

Heck, Suzuki and Kumada–Corriu cross-coupling reactions mediated by complexes based on the upper rim of diphosphinated calix[4]arenes

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Abstract

Two bis-triarylphosphines [5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**) and 5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxy-calix[4]arene (**2**)] were assessed in metal-catalysed cross-coupling reactions. Effective Heck couplings between aryl bromides and styrene were achieved when operating in DMF at 110 °C with 2 mol% of Pd(OAc)₂ in the presence of Cs₂CO₃; the highest TOF values (ca. 50) being observed with *activated* aryl bromides. The coupling reaction could be extended to aryl chlorides (conversions of ca. 20% within 24 h) with both ligands, provided the reaction was carried out with NaOAc in a DMF/water mixture. The two phosphines were also found to be efficient in Suzuki cross-coupling of aryl halides with phenyl boronic acid, the turnovers being somewhat lower than those observed in Heck couplings. In Kumada–Corriu cross-coupling of aryl halides with phenylmagnesium bromide, remarkable activities were reached in the presence of palladium or nickel. TONs up to 800 mol(converted PhCl)·mol(Ni)⁻¹ were observed for the conversion of chlorobenzene into biphenyl. Unlike the mono-triaryl phosphine PPh₃, ligands **1** and **2** both promote palladium-catalysed Suzuki and Kumada–Corriu couplings involving chlorobenzene.

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Keywords: Diphosphines; Calixarenes; Cross-couplings; Aryl halides

1. Introduction

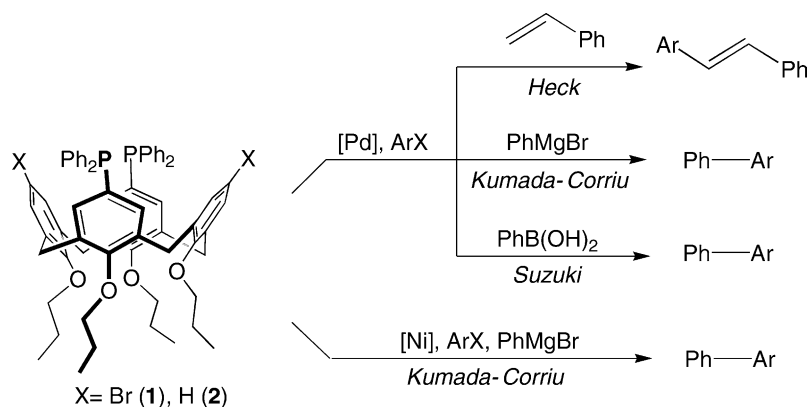
Generic calix[*n*]arenes are cyclic, basket-shaped polyphenols which are receiving extensive attention in all fields of molecular chemistry [1,2]. Over the last decade, methodology became available that allowed their easy, multiple functionalisation, hence providing access to novel and sophisticated podands, the properties of which were mainly exploited in areas such as solvent extraction and ion sensors. The utility of calixarene-based ligands in catalytic applications has been recognised more recently [3] and their potential has already been evaluated in several fields of catalysis including olefin hydroformylation [4,5], oligomerisation and polymerisation reactions [6,7], hydrogenations [5,8], olefin oxidations [9] and carbon–carbon bond forming reactions [10,11].

The present study is aimed at assessing the calix[4]arene derived diphosphines **1** and **2** in several cross-coupling reactions. It follows a previous study [6] that showed that these diphosphines are thermally robust and highly efficient in the nickel-catalysed ethylene dimerisation, their activity being higher than those observed with the more basic dppe and PCy₃ ligands [12]. This effect was assigned to the particular dynamics of the corresponding Ni-chelate complexes in which the metal centre moves from one side to the other of the calixarene, a motion characterized by a cyclic variation of the ligand's bite angle reaching a maximum value when the metal crosses the calixarene axis. This bite angle variation causes a temporary electron density decrease at the metal centre and incidentally facilitates the ethylene insertion step.

The present work focusses on Heck [13], Suzuki [14] and Kumada–Corriu [15,16] cross-coupling reactions of various arylhalides (Scheme 1). Although these reactions are most often carried out in the presence of phosphine ligands, rarely diphosphines with a flexible bite angle, such as, e.g. **1**

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Scheme 1.

and **2**, have been employed. Note, the only calixarene ligand reported to date that was used in cross-coupling reactions is a bis-imidazolium ligand, synthesised by Schatz et al. [11].

