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Switchable Selectivity in the Pd-Catalyzed Alkylative Cross-Coupling of Esters

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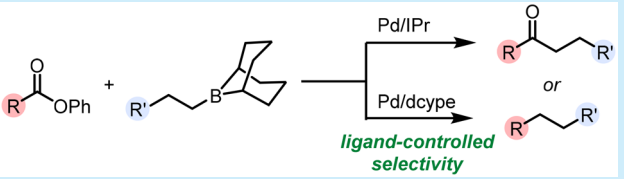
Supporting Information

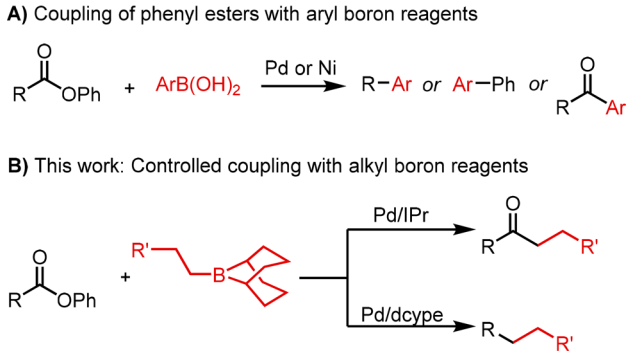
ABSTRACT: The Pd-catalyzed cross-coupling of phenyl esters and alkyl boranes is disclosed. Two reaction modes are rendered accessible in a selective fashion by interchange of the catalyst. With a Pd−NHC system, alkyl ketones can be prepared in good yields via a Suzuki−Miyaura reaction proceeding by activation of the C(acyl)−O bond. Use of a Pd−dcype catalyst enables alkylated arenes to be synthesized by a modified pathway with extrusion of CO. Applications of this divergent coupling strategy and the origin of the switchable selectivity are discussed.



Pd-catalyzed cross-coupling reactions have greatly simplified the way we construct C(sp^2)−C(sp^2) and C(sp^2)−C(sp^3) bonds. Initially, developments in the field were mostly focused on expanding the scope of the nucleophilic agent, with organoboron reagents now being the most utilized coupling partner due to their accessibility and effectiveness for the construction of complex molecules.[1] While aryl and vinyl halides are traditionally utilized as the electrophilic reaction component, the development of cross-coupling reactions that feature alternative electrophiles can further extend the impact and utility of the Suzuki−Miyaura reaction by enabling even more diverse products to be reliably formed from simple starting materials. Owing to their ubiquity, carboxylic acid derivatives represent a useful family of alternative coupling partners. While cross-coupling of acid chlorides has been known since the pioneering work of Stille[2] and recent research has focused on the use of more robust substrates such as acid anhydrides,[3] thioesters,[4] select amides,[5] and esters.[6] In particular, the use of phenyl ester coupling partners has recently been exploited in an array of diverse reactions.[7] In contrast to aryl halides, phenyl esters can be activated by different reaction modes depending on the choice of catalyst (Scheme 1A). For instance, Garg and Shi independently demonstrated activation of the C(aryl)−O bond in couplings with arylboron reagents.[8] Love and Itami later demonstrated formal cleavage of the C(aryl)−C bond to form biaryls,[9] while our group, in collaboration with the Houk laboratory, recently disclosed that aryl ketones could be selectively prepared.[10]

Although a wealth of mechanistic information has accumulated over the last couple of years on these and related reactions,[11] rationally predicting and controlling selectivity in cross-couplings of esters remains a considerable challenge. Moreover, couplings with alkyl nucleophiles constitutes an underdeveloped area in the field[12] due to several challenges with the use of alkyl boron reagents such as their reluctance to transmetalate relative to their aryl counterparts and the intermediacy of alkylmetal species that are prone to β-hydride elimination.[13] Nonetheless, the formation of C(sp^2)−C(sp^3) bonds is an important goal due to the prevalence of these types of linkages in pharmaceuticals and other valuable materials.

Scheme 1. Different Reaction Modes in the Cross-Couplings of Esters



In this work, we disclose the first Pd-catalyzed coupling of phenyl esters with alkyl boranes (Scheme 1B).[14] A bulky NHC ligand enables the reaction to proceed with carbonyl retention to afford ketones. In contrast, the use of a hemilabile bidentate phosphine ligand provides the decarbonylated adduct selectively. Remarkably, β-hydride elimination can be minimized in the latter reaction mode, even at the high temperature required for decarbonylation.

