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Efficient, Nickel-Catalysed Kumada–Tamao–Corriu Cross-Coupling with a Calix[4]arene-Diphosphine Ligand

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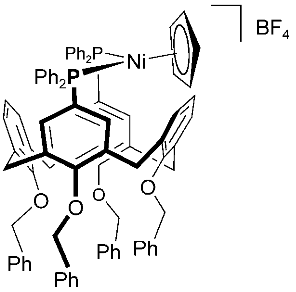
Abstract: The dynamic complex *cis-P,P′*-(η^5-cyclopentadienyl)-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxycalix[4]arene}nickel(II) tetrafluoroborate (**2**) in which the PNiP plane undergoes a rapid fanning motion was assessed in the cross-coupling reacting between phenylmagnesium bromide (PhMgBr) and aryl halides (ArX). TOFs, of up to 21250 mol(converted ArBr)·mol(**2**)$^{-1}$·h^{-1}, were obtained with electron-rich as well as congested bromoarenes using catalyst loadings as low as 1×10^{-3} mol%, provided that the reactions were carried out at 100 °C in dioxane with a PhMgBr/ArX ratio of 2:1. The high activities observed contrast with those observed for triphenylphosphine-based catalysts and furthermore, outperforms the fastest diphosphine-based catalysts reported, a behaviour which is likely to rely on a bite angle effect.

Keywords: calixarenes; Kumada–Tamao–Corriu coupling; nickel; strained chelating diphosphines

Introduction

The Kumada–Tamao–Corriu cross-coupling[1–3] is the reaction between a Grignard reagent and an aryl or vinyl halocarbon catalysed by nickel or palladium complexes.[4–8] In the last three decades this valuable synthetic tool has been applied to the preparation of a variety of organic molecules, including natural products, polymers, and liquid crystals. First reported in 1972, it constituted at that time the starting point for the discovery of many new cross-coupling reactions.[9,10] In most systems, the active catalyst is based on a tertiary monophosphine, as such ligands are particularly suited for the stabilisation of zero-valent metal intermediates. A rapid survey of the literature shows that PPh_3 is a commonly employed phosphine, although some chelating diphosphines are known to be superior to monophosphines.[11] Prominent diphosphines for this reaction include dppp, dppb, dppf, and DPEphos.[12]

Independently, our group[13] and that of Tsuji[14] recently described the synthesis of diphosphines based on a conical calix[4]arene unit, in which diphenylphosphino substituents are attached to the *p*-carbon atoms of two distal phenoxy rings. For convenience, these phosphines will be termed here "1,3-calixdiphosphines". These ligands, when associated with nickel(II), result in remarkably fast catalysts for C−C bond-forming reactions, notably ethylene[15] and propylene dimerisation[16] as well as norbornene polymerisation.[17] A major practical advantage of the 1,3-calixdiphosphines is their high stability towards oxidation, which makes them attractive with respect to the ligands usually employed for efficient coupling reactions based on Ni/phosphine systems, e.g., PCy_3.[18] The high performance of the 1,3-calixdiphosphine/Ni catalysts was attributed, in part, to the dynamics of the complexes formed in solution, during which time the ligand bite angle periodically increases, thus favouring the insertion step as a result of increased steric interactions between the P substituents and the two coupling partners. In our first report on this topic, which mainly focussed on dimerisation reactions, we had briefly mentioned that Kumada–Tamao–Corriu cross-coupling reactions can also be performed with such ligands, but the catalyst activity was moderate.[19] As an extension of this preliminary study, we now show that high activities can be reached under appropriate reaction conditions. The present study further shows that the size of the substituents grafted onto the lower rim may also influence the catalytic outcome. All catalytic runs were performed with a well-defined precursor, namely the *cationic* complex **2**.



