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High efficiency of cavity-based triaryl-phosphines in nickel-catalysed Kumada–Tamao–Corriu cross-coupling†

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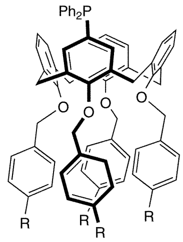
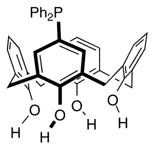
Combining diaryl-calixarenyl phosphines with [Ni(cod)$_2$] resulted in highly active Kumada–Tamao–Corriu cross-coupling catalysts. With one of the ligands, TOFs up to 439 000 mol(ArBr) mol(Ni)$^{-1}$ h^{-1} were observed in the reaction of 1-bromonaphthalene with PhMgBr. The systems were also found to be active at room temperature with aryl chlorides.

Metallation-cross-coupling strategies dominate in the construction of numerous sophisticated molecules, including natural products, organic materials, polymers, and building blocks for supramolecular chemistry.[1–8] One of the methodologies that still plays a prominent role in aryl–aryl coupling is the Kumada–Tamao–Corriu (KTC) reaction, that is the coupling of a Grignard reagent (ArMgX) with an aryl halide.[9–12] The continuous interest for these reactions is mainly due to the fact that Grignards are among the most easily prepared and least expensive arylmetals. In this chemistry the efficacy of nickel catalysts is well-documented,[13] although palladium remains the most frequently employed metal.[14] Until recently, it was commonly accepted that the best results arise from a combination of nickel with diphosphines, especially if these display a large bite angle, *e.g.* as with $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_4PPh_2$, or $[Fe(C_5H_4PPh_2)_2]$. Such diphosphines may assist the reductive elimination step, as they force the organic fragments to be *cis* and rather close to one another.[15–17] Other authors have shown that monodentate ligands with strong donor properties, *e.g.*, *N*-heterocyclic carbenes,[18,19] or diaminophosphine oxide derivatives,[20] may also efficiently accelerate this reaction.

We have recently shown that a particular class of chemically robust aryl-monophosphines, namely calix[4]arenes substituted at their upper rim by a diarylphosphino group, promote the palladium-catalysed cross-coupling between arylboronic acids and aryl halides.[21] One factor which may contribute to the high reaction rates observed arises from the receptor properties of the calixarenyl fragment, which is able to temporarily entrap the phosphorus-bonded "M(π-arene)" unit, thereby increasing the bulkiness of the ligand and consequently favouring the formation of monoligand-M(0) species. It is noteworthy that Pd(0)-monophosphine complexes have been recognised as key intermediates in Suzuki–Miyaura cross-coupling with arylbromides.[22–28] A monophosphine pathway has also been proposed by Liu for the Ni-catalyzed cross-coupling between various ArX substrates and arylboronic acids in the presence of a bulky monophosphine.[29] It should further be mentioned here that the capacity of phosphino-substituted calix[4]arenes to bind in solution metal–arene units in a supramolecular fashion was structurally proven (by NMR and X-ray analysis) in the case of Ru(*p*-cymene) complexes, arene binding involving interactions with two distal phenoxy rings.[30,31]



1 R = H
2 R = OMe



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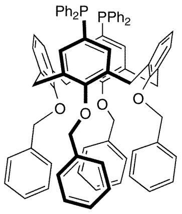

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Aiming to enlarge the scope of applications of calixarene-based monophosphines, we have now investigated the performance of the three receptors **1–3** in nickel-catalysed Kumada–Tamao–Corriu (KTC) coupling. It is worth mentioning here that bulky monophosphines able to promote the formation of monoligand-M(0) intermediates (*e.g.* Buchwald ligands) are now classically used in palladium-catalysed Kumada–Tamao–Corriu cross-coupling, but surprisingly, to date, this ligand-type has not been considered for nickel-catalysed, Grignard mediated aryl–aryl couplings. While the more recent developments in the nickel-catalysed KTC couplings are focusing on electron-rich ligands, the ligands of this study are triaryl-phosphines, which makes them particularly easy to handle.