2. Experimental

All reactions were performed in Schlenk flasks under dry nitrogen. Solvents were dried by conventional methods and distilled under nitrogen immediately prior to use. Gas chromatographic analyses were performed on a VARIAN 3900 gas chromatograph using a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). 5,17-Dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**1**) [2], 5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene (**2**) [2] and *cis-P,P'*-dibromo- $\{5,17\}$ -bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel(II) (**3**) [6] were prepared according to previously published methods. Pd(OAc)₂, Cs₂CO₃, PhMgBr, PhB(OH)₂, styrene and arylhalides were purchased and used as received. Catalytic products were purified by silica gel chromatography, NMR spectroscopy corresponds to the literature [17].

2.1. General procedure for Heck cross-coupling reaction

Into a Schlenk tube, Pd(OAc)₂ (0.0045 g, 0.02 mmol, 2 mol%), ligand **1** or **2** (0.02 mmol, 2 mol%) and Cs₂CO₃ (0.358 g, 1.10 mmol) were introduced under nitrogen. The Schlenk tube was purged three times with nitrogen, then DMF (3 mL), styrene (0.17 mL, 1.50 mmol) and the aryl halide (1.00 mmol) were added. The reaction mixture was heated at 110 °C for the desired time (1–24 h). After cooling, decane (0.10 mL) was added as an internal reference. A sample of 0.5 mL was taken, filtered and analysed by GC.

2.2. General procedure for Suzuki cross-coupling reactions

Into a Schlenk tube, Pd(OAc)₂ (0.0045 g, 0.02 mmol, 2 mol%), ligand **1** or **2** (0.02 mmol, 2 mol%), Cs₂CO₃

(0.358 g, 1.10 mmol) and 0.122 g (1.00 mmol) of phenylboronic acid were introduced under nitrogen. After purging three times with nitrogen, DMF (3 mL) and aryl halide (1.5 mmol) were added. The reaction mixture was heated at 110 °C for the desired time (1–15 h) and after cooling to room temperature, 0.10 mL of decane (internal reference) was added. A sample of 0.5 mL of the resulting solution was taken, filtered and analysed by GC.

2.3. General procedure for Kumada–Corriu cross-coupling reaction catalysed by palladium

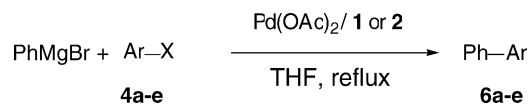
Into a Schlenk tube, Pd(OAc)₂ (0.0045 g, 0.02 mmol, 2 mol%) and ligand **1** or **2** (0.02 mmol, 2 mol%) were introduced under nitrogen. After purging three times with nitrogen, THF (6 mL), a 3.0 M solution of PhMgBr in Et₂O (0.5 mL, 1.5 mmol) and aryl halide (1 mmol) were added. The reaction mixture was refluxed for the desired time (1–15 h) and after cooling to room temperature, decane (0.10 mL, internal reference) and methanol (2 mL) were added. A sample of 0.5 mL of the resulting solution was taken, filtered and analysed by GC.

2.4. General procedure for the nickel-catalysed Kumada–Corriu cross-coupling reaction

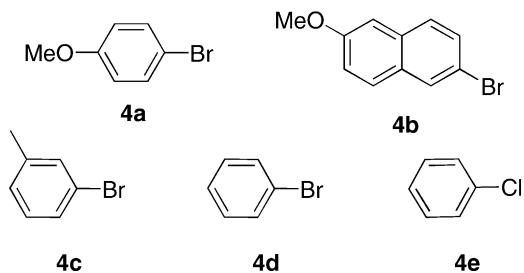
To a Schlenk tube containing complex **3** (0.005 g, 3.39 μmol, 2 mol%), THF (1 mL), PhMgBr 3 M in Et₂O (0.1 mL, 0.33 mmol) and aryl halide (0.17 mmol) were added. The reaction mixture was refluxed for 1 h and after cooling to room temperature, decane (0.05 mL, internal reference) and methanol (1 mL) were added. A small amount (0.5 mL) of the resulting solution was taken, filtered and analysed by GC.

3. Results and discussion

The diphosphines **1** and **2** were first assessed in Heck reactions of aryl halides with styrene in DMF (Scheme 2). The runs were achieved at 110 °C with 2 mol% of Pd(OAc)₂ in the presence of a base. With Cs₂CO₃ for example, 98% of 4-



Scheme 4.



