %), monophosphane (1×10^{-5} mmol, 2 equiv/Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane. The TOFs were expressed in mol(ArBr).mol(Pd)$^{-1}$.h^{-1}. Conv. = conversion [b] $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol %), monophosphane (1×10^{-4} mmol, 2 equiv/Pd).

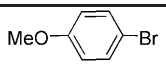
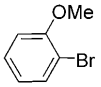
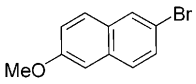
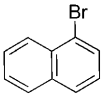
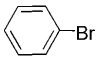
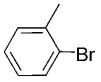
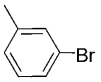
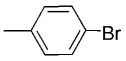
To find the highest catalytic activity, the ArBr/Pd ratio was raised to 10^6:1 (Table 4). With this catalyst loading, the conversions remained significant; moreover, the differences in activity between the five monophosphanes tested (**6–10**) were more pronounced. Monophosphane **6**, which has O-hexyl substituents, was the one that gave the highest activities for substrates substituted by a methoxy function (4-bromoanisole, 2-bromoanisole, 2-bromo-6-methoxynaphthalene; Table 4, entries 1–3). The *p*-methoxybenzyl-substituted monophosphane **8** gave the higher conversions for bromobenzene as well as for 2-, 3-, and 4-bromotoluene (Table 4, entries 5–8). 1-Bromonaphthalene was converted more efficiently with monophosphane **9**, which has four *m*-methoxybenzyl substituents (Table 4, entry 4). The tetrabenzylated monophosphane **7** gave, in general, lower conversions than the other phosphanes, this trend being particularly marked with the two hindered substrates 2-bromoanisole and 2-bromotoluene (Table 4, entries 2 and 6). The highest catalytic activity of all runs was measured for monophosphane **8** when used in the arylation of 4-bromotoluene (TOF = 321 000 mol(converted ArBr).mol(Pd)$^{-1}$.h^{-1}; Table 4, entry 8). The observed activity differences between the individual phosphanes could, subsequently, reflect differences in the strength of the steric interactions between the lower-rim substituents, which might modify the shape of the calixarene backbone, and incidentally its overall encumbrance. This interpretation, however, does not hold if the results obtained with phosphane **8** are considered, which performs only with non-methoxylated substrates. The observation that methoxy-containing arylbromides lower the reactivity of catalytic systems based on this particular phosphane was corroborated by another test. Thus, repeating the run described in entry 8 of Table 4 (substrate: 4-bromotoluene) in the presence of 1,4-dimethoxybenzene (0.5 equiv with respect to the substrate), led to a significant activity decrease (ca. 30%). We have no rational explanation for the lower activities of the sole ligand **8** in the presence of anisole derivatives. Possibly, the methoxy substituents of **8** form a ternary complex with anisole derivatives and the sodium ions present in solution in which the shape of the calixarene core is strongly modified, and incidentally also the bulkiness of the ligand.

We further observed that all the catalytic systems presented above displayed remarkably long lifetimes. For example, carrying out the arylation of 4-bromotoluene with ligand **8** and a palladium loading of 2.10^{-6} mol % led to a conversion of 10.3% after 16 h (Table 5, entry 1). This corresponds to a TOF of 322 000 mol(ArBr).mol(Pd)$^{-1}$.h^{-1}, a value that is nearly identical with the one measured after 1 h (Table 4, entry 8). After three days, the activity was still high, the TON having then reached a value of 14.55×10^6 mol(ArBr).mol(Pd)$^{-1}$ (Table 5, entry 4).

Finally, several runs that used a low Pd concentration (ArBr/Pd = 10^6) were repeated in the presence of a drop of mercury. No significant change in activities were observed, suggesting that no palladium nanoparticles were present.[18]

Suzuki–Miyaura cross-coupling at room temperature: The monophosphanes were further assessed for use in reactions that were carried out at room temperature. These runs were performed with an ArBr/Pd ratio of 1000 (0.1 mol %). In Table 6 the results obtained for various arylbromides are listed, with each entry corresponding to a test achieved in the presence of the ligand that gave the best results at 100 °C. Under these conditions, good conversions were ob-

Table 4. Palladium-catalysed Suzuki–Miyaura cross-coupling of arylbromides by using monophosphanes **6–10** and applying a ArBr/Pd ratio of 10^6:1.[a]

Entry	ArBr		Calix[4]arene monophosphane				
			6	**7**	**8**	**9**	**10**
1		conv. [%]	25.4	21.1	6.2	20.8	21.2
		TOF	254000	211000	62000	208000	212000
2		conv. [%]	13.0	3.8	5.7	11.6	4.5
		TOF	130000	38000	57000	116000	45000
3		conv. [%]	26.1	20.6	6.4	21.6	20.3
		TOF	261000	206000	64000	216000	203000
4		conv. [%]	13.7	6.5	16.6	17.0	10.5
		TOF	137000	65000	166000	170000	105000
5		conv. [%]	6.7	5.3	14.5	8.8	10.8
		TOF	67000	53000	145000	88000	108000
6		conv. [%]	5.4	3.6	16.4	7.9	3.2
		TOF	54000	36000	164000	79000	32000
7		conv. [%]	16.2	9.8	20.1	14.6	10.5
		TOF	162000	98000	201000	146000	105000
8		conv. [%]	21.4	15.2	32.1	18.8	20.9
		TOF	214000	152000	321000[b]	188000	209000

[a] $[Pd(OAc)_2]$ (5×10^{-7} mmol, 1×10^{-4} mol%), monophosphane (1×10^{-6} mmol, 2 equiv/Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane. The TOFs were expressed in mol(ArBr).mol(Pd)$^{-1}$.h^{-1}. Conv. = conversion. [b] Repeating this experiment during a 5 h reaction period led to full conversion.