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Results and Discussion

For the present study we started from the tetrabenzyl-substituted 1,3-calixdiphosphine **1**.[14] Reaction of the latter with $[(\eta^5\text{-}C_5H_5)Ni(COD)]BF_4$ (COD = 1,5-cyclooctadiene) afforded quantitatively complex **2** (Scheme 1), which can be handled in air. The mass spectrum of **2** shows a strong peak at 1275.38 with an isotopic profile exactly as expected for the corresponding $[M]^+$ ion. The NMR spectra at room temperature of **2** are consistent with a C_2-symmetrical molecule. Thus, the ^{1}H NMR spectrum displays a single AB pattern for all Ar*CH*$_2$Ar protons, while the ^{31}P NMR spectrum exhibits a singlet at $\delta = 30.8$ ppm. In the ^{13}C NMR spectrum, the Ar*C*H$_2$Ar signal appears at $\delta = 31.60$ ppm, a value which is in accord with a calixarene in the cone conformation.[20]

The molecular structure of **2** was determined by a single X-ray diffraction study (Figure 1 and Table 1). The complex displays C_1-symmetry in the solid state. The calixarene fragment adopts a pinched cone conformation, with interplanar angles between opposite phenoxy rings of 26.3 and 69.0°, respectively. As already observed in *cis*-chelate complexes obtained from related "1,3-calixdiphosphines",[15,21] the metal unit is turned away from the calixarene axis (distance to the axis: *ca.* 1.35 Å). The dihedral angle between the PNiP plane and the calixarene reference plane, that is the mean plane of the bridging Ar*C*H$_2$ carbon atoms, is only 23°. The bite angle of the chelating unit, 102.8°, compares with that found in other complexes of general formula $[NiCp(PPh_3)_2]^+$ ($Cp = C_5H_5$ or Cp-derived ligand).[22] Calixarene **2** contains a unique PPh ring oriented towards the centre of the cavity (ring containing C75), hence rendering the two phosphorus atoms non-equivalent.

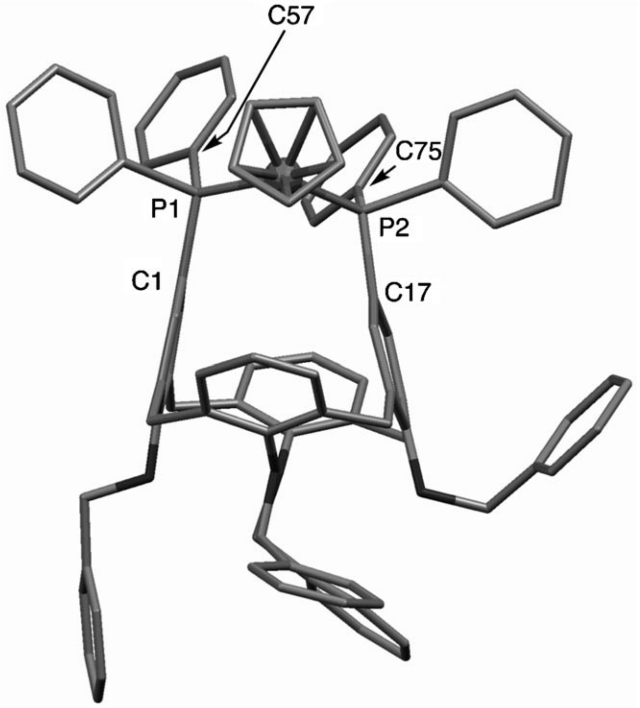
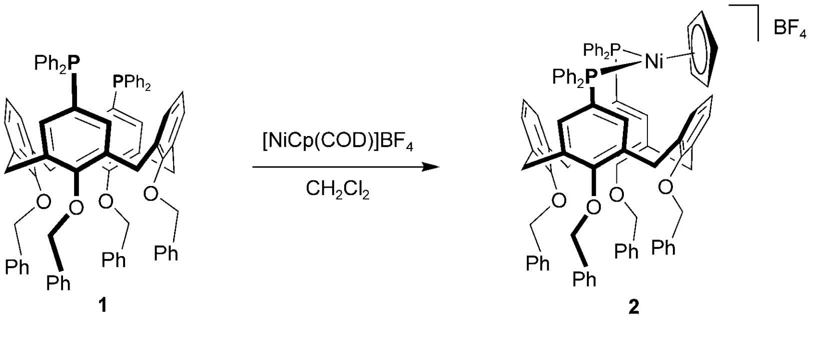


Figure 1. Molecular structure of the cationic nickel complex **2**. The BF$_4$ anion, the CH$_2$Cl$_2$ and the hexane solvent molecules are omitted for clarity

The non-equivalence of the P atoms was also displayed in solution at low temperatures. Thus, the ^{31}P NMR (CD$_2$Cl$_2$, 162 MHz) spectrum measured at



Scheme 1. Synthesis of the chelate complex **2**.

