Carboxylic–Phosphoric Anhydrides as Direct Electrophiles for Decarbonylative Hirao Cross-Coupling of Carboxylic Acids: DFT Investigation of Mechanistic Pathway

Chengwei Liu,*[a,d]† Yang-Yang Xing,[b]† Tongliang Zhou,[d] Tieqiao Chen,*[c] Xin Hong,*[e,f,g] and Michal Szostak*[d]

Dedicated to Professor Kendall N. Houk in celebration of his 80th birthday

[a] Prof. Dr. C. Liu
Department of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444 (China), E-mail: chengwei_liu@shu.edu.cn

[b] Dr. Y.-Y. Xing
College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Shandong Normal University, Jinan 250014 (China)

[c] Prof. Dr. T. Chen
Hainan Provincial Key Lab of Fine Chem, Hainan University, Haikou, 570228 (China)
E-mail: chentieqiao@hnu.edu.cn

[d] Dr. C. Liu, T. Zhou, Prof. Dr. M. Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102 (United States)
E-mail: michal.szostak@rutgers.edu
Homepage: http://chemistry.rutgers.edu/szostak/

[e] Prof. Dr. X. Hong
Center of Chemistry for Frontier Technologies, Department of Chemistry, State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027 (China)
E-mail: hxchem@zju.edu.cn

[f] Prof. Dr. X. Hong
Beijing National Laboratory for Molecular Sciences, Zhongguancun North First Street NO. 2, Beijing 100190 (China)

[g] Prof. Dr. X. Hong
Key Laboratory of Precise Synthesis of Functional Molecules of Zhejiang Province, School of Science, Westlake University, 18 Shilongshan Road, Hangzhou 310024, Zhejiang Province (China)

† These authors contributed equally to this work.

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Abstract: *In this anniversary issue, we present DFT study of the mechanism of decarbonylative Hirao cross-coupling of carboxylic–phosphoric anhydrides to afford aryl phosphonates. Traditionally, the direct activation of carboxylic acids to participate in decarbonylative couplings is performed in the presence of carboxylic acid anhydride activators. We discovered that direct dehydrogenative decarbonylative phosphorylation of benzoic acid can be performed in high yield via dehydrogenative and decarbonylative coupling in the presence of phosphite as dual activating and nucleophilic reagent, enabling direct decarbonylative phosphorylation. Control studies demonstrated that carboxylic-phosphoric anhydride (acyl phosphate) is an intermediate in this process. DFT studies were conducted to gain insight into this decarbonylative process and compare the selectivity of C–O and P–O bond activations. Considering the utility of ubiquitous carboxylic acids, this alternative activation pathway may find applications in decarbonylative coupling of carboxylic acids for the synthesis of valuable molecules in organic synthesis.*

The 2010 Nobel Prize winning cross-coupling of aryl halides have become cornerstone of organic synthesis, providing key mechanistic background for the activation of other classes of electrophiles (Figure 1A).[1,2] In this context, many different nucleophilic and electrophilic cross-coupling partners have been invented in the last decade, expanding the cross-coupling toolbox to nonclassical cross-coupling partners.[3,4] In particular, decarbonylative cross-coupling of carboxylic acids have received major attention owing to the ubiquity of carboxylic acids in organic synthesis, natural products and pharmaceuticals and the potential to access the common Ar–[M] intermediates.[5] To achieve activation of carboxylic acids for decarbonylative pathway, a range of carboxylic acid derivatives, such as acyl fluorides,[6] acyl chlorides,[7] anhydrides,[8] esters,[9] thioesters,[10] and amides,[11] have been employed as electrophiles in cross-coupling reactions for the construction of new C–C and C–X bonds (Figure 1B). The use of carboxylic acids as electrophiles after CO deinsertion offers a major advantage since carboxylic acids are highly stable, non-toxic and orthogonal to aryl halides.[12] Due to these beneficial features, carboxylic acids have been referred to as ideal substrates for organic synthesis.[13] Perhaps most importantly, carboxylic acids are commonly present in complex pharmaceuticals, which allows for the direct late-stage-functionalization strategies not available from aryl halides.[14]

