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Cross-Coupling Reactions

"(Diphosphine)Nickel"-Catalyzed Negishi Cross-Coupling: An Experimental and Theoretical Study

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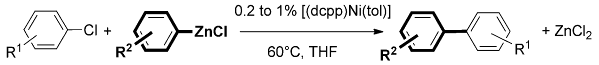
Abstract: The use of a strongly donating "(bis-dialkylphosphine)Ni" fragment promotes the catalytic coupling of a large range of ArCl and ArZnCl derivatives under mild conditions. Stoichiometric mechanistic investigations and DFT calculations prove that a Ni^0/Ni^{II} cycle is operative in this system.

Over the past 40 years, Pd-catalyzed cross-coupling reactions have been extensively studied.[1] This is especially true for Csp^2–Csp^2 bond forming processes, because unsymmetrical biaryl compounds are found in attractive targets ranging from liquid crystals to pharmaceuticals.[2] Among them, the Negishi reaction, involving organozinc derivatives, has been studied to a lesser extent than the Suzuki–Miyaura reaction, involving organoboron species. The most active catalyst systems have been devised from the early 2000s, and feature a single bulky phosphine-like[3–5] or N-heterocyclic carbene (NHC)[6–8] ligands bound to the Pd center.[9–12] It is, however, still desirable to develop the chemistry of related Ni complexes because of the much lower cost. Negishi et al. reported such aryl–aryl coupling using a catalytic Ni^0 precursor, $[Ni(PPh_3)_4]$, generated in situ from commercially available $[Ni(acac)_2]$, PPh_3, and diisobutylaluminum hydride (DIBALH) as early as 1977.[13] In terms of catalytic efficiency, until recently, somewhat high catalytic loadings (ca. 5%) were necessary for efficient coupling processes.[14] Ligand optimizations have resulted in significant lowering of the Ni precatalyst amounts (typically ca. 1%, but down to 0.01% in the most favorable cases).[15–21] In terms of mechanism, the possibility for Ni complexes to reach all oxidation states ranging from Ni^0 to Ni^{III} makes the understanding of the cross-coupling reaction involving a Ni catalyst undoubtedly more complex than the related Pd one. Kochi et al. showed in the late 1970s in seminal contributions that in the case of reactions of ArBr and Ni complexes featuring monophosphine ligands (such as PPh_3), a single electron transfer (SET) process could occur between the Ni^{II} complex generated by oxidative addition of ArBr, resulting in the formation of a Ni^I complex.[22,23] This SET is kinetically favorable over the transmetalation/reductive elimination sequence, and hence the overall catalytic process then involves Ni^I/Ni^{III} species. In a 1986 study dealing with the coupling of ArCl using Ni catalysts and reducing agents, Colon and Kelsey proposed a slightly different mechanism in which the Ni^{II} complex is reduced by the reducing agent and not the ArCl.[24] Interestingly, ligand effects were also studied and they concluded that triarylphosphines were the best ligands, with trialkylphosphines resulting in much slower reaction and poorer yield, and bidentate diarylphosphines being inefficient.

In the present contribution, we report an efficient Ni-catalyzed Negishi cross-coupling process between $R^1C_6H_4Cl$ and $R^2C_6H_4ZnCl$ derivatives under mild conditions, using the chosen Ni^0 precatalyst $[(dcpp)Ni(\eta^2\text{-toluene})]$ (dcpp = 1,3-bis(dicyclohexylphosphino)propane; Scheme 1).[25] We show here the successful use of strongly donating bis-dialkylphosphine ligand, well known to stabilize unsaturated Ni^0 complexes unlike the bis-diarylphosphines. Preliminary mechanistic investigations as well as a full computational analysis of the complete catalytic cycle support a Ni^0/Ni^{II} cycle.



Scheme 1. The nickel-catalyzed process studied.

The coupling with the cheapest and most accessible, but still challenging, derivatives $R^1C_6H_4Cl$ was studied. Most satisfyingly, the reaction between 4-chlorotoluene and phenylzinc chloride yielded the expected biphenyl in an excellent yield of 93% within 6 h (entry 1, Table 1; 1% cat., 97% GC yield, together with 3% of the homocoupling product Ph–Ph). The quantity of Ni complex can be reduced to 0.2%, but the reaction required 19 h (turnover frequency (TOF): 26 h^{-1}) to be complete (entry 2). When the quantity is lowered down to 0.01%, the yield was 21% after 58 h (TOF: 36 h^{-1}) and 47% after 138 h (TOF: 34 h^{-1}), showing that no catalyst decomposi-

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Table 1. Scope of the coupling reaction.