Scheme 2.

bromoanisole (**4a**) was consumed after 1 h, while in the same period the conversion dropped to 8% when using K_2CO_3 . The higher conversions observed with Cs_2CO_3 versus K_2CO_3 possibly arise from a better solubility of the cesium salt in DMF [18]. Similarly, when employing Cs_2CO_3 , 2-bromo-6-methoxynaphthalene (**4b**) and 3-bromotoluene (**4c**) were consumed almost quantitatively after 1 h with either ligand **1** or **2**. As anticipated, the reaction with the non-activated aryl halide bromobenzene (**4d**) (in the presence of Cs_2CO_3) proceeded a little slower, *trans*-stilbene (**5d**) being formed in 46 and 40% conversion with ligands **1** and **2**, respectively, after 1 h. Under identical conditions, the less reactive chlorobenzene (**4e**) was not converted to stilbene, but conversions of ca. 20% were observed for both ligands when carrying out the reaction with NaOAc in a DMF/water mixture. Overall, the performances of **1** and **2** in Heck cross-couplings are superior to those of PPh_3 (Table 1) and compare with those reported for $\text{Ph}_2\text{PCH=CHPh}_2$ [19].

The diphosphines **1** and **2** were further tested in Suzuki cross-coupling of aryl halides with phenyl boronic acid. Again, the reaction was carried out in the presence of Cs_2CO_3 in anhydrous DMF (Scheme 3). The rate of these reactions were found to be lower than those of the Heck reaction described above. In a typical example, 4-bromoanisole (**4a**) had a conversion rate of ca. 65% after 1 h, quantitative conversion into biaryl **6a** requiring a period of 5 h (Table 2). Whichever aryl halide was used, the sterically less encumbered diphosphine **2** turned out to be the more efficient ligand. Thus, with ligand **2**, conversion of the brominated naphthalene **4b** was completed after 3 versus 5 h when using **1**. With the less activated aryl bromides **4c** and **4d**, the coupling reac-

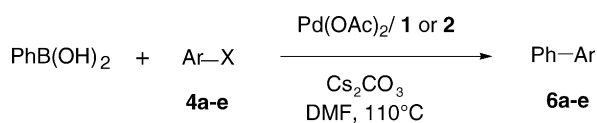
tions proceeded slower. For example with **2**, compounds **4c** and **4d** were converted into the corresponding biaryls in 71% (after 5 h) and 98% (after 15 h), respectively. Under the same conditions, reactions of chlorobenzene and phenyl boronic acid were achieved in moderate yield (30% in 15 h).

It is interesting to note that the activities observed with **1** or **2** are close to those produced with PPh_3 when performing the Suzuki coupling with an aryl bromide (Table 2). The fact that cross-coupling occurred with **1** or **2** when using chlorobenzene while no reaction was observed with PPh_3 under similar conditions, suggests that the presence of a chelating unit is required for this reaction.

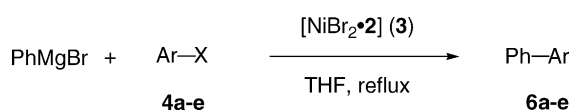
Aiming at producing the biaryls **6** in better yields, we decided to evaluate diphosphines **1** and **2** in Kumada–Corriu cross-coupling reactions (Scheme 4). Kumada–Corriu couplings can be achieved both with nickel [20] and palladium catalysts [21]. In the following, the results obtained with palladium are given first.

Mixing diphosphines **1** and **2** with Pd(OAc)_2 gave systems that very efficiently catalyse the cross-coupling of aryl halides with phenylmagnesium bromide. All runs were carried out in refluxing THF. In the presence of 2 mol% Pd, the activated aryl bromides **4a–c** were almost fully converted into the biaryls **6a–c** within 1 h (Table 3). We observed that with either ligand the non-activated bromide (**4d**) was fully converted within 1 h, even in the presence of only 1 mol% of palladium. In order to determine the true activity of these catalytic systems, the catalyst loading was reduced to 0.02 mol%. This led to a TON of 1100 mol (converted **4d**)·mol(Pd)^{−1} for diphosphine **1** (corresponding to a conversion of 22%) and 1450 mol(converted **4d**)·mol(Pd)^{−1} for ligand **2** (conversion of 29%). As for PhBr, the rate of the Kumada–Corriu reaction with PhCl (**4e**) is higher than that of the corresponding Suzuki reaction. In this case biphenyl was obtained either in 28% (using **1**) or 38% (using **2**) yield after 15 h. As in the Suzuki coupling, with all substrates tested, the catalytic systems based on diphosphine **2** showed higher activities than those observed with ligand **1**. Again, no reaction occurred with chlorobenzene when using PPh_3 as the ligand.

