Bond Activation

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# Cross-Coupling of Aryl/Alkenyl Pivalates with Organozinc Reagents through Nickel-Catalyzed C−O Bond Activation under Mild Reaction Conditions**

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Biaryls have been widely applied in the syntheses of natural products, polyaromatic molecules, and pharmaceuticals.[1,2] Transition-metal-catalyzed cross-coupling reactions are among the most powerful tools used to construct such structural units. In the last decades, significant effort has been directed towards cross-coupling reactions, thus allowing the coupling partners to be extended from aryl iodides, bromides, and triflates to relatively unreactive chlorides and tosylates/mesylates.[3] The complexes of first-row transition metals, such as iron, cobalt, and nickel, also exhibited promising catalytic reactivities to take the place of late-transition-metal complexes.[4] Despite these noteworthy advances, aryl carboxylates (one family of the most easily available and useful compounds) have not yet been successfully employed as coupling partners in cross-coupling reactions.[5] Their simplicity as well as ready availability make carboxylates particularly attractive for use in synthetic chemistry. For example, aryl/alkenyl carboxylates can be easily derived from phenols and carbonyl compounds in a single step.[6] Also, the application of carboxylates in coupling reactions could reduce the use of halides, which are environmentally unfriendly. Ironically, the inertness of aryl carboxylates has long been viewed as a vivid testimony of their functional group tolerance in many reactions. Owing to their stability, carboxylates such as acetates and pivalates are generally applied to synthetic chemistry as protecting groups.

After the pioneering studies of Wenkert et al. on nickel-catalyzed arylation of aryl/vinyl methyl ethers in the late 1970s,[7a,b] the field of C−O bond activation remained dormant for nearly three decades. The vast synthetic potential of this activation-type chemistry has been rarely explored until the recent appearance of several impressive examples. It is apparent that a renaissance in the activation of an unreactive C−O bond is on the way. The studies of Dankwardt and co-workers have greatly broadened the substrate scope to a wide range of nonactivated aromatic ethers in nickel-catalyzed coupling with Grignard reagents.[7c] Kakiuchi et al. first reported chelation-assisted ruthenium-catalyzed coupling of aromatic ethers with organoboron reagents.[7d] Very recently, Chatani and co-workers made advances in the nickel-catalyzed cross-coupling between aromatic methyl ethers and arylboronic esters.[7e] Our recent studies also showed that nickel catalyzed the efficient alkylation of aromatic as well as benzylic methyl ethers with Grignard reagents.[7f,g] As part of a program aimed at the activation of otherwise unreactive C−O bond to enable synthetically useful transformations, we have disclosed the first successful cross-coupling of aryl carboxylates with aryl boroxines.[8] However, several issues remained to be addressed such as high catalyst loading and elevated temperature. Given their easy preparation and high functional group tolerance, organozinc reagents have proved to be quite useful in cross-coupling reactions to construct biaryl and aryl–vinyl structural scaffolds.[9] To the best of our knowledge, aryl carboxylates have never been used to couple with organozinc reagents. Herein, we reported the unprecedented cross-coupling of aryl/alkenyl pivalates with arylzinc reagents to construct C−C bonds under mild reaction conditions.

On the basis of our previous studies, 2-naphthyl carboxylates **1** were chosen as model substrates because of their higher reactivity in related C−O activation transformations.[8] Gratifyingly, when 2-naphthyl acetate (**1a**) was used as a substrate, the desired coupling product **3a** was obtained in the presence of a catalytic amount of $[NiCl_2(PCy_3)_2]$ in DMA, albeit in a low yield, accompanied by the hydrolyzed 2-naphthol as a by-product (Table 1, entry 1). The increased steric bulk of the carboxylates dramatically improved the yield of the reaction, presumably by inhibiting the direct attack of the arylzinc reagents on carbonyl groups (Table 1, entry 3 versus entries 1 and 2). When 2-naphthyl pivalate (**1c**) was applied, the reaction reached full conversion and gave the isolated product in 84% yield. Other ligands such as $PPh_3$, $P(n\mathrm{Bu})_3$, and $P(t\mathrm{Bu})_3$ were tested but gave lower yields (Table 1, entries 4–7), thus suggesting that the $PCy_3$ ligand had a balance between both steric and electronic effects. Furthermore, other nonpolar solvents were not appropriate for this transformation, meanwhile the polar solvents such as DMF and NMP were efficient (Table 1, entries 8–12). Notably, the reaction proceeded at as low as 30 °C without

