Tetra-hydroxy-calix[4]arene derivatives with two P(III) or P(V) units attached at the upper rim

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Calixarene-Derived Mono-Iminophosphoranes: Highly Efficient Ligands for Palladium- and Nickel-Catalysed Cross-Coupling

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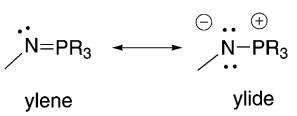
Abstract: The first mono-iminophosphoranes based on a calix[4]arene skeleton have been synthesised and tested in the arylation of aryl bromides and aryl chlorides. Combining these ligands with $[Pd(OAc)_2]$ or $[Ni(cod)_2]$ resulted in highly active Suzuki–Miyaura and Kumada–Tamao–Corriu cross-coupling catalysts, respectively. TOFs up to *ca.* 4×10^5 mol(ArBr)·mol(M)$^{-1}$·h^{-1} were obtained in each case. The remarkable activities observed probably arise from the ligands' ability to form complexes with cavity-entrapped "MArX" moieties (*endo*-complexes), their highly crowded metal environment favouring formation of mono-ligated intermediates over that of less reactive bis-ligated ones. Possible supramolecular interactions within the cavity involving the receptor wall and the aromatic substrate may also significantly influence the reaction rates, notably by increasing the proportion of *endo*-complexes.

Keywords: calix[4]arenes; cross-coupling; iminophosphoranes; Kumada–Tamao–Corriu reaction; nickel; palladium; supramolecular catalysis; Suzuki–Miyaura reaction

Introduction

Iminophosphoranes, also termed phosphazenes or phosphinimines, are analogues of Wittig compounds ($R_3P{=}CR'_2$) in which the alkylidene group has been substituted by an NR unit. They are generally described in terms of two mesomeric forms, one containing a P=N double bond (ylene), the other having a zwitterionic ylidic (P^+–N^-) structure (Scheme 1). The phosphorus substituents strongly influence the P–N bond length and polarisation, and therefore play a major role in controlling the relative weight of the two mesomeric forms. Iminophosphoranes are usually represented as possessing a phosphorus-nitrogen double bond, this accounting for its short length. However, this representation is only used for the sake of simplicity, theoretical analysis showing that the P–N bond is in fact a single bond reinforced by negative hyperconjugation of the lone pair of the nitrogen atom onto other orbitals centred on the phosphorus atom.[1,2]

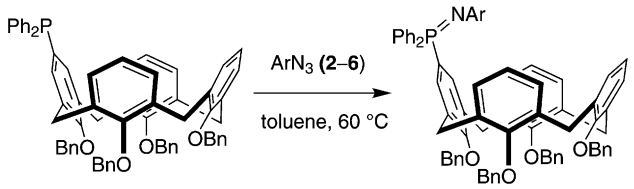


Scheme 1. The two low-energy mesomeric forms of an iminophosphorane.

Iminophosphoranes can bind transition metals *via* their nitrogen atom,[3–12] but their binding strength is rather weak in comparison with that of imines. To increase their capacity to form metal complexes, they are often covalently associated with another, stronger donor that enables them to bind as chelate species. It is noteworthy that this class of ligands has only sparingly been investigated in homogeneous catalysis. A few studies have focussed on their use in cross-coupling reactions, in which the iminophosphoranes employed were all potential chelators, particular examples being bis-iminophosphoranes[13] or iminophosphoranes containing another coordinating function.[14–16] In the present study, we describe the synthesis of the first mono-iminophophoranes based on a calix[4]arene unit and their use in Suzuki–Miyaura and Kumada–Tamao–Corriu (KTC) cross-coupling. Calixarenes are valuable synthons for the construction of receptor ligands and/or of sterically demanding ligands.[17–19]

Results and Discussion

Staudinger condensation[20] of calixarenyl-phosphine **1** with aryl azides **2**–**6** led quantitatively to the iminophosphorane-calix[4]arenes **7**–**11**, respectively (Scheme 2). Their formation was confirmed by MALDI-TOF analysis, each mass spectrum being characterised by a single peak with the isotopic pattern exactly as expected for the corresponding $[M+H]^+$ ion. The ^{31}P NMR spectra all displayed a singlet appearing in a range (−11–0 ppm) that is typical for iminophosphoranes.[7] Each ^{1}H NMR spectrum was consistent with a C_s-symmetrical molecule. The conical conformation of the calix[4]arene moieties was inferred from the ^{13}C NMR spectra, in which the two ArCH_2Ar signals appeared at *ca.* 31 ppm.[21] The synthesised iminophosphoranes were only moderately stable when not kept under nitrogen, their reaction with air leading quantitatively after few hours to phosphine oxide **12** and the corresponding aniline derivative.