Entry	R^1PhCl	$R^2PhZnCl$ R^2:	Cat. [%]	*t* [h]	Yield [%] (GC conversion [%])
1	4-CH_3PhCl	H	1	6	93 (97)
2	4-CH_3PhCl	H	0.2	19	93 (98)
3	4-CH_3PhCl	H	0.01	58	(21)
4	4-CH_3PhCl	H	0.01	138	(47)
5	4-CF_3PhCl	H	0.2	1	94 (98)
6	4-$CO_2MePhCl$	H	0.2	6	92 (96)
7	PhCl	H	0.2	16	98 (100)
8	4-OMePhCl	H	0.2	32	90 (93)
9[a]	2,6-$(Me)_2PhCl$	H	1	7	75 (81)
10	2-ClPy	H	1	2	96 (100)
11	2,6-Cl_2Py	H	1	6	58 (73)
12	2-Cl-3-NH_2Py	H	1	4	90 (100)
13	4-CF_3PhCl	4-OMe	0.2	0.5	91 (97)
14	4-$CO_2MePhCl$	4-OMe	0.2	1.5	89 (94)
15	PhCl	4-OMe	0.2	4	90 (97)
16	4-CH_3PhCl	4-OMe	0.2	8	88 (95)
17[b]	4-CH_3PhCl	H	1	2	(97)
18[c]	4-CH_3PhCl	H	1	6	(95)
19[d,e]	4-CH_3PhCl	H	1	72	(7)

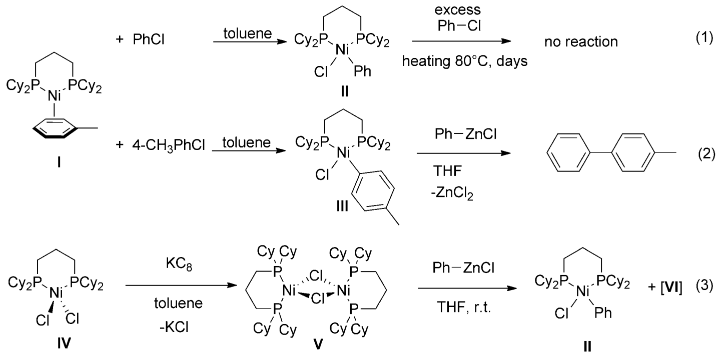
Reaction conditions: R^1ArCl (1 mmol, 1 equiv), $R^2ArZnCl$ (1.1 mmol, 1.1 equiv), cat. [(dcpp)Ni(tol)], THF (2 mL), 60 °C. The difference between the conversion measured by GC and the yield is accounted for by the formation of the homocoupled product, Ph–Ph. [a] 1.8 equiv PhZnCl used. [b] [(dcpp)$NiCl_2$] as catalyst. [c] [(dcpp)Ni(Ph)Cl] as catalyst. [d] [(dcpp)Ni(μ_2-Cl)$_2$Ni(dcpp)] as catalyst. [e] Ph–Ph is also formed in 33% yield.

tion occurred. In a second set of experiments, the electronic nature of the *para* substituent in $R^1C_6H_4Cl$ was modulated. As classically observed, increasing the electron density of the aryl moiety resulted in a slower reaction (compare entries 2, 7, and 8). On the other hand, increasing the electron density of the zinc partner resulted in faster reaction (compare entries 5–7 to 13–15). Nevertheless, because of the stability of the complex over time, near quantitative yields of coupled products were obtained in every case. Importantly, more challenging substrates, *ortho*-substituted as well as heteroaryl or even amino-containing derivatives, proved successful in the coupling process (entries 9–12).

In summary, the representative examples provided here show that the new catalytic process, based on a well-defined Ni^0 complex, allows the formation of biaryl compounds under mild conditions with very low catalyst loading. It was then verified that similar results were obtained by using more readily manipulated Ni^{II} precursors, namely [(dcpp)$NiCl_2$] or [(dcpp)Ni(Ph)Cl] (entries 17 and 18). Most importantly, isolated Ni^I precursor [(dcpp)Ni(μ_2-Cl)$_2$Ni(dcpp)][26] not only performed sluggishly (40% conversion after 72 h with 1% cat.), but also less selectively (7% of the desired 4-CH_3Ph–Ph compound versus 33% of the homocoupling product Ph–Ph), proving that the Ni^I/Ni^{III} cycle is much less efficient in this reaction (entry 19). These latter experiments are in contrast with some literature precedence. Indeed, Ni-catalyzed Negishi cross-coupling processes have been shown to involve a Ni^I/Ni^{III} cycle with many ligand systems.[14,27] Nonetheless, the use of [(BINAP)Ni(η^2-NC-Ph)] (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) in the catalytic coupling of ArCl with amines was recently reported and shown to occur via a Ni^0/Ni^{II} pathway.[28]