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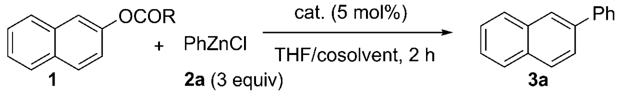
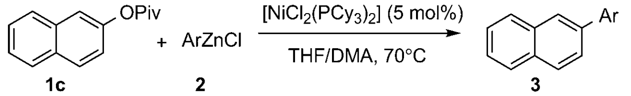
***Table 1:*** Cross-coupling reaction between **1** and **2a** under different reaction conditions.[a]

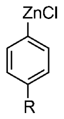
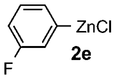
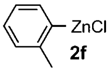
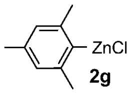
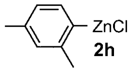
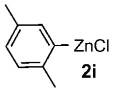
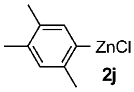
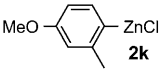
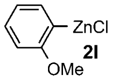


| Entry | Carboxylate | Catalyst | Cosolvent | $T$ [°C] | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | R = Me, **1a** | $[NiCl_2(PCy_3)_2]$ | DMA | 70 | 21 |
| 2 | R = *i*Pr, **1b** | $[NiCl_2(PCy_3)_2]$ | DMA | 70 | 73 |
| 3 | R = *t*Bu, **1c** | $[NiCl_2(PCy_3)_2]$ | DMA | 70 | 100 (84)[c] |
| 4 | **1c** | $NiCl_2 + 2\ PCy_3$ | DMA | 70 | 100 (78)[c] |
| 5 | **1c** | $NiCl_2 + 2\ PPh_3$ | DMA | 70 | 19 |
| 6 | **1c** | $NiCl_2 + 2\ PnBu_3$ | DMA | 70 | 38 |
| 7 | **1c** | $NiCl_2 + 2\ PtBu_3$ | DMA | 70 | 47 |
| 8 | **1c** | $[NiCl_2(PCy_3)_2]$ | THF | 70 | 6 |
| 9 | **1c** | $[NiCl_2(PCy_3)_2]$ | DCE | 70 | < 5 |
| 10 | **1c** | $[NiCl_2(PCy_3)_2]$ | toluene | 70 | < 5 |
| 11 | **1c** | $[NiCl_2(PCy_3)_2]$ | DMF | 70 | 100 (85)[c] |
| 12 | **1c** | $[NiCl_2(PCy_3)_2]$ | NMP | 70 | 100 (82)[c] |
| 13 | **1c** | $[NiCl_2(PCy_3)_2]$ | DMA | 50 | 89 |
| 14 | **1c** | $[NiCl_2(PCy_3)_2]$ | DMA | 30 | 71 |
| 15[d] | **1c** | $[NiCl_2(PCy_3)_2]$ | DMA | 70 | 70 |
| 16[e] | **1c** | $[NiCl_2(PCy_3)_2]$ | DMA | 70 | 84 |
| 17 | **1c** | $[FeCl_3(PCy_3)_3]$ | DMA | 70 | 0 |
| 18 | **1c** | $[CoCl_2(PCy_3)_2]$ | DMA | 70 | < 5 |
| 19 | **1c** | $[PdCl_2(PCy_3)_2]$ | DMA | 70 | 0 |

[a] Reaction conditions: 0.5 mmol of 2-naphthyl carboxylate **1**, 1.5 mmol of PhZnCl **2a**, 0.025 mmol of catalyst in 1 mL of THF and 2 mL of cosolvent. [b] Yield determined by GC analysis. [c] Yield of isolated product. [d] 1 mol% of catalyst. [e] 2 equivalents of PhZnCl. Cy = cyclohexyl, DCE = 1,2-dichloroethane, DMA = dimethylacetamide, DMF = *N*,*N*-dimethylformamide, NMP = *N*-methylpyrrolidine.

