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Rh(I)-Catalyzed P(III)-Directed C–H Bond Alkylation: Design of Multifunctional Phosphines for Carboxylation of Aryl Bromides with Carbon Dioxide

Zhuan Zhang,^[a] Thierry Roisnel,^[a] Pierre H. Dixneuf,^[a] and Jean-François Soulé*^[a]

Abstract: We report herein the C–H bond alkylation with alkenes of biarylphosphines at *ortho*-position(s) using rhodium(I) catalysis providing a straightforward access to a large library of multifunctionalized phosphines. Some of these modified ligands have outperformed commercially available phosphines in Pd-catalyzed carboxylation of aryl bromides with carbon dioxide in the presence of a photoredox catalyst.

In transition-metal catalysis, the discovery of novel reactivities and the tuning of chemo- or regioselectivity often relies on the ligand design.^[1] The quest to find highly effective phosphines remains an intensive research topic, as illustrated by the recent reports describing the catalytic performance of biarylphosphines in cross-coupling couplings,^[2] Lipshutz's phosphine for reaction in water,^[3] Beller's hybrid pyridine-phosphine for carbonylation reactions,^[4] or pincer ligands for mild hydrogenation reactions (Figure 1a).^[5] Besides the steric and electronic factor modulations, the presence of a peripheral functional group is responsible for the high catalytic performance owing to hemilabile behaviors,^[6] or metal-ligand cooperation.^[7] This strategy has been recently applied for the reduction of CO₂ using metal catalysts with nitrogen-based ligands bearing a functional group (amine, amide, ether, imidazolium, phenol, or thiourea) able to activate the CO₂ or to stabilize intermediates *via* secondary coordination sphere interactions.^[8] However, the preparation of phosphines with pendant functional groups remains challenging owing to their synthetic schemes, which rely on multi-steps synthesis with polar reagents (*i.e.*, Grignard or organolithium).

Late-stage diversification, *via* a regioselective C–H bond functionalization of phosphorus compounds has recently emerged as a suitable alternative to prepare new phosphines.^[9] However, in most of the cases, phosphorus atom has to be oxidized to act as a P(V) directing group.^[10] The use of P(III) as a directing group is highly desirable to avoid the phosphorus protection-deprotection sequence (Figure 1c). In 2014, Clark *et al.* demonstrated that P(III) could act as a directing group in Ir(I)-catalyzed C–H bond borylation of JohnPhos derivatives.^[11] In 2019, Takaya's and Shi's groups have independently reported the *ortho*-borylation of triarylphosphines using Ru(II) or Rh(I) catalysis.^[12] In 2017, Shi's group reported the Rh(I)-catalyzed C–H bond arylation of biarylphosphines at *ortho*-position, offering

efficient access to triarylphosphines.^[13] While useful in the tuning of electronic and steric properties of biarylphosphines, this method did not allow yet the preparation of phosphines bearing flexible cooperative ligand(s). The same group also reported the hydroarylation of activated olefins with indoles using P(III) as directing group but did not attend to alkylate biaryl phosphine.^[14]

We herein develop a method to incorporate functional group(s) to phosphine ligands using Rh(I)-catalyzed C–H bond alkylation(s) with functional alkenes (Figure 1d). We report a fast preparation of a library of phosphines bearing cooperative site(s). We also showed the benefit of this multifunctional phosphines to build efficient palladium catalyst for Iwasawa's carboxylation of aryl bromides with CO₂.^[15]