We first investigated the possibility of performing alkylative carbonyl-retentive couplings with phenyl esters and alkyl boranes. Given the efficiency of Pd−NHC complexes in related cross-couplings,[10,15] we elected Pd(IPr)(cinnamyl)Cl as a potential catalyst. No conversion was observed in the absence of base (Table 1, entry 1). However, upon incorporation of cesium carbonate, **3a** was obtained in high

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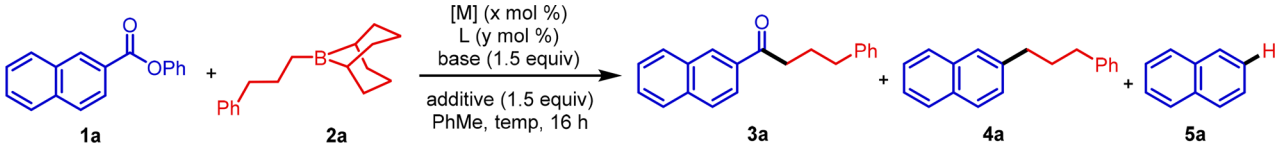
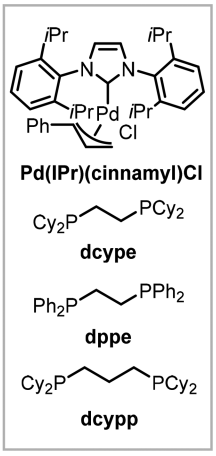
Table 1. Optimization of the Pd-Catalyzed Coupling of Phenyl Esters and Alkyl Boranes[a]



1a 2a 3a 4a 5a

entry	metal source	x	ligand	y	base/additive	temp (°C)	yield (%) 3a[b]	yield (%) 4a[b]	yield (%) 5a[c]
1	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	none	60	0	0	0
2	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	Cs_2CO_3	60	74	0	0
3	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	Cs_2CO_3/H_2O	60	96	0	0
4	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	Cs_2CO_3/H_2O	80	77	0	0
5	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	Cs_2CO_3/H_2O	110	57	0	0
6	$Pd(OAc)_2$	5	dcype	10	none	130	0	58	21
7	$Pd(OAc)_2$	5	dcype	10	KF	130	0	66	7
8	$Pd(OAc)_2$	5	dcype	10	KF	160	0	82	13
9	$Pd(OAc)_2$	5	dppe	10	KF	160	0	0	0
10	$Pd(OAc)_2$	5	dcypp[d]	10	KF	160	0	20	16
11	$Ni(cod)_2$	10	dcype	20	KF	160	0	12	60
12	Pd(IPr)(cinnamyl)Cl	5	n/a	n/a	KF	160	0	0	0
13	$Pd(OAc)_2$	5	dcype	10	Cs_2CO_3/H_2O	60	0	0	0