Table 1. Selected bond lengths [Å] and angles [°] for **2**.

Distances			
Ni1−P1	2.2031(12)	Ni1−P2	2.2013(11)
P1−C1	1.823(4)	P2−C17	1.821(4)
P1−C57	1.814(4)	P2−C69	1.833(4)
P1−C63	1.843(4)	P2−C75	1.832(4)
Angles			
P1−Ni1−P2	102.84(4)	C1−P1−Ni1	111.71(14)
C17−P2−Ni1	113.49(13)		

−80 °C shows an AB quartet ($\delta_A = 34.7$; $\delta_B = 28.6$ ppm) with $^2J(PP') = 41$ Hz (Figure 2, *left*). The observed coupling constant reflects the presence of *cis*-configured phosphorus atoms. Upon raising the temperature the four signals collapse near −10 °C, before merging into a singlet at higher temperatures. This observation can be interpreted in terms of a fast oscillation of the two PPh_2 units about their respective P−Ni bonds, a motion taking alternately each of the *endo*-PPh rings from directly above towards one side of the cavity (Scheme 2). The energy barrier for this phenomenon, as inferred from the NMR study, is 11.3 kcal·mol^{-1}. As expected for a C_1-symmetrical structure, the ^{1}H NMR spectrum measured at −80 °C distinctly shows four poorly resolved AB systems for the ArCH_2Ar protons (Figure 2, *right*). By raising the temperature, the four AB systems broaden, coalesce and eventually result in a single AB quartet at room temperature.[23] These observations taken together with the conclusion inferred from the ^{31}P NMR spectrum, imply that a second motion takes place. The latter corresponds to a fanning motion of the metal, which displaces the nickel atom from one side to the other of the calix axis. In these dynamics, the P−Ni−P bite angle periodically increases and decreases as shown in Scheme 3, reaching its highest value when the metal crosses the calixarene axis. Similar findings have been made previously for an analogue of **2**, containing four *n*-propyl substituents instead of benzyl ones.[15] Note that at −80 °C (CD_2Cl_2, 400 MHz) the second motion of the benzyl-substituted molecule **2**