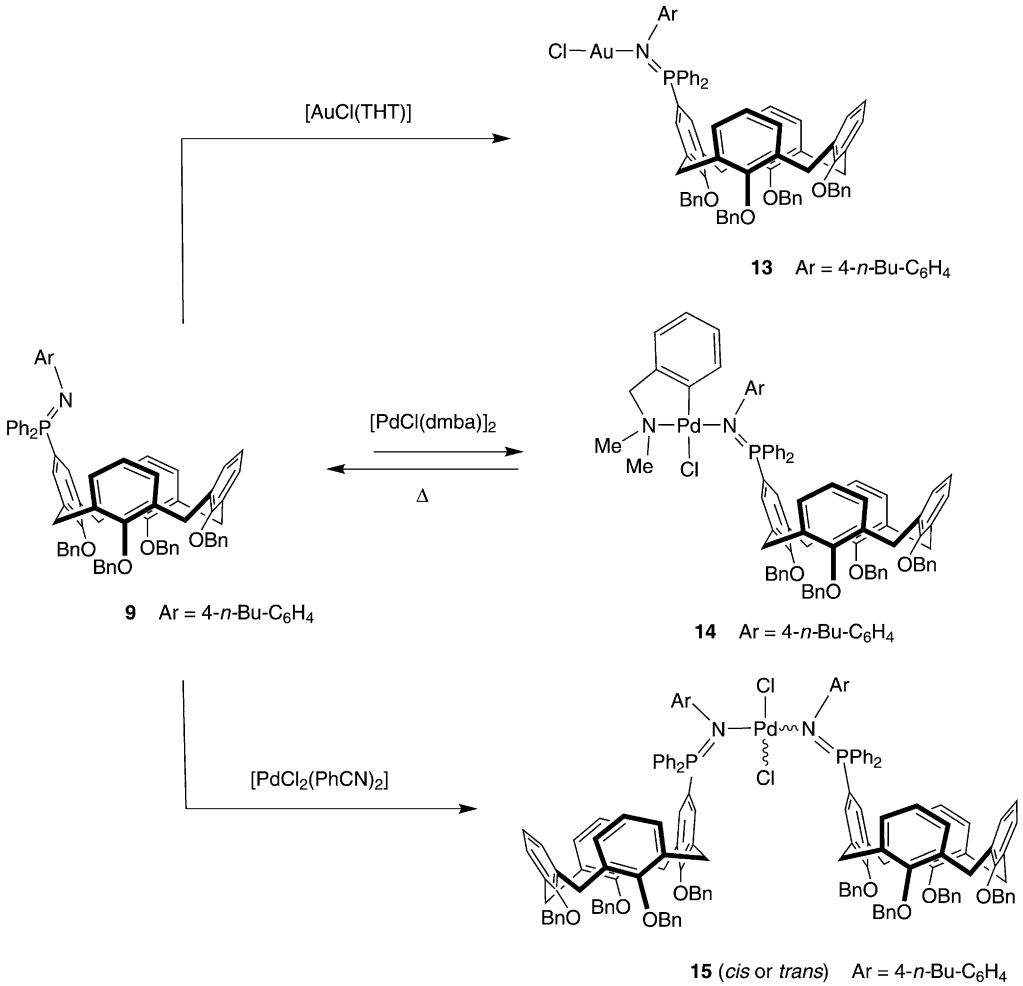


1

Ar = 2,4,5-Me_3-C_6H_2 **7**
= 2,6-(*i*-Pr)$_2$-C_6H_3 **8**
= 4-*n*-Bu-C_6H_4 **9**
= 2-MeO-C_6H_4 **10**
= 4-MeO-C_6H_4 **11**

Scheme 2. Synthesis of iminophosphoranes **7**–**11**.

The five iminophosphoranes were found to be suitable for metal binding (Scheme 3). For example, iminophosphorane **9** gave quantitatively complex **13** when reacted with [AuCl(THT)] (THT: tetrahydrothiophene). Reaction of **9** with $[PdCl(dmba)]_2$ (dmbaH: *N,N*-dimethylbenzylamine) led to a partial conversion to the complex [PdCl(dmba)(**9**)] (**14**) (see the Supporting Information, Schemes S-2 and S-3). Reaction of two equiv. of **9** with $[PdCl_2(PhCN)_2]$ gave the



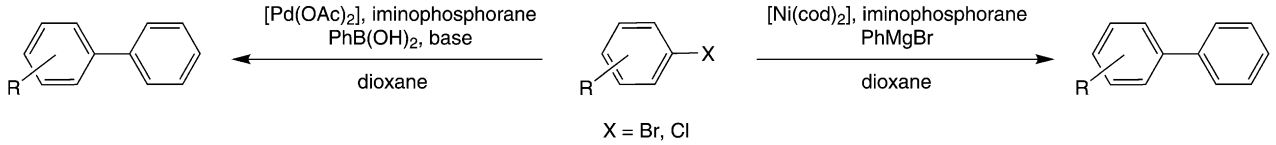
13 Ar = 4-*n*-Bu-C_6H_4

9 Ar = 4-*n*-Bu-C_6H_4

14 Ar = 4-*n*-Bu-C_6H_4

15 (*cis* or *trans*) Ar = 4-*n*-Bu-C_6H_4

Scheme 3. Synthesis of complexes **13**–**15**.



Scheme 4. Suzuki–Miyaura and Kumada–Tamao–Corriu cross-coupling reactions.

bis-iminophosphorane complex **15**, which in contrast to **14** did not undergo ligand dissociation in solution. The ^{31}P NMR spectrum revealed that the phosphorus signal of ligand **9** had undergone a downfield shift of 30.8 ppm upon metal complexation ($\delta = 29.9$ ppm in **15**). Whether this shift is typical of a *cis* or *trans* complex species is unknown. Dissociation of both iminophosphorane ligands was observed upon addition of PPh_3 or tetrahydrothiophene in excess to **15**, but the complex was stable in tetrahydrofuran as well as dioxane.

Iminophosphoranes **7**–**11** were assessed both in palladium-catalysed Suzuki–Miyaura and nickel-catalysed Kumada–Tamao–Corriu cross-coupling reactions (Scheme 4). Each catalyst was generated *in situ* by mixing the ligand and a metal precursor.

Suzuki–Miyaura Cross-Coupling with Aryl Bromides

These runs were carried out in dioxane at 100 °C for 1 hour using two equivalents of iminophosphorane **9** per palladium atom. The highest conversion observed for 4-bromoanisole (91.1%) was obtained in the presence of NaH as base (Table 1, entries 1–5 and 8). No significant differences in activity were seen for ligand/palladium ratios between 1 and 2.5, indicating that the active species contains only one iminophosphorane ligand (Table 1, entries 6–9). A large excess of ligand inhibited the catalytic reaction (Table 1, entry 10). In view of these findings, the following runs were carried out with an L:Pd ratio of 2:1.

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

Entry	**9**/Pd	Base	Conversion [%]
1	2/1	K_3PO_4	61.3
2	2/1	Cs_2CO_3	50.1
3	2/1	K_2CO_3	42.1
4	2/1	KOH	40.6
5	2/1	NEt_3	15.5
6	1/1	NaH	84.3
7	1.5/1	NaH	90.8
8	2/1	NaH	91.1
9	2.5/1	NaH	88.2
10	5/1	NaH	54.6

[a] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol%), **9**, ArBr (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 being based on decane.

Using the optimal conditions defined above (2 equiv. of ligand per palladium atom, NaH, 100 °C, 1 h reaction time), the following runs were carried out using an ArBr/Pd ratio of 10^5 (10 ppm of palladium). The highest conversions were obtained with ligand **10** (Table 2). For example, while this ligand gave full conversion of 2-bromo-6-methoxynaphthalene and 1-bromonaphthalene (Table 2, entries 3 and 4), the less reactive substrates 2-bromoanisole and 2-bromotoluene resulted in conversions of 59.7 and 76.4%, respectively (Table 2, entries 2 and 6).

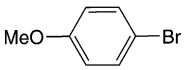
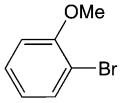
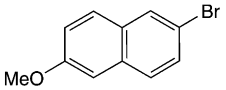
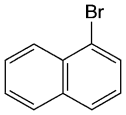
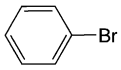
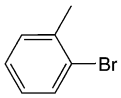
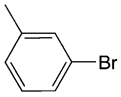
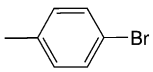
Another series of runs was carried out with iminophosphoranes **9** and **10** by applying a palladium loading of only 1 ppm (ArBr/Pd ratio of 10^6) and (Scheme 5 and Supporting Information, Table S-3). With the unhindered substrates, the observed activities were higher than 2.1×10^5 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}. The highest activity was found in the arylation of 2-bromo-6-methoxynaphthalene with ligand **10** [TOF = 4×10^5 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}].

