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Upgrading Carbazolyl-Derived Phosphine Ligands using Rh^I-Catalyzed P^{III}-Directed C–H Bond Alkylation for Catalytic CO₂-Fixation Reactions

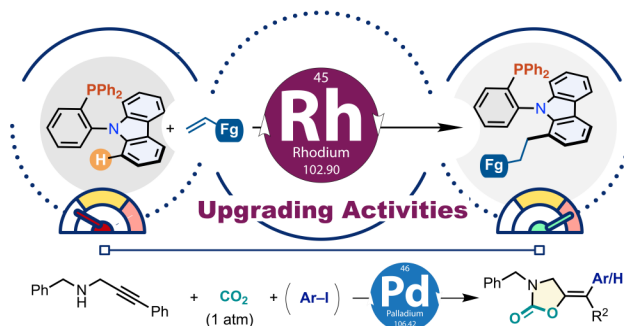
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ABSTRACT: We report a rh(I)-catalyzed C–H bond alkylation of PhenCarPhos [= *N*-(2-(diphenylphosphanyl)phenyl)carbazole] and some congener phosphine ligands with alkenes. The C–H bond functionalization occurred exclusively at the C1 position of the carbazolyl unit because the trivalent phosphine acts as a directed group. This protocol provides straightforward access to a large library of C1-alkyl substituted PhenCarPhos, which outperformed common commercial or unfunctionalized phosphines and their precursors in the Pd-catalyzed carbon dioxide-fixation reactions with propargylic amines.

Designing more active ligands is one of the most important fields of catalysis and organometallic chemistry. Despite numerous advances in transition metal-catalyzed reactions, developing efficient catalytic systems is still highly desirable for industrial application, significantly decreasing their environmental impact. Among the different classes of ligands, phosphines remain the most popular with several well-established industrial processes.¹ It is admitted that the associated phosphines can modulate the activity of metal centers of catalysts through fine-tuning of their steric and electronic properties or by weak interactions in the second coordination sphere. However, the synthesis of such multifunctional phosphines with different substituents often requires multistep synthesis and the use of organometallic reagents may limit the diversity of the functional group that can be introduced in the phosphine scaffold.

Since the pioneer observation by Hartwig and co-workers on Pd-catalyzed direct polyarylation of 1-(di-*tert*-butylphosphino)ferrocene,² P(III)-chelation-assisted C–H bond functionalization has become a straightforward strategy to

quickly generate vast libraries of functionalized phosphines allowing to discover upgraded ligand exhibiting higher catalytic activity in among others Pd catalysis.³ To date, C–H bond functionalizations of phosphines is limited to arylphosphines (borylation,⁴ silylation⁵ and arylation⁶), biarylphosphines (borylation,⁷ silylation, arylation,⁸ alkylation,⁹ alkenylation¹⁰ and carbonylation¹¹) and 1-naphtylphosphines (arylation¹² and alkylation¹³) (Figure 1). Interestingly, in some cases, the C–H bond functionalizations of phosphines give birth to a better ligand in transition-metal catalyzed reactions.¹⁴ For instance, we have demonstrated that C–H bond alkylation of CyJohnPhos (= (2-biphenyl)dicyclohexylphosphine) morphs this inactive ligand into a very active phosphine in Pd-catalyzed carboxylation of aryl bromides with carbon dioxide due to incorporation of amide and ester groups as a basic pendant unit.^{9a} Continuing our efforts to modify phosphines through their C–H bond functionalizations, we turned our attention to PhenCarPhos [= *N*-(2-(diphenylphosphanyl)phenyl)carbazole]. Associated with palladium, this ligand, developed by Kwong,¹⁵ exhibits high catalytic activities taking advantage of the introduced carbazolyl unit that *i*) facilitates the reductive elimination process due to an extended flat-wall-like rigidity and *ii*) stabilizes active Pd catalytic species during the catalytic cycle through weak interactions with the sp³- hybridized nitrogen atom.

Surprisingly, carbazolyl-derived phosphines have never been subjected to the C–H bond functionalization yet. One reason lie with forming an unconventional 7-membered ring cyclometalated phosphine-metal intermediate. Herein, we report an Rh(I)-catalyzed P(III)-directed C1-alkylation of carbazolyl-derived phosphines with olefins (Figure 1, blue box). This method allows the rapid synthesis of functionalized PhenCarPhos. These modified ligands show promising activity in the Pd-catalyzed CO₂-fixation reaction.