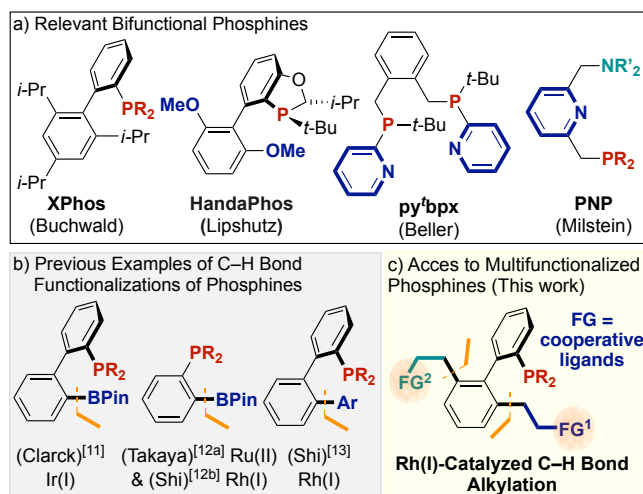


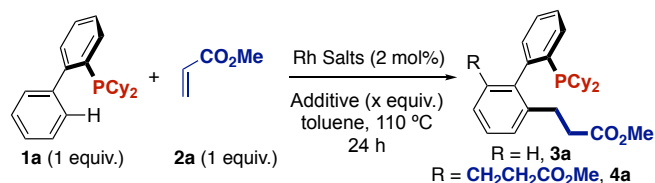
Figure 1. Multifunctional Phosphines and Their Modifications

To explore the C–H bond alkylation of phosphines, we choose cyclohexyl JohnPhos (**1a**) and methylacrylate (**2a**) as the model substrates (Table 1). Among the different Rh(I) catalysts, the best conversion is obtained using [Rh(OAc)(COD)]₂. Notably using a stoichiometric ratio between **1a** and **2a**, only the mon-alkylated phosphine **3a** is observed (**3a/4a** ratio > 95:5) (entries 1-5).^{[16],[17]} Under basic conditions (AcOK), a full conversion is observed but with a lower **3a/4a** ratio of 85:15; while in the presence of 1 equivalent of AcOH, **3a** is isolated in 96% yield (entries 6 and 7). The use of more congested acid, such as PivOH, gives a similar yield (entry 8). Under basic conditions and in the presence of 3 equiv. of **2a** with 4 mol% of catalyst, the dialkylated phosphine **4a** is formed with 55% selectivity (entry 9). When the reaction is performed at 160 °C, a higher selectivity of 90% is observed leading to the formation of **4a** in 85% isolated yield (entry 10).

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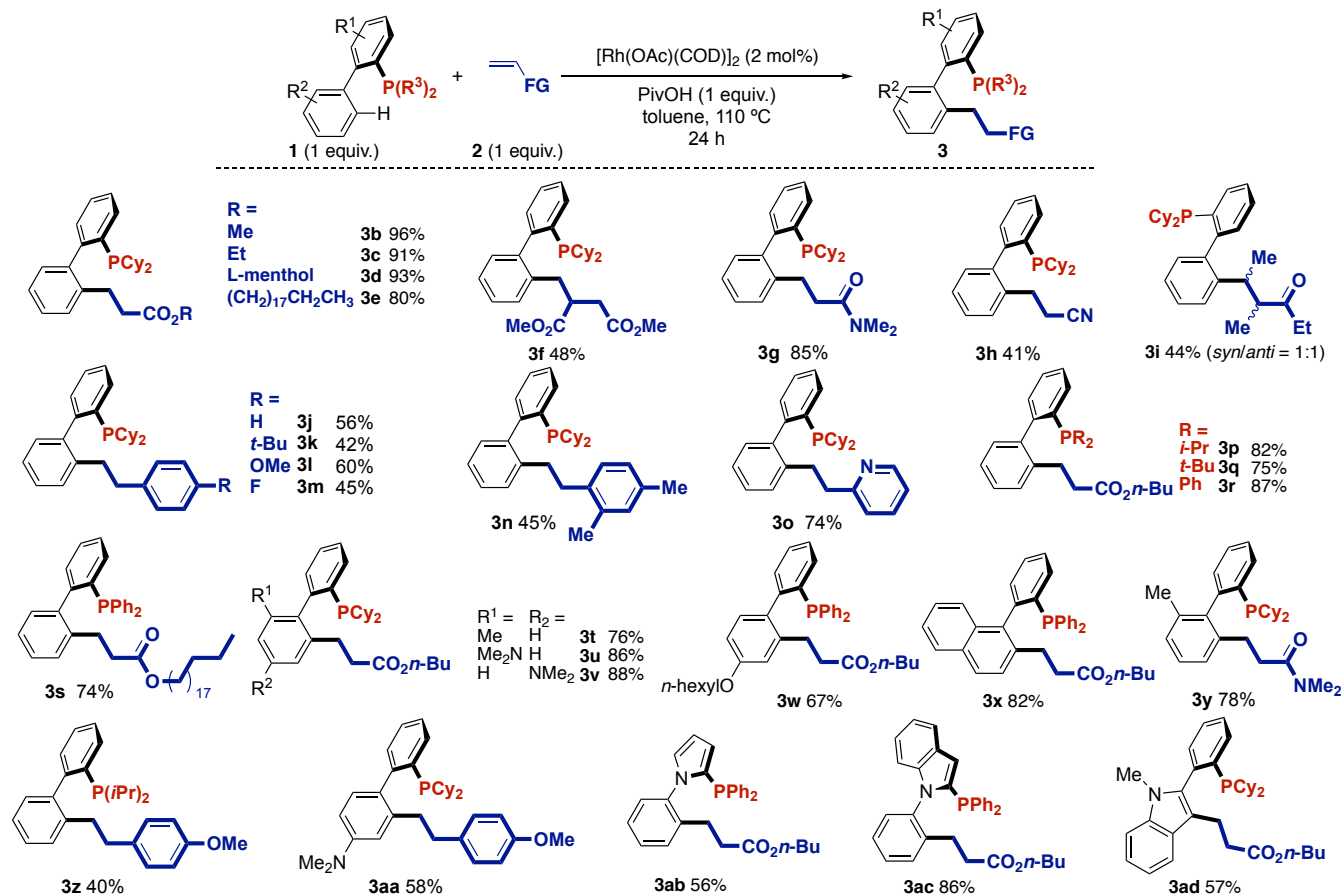
Table 1. Optimization of Rh(I)-Catalyzed C–H Bond Mono-Alkylation and Di-Alkylation of JohnPhos (**1a**) with Methylacrylate (**2a**)