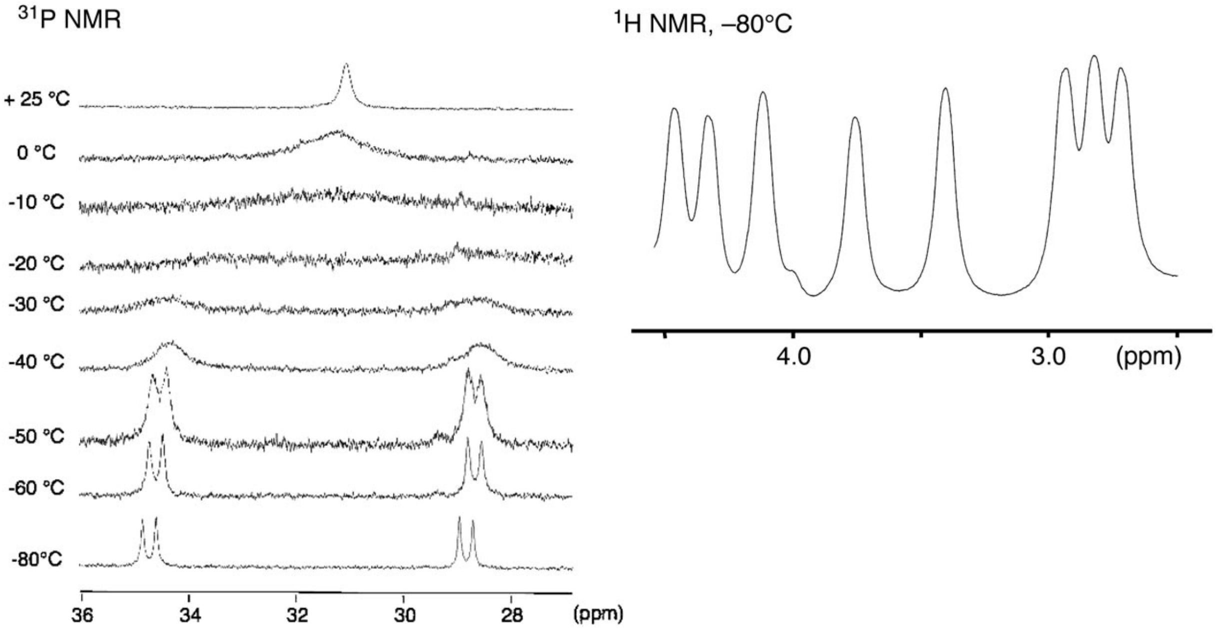
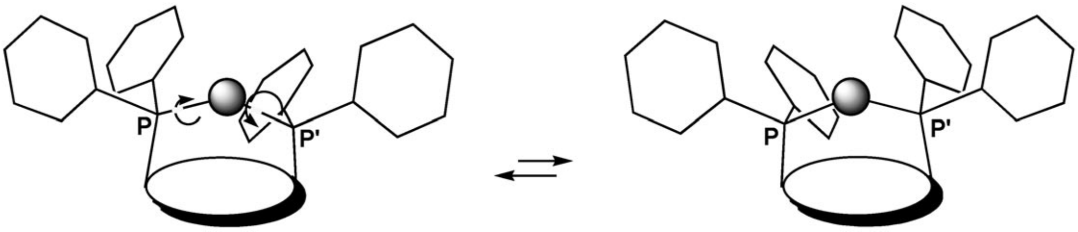
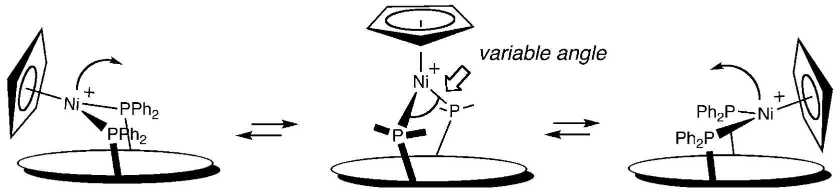


Figure 2. NMR spectra of **2** in CD_2Cl_2. *left:* ^{31}P NMR (162 MHz, variable T); *right*: ^{1}H NMR (400 MHz, −80 °C).



Scheme 2. Restricted rotation about the Ni−P bonds leads to alternative displacement of each *endo*-oriented PPh ring above the cavity entrance.



Scheme 3. Fanning motion of the PNiP plane.

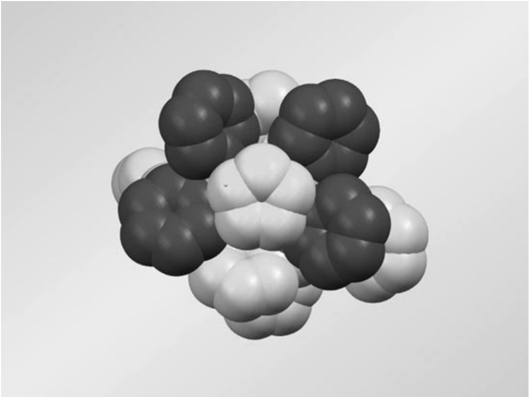


Figure 3. Instant view of the dynamic complex **2**, with the nickel atom located on the calixarene axis (PM3 calculation).

was not totally frozen out, contrary to the observations made for propyl analogue. In other words, the flipping motion is a little faster in the benzyl-substituted complex. Semi-empirical PM3 calculations[24] made for **2** indicate that during the dynamic process the P−Ni−P angle increases up to *ca.* 109°. In the corresponding transition state,[25] in which the metal atom is located on the calixarene axis, each of the four PPh rings closely comes in contact with the Cp ring, which may then be viewed as sitting in the heart of a flower with four C_6H_5 petals (Figure 3). Note that the PM3 study led to an energy barrier of 9.1 kcal·mol^{-1}, which is relatively close to the experimental value.