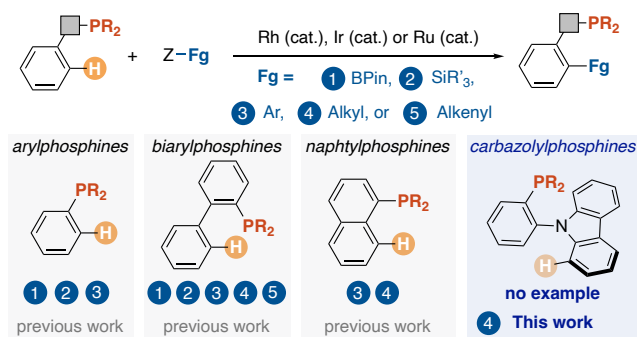
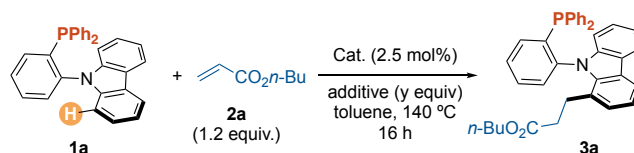


Figure 1. TM-Catalyzed P(III)-Directed C–H Functionalizations

To explore the C–H bond alkylation of carbazolyl-derived phosphine, we choose PhenCarPhos (**1a**) and *n*-butyl-acrylate (**2a**) as the model substrates (Table 1). Based on our previous work on C–H bond alkylation of biarylphosphines,^{9a} we tested firstly the same conditions, namely, [Rh(OAc)(COD)]₂, PivOH in toluene at 140 °C, but no reaction occurred (entry 1). The desired alkylated phosphine **3a** was obtained with a conversion of 50% using KOAc instead of PivOH (entry 2). Increasing the amount of KOAc (2 equi.) gave a better conversion (entry 3). Then, we ran the reaction in different solvents (1,4-dioxane, DMF, 1,2-dichloroethane), but none of them outperformed toluene (entries 4–6). NaHCO₃ as a base gives a slightly better result (92% yield, entry 7). Interestingly, commercially available [RhCl(COD)]₂ catalyst displays a similar catalytic activity affording **3a** in 87% isolated yield (entry 8). Other Rh(I)-catalysts such as [RhCl(NBE)]₂, [RhCl(COE)]₂, and RhCl(PPh₃)₃ were less efficient, while no reaction occurred with Cp*Rh(III) catalyst (entries 9–12). Besides, C–H bond alkylation of PhenCarPhos (**1**) was also achieved using 5 mol% [RuCl₂(*p*-cymene)]₂ catalyst in conjunction with 15 mol%

of AgSbF₆ and 2 equivalents of KOAc (entry 13). However, our attempt to obtain the dialkylation product through increasing the amount of both base and butyl-acrylate or even starting the reaction from **3a** remained unsuccessful (entry 14). Moreover, the phenyl substituents on the phosphorus group are very important, as with two cyclohexyl groups on the phosphorus, no reaction occurred either with rhodium or ruthenium conditions (entries 15 and 16).