Several experiments, stoichiometric as well as catalytic, were carried out to further prove the involvement of the Ni^0/Ni^{II} cycle using the strongly donating bidentate phosphine dcpp, as well as to identify likely intermediates in the catalytic process (Scheme 2).

Firstly, the stoichiometric addition of chlorobenzene to [(dcpp)Ni(η^2-toluene)] at 40 °C resulted in the quantitative formation of the [(dcpp)Ni(Ph)Cl] complex, **II**, within minutes. This complex is square planar as shown by its diamagnetism; two sets of doublets are observed in the $^{31}P\{^1H\}$ NMR spectrum at 5.8 and 19.0 ppm, $^2J_{P,P}$ = 48.4 Hz, see the Supporting Information). The analogous complex, **III**, was obtained through the reaction between complex **I** and 4-CH_3PhCl. The oxidative addition of ArCl to the Ni^0 fragment is therefore a low energy process. Then, the possibility of a redox process between Ni^{II} complex **II** and ArCl was studied. Despite heating for days at 80 °C, no evolution of **II** was observed (Scheme 2, Eq. (1)), which shows that the strong coordination of the bidentate phosphine prevents reduction to a Ni^I species, observed in the case of monophosphines. On the other hand, addition of one equivalent of PhZnCl to complex **III** resulted in the quantitative formation of the expected 4-CH_3Ph–Ph, without any formation of the homocoupling product Ph–Ph (Scheme 2, Eq. (2)). The formation of the latter compound is indicative of the intermediate formation of a Ni^I species (see above). To further test the involvement of a Ni^I/Ni^{III} cycle, the known dimeric Ni^I complex [(dcpp)Ni(μ_2-Cl)$_2$Ni(dcpp)], **V**, was reacted with a stoichiometric amount of PhZnCl at room temperature. A mixture of complex [(dcpp)Ni(Ph)Cl], **II**, and a second species, **VI**, characterized by a singlet in $^{31}P\{^1H\}$ NMR spectrum at 56 ppm, was formed within minutes as shown by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2, Eq. (3)). This mixture rapidly evolved as complex **II** reacted further with PhZnCl to form the homocoupled product Ph–Ph, preventing further characterization of compound **VI**.

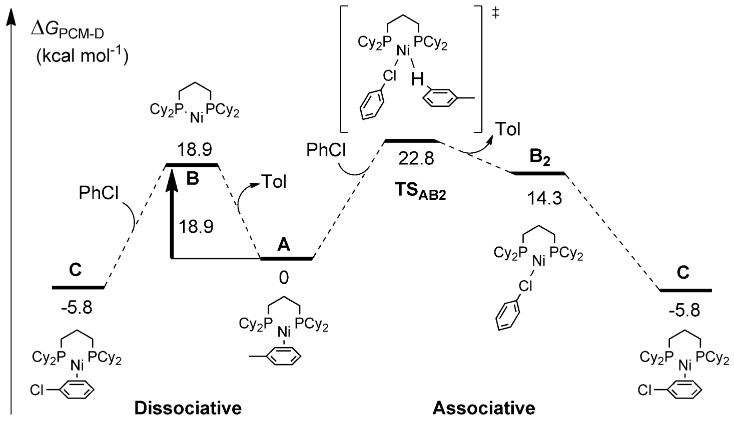


Scheme 2. Mechanistic investigations.