Entry	Rh Salts	Additive	Conv. (%) ^[a]	3a/4a ^[a]
1	[Cp*RhCl ₂] ₂	–	18	>95:5
2	[RhCl(COD)] ₂	–	31	>95:5
3	RhCl(PPh ₃) ₃	–	28	>95:5
4	[Rh(OAc)(COD)] ₂	–	56	>95:5
5	[Rh(OAc)(NBE)] ₂	–	52	>95:5
6	[Rh(OAc)(COD)] ₂	KOAc (0.25)	100	>85:15
7	[Rh(OAc)(COD)] ₂	AcOH (1)	100	>95:5 (96%) ^[b]
8	[Rh(OAc)(COD)] ₂	PivOH (1)	100	>95:5 (91%) ^[b]
9 ^[c]	[Rh(OAc)(COD)] ₂	KOAc (0.50)	100	>45:55
10 ^[c,d]	[Rh(OAc)(COD)] ₂	AcOH (0.50)	100	>10:90 (85%) ^[e]

[a] Determined by ³¹P NMR using PPh₃ as internal standard. [b] Isolated yield of **3a**. [c] Using 4 mol% of [Rh(OAc)(COD)]₂ and 3 equiv. of **2a** over 48 h. [d] At 160 °C. [e] Isolated yield of **4a**.

With the optimal conditions, we move on the scope of the reaction (Scheme 1). First methyl, ethyl, and L-menthyl acrylates are efficiently employed as alkyl sources to afford the JohnPhos congeners **3b–3d** with a pendant ester group in excellent yields. Interestingly, from eicosyl acrylate, a long aliphatic chain (C₂₀H₃₈)