Table 1. Optimization of C–H Alkylation of PhenCarPhos

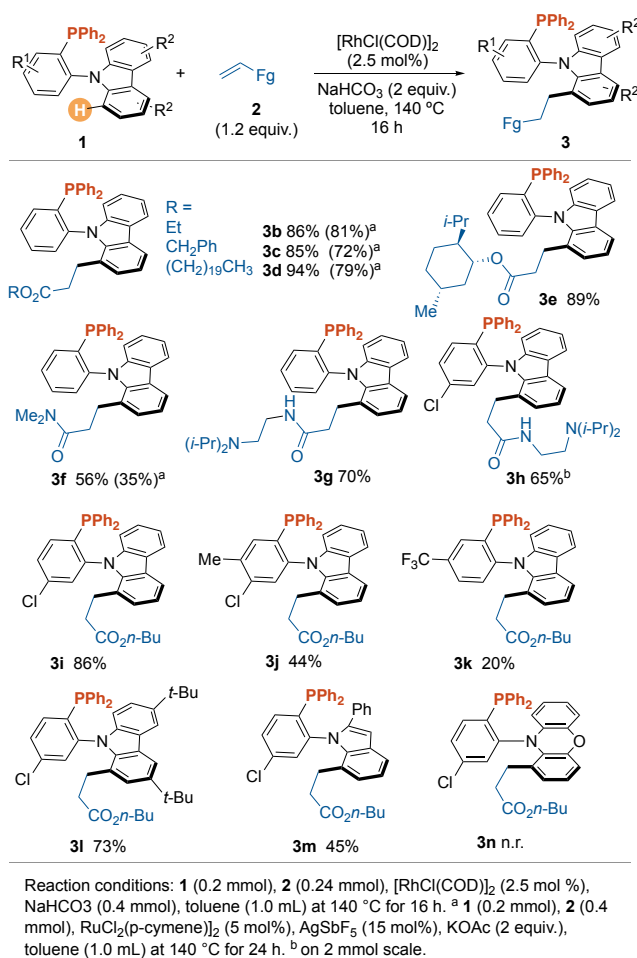


Entry	Cat	Additive (y)	Conv. (%) ^a	3a (%) ^a
1	[Rh(OAc)(COD)] ₂	PivOH (1)	0	0
2	[Rh(OAc)(COD)] ₂	KOAc (0.25)	50	45
3	[Rh(OAc)(COD)] ₂	KOAc (2)	89	82
4 ^b	[Rh(OAc)(COD)] ₂	KOAc (2)	75	73
5 ^c	[Rh(OAc)(COD)] ₂	KOAc (2)	18	15
6 ^d	[Rh(OAc)(COD)] ₂	KOAc (2)	0	0
7	[Rh(OAc)(COD)] ₂	NaHCO ₃ (2)	100	92
8	[RhCl(COD)] ₂	NaHCO ₃ (2)	100	92 (87)
9	[RhCl(NBE)] ₂	NaHCO ₃ (2)	85	81
10	[RhCl(COE)] ₂	NaHCO ₃ (2)	84	79
11	RhCl(PPh ₃)	NaHCO ₃ (2)	10	8
12	[Cp*RhCl ₂] ₂	NaHCO ₃ (2)	0	0
13	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5)	AgSbF ₆ (15 mol%) + KOAc (2)	100	86 (72)
14 ^e	[RhCl(COD)] ₂	NaHCO ₃ (2)	0	0
15 ^f	[RhCl(COD)] ₂	NaHCO ₃ (2)	0	0
16 ^f	[Ru(<i>p</i> -cymene)Cl ₂] ₂ (5)	AgSbF ₆ (15 mol%) + KOAc (2)	0	0

^a determined by ³¹P NMR using PPh₃ as internal standard, isolated yield is shown in parentheses; ^b in 1,4-dioxane; ^c in DMF; ^d in 1,2-dichloroethane; ^e reaction from **3a**; ^f reaction from (*N*-(2-(dicyclohexylphosphanyl)phenyl)carbazole

Next, we turned our attention to the scope of the reaction (Scheme 1). PhenCarPhos (**1a**) was alkylated with ethyl (**2b**), benzyl (**2c**) and eicosyl (**2d**) acrylates providing the carbazolyl-derived phosphine-ester ligands **3b–3d** in 85–94% yields. Ru(II) conditions afford the same products, albeit in slightly lower yields. We also incorporated enantiopure L-menthyl acrylate unit on this phosphine scaffold to afford the chiral phosphine-ester **3e** in 89% of yield. We also coupled **1a** with acrylamides using either Rh or Ru to give phosphine-amide hybrid ligands **3f** and **3g** in 56% and 70% yield, respectively.

The conditions tolerate a chloro-substituent at the *para*-position of the PPh₂ group, providing phosphine-amide ligand **3h** and phosphine-ester ligand **3i** in 65% (on 2 mmol scale) and 86% yield, respectively. From 9-(2-(diphenylphosphaneyl)-5-chloro-4-methylphenyl)carbazole (**1c**) and 9-(2-(diphenylphosphaneyl)-4-(trifluoromethyl)phenyl)carbazole (**1d**), phosphine-ester ligands **3j** and **3k** was isolated in moderate yields. There is no major influence to introduce substituents, like tertbutyl, on the carbazolyl unit at C3 and C6 positions, as alkylated carbazolylphosphine **3l** was isolated in 73% yield. This alkylation method was also transferable to the modification of indolyl-derived phosphine (**1f**), resulting in **3m**. However, no reaction occurred when the carbazolyl part was replaced by phenoxazinyl unit. The size of the *N*-heterocycles might explain this lack of reactivity: C–H bond alkylation is limited to using 5-membered ring *N*-heterocycles due to the possible formation of conformationally constrained conformational strengths 7-membered rodacycle intermediates.