Table 5. Stability of the catalytic species formed with monophosphane **8**.[a]

Entry	Time [h]	Conversion [%]	TON [mol(ArBr).mol(Pd)$^{-1}$]	TOF [mol(ArBr).mol(Pd)$^{-1}$.h^{-1}]
1	16	10.3	5150000	322000
2	24	14.5	7250000	302000
3	48	25.3	12660000	264000
4	72	29.1	14550000	202000

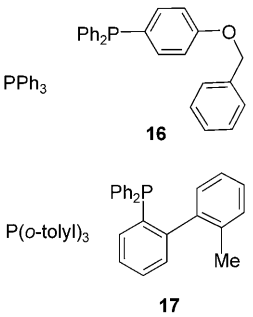
[a] $[Pd(OAc)_2]$(2×10^{-8} mmol, 2×10^{-6} mol%, 4-bromotoluene/Pd ratio = 50×10^6), monophosphane **8** (4×10^{-8} mmol, 2 equiv/Pd), 4-bromotoluene (1.0 mmol), $PhB(OH)_2$ (0.244 g, 2.0 mmol), NaH (60% dispersion in mineral oil; 0.080 g, 2.0 mmol), dioxane (3.0 mL), decane (0.10 mL), 100 °C. The conversions were determined by GC; the calibrations were based on decane.

served for the whole range of substrates employed. The highest conversion was again observed in the arylation of 4-bromotoluene in the presence of ligand **8** (TOF = 490 mol(ArBr).mol(Pd)$^{-1}$.h^{-1}). Note that the systems based on monophosphanes **6** and **8** were particularly efficient towards the sterically hindered 2-bromoanisole and 2-bromotoluene (conversions of 32.9 and 24.2%, respectively, after one hour; see Table 6, entries 2 and 6).

Suzuki–Miyaura cross-coupling of arylchlorides: The more challenging arylchlorides could also be converted conveniently into biaryls, as long as a catalyst loading of 1 mol% was applied (Table 7). For all the substrates tested (4-chloroanisole, 1-chloro-4-nitrobenzene, 4-chlorotoluene and chlorobenzene), monophosphane **8** led to good conversions. For example, for 1-chloro-4-nitrobenzene, the conversion was 41.0% after 1 hour (Table 7, entry 1). The higher reactivity of 1-chloro-4-nitrobenzene with respect to the other substrates arises from an easier oxidative addition step with this particular arylchloride. Increasing the reaction time allowed full transformation of all substrates. Thus by using **7**, for example, 100% conversions were observed after approximately 5 h in the case of 1-chloro-4-nitrobenzene and chlorobenzene, and after 16 h for 4-chloroanisole and 4-chlorotoluene.

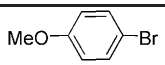
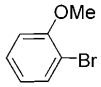
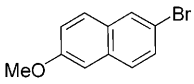
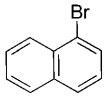
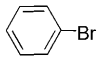
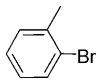
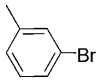
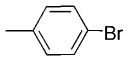
Comparison with other arylphosphanes: The results outlined above demonstrate that the combination of $[Pd(OAc)_2]$ with monophosphanes **6–10** results in highly active catalysts for Suzuki–Miyaura cross-coupling reactions of arylbromides. Ligands **6** and **8**, which were the ligands that gave the best results for the arylation of bromoanisole and bromotoluene, respectively, were compared with two non-bulky arylphosphanes, PPh_3 and (4-benzyloxyphenyl)diphenylphosphane (**16**), and two sterically demanding ones, P(*o*-tolyl)$_3$ and 2-diphenylphosphanyl-2'-methylbiphenyl (**17**; see Scheme 6). The results of the runs performed with these ligands are reported in Table 8.

The systems based on **6** and **8** led to activities that were approximately 3–4 times higher than those obtained with PPh_3 and **16** (Table 8, entries 1 and 2). Interestingly, the activities are comparable with those of phosphane **17**, which belongs to the very efficient Buchwald-type phosphanes.[14] In the case of 4-bromotoluene, monophosphane **8** led to conversions that were even significantly higher than those obtained with **17** (conversion: 32.1% vs. 21.4%;



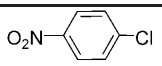
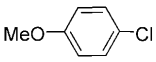
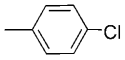
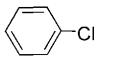
Scheme 6. Ligands used for ranking the calixarene monophosphanes.

Table 6. Suzuki–Miyaura cross-coupling reactions carried out at room temperature by using monophosphanes **6**, **8** and **9**.[a]

entry	ArBr	Calix[4]arene monophosphane	Conversion [%]	TOF
1		**6**	44.3	440
2		**6**	32.9	330
3		**6**	44.8	450
4		**9**	38.6	390
5		**8**	22.8	230
6		**8**	24.2	240
7		**8**	37.3	370
8		**8**	48.7	490

[a] $[Pd(OAc)_2]$ (5×10^{-4} mmol, 0.1 mol%, ArBr/Pd ratio of 1000), monophosphane (1×10^{-3} mmol, 2 equiv/Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), room temperature, 1 h. The conversions were determined by GC; the calibrations were based on decane. The TOFs are expressed in $mol(ArBr).mol(Pd)^{-1}.h^{-1}$.

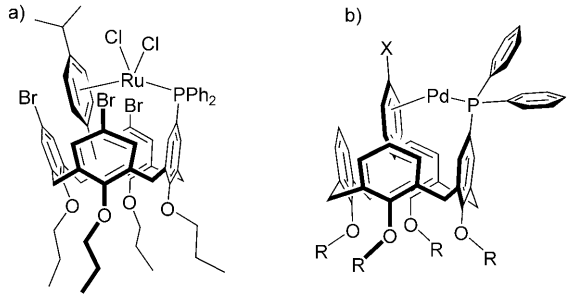
Table 7. Palladium-catalysed Suzuki–Miyaura cross-coupling of arylchlorides in the presence of monophosphanes **6**–**10**.[a]

Entry	ArCl		Calix[4]arene monophosphane				
			6	**7**	**8**	**9**	**10**
1		conv. [%]	5.0	36.2	41.0	25.7	4.2
2		conv. [%]	1.9	9.4	12.0	7.6	3.0
3		conv. [%]	5.6	9.9	26.6	16.4	7.3
4		conv. [%]	9.8	37.1	34.7	33.8	19.6

[a] $[Pd(OAc)_2]$ (2.5×10^{-3} mmol, 1 mol%, ArCl/Pd ratio of 100), monophosphane (5×10^{-3} mmol, 2 equiv/Pd), ArCl (0.25 mmol), $PhB(OH)_2$ (0.061 g, 0.5 mmol), NaH (60% dispersion in mineral oil) (0.020 g, 0.5 mmol), dioxane (0.75 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane. Conv. = conversion.

see Table 8, entry 2). The efficiency of Buchwald phosphanes is generally attributed to their ability to bind the palladium centre in a hemilabile manner, thereby stabilising a reactive monophosphane palladium(0) precursor.[12,29] Possibly, the activation barrier of the oxidative addition step is lower for this monoligand species than for the corresponding bis(phosphane) complex.[30] Note that bulky arylphosphanes with no secondary binding function are usually less efficient than Buchwald phosphanes of comparable steric encumbrance. In keeping with this belief, we found that P-(*o*-tolyl)$_3$[31] led to activities that were approximately three times lower than those of monophosphanes **6** and **8** (Table 8, entries 1 and 2).