To complete the evaluation of the ligands, the sterically unhindered substrates were also tested at *room temperature*. For each individual substrate, the catalytic tests were carried out with the ligand that gave the highest conversion when operating at 100 °C (Table 3). The 1 h runs were achieved with a palladium loading of 0.1 mol%. Under these conditions, the observed conversions lay in the range 40.2–86.6%. The highest conversion was observed in the arylation of 2-bromo-6-methoxynaphthalene (Table 3, entry 3). Full conversions were reached after 2–3 h (Supporting Informatiion, Table S-4). The catalytic system still remained satisfactory when using a catalyst loading of only 0.01 mol% (Table 3).

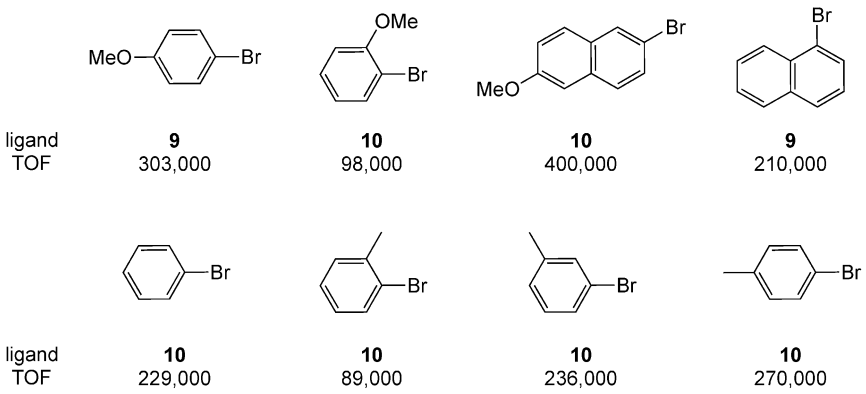
Suzuki–Miyaura Cross-Coupling with Aryl Chlorides

The two iminophosphoranes bearing *p*-butylphenyl (**9**) and *o*-anisyl (**10**) substituents, respectively, were tested in the cross-coupling of $PhB(OH)_2$ with aryl chlorides (Table 4). Applying a palladium loading of 1 mol% resulted in good conversions after 5 h for the activated aryl chlorides (1-chloro-4-nitrobenzene, 4-chloroacetophenone and 4-chlorobenzonitrile;

Table 2. Palladium-catalysed Suzuki–Miyaura cross-coupling of aryl bromides using iminophosphoranes **7**-**11** and applying a ArBr/Pd ratio of 10^5.[a]

Entry	ArBr		Iminophosphorane				
			7	**8**	**9**	**10**	**11**
1		conv. [%]	80.8	72.9	91.1	87.1	81.7
2		conv. [%]	46.1	27.3	40.2	59.7	5.8
3		conv. [%]	100	80.0	100	100	100
4		conv. [%]	65.6	55.8	100	100	30.5
5		conv. [%]	87.6	39.9	44.3	99.7	29.5
6		conv. [%]	42.3	65.9	38.5	76.4	34.3
7		conv. [%]	55.8	68.3	86.8	100	41.5
8		conv. [%]	90.4	75.5	93.7	98.5	70.9

[a] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol%), iminophosphorane (1×10^{-5} mmol, 2×10^{-3} mol%), 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 being based on decane.



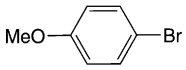
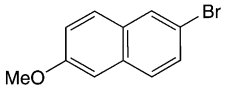
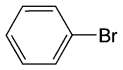
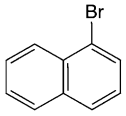
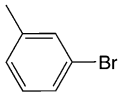
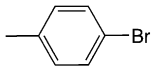
Scheme 5. Maximal activities observed for the cross-coupling product formed in the Suzuki–Miyaura reaction using 1 ppm of $[Pd(OAc)_2]$ (*cf.* Supporting Information, Table S-3). TOFs expressed in $mol(ArBr)\cdot mol(Pd)^{-1}\cdot h^{-1}$.

Table 4, entries 1, 2, 4, 5, 7 and 8) and after 24 h for the deactivated ones (4-chloroanisole and 4-chlorotoluene; Table 4, entries 9–13). When the tests with the activated aryl chlorides were carried at room temperature, the conversions dropped significantly (Table 4, entries 3, 6 and 9).

Kumada–Tamao–Corriu Cross-Coupling with Aryl Bromides

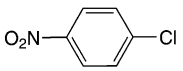
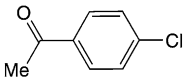
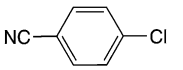
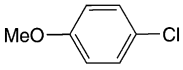
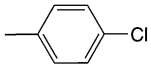
For the Kumada–Tamao–Corriu cross-coupling of aryl bromides, the catalytic system was generated *in situ* starting from $[Ni(cod)_2]$ and iminophosphoranes **7**, **10** or **11** in 1,4-dioxane at 100 °C. To prevent decomposition of the active species, the runs were performed

Table 3. Suzuki–Miyaura cross-coupling carried out at room temperature.[a]

Entry	ArBr	Iminophosphorane	$[Pd(OAc)_2]$ [mol%]	Conv. [%]	TOF [mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}]
1		**9**	0.1	41.7	420
2			0.01	12.0	1200
3		**10**	0.1	86.6	870
4			0.01	48.2	4820
5		**10**	0.1	67.1	670
6			0.01	20.8	2080
7		**9**	0.1	52.0	520
8			0.01	15.9	1590
9		**10**	0.1	40.2	400
10			0.01	12.0	1200
11		**10**	0.1	78.0	780
12			0.01	29.8	2980

[a] $[Pd(OAc)_2]$, iminophosphorane (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), 25 °C, 1 h.

Table 4. Palladium-catalysed Suzuki–Miyaura cross-coupling of aryl chlorides.

Entry	ArCl	Iminophosphorane	Temperature [°C]	Time [h]	Conversion [%]
1[a]		**9**	100	5	87.6
2[a]		**10**	100	5	78.3
3[b]		**9**	25	24	28.9
4[a]		**9**	100	5	85.7
5[a]		**10**	100	5	67.5
6[b]		**9**	25	24	14.2
7[a]		**9**	100	5	76.2
8[a]		**10**	100	5	73.1
9[b]		**9**	25	24	11.3
10[a]		**9**	100	24	73.3
11[a]		**10**	100	24	66.0
12[a]		**9**	100	24	66.3
13[a]		**10**	100	24	51.0

[a] $[Pd(OAc)_2]$ (2.5×10^{-3} mmol, 1 mol%), iminophosphorane (5×10^{-3} mmol, 2 mol%), dioxane (0.75 mL), 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), decane (0.025 mL). The conversions were determined by GC, the calibrations being based on decane.