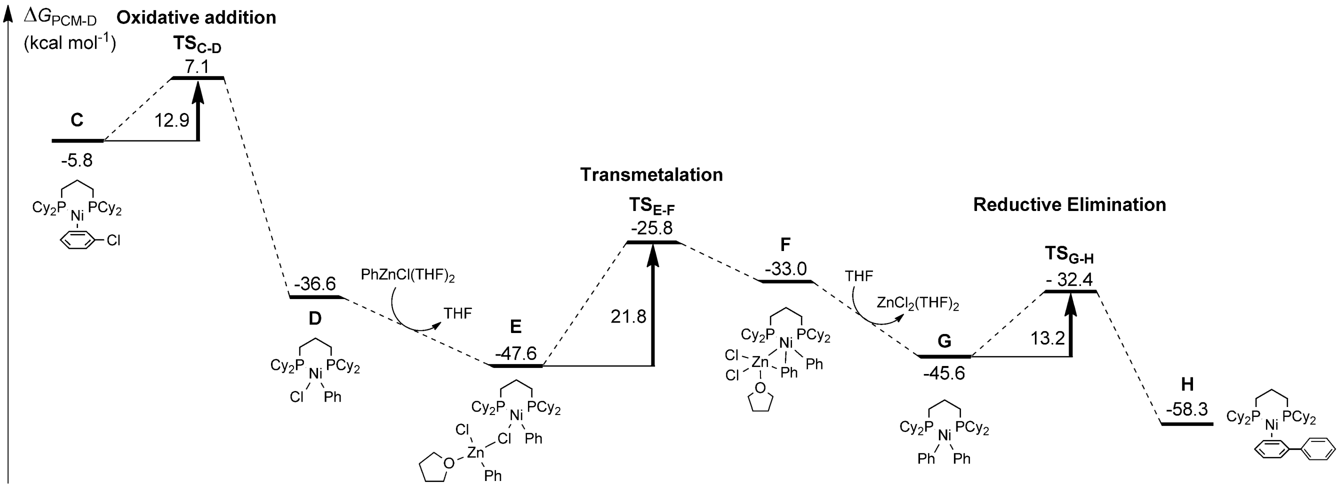
Nonetheless, this latter experiment is crucial for mechanistic understanding as it shows that the present “(dcpp)Ni” system readily evolves from Ni^{I} species to mixtures of diamagnetic complexes (Ni^{II} and/or Ni^{0} complexes) in the presence of PhZnCl. This reaction provides a rationale for the formation of the homocoupled product of PhZnCl. Together, these experiments are in full accord with the catalytic reaction presented above (Table 1, entry 19), explaining the formation of mixtures of homo- and heterocoupling products when Ni^{I} complex **V** was used in catalytic amounts. In summary, these stoichiometric experiments prove that all three steps of the Ni^{0}/Ni^{II} cycle are facile at room temperature: oxidative addition of PhCl to Ni^{0}; transmetalation at Ni(Ar)(Cl) with Ar′ZnCl; and reductive elimination from Ni(Ar)(Ar′). These experiments also show that Ni^{I} complexes can be involved in cross-coupling, but they then lead to a poor selectivity of heterocoupling versus homocoupling, favoring the homocoupling product. Given the low yield of homocoupled product in the catalytic experiments, the involvement of Ni^{I} in the present catalytic process can be safely ruled out. In an additional effort to identify the resting state of the catalyst, we monitored the reaction of 4-CF_3PhCl with PhZnCl catalyzed by 1 % of [(dcpp)Ni(η^2-toluene)] at 60 °C by $^{31}P\{^1H\}$ NMR spectroscopy. The only species that was observed during the whole reaction (after 30 %, 70 %, and ca. full conversion) was characterized by two doublets at 5.9 and 19.7 ppm, $^2J_{P,P} = 56.0$ Hz. This complex has almost identical spectroscopic features to [(dcpp)Ni(4-CF_3-Ph)Cl], that is, two doublets at 5.9 and 19.3 ppm, $^2J_{P,P} = 53.0$ Hz, in C_6D_6 (see the Supporting Information. We, thus, propose that it corresponds to either complex **D** or the heterobimetallic adduct [(dcpp)Ni(4-CF_3-Ph)(μ-Cl)Zn(Cl)(Ph)(THF)] **E** (Scheme 5, see below). Importantly, in contrast to Hartwig’s recent report, wherein the [(BINAP)Ni(η^2-NC-Ph)] partly evolves during the course of catalysis to [(BINAP)$_2$Ni], the bis-dialkylphosphine ligand dcpp prevents decomposition of the catalytic species.[28]

As a final investigation of the mechanism, a full DFT study has been performed on the catalytic system (for details see the Supporting Information). First, the entry into the catalytic cycle was computed. The results implied displacement of the toluene ligand from the 16-electron complex (η^2 coordination) by the ArCl substrate. Both dissociative and associative mechanisms were envisaged (Scheme 3). Dissociation of toluene to form **B** is endergonic, but the energy required is low (18.9 kcal mol^{-1}). The associative mechanism involves an 18-electron transition state, **TS$_{AB2}$**. It features both incoming PhCl and toluene ligands as η^1 coordinated species (see the Supporting Information). Evolution to complex **C** occurs via the PhCl η^1-coordinated intermediate complex **B$_2$**. Overall, the two mechanisms are close in energy (less than 4 kcal mol^{-1} difference), but more importantly the activation energy required to enter the catalytic cycle is very low (18.9 kcal mol^{-1}).