For the nickel-catalysed Kumada–Corriu reaction (Scheme 5), the tests were carried out with a single catalyst precursor, namely $\text{NiBr}_2 \cdot \mathbf{2}$ (**3**) [6]. It is noteworthy that in



Scheme 3.



Scheme 5.

Table 1
Pd(OAc)₂/1 or 2 catalysed Heck cross-coupling aryl halides 4 with styrene^a

4	Ligand	Time (h)	Conversion into 5 ^b (%)	TON (mol(converted 4)-mol(Pd ⁻¹))
4a	1	1	87	43
4a	1	2	100 (98% isolated yield)	50
4a ^c	2	15	8	4
4a	2	1	98	49
4a	2	2	100	50
4a ^d	PPh ₃ (2 eq./Pd)	1	90	45
4b	1	1	99	49
4b	1	2	100 (94% isolated yield)	50
4b	2	1	99	49
4b	2	2	100	50
4c	1	1	100 (94% isolated yield)	50
4c	2	1	99	49
4c ^d	PPh ₃ (2 eq./Pd)	1	44	22
4d	1	1	46	23
4d	1	5	98 (96% isolated yield)	49
4d	2	1	40	20
4d	2	5	77	38
4d ^d	PPh ₃ (2 eq./Pd)	1	11	5
4e ^e	1	24	20	10
4e ^e	2	24	22	11

^a Reaction conditions: Pd(OAc)₂ (0.004 g, 20 μmol, 2 mol%), 1 or 2 (20 μmol, 2 mol%), styrene (1.50 mmol, ~0.17 mL), ArX (1.00 mmol), Cs₂CO₃ (0.358 g, 1.10 mmol), decane (0.10 mL), DMF (3 mL), 110 °C.

^b Determined by GC, calibration based on decane.

^c K₂CO₃ (0.207 g, 1.50 mmol) instead of Cs₂CO₃.

^d PPh₃ (0.011 g, 40 μmol, 4 mol%).

^e 1 or 2 (30 μmol, 3 mol%), styrene (1.10 mmol, ~0.126 mL), NaOAc (0.090 g, 1.10 mmol), DMF/H₂O (0.66 mL, 2:1, v/v), 130 °C.

Table 2
Pd(OAc)₂/1 or 2 catalysed Suzuki cross-coupling aryl halides 4 with phenylboronic acid^a

4	Ligand	Time (h)	Conversion into 6 ^b (%)	TON (mol(converted 4)-mol(Pd ⁻¹))
4a	1	1	63	31
4a	1	2	78	39
4a	1	5	94	47
4a	2	1	70	35
4a	2	2	86	43
4a	2	5	100	50
4a ^c	PPh ₃ (2 eq./Pd)	1	75	37
4b	1	2	45	22
4b	1	5	100	50
4b	2	1	52	26
4b	2	3	100	50
4b ^c	PPh ₃ (2 eq./Pd)	1	82	41
4c	1	5	68	34
4c	2	5	71	35
4c ^c	PPh ₃ (2 eq./Pd)	5	71	35
4d	1	15	81	20
4d	2	15	98	49
4d ^c	PPh ₃ (2 eq./Pd)	15	90	45
4e	1	15	16	8
4e	2	15	30	15
4e ^c	PPh ₃ (2 eq./Pd)	15	0	0

^a Pd(OAc)₂ (0.004 g, 20 μmol, 2 mol%), ligand (20 μmol, 2 mol%), PhB(OH)₂ (0.122 g, 1.00 mmol), ArX (1.5 mmol), Cs₂CO₃ (0.358 g, 1.10 mmol), decane (0.10 mL), DMF (3 mL), 110 °C.

^b Determined by GC, calibration based on decane.

^c PPh₃ (0.011 g, 40 μmol, 4 mol%).