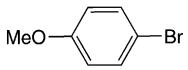
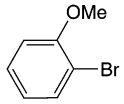
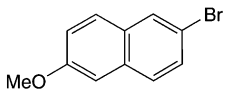
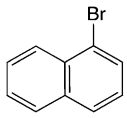
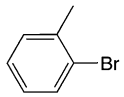
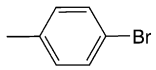
[b] $[Pd(OAc)_2]$ (7.5×10^{-3} mmol, 3 mol%), iminophosphorane (1.5×10^{-2} mmol, 6 mol%).

using two equiv. of ligand per nickel. Applying a ArBr/Ni ratio of 10^5 (10 ppm of nickel), resulted in moderate to good conversions after 1 h reaction time (Table 5). The highest activities were obtained in the arylation of 2-bromo-6-methoxynaphthalene and 1-bromonaphthalene, which were converted in 68.8 and 85.6% yield, respectively (Table 5, entries 3 and 5). Reducing the metal loading to 1 ppm led to activities that remained remarkably high, 3.04×10^5 mol(ArBr)·mol(Ni)$^{-1}$·h^{-1} for 2-bromo-6-methoxynaphthalene and 3.9×10^5 mol(ArBr)·mol(Ni)$^{-1}$·h^{-1} for 1-bromonaphthalene (Table 5, entries 4 and 6).

Comparison with Other Ligands

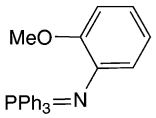
In a recent study, we have shown that calixarenyl-monophosphine **1** is *ca.* 2.3 times more active than PPh_3 in the cross-coupling of 4-bromotoluene with phenylboronic acid.[17] Interestingly, the arylation of 4-bromotoluene led to higher activities when iminophosphorane **10** [2.7×10^5 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}] was employed instead of calixarenyl-monophosphine **1** [TOF = 1.52×10^5 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}] (Table 6, entries 2 and 3). For comparison, the runs carried out with the PPh_3-derived iminophosphorane

Table 5. Nickel-catalysed Kumada–Tamao–Corriu cross-coupling of aryl bromides.

Entry	ArBr		Iminophosphoranes 7	10	11
1[a]		conv. [%]	37.9	46.1	42.6
		TOF	37900	46100	42600
2[a]		conv. [%]	20.8	32.7	23.9
		TOF	20800	32700	23900
3[a]		conv. [%]	68.8	60.7	68.7
		TOF	68800	60700	68700
4[b]		conv. [%]	30.4	17.3	29.7
		TOF	304000	173000	297000
5[a]		conv. [%]	77.7	85.6	85.5
		TOF	77700	85600	85500
6[b]		conv. [%]	34.4	38.1	39.0
		TOF	344000	381000	390000
7[a]		conv. [%]	19.5	20.5	22.4
		TOF	19500	20500	22400
8[a]		conv. [%]	49.3	45.7	45.5
		TOF	49300	45700	45500

[a] $[Ni(cod)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol%), iminophosphorane (1×10^{-5} mmol, 2×10^{-3} mol%), dioxane (1.5 mL), ArBr (0.5 mmol), PhMgBr (1 mmol), decane (0.050 mL), 100 °C, 1 h. The conversions were determined by GC, the calibrations being based on decane. TOFs expressed in mol(ArBr)·mol(Ni)$^{-1}$·h^{-1}.

[b] $[Ni(cod)_2]$ (5×10^{-7} mmol, 1×10^{-4} mol%), iminophosphorane (1×10^{-6} mmol, 2×10^{-4} mol%).



16

Figure 1. Ligand **16** used for ranking the calixaryl-iminophosphoranes.

16 (Figure 1) led to a TOF of only 2.41×10^4 mol(ArBr)·mol(Pd)$^{-1}$·h^{-1}, which corrresponds to a 10-fold lower activity than that of **10** (Table 6, entries 3 and 5). We also observed that the catalytic reactions performed in the absence of **10** but in the presence of its hydrolysis products (namely **12** or *o*-methoxyaniline) led to considerably lower activities: thus, with phosphine oxide **12** the reaction rate dropped by a factor of 5. With *o*-methoxyaniline, the activity was reduced by a factor of 100 (Table 6, entries 4 and 6). These findings are a good indication that during the catalytic runs with iminophosphoranes **7**–**11**, these ligands had not undergone hydrolysis. Similar observations were made for the nickel-catalysed Kumada–Tamao–Corriu coupling reactions (Table 6, entries 7–12).

Is it possible to rationalise the high activities observed with iminophosphoranes **7**–**11** compared to those with PPh_3? In principle, we have to distinguish between the Suzuki–Miyaura cross-coupling and the Kumada–Tamao–Corriu reaction, the corresponding mechanisms and energetics being different. It is now well-accepted that in the former reaction, bulky ligands, notably phosphines, promote the oxidative addition step (which is the key step) by facilitating the formation of mono-ligand Pd(0)-arene complexes,

Table 6. Suzuki–Miyaura and Kumada–Tamao–Corriu cross-coupling reactions - comparison with other ligands.

Entry	Ligand	Metal precursor [mol%]	Conversion [%]	TOF [mol(ArBr)·mol(M)$^{-1}$·h^{-1}]
$[Pd(OAc)_2]$ and 4-bromotoluene[a]				
1	/	1×10^{-2}	16.7	1670
2	**1**	1×10^{-4}	15.2	152000
3	**10**	1×10^{-4}	27.0	270000
4	**12**	1×10^{-3}	49.3	49300
5	**16**	1×10^{-3}	24.1	24100
6	*o*-MeO-C_6H_4-NH_2	1×10^{-2}	27.3	2730
$[Ni(cod)_2]$ and 1-bromonaphthalene[b]				
7	/	1×10^{-2}	56.0	5600
8	**1**	1×10^{-4}	38.6	386000
9	**10**	1×10^{-4}	38.1	381000
10	**12**	1×10^{-3}	53.0	53000
11	**16**	1×10^{-4}	5.6	56000
12	*o*-MeO-C_6H_4-NH_2	1×10^{-2}	63.1	6310

[a] $[Pd(OAc)_2]$, ligand (2 equiv./Pd), 4-bromotoluene (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 being based on decane.

[b] $[Ni(cod)_2]$, ligand (2 equiv./Ni), 1-bromonaphthalene (0.5 mmol), PhMgBr (1.0 mmol), dioxane (1.5 mL), decane (0.050 mL), 100 °C, 1 h.