To rationalise the abnormal high performance towards arylbromides of monophosphanes **6** and **8**, which unlike **17** are unable to coordinate metals in a hemilabile/chelating fashion, it might be considered that in the corresponding catalytic intermediates, the P–M vector remains preferentially directed towards the calixarene axis rather than pointing away from the cavity. In such a species the conical calixarenyl fragment would then considerably increase the time-averaged bulkiness of the phosphane (over, for example, that of **16**), and therefore favour the formation of a zerovalent monoligand species, which is regarded as the key step in the activation of aryl bromides.[29] With Buchwald-type ligands such as **17**, the formation of monoligand complexes is seemingly promoted by transient binding of the remote aryl ring, which then makes the phosphane artificially more bulky. One factor that could contribute to the formation of monoligand phosphane complexes with **6**–**10** is the ability of the latter ligands to bind metal–π–arene fragments, thereby forming complexes in which the M–arene unit is permanently held inside the calixarene cavity. This finding was made recently by Jeunesse et al. for some ruthenium-(*p*-cymene) complexes obtained from closely related ligands (Scheme 7).

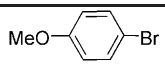
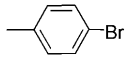
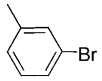
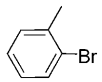


Scheme 7. a) Typical structure of $RuCl_2$(*p*-cymene) complexes that were obtained from calixarenyl monophosphanes;[19] b) Proposed monophosphane palladium(0) intermediate formed in Suzuki–Miyaura cross-coupling before the oxidative addition step.

The entrapment of the η^6-bonded arene results from π–π interactions between the *p*-cymene ligand and two phenolic rings of the calixarene backbone.[20,32] A similar supramolecular interaction may, in principle, also occur in transient $[Pd^0(ArX)L]$ complexes obtained from the calixarenyl phosphanes **6**–**10** (Scheme 7). Although this hypothesis remains speculative, it is consistent with the observation that subtle size modifications of the lower-rim substituents do improve the catalytic outcome, probably as a result of an induced shape modification of the calixarene receptor, which may then operate as a better receptor.

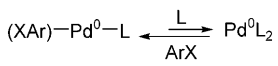
Of course, it may be questioned why **17** is more efficient[33] than monophosphanes **6**–**10** in cross-coupling reac-

Table 8. Comparison of monophosphanes in Suzuki–Miyura cross-coupling of arylbromides.[a]

Entry	ArBr		PPh_3	**16**	P(*o*-tolyl)$_3$	**17**	Calixarene monophosphane
1		conv. [%]	7.0	8.6	9.6	35.5	25.4 (**6**)
		TOF	70000	86000	96000	355000	254000
2		conv. [%]	6.5	7.5	10.3	21.4	32.1 (**8**)
		TOF	65000	75000	103000	214000	321000
3		conv. [%]	–	–	–	11.9	16.4 (**8**)
		TOF	–	–	–	119000	164000
4		conv. [%]	–	–	–	9.7	20.1 (**8**)
		TOF	–	–	–	97000	201000

[a] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-4} mol%), monophosphane (1×10^{-5} mmol, 2 equiv/Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), NaH (60% dispersion in mineral oil; 0.040 g, 1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC; the calibrations were based on decane. The TOFs were expressed in mol(ArBr).mol(Pd)$^{-1}$.h^{-1}. Conv. = conversion.

tions with aryl chlorides. According to Hartwig, the rate-limiting step with aryl chlorides is the oxidative addition step that occurs after formation of the monoligand species.[29] Actually, **17** may act as a chelator, and when behaving so it becomes a better donor than its P monodentate counterpart, hence the oxidative addition step should be facilitated with respect to systems based on purely monodentate phosphanes such as **6**–**10**. Note, however, that recent investigations on bowl-shaped triarylphosphanes in which the P atom sits deep inside a pocket[13,15,16,34] have clearly demonstrated that the presence of additional donors that may render the phosphane a chelating ligand is not a prerequisite for the oxidative addition to occur effectively. It is likely that with these extremely crowded ligands, the palladium(0) complexes that may form are exclusively monophosphane species, the formation of the less-reactive PdL_2 intermediate being totally prevented. These findings suggest that, in principle, any phosphane (L) of medium basicity that is able to shift the equilibrium shown in Scheme 8 towards the formation of the $Pd^0L(ArX)$ species effectively should also be efficient in Suzuki–Miyaura cross-coupling of aryl chlorides.



Scheme 8. Possible key equilibrium preceding the oxidative addition step in Suzuki–Miyaura cross-coupling.

Conclusion

We have described the synthesis of five new, conical *p*-$(H)_3$-calix[4]arenes that have a PPh_2 group anchored at their upper rim. X-ray diffraction studies carried out on three palladium complexes containing monophosphane **7** suggest that the PPh_2 moiety may freely rotate in solution about the P–C_{calix} axis, and therefore position a coordinated metal ion either above or outside the cone that is delineated by the calixarene cavity. This peculiarity makes any attempt to determine a cone angle value for this kind of bulky ligands worthless. Combining any of these monophosphanes with $[Pd(OAc)_2]$ and NaH at 100 °C in 1,4-dioxane gave a highly efficient catalytic system for the Suzuki–Miyaura cross-coupling of phenylboronic acid with aryl bromides, which moreover was stable over several days. The observed activities, which compare with those of another triarylphosphane, the Buchwald-type ligand **17**, were found to be three times higher than those of systems based on the bulky phosphane P(*o*-tolyl)$_3$. Because, unlike Buchwald-type ligands, the reported calixarenyl phosphanes cannot act as chelators, it is likely that their high efficiency relies on the ability of the calixarene to act as a second-sphere ligand towards a P-coordinated {Pd^0-(ArX)} moiety, thereby considerably increasing the crowding about the catalytic centre and incidentally favouring the formation of a more active monoligand complex. However, the proportion of monoligand species formed before the oxidative addition step is probably not sufficient to make theses phosphanes competitive with the formally more electron rich **17** in cross-coupling reactions with aryl chlorides. Further work is aimed at modifying the calixarene backbone to get new triarylphosphane ligands that operate in a supramolecular fashion for the efficient activation of aryl chlorides.

Experimental Section

General methods: All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded by using a Bruker AVANCE 300 spectrometer. ^{1}H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$), ^{13}C 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. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm). 5-Bromo-25,26,27,28-tetrahydroxy-calix[4]arene (**1**),[35] and (4-benzyloxyphenyl)diphenylphosphane (**16**)[36] were prepared according to literature procedures. In the NMR data given hereafter, the bridging CH_2 groups of the calixarene backbone are designated by the abreviation $ArCH_2Ar$.

