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Synthesis of Calixarene-Based Bis(iminophosphoranes) and Their Use in Suzuki–Miyaura Cross-Coupling

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Calix[4]arene-derived bis(iminophosphoranes) have been synthesised and assessed in palladium-catalysed cross-couplings between phenylboronic acid and aryl bromides or chlorides. TOFs of up to 35100 mol(ArPh formed) mol(Pd)⁻¹ h^{-1} were observed in the reaction with 4-bromoanisole. The li-

diphosphanes. Their relatively good performances possibly arise from their ability to generate chelated intermediates in highly crowded metal environments, which incidentally facilitates the reductive elimination step.

gands showed higher activities than the parent calixarene-

Introduction

Organic imines are commonly used as ligands in homogeneous catalysis, in particular for carbon–carbon bondforming reactions.^[1–8] In comparison, the related iminophosphoranes $R_3P=NR$, also termed phosphazenes, have only rarely been employed for the preparation of transitionmetal-based catalysts.^[9–16] This is mainly due to the nature of the P=N bond, which involves a zwitterionic contribution, thus making stabilisation of coordinated metal atoms in low oxidation states difficult.^[17,18] However, recent studies have shown that functionalised iminophosphoranes capable of forming chelate complexes can be used both in carbon–carbon and carbon–heteroatom bond formation.^[19–26]

We have recently described conical calix[4]arenes in which two distal phosphanyl groups are attached at the upper rim of the macrocycle and have shown that such phosphanes, when associated with palladium, could function as efficient cross-coupling catalysts.^[27,28] The good performances of the catalysts were shown to be related to the size and structural properties of the calixarene backbone. As a logical extension of these studies, we embarked on the synthesis of the corresponding iminophosphorane derivatives, which were assessed in Suzuki–Miyaura cross-couplings. The five ligands reported in this study are the first bis-(iminophosphoranes) based on a calix[4]arene skeleton. It should be noted that an iminophosphorane based on a closely related resorcin[4]arene has been reported recently.^[29]

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Results and Discussion

The bis(iminophosphoranyl)calix[4]arenes 2-6 were prepared through Staudinger condensations^[30] of calixarenylphosphane 1 with the appropriate aryl azides (Scheme 1). The azides themselves were obtained by treatment of substituted anilines with freshly prepared TfN_3 (Tf = CF₃SO₂) in the presence of CuSO₄ and NEt₃.^[31] The products were characterised by elemental analyses, mass spectrometry (MALDI-TOF) and NMR spectroscopy. Each mass spectrum displays a strong peak corresponding to the expected $[M + H]^+$ ion. In the ³¹P NMR spectra the phosphorus atoms appear in each case as a singlet in the $\delta = -10$ to +1 ppm range. The conical structure of the calixarene unit was maintained in each case, as deduced from the ¹³C NMR spectra, all of which display Ar*C*H₂Ar signals at $\delta \approx$ 31 ppm.^[32] The ¹H NMR spectra are consistent with C_{2v} symmetrical compounds. The bis(iminophosphoranes) were only moderately air-stable, contact with air leading to the the expected hydrolysis products - namely the corresponding aniline and the bis(phosphane oxide) 7. They were therefore stored under nitrogen.



Scheme 1. Synthesis of bis(iminophosphoranes) 2-6.

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The above ligands were found to be suitable for metal binding. For example, upon treatment of **2** (Scheme 2) with 2 equiv. of [AuCl(THT)] (THT = tetrahydrothiophene), the dinuclear complex **8** was formed quantitatively. In the corresponding ³¹P NMR (C₆D₆) spectrum, the phosphorus atoms appear as a singlet at δ = 28.6 ppm (cf. δ = -9.2 ppm for the free ligand).



Scheme 2. Synthesis of the digold complex 8.

Whereas the above reaction led to a single product, the reaction between 6 and [PdCl₂(MeCN)₂] (1 equiv.) gave a mixture of complexes that could not be separated. The ³¹P NMR spectrum of the crude reaction mixture revealed the presence of three peaks at δ = 34.2, 31.0 and 30.6 ppm, all consistent with the presence of coordinated palladium.^[33] Unreacted iminophosphorane was not detected. The mass spectrum of the reaction mixture showed a peak at m/z =1573.41, corresponding to the cation $[PdCl_2(6) + H]^+$ (see Scheme 2 in the Supporting Information) and therefore suggesting the formation of a $[PdCl_2(6)]$ complex with a chelated structure. The ability of 6 to form chelate complexes was formally demonstrated by treatment with AgBF₄ (Scheme 3), which quantitatively gave complex 9 (see the Experimental Section). The ¹H and ³¹P NMR spectra of 9 are consistent with a complex of C_{2v} -symmetrical structure. It is likely that the apparent C_{2v} symmetry reflects a dynamic structure in which the linear N-Ag-N system undergoes a fast balance-wheel motion centred on the calixarene axis (Scheme 3).