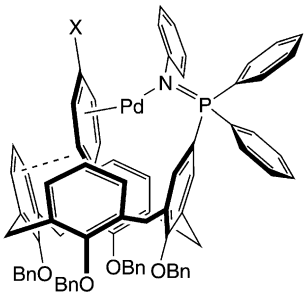


Figure 2. Proposed mono-iminophosphorane palladium(0) *endo*-intermediate formed in cross-coupling reactions before the oxidative addition step.

which are more reactive than the related Pd complexes bearing two ligands (in equilibrium with the mono-ligated ones).[22–28] Molecular modelling revealed that the above iminophosphoranes (L) can result in [LPd(0)(arene)] fragments with two distinct structures, namely those with the coordinated "Pd(0)-(arene)" moiety located inside the cavity and those with it lying outside. The crowding about the metal centre is substantially larger in the isomers with the "Pd(arene)" entrapped in the cavity (Figure 2) than in the *exo*-species, so that *endo*-coordination should favour the formation of mono-ligated intermediates. Furthermore, preliminary calculations showed that in *endo* intermediates, pi–pi stacking interactions may occur between the coordinated ArX unit and a phenoxy ring of the cavity wall. This supramolecular interaction may thus directly contribute to the stabilisation of *endo*-coordinated species, and indirectly increase the proportion of mono-ligated species. Interestingly, we observed that in the presence of calixarene **10**, the arylation of 1-bromo-3,5-di-*tert*-butylbenzene, a *large* substrate which cannot enter the cavity, occurred with only 65.3% conversion under the conditions described in Table 7, *vs.* 98.8% in the presence of the cavity-free iminophosphorane **16** (Table 7, entries 1 and 2). These findings support the idea that supramolecular assistance of the cavity-receptor interaction may be helpful for increasing the reaction rate of Suzuki–Miyaura reactions performed with "small" aromatic substrates.

Table 7. Suzuki–Miyaura cross-coupling of 1-bromo-3,5-di-*tert*-butylbenzene with phenylboronic acid - comparison with other ligands.[a]

Entry	Ligand	Conversion [%]
1	**10**	65.3
2	**16**	98.8

[a] $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol%), ligand (1×10^{-4} mmol, 2×10^{-2} mol%), 1-bromo-3,5-di-*tert*-butylbenzene (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 being based on decane.

The results obtained in the Kumada–Tamao–Corriu reactions further demonstrate the high efficiency of the calixarene derivatives **7**–**11** in cross-coupling reactions. Any explanation of their high efficiency can only be speculative, as in this reaction the *first, irreversible step* is substrate coordination, and not oxidative addition.[29] Possibly, (Ar−Ar′) product dissociation from the nickel centre is significantly accelerated by steric effects for those bis-aryls that have been generated in an *endo*-complex. In view of the receptor properties of calixarenes **7**–**11**, it is likely that, as for the above Pd catalysts, the formation of *endo*-Ni-(ArX) complexes occurring after product decomplexation can be supramolecularly assisted. Of course, for such *endo* species, mono-ligated intermediates would again be favoured, these necessarily rendering the transformation Ni(ArX)→Ni(Ar)(X) more facile.[30]

Conclusions

In summary, we have described the synthesis of the first mono-iminophosphoranes based on a calix[4]arene platform. Combined with palladium or nickel, these led to remarkably efficient catalysts for Suzuki–Miyaura (Pd) as well as Kumada–Tamao–Corriu (Ni) cross-coupling reactions. In both reactions, up to tenfold enhancement in catalytic activity was achieved with respect to catalysts based on the cavity-free iminophosphorane $Ph_3P{=}N(o\text{-anisyl})$. The origin of their catalytic performance is likely to arise from their ability to form complexes having cavity-entrapped MArX units that result in a highly crowded metal environment and therefore favour the formation of mono-ligated intermediates, these being more reactive than bis-ligated complexes. A feature which should increase the formation of *endo*-complexes, whatever the metal, is the cavity's ability to supramolecularly bind the aromatic substrate. In the case of the Kumada–Tamao–Corriu reaction, the key step in the catalytic cycle is the formation of an "Ni(ArX)" moiety after decomplexation of the Ar−Ar′ product, this being facilitated with intermediates having *endo*-located metal centres. Further studies are aimed at exploiting the supramolecular potential of iminophosphoranes built on macrocyclic platforms in carbon-carbon bond forming reactions.

Experimental Section

General Experimental Methods

All reactions were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods

and distilled immediately prior to use. Routine ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with an FT Bruker AV-300. ^{1}H NMR spectra were referenced to residual protiated solvent (7.16 ppm for C_6D_6 and 7.26 ppm for $CDCl_3$), ^{13}C NMR chemical shifts are reported relative to deuterated solvent (128.0 ppm for C_6D_6 and 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. Infrared spectra were recorded with a Bruker FT-IR Alpha-P spectrometer. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm, 0.25 μm film thickness). The elemental analysis was performed by the Service de Microanalyse, Université de Strasbourg. 5-Diphenylphosphino-25,26,27,28-tetrabenzyloxycalix[4]arene (**1**)[17] and [Ni(cod)$_2$][31] were prepared according to literature procedures. Aryl azides were synthesized according to a procedure based on the use of TfN_3.[32]

Although we have not experienced any problems in handling TfN_3, care should be taken due to its potentially explosive nature. This reagent should be kept in solution and used immediately after its synthesis.

NMR spectral data of 2-azido-1,3,5-trimethylbenzene (**2**),[33] 1-azido-2,6-diisopropylbenzene (**3**),[32] 1-azido-4-butylbenzene (**4**),[32] 1-azido-2-methoxy-benzene (**5**),[33] and 1-azido-4-methoxybenzene (**6**)[32] were in agreement with those reported in the literature.

General Procedure for the Synthesis of 5-(Aryliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix[4]arenes (7–11)

To a solution of **1** (1.00 mmol) in toluene (10 mL) was added a solution of aryl azide (1.00 mmol) in toluene (10 mL). After stirring the solution for 16 h at 60 °C, the reaction mixture was evaporated to dryness under vacuum to afford quantitatively the iminophosphorane.

5-(Mesityliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix[4]arene (7): ^{1}H NMR (300 MHz, C_6D_6): δ = 7.76–7.69 (4H, arom. CH), 7.34–7.28 (6H, arom. CH), 7.20–6.99 (24H, arom. CH), 6.74 (d, 2H, arom. CH, ^{3}J = 7.5 Hz), 6.61–6.54 (5H, arom. CH), 6.35–6.32 (2H, arom. CH), 4.97 (s, 2H, CH_2Ph), 4.93 (s, 2H, CH_2Ph), 4.94 and 4.89 (AB spin system, 4H, CH_2Ph, ^{2}J = 11.5 Hz), 4.33 and 2.94 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.4 Hz), 4.18 and 2.67 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.4 Hz), 2.29 (s, 6H, *o*-CH_3 of mesityl), 2.12 (s, 3H, *p*-CH_3 of mesityl); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ = 158.14 (d, arom. $C_{quart.}$-O, $^{4}J_{P,C}$ = 3.1 Hz), 155.86, 155.44 (2 s, arom. $C_{quart.}$-O), 145.89–122.88 (arom. C), 76.95 (s, OCH_2Ph), 76.77 (s, OCH_2Ph), 76.66 (s, OCH_2Ph), 31.86 (s, ArCH_2Ar), 31.76 (s, ArCH_2Ar), 22.05 (s, *o*-CH_3 of mesityl), 21.08 (s, *p*-CH_3 of mesityl); $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6): δ = −10.8 (s, PPh_2); IR: ν = 1329 cm^{-1} (P=N); anal. calcd. for $C_{77}H_{68}O_4PN$ (*M*r = 102.34): C 83.90, H 6.22, N 1.27%; found: C 84.01, H 6.25, N 1.30%; MS (Maldi-TOF): *m*/*z* = 1102.39 $[M+H]^+$ expected isotopic profile.