Table 3

Pd(OAc)₂/1 or 2 catalysed Kumada–Corriu cross-coupling aryl halides **4** with phenylmagnesium bromide^a

4	Ligand	Pd(OAc) ₂ (mol%)	Time (h)	Conversion into 6 ^b (%)	TON (mol(converted 4)-mol(Pd ⁻¹))
4a	1	2	1	98 (94% isolated yield)	49
4a	2	2	1	99	49
4a ^d	PPh ₃ (2 eq./Pd)	2	1	88	44
4b	1	2	1	100 (95% isolated yield)	50
4b	2	2	1	100	50
4c	1	2	1	100 (95% isolated yield)	50
4c	2	2	1	82	41
4c	2	2	2	100	50
4c ^d	PPh ₃ (2 eq./Pd)	2	1	99	49
4d ^c	1	1	1	100	100
4d	1	0.1	1	28	280
4d	1	0.02	1	22	1100
4d ^c	2	1	1	100 (96% isolated yield)	100
4d	2	0.1	1	33	330
4d	2	0.02	1	29	1450
4d ^d	PPh ₃ (2 eq./Pd)	2	1	100	50
4e	1	2	1	13	6
4e	1	2	5	18	9
4e	1	2	15	28	14
4e	2	2	1	14	7
4e	2	2	5	22	11
4e	2	2	15	38	19
4e ^d	PPh ₃ (2 eq./Pd)	2	5	0	0

^a Pd(OAc)₂/ligand: 1/1, PhMgBr (0.5 mL, 1.50 mmol, 3 M in Et₂O), ArX (1.00 mmol), decane (0.10 mL), THF (6 mL), reflux.^b Determined by GC, calibration based on decane.^c PhMgBr (1 mL, 3.00 mmol, 3 M in Et₂O), PhBr (2.00 mmol, ~0.21 mL).^d PPh₃ (0.011 g, 40 μmol, 4 mol%).

all cases, this complex afforded better results than those observed for the Pd(OAc)₂/2 system described above. Operating in the presence of 2 mol% **3**, high conversions, all superior to 92% (TON > 46), were observed after 1 h, with the aryl bromides **4a–d** as well as with chlorobenzene (Table 4). Using 0.02 mol% of **3**, 16% of the chlorobenzene loaded were converted after 1 h. This corresponds to a TON of 800 mol(converted **4e**)-(mol of Ni)⁻¹. For comparison, using 2 mol% of metal, afforded biphenyl in 14% yield after 1 h with palladium, while full conversion was observed in the same period with nickel.

Table 4

Nickel complex **3** catalysed Kumada–Corriu cross-coupling aryl halides **4** with phenylmagnesium bromide^a

4	Ni complex 3 (mol%)	Conversion into 6 ^b (%)	TON (mol(converted 4)-mol(Pd ⁻¹))
4a	2	92	46
4b	2	100	50
4c	2	99	49
4d	2	99	49
4e	2	100	50
4e	0.1	74	740
4e	0.02	16	800

^a Ni complex **3**, PhMgBr (0.1 mL, 0.33 mmol, 3 M in Et₂O), ArX (0.17 mmol), decane (0.05 mL), THF (1 mL), 1 h, reflux.^b Determined by GC, calibration based on decane.

4. Concluding remarks

The present work is a further confirmation that conical calixarenes in which two distal positions of the upper rim are substituted by phosphino groups hold promise as catalysts for C–C bond forming reactions. The most striking results of this study are the remarkable activities of diphosphines **1** and **2** in Kumada–Corriu couplings. The exact origin of the observed performances is not known at the present stage, but could rely on the bite angles of these ligands. Kamer et al. have recently studied the effect of the natural bite angle (β_n) of diphosphane ligands in the palladium catalyzed cross-coupling of *sec*-butyl magnesium chloride with bromobenzene and shown that the reaction rate reaches a maximum with the diphosphane Ph₂P{C₆H₄-*o*-OC₆H₄(-*o*-PPh₂)}, the natural bite angle of which is 102.7° [22]. The β_n values of **1** and **2** have not been calculated, but can be estimated from the PMP angle found in PtCl₂•**1** in the solid state, $\alpha = 99.7^\circ$, a value, which, due to the inherent dynamics of this complex in solution corresponds to a minimum [2]. In view of the cyclic variation of the ligand's bite angle in square planar MX₂• (**1** or **2**) complexes, the PMP angle of the palladium complexes considered here is likely to easily reach the optimum value determined by Kamer. Of course, further studies are needed to confirm that the flexibility of diphosphines **1** and **2** is a crucial feature for the observed

catalytic properties. Future work will focus in particular on non flexible analogues of **1** or **2**.

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