The five bis(iminophosphoranes) 2-6 were assessed in palladium-catalysed Suzuki–Miyaura couplings (Scheme 4). The catalytically active species were generated in situ by mixing [Pd(OAc)₂] and the iminophosphoranes.



Scheme 4. Suzuki-Miyaura cross-coupling.

To determine optimal catalytic conditions, we first investigated the reaction between 4-bromoanisole and phenylboronic acid in the presence of bis(iminophosphorane) **3** (Table 1). With Cs_2CO_3 as base, higher levels of conversion were observed at 100 °C in dioxane than at 130 °C in DMF (Table 1, Entries 1 and 2). Replacement of the base by NaH slightly increased the level of conversion (Table 1, Entries 2 and 6). The other bases tested – K_2CO_3 , KOH and NEt₃ – did not improve the levels of conversion (Table 1, Entries 3– 5). As expected, reduction of the temperature decreased the reaction rate (Table 1, Entries 6–8). We also found that the kinetics were not affected by use of more than 1 equiv. of ligand relative to palladium (Table 1, Entries 9–11).

Finally, we observed that the absence of any ligand drastically reduced the catalytic outcome (Table 2, Entry 1). This was also the case when the catalytic runs were carried out in the presence of palladium associated either with bis(phosphane oxide) 7 or with 2-methoxyaniline, two products that should be formed upon hydrolysis of 5 during catalysis (Table 2, Entries 4 and 5).

The bis(iminophosphoranes) **2–6** were then tested in palladium-catalysed Suzuki–Miyaura cross-coupling reactions of aryl bromides under the optimised conditions (NaH as base, dioxane, 100 °C, 1 h). An ArBr/Pd ratio of 10000, corresponding to a palladium loading of 0.01 mol-%, was applied for the runs (Table 3). Under these conditions, even for the hindered 2-bromoanisole and 2-bromotoluene, levels of conversion >51% were obtained within 1 h. As expected, increasing the reaction time to 2 h led to almost full conversion. The highest level of conversion was observed in the arylation of 4-bromoanisole in the presence of bis(iminophosphorane) **6**, with *p*-anisole substituents (Table 3, En-



Scheme 3. Synthesis of the chelate complex 9 and proposed molecular motion of 9.

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Table 1. Suzuki–Miyaura cross-coupling between 4-bromoanisole and phenylboronic acid – search for optimal conditions in the presence of bis(iminophosphorane) $3^{[a]}$

Entry	Solvent	Base	[Pd(OAc) ₂] [%]	3 [mol-%]	<i>T</i> [°C]	Conversion [%]
1	DMF	Cs ₂ CO ₃	1.0	1.0	130	34.6
2	dioxane	Cs_2CO_3	1.0	1.0	100	96.6
3	dioxane	K_2CO_3	1.0	1.0	100	88.8
4	dioxane	KOH	1.0	1.0	100	21.4
5	dioxane	NEt ₃	1.0	1.0	100	4.6
6	dioxane	NaH	1.0	1.0	100	99.2
7	dioxane	NaH	1.0	1.0	80	73.0
8	dioxane	NaH	1.0	1.0	65	34.3
9	dioxane	NaH	0.01	0.01	100	57.3
10	dioxane	NaH	0.01	0.015	100	54.9
11	dioxane	NaH	0.01	0.02	100	55.4

[a] $[Pd(OAc)_2]$, bis(iminophosphorane) **3**, 4-bromoanisole (0.25 mmol), PhB(OH)₂ (0.061 g, 0.50 mmol), NaH (60% dispersion in mineral oil, 0.040 g, 1.0 mmol), decane (0.050 mL), solvent (0.75 mL), 1 h. The levels of conversion were determined by GC, with calibrations based on decane.