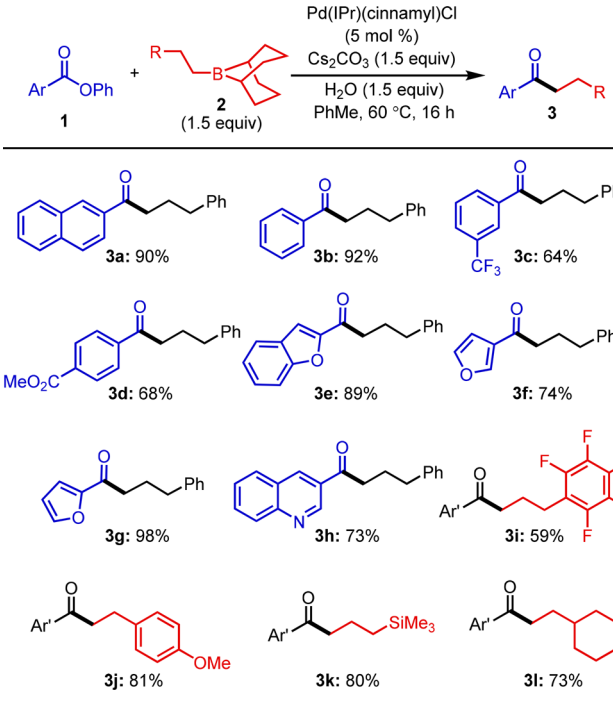


[a]General reaction conditions: ester **1a** (0.10 mmol), alkyl borane **2a** (0.15 mmol), Pd or Ni catalyst, ligand, base (0.15 mmol), additive (0.15 mmol), toluene (0.11 M), 16 h, under nitrogen atmosphere. [b]Yield determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard. [c]Yield determined by GC/FID with 1,3,5-trimethoxybenzene as the internal standard. [d]dcypp·HBF_4 was used along with 20 mol % of K_2CO_3.

yield (entry 2). Further addition of water reached near quantitative yield of **3a** (entry 3). Increasing the temperature was found to lead to reduced yields of the ketone product without any detectable formation of decarbonylated products (entries 4 and 5). Next, we turned our attention to decarbonylative alkylative couplings. With the net majority of decarbonylative couplings of esters occurring at elevated temperatures >140 °C, it was suspected that preventing β-hydride elimination under such conditions would pose a significant challenge. We envisioned that an optimal catalyst would bear a ligand that favors reductive elimination while being labile enough to allow decarbonylation. Rationally designed screenings were conducted on the basis of previous reports and the mechanistic studies of related couplings.[6−10] An initial hit was found with $Pd(OAc)_2$ (5 mol %) and dcype (10 mol %). As is shown in Table 1, a moderate yield of **4a** can be obtained in the absence of any base or additive (entry 6). Interestingly, KF was found to both increase the yield and lead to better selectivity for the formation of the desired adduct **4a** over the reduced product **5a** (entry 7). Better conversion was obtained at higher temperatures, reaching a satisfactory yield of 82% of **4a** at 160 °C (entry 8). Among the diverse array of ligands screened, dcype was found to be uniquely effective for this transformation (Table S3). For instance, the use of dppe as the ligand led to full recovery of the starting material **1a** (entry 9), while dcypp was unselective for the formation of arenes **4a** and **5a** (entry 10). Interestingly, the replacement of $Pd(OAc)_2$ by $Ni(cod)_2$ reversed the selectivity, favoring beta-hydride elimination over reductive elimination to give 60% of naphthalene **5a** (entry 11). To further corroborate that the selectivity switch between the formation of **3a** vs **4a** was not solely temperature-dependent, both catalysts were tried at different temperatures. At 160 °C, no trace of decarbonylated adduct **4a** was observed with the Pd-NHC catalyst (entry 12). Conversely, the Pd-dcype catalyst did not provide any ketone **3a** at 60 °C (entry 13). Thus, we attribute the requirement for elevated temperatures in the decarbonylative pathway to the challenging liberation of CO from the metal center.

The scope of the carbonyl-retentive couplings is illustrated in Scheme 2. Different esters were tested with alkyl borane **2a**. Simple phenyl naphthoate and benzoate derivatives provided good to excellent yields (**3a**−**d**). Heteroaryl esters such as

Scheme 2. Scope of Carbonyl-Retentive Coupling[a]



[a]General reaction conditions: ester (0.20 mmol), alkyl borane (0.30 mmol), Pd(IPr)(cinnamyl)Cl (5 mol %), Cs_2CO_3 (0.30 mmol), water (0.30 mmol), toluene (0.22 M), 16 h, at 60 °C, under nitrogen atmosphere. Ar′ = 2-naphthyl.