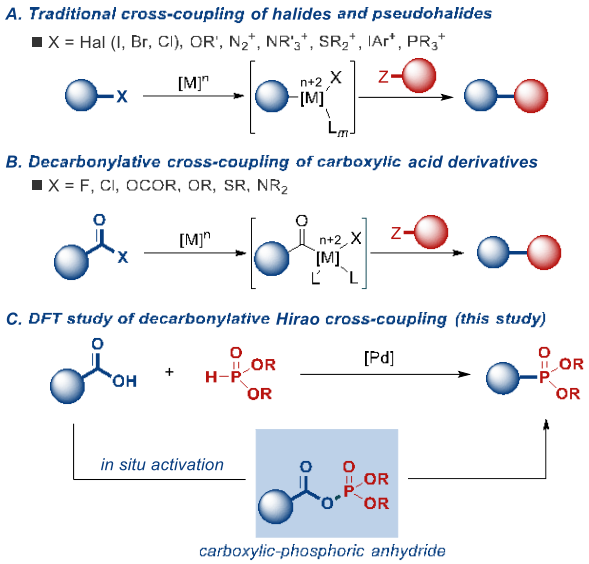


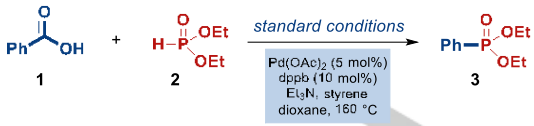
Figure 1. (A) Cross-coupling of aryl halides. (B) Decarbonylative cross-coupling of carboxylic acid derivatives. (C) This study: DFT mechanism of decarbonylative Hirao cross-coupling of carboxylic–phosphoric anhydrides.

Traditionally, direct cross-coupling of carboxylic acids requires activation of the carboxylic acid with carboxylic acid anhydride activators. Mechanistically, in order to achieve decarbonylative coupling, the Ar–C(O)–OH bond of carboxylic acid must undergo oxidative addition to give acyl–metal intermediate, followed by decarbonylation.[15] The direct insertion into the C–OH bond energetically unfavorable with additional formation of carboxylate; thus, the most common strategy is to convert carboxylic acids in a separate step into activated carboxylic acid derivatives, such as acyl fluorides, chlorides, esters or amides.[6–11] Alternatively, in situ activation has been deployed. This mode of activation is most successful with unsymmetrical carboxylic acid anhydrides, where the combination of nucleophilic acylation and decarbonylative coupling, permits to access Ar electrophiles under Pd(0)/(II), Ni(0)/(II) and Rh(I)/(III) catalytic cycles.[8]

Herein, we present DFT study of the mechanism of decarbonylative Hirao cross-coupling of carboxylic–phosphoric anhydrides to afford aryl phosphonates (Figure 1C). We serendipitously discovered that direct dehydrogenative decarbonylative phosphorylation of benzoic acid can be performed in high yield via dehydrogenative and decarbonylative coupling in the presence of phosphite as dual activating and nucleophilic reagent, enabling direct decarbonylative phosphorylation. Control studies demonstrated that carboxylic–phosphoric anhydride (acyl phosphate) is an intermediate in this process. DFT studies were conducted to gain insight into this decarbonylative process and compare the selectivity of C–O and P–O bond activations. Considering the utility of ubiquitous carboxylic acids, this alternative activation pathway may find applications in decarbonylative coupling of carboxylic acids for the synthesis of valuable molecules in organic synthesis.

First, this decarbonylative phosphorylation was examined using benzoic acid (**1**) and diethyl phosphite (**2**) (Table 1). We identified the combination of $Pd(OAc)_2$ (5 mol%), dppb (5 mol%) in the presence of Et_3N (2.0 equiv) and styrene (2.0 equiv) in dioxane at 160 °C as the optimal system to deliver the desired phenyl phosphonate (**3**) in 97% yield (Table 1, entry 1).[16,17]

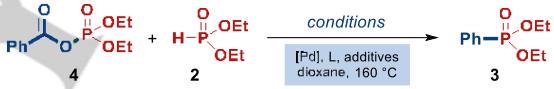
Table 1. Optimization Experiments.[a]



Entry	Change from the standard conditions	Yield[b] [%]
1	none	>98
2	no $Pd(OAc)_2$	<2
3	no dppb	<2
4	no Et_3N, no styrene, **2** (3.0 equiv)	77
5	no Et_3N, no styrene, **2** (2.0 equiv)	52
6	**2** (1.0 equiv) instead of **2** (2.0 equiv)	31
7	**2** (1.2 equiv) instead of **2** (2.0 equiv)	54
8	**2** (1.5 equiv) instead of **2** (2.0 equiv)	77
9	styrene (20 mol%) instead of styrene (2.0 equiv)	80
10	4-MeO-styrene instead of styrene	76
11	4-CF_3-styrene instead of styrene	40
12	stilbene instead of styrene	38
13	norbornene instead of styrene	35
14	Na_2CO_3, K_2CO_3, K_3PO_4 instead of Et_3N	26-41
15	120-140 °C instead of 160 °C	25-56