General procedure for the synthesis of 5-bromo-25,26,27,28-tetraalkyloxy-calix[4]arenes (2–5): A solution of **1** (1.000 g, 2.0 mmol), NaH (60% in mineral oil; 0.357 g, 8.9 mmol) and the corresponding alkylbromide (8,9 mmol) in DMF (50 mL) was heated at 60 °C during 3 h. After cooling to room temperature, excess NaH was hydrolysed with water (2 mL) and the reaction mixture was evaporated to dryness. The resulting oily product was treated with a mixture of CH_2Cl_2 (50 mL) and water (20 mL). After extraction of the aqueous layer with CH_2Cl_2 (2 × 50 mL), the organic phases were combined. The resulting solution was washed

with water (4×50 mL), then dried over Na_2SO_4 and evaporated under reduced pressure. The products **2–5** were purified by column chromatography on silica gel by using petroleum ether (100%) as the eluent for **2** and **3** or ethyl acetate/petroleum ether (20:80, v/v) as the eluent for **4** and **5**.

5-Bromo-25,26,27,28-tetrahexyloxy-calix[4]arene (2): Yield: 1.529 g, 91%; R_f=0.73 (AcOEt/petroleum ether, 20:80, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.82–6.68 (6H; Ar H), 6.58 (d, ^3J=7.5 Hz, 1H; Ar H), 6.49 (s, 2H; Ar H *ortho* to Br), 6.41 (d, ^3J=7.5 Hz, 2H; Ar H), 4.44 and 3.16 (2×d, ^2J=13.6 Hz, 4H; AB spin system, ArCH_2Ar), 4.39 and 3.09 (2×d, ^2J=13.6 Hz, 4H; AB spin system, ArCH_2Ar), 3.96–3.89 (m, 4H; OCH_2), 3.83 (t, ^3J=7.3 Hz, 2H; OCH_2), 3.80 (t, ^3J=7.3 Hz, 2H; OCH_2), 1.92–1.85 (m, 8H; OCH_2CH_2), 1.50–1.31 (m, 24H; $CH_2CH_2CH_2CH_2CH_3$), 0.96–0.89 ppm (m, 12H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=157.21, 156.24 and 155.51 (3×s; Ar Cq-O), 137.04–114.82 (Ar C), 75.29 (s; OCH_2), 75.17 (s; 2×OCH_2), 32.26 (s; $CH_3CH_2CH_2$), 32.18 (s; $CH_3CH_2CH_2$), 32.14 (s; $CH_3CH_2CH_2$), 31.17 (s; ArCH_2Ar), 31.04 (s; ArCH_2Ar), 30.51 (s; OCH_2CH_2), 30.39 (s; OCH_2CH_2), 30.32 (s; OCH_2CH_2), 26.24 (s; $OCH_2CH_2CH_2$), 26.18 (s; $OCH_2CH_2CH_2$), 25.97 (s; $OCH_2CH_2CH_2$), 23.02 (s; CH_2CH_3), 22.96 (s; CH_2CH_3), 22.94 (s; CH_2CH_3), 14.23 (s; CH_2CH_3), 14.22 ppm (s; CH_2CH_3); elemental analysis calcd (%) for $C_{52}H_{71}O_4Br$ (M_r=840.02): C 74.35, H 8.52; found: C 74.20, H 8.67.

5-Bromo-25,26,27,28-tetrabenzyloxy-calix[4]arene (3): Yield: 1.624 g, 94%; R_f=0.75 (CH_2Cl_2-petroleum ether, 50:50, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.38–7.35 (2H; benzyl Ar H), 7.30–7.22 (14H; benzyl Ar H), 7.16 (d, ^3J=7.1 Hz, 4H; benzyl Ar H), 6.76–6.60 (m, 7H; calix Ar H), 6.43 (s, 2H; Ar H *ortho* to Br), 6.37 (d, ^3J=7.5 Hz, 2H; calix Ar H), 5.02 and 4.97 (2×d, ^2J=11.9 Hz, 4H; AB spin system, CH_2Ph), 4.86 (s, 2H; H_2Ph), 4.80 (s, 2H; CH_2Ph), 4.25 and 3.00 (2×d, ^2J=13.7 Hz, 4H; AB spin system, ArCH_2Ar), 4.10 and 2.83 ppm (2×d, ^2J=13.7 Hz, 4H; ArCH_2Ar, AB spin system); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=155.71, 155.39 and 154.54 (3×s; Ar Cq-O), 137.99–115.28 (Ar C), 76.95 (s; OCH_2Ph), 76.89 (s; OCH_2Ph), 76.31 (s; OCH_2Ph), 31.56 (s; ArCH_2Ar), 31.41 ppm (s; ArCH_2Ar); elemental analysis calcd (%) for $C_{56}H_{47}O_4Br$ (M_r=863.87): C 77.86, H 5.48; found: C 77.67, H 5.61.

5-Bromo-25,26,27,28-tetra(*p*-methoxy)benzyloxy-calix[4]arene (4): Yield: 1.751 g, 89%; R_f=0.52 (CH_2Cl_2-petroleum ether, 60:40, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.31 (d, ^3J=8.6 Hz, 2H; benzyl Ar H), 7.23 (d, ^3J=8.5 Hz, 2H; benzyl Ar H), 7.18 (d, ^3J=8.6 Hz, 4H; benzyl Ar H), 6.84 (d, ^3J=8.5 Hz, 2H; benzyl Ar H), 6.82 (d, ^3J=8.5 Hz, 2H; benzyl Ar H), 6.78–6.69 (m, 10H; benzyl and calix Ar H), 6.64 (t, ^3J=7.6 Hz, 1H; calix Ar H of), 6.46 (s, 2H; calix Ar H *ortho* to Br), 6.40 (d, ^3J=7.6 Hz, 2H; calix Ar H), 4.96 and 4.92 (2×d, ^2J=12.1 Hz, 4H; AB spin system, CH_2Ar), 4.83 (s, 2H; CH_2Ar), 4.77 (s, 2H; CH_2Ar), 4.27 and 3.01 (2×d, ^2J=13.7 Hz, 4H; AB spin system, ArCH_2Ar), 4.12 and 2.85 (2×d, ^2J=13.7 Hz, 4H; AB spin system, ArCH_2Ar), 3.82 (s, 3H; CH_3OAr), 3.81 (s, 3H; CH_3OAr), 3.78 ppm (s, 6H; CH_3OAr); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=159.61, 159.49 and 159.43 (3×s; Ar Cq-OMe), 155.71, 155.40 and 154.54 (3×s; Ar Cq-Ocalix), 137.43–113.40 (Ar C), 76.44 (s; OCH_2Ar), 76.34 (s; OCH_2Ar), 75.70 (s; OCH_2Ar), 55.44 (s; CH_3OAr), 55.37 (s; CH_3OAr), 31.60 (s; ArCH_2Ar), 31.48 ppm (s; ArCH_2Ar); elemental analysis calcd (%) for $C_{60}H_{55}O_8Br$ (M_r=983.98): C 73.24, H 5.63; found: C 73.16, H 5.72.

