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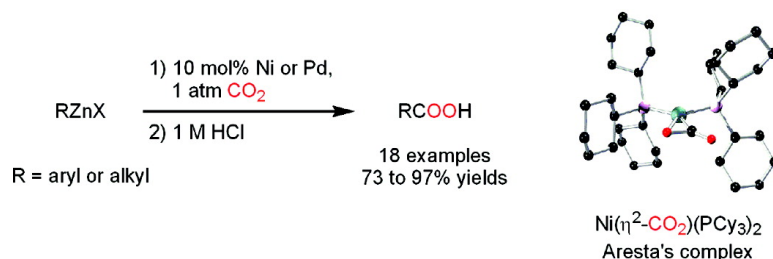
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Beyond Aresta's Complex: Ni- and Pd-Catalyzed Organozinc Coupling with CO_2

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Carbon dioxide is the ideal C1 source for organic synthesis because of its abundance, nontoxicity, and potential as a renewable resource.[1] Thus, designing mild methods to catalytically activate CO_2 and form C−C bonds represents a challenge of both academic and practical importance. Grignard and organolithium reagents are strong nucleophiles which react with CO_2 directly to form valuable carboxylic acid products and derivatives; however, their poor functional group compatibility ultimately limits their use.[2] Iwasawa and co-workers recently reported a Rh-catalyzed carboxylation of aryl- and alkenylboronic esters.[2b] Herein, we report a complementary and mechanistically distinct protocol—a Ni- and Pd-catalyzed cross-coupling between organozinc reagents and CO_2.[3] Our transformation represents a mild and functional group tolerant strategy for carboxylation.[2,4] Moreover, this process can be considered an extension of the Negishi cross-coupling to include CO_2 as the electrophilic partner (Scheme 1).

We initially focused our attention on Aresta's complex, $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (**1**), the first metal−CO_2 complex to be isolated and characterized.[5a] Aresta's report in 1975 sparked a general interest in using transition metals to activate and fixate CO_2.[6] Ironically, no method for using **1** in catalytic transformations with CO_2 had been developed.[5,7] It appeared to us that Aresta's complex (**1**) could undergo transmetalation with organozinc reagents to form organonickel species **2** (Scheme 2).[8] Reductive elimination from **2** would furnish a new C−C bond, generating a zinc carboxylate and low valent $Ni(PCy_3)_2$ (**3**), which would bind another molecule of CO_2 through an oxidative cycloaddition to regenerate **1**.

Control experiments confirmed that no background reaction occurs between phenylzinc bromide and CO_2 under mild conditions (Table 1, entry 1). In agreement with our proposal, treatment of $PhZnBr$ with a *catalytic* amount of **1** (10 mol %) under an atmosphere of CO_2 resulted in the desired benzoic acid in >95% after acidic workup (entry 2). While catalytic fixation of CO_2 by way of insertion to M−C bonds[2b] or by Lewis acid activation[9] has been proposed, this is a rare example of catalytic activation by η^2-coordination of CO_2 to a transition metal.[10] Rather than using the Aresta's complex directly, we examined the use of $[Ni(PCy_3)_2](N_2)$[11] to generate **1** in situ. Under these conditions, the product was formed in >95% (entry 3). For convenience, we also examined the use of commercially available $Ni(COD)_2$ as a catalyst (entry 4). These results support that complexes **1** and **3** are intermediates in the catalytic cycle.

Due to their high versatility and robustness, we next examined the use of Pd salts as catalyst for CO_2 activation (Table 1). Notably, $Pd(\eta^2\text{-}CO_2)(PMePh_2)_2$ has previously been isolated and characterized.[12] We now report that $Pd(PCy_3)_2$ is catalytically competent,[12] affording carboxylation in high yields (entry 5). $Pd_2(dba)_3$ as a Pd(0) source was ineffective presumably due to competitive binding of *trans,trans*-dibenzylideneacetone (dba) and CO_2 (entry 6). Indeed, the addition of small amounts of dba completely inhibits the reaction. $Pd(OAc)_2$ serves as a convenient and easily handled

Scheme 1. Analogy to the Negishi Cross-Coupling
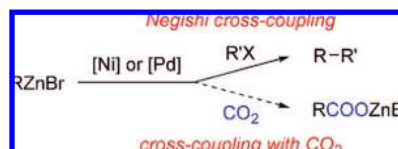
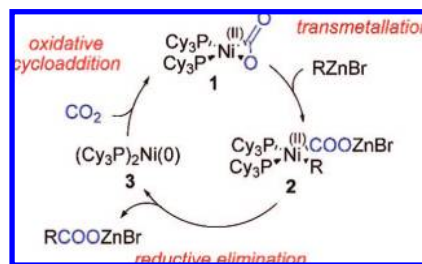**Scheme 2.** Proposed Catalysis with Aresta's Complex

Table 1. CO_2 Activation with Nickel and Palladium

entry	x	[M]	ligand	yield (%)^a
1	0	none	none	0^b
2	10	$Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (**1**)	−	$>95^c$
3	5	$[Ni(PCy_3)_2]_2(N_2)$	−	$>95^b$
4	10	$Ni(COD)_2$	PCy_3	78^b
5	10	$Pd(PCy_3)_2$	−	>95
6	5	$Pd_2(dba)_3$	PCy_3	<5
7	1	$Pd(OAc)_2$	PCy_3	$>95\ (90^d)$
8	1	$Pd(OAc)_2$	P^tBu_2Me	>95
9	1	$Pd(OAc)_2$	PPh_3	7
10	1	$Pd(OAc)_2$	$AsPh_3$	2
11	1	$Pd(OAc)_2$	TMI^e	6
12	1	$Pd(OAc)_2$	bpy	4