Table 2. Suzuki–Miyaura cross-coupling between 4-bromotoluene and phenylboronic acid – comparison with other ligands.^[a]

Entry	Ligand	Conversion [%]
1	none	16.7
2	1 (1 equiv.)	35.4
3	5 (1 equiv.)	56.3
4	7 (1 equiv.)	30.7
5	$o-MeOC_6H_4NH_2$ (2 equiv.)	27.3

[a] $[Pd(OAc)_2]$ (5×10⁻⁵ mmol, 0.01 mol-%), ligand, 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 levels of conversion were determined by GC, with calibrations based on decane.

try 1). With this substrate, the activity reached 35100 mol- $(ArBr)mol(Pd)^{-1}h^{-1}$ when the palladium loading was reduced to 0.001 mol-% (Table 3, Entry 2).

The calixarenyl-iminophosphoranes **3** and **6** were further tested in arylations of aryl chlorides, which are less reactive substrates (Table 4). Use of a palladium loading of 1 mol-% led, after 3 h, to good levels of conversion in the case of the three activated aryl chlorides 1-chloro-4-nitrobenzene, 4-chloroacetophenone and 4-chlorobenzonitrile (Table 4, Entries 1–6). Lower levels of conversion were obtained in arylations of 4-chloroanisole and 4-chlorotoluene (Table 4, Entries 7–10). We further noted that bis(iminophosphorane) **6** gave slightly higher levels of conversion than ligand **3**: whereas 1-chloro-4-nitrobenzene, for example, was 61.4% converted with **3**, its degree of conversion reached 73.1% with **6** (Table 4, Entries 1 and 2).

The results outlined above clearly show that combinations of $[Pd(OAc)_2]$ with the bis(iminophosphoranes) **2–6** functioned as active Suzuki–Miyaura cross-coupling catalysts. In order to rank these ligands, the arylation of 4-bromotoluene was carried out with the previously reported high-performing bis(phosphane) **1**, a ligand that quantitatively forms chelate complexes upon reaction with Pd^{II}. The high activities observed with these complexes arise from their dynamic behaviour in solution, which periodically generates increased ligand bite-angle values that impact on the reductive elimination step.^[28] Significantly, whereas diphosphane **1** gave 35.4% conversion under the conditions Table 3. Palladium-catalysed Suzuki–Miyaura cross-couplings of aryl bromides in the presence of bis(iminophosphoranes) 2-6 and with an ArBr/Pd ratio of 10000:1.^[a]

Enter	4.0		Bis(iminophosphorane)				
Entry	ArBr		2	3	4	5	6
1		conv. (%)	81.1	56.5	82.6	77.4	84.4
	MeO-	TOF	8110	5650	8260	7740	8440
2 ^[b]		conv. (%)	33.2	14.9	32.9	28.9	35.1
		TOF	33200	14900	32900	28900	35100
3	OMe	conv. (%)	46.1	39.8	63.9	41.1	59.3
	⟨Br	TOF	3610	4980	6390	4110	5930
4	—Вr	conv. (%)	42.9	23.5	51.1	49.3	49.6
		TOF	4290	2350	5110	4930	4960
5		conv. (%)	58.8	33.7	36.1	39.0	43.7
	Br	TOF	5880	3370	3610	3900	4370
6	\rightarrow	conv. (%)	63.9	67.2	56.2	50.6	45.4
	Br	TOF	6390	6720	5620	5060	4540
7	Br	conv. (%)	67.2	71.1	62.8	56.3	61.7
		TOF	6720	7110	6280	5630	6170

[a] $[Pd(OAc)_2]$ (5×10⁻⁵ mmol, 0.01 mol-%), bis(iminophosphorane) (5×10⁻⁵ mmol, 0.01 mol-%), dioxane (1.5 mL), ArBr (0.5 mmol), PhB(OH)₂ (0.092 g, 0.75 mmol), NaH (60% dispersion in mineral oil) (0.040 g, 1.0 mmol), decane (0.050 mL), 100 °C, 1 h. The levels of conversion were determined by GC, with calibrations based on decane. TOFs expressed in mol(ArBr)mol(Pd)⁻¹ h⁻¹. [b] $[Pd(OAc)_2]$ (5×10⁻⁶ mmol, 0.001 mol-%), bis(iminophosphorane) (5×10⁻⁶ mmol, 0.001 mol-%).

shown in Table 2, the degree of conversion obtained with the bis(iminophosphorane) **6** reached 61.7% (Table 2, Entry 2 and Table 3 Entry 7). The reason why **6** performs better than **1** is a matter for discussion. According to molecular mechanics calculations,^[34] the hypothetical chelate com-

Table 4. Palladium-catalysed Suzuki–Miyaura cross-couplings of aryl chlorides in the presence of bis(iminophosphoranes) $\bf 3$ and $\bf 6$.^[a]