5-Bromo-25,26,27,28-tetra(*m*-methoxy)benzyloxy-calix[4]arene (5): Yield: 1.732 g, 88%; R_f=0.5 (CH_2Cl_2-petroleum ether, 60:40, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.24 (t, ^3J=7.2 Hz, 1H; benzyl Ar H), 7.21 (t, ^3J=7.5 Hz, 1H; benzyl Ar H), 7.13 (t, ^3J=7.9 Hz, 2H; benzyl Ar H), 7.04–6.64 (m, 19H; benzyl and calix Ar H), 6.48 (s, 2H; calix Ar H *ortho* to Br), 6.42 (d, ^3J=7.5 Hz, 2H; calix Ar H), 5.10 and 5.04 (2×d, ^2J=11.9 Hz, 4H; AB spin system, CH_2Ar), 5.02 (s, 2H; CH_2Ar), 4.93 (s, 2H; CH_2Ar), 4.28 and 3.02 (2×d, ^2J=13.6 Hz, 4H; AB spin system, ArCH_2Ar), 4.12 and 2.83 (2×d, ^2J=13.7 Hz, 4H; AB spin system, ArCH_2Ar), 3.73 (s, 3H; CH_3OAr), 3.73 (s, 3H; CH_3OAr), 3.68 ppm (s, 6H; CH_3OAr); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=159.51, 159.47 and 159.22 (3×s; Ar Cq-OMe), 155.65, 155.32 and 154.45 (3×s; Ar Cq-Ocalix), 139.45–113.62 (Ar C), 76.70 (s; OCH_2Ar), 76.62 (s; OCH_2Ar), 76.12 (s; OCH_2Ar), 55.27 (s; CH_3OAr), 55.26 (s; CH_3OAr), 55.20 (s; CH_3OAr), 31.59 (s; ArCH_2Ar), 31.45 ppm (s; ArCH_2Ar); elemental analysis calcd (%) for $C_{60}H_{55}O_8Br$ (M_r=983.98): C 73.24, H 5.63; found: C 73.28, H 5.75.

General procedure for the synthesis of 5-diphenylphosphanyl-25,26,27,28-tetraalkyloxy-calix[4]arenes (6–9): *n*-Butyllithium (2.1 mmol) was slowly added to a solution of 5-bromo-25,26,27,28-tetraalkyloxy-calix[4]arene (1 mmol) in THF (50 mL) at −78°C. After 0.5 h, the generated carbanion was quenched with chlorodiphenylphosphane (2.5 mmol). The mixture was stirred at room temperature for 3 h. After completion of the reaction (monitored by TLC), water (20 mL) was added. The aqueous phase was washed with CH_2Cl_2 (2×50 mL). The combined organic phases were dried over Na_2SO_4 and were evaporated under reduced pressure. The calixarene monophosphanes **6–9** were purified by column chromatography on silica gel by using petroleum ether (100%) as the eluent for **6** and **7** and ethyl acetate/petroleum ether (20:80, v/v) as the eluent for **8** and **9**.

5-Diphenylphosphanyl-25,26,27,28-tetrahexyloxy-calix[4]arene (6): Yield: 0.850 g, 90%; R_f=0.80 (CH_2Cl_2-petroleum ether, 40:60, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.35–7.29 (m, 6H; PPh_2 Ar H), 7.22–7.17 (m, 4H; PPh_2 Ar H), 6.80 (d, ^3J=7.3 Hz, 2H; calix Ar H), 6.72–6.65 (m, 5H; calix Ar H), 6.61–6.52 (m, 4H; Ar H of calix), 4.53 and 3.24 (2×d, ^2J=13.3 Hz, 4H; AB spin system, ArCH_2Ar), 4.48 and 3.12 (2×d, ^2J=13.2 Hz, 4H; AB spin system, ArCH_2Ar), 3.96 (pseudo t, ^3J=7.3 Hz, 8H; OCH_2), 2.05–1.94 (m, 8H; OCH_2CH_2), 1.50–1.39 (m, 24H; $CH_2CH_2CH_2CH_2CH_3$), 0.99 ppm (t, ^3J=6.0 Hz, 12H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=157.58, 156.66 and 156.48 (3×s; Ar Cq-O), 138.50–122.18 (Ar C), 75.50 (s; OCH_2), 75.42 (s; OCH_2), 75.33 (s; OCH_2), 32.23 (s; 2×$CH_2CH_2CH_3$), 32.19 (s; $CH_2CH_2CH_3$), 31.13 (s; ArCH_2Ar), 30.99 (s; ArCH_2Ar), 30.48 (s; OCH_2CH_2), 30.43 (s; OCH_2CH_2), 30.38 (s; OCH_2CH_2), 26.12 (s; 2×$OCH_2CH_2CH_2$), 26.07 (s; $OCH_2CH_2CH_2$), 23.00 (s; 2×CH_2CH_3), 22.96 (s; CH_2CH_3), 14.23 ppm (s; CH_2CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ=−5.4 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{64}H_{81}O_4P$ (M_r=945.30): C 81.32, H 8.64; found: C 81.41, H 8.75.

5-Diphenylphosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]arene (7): Yield: 0.727 g, 75%; R_f=0.37 (CH_2Cl_2-petroleum ether, 40:60, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.39–7.17 (m, 30H; benzyl and PPh_2 Ar H), 6.78–6.73 (m, 3H; calix Ar H), 6.67 (d, ^3J=7.9 Hz, 2H; calix Ar H), 6.58–6.52 (s, 4H; calix Ar H), 6.42–6.38 (m, 2H; calix Ar H), 5.04 (s, 4H; CH_2Ph), 5.00 and 4.95 (2×d, ^2J=11.5 Hz, 4H; AB spin system, CH_2Ph), 4.30 and 3.03 (2×d, ^2J=13.3 Hz, 4H; AB spin system, ArCH_2Ar), 4.22 and 2.88 ppm (2×d, ^2J=13.4 Hz, 4H; AB spin system, ArCH_2Ar); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=156.35, 155.56 and 155.17 (3×s; Ar Cq-O), 138.31–122.39 (Ar C), 76.57 (s; OCH_2Ph), 76.46 (s; OCH_2Ph), 76.21 (s; OCH_2Ph), 31.44 (s; ArCH_2Ar), 31.37 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ=−5.9 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{68}H_{57}O_4P$ (M_r=969.15): C 84.27, H 5.93; found: C 84.39, H 5.92.