***Table 2:*** Nickel-catalyzed C−C bond formation with various arylzinc reagents.[a]



| Entry | ArZnCl | | Product (yield [%])[b] |
|---|---|---|---|
| 1 |  | R = H, **2a** | **3a** (84) |
| 2 | | R = Me, **2b** | **3b** (80) |
| 3 | | R = OMe, **2c** | **3c** (85) |
| 4 | | R = $CH_2OMe$, **2d** | **3d** (66) |
| 5 |  **2e** | | **3e** (69) |
| 6 |  **2f** | | **3f** (81) |
| 7[c] |  **2g** | | **3g** (< 5) |
| 8 |  **2h** | | **3h** (80) |
| 9 |  **2i** | | **3i** (82) |
| 10 |  **2j** | | **3j** (84) |
| 11 |  **2k** | | **3k** (85) |
| 12 |  **2l** | | **3l** (69) |

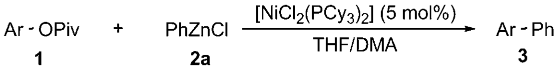
[a] Reaction conditions: 0.5 mmol of naphthyl pivalate, 1.5 mmol of ArZnCl, 0.025 mmol of catalyst in 1 mL of THF and 2 mL of DMA. [b] Yield of isolated product. [c] Yield determined by GC analysis with the use of *n*-dodecane as an internal standard. Piv = pivalate.

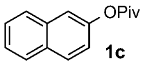
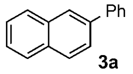
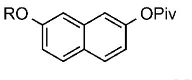
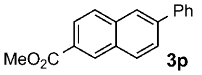
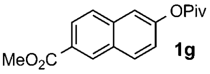
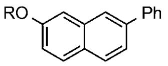
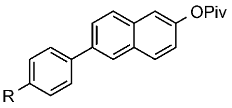
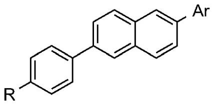
significant loss of catalytic reactivity (Table 1, entries 13 and 14). Lowering the catalyst loading to 1 mol% or the amount of arylzinc reagent to 2 equivalents led to slightly lower yields (Table 1, entries 15 and 16). For this transformation other transition-metal complexes did not show comparable catalytic reactivity (Table 1, entries 17–19).

With the optimized reaction conditions in hand, the reactivity of different arylzinc reagents were subsequently investigated (Table 2). 2-Naphthyl pivalate (**1c**) was coupled with a variety of arylzinc reagents in good efficiency. The electronic nature of the arylzinc reagents did not play a significant role in the reaction. Arylzinc reagents bearing *para* substituents, such as methyl and methoxyl groups, were suitable for this transformation and the desired products were obtained in good to excellent yields (Table 2, entries 2–4). During this transformation, C−O and C−F bonds survived, and they could be further transformed into different functionalities (Table 2, entries 3–5). Interestingly, an *ortho* substituent on the phenyl ring of the arylzinc reagent increased the reaction efficiency and exerted a marked rate acceleration (Table 2, entries 6, 8–12)—presumably because steric repulsion enhanced the reductive elimination step.[10] However, further increase of the steric bulk led to the termination of the cross-coupling, as was demonstrated by the reaction of the 2-mesitylzinc chloride (**2g**), which gave no desired product (Table 2, entry 7). This outcome suggests that the transmetalation of extremely bulky arylzinc reagent might be problematic before reaching the reductive elimination step.[10] Unfortunately, functionalized arylzinc reagents such as *p*-cyano and *p*-methoxycarbonyl phenylzinc chlorides, which can be prepared through halide/Mg exchange and subsequent Mg/Zn transmetalation,[11] can not successfully undergo the desired cross-coupling reaction.