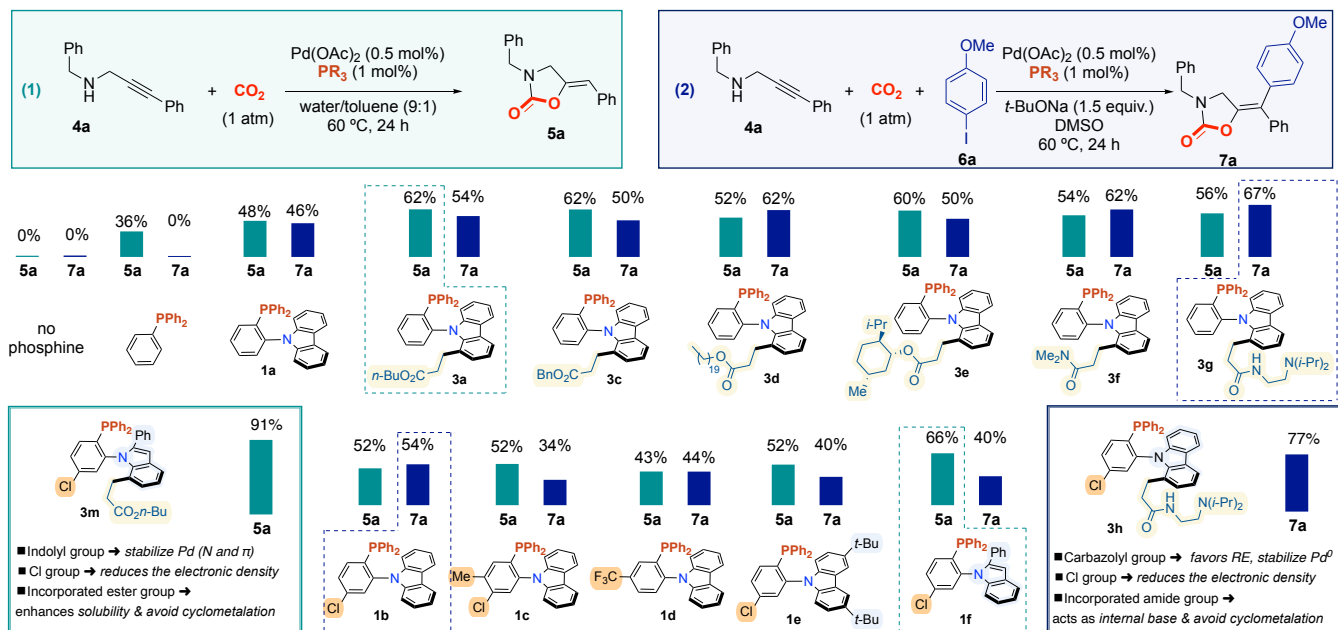


Scheme 1. Scope of Rh(I)-Catalyzed C–H Bond Alkylation of Carbazolyl-Derived Phosphine Ligands

Over the last decades, the development of eco-friendly catalytic CO₂-fixation reactions has garnered a new vision for the economy of CO₂ from a waste product toward an abundant, nontoxic C1 feedstock for constructing synthetic intermediates.¹⁶ In line with our previous discovery on upgrading catalytic activities of biarylphosphines for Pd-catalyzed carboxylation of aryl bromides with CO₂^{9A} we firstly investigated the effect of C–H bond alkylation of PhenCarPhos in Pd-catalyzed