In a second stage, the catalytic process was computed and the reaction profile is depicted in Scheme 4. The previous step forms **C**, which is electron rich enough to perform an oxidative addition in the carbon–chloride bond leading to Ni^{II} complex **D**, which has been experimentally observed. The transi-



Scheme 3. Reaction pathways for the coordination of chlorobenzene.



Scheme 4. Reaction pathway for one catalytic cycle starting from complex C.

tion state situated 12.9 kcal mol^{-1} above **C** is very low despite the classical difficulty in performing oxidative addition with C–Cl bonds, proving the electron-rich nature of the (dcpp)Ni fragment, **B**. This reaction is quite exergonic, liberating 30.8 kcal mol^{-1} from **C**. Once the C–Cl bond has been activated, the next steps consist of the approach and reaction with the organozinc reagent. The coordination of the arylzinc chloride to **D** leads to heterobimetallic complex **E** (Figure 1), which features a tetrahedral zinc derivative having for ligands one phenyl, one chloride, one THF molecule, and the chlorine (bridging) atom from **D** behaving as an L-type ligand. This coordination is again exergonic, **E** being 9.0 kcal mol^{-1} lower in energy than **D**, a fact that is directly linked to the strength of the Zn–Cl bond. A transition state for the key transmetalation step could be located on the potential energy surface: **TS$_{E-F}$** (Figure 1) is situated 21.8 kcal mol^{-1} higher in energy than **E**. In **TS$_{E-F}$**, the Ni–Cl and Zn–Cl bonds are 0.10 Å longer and 0.16 Å shorter than in **E** respectively, showing the Cl transfer. In parallel, the Ph–Zn bond is only marginally elongated (0.07 Å) and the Ph–Ni bond is rather long (2.58 Å). Most interestingly, a very short Ni–Zn intermetallic distance of 2.59 Å is calculated, much shorter than the sum of the van der Waals radii (3.02 Å), and in fact only marginally longer than the sum of the covalent radii (2.52 Å), suggesting metallophilic interaction in the transition state. Related transition states featuring such short interactions have been calculated for Pd–Zn[29] or Pd–Au/Sn–Au species,[30] whereas they are absent in the Pd–Sn[30] transmetalation processes, and were linked to lower activation energies. The transition state **TS$_{E-F}$** leads to **F**, which lies 14.6 kcal mol^{-1} higher than **E**. Complex **F** is an interesting heterobimetallic complex with one bridging phenyl ring between the Ni and the Zn centers (Figure 1). The Ni–C (2.04 Å) and Zn–C (2.20 Å) bond lengths indicate that the phenyl is almost fully transferred to Ni. This bridging Ph moiety is thus clearly a weaker ligand than THF, as elimination of $ZnCl_2(THF)_2$ leads to **G**, lying 12.6 kcal mol^{-1} lower than **F**. The whole transmetalation step is rather exergonic, with an overall energy gain from **D** to **G** of 9.0 kcal mol^{-1}. Finally, reductive elimination of biphenyl from **G** is facile as the transition state **TS$_{G-H}$** lies 13.2 kcal mol^{-1} higher than **G**. Interestingly, the biphenyl remains coordinated through two electrons of one aromatic ring, in a similar way than in complex **A**, to form **H** (see the Supporting Information). Overall, each catalytic cycle is strongly exergonic, by 52.5 kcal mol^{-1}, and the transmetalation step possesses the highest barrier **within the cycle** (21.8 kcal mol^{-1}).