We began our investigations by studying the reaction of PhMgBr with 4-bromoanisole in the presence of a mixture of [Ni(cod)$_2$] and two equiv. of phosphine **1**.[32] The 1 h-test reactions were carried out in dioxane (Table 1). Using a catalyst loading of 0.002% and operating at 100 °C gave the expected coupling product in 50.6% yield, a result which corresponds to a TOF of 25 300 mol(ArBr) mol(Ni)$^{-1}$ h^{-1}

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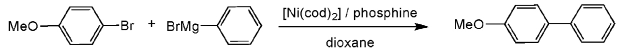
† Electronic supplementary information (ESI) available: Experimental details for the synthesis of **6** and catalytic runs. See DOI: 10.1039/c0cc05805j

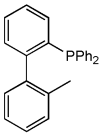
Table 1 Kumada–Tamao–Corriu cross-coupling of 4-bromoanisole with phenyl boronic acid—the search for optimal conditions[a]



Entry	Precatalyst	ArBr/[Ni]	*T*/°C	Conv. (%)	TOF[b]
1	[Ni]/**1** (2 equiv.)	50 000	100	50.6	25 300
2	[Ni]/**1** (2 equiv.)	50 000	80	41.4	20 700
3	[Ni]/**1** (2 equiv.)	50 000	60	19.9	9950
4	[Ni]/**1** (2 equiv.)	100 000	100	31.3	31 300
5	[Ni]/PPh$_3$ (2 equiv.)	100 000	100	8.3	8300
6	[Ni]/P(*o*-tol)$_3$ (2 equiv.)	100 000	100	14.4	14 400
7	[Ni]/**4** (1 equiv.)	100 000	100	26.2	26 200

[a] Conditions: [Ni(cod)$_2$], 4-bromoanisole, PhMgBr (2 equiv./ArBr), dioxane (1.50 mL), decane (0.05 mL), 1 h. Conversions by GC; calibrations based on decane. [b] mol(ArBr) mol(Ni)$^{-1}$ h^{-1}.

(Table 1, entry 1). Operating at lower temperatures led to significantly lower activities (Table 1, entries 2 and 3). A temperature of 100 °C was therefore applied to all the following runs. When reducing the catalyst loading by a factor of two the conversion still reached 31% after 1 h (TOF = 31 300 mol(ArBr) mol(Ni)$^{-1}$ h^{-1}). In comparison, under similar conditions, PPh$_3$ and the bulky P(*o*-tolyl)$_3$ ligand led to significantly lower conversions, 8.3% and 14.4%, respectively (TOFs = 8300 and 14 400 mol(ArBr) mol(Ni)$^{-1}$ h^{-1}). The remarkable efficiency of ligand **1** was further confirmed by a comparison with calixarenyl-diphosphine **4** (1 equiv.), a chelating ligand which was previously shown to be highly efficient in other C–C bond forming reactions as a result of its large bite angle.[33]



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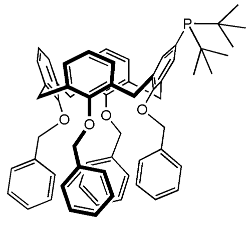

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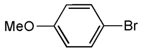
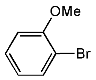
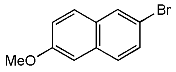
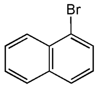
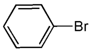
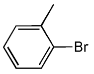
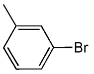
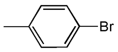
Ligand **4** led to a *ca.* 20% lower TOF than that obtained with **1** (Table 1, entry 7). Note that some homocoupling product (Ph–Ph) also formed, but in none of the above runs did the ratio Ph–Ph : Ar–Ph exceed 9% (see ESI†).

As a next step, we assessed the efficiency of ligands **1–3** in reactions with various aryl bromides using catalyst loadings of 0.01% (Table 2). For each non-encumbered aryl bromide, at least one of the three phosphines led to conversions superior to 85%. With sterically hindered substrates, the conversions, although lower, remained satisfactory (44.4–71.7%; Table 2, entries 2 and 6). Interestingly, 1-bromonaphthalene (naphtBr) gave the fastest reactions, full conversion being observed for this substrate under the above conditions whatever the phosphine employed (Table 2, entry 4). Remarkably, when the experiments carried out with naphtBr were repeated with a Ni/ArBr ratio of 1 : 10^6, the conversions still reached 40% after 1 h (TOF = 386 000 (**1**), 439 000 (**2**) and 426 000 (**3**) mol(naphtBr) mol(Ni)$^{-1}$ h^{-1}, see Table S3, ESI†). In comparison, the Buchwald-type triarylphosphine **5**[34] led in this case to an activity of 253 000 mol(naphtBr) mol(Ni)$^{-1}$ h^{-1}.