5-(2,6-Diisopropylphenyliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix [4]arene (8): ^{1}H NMR (300 MHz, C_6D_6): δ = 7.68–7.62 (4H, arom. CH), 7.33–7.28 (6H, arom. CH), 7.24 (d, 2H, arom. CH, ^{3}J = 7.7 Hz), 7.16–7.00 (23H, arom. CH), 6.78 (d, 2H, arom. CH, ^{3}J = 7.3 Hz), 6.67–6.50 (5H, arom. CH), 6.42–6.39 (2H, arom. CH), 4.99 (s, 2H, CH_2Ph), 4.96 (s, 2H, CH_2Ph), 4.92 and 4.86 (AB spin system, 4H, CH_2Ph, ^{2}J = 11.6 Hz), 4.33 and 2.93 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.4 Hz), 4.17 and 2.69 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.5 Hz), 3.68 (hept, 2H, CH-$(CH_3)_2$, ^{3}J = 6.8 Hz), 1.20 (d, 12H, CH(CH_3)$_2$, ^{3}J = 6.8 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 158.21 (d, arom. $C_{quat.}$-O, $^{4}J_{PC}$ = 3.1 Hz), 155.95, 155.41 (2 s, arom. $C_{quat.}$-O), 145.64–119.55 (arom. C), 76.99 (s, OCH_2Ph), 76.89 (s, OCH_2Ph), 76.59 (s, OCH_2Ph), 31.86 (s, ArCH_2Ar), 29.13 (s, CH(CH$_3$)$_2$), 24.18 (s, CH(CH_3)$_2$); $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6): δ = −8.6 (s, PPh_2); IR: ν = 1327 cm^{-1} (P=N); anal. calcd. for $C_{80}H_{74}O_4PN$ (*M*r = 1144.42): C 83.96, H 6.52, N 1.22%; found: C 84.02, H 6.38, N 1.10%; MS (Maldi-TOF): *m*/*z* = 1141.41 $[M+H]^+$ expected isotopic profile.

5-(4-Butylphenyliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix[4]arene (9): ^{1}H NMR (300 MHz, C_6D_6): δ = 7.77–7.71 (4H, arom. CH), 7.32–7.26 (6H, arom. CH), 7.19–7.00 (26H, arom. CH), 6.77–6.68 (4H, arom. CH), 6.61 (t, 2H, arom. CH, ^{3}J = 7.5 Hz), 6.54 (t, 1H, arom. CH, ^{3}J = 7.5 Hz), 6.41 (d, 2H, arom. CH, ^{3}J = 6.6 Hz), 5.08 (s, 4H, CH_2Ph), 4.84 (s, 2H, CH_2Ph), 4.70 (s, 2H, CH_2Ph), 4.33 and 2.93 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.3 Hz), 4.15 and 2.64 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.3 Hz), 2.57 (t, 2H, $C_6H_4CH_2$, ^{3}J = 7.3 Hz), 1.59 (quint, 2H, $C_6H_4CH_2CH_2$, ^{3}J = 7.3 Hz), 1.30 (hex, 2H, CH_2CH_3, ^{3}J = 7.2 Hz), 0.84 (t, 3H, CH_2CH_3, ^{3}J = 7.3 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ = 158.24 (d, $C_{quat.}$-O, $^{4}J_{P,C}$ = 3.1 Hz), 155.66, 155.51 (2s, $C_{quat.}$-O), 150.09–123.00 (arom. C), 77.38 (s, OCH_2Ph), 77.11 (s, OCH_2Ph), 76.44 (s, OCH_2Ph), 35.58 (s, $C_6H_4CH_2$), 34.62 (s, $C_6H_4CH_2CH_2$), 31.93 (s, ArCH_2Ar), 31.63 (s, ArCH_2Ar), 22.76 (s, CH_2CH$_3$), 14.29 (s, CH$_2$CH_3); $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6): δ = −0.9 (s, PPh_2); IR: ν = 1329 cm^{-1} (P=N); anal. calcd. for $C_{78}H_{70}O_4PN$ (*M*r = 1116.37): C 83.92, H 6.32, N 1.25%; found: C 84.04, H 6.23, N 1.12%; MS (Maldi-TOF): *m*/*z* = 1116.39 $[M+H]^+$ expected isotopic profile.

5-(2-Methoxyphenyldiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix[4]arene (10): ^{1}H NMR (300 MHz, C_6D_6): δ = 7.79–7.73 (4H, arom. CH), 7.33–7.27 (9H, arom. CH), 7.16–7.00 (21H, arom. CH), 6.84–6.70 (6H, arom. CH), 6.61 (t, 2H, arom. CH, ^{3}J = 7.0 Hz), 6.58 (t, 1H, arom. CH, ^{3}J = 7.5 Hz), 6.40 (d, 2H, arom. CH, ^{3}J = 6.6 Hz), 5.06 (s, 4H, CH_2Ph), 4.87 (s, 2H, CH_2Ph), 4.73 (s, 2H, CH_2Ph), 4.33 and 2.94 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.3 Hz), 4.16 and 2.64 (AB spin system, 4H, ArCH_2Ar, ^{2}J = 13.3 Hz), 3.31 (s, 3H, CH_3OC$_6$H$_4$); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ = 157.94 (d, arom. $C_{quart.}$-O, $^{4}J_{P,C}$ = 3.1 Hz), 155.68, 155.48 (2s, arom. $C_{quart.}$-O), 153.76–112.20 (arom. C), 77.29 (s, OCH_2Ph), 76.99 (s, OCH_2Ph), 76.50 (s, OCH_2Ph), 54.91 (s, CH_3OC$_6$H$_4$), 31.91 (s, ArCH_2Ar), 31.67 (s, ArCH_2Ar); $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6): δ = 0.0 (s, PPh_2); IR: ν = 1327 cm^{-1} (P=N); anal. calcd. for $C_{75}H_{64}O_5PN$ (*M*r = 1090.29): C 82.62, H 5.92, N 1.28%; found: C 82.75, H 5.79, N 1.21%; MS (Maldi-TOF): *m*/*z* = 1090.30 $[M+H]^+$ expected isotopic profile.