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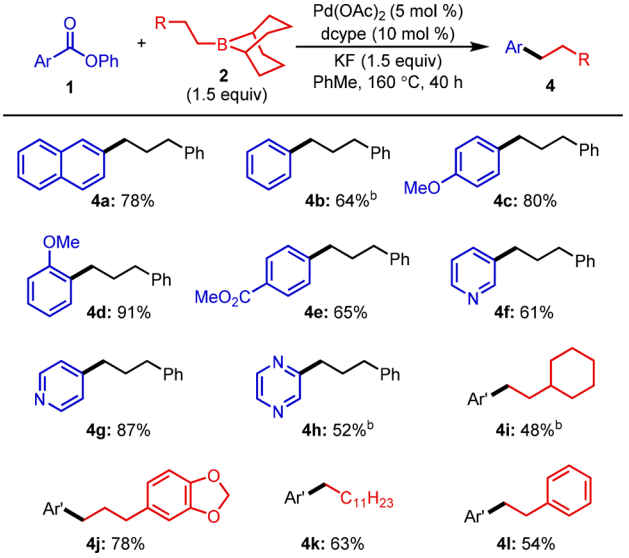
furans, benzofurans, and quinolines were also compatible under the reaction conditions (**3e–h**). Different B-alkyl-9-BBN reagents were then tested. A B-alkyl-9-BBN bearing a perfluorophenyl ring provided **3i** in a moderate yield. Styrenyl-derived and aliphatic boranes also provided good yields (**3j–l**).

We next explored the scope of the decarbonylative couplings (Scheme 3). Both electron-neutral (**4a** and **4b**) and electron-

Scheme 3. Scope of Decarbonylative Coupling[a]



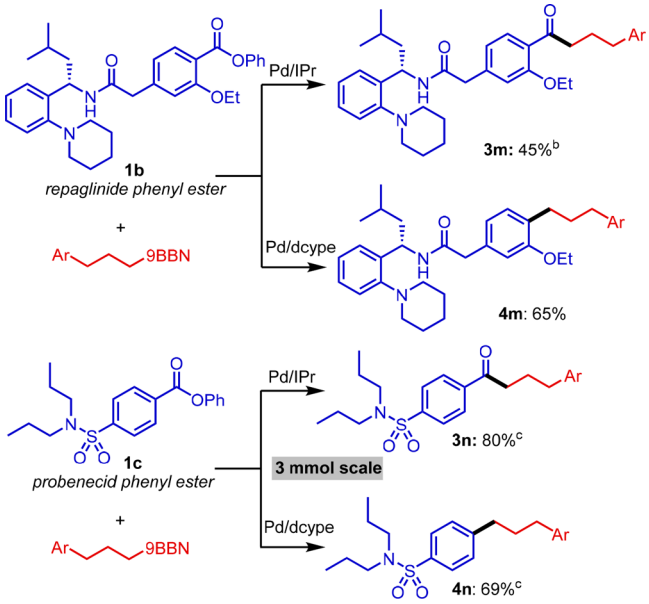
[a]General reaction conditions: ester (0.20 mmol), alkyl borane (0.30 mmol), $Pd(OAc)_2$ (5 mol %), dcype (10 mol %), KF (0.30 mmol), toluene (0.22 M), 40 h, at 160 °C, under nitrogen atmosphere. Ar′ = 2-naphthyl. [b]$Pd(COD)(CH_2TMS)_2$ (5 mol %) was used instead of $Pd(OAc)_2$.

rich (**4c** and **4d**) arenes provided good to excellent yields. An ester bearing a methyl ester functionality selectively reacted with the phenyl ester moiety (**4e**). Pleasingly, heteroaryl esters with pyridine and pyrazine motifs were suitable coupling partners (**4f–h**). Aliphatic boranes provided moderate yields under the reaction conditions (**4i** and **4k**), while a safrole-derived B-alkyl-9-BBN nucleophile provided high yield of product **4j**. Notably, an alkyl borane having a benzylic β-hydrogen was also an efficient coupling partner (**4l**).

The ability to transform a single starting material into different classes of products is most powerful when the preparation of diverse, potentially bioactive molecules is sought (Scheme 4). Toward this goal, functional group-rich phenyl ester **1b**, derived from the antidiabetic drug repaglinidine, could be utilized to form both the ketone **3m** and decarbonylated product **4m**. Ester **1c**, derived from the gout and hyperuricemia drug probenecid, could be similarly diversified to **3n** and **4n** on 3 mmol scale with reduced catalyst loading, providing good yields of both products.