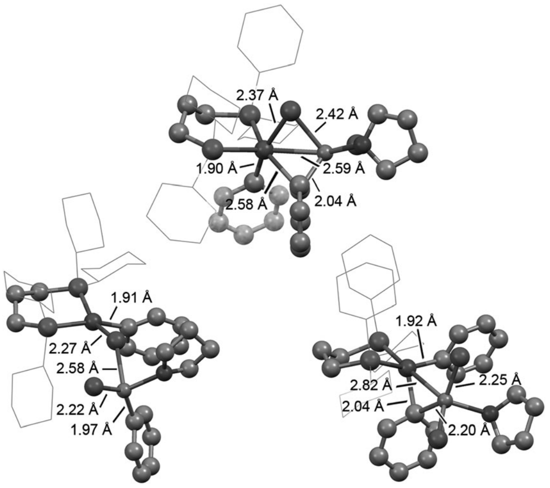
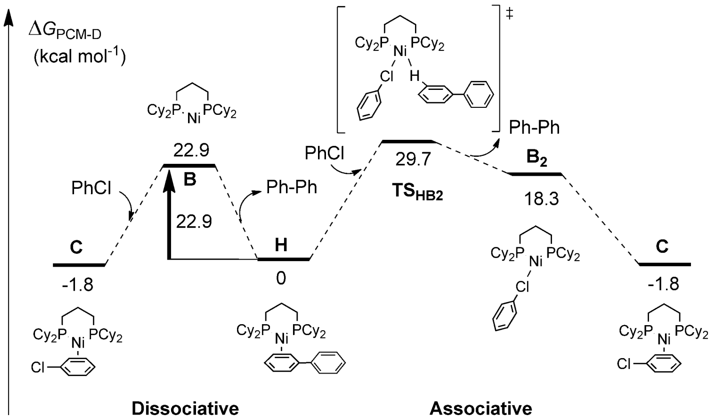


Figure 1. Computed structures of **E** (left), **TS$_{E-F}$** (top), and **F** (right).

In a third stage, the product to reagent exchange that connects the biphenyl complex **H** to **C** was computed. This process allows a new catalytic cycle to occur. Here also, the dissociative and associative mechanisms were computed and the reaction profile is depicted in Scheme 5. Note that, for clarity, the energy of **H** is set at 0. The dissociative process involves the intermediacy of the 14-electron complex **B**, is calculated to be 22.9 kcal mol^{-1} higher in energy than **H** and leads to **C**, located 1.8 kcal mol^{-1} lower than **H**, making the exchange exergonic.

In the associative process, a transition state, **TS$_{HB2}$**, was located at 29.7 kcal mol^{-1} above **H**. In **TS$_{HB2}$**, the biphenyl and the PhCl ligands are coordinated to the Ni center in an η^1 fashion (see the Supporting Information). This transient complex evolves to the η^1 complex **B$_2$** on the way to **C**. The dissociative mechanism is calculated to be 6.8 kcal mol^{-1} lower than the associative one, making the former process favorable. Overall, the regeneration of **C** and liberation of the biphenyl product is a favorable and facile process, thereby allowing further catalytic cycles to proceed.



Scheme 5. Reaction pathways for the product to reagent exchange: regeneration of η^2 ArCl complex C.

In conclusion, we present here an efficient nickel-based catalytic system to perform a Negishi-type cross-coupling of aryl chlorides with equimolar arylzinc chlorides. It is shown here for the first time that strongly electron donating diphosphine ligands are in fact excellent ligands for this nickel-catalyzed process. Mechanistic investigations prove the involvement of Ni^0 and Ni^{II} intermediates, confirmed by the DFT analysis of the whole catalytic process. The use of a bidentate diphosphine is the key to shut down the Ni^{I}/Ni^{III} catalytic cycle. The calculations show that both the oxidative addition and reductive elimination processes are facile. The barrier for transmetalation is very similar to the barrier needed for the product to reagent exchange (21.8 and 22.9 $kcal\,mol^{-1}$, respectively), making them the rate-determining steps. The magnitude of these barriers is fully consistent with the fact that the reaction occurs under mild conditions.

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Keywords: cross-coupling · dft · diphosphine ligands · mechanistic study · Negishi coupling · Ni catalysis

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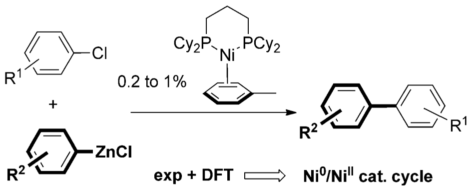
“(Diphosphine)Nickel”-Catalyzed Negishi Cross-Coupling: An Experimental and Theoretical Study



The use of a strongly donating “(bis-dialkylphosphine)Ni” fragment promotes the catalytic coupling of a large range of ArCl and ArZnCl derivatives under mild conditions. Stoichiometric mechanistic investigations and DFT calculations prove that a Ni^0/Ni^{II} cycle is operative in this system.