^{a} Yields determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ^{b} Toluene used as solvent. ^{c} Toluene-d_8 used as solvent. ^{d} Isolated yield. ^{e} TMI = 1,3,4,5-tetramethylimidazol-2-ylidene.

precatalyst (entries 7 and 8), presumably forming Pd(0) in situ.[13] With this catalyst, use of a simple balloon filled with CO_2 allows efficient carboxylation.[14] A significant ligand effect was observed; PPh_3, $AsPh_3$, 1,3,4,5-tetramethylimidazol-2-ylidene (TMI), and 2,2′-bipyridine (bpy) ligands resulted in less than 10% of the carboxylated product (entries 9−12). These observations support the idea that electron-rich phosphines (e.g., PCy_3 and P^tBu_2Me) are necessary for oxidative addition to occur between Ni(0) or Pd(0) and CO_2.[6]

Next, we prepared a range of arylzinc bromides by the Gosmini method (Co-catalyzed insertion of zinc into C−Br bonds)[15] to

Table 2. Pd-Catalyzed Arylzinc Carboxylations
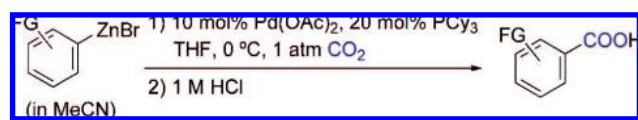
| entry	functional group (FG)	yield (%)[a]
1	none	90[b,c]
2	p-OMe	90
3	m-OMe	97
4	o-OMe	80
5	p-OAc	97[d]
6	p-Me	81[e]
7	p-CF$_3$	90
8	p-Cl	88
9	p-F	94
10	p-CN	73
11	p-COMe	75
12	p-COOEt	76[e]

[a] Isolated yields. [b] Organozinc solution in THF. [c] With 1 mol % of [Pd], 2 mol % of PCy$_3$. [d] Isolated as 4-hydroxybenzoic acid after saponification with 1 M NaOH. [e] With 5 mol % of [Pd], 10 mol % of PCy$_3$.

Table 3. Ni-Catalyzed Aryl- and Alkylzinc Carboxylations
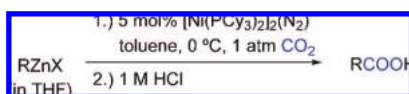
entry	RZnX	yield(%)[a]
1	PhZnBr	74[b]
2	PhZnPh[c]	80
3	n-C$_5$H$_{11}$ZnBr	90
4	Ph(CH$_2$)$_2$ZnBr•LiCl[d]	80
5	Cl(CH$_2$)$_3$ZnI•LiCl[d]	92
6	AcO(CH$_2$)$_4$ZnBr•LiCl[d]	75
7	EtOOC(CH$_2$)$_4$ZnBr•LiCl[d]	86

[a] Isolated yields. [b] With 10 mol % of Ni(COD)$_2$ and 20 mol % of PCy$_3$. [c] In situ prepared PhZnEt reacts poorly. [d] See ref 18 for preparation.

investigate the scope of our carboxylation (Table 2). Arylzinc reagents prepared by this route reacted well with Pd(OAc)$_2$ as the precatalyst,[16] although higher loadings were required. Both electron-rich and electron-poor organozinc reagents were carboxylated in good to excellent yields (entries 1−9), while aromatic rings bearing π-acceptors gave moderate yields (entries 10−12). Notably, substituents at *ortho*, *meta*, and *para* positions can be tolerated (entries 2−4). The carboxylation of arylzinc bromides displayed a significant scope, allowing functionalities traditionally incompatible with Grignard reagents (e.g., ketones, esters, nitriles; entries 10−12).[2] A heteroaromatic reagent could also be effectively carboxylated (eq 1).
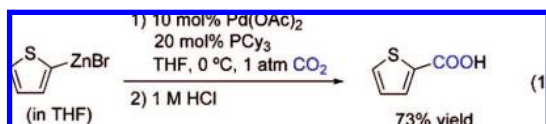
Complimentary to our Pd-based protocol,[17] we found that, under Ni catalysis, both aromatic and aliphatic zinc reagents could be tolerated (Table 3). Commercially available PhZnBr, Ph$_2$Zn, and n-C$_5$H$_{11}$ZnBr underwent CO$_2$ incorporation to produce the corresponding carboxylic acids in good yields (entries 1−3). Alkylzinc reagents (prepared by Knochel's method)[18] bearing various functionality (e.g., Ph, Cl, AcO, EtCOO substituents) were also well-tolerated (entries 4−7). In contrast to Iwasawa's Rh-catalyzed

method,[3] this approach enables carboxylation of functional group compatible aliphatic nucleophiles.[19]

In summary, we have presented a novel catalytic strategy for carbon dioxide incorporation. Aresta's complex can catalyze the cross-coupling of organozinc reagents with CO$_2$, and Pd(OAc)$_2$ is shown to be a convenient catalyst precursor for carbon dioxide activation. We are further investigating the mechanism of this process and plan to use this concept toward asymmetric carboxylation.

Supporting Information Available: General procedures for carboxylations, organozinc synthesis, catalyst preparation, spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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