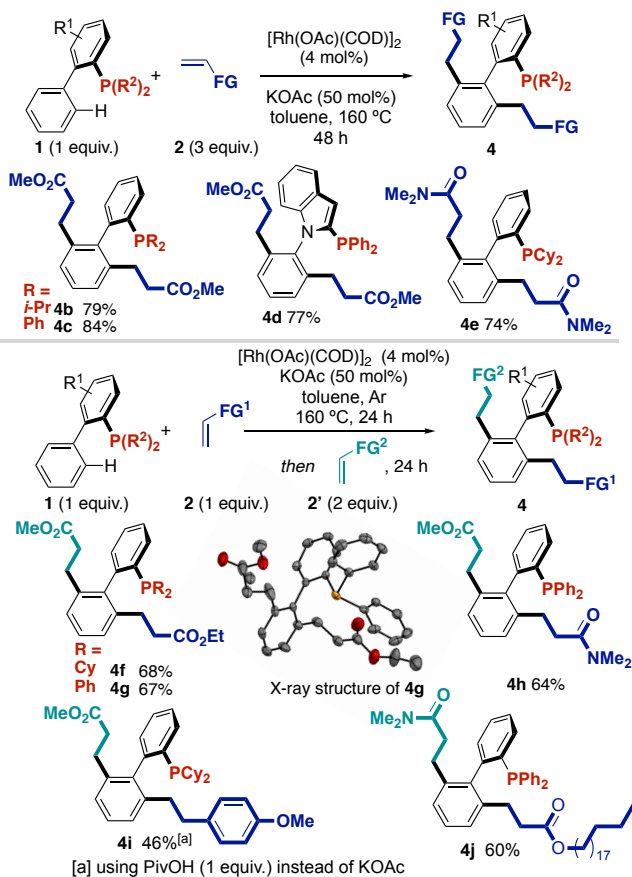
is introduced on phosphine scaffold leading to the potential surfactant phosphine **3e** in 80% yield. Dimethyl itaconate is also successfully coupled to give the bifunctional phosphine-diester **3f** in 48% yield. We also prepared phosphines bearing dimethylacrylamide (**3g**) or nitrile (**3h**) group in good yields from *N,N*-dimethylacrylamide, acrylonitrile. **1a** also undergoes C–H bond alkylation with an internal 1,2-disubstituted alkene, such as 4-methylhex-4-en-3-one, to afford *ortho*-tertiary alkyl-substituted cyclohexyl JohnPhos **3i** in 44% yield as an equimolar mixture of *syn/anti* products. Styrene derivatives also react with **1a** to provide the phosphines bearing a peripheral arene ring **3j–3n** in 42–60% yields. The incorporation of pyridine ring into phosphine scaffold often gives a rise of the catalytic activity in carbonylation reactions^[18] owing to metal-ligand cooperativity.^[19] The coupling of **1a** with 2-vinylpyridine affords the hybrid phosphine-pyridine ligand **3o** in 74% yield. Other substituents of the phosphorus atom, such as *i*-propyl, *t*-butyl or phenyl groups are also tolerated allowing the preparation of phosphine–ester ligands **3p–3r** in 75%–87% yields. Notably, the lowest yield is observed when the P atom is substituted by the more steric hindered *tert*-butyl group. Biarylphosphines substituted at *ortho*' or *para*' position by methyl, dimethylamino or hexyloxy group nicely react with **2b** to give **3t–3w** in good yields. More congested C(naphthyl)–H bond is also alkylated to give **3x** in 82% yield. The reaction between cyclohexyl MePhos and acrylamide afforded **3y**, an analog of XPhos bearing an amide group, in 78% yield.

**Scheme 1.** Scope of Rh(I)-Catalyzed 2'-Alkylation of Biarylphosphines with Alkenes

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The diversification of biarylphosphines with less reactive 1-methoxy-4-vinylbenzene gives **3z** and **3aa** in good yields. It is noteworthy that *N*-phenylpyrrole (cataCXium®P) and *N*-phenylindole (cataCXium®Pin)-based phosphines—developed by Beller's group for cross-coupling reactions with less reactive aryl chlorides—^[2c, 2d, 4b] are alkylated on the phenyl ring to provide the hemilabile phosphine-esters **3ab** and **3ac** in 56% and 86% yield, respectively. CM-Phos developed by Kwong for cross-coupling reactions with aryl mesylates,^[2e] undergoes C3–H bond alkylation of indolyl unit with **2b** to afford the CM-Phos congener **3ad** with pendant ester in 57% yield.

We next explore the one-step synthesis of XPhos congeners bearing two functional groups *via* double alkylations of JohnPhos at 2' and 6' positions (Scheme 2, up). The dialkylation reaction is more sensitive to the steric hindrance of the P-substituent as *t*-butyl JohnPhos did not afford the second alkylation, while the reaction with *i*-propyl, phenyl JohnPhos and cataCXium®P afford the difunctionalized XPhos analogs **4b–4d** in 77–84% yields. The diamide-phosphine **4e** is obtained from *N,N*-dimethylacrylamide.