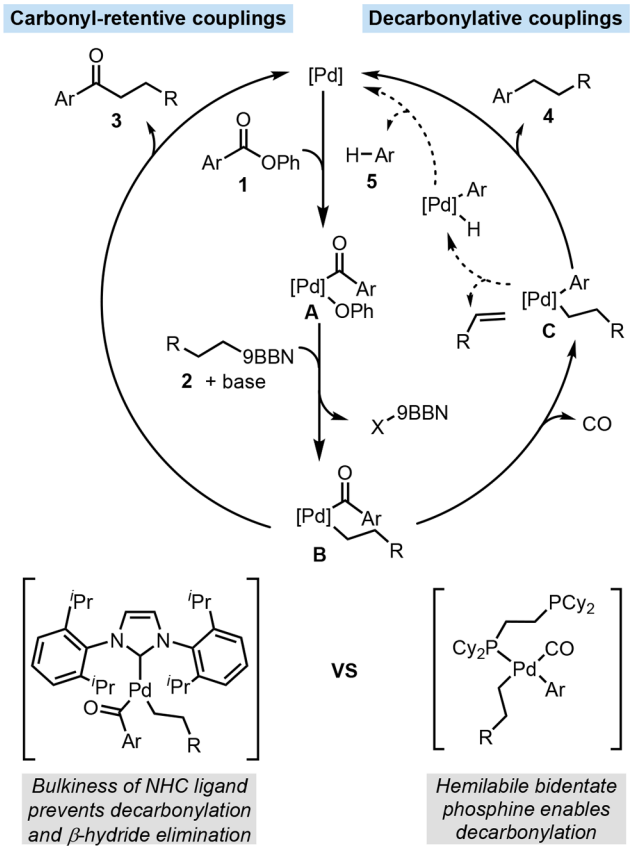
A general mechanism outlining the different reaction modes is proposed in Scheme 5. Three products were observed in the coupling of phenyl esters and B-alkyl-9-BBN reagents: ketone adduct **3**, alkylated arene **4**, or reduced product **5**. All mechanisms can begin with oxidative addition of the catalyst into the weak C(acyl)–O bond, as has been proposed in related couplings[10,16] and demonstrated experimentally in stoichiometric studies with Ni/ICy.[6d]

Scheme 4. Derivatization of Bioactive Molecules[a]



[a]General conditions as described in Schemes 1 and 2. Ar = Ph for **3m** and **3n**, Ar = 3,4-methylenedioxyphenyl for **4m** and **4n**. [b]10 mol % of Pd(IPr)(cinnamyl)Cl was used. [c]3.0 mmol scale with 3 mol % of [Pd].

Scheme 5. Proposed Mechanism



The palladium acyl intermediate **A** can then undergo transmetalation with the organoboron species to form **B**, with the respective additives facilitating transmetalation (X = OPh, F, OH, or carbonate).[17] Depending on the nature of the

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ligand, direct reductive elimination leads to ketone **3**, or decarbonylation and CO extrusion can occur to form intermediate **C**. Most reported cross-couplings of phenyl esters proceed by the decarbonylative pathway, many of which utilize dcype as a ligand.[18] Previous DFT calculations on similar transformations with carbon-based nucleophiles suggest transmetalation occurs prior to decarbonylation.[9a,11a,d] The dissociation of one of the phosphine arms of dcype is subsequently required to open up a coordination site for the challenging decarbonylation/extrusion.[11a,b] In contrast, the electron-rich Pd-IPr catalyst blocks decarbonylation due to the steric bulk of the NHC ligand, favoring reductive elimination.[10] Lastly, after decarbonylation, there are again two possibilities. Reductive elimination yields the desired product **4**, while β-hydride elimination would lead to the reduced product **5**. The minimization of β-hydride elimination at elevated temperatures with Pd−dcype is particularly notable.

In summary, the use of esters as electrophilic coupling partners in the Pd-catalyzed Suzuki−Miyaura with alkyl nucleophiles was developed. While many related cross-couplings of carboxylic acid derivatives have been reported, controlling which product class forms is challenging. In this work, two reaction modes can be accessed selectively by interchange of the ligands. An air-stable Pd−NHC catalyst enabled carbonyl-retentive coupling to form a broad range of alkyl ketones. In parallel, a Pd−dcype catalyst was shown to selectively form alkylated arenes via a decarbonylative pathway. We expect that these disclosed transformations will provide rapid access of diverse product-types from a single starting material and will encourage academic chemists to exploit the broad knowledge accumulated in the field to rationally design selective cross-coupling reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01646.

Experimental procedures, characterization of organic molecules, and optimization tables (PDF)

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Notes

The authors declare no competing financial interest.

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