Entry	ArCl	Bis(iminophosphorane)	Time [h]	Conv. (%)
1		3	3	61.4
2		6	3	73.1
3		3	3	71.7
4	Me	6	3	65.3
5		3	3	65.2
6		6	3	71.3
7		3	16	57.6
8		6	16	61.4
9		3	16	37.9
10		6	16	44.2

[a] [Pd(OAc)₂] $(2.5 \times 10^{-3} \text{ mmol}, 1 \text{ mol-}\%)$, bis(iminophosphorane) $(2.5 \times 10^{-3} \text{ mmol}, 1 \text{ mol-}\%)$, 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), 100 °C. The levels of conversion were determined by GC, with calibrations based on decane.

plex [*cis*-PdCl₂(**6**)] (Figure 1) displays a sterically more crowded metal environment (presence of six phenyl rings close to the palladium atom) than in the related chelate complexes derived from **1**. Steric crowding is known to favour the reductive elimination step, namely the coupling of two *cis*-positioned aryl moieties.^[35,36] However, the ability of **6** to operate as a ligand with two η^1 -coordination sites during catalysis cannot be ruled out at this stage.



Figure 1. Calculated structure of [*cis*-PdCl₂(**6**)]. Left: side view; right: partial view from top.

Conclusions

We have described the synthesis of the first bis(iminophosphoranes) based on a calix[4]arene platform. In combinations with $[Pd(OAc)_2]$ and a base, these ligands efficiently catalyse Suzuki–Miyaura cross-coupling reactions of aryl bromides and aryl chlorides. The highest activity [TOF =35100 mol(ArPh formed)mol(Pd)⁻¹ h⁻¹] was observed in the arylation of 4-bromoanisole. The origin of the good performances of these ligands can reasonably be ascribed to the formation of intermediate chelate complexes, which creates a highly crowded metal environment and incidentally facilitates the reductive elimination step.

Experimental Section

General 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 ¹H, ¹³C and ³¹P NMR spectra were recorded with an FT Bruker AV-300 instrument. ¹H NMR spectra were referenced to residual protiated solvent (δ = 7.16 ppm for C₆D₆, 7.26 ppm for CDCl₃ and 5.32 ppm for CD₂Cl₂), ¹³C chemical shifts are reported relative to deuterated solvent ($\delta = 128.0$ ppm for C₆D₆, 77.16 ppm for CDCl₃ and 53.8 ppm for CD_2Cl_2) and the ³¹P data are given relative to external H₃PO₄. 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 with a Varian 3900 gas chromatograph fitted with a WCOT fused silica column ($25 \text{ m} \times 0.25 \text{ mm}$, $0.25 \mu \text{m}$ film thickness). Elemental analyses were performed by the Service de Microanalyse, Université de Strasbourg. 5,17-Bis(diphenylphosphanyl)-25,26,27,28-tetrabenzyloxycalix[4]arene (1),[37] [AuCl(THT)][38] and [PdCl₂(MeCN)₂]^[39] were prepared according to literature procedures. Aryl azides were synthesized by using TfN₃ according to a procedure developed by Tor.^[31] Although we have not experienced any difficulty in handling TfN_3 , care should be taken owing to the potentially explosive natures of certain azides. The reagent should be kept in solution and used immediately after its synthesis. NMR spectroscopic data for the formed 1-azido-4-butylbenzene,[31] 1azido-4-methoxybenzene,^[31] 1-azido-2,6-diisopropylbenzene,^[31] 1azido-2-methoxybenzene^[40] and 2-azido-1,3,5-trimethylbenzene^[40] were in agreement with those reported in the literature.

General Procedure for the Synthesis of 25,26,27,28-Tetrabenzyloxy-5,17-bis(aryliminodiphenylphosphoranyl)calix[4]arenes 2–6: A solution of aryl azide (2.00 mmol) in toluene (10 mL) was added to a solution of 1 (1.00 mmol) in toluene (10 mL). After the solution had been stirred at 60 °C for 16 h, the reaction mixture was concentrated to dryness under vacuum to afford the bis(iminophosphorane) in quantitative yield.