In the present study we started the Kumada–Tamao–Corriu cross-coupling tests using 4-bromoanisole and phenylmagnesium bromide (Scheme 4). The runs were achieved in refluxing THF with 2 mol% of **2**. We found that using a PhMgBr/4-bromoanisole ratio of 2:1 resulted in higher yields than with a 1:1 ratio (Table 2, entries 2–6) and also noted that higher conversions were obtained when precatalyst **2** was activated for one hour at 65 °C before addition of the reagents (Table 2, entries 1 and 2). However, in comparison with our previous results based on a neutral $NiBr_2$ complex containing a related, tetra-*O*-propylated calixarene, the reaction rate of the present catalytic system was found a little lower. This difference simply reflects the difficulty of a full activation of the NiCp complex **2** at 65 °C. Indeed, careful NMR analysis of the catalyst solution after the one-hour activation period revealed that some starting NiCp complex was still present. Monitoring during 4 days by ^{31}P NMR a solution of **2** in dioxane heated at 100 °C, showed that a single product formed, characterised by a singlet at 41.8 ppm. Clearly, no partial or full decoordination of the ligand can be seen. Furthermore, it is worth mentioning that when the catalytic reaction was carried out at 65 °C with $[NiCp(COD)]BF_4$ in the absence of diphosphine **1** (conditions as defined in Table 2, entry 2), the catalyst was about 4 times less active.

$$\text{PhMgBr} + \text{Ar—X} \xrightarrow{[(\eta^5\text{-}C_5H_5)Ni(\mathbf{1})]BF_4\ (\mathbf{2})} \text{Ph—Ar}$$

Scheme 4. Kumada–Tamao–Corriu cross coupling reaction catalysed by the nickel complex **2**.

Table 2. Screening for the optimal catalytic conditions for the Kumada–Tamao–Corriu cross-coupling catalysed by the nickel complex **2**.[a]

Entry	PhMgBr/ 4-bromoanisole	Activation[b]	Solvent	*T* [°C]	Conversion[c] [%]
1	2	no	THF	65	60.4
2	2	yes	THF	65	81.3
3	1	yes	THF	65	43.4
4	1	yes	dioxane	80	44.3
5	1.5	yes	dioxane	80	76.3
6	2	yes	dioxane	80	79.4
7	2	yes	dioxane	100	100

[a] **2** (0.014 g, 1.10^{-2} mmol, 2 mol%), solvent (1.5 mL), PhMgBr (in THF solution), 4-bromoanisole (0.061 mL, 0.5 mmol), decane (0.050 mL), 1 h.

[b] Complex **2** was heated for 1 hour at the reaction temperature before addition of the reagents

[c] Determined by GC, calibration based on decane.

The observation that a 2:1 PhMgBr/ArBr ratio results in higher conversions also holds for runs carried out in dioxane. We then found that operating at 100 °C in dioxane significantly increased the conversions (Table 2, entries 6 and 7). In all runs, the amount of homocoupling product was lower than 3%.

Table 3. Kumada–Tamao–Corriu cross-coupling reaction catalysed by the nickel complex **2**.[a]

Entry	ArBr	ArBr/**2**	Conversion[b] [%]	TOF [mol(ArBr)·mol(**2**)$^{-1}$·h^{-1}]
1	4-bromoanisole	5000	50.9	2540
2	4-bromoanisole	50000	15.1	7530
3	2-bromoanisole	5000	58.0	2890
4	2-bromo-6-methoxynaphthalene	5000	60.2	3010
5	2-bromo-6-methoxynaphthalene	50000	11.6	5810
6	2-bromotoluene	5000	35.2	1760
7	3-bromotoluene	5000	36.2	1810
8	4-bromotoluene	5000	95.6	4780
9	4-bromotoluene	50000	37.4	18700
10	bromomesitylene	5000	15.6	780
11	bromobenzene	5000	44.6	2220
12	1-bromonaphthalene	5000	92.9	4645
13	1-bromonaphthalene	50000	42.5	21250
14	4-chloroanisole	5000	7.0	350
15	1-chloro-4-nitrobenzene	5000	27.7	1380
16	4-chlorotoluene	5000	7.6	380
17	chlorobenzene	5000	34.1	1710