Different carboxylates were further explored to examine the functional group tolerance of the reaction (Table 3). Several phenol protecting groups including methyl, benzyl, and MOM were tested and all of them survived (Table 3, entries 2–4). Notably, the ester functionality remained untouched in the reaction, thus suggesting an orthogonal reactivity (for the current system) towards two different types of ester groups (Table 3, entry 5). Moreover, the coupling reaction could also be applied to larger conjugated system. 2,4,5-Trimethylphenylzinc chloride (**2j**) was chosen as the coupling partner with 6-aryl-2-naphthyl pivalates (**1h**–**k**) because of concern about both the reactivity of the substrate and solubility of the product (Table 3, entries 6–9). Significantly, only 5 mol% of the catalyst and 3 equivalents of

**Table 3:** Nickel-catalyzed C–C bond formation with different 2-naphthyl pivalates.[a]

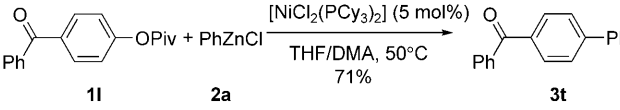


| Entry | ArOPiv | | Product | | Yield [%][b] |
|---|---|---|---|---|---|
| 1 |  **1c** | |  **3a** | | 84 |
| 2 |  | R = Me, **1d** |  **3p** | R = Me, **3m** | 70 |
| 3 | | R = Bn, **1e** | | R = Bn, **3n** | 77 |
| 4 | | R = MOM, **1f** | | R = MOM, **3o** | 79 |
| 5[c] |  **1g** | |  | | 82 |
| 6[d] |  | R = H, **1h** |  | R = H, **3q** | 82 |
| 7[d] | | R = OMe, **1i** | | R = OMe, **3r** | 81 |
| 8[d] | | R = F, **1j** | | R = Ar, **3s** | 81 |
| 9[d] | | R = Cl, **1k** | | R = Ar, **3s** | 79 |

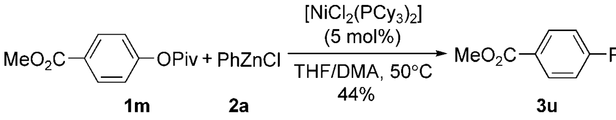
[a] Reaction conditions: 0.5 mmol of naphthyl pivalate, 1.5 mmol of ArZnCl, 0.025 mmol of catalyst in 1 mL of THF and 2 mL of DMA. [b] Yield of isolated product. [c] Reaction carried out at 50 °C. [d] Arylzinc reagent **2j** was used. Ar = 2,4,5-Me$_3$C$_6$H$_2$, Bn = benzyl, MOM = methoxymethyl.

arylzinc reagent were sufficient for double arylations, thus highlighting the effectiveness of the catalytic system (Table 3, entries 8 and 9). Although the concomitant arylation of the aryl C–Cl bond was not surprising, the activation of the C–F bond was somewhat unexpected because the aryl C–F bond survived when it was present in the arylzinc counterpart (Table 2, entry 5 and see the Supporting Information). On the other hand, activation of the C–F bond turned out to be an additional bonus which represented a rare example for normally unactivated aryl C–F arylation.[12] This reaction has also set a boundary for tolerance towards aryl halides used in the current system.

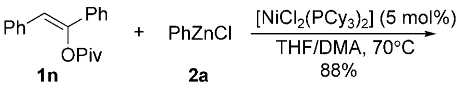
Besides naphthyl pivalates, phenyl pivalates were also suitable substrates as long as an electron-withdrawing substituent was incorporated on the phenyl ring to activate the substrates. For example, the coupling of 4-phenylcabonylphenyl pivalate (**1l**) and 4-methoxylcarbonylphenyl pivalate (**1m**) proceeded well [Eqs. (1) and (2)]. The current catalytic system was by no means limited to aryl–aryl coupling, as it could also be extended to vinyl–aryl coupling. The coupling of acyclic as well as cyclic vinyl pivalate (**1n** and **1o**) with phenylzinc chloride turned out to be highly efficient, and provided the styryl derivatives in high yields [Eqs. (3) and (4)].