5-(4-Methoxyphenyliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxycalix[4] arene (11): ^{1}H NMR (300 MHz, C_6D_6): δ = 7.78–7.71 (4H, arom. CH), 7.32–7.27 (6H, arom. CH), 7.16–7.00 (24H, arom. CH), 6.87 (d, 2H, arom. CH, ^{3}J = 6.3 Hz), 6.77–6.68 (4H, arom. CH), 6.61 (t, 2H, arom. CH, ^{3}J = 7.4 Hz), 6.54 (t, 1H, arom. CH, ^{3}J =

7.3 Hz), 6.40 (d, 2H, arom. CH, $^3J=6.4$ Hz), 5.08 (s, 4H, CH_2Ph), 4.84 (s, 2H, CH_2Ph), 4.71 (s, 2H, CH_2Ph), 4.32 and 2.93 (AB spin system, 4H, ArCH_2Ar, $^2J=13.3$ Hz), 4.15 and 2.64 (AB spin system, 4H, ArCH_2Ar, $^2J=13.3$ Hz), 3.43 (s, 6H, CH_3OC$_6$H$_4$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta=158.25$ (d, arom. $C_{quart.}$-O, $^4J_{P,C}=2.9$ Hz), 155.65, 155.52 (2s, arom. $C_{quart.}$-O), 152.69–114.63 (arom. C), 77.38 (s, OCH_2Ph), 77.11 (s, OCH_2Ph), 76.43 (s, OCH_2Ph), 55.33 (s, CH_3OC$_6$H$_4$), 31.92 (s, ArCH_2Ar), 31.65 (s, ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta=-1.2$ (s, PPh$_2$); IR: $\nu=1327$ cm^{-1} (P=N); anal. calcd. for. $C_{75}H_{64}O_5PN$ ($Mr=1090.29$): C 82.62, H 5.92, N 1.28%; found: C 82.51, H 5.98, N 1.33%; MS (Maldi-TOF): $m/z=1090.30$ $[M+H]^+$ expected isotopic profile.

5-Diphenylphosphinoyl-25,26,27,28-tetrabenzyloxycalix[4]arene (12): To a solution of 5-diphenylphosphino-25,26,27,28-tetrabenzyloxycalix[4]arene (**1**) (0.5 mmol) in CH_2Cl_2 (10 mL) was added H_2O_2 (30% in water, 4 mL, 5.0 mmol). The resulting solution was stirred at room temperature for 2 h. The resulting mixture was treated with a mixture of CH_2Cl_2 (10 mL) and water (20 mL). After extraction of the aqueous layer with CH_2Cl_2 (2×10 mL), the organic phases were combined. The resulting solution was washed with water (2×10 mL), then dried over Na_2SO_4 and evaporated under reduced pressure to afford quantitatively phosphine oxide **12** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.43$–7.23 (32H, arom. CH), 6.84 (d, 2H, arom. CH, $^3J=12.3$ Hz), 6.74–6.70 (3H, arom. CH), 6.59–6.53 (2H, arom. CH), 6.44 (d, 2H, arom. CH, $^3J=7.5$ Hz), 5.08 and 5.01 (AB spin system, 4H, CH_2Ph, $^2J=11.6$ Hz), 4.94 (s, 2H, CH_2Ph), 4.91 (s, 2H, CH_2Ph), 4.29 and 3.02 (AB spin system, 4H, ArCH_2Ar, $^2J=13.3$ Hz), 4.14 and 2.83 (AB spin system, 4H, ArCH_2Ar, $^2J=13.4$ Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta=158.75$, 155.46, 155.10 (3s, arom. $C_{quart.}$-O), 137.63–122.49 (arom. C), 77.07 (s, OCH_2Ph), 76.75 (s, OCH_2Ph), 76.34 (s, OCH_2Ph), 31.45 (s, ArCH_2Ar), 31.36 (s, ArCH_2Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): $\delta=29.1$ (s, O=PPh$_2$); anal. calcd. for. $C_{68}H_{57}O_5P$ ($Mr=985.15$): C 82.90, H 5.83%; found: C 83.03, H 5.71%.

N-Chlorido-{5-(4-butylphenyliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyl-oxycalix[4]arene}gold(I) (13)

To a stirred solution of **9** (0.100 g, 0.09 mmol) in CH_2Cl_2 (15 mL) was added a solution of [AuCl(THT)] (0.029 g, 0.09 mmol) in THF (5 mL). After stirring for 5 h, the solution was concentrated to 1 mL. Addition of *n*-hexane afforded **13** as a white solid; yield: 0.111 g (93%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=7.44$ (d, 2H, arom. CH, $^3J=11.7$ Hz), 7.41 (dd, 2H, arom. CH, $^3J=11.7$ Hz, $^4J=1.2$ Hz), 7.29–7.24 (8H, arom. CH), 7.13–6.93 (22H, arom. CH), 6.75 (d, 4H, arom. CH, $^3J=7.8$ Hz), 6.63 (t, 2H, arom. CH, $^3J=7.3$ Hz), 6.47 (dd, 2H, arom. CH, $^3J=7.5$ Hz, $^4J=1.8$ Hz), 6.36 (d, 2H, arom. CH, $^3J=7.8$ Hz), 6.04 (t, 1H, arom. CH, $^3J=7.5$ Hz), 5.14 and 5.07 (AB spin system, 4H CH_2Ph, $^2J=12.0$ Hz), 4.77 (s, 2H, CH_2Ph), 4.70 (s, 2H, CH_2Ph), 4.26 and 2.87 (AB spin system, 4H, ArCH_2Ar, $^2J=13.3$ Hz), 4.03 and 2.60 (AB spin system, 4H, ArCH_2Ar, $^2J=13.6$ Hz), 2.36 (t, 2H, C$_6$H$_4$CH_2, $^3J=7.6$ Hz), 1.49–1.42 (2H, C$_6$H$_4$CH$_2$CH_2), 1.30–1.20 (2H, CH_2CH$_3$), 0.84 (t, 3H, CH$_2$CH_3, $^3J=7.1$ Hz); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta=159.91$ (d, $C_{quat.}$-O, $^4J_{P,C}=2.5$ Hz), 155.88, 155.77 (2s, $C_{quat.}$-O), 146.05–119.10 (arom. C), 78.12 (s, OCH_2Ph), 78.02 (s, OCH_2Ph), 76.61 (s, OCH_2Ph), 35.51 (s, C$_6$H$_4$CH_2), 34.40 (s, C$_6$H$_4$CH$_2$CH_2), 32.13 (s, ArCH_2Ar), 31.82 (s, ArCH_2Ar), 23.40 (s, CH_2CH$_3$), 14.71 (s, CH$_2$CH_3); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta=33.4$ (s, PPh$_2$); anal. calcd. for $C_{78}H_{70}AuClNO_4P$ ($Mr=1348.79$): C 69.46, H 5.23, N 1.04%; found: C 69.58, H 5.47, N 0.88%.