5-Diphenylphosphanyl-25,26,27,28-tetra(*p*-methoxy)benzyloxy-calix[4]arene (8): Yield: 0.163 g, 15%; R_f=0.90 (CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.30 (d, 4H; PPh_2 Ar H), 7.24 (^3J=8.6 Hz, d, 4H; methoxybenzyl Ar H), 7.23–7.12 (m, 4H; PPh_2 Ar H), 7.22 (d, ^3J=8.6 Hz, 2H; methoxybenzyl Ar H), 7.16 (d, ^3J=8.0 Hz, 2H; methoxybenzyl Ar H), 6.80 (d, ^3J=8.6 Hz, 4H; methoxybenzyl Ar H), 6.77–6.67 (m, 4H; PPh_2 and calix Ar H), 6.72 (d, ^3J=8.6 Hz, 4H; methoxybenzyl Ar H), 6.62 (d, ^3J=7.9 Hz, 2H; calix Ar H), 6.56–6.46 (m, 5H; calix Ar H), 6.37–6.34 (m, 2H; calix Ar H), 4.92 (s, 4H; CH_2Ar), 4.87 and 4.83 (2×d, ^2J=12 Hz, 4H; AB spin system, CH_2Ar), 4.24 and 2.98 (2×d, ^2J=13.3 Hz, 4H; AB spin system, ArCH_2Ar), 4.16 and 2.83 (2×d, ^2J=13.4 Hz, 4H; AB spin system, ArCH_2Ar), 3.80 (s, 6H; CH_3OAr), 3.79 ppm (s, 6H; CH_3OAr); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ=159.49 and 159.44 (2×s; Ar Cq-OMe), 156.52, 155.70 and 155.32 (3×s; Ar Cq-Ocalix), 138.48–113.41 (Ar C), 76.16 (s; OCH_2Ar), 76.01 (s; OCH_2Ar), 75.76 (s; OCH_2Ar), 55.50 (s; CH_3OAr), 55.42 (s; CH_3OAr), 55.40 (s; CH_3OAr), 31.64 (s; ArCH_2Ar), 31.59 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ=−5.8 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{72}H_{65}O_8P\cdot{}^1/_2CH_2Cl_2$ (M_r=1089.25+42.47): C 76.94, H 5.88; found: C 76.87, H 5.76.

5-Diphenylphosphanyl-25,26,27,28-tetra(*meta*-methoxy)benzyloxy-calix[4]arene (9): Yield: 0.272 g, 25%; R_f=0.70 (AcOEt-petroleum ether,

40:60, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (12H; Ar H), 7.09 (t, ^3J = 6.8 Hz, 6H; Ar H), 6.97–6.88 (m, 13H; Ar H), 7.80–6.60 (m, 14H; Ar H), 6.51 (d, ^3J = 6.2 Hz, 2H; Ar H), 5.13–5.06 (m, 8H; CH_2Ar), 4.36 and 3.08 (2×d, ^2J = 13.4 Hz, 4H; AB spin system, ArCH_2Ar), 4.27 and 2.92 (2×d, ^2J = 13.4 Hz, 4H; AB spin system, ArCH_2Ar), 3.77 (s, 6H; CH_3OAr), 3.76 ppm (s, 6H; CH_3OAr); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 159.29, 159.25 and 159.22 (3×s; Ar Cq-OMe), 156.26, 155.42 and 155.17 (3×s; Ar Cq-Ocalix), 139.35–113.50 (Ar C), 76.31 (s; OCH_2Ar), 76.22 (s; OCH_2Ar), 76.18 (s; OCH_2Ar), 55.10 (s; CH_3OAr), 31.53 (s; ArCH_2Ar), 31.43 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −5.6 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{72}H_{65}O_8P$ (M_r = 1089.25): C 79.39, H 6.01; found: C 79.34, H 5.93.

5-Diphenylphosphanyl-25,26,27,28-tetrahydroxy-calix[4]arene (10): A Schlenk tube was filled with phosphane **7** (0.500 g, 0.5 mmol), $AlCl_3$ (0.267 g, 2.0 mmol) and toluene (50 mL). After stirring this suspension for 16 h, a saturated solution of NaCl (15 mL) was slowly added. The aqueous layer was extracted with CH_2Cl_2 (2×15 mL), then the combined organic layers were dried over Na_2SO_4. Evaporation under vacuum afforded a pale-yellow solid, which was recrystallised from diethylether/petroleum ether (1:1, v/v). The product was collected by filtration and dried under vacuum (yield: 0.314 g, 100%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (s, 4H; OH), 7.33–6.67 (m, 21H; Ar H), 4.20 and 3.49 ppm (2× br signals, 8H; AB spin system, ArCH_2Ar); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 150.05, 149.21 and 148.67 (3×s; Ar Cq-OH), 137.94–122.32 (Ar C), 31.85 (s; ArCH_2Ar), 31.74 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −5.9 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{40}H_{33}O_4P$ (M_r = 608.66): C 78.93, H 5.46; found: C 78.84, H 5.33.

***trans-P,P*-Dichlorido-bis{5-diphenylphosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]are ne}-palladium(II) (11)**: A solution of [$PdCl_2$(cod)] (0.012 g, 0.04 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **7** (0.079 g, 0.08 mmol) in CH_2Cl_2 (5 mL) that was maintained at −78°C. After stirring the solution for a further 0.5 h at −78°C, the reaction mixture was concentrated to ca. 2 mL, upon which *n*-hexane (20 mL) was added. The yellow precipitate was separated by filtration and dried under vacuum (yield: 0.085 g, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.56 (m, 8H; Ar CH), 7.45–7.12 (m, 52H; Ar CH), 6.81 (d, ^3J = 7.5 Hz, 8H; Ar CH), 6.64 (t, ^3J = 7.4 Hz, 2H; Ar CH), 6.44–6.40 (m, 8H; Ar CH), 6.34–6.30 (m, 4H; Ar CH), 5.05 (s, 4H; OCH_2Ph), 5.02 (s, 4H; OCH_2Ph), 4.87 and 4.81 (2×d, ^2J = 11.5 Hz, 8H; AB spin system, OCH_2Ph), 4.24 and 2.97 (2×d, ^2J = 13.6 Hz, 8H; AB spin system, ArCH_2Ar), 4.18 and 2.79 ppm (2×d, ^2J = 13.6 Hz, 8H; AB spin system, ArCH_2Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 157.81, 155.70 and 155.00 (3×s; Ar Cq-O), 137.83–122.20 (Ar C), 76.78 (s; OCH_2Ph), 76.33 (s; OCH_2Ph), 76.17 (s; OCH_2Ph), 31.47 ppm (s; ArCH_2Ar) (only one signal is seen of the ArCH_2Ar carbon atoms); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 22.7 ppm (s; PPh_2); MS (MALDITOF): *m/z*: 2079.52 [*M*−Cl]$^+$ expected isotopic profiles; elemental analysis calcd (%) for $C_{136}H_{114}Cl_2O_8P_2Pd$ (M_r = 2115.63): C 77.21, H 5.43; found: C 77.29, H 5.56.