High conversions were also obtained with the more challenging aryl chlorides (Table 3). Thus, for example, using phosphine **1** and applying a catalyst loading of 1% led straightforwardly (1–3 h; 100 °C) to conversions close to 100% for all substrates, except for 2-chlorotoluene (24.6% after 1 h), which is more encumbered than the other chloroarenes. As expected, better activities were observed for the electron-deficient 4-nitrochlorobenzene (Table 3, entry 9) than for the electron-rich substrates 4-chloroanisole and chlorotoluene (Table 3, entries 1–6). Reducing the catalyst concentration by a factor 100 still led to high conversions (Table 3). Similar trends and activities were observed with the other two ligands. The reactions with aryl chlorides could also be performed in moderate-to-good conversions at 25 °C (Table 4). Replacing the triarylphosphine ligand **1** with the more basic ligand **6** accelerated these reactions by *ca.* 30% (Table 4). The moderate increase of reaction rate observed with **6** is in line with the studies by Liu *et al.* who suggested (a) that a monophosphine mechanism is favoured in the case of bulky phosphines and (b) that oxidative addition of ArX (X = Cl, Br) to nickel(0) is only weakly influenced by the basicity of the phosphine used.[31] Finally, we found that using PPh$_3$ resulted in a catalytic system which turned out to be 4 times less active than **1** at room temperature.

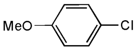
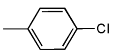
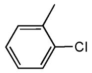
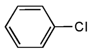
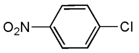
Overall, the above results show that ligands **1–3** display activities in KTC cross-coupling catalysis that are unusually high for a triarylphosphine ligand. We tentatively propose the formation of a transient [Ni(π-ArX)(calix-phosphine)] intermediate[35] having the coordinated ArX entrapped in a supramolecular

Table 2 Kumada–Tamao–Corriu cross-coupling of aryl bromides using a ArBr/Ni ratio of 10 000[a]

Entry	ArBr	Conversion (%)		
		1	**2**	**3**
1		86.4	89.4	88.4
2		52.3	54.5	59.3
3		85.3	88.9	86.8
4		95.5	96.9	98.2
5		80.8	96.3	49.3
6		58.1	71.7	44.4
7		76.2	85.7	73.6
8		82.7	90.0	87.7

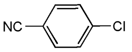
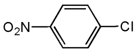
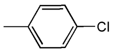
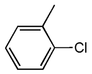
[a] Conditions: [Ni(cod)$_2$] (5 × 10^{-5} mmol, 1 × 10^{-2} mol%), phosphine (2 equiv./Ni), ArBr (0.5 mmol), PhMgBr (1 mmol), dioxane (1.50 mL), decane (0.05 mL), 100 °C, 1 h. Conversions by GC; calibrations based on decane.

Table 3 Kumada–Tamao–Corriu cross-coupling of arylchlorides catalyzed by [Ni(cod)$_2$]/**1**[a]

Entry	ArCl	[Ni(cod)$_2$] (mol%)	Reaction time/h	Conversion (%)
1		1	3	98.5
2		0.01	16	37.4
3		1	3	99.6
4		0.01	16	42.2
5		1	1	24.6
6		1	5	75.4
7		1	1	97.9
8		0.01	5	69.2
9		1	1	99.2
10		0.01	5	60.3

[a] Conditions: [Ni(cod)$_2$], monophosphine **1** (2 equiv./Ni), ArCl (0.25 mmol), PhMgBr (0.5 mmol), dioxane (0.75 mL), decane (0.025 mL), 100 °C. The conversions were determined by GC, the calibrations being based on decane. At 100 °C, the nitro group did not undergo nucleophilic attack.

Table 4 Kumada–Tamao–Corriu cross-coupling of aryl chlorides in the presence of monophosphines **1** and **6** at 25 °C[a]

Entry	ArCl		Monophosphine **1**	Monophosphine **6**
1		conv. (%) (6 h)	72.2	88.2
2		conv. (%) (6 h)	66.7	92.3
3		conv. (%) (24 h)	62.5	80.9
4		conv. (%) (24 h)	45.2	64.4

[a] Conditions: [Ni(cod)$_2$] (7.5×10^{-3} mmol, 3 mol%), monophosphine (2 equiv./Ni), ArCl (0.25 mmol), PhMgBr (0.5 mmol), dioxane (0.75 mL), decane (0.025 mL), 25 °C. Conversions determined by GC; calibrations based on decane. At 25 °C, neither the cyano nor the nitro groups were found to undergo nucleophilic attack.

manner in the cavity. The resulting orientation of the P–M bond in this complex, turned towards the calixarene axis (and not outwards), should artificially increase the ligand bulk, and incidentally favour the formation of a mono-ligand Ni(0) intermediate.

In summary, we have reported the first examples of highly efficient Kumada–Tamao–Corriu cross-coupling reactions carried out by combining a nickel centre with a triaryl monophosphine. The systems described are particularly easy to handle as the reported calixarene-phosphines are chemically exceptionally robust. Further studies are aimed at the discovery of other catalytic reactions exploiting the supramolecular potential of calixarenyl-monophosphines.

This work was supported by the French ANR (Program MATCALCAT) and University Louis Pasteur (grant to LM).

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