[a]Conditions: $PhCO_2H$ (**1**) (1.0 equiv), $HP(O)P(OEt)_2$ (**2**) (2 equiv), $Pd(OAc)_2$ (5 mol%), dppb (10 mol%), Et_3N (2.0 equiv), styrene (2.0 equiv), dioxane, 160 °C, 15 h. [b]Determined by ^1H NMR and/or GC.

Table 2. Control Experiments.[a]



Entry	[Pd]	Ligand	Base	Additive	Yield[b] [%]
1	$Pd(OAc)_2$	-	-	-	<2
2	$Pd(OAc)_2$	dppb	-	-	89
3	$Pd(OAc)_2$	-	Et_3N	-	17
4	$Pd(OAc)_2$	dppb	Et_3N	-	76
5	$Pd(OAc)_2$	dppb	Et_3N	styrene	98
6[c]	$Pd(OAc)_2$	dppb	Et_3N	styrene	<2

[a]Conditions: $PhCO_2P(O)(OEt)_2$ (**4**) (1.0 equiv), $HP(O)P(OEt)_2$ (**2**) (1.1 equiv), $Pd(OAc)_2$ (5 mol%), dppb (10 mol%), Et_3N (2.0 equiv), styrene (2.0 equiv), dioxane, 160 °C, 15 h. [b]Determined by ^1H NMR and/or GC. [c]Without **2**.

Control experiments showed that there is no reaction in the absence of Pd source or phosphine ligand (Table 1, entries 2-3). The reaction proceeded in the absence of any additives (only $Pd(OAc)_2$/dppb, 77% yield) ($HP(O)(OEt)_2$, 3 equiv) and 52% yield ($HP(O)(OEt)_2$, 2 equiv) (Table 1, entries 4-5). There was a significant effect of increasing stoichiometry of $HP(O)(OEt)_2$ (31% to 98% yield, from 1.0 to 2.0 equiv) (Table 1, entry 1 and 6-8). Catalytic amount of styrene (20 mol%) was sufficient to improve the yield (Table 1, entry 9 vs. entry 1). Other olefin additives were tested (4-MeO-styrene, 76%; 4-CF_3-styrene, 40%; stilbene, 38%; norbornene, 35%) (Table 1, entries 10-13) and their effect was consistent with coordination to Pd to facilitate reductive elimination.[18] Olefin additives were not required, but in general, the reactions were cleaner. Et_3N was also not required (Table 1, entries 4-5), but the reactions were cleaner in its presence. Inorganic bases (Na_2CO_3, 41%; K_2CO_3, 26%; K_3PO_4, 33%) were ineffective (Table 1, entry 14). The reaction proceeded at lower temperatures with modest yield (140 °C, 56%, 120 °C, 25%) (Table 1, entry 15), and no reaction was observed at 100 °C (not