Reaction of 9 with [PdCl(*o*-C$_6$H$_4$CH$_2$NMe$_2$]$_2$

To a stirred solution of **9** (0.050 g, 0.045 mmol) in CH_2Cl_2 (5 mL) was added a solution of [PdCl(*o*-C$_6$H$_4$CH$_2$NMe$_2$]$_2$ (0.012 g, 0.022 mmol) in CH_2Cl_2 (5 mL). After stirring for 0.5 h, the solvent was removed under vacuum to afford a mixture of complex **14** and free ligand **9**. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): $\delta=26.1$ (s, N=PPh$_2$ coordinated to Pd) and −0.9 (s br, N=PPh$_2$ free); MS (Maldi-TOF): $m/z=1355.44$ $[M-Cl]^+$ expected isotopic profile for **14** (*cf.* the Supporting Information).

N,N′-Dichlorido-bis{5-(4-butylphenyliminodiphenylphosphoranyl)-25,26,27,28-tetrabenzyloxy-calix[4]arene}palladium(II) (15)

To a stirred solution of **9** (0.050 g, 0.045 mmol) in CH_2Cl_2 (10 mL) was added a solution of [PdCl$_2$(PhCN)$_2$]$_2$ (0.012 g, 0.022 mmol) in CH_2Cl_2 (5 mL). After stirring for 0.5 h, the solution was concentrated to *ca.* 1 mL. Addition of *n*-hexane (20 mL) afforded **15** as a brown solid; yield: 0.046 g (75%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=7.97$ (d, 4H, arom. CH, $^3J=8.4$ Hz), 7.79 (d, 4H, arom. CH, $^3J=8.1$ Hz), 7.76 (d, 4H, arom. CH, $^3J=8.0$ Hz), 7.32–7.06 (56H, arom. CH), 6.88(d, 4H, arom. CH, $^3J=8.1$ Hz), 6.75–6.67 (12H, arom. CH), 6.44 (d, 4H, arom. H, $^3J=6.6$ Hz), 6.02 (t, 2H, arom. CH, $^3J=7.3$ Hz), 5.08 (s, 8H, CH_2Ph), 4.87 (s, 4H, CH_2Ph), 4.74 (s, 24, CH_2Ph), 4.28 and 2.87 (AB spin system, 8H, ArCH_2Ar, $^2J=13.4$ Hz), 4.12 and 2.82 (AB spin system, 8H, ArCH_2Ar, $^2J=13.4$ Hz), 2.47 (t, 4H, C$_6$H$_4$CH_2, $^3J=7.3$ Hz), 1.59–1.49 (4H, C$_6$H$_4$CH$_2$CH_2), 1.31–1.15 (4H, CH_2CH$_3$), 0.86 (t, 6H, CH$_2$CH_3, $^3J=6.4$ Hz); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta=159.04$ (d, $C_{quat.}$-O, $^4J_{P,C}=2.4$ Hz), 155.22 and 155.10 (2s, $C_{quat.}$-O), 145.88–122.14 (arom. C), 77.34 (s, OCH_2Ph), 77.07 (s, OCH_2Ph), 76.00 (s, OCH_2Ph), 35.09 (s, C$_6$H$_4$CH_2), 33.80 (s, C$_6$H$_4$CH$_2$CH_2), 31.46 (s, ArCH_2Ar), 31.25 (s, ArCH_2Ar), 22.52 (s, CH_2CH$_3$), 13.92 (s, CH$_2$CH_3); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta=29.9$ (s, PPh$_2$); anal. calcd. for $C_{156}H_{140}PdCl_2N_2O_8P_2$ ($Mr=2410.06$): C 77.74, H 5.85, N 1.16%; found: C 77.84, H 5.98, N 1.04%.

2-Methoxyphenyliminotriphenylphosphorane (16)

To a solution of triphenylphosphine (0.262 g, 1.00 mmol) in toluene (10 mL) was added a solution of 2-methoxyphenyl azide (0.149 g, 1.00 mmol in toluene (10 mL). After stirring the solution for 16 h at 60 °C, the reaction mixture was evaporated to dryness under vacuum to afford quantitatively **16**; yield: 0.382 g (100%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=7.84$–7.77 (6H, arom. CH), 7.46 (d, 1H, arom. CH *ortho* to N, $^3J=7.8$ Hz), 7.40–7.35 (1H, arom. CH *para* to CH$_3$O), 7.04–6.96 (9H, arom. CH), 6.80 (dd, 1H, arom. CH *para* to N, $^3J=7.8$ Hz, $^3J=7.8$ Hz), 6.67 (d, 1H, arom. CH *ortho* to CH$_3$O, $^3J=7.8$ Hz), 3.08 (s, 3H, CH$_3$O); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta=159.01$ (s, arom. $C_{quat.}$-O), 134.44 (d, arom. $C_{quat.}$-P, $^1J_{C,P}=71.9$ Hz), 132.38 (d, arom. CH *ortho* to

P, $^{2}J_{C,P}=9.4$ Hz), 130.49 (s, arom. CH *para* to P), 128.50 (d, arom. CH *ortho* to N, $^{3}J_{C,P}=7.4$ Hz), 127.94 (d, arom. CH *meta* to P, $^{3}J_{C,P}=11.5$ Hz), 125.34 (d, arom. $C_{quat.}$-N, $^{2}J_{C,P}=19.8$ Hz), 121.64 (s, arom. CH *para* to N), 117.77 (s, arom. CH *ortho* to CH_3O), 54.03 (s, CH_3O); $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6): $\delta=-0.3$ (s, PPh_2). IR: $\nu=1328\ cm^{-1}$ (P=N); anal. calcd. for $C_{25}H_{22}OPN$ ($Mr=383.42$): C 78.31, H 5.78, N 3.65%; found: C 78.22, H 5.84, N 3.78%.

Typical Procedure for Palladium-Catalysed Suzuki–Miyaura Cross-Coupling Reactions

A 10-mL Schlenk tube was charged with a solution of [Pd(OAc)$_2$] in dioxane, a solution of the ligand in dioxane, aryl halide (0.5 mmol), phenylboronic acid (0.122 g, 1.0 mmol), base (1.0 mmol), and decane (0.05 mL, internal reference). Dioxane was then added so that the total reaction volume was 1.5 mL. The reaction mixture was heated for 1 h at 100 °C. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analysed by GC. Some homocoupling product (Ph–Ph) was detected in each run, but the Ph–Ph:Ar–Ph ratio never exceeded 10% (see the Supporting Information).

Typical Procedure for Nickel-Catalysed Kumada–Tamao–Corriu Cross-Coupling Reactions

A 10-mL Schlenk tube was charged with a solution of [Ni(cod)$_2$] in dioxane, a solution of the ligand in dioxane, aryl halide (0.5 mmol), PhMgBr (1 mL, 1.0 mmol, 1 M solution in THF), and decane (0.05 mL, internal reference). Dioxane was then added so that the total reaction volume was 1.5 mL. The reaction mixture was heated for 1 h at 100 °C. After cooling to room temperature, a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analysed by GC. Some homocoupling product (Ph–Ph) was detected in each run, but the Ph–Ph:Ar–Ph ratio never exceeded 15 % (see the Supporting Information).

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