25.26.27.28-Tetrabenzyloxy-5.17-bis(mesityliminodiphenylphosphoranyl)calix[4]arene (2): ¹H NMR (300 MHz, C_6D_6): $\delta = 7.99-7.93$ (8 H, arom. CH), 7.41 (d, ${}^{3}J$ = 11.5 Hz, 4 H, arom. CH), 7.30 (d, ${}^{3}J = 6.3$ Hz, 4 H, arom. CH), 7.21–6.97 (arom., 32 H CH), 6.49 (t, ${}^{3}J$ = 7.6 Hz, 2 H, arom. CH), 6.06 (d, ${}^{3}J$ = 7.6 Hz, 4 H, arom. CH), 5.22 (s, 4 H, CH₂Ph), 4.40 (s, 4 H, CH₂Ph), 4.21 and 2.70 (AB spin system, ${}^{2}J$ = 13.6 Hz, 8 H, ArCH₂Ar), 2.44 (s, 12 H, *o*-CH₃ of mesityl), 2.32 (s, 6 H, p-CH₃ of mesityl) ppm. ¹³C {¹H} NMR (75 MHz, C₆D₆): δ = 158.76 (d, ⁴J_{P,C} = 3.1 Hz, arom. C_{quat.}-O), 154.67 (s, arom. C_{quat.}-O), 145.52-122.89 (arom. C), 77.19 (s, OCH₂Ph), 75.23 (s, OCH₂Ph), 31.36 (s, ArCH₂Ar), 21.69 (s, o-CH₃ of mesityl), 20.70 (s, p-CH₃ of mesityl) ppm. ³¹P {¹H} NMR (121 MHz, C₆D₆): $\delta = -9.6$ (s, PPh₂) ppm. IR: $\tilde{v} = 1328$ (P=N) cm^{-1} . MS (MALDI-TOF): $m/z = 1419.63 [M + H]^+$ (expected isotopic profile). C₉₈H₈₈N₂O₄P₂ (1419.71): calcd. C 82.91, H 6.25, N 1.97; found C 83.01, H 6.24, N 1.80.

25,26,27,28-Tetrabenzyloxy-5,17-bis(2,6-diisopropylphenyliminodiphenylphosphoranyl)calix[4]arene (3): ¹H NMR (300 MHz, C₆D₆): δ = 7.83–7.78 (8 H, arom. CH), 7.52 (d, ³*J* = 11.8 Hz, 4 H, arom. CH), 7.30–6.97 (38 H, arom. CH), 6.51 (t, ³*J* = 7.6 Hz, 2 H, arom. CH), 6.21 (d, ${}^{3}J$ = 7.6 Hz, 4 H, arom. CH), 5.29 (s, 4 H, *CH*₂Ph), 4.42 (s, 4 H, *CH*₂Ph), 4.25 and 2.78 (AB spin system, ${}^{2}J$ = 13.6 Hz, 8 H, ArCH₂Ar), 3.83 [sept, ${}^{3}J$ = 6.8 Hz, 4 H, *CH*(CH₃)₂], 1.12 [d, ${}^{3}J$ = 6.8 Hz, 24 H, CH(CH₃)₂] ppm. ${}^{13}C$ {¹H} NMR (75 MHz, CDCl₃): δ = 157.65, 153.86 (2 s, arom. C_{quat.}-O), 142.56–118.62 (arom. C), 76.77 (s, OCH₂Ph), 74.40 (s, OCH₂Ph), 30.53 (s, Ar-CH₂Ar), 27.49 [s, CH(CH₃)₂], 22.78 [s, CH(CH₃)₂] ppm. ${}^{31}P$ {¹H} NMR (121 MHz, C₆D₆): δ = -3.3 (s, PPh₂) ppm. IR: \tilde{v} = 1329 (P=N) cm⁻¹. MS (MALDI-TOF): *m*/*z* = 1503.69 [M + H]⁺ (expected isotopic profile). C₁₀₄H₁₀₀N₂O₄P₂ (1503.86): calcd. C 83.06, H 6.70, N 1.82; found C 82.82, H 6.54, N 1.80.