Scheme 2. Scope of Rh(I)-Catalyzed Twofold 2',6'-Dialkylation of Biarylphosphines

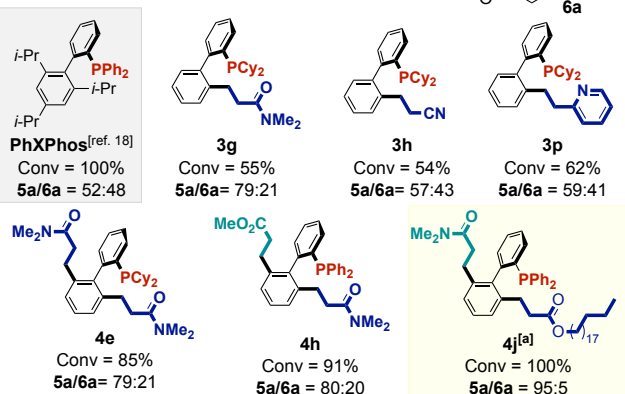
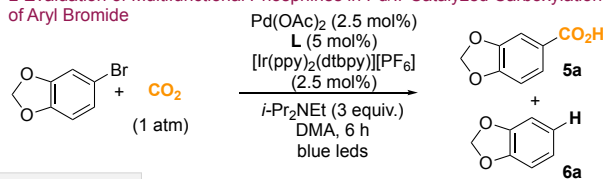
Then, iterative one-pot reactions with two different alkenes are carried out by the introduction of a second alkene after 24 h (Scheme 2, bottom). The couplings of cyclohexyl or phenyl JohnPhos with two different acrylate esters afforded the dissymmetrical diester-phosphine **4f** and **4g** in good yields. The

structure of **4g** was confirmed by X-ray diffraction analysis.^[20] Unprecedented phosphine **4h**—which contains multiple hemilabile groups—is prepared in 64% yield *via* iterative two-fold C–H bond alkylations using firstly acrylamide followed by methylacrylate. The multifunctional phosphine **4i** is obtained by the alkylation of **1a** with 4-methoxystyrene and methylacrylate. To produce long chain bifunctional phosphine for catalyst to operate in water, the multifunctional phosphine **4j** is prepared using eicosyl acrylate and acrylamide as both alkene sources.

We further investigated the catalytic activity of these multifunctional phosphines in Pd-catalyzed carboxylation of aryl bromides using CO₂ as a C1 source (Figure 2). Iwasawa and co-workers have reported an elegant protocol for the Pd-catalyzed carboxylation of aryl bromides in the presence of a photoredox catalyst.^[15] However, 3 equivalents of Cs₂CO₃ as base are required to decrease the formation of the hydrogenated product. We could expect that using our multifunctional phosphine bearing a basic unit, the reaction might be performed in absence of a base. Moreover, further interactions between the functional group on the phosphine with CO₂ can provide higher catalytic activity.^[8a–d] Therefore, we evaluated the potential of JohnPhos and XPhos congeners in the carboxylation of 5-bromo-1,3-benzodioxole, albeit in absence of Cs₂CO₃ (Figure 2, top). Interestingly, the Johnphos ligands bearing an amide (**3g**), cyano (**3h**) or pyridine group (**3p**) associated to Pd(OAc)₂ give better selectivities in favor of the formation of the carboxylated product **5a** than the commercially available PhXPhos, albeit in lower conversions. Notably, the phosphine-amide **3g** furnishes the best selectivity (**5a/5a'** = 79:21).^[21] The phosphine-diamide **4e** gives good conversion and selectivity (85%, 79:21), as the formation of the Pd-cyclometalated phosphine complex is avoided owing to the both phosphine *ortho*'-positions are substituted.^[22] The hybrid ligand **4h** containing an ester and an amide group affords a slightly better conversion with similar **5a** selectivity (91%, 80:20). There are many advantages to perform transition metal-catalyzed reactions in water media (e.g., products separation, lower catalyst loading, selectivity improvement, ...) proved that suitable ligands have to be designed.^[23] Therefore, we decided to carry out this carboxylation in toluene/water using the surfactant containing phosphine **4j**, which bears an amide group. Under these conditions, **5a** was obtained in 95:5 selectivity with a full conversion and we were able to decrease the catalyst loading to 0.5 mol%. The higher catalytic activity observed with **4j** can be attributed to a unique CO₂-responsive surfactant behavior.^[24] The interfacial tension (IFT) of a biphasic system in water/toluene in the presence of CO₂; while with **3e** (which does not have the amide group) the IFT varies only from 10.4 to 7.9 mN/M and almost no variation is observed without phosphine (Figure 2, middle). Using the most active bifunctional phosphine **4f** with low Pd catalyst loading in water media, the carboxylic acids **5a–5e** are isolated in high yields without the use of Cs₂CO₃ as an additive by simple extraction (Figure 2, bottom)