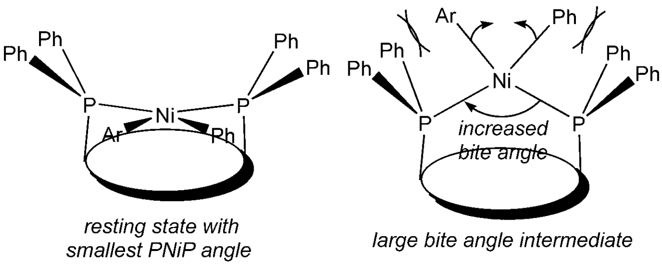
[a] i) **2**, dioxane (1 mL), 100 °C, 1 h; ii) PhMgBr (1 mL in THF solution, 1 mmol), ArBr (0.5 mmol), decane (0.05 mL), dioxane (0.5 mL), 100 °C, 1 h. For the calculation of the TOF, we considered that the reaction began only once the substrates had been added to the reaction mixture.

[b] Determined by GC, calibration based on decane.

Using the above optimised reaction parameters (dioxane, 100 °C, PhMgBr/ArBr = 2:1, activation of the precatalyst), we then chose to apply an ArBr/catalyst ratio of 5000. We found that for 4-bromoanisole, 2-bromo-6-methoxynaphthalene, 4-bromotoluene, and bromobenzene, the conversions were still high (>45%), the highest conversions being observed for activated 4-bromotoluene (95.6%) (Table 3, entries 1, 4, 8 and 11). In our quest to find the highest catalytic activity of the system, we decided to reduce the catalyst loading to 1×10^{-3} mol% (which corresponds to an ArBr/catalyst ratio of 50000). This led to turnover frequencies (TOFs) of 7530, 5810 and 18700 mol(converted ArBr)·mol(**2**)$^{-1}$·h^{-1}, for 4-bromoanisole, 2-bromo-6-methoxynaphthalene and 4-bromotoluene, respectively (Table 3, entries 2, 5 and 9). Complex **2** furthermore turned out to efficiently promote the reaction of PhMgBr with congested aryl bromides, notably 2-bromoanisole, 2-bromotoluene, bromomesitylene and 1-bromonaphthalene (Table 3, entries 3, 6, 10 and 12). Thus, for example, TOFs up to 21250 mol(converted ArBr)·mol(**2**)$^{-1}$·h^{-1} were obtained with 1-bromonaphthalene using a catalyst loading of 1×10^{-3} mol%, which corresponds to a conversion of 42.5% (Table 3, entry 13).

The more challenging aryl halides 4-chloroanisole, 1-chloro-4-nitrobenzene, 4-chlorotoluene, and chlorobenzene could also efficiently be converted into biaryls (Table 3, entries 14–17). The highest conversion observed after 1 hour reaction time was observed for chlorobenzene [conversion 34.1% and TOF = 1710 mol(converted PhCl)·mol(**2**)$^{-1}$·h^{-1}] (Table 3, entry 17). As expected, the electron-deficient 1-chloro-4-nitrobenzene reacted faster than the electron-rich 4-chloroanisole and 4-chlorotoluene, the corresponding TOFs being 1380, 350 and 380 mol(converted ArCl)·mol(**2**)$^{-1}$·h^{-1}, respectively (Table 3, entries 14–16). These results strongly suggest that the rate-limiting step of the catalytic cycle is the oxidative addition of the aryl chloride to the nickel.