25,26,27,28-Tetrabenzyloxy-5,17-bis(4-butylphenyliminodiphenylphosphoranyl)calix[4]arene (4): ¹H NMR (300 MHz, C_6D_6): $\delta =$ 8.04–7.98 (8 H, arom. CH), 7.64 (d, ${}^{3}J$ = 11.5 Hz, 4 H, arom. CH), 7.37 (d, ${}^{3}J$ = 8.0 Hz, 4 H, arom. CH), 7.29 (d, ${}^{3}J$ = 7.0 Hz, 4 H, arom. CH), 7.19–6.96 (32 H, arom. CH), 6.45 (t, ³J = 7.6 Hz, 2 H, arom. CH), 6.18 (d, ${}^{3}J$ = 7.6 Hz, 4 H, arom. CH), 5.19 (s, 4 H, CH₂Ph), 4.45 (s, 4 H, CH₂Ph), 4.20 and 2.70 (AB spin system, ²J = 13.7 Hz, 8 H, ArC H_2 Ar), 2.60 (t, ${}^{3}J$ = 6.5 Hz, 4 H, C₆H₄C H_2), 1.62 (quint, ${}^{3}J$ = 6.5 Hz, 4 H, C₆H₄CH₂CH₂), 1.33 (sext, ${}^{3}J$ = 6.4 Hz, 4 H, CH_2CH_3), 0.86 (t, ${}^{3}J$ = 6.4 Hz, 6 H, CH_2CH_3) ppm. ¹³C {¹H} NMR (75 MHz, C₆D₆): δ = 159.74 (d, ⁴J_{PC} = 3.1 Hz, arom. Cquart.-O), 155.08 (s, arom. Cquart.-O), 150.22-123.28 (arom. C), 77.63 (s, OCH₂Ph), 75.80 (s, OCH₂Ph), 35.60 (s, C₆H₄CH₂), 34.63 (s, C₆H₄CH₂CH₂), 31.66 (s, ArCH₂Ar), 22.79 (s, CH₂CH₃), 14.31 (s, CH₂*C*H₃) ppm. ³¹P {¹H} NMR (121 MHz, C₆D₆): δ = -0.4 (s, PPh₂) ppm. IR: $\tilde{v} = 1325$ (P=N) cm⁻¹. MS (MALDI-TOF): $m/z = 1447.59 [M + H]^+$ (expected isotopic profile). $C_{100}H_{92}N_2O_4P_2$ (1447.76): calcd. C 82.96, H 6.40, N 1.93; found C 82.83, H 6.25, N 1.92.

25,26,27,28-Tetrabenzyloxy-5,17-bis(2-methoxyphenyldiphenylphosphoranyl)calix[4]arene (5): ¹H NMR (300 MHz, C_6D_6): $\delta =$ 8.04–7.98 (8 H, arom. CH), 7.63 (d, ${}^{3}J$ = 11.8 Hz, 4 H, arom. CH), 7.50 (d, ${}^{3}J$ = 7.6 Hz, 2 H, arom. CH), 7.29 (d, ${}^{3}J$ = 7.3 Hz, 4 H, arom. CH), 7.20–6.80 (34 H, arom. CH), 6.38 (t, ³J = 7.5 Hz, 2 H, arom. CH), 6.15 (d, ${}^{3}J$ = 7.5 Hz, 4 H, arom. CH), 5.19 (s, 4 H, CH₂Ph), 4.46 (s, 4 H, CH₂Ph), 4.21 and 2.72 (AB spin system, ²J = 13.6 Hz, 8 H, ArC H_2 Ar), 3.32 (s, 6 H, C H_3 OC₆H₄) ppm. ¹³C {¹H} NMR (75 MHz, C₆D₆): δ = 159.17 (d, ⁴J_{P,C} = 3.7 Hz, arom. Cquart.-O), 155.08 (s, arom. Cquart.-O), 153.58-112.20 (arom. C), 77.63 (s, OCH₂Ph), 75.74 (s, OCH₂Ph), 54.84 (s, CH₃OC₆H₄), 31.70 (s, Ar*C*H₂Ar) ppm. ³¹P {¹H} NMR (121 MHz, C₆D₆): $\delta = 0.5$ (s, PPh₂) ppm. IR: $\tilde{v} = 1326$ (P=N) cm⁻¹. MS (MALDI-TOF): m/z =1395.50 $[M + H]^+$ (expected isotopic profile). $C_{94}H_{80}N_2O_6P_2$ (1395.60): calcd. C 80.90, H 5.78, N 2.01; found C 80.79, H 5.90, N 1.81.