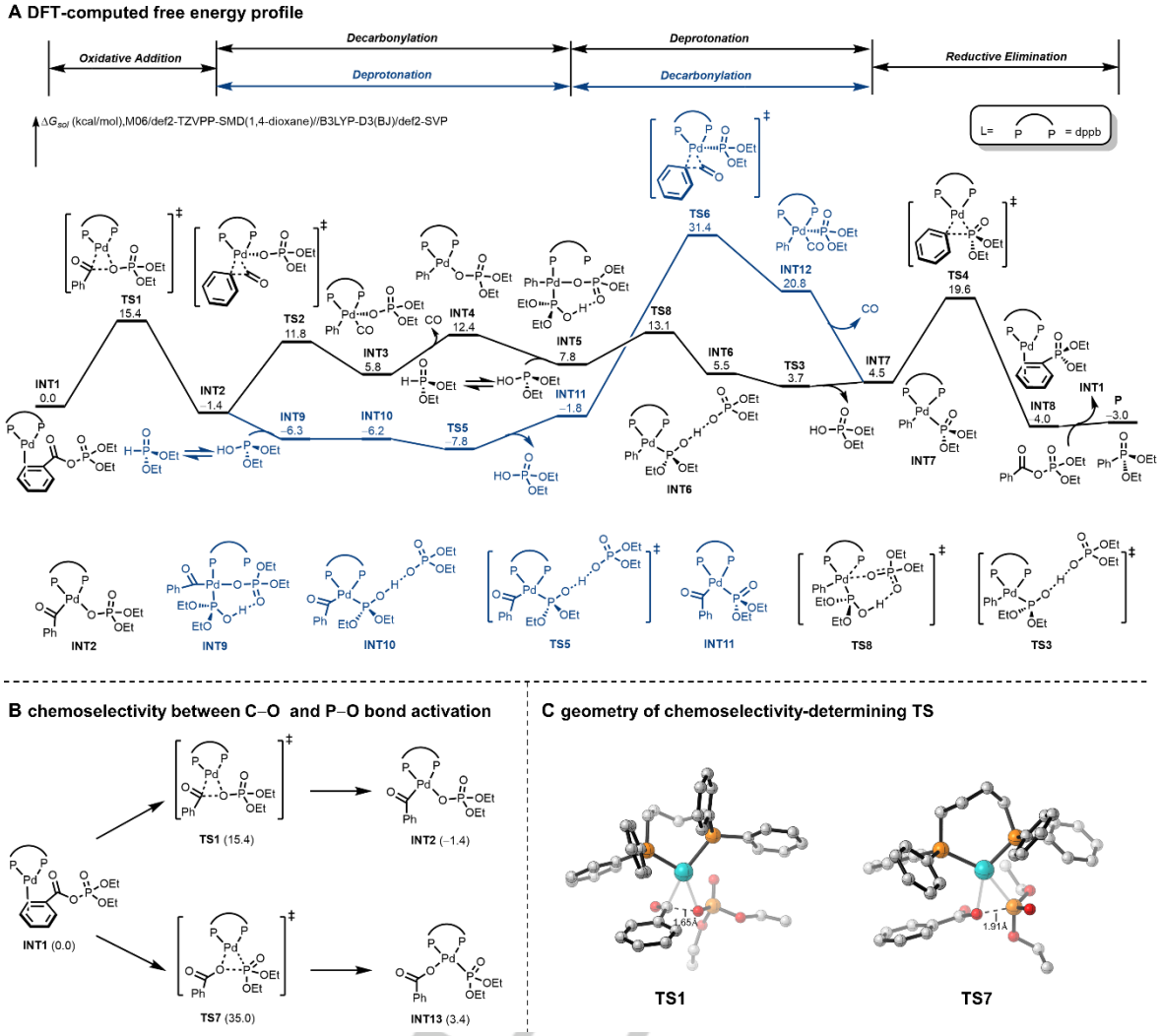


Figure 2. Computational results on the mechanism and chemoselectivity of Pd-catalyzed dehydrogenative decarbonylative coupling of carboxylic acids.

shown). Overall, these optimization studies were consistent with dehydrogenative O–H/H–P coupling to give benzoic–phosphoric anhydride as a direct electrophile,[20] followed by decarbonylative coupling. To validate this hypothesis, benzoic–phosphoric anhydride (**4**) was synthesized and subjected to control reaction conditions (Table 2). As expected, we found that although no reaction was observed using palladium catalyst (Table 2, entry 1), efficient decarbonylation took place in the presence of Pd/dppb (Table 2, entry 2), establishing benzoic–phosphoric anhydrides (acyl phosphates) as a new class of electrophiles for decarbonylative cross-coupling. Further control experiments demonstrated that the combination of Et_3N and styrene additives (Table 2, entries 3-5) is ideal for the coupling, in agreement with the previous optimization studies (Table 1). As expected, external phosphite must be used to achieve decarbonylative coupling (Table 2, entry 6). The dehydrogenation step is well-established by O–H/H–P coupling.[19,20] Control experiments demonstrated that palladium and phosphine are needed for the formation of the mixed anhydride (not shown). At this stage, scope studies have not been performed.