From studies by Tamao et al., it is known that the nickel-catalysed coupling reaction is markedly dependent on the phosphine used, its rate varying according to the order [NiCl$_2$(dppp)] > [NiCl$_2$(dppe)] > [NiCl$_2$(dmpe)] ≈ [NiCl$_2$(PPh$_3$)$_2$] ≫ [NiCl$_2$(PEt$_3$)$_2$] ≈ [NiCl$_2$(PPh$_2$Me)$_2$] [dmpe = 1,2-bis(dimethylphosphino)ethane].[1] Using the fastest of these catalysts, namely [NiCl$_2$(dppp)], and applying the catalytic conditions defined in entry 1 of Table 3, led to a conversion of 47.1%, which is about 10% lower than that of complex **2**. Note that unlike [NiCl$_2$(dppp)], complex **2** relies on an air-stable bis(triarylphosphine) ligand. A parameter which could contribute to the rather high catalytic activity of **2** is the intrinsic motion of the catalytic species. If one assumes that during catalysis a square planar [Ni(Ar)(Ar′)·**1**] complex is formed, itself displaying dynamics similar to that of **2** with temporarily enlarged PNiP angles, then it becomes clear that when the metal crosses the calixarene axis, the steric pressure exerted by the PPh$_2$ groups on the two Ni–aryl moieties becomes particularly strong and consequently facilitates the coupling step (Scheme 5).[26] These findings are in keeping with the observations made by Marcone and Moloy,[27] as well as by Hartwig et al.[28] on diphosphines with large bite angles. The question whether the presence of the



Scheme 5. Proposed catalytic intermediates with minimum (*left*) and maximum (*right*) bite angles according to the position of the nickel atom.

benzyl substituents, which were found to accelerate the flipping of the PNiP plane with respect to that of the corresponding tetrapropylated complex, has a beneficial role on the coupling step remains open. In this context, investigations on non-dynamic versions of complex **2**, obtained for example, by rigidifying the calixarene backbone, would certainly be very useful. Such complexes would also provide an answer to the question whether a blocked system in which the bite angle is close to that found in **2** in the solid state (102.8°) can compete with dppp.

Conclusions

In this work we have shown that the air-stable, cationic nickel complex **2**, once thermally activated, efficiently catalyses Kumada–Tamao–Corriu coupling reactions. High TOFs, of up to 21250 mol(converted ArBr)$\cdot$mol(**2**)$^{-1}\cdot$h^{-1}, were obtained with various electron-rich and congested bromoarenes using catalyst loading as low as 1×10^{-3} mol%, provided that the reactions were carried out at 100 °C in dioxane with a PhMgBr/ArX ratio of 2:1. The high activities of our system contrast with those observed for triphenylphosphine-based catalysts and furthermore, our system outperforms the fastest catalysts reported, a behaviour which is likely to rely on the intrinsic dynamics of the calixarene core. The latter possibly facilitates the coupling step by causing a temporary increase of the PNiP angle and hence an increase of the steric pressure of the P-substituents on the organic ligands. We anticipate that "1,3-calixdiphosphines" with bulkier P substituents would lead to even higher reaction rates.

Experimental Section

General Aspects

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 or AV-400 spectrometer. ^{1}H NMR spectra were referenced to residual protiated solvent (5.32 ppm for CD_2Cl_2), ^{13}C NMR chemical shifts are reported relative to deuterated solvent (53.8 ppm for CD_2Cl_2) and the ^{31}P data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. 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 µm film thickness). Mass spectra were recorded on a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2 as a solvent. The elemental analysis was performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. 5,17-Bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxycalix[4]arene (**1**)[14] and [Ni(η^5-C_5H_5)(COD)]BF_4[29] were prepared according to methods reported in the literature.

Preparation of *cis-P,P'*-(η^5-Cyclopentadienyl)-{5,17-bis(diphenylphosphino)-25,26,27,28-tetrabenzyloxy-calix[4]arene}nickel(II) Tetrafluoroborate (2)