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■ Evaluation of Multifunctional Phosphines in Pd/Ir-Catalyzed Carboxylation of Aryl Bromide



[a] Using Pd(OAc)₂ (0.5 mol%), 4j (1 mol%) in toluene/water (1:1)

■ Interfacial Tension of Water/Toluene and Carbonated Water/Toluene in the Presence of Phosphines (conc. 5 mg/mL) at 25 °C

Entry	Ligand	IFT water/toluene (mN/M)	IFT CO ₂ -water/toluene (mN/M)
1	–	10.5	9.5
3	3e	10.4	7.9
4	4j	8.7	3.9

Pendant Drop image of 4j in CO₂-Water/Toluene

■ Scope of Pd-Catalyzed Carboxylation of ArBr in Water Media using the Surfactant Phosphine 4j

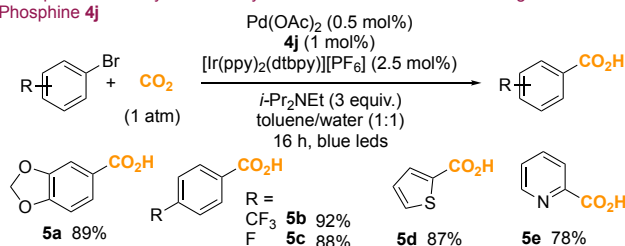


Figure 2. Application of (Multi)-Functionalized Phosphines in Pd-Catalyzed Carboxylation of Aryl Bromides in the Presence of Photoredox Catalyst.

In summary, we have developed a new method to quickly functionalize biarylphosphines using Rh(I)-catalyzed C–H bond alkylation directed by P(III) atom with alkenes. We can control the mono- or di-selectivity, as well as to perform one-pot dialkylation allowing to the formation of multi-functionalized phosphines. This technology has several advantages: *i*) to allow the one-step diversifications of commercially available phosphines (40 examples), *ii*) to exhibit high functional group tolerance, *iii*) to modulate the catalytic activity of phosphines *via* secondary coordination sphere interactions, *iv*) to modify the physical properties (i.e., solubility, hydrophilicity) of the ligands. Thanks to the late-stage diversification, a surfactant phosphine with amide group exhibiting high catalytic activity in carboxylation reaction was prepared. In the near future, the easy preparation of a broader library of phosphines bearing multiple functional groups should create new catalysts to transform CO₂ *via* C–C bond formation.

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Keywords: Phosphine • Rhodium • C–H Bond Functionalization • Carbon Dioxide • Alkylation

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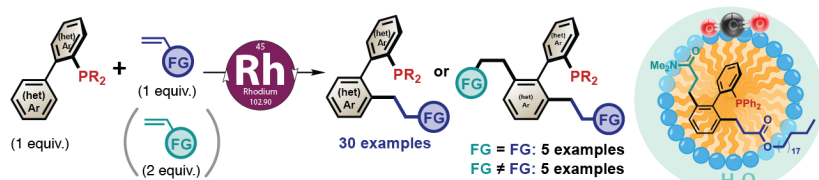
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Layout 1:

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Multifunctional phosphines –bearing flexible pendant co-catalyst(s) (e.g., ester, amide, pyridine, aryl, cyano, etc.)– are synthesized *via* Rh(I)-catalyzed C–H bond alkylation of biarylphosphines using functionalized alkenes (40 examples). Unprecedented carbon dioxide-responsive surfactant is prepared and exhibited high catalytic activity in Pd-catalyzed carboxylation of aryl bromides in aqueous media.

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 Rh(I)-Catalyzed P(III)-Directed C–H Bond Alkylation: Design of Multifunctional Phosphines for Carboxylation of Aryl Bromides with Carbon Dioxide