To gain insight into the mechanism of this intriguing process, computational studies were performed (Figure 2). It is well-established that computational approaches provide a powerful tool for understanding the mechanisms in organometallic catalysis. The density functional theory (DFT)-calculated free energy profile of the operative reaction mechanism of Pd-catalyzed dehydrogenative decarbonylative cross coupling of carboxylic acids is shown in Figure 4A. From the (dppb)Pd^0(substrate) active complex **INT1**, the oxidative addition via **TS1** is facile and reversible, which cleaves the C–O bond and generates the acylpalladium(II) intermediate **INT2**. Decarbonylation through **TS2** leads to the arylpalladium(II) species **INT3**, and **INT3** undergoes CO dissociation to produce **INT4**. Subsequently, the phosphite isomerization from $HP(O)(OEt)_2$ to $HOP(OEt)_2$ is necessary to transfer the hydridic hydrogen to the protic hydrogen, and the isomerized $HOP(OEt)_2$ coordinates to **INT4** to give the intermediate **INT5**. **INT5** further isomerizes to **INT6**, which is essentially a coordination change of palladium. Subsequent deprotonation step via **TS3** leads to the pre-reductive elimination intermediate **INT7**, and the reductive elimination through **TS4** generates the product-coordinated complex **INT8**. **INT8** eventually liberates the cross-coupling product and regenerates the active palladium(0) species **INT1**. We also investigated the alternative mechanism that reverses the sequence of decarbonylation and deprotonation (blue pathway, Figure 2A). This pathway is unlikely due to the high barrier associated with the decarbonylation step via **TS6**. Based on the DFT-computed free energy profile, the turn-over limiting step is the C–P reductive elimination step via **TS4**.

Our mechanistic model also elucidated the origins of chemoselectivity between C–O and P–O bond activations. Figure 2B elaborates the details of the free energy changes of the competing C–O and P–O bond activations, and Figure 2C shows the optimized geometry of the key bond activation transition states. From **INT1**, the C–O bond activation is facile with a 15.4 kcal/mol, which produces the acylpalladium(II) intermediate **INT2** in equilibrium. In contrast, the P–O bond activation through **TS7** requires a barrier of 35.0 kcal/mol, despite the generated palladium(II) intermediate **INT13** has a reasonable stability (3.4 kcal/mol higher in free energy comparing with **INT1**). These results highlighted the strong chemoselectivity of bond activation of the *in situ* generated C(O)–OR electrophile, which also emphasizes that the rational design of leaving group in anhydride has great potential to expand the scope of transition metal-catalyzed decarbonylative coupling of carboxylic acids.

Several additional points are worth noting: (1) the reaction works at as low temperatures as 120 ºC. However, higher yields are observed at higher temperatures; (2) styrene is not essential for the reaction. The yields are slightly better in the presence of styrene. (3) three-dimensional optimized structures have been drawn out in the supporting information (cf. Figure 2). Our ongoing studies are focused on addressing the effect of π-accepting ligands on CO deinsertion.

In conclusion, we have reported DFT study on the mechanism of Hirao cross-coupling of carboxylic–phosphoric anhydrides. This reaction can be performed in high yield by decarbonylative phosphorylation of benzoic acid. Control studies demonstrated that carboxylic–phosphoric anhydride is an intermediate in this process. DFT studies provided key insights into the mechanism and selectivity of C–O and P–O bond activations. We expect this alternative activation pathway may find applications in decarbonylative coupling of carboxylic acids. Our ongoing studies are focused on investigation the substrate scope of this and related decarbonylative cross-couplings of carboxylic acids and the development of new activation modes of the C–OH bond for decarbonylation.

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Keywords: DFT • decarbonylation • selectivity • cross-coupling • carboxylic acids • dehydrogenation • acyl phosphates

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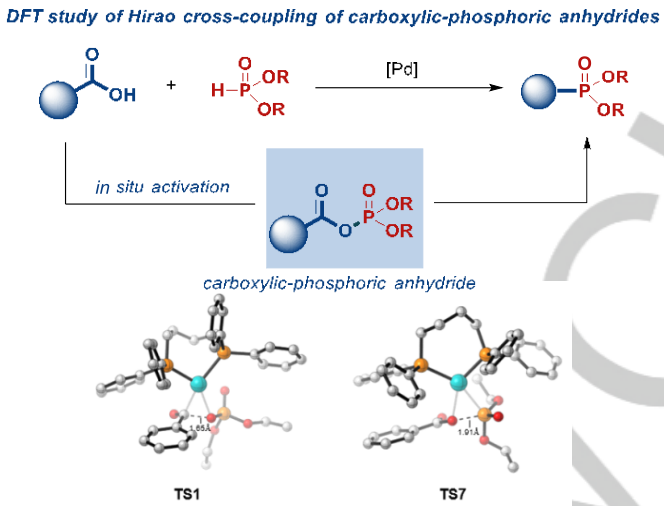

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