25,26,27,28-Tetrabenzyloxy-5,17-bis(4-methoxyphenyliminodiphenylphosphoranyl)calix[4]arene (6): ¹H NMR (300 MHz, C₆D₆): δ = 8.04–7.98 (8 H, arom. CH of PPh₂), 7.63 (d, ³J = 11.7 Hz, 4 H, arom. CH), 7.30 (d, ${}^{3}J$ = 6.3 Hz, 4 H, arom. CH), 7.28 (d, ${}^{3}J$ = 6.3 Hz, 4 H, arom. CH), 7.20–6.91 (32 H, arom. CH), 6.44 (t, ${}^{3}J$ = 7.6 Hz, 2 H, arom. CH), 6.14 (d, ${}^{3}J$ = 7.6 Hz, 4 H, arom. CH), 5.19 (s, 4 H, CH₂Ph), 4.45 (s, 4 H, CH₂Ph), 4.21 and 2.71 (AB spin system, ${}^{2}J = 13.5 \text{ Hz}$, 8 H, ArCH₂Ar), 3.46 (s, 6 H, CH₃OC₆H₄) ppm. ¹³C {¹H} NMR (75 MHz, C₆D₆): δ = 159.33 (d, ⁴J_{P,C} = 3.1 Hz, arom. C_{quart.}-O), 154.64 (s, arom. C_{quart.}-O), 152.45-114.63 (arom. C), 77.24 (s, OCH₂Ph), 75.41 (s, OCH₂Ph), 54.93 (s, CH₃OC₆H₄), 31.29 (s, ArCH₂Ar) ppm. ³¹P {¹H} NMR (121 MHz, C_6D_6): $\delta = -0.5$ (s, PPh₂) ppm. IR: $\tilde{v} = 1328$ (P=N) cm⁻¹. MS (MALDI-TOF): $m/z = 1395.54 [M + H]^+$ (expected isotopic profile). C₉₄H₈₀N₂O₆P₂ (1395.60): calcd. C 80.90, H 5.78, N 2.01; found C 80.96, H 5.95, N 1.88.

25,26,27,28-Tetrabenzyloxy-5,17-bis(diphenylphosphinoyl)calix[4]arene (7): H_2O_2 (30% in water, 4 mL, 5.0 mmol) was added to a solution of 25,26,27,28-tetrabenzyloxy-5,17-bis(diphenylphosphanyl)calix[4]arene (1, 0.576 g, 0.5 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 2 h. The mixture was treated with a mixture of CH2Cl2 (10 mL) and water (20 mL). After extraction of the aqueous layer with CH₂Cl₂ $(2 \times 10 \text{ mL})$, the organic phases were combined. The resulting solution was washed with water $(2 \times 10 \text{ mL})$, dried with Na₂SO₄ and concentrated under reduced pressure to afford the bis(phosphane oxide) 7 as a white solid in quantitative yield. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 7.58-7.34$ (20 H, arom. CH), 7.24-6.96 (24 H, arom. CH), 6.16 (t, ${}^{3}J$ = 7.5 Hz, 2 H, arom. CH), 5.90 (d, ${}^{3}J$ = 7.5 Hz, 4 H, arom. CH), 5.12 (s, 4 H, CH₂Ph), 4.56 (s, 4 H, CH_2Ph), 4.12 and 2.82 (AB spin system, $^2J = 13.8$ Hz, 8 H, Ar- CH_2Ar) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 158.97 (d, ${}^{4}J_{P,C}$ = 2.8 Hz, arom. C_{quart.}-O), 154.29 (s, arom. C_{quart.}-O), 137.64-122.21 (arom. C), 77.12 (s, OCH₂Ph), 75.03 (s, OCH₂Ph), 30.89 (s, Ar*C*H₂Ar) ppm. ³¹P {¹H} NMR (121 MHz, CDCl₃): δ = 31.0 (s, O=PPh₂) ppm. $C_{80}H_{66}O_6P_2$ (1185.32): calcd. C 81.06, H 5.61; found C 80.89, H 5.72.

Digold Complex 8: A solution of [AuCl(THT)] (0.045 g, 0.14 mmol) in THF (5 mL) was added to a stirred solution of 2 (0.100 g, 0.07 mmol) in CH₂Cl₂ (15 mL). After 5 h, the solution was concentrated to ca. 1 mL. Addition of hexane afforded 8 as a white solid (0.112 g, 86%). ¹H NMR (300 MHz, C_6D_6): $\delta = 7.93-7.72$ (8 H, arom. CH), 7.54–7.42 (4 H, arom. CH), 7.32 (d, ${}^{3}J$ = 6.3 Hz, 4 H, arom. CH), 7.18-6.96 (30 H, arom. CH), 6.71 (s, 4 H, arom. CH), 6.22–6.09 (4 H, arom. CH), 5.25 and 5.21 (AB spin system, ${}^{2}J$ = 13.1 Hz, 4 H, CH₂Ph), 4.43 (s, 4 H, CH₂Ph), 4.20 and 2.74 (AB spin system, ${}^{2}J = 13.8$ Hz, 8 H, ArCH₂Ar), 2.33 (s, 12 H, o-CH₃) of mesityl), 2.17 (s, 6 H, p-CH₃ of mesityl) ppm. ¹³C {¹H} NMR (75 MHz, C₆D₆): δ = 159.85 (d, ⁴J_{P,C} = 3.7 Hz, arom. C_{quat.}-O), 155.36 (s, arom. $C_{quat.}{-}O),\ 141.59{-}124.31$ (arom. C), 78.07 (s, OCH₂Ph), 76.06 (s, OCH₂Ph), 32.31 (s, ArCH₂Ar), 23.40 (s, o-CH3 of mesityl), 21.54 (s, p-CH3 of mesityl) ppm. ^{31}P $\{^{1}H\}$ NMR (121 MHz, C_6D_6): δ = 28.6 (s, PPh₂) ppm. C₉₈H₈₈Au₂Cl₂N₂O₄P₂·C₆H₁₄ (1884.54 + 86.17): calcd. C 63.38, H 5.22, N 1.42; found C 63.12, H 5.36, N 1.67.