***cis-P,P*-Dichlorido-bis{5-diphenylphosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]arene}-palladium(II) (12)**: A solution of [$PdCl_2$(cod)] (0.012 g, 0.04 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of **7** (0.079 g, 0.08 mmol) in CH_2Cl_2 (5 mL) at 40°C. After stirring for 0.5 h at 40°C, the reaction mixture was concentrated to ca. 2 mL, upon which *n*-hexane (20 mL) was added. The orange precipitate that formed was separated by filtration and dried under vacuum (yield: 0.084 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.44–7.38 (m, 12H; Ar CH), 7.29–7.20 (m, 44H; Ar CH), 7.13–7.11 (m, 4H; Ar CH), 6.71–6.66 (m, 8H; Ar CH), 6.56 (t, ^3J = 7.4 Hz, 4H; Ar CH), 6.49 (d, ^3J = 7.5 Hz, 4H; Ar CH), 6.45 (d, ^3J = 7.5 Hz, 4H; Ar CH), 6.22 (t, ^3J = 7.4 Hz, 2H; Ar CH), 5.02 and 4.95 (2×d, ^2J = 11.6 Hz, 8H; AB spin system, OCH_2Ph), 4.83 (s, 4H; OCH_2Ph), 4.82 (s, 4H; OCH_2Ph), 4.19 and 2.92 (2×d, ^2J = 13.3 Hz, 8H; AB spin system, ArCH_2Ar), 3.99 and 2.72 ppm (2×d, ^2J = 13.5 Hz, 8H; AB spin system, ArCH_2Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 157.87, 155.26 and 155.02 (3×s; Ar Cq-O), 137.64–122.34 (Ar C), 77.07 (s; OCH_2Ph), 76.95 (s; OCH_2Ph), 76.16 (s; OCH_2Ph), 31.41 (s; ArCH_2Ar), 31.26 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 31.9 ppm (s; PPh_2); MS (MALDITOF): *m/z*: 2079.52 [*M*−Cl]$^+$ expected isotopic profiles; elemental analysis calcd (%) for $C_{136}H_{114}Cl_2O_8P_2Pd$ (M_r = 2115.63): C 77.21, H 5.43; found: C 77.15, H 5.56.

Chlorido-(*o*-dimethylaminomethylphenyl-*C*,*N*)-{5-diphenylphosphanyl-25,26,27,28-tetra benzyloxy-calix[4]arene} palladium(II) (13): A solution of [PdCl(*o*-$C_6H_4CH_2NMe_2$]$_2$ (0.035 g, 0.06 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of **7** (0.122 g, 0.13 mmol) in CH_2Cl_2 (5 mL). After stirring for 0.5 h, the reaction mixture was concentrated to ca. 2 mL, upon which *n*-hexane (20 mL) was added. The yellow precipitate that formed was separated by filtration and was dried under vacuum (yield: 0.157 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.58–7.54 (m, 4H; Ar CH), 7.52–7.10 (m, 27H; Ar CH), 6.99 (d, ^3J = 7.1 Hz, 1H; Ar CH), 6.87 (d, ^3J = 7.1 Hz, 4H; Ar CH), 6.74 (t, ^3J = 7.4 Hz, 1H; Ar CH), 6.51–6.42 (m, 2H; Ar CH), 6.26–6.23 (m, 4H; Ar CH), 5.78 (t, ^3J = 4.6 Hz, 2H; Ar CH), 5.07 (s, 2H; OCH_2Ph), 5.04 (s, 2H; OCH_2Ph), 4.81 and 4.74 (2×d, ^2J = 11.3 Hz, 4H; AB spin system, OCH_2Ph), 4.19 and 2.95 (2×d, ^2J = 13.5 Hz, 4H; AB spin system, ArCH_2Ar), 4.07 and 2.80 (2×d, ^2J = 13.4 Hz, 4H; AB spin system, ArCH_2Ar), 4.03 (br s, 2H; CH_2N), 2.85 ppm (d, ^4J(P,H) = 2 Hz, 6H; N(CH_3)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 157.80, 155.87 and 154.94 (3×s; Ar Cq-O), 150.97 (s; Ar Cq-CH_2N), 148.52 (d; Ar Cq-Pd), 138.37–122.32 (Ar C), 76.99 (s; OCH_2Ph), 76.21 (s; OCH_2Ph), 75.71 (s; OCH_2Ph), 73.21 (s; CH_2N), 50.64 (s; N(CH_3)$_2$), 31.43 ppm (s; ArCH_2Ar); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 43.1 ppm (s; PPh_2); MS (MALDITOF): *m/z*: 1208.86 [*M*−Cl]$^+$ expected isotopic profiles; elemental analysis calcd (%) for $C_{77}H_{69}ClNO_4PPd{\cdot}CH_2Cl_2$ (M_r = 1245.22 + 84.93): C 70.43, H 5.38, N 1.05; found: C 70.56, H 5.12, N 0.96.