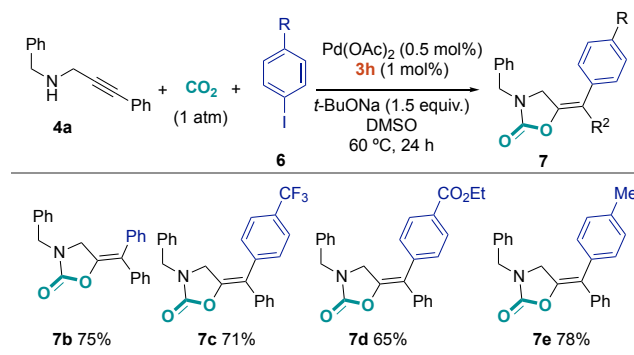
synthesis of oxazolidinones, which are essential building blocks, using CO₂ and propargylic amines. Several reports on carboxylation of propargylamines or aminoalcohols with CO₂ to access oxazolidinones have appeared during the last decade.¹⁷ In most of the cases, *p*-acid catalysis (silver¹⁸ or gold¹⁹) was employed with a stoichiometric amount of organic bases. In 2017, Bourissou and co-workers carried out this transformation under base-free conditions using a well-defined SCS indenediide Pd complex.²⁰ Moreover, in all cases, DMSO is employed as the solvent. We resonated that PhenCarPhos may be a better ligand, as the carbazolyl unit will play the role of a basic residue. Therefore, we elevated our library of phosphines for the coupling of *N*-benzyl-3-phenylprop-2-yn-1-amine (**4**) in the presence of CO₂ (1 atm) in a water media using 0.5 mol% Pd(OAc)₂ (Scheme 2, green). No reaction occurred in the absence of phosphine, while a low yield of 36% was obtained with PPh₃. Interestingly, a better yield of 48% was obtained with PhenCarPhos. Chasing the best ligand for this carboxylation-cyclization reaction, we next evaluated the effect of modifications on the PhenCarPhos scaffold. The phosphine-ester hybrid ligands **3a**, **3c-e** exhibited higher catalytic activities for the formation of **5a** than the parent phosphine. The best modification was with *n*-butyl acrylate or benzyl acrylate. Reactions performed with phosphine-amide hybrid ligands **3f** and **3g** were less performant. Then, we demonstrate that there the incorporation of Cl substituent on *N*-aryl group at the *para*-position of PPh₂ group slightly increased the yield of **5a** (52% with **3i** or **3j**), while the introduction of CF₃ group has a deleterious effect (42% with **3k**). Next, we studied the effect of the heterocycle; the substitution of carbazolyl by its 3,6-di-*tert*-butyl congener did not a significantly impact. However, the installation of the 2-phenylindolyl group improves the catalytic performance, as with phosphine **1f**, oxazolidinone **5a** was isolated in 66% yield. Finally, a spectacular catalytic property's upgrading was observed through the C–H bond alkylation of **1f** with *n*-butyl acrylate, as phosphine-ester hybrid ligand **3m** gives **5a** in 91% yield.

As the upgrading of carbazolyl-phosphines through Rh(I)-catalyzed C–H bond alkylation morphs moderate active ligand into very active bifunctional phosphine in Pd-catalyzed carboxylation-cyclization reaction, we also investigate this strategy in Pd-catalyzed 3-component carboxylation-cyclization-cross-coupling reaction, which was initially developed by Nevado and co-workers using well-defined [PdCl₂(dppf)] catalyst.²¹ This reaction prepares functionalized oxazolidinones from CO₂, propargylamines, and aryl iodides. Propargylamine **4a**, iodoanisole(**6a**) in the presence of *t*-BuONa (1.5 equiv) and Pd(OAc)₂ (0.5 mol%) in DMSO at 60 °C were chosen as standard conditions to evaluate (alkylated) carbazolyl-phosphines (Scheme 2, blue). Again, PhenCarPhos outperformed PPh₃. Delving into the screening of the effect post-modification of PhenCarPhos and then scaffold revealed that the best ligand for this 3-component reaction should hold an *N*-(2-(diisopropylamino)ethyl), a carbazolyl and a chloro groups. Indeed, the phosphine **3h**, specifically designed for this reaction, allowed to isolate **7a** in 77% yield.



Scheme 2. Catalytic Activities of Modified Phosphines in (1) Pd-Catalyzed Carboxylation-Cyclization of Propargylamine (**4a**) with CO₂ & (2) Pd-Catalyzed 3-Component Carboxylation-Cyclization-Cross-Coupling Reaction

With the optimized ligand in hand, we explored the scope of aryl iodides under these conditions (Scheme 2). Reactions with aryl iodide bearing electron-donating or withdrawing groups give the corresponding oxazolidinones **7b-e** in good to excellent yields. However, the reaction with bromobenzene or chlorobenzene was unsuccessful, leading only to the formation of **5a**.



Scheme 3. Scope of Pd-catalyzed 3-Component Carboxylation-Cyclization-Cross-Coupling Reaction using **3m**

In summary, we reported the first example of the C–H bond functionalization of carbazolyl-derived phosphines (PhenCarPhos). This C–H bond alkylation using activated alkenes occurs at the C1-position of the carbazolyl ring through P^{III}-assisted C–H bond cleavage using [RhCl(COD)]₂. This direct approach paves the way to quickly preparing a library of new phosphine hybrid ligands. Some of them have outperformed their parent ones in Pd-catalyzed CO₂-fixations reactions to prepare oxazolidinones from alkynes and (aryl iodides). Together these results suggest that a better solubility might explain

the upgrading of catalytic performances after incorporating an ester group. Besides, the introduction of an amino group might participate in the stabilization of active Pd catalytic species or interact with CO₂. Another explanation could be that introducing an alkyl group on the carbazole could prevent the cyclometallation with palladium like the *i*-Pr group in the XPhos ligand. This late-stage functionalization of phosphines will help to design new phosphines to discover novel reactivity, especially for CO₂-fixation reactions.

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