Reaction of 6 with [PdCl₂(CH₃CN)₂]: A solution of **6** (0.150 g, 0.011 mmol) in CH₂Cl₂ (100 mL) was added slowly to a solution of [PdCl₂(CH₃CN)₂] (0.028 mg, 0.011 mmol) in CH₂Cl₂ (200 mL). The resulting solution was stirred overnight and then concentrated to ca. 5 mL. Addition of hexane (100 mL) afforded a brown precipitate, which turned out to contain several complexes that could not be separated. MS (ESI-TOF, crude reaction mixture): m/z (%) = 1573.41 (1) ([PdCl₂(**6**) + H]⁺ requires 1573.40; expected isotopic profile; see Scheme S2 in the Supporting Information).

Silver Complex 9: A solution of AgBF₄ (0.028 g, 0.14 mmol) in THF (10 mL) was added to a stirred solution of **6** (0.200 g, 0.14 mmol) in THF (40 mL). After 2 h, the solution was concentrated to ca. 1 mL. Addition of hexane afforded **9** as a white solid (0.208 g, 92%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.73–7.15 (45 H, arom. CH), 7.01–6.96 (6 H, arom. CH), 6.92 (d, ³J = 12.4 Hz, 2 H, arom. CH), 6.79 (d, ³J = 7.2 Hz, 2 H, arom. CH), 6.58–6.52 (4 H, arom. CH), 6.54 (s, 4 H, CH₂Ph), 4.88 (s, 4 H, CH₂Ph), 4.22 and 2.89 (AB spin system, 8 H, ArCH₂Ar, ²J = 13.4 Hz), 3.70 (s, 6 H, CH₃OC₆H₄) ppm. ¹³C {¹H} NMR (75 MHz, CD₂Cl₂): δ = 159.68 (s, arom. C_{quart}–O), 155.50 (s, arom. C_{quart}–O), 152.50–114.30 (arom. C), 78.49 (s, OCH₂Ph), 76.12 (s, OCH₂Ph), 55.87 (s, CH₃OC₆H₄), 31.89 (s, ArCH₂Ar) ppm. ³¹P {¹H} NMR (121 MHz, CD₂Cl₂): δ = 24.8 [d, PPh₂, ²J(P¹⁰⁷,Ag) ≈ ²J(P¹⁰⁹,Ag) = 7.7 Hz].

 $C_{94}H_{80}AgBF_4N_2O_6P_2$ (1590.27): calcd. C 70.99, H 5.07, N 1.76; found C 71.04, H 4.92, N 1.80. MS (MALDI-TOF): m/z = 1503.45[M – BF₄]⁺ (expected isotopic profile).

Typical Procedure for Palladium-Catalysed Suzuki–Miyaura Cross-Coupling Reactions: A solution of $[Pd(OAc)_2]$ in dioxane, a solution of the ligand in dioxane, the aryl halide (0.5 mmol), phenylboronic acid (0.122 g, 1.0 mmol), the base (1.0 mmol), decane (0.05 mL), internal reference) and a complementary amount of dioxane (so that the total reaction volume was 1.5 mL) were placed in a Schlenk tube under an inert gas. The reaction mixture was then heated at $100 \,^{\circ}$ C for 1 h. 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. In these catalytic tests some homocoupling product (Ph–Ph) was concomitantly formed, but in none of the above runs did the Ph–Ph/Ar–Ph ratio exceed 10% (see the Supporting Information).

Supporting Information (see footnote on the first page of this article): NMR spectra and MS (ESI-TOF), details for various cross-coupling experiments.

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