To a solution of **1** (0.242 g, 0.210 mmol) in CH_2Cl_2 (50 mL) was added a solution of [(η^5-C_5H_5)Ni(COD)]BF_4 (0.067 g, 0.210 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 16 h. The solution was then evaporated under reduced pressure, the residue was washed with Et_2O (15 mL) then dried under vacuum to afford **2** as a brownish solid; yield: 0.281 g (98%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): $\delta=7.45$ (s, arom. CH, 8H), 7.40–7.34 (m, arom. CH, 6H), 7.30–7.21 (m, arom. CH, 12H), 7.12–7.04 (m, arom CH, 12H), 6.98–6.93 (m, arom. CH, 2H), 6.88–6.80 (m, arom. CH, 6H), 6.50 (t, $J=5.0$ Hz, arom. CH, 4H), 5.35 (s, OCH_2Ph, 4H), 4.95 (s, OCH_2Ph, 4H), 4.93 (s, C_5H_5, 5H), 4.31 and 2.98 (2d, AB spin system, $J=14.2$ Hz, ArCH_2Ar, 8H); ^{1}H NMR (CD_2Cl_2, 400 MHz, 193 K): $\delta=$ 7.44–6.28 (m, arom. CH, 48H), 6.28 (s br, arom. CH of calixarene, 1H), 5.79 (s br, arom. CH of calixarene, 1H), 5.41 (s br, OCH_2Ph, 4H), 5.10 (s br, OCH_2Ph, 2H), 4.99 (s br, OCH_2Ph, 2H), 4.82 (s, C_5H_5, 5H), 4.44 (s br, ArCH_2Ar, 1H), 4.33 (s br, ArCH_2Ar, 1H), 4.12 (s br, ArCH_2Ar, 1H), 3.75 (s br, ArCH_2Ar, 1H), 3.34 (s br, ArCH_2Ar, 1H), 2.86 (s br, ArCH_2Ar, 1H), 2.74 (s br, ArCH_2Ar, 1H), 2.64 (s br, ArCH_2Ar, 1H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz, 298 K): $\delta=157.94$ and 155.71 (2 s, arom Cq-O), 137.75–123.66 (arom. *C*s), 97.07 (s, C_5H_5), 77.59 (s, OCH_2Ph), 75.77 (s, OCH_2Ph), 31.60 (s, ArCH_2Ar); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 298 K): $\delta=30.8$ (s, PPh_2); ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, 193 K): $\delta=34.8$ (d, $J_{PP}=34.8$ Hz, PPh_2), 18.8 (d, $J_{PP}=34.8$ Hz, PPh_2); MS (ESI TOF): *m/z* = 1275.3844 $[M-BF_4]^+$ expected isotopic profiles; anal. calcd. for $C_{85}H_{71}O_4P_2NiBF_4\cdot2H_2O$: (*M*r = 1363.92 + 36.03): C 72.92, H 5.40%; found: C 72.97, H 5.64%.

General Procedure for the Nickel-Catalysed Kumada–Tamao–Corriu Cross-Coupling Reaction

A solution of complex **2** in the appropriate solvent (1 mL, THF or dioxane) was heated for 1 hour at the reaction temperature (see Table 2 and Table 3) before adding a solution of PhMgBr (1 mL, 1.0 mmol, 1 M solution in THF) and a solution (0.5 mL) of aryl bromide (0.5 mmol). The reaction mixture was then heated for 1 h. 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 analyzed by GC.

Crystallography

Single crystals of **2** (yellow) suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature. Data were collected at 100 K on a Nonius Kappa CCD diffractometer using a Mo-Kα ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. Formula: $C_{89}H_{71}BF_4NiO_4P_2 \cdot 1/2\,C_6H_{14} \cdot CH_2Cl_2$; $M = 1491.89$ g mol^{-1}; triclinic; space group *P-1*; $a = 13.3471(9)$ Å, $b = 14.2768(8)$ Å, $c = 22.8424(9)$ Å, $\alpha = 98.770(4)°$, $\beta = 104.362(5)°$, $\gamma = 109.144(5)°$, $V = 3851.3(4)$ Å^3; $Z = 2$; $D = 1.287$ g cm^{-3}; $\mu = 0.424$ mm^{-1}; $F(000) = 1558$. Crystal dimensions $0.18 \times 0.12 \times 0.10$ mm. Total reflections collected 21370 and 7361 with $I > 2\sigma(I)$. Goodness of fit on F^2 0.882; $R(I > 2\sigma(I)) = 0.0663$, $wR2 = 0.1748$ (all data), 965 parameters; maximum/minimum residual density 1.401/−0.971 e Å^{-3}. The crystal structure was solved in SIR 97[30] and refined in SHELXL97[31] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. CCDC 680939 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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