(*o*-Dimethylaminomethylphenyl-*C*,*N*)-{5-diphenylphosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]arene}-tetrahydrofurane palladium(II) tetrafluoroborate (14): Asolution of $AgBF_4$ (0.024 g, 0.13 mmol) in THF (2 mL) was added to a solution of **13** (0.161 g, 0.13 mmol) in CH_2Cl_2 (5 mL). After 0.5 h, the solution was filtered through Celite and concentrated to ca. 2 mL. Addition of *n*-hexane (20 mL) afforded **14** as a brown precipitate, which was filtered off and dried under vacuum (yield: 0.168 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.42–7.12 (m, 30H; Ar CH), 6.97–6.93 (m, 3H; Ar CH), 6.88 (d, ^3J = 7.2 Hz, 1H; Ar CH), 6.68 (d, ^3J = 6.9 Hz, 2H; Ar CH), 6.58–6.31 (m, 6H; Ar CH), 6.23 (t, ^3J = 7.0 Hz, 1H; Ar CH), 5.98 (d, ^3J = 7.0 Hz, 2H; Ar CH), 4.95 (s, 2H; OCH_2Ph), 4.93 and 4.84 (2×d, ^2J = 11.5 Hz, 4H; AB spin system, OCH_2Ph), 4.89 (s, 2H; OCH_2Ph), 4.19 and 2.93 (2×d, ^2J = 13.3 Hz, 4H; AB spin system, ArCH_2Ar), 4.09 and 2.76 (2×d, ^2J = 13.3 Hz, 4H; AB spin system, ArCH_2Ar), 3.95 (br s, 2H; CH_2N), 3.67–3.63 (m, 4H; CH_2O of THF), 2.74 (s, ^4J (P,H) < 1 Hz, 6H; N(CH_3)$_2$), 1.79–1.74 ppm (m, 4H; CH_2CH$_2$O of THF); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 158.30, 155.66 and 155.10 (3×s; Ar Cq-O), 148.07 (s; Ar Cq-CH_2N), 139.30 (d; Cq-Pd), 137.87–122.30 (Ar C), 76.71 (s; OCH_2Ph), 76.61 (s; OCH_2Ph), 76.18 (s; OCH_2Ph), 71.07 (s; CH_2N), 68.50 (s; CH_2O of THF), 49.67 (s; N(CH_3)$_2$), 31.45 (s; ArCH_2Ar), 25.65 ppm (s; CH_2CH$_2$O of THF); ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ = 39.1 ppm (s; PPh_2); elemental analysis calcd (%) for $C_{81}H_{77}BF_4NO_5PPd$ (M_r = 1337.71): C 72.73, H 5.80, N 1.05; found: C 72.85, H 5.71, N 0.99.

General procedure for palladium-catalysed Suzuki–Miyaura cross-coupling reactions: In a Schlenk tube in an inert atmosphere a solution of [$Pd(OAc)_2$] in dioxane, a solution of the ligand (2 equiv/Pd) in dioxane, aryl halide (0.5 mmol), phenylboronic acid (0.122 g, 1.0 mmol), base (1.0 mmol), decane (0.05 mL, internal reference) and a complementary amount of dioxane were introduced so that the total reaction volume was 1.5 mL. The reaction mixture was then 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 analyzed by GC.

Crystal structure of 11: Single crystals of **11** that were suitable for diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. M_r = 1057.76; triclinic; space group $P\bar{1}$; a = 12.6332(4), b = 14.0161(3), c = 15.2785(3) Å; α = 88.749(2), β = 77.488(2), γ = 87.409(2)°; V = 2636.10(11) Å^3; Z = 2; D_x = 1.333 mg m^{-3}; λ ($Mo_{K\alpha}$) = 0.71073 Å; μ = 0.32 mm^{-1}; F(000) = 1104; T = 120(2) K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite $Mo_{K\alpha}$ radiation, λ = 0.71073 Å). The structure was solved with

SIR-97,[37] 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[38] and full-matrix least-square techniques (use of F^2; x, y, z, b_{ij} for C, Cl, O, P and Pd atoms; x, y, z in riding mode for H atoms; 673 variables and 8124 observations with $[I>2.0\sigma(I)]$; calcd $w=1/[\sigma^2(F_o^2)+(0.033P)^2]$ in which $P=(F_o^2+2F_c^2)/3$; $R1=0.036$, $wR2=0.071$, $S_w=0.887$; $\Delta\rho<0.63$ e Å^{-3}.

Crystal structure of 15a: Single crystals of **15a** suitable for diffraction study were obtained by slow diffusion of hexane into a commercial (undried) dichloromethane solution of the complex. $M_r=1312.51$; triclinic; space group $\bar{P}1$; $a=13.5768(6)$, $b=14.6696(4)$, $c=18.9840(6)$ Å; $\alpha=94.706(3)$, $\beta=110.158(4)$, $\gamma=111.821(4)°$; $V=3197.83(19)$ Å^3; $Z=2$; $D_x=1.363$ mg m^{-3}; $\lambda(Mo_{K\alpha})=0.71073$ Å; $\mu=0.381$ mm^{-1}; $F(000)=1360$; $T=150(2)$ K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å). The structure was solved with SIR-97,[37] 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[38] and full-matrix least-square techniques (use of F^2; x, y, z, b_{ij} for C, B, F, N, O, P and Pd atoms; x, y, z in riding mode for H atoms; 811 variables and 6709 observations with $[I>2.0\sigma(I)]$; calcd $w=1/[\sigma^2(F_o^2)+(0.0369P)^2]$ in which $P=(F_o^2+2F_c^2)/3$; $R1=0.048$, $wR2=0.081$, $S_w=0.795$; $\Delta\rho<0.643$ e Å^{-3}.

Crystal structure of 15b: Single crystals of **15b**·CH_2Cl_2 that were suitable for diffraction were obtained by slow diffusion of hexane into a commercial (undried) dichloromethane solution of the complex. $M_r=1397.44$; triclinic; space group $\bar{P}1$; $a=13.3935(3)$, $b=14.9355(3)$, $c=18.1936(4)$ Å; $\alpha=90.332(2)$, $\beta=110.253(2)$, $\gamma=98.837(2)°$; $V=3367.04(13)$ Å^3, $Z=2$; $D_x=1.378$ mg m^{-3}; $\lambda(Mo_{K\alpha})=0.71069$ Å; $\mu=0.443$ mm^{-1}; $F(000)=1444$; $T=150(2)$ K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite $Mo_{K\alpha}$ radiation, $\lambda=0.71069$ Å). The structure was solved with SIR-97,[37] 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[38] and full-matrix least-square techniques (use of F^2; x, y, z, b_{ij} for C, B, Cl, F, N, O, P and Pd atoms; x, y, z in riding mode for H atoms; 838 variables and 8650 observations with $[I>2.0\sigma(I)]$; calcd $w=1/[\sigma^2(F_o^2)+(0.0332P)^2]$ in which $P=(F_o^2+2F_c^2)/3$; $R1=0.038$, $wR2=0.070$, $S_w=0.779$; $\Delta\rho<0.666$ e Å^{-3}.

CCDC-738628 (**11**), 745119 (**15a**) and 744881 (**15b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This study was supported by the French Agence Nationale de la Recherche (ANR MATCALCAT). We thank Dr. C. Jeunesse for helpful discussion. The University of Strasbourg is gratefully acknowledged for a grant to L.M.

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Received: December 10, 2009
Published online: June 25, 2010