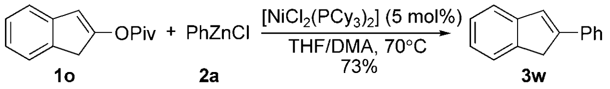
(1)



(2)



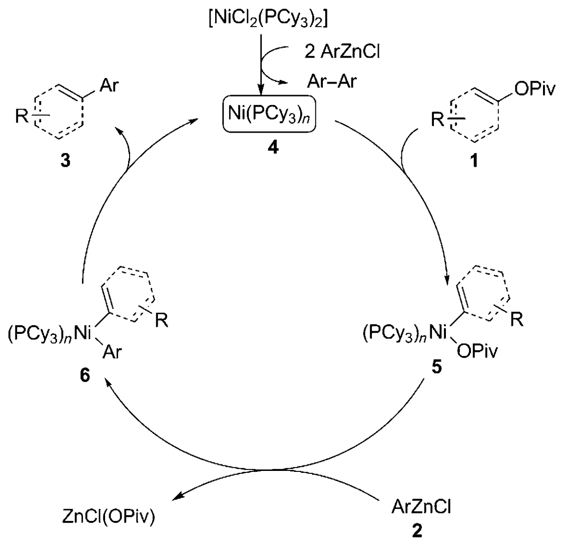
(3)



(4)

A proposed mechanistic model for the cross-coupling reaction is outlined in Scheme 1. It is anticipated that the nickel-catalyzed arylation of aryl carboxylates proceeds through a classic cross-coupling mechanism. First, in situ reduction of Ni$^{II}$ by the organozinc reagent generates the active Ni$^0$ catalytic species **4**, which was evidenced by the generation of homocoupling biaryls in the presence of ArZnCl and [NiCl$_2$(PCy$_3$)$_2$]. [13a] Subsequently, oxidative addition of aryl carboxylates **1** to Ni$^0$ furnishes aryl nickel species **5**, which further undergoes transmetalation with the organozinc reagent to produce the biaryl nickel intermediate **6**.[13b] Finally, upon reductive elimination, the desired product **3** is obtained along with regeneration of the active catalyst to facilitate the catalytic cycle.[13c] Similarly, the coupling of alkenyl pivalates with arylzinc reagents follows the same pathway.

In summary, we have demonstrated the first example of catalytic cross-coupling using aryl/alkenyl pivalates (as aryl/alkenyl electrophile surrogates) with arylzinc reagents. The simple and efficient catalytic system allowed the coupling to



***Scheme 1.*** Proposed mechanism for the direct arylation of aryl/alkenyl pivalates with organozinc reagents.

precede under mild reaction conditions, and exhibited good level of functional group tolerance. Ongoing work will seek further extension of other coupling reactions with aryl carboxylates as well as deeper mechanistic insight into this novel reaction.

## *Experimental Section*

A representative procedure (Table 2): A solution of *t*BuLi (2.0 mL, 3.0 mmol; 1.5 M solution in pentane) was added dropwise to a solution of aryl bromide (1.5 mmol) in THF (2 mL) in a Schlenk tube at −78 °C. The resulting mixture was stirred for 30 min at −78 °C, and then for a further 30 min at room temperature. Next, ZnCl$_2$ (230 mg, 1.7 mmol) was added in one portion at 0 °C to the aryllithium solution thus obtained. After stirring at room temperature for an additional 15 min, the reaction mixture was charged with [NiCl$_2$(PCy$_3$)$_2$] (17.0 mg, 0.025 mmol), arylcarboxylate (0.5 mmol), and anhydrous DMA (2 mL). A balloon containing N$_2$ (1 atm) was connected to the Schlenk tube before it was immediately heated to 70 °C, thus ensuring the pentane evaporated into the balloon. After the reaction was complete (as evident by TLC), the mixture was quenched with aqueous HCl (2 M, 5 mL) and then EtOAc (80 mL) was added. The organic phase was washed with water (30 mL × 3), dried over MgSO$_4$, concentrated and purified by flash column chromatography on silica gel.

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**Keywords:** C−O activation · cross-coupling · homogeneous catalysis · nickel · organozinc reagents

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