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Base-Induced Mechanistic Variation in Palladium-Catalyzed Carbonylation of Aryl Iodides

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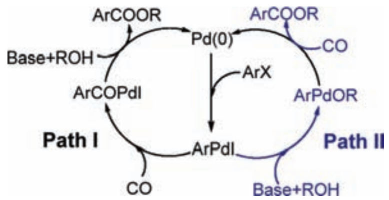
Abstract: A mechanism, which is distinct from the traditional one when sodium alkoxide was used instead of tertiary amines, was proposed for the alkoxycarbonylation of aryl iodides. The catalytic cycle was composed of oxidative addition, subsequent ArPdOR formation, CO insertion to Pd-OR, and final reductive elimination of ArPdCOOR. The kinetic simultaneity of the formation of deiodinated side product from the aryl iodide and aldehyde from corresponding alcohol provided strong evidence for the existence of ArPdOR species. The observation of thioether, as the other competitive product in palladium catalyzed thiocarbonylation of aryl iodides and sodium alkylthiolate, also indicate the possibility of metathesis between ArPdI and sodium alkylthiolate. Preliminary kinetic studies revealed that neither oxidative addition nor reductive elimination was rate limiting. DFT calculation displayed preference for CO insertion into Pd-OR bond. The advantage of this novel mechanism had been demonstrated in the facile alkoxycarbonylation and thiocarbonylation. The ethoxycarbonylation of aryl iodides under room temperature and balloon pressure of CO in the presence of EtONa were examined, and good to high yields were obtained; the *t*-butoxycarbonylation reactions in the presence of *t*-BuONa were achieved, and the alkylthiocarbonylation (including the *t*-butylthiocarbonylation) of aryl iodides in the presence of sodium alkylthiolate were also investigated.

Introduction

Palladium catalyzed alkoxycarbonylation of organic halides is an important method for fine chemical synthesis.[1−9] Previously, many mechanistic studies have used tertiary and secondary amines as bases, and the mechanism is generally accepted to consist of oxidative addition of the aryl halide, CO coordination and insertion, and alcoholysis of the resulted acyl palladium complex (Scheme 1, Path I).[10−16]

Scheme 1. Traditional Mechanism and Postulated Pathway for Alkoxycarbonylation of Aryl Halides



Theoretically, another pathway is possible where the ArPdOR species forms via metathesis from the oxidative addition intermediate ArPdI (Scheme 1, Path II). Milstein postulated the pathway during investigation of the alkoxycarbonylation using organic bases but excluded it finally by the experimental results.[17] To the best of our knowledge, compelling evidence is still demanded for the alternative Path II. Our recent studies toward the Pd-catalyzed alkoxylcarbonylation of aryl iodides

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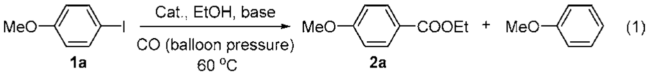
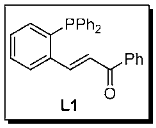
Scheme 2. Product Distribution of Carbonylations of 4-Iodoanisole **1a** Catalyzed by $PdCl_2(MeCN)_2$/**L1** or $PdCl_2(PPh_3)_2$





Cat.1: $PdCl_2(MeCN)_2$ / **L1**
Cat. 2: $PdCl_2(PPh_3)_2$

Cat.	base	**2a**	**anisole**
Cat. 1	NaOEt	83%	16%
	NEt_3	24%	0%
Cat. 2	NaOEt	95%	4%
	NEt_3	8%	0%

with sodium alkoxides as the base revealed a mechanism distinct from Path I and consistent with Path II. Herein, we report our recent results.

Results and Discussion

1. Differences Caused by the Employed Bases (NaOEt vs NEt_3). Organic bases, mostly tertiary amines, are commonly employed in alkoxycarbonylation,[18−20] yet inorganic bases under some conditions display comparable or even better activities in catalytic carbonylations.[21] Studies by Yamamoto[14] and Moser[16] indicate that sodium alkoxides react faster than organic bases. However, to the best of our knowledge, no detailed investigation of the alkoxide bases has been reported yet.

Prompted by our interests in the mechanism of alkoxycarbonylation, we chose ethoxycarbonylation of 4-iodoanisole **1a** as the model and tested the reaction with NEt_3 and EtONa as the base, respectively. $PdCl_2(CH_3CN)_2$/**L1** (**L1** = (*E*)-3-(2-(diphenyl-phosphino)phenyl)-1-phenyl-prop-2-en-1-one) combination was employed as the catalyst.[22,23] In the EtONa system, ethyl 4-methoxybenzoate **2a** was obtained in 83% yield within 60 min, while only 24% of **2a** was detected after 300 min in the NEt_3 system. Notably, in the EtONa system, 16% of anisole was formed as side product from deiodination of **1a** but anisole was not observed in the NEt_3 system (Scheme 2). In $PdCl_2(PPh_3)_2$-catalyzed reactions, 95% of **2a** and 4% of anisole were gained after 20 min in EtONa system, and only 8% of **2a** was detected after 300 min in NEt_3 system (Scheme 2).

Yamamoto et al. investigated the kinetics of ethoxylcarbonylation and concluded that the ArCOPdI species was the main resting Pd-species in the catalytic cycle. The rate-determining step involves the reaction of the alcohol with the ArCOPdI using NEt_3 as the base, where both alcohol and NEt_3 show first-order dependence.[14] Notably, in the presence of [$PdCl_2(MeCN)_2$/**L1**] as the catalyst, and when NEt_3 was used instead of EtONa, we observed zero-order kinetics for the ethoxylcarbonylation of **1a** (Figure 1a). This kinetic behavior is obviously different from the above system employing NEt_3 as the base.[14] Furthermore, we did study the [$PdCl_2(MeCN)_2$/**L1**]-catalyzed ethoxylcarbonylation employing NEt_3 as the base and found that the rate of this reaction was much slower. The first-order kinetic behavior was observed (Figure 1a), which is consistent with Yamamoto's observation.[14] Similar kinetic trends were observed in the $PdCl_2(PPh_3)_2$ system (Figure 1b). These results indicated that the mechanism or rate-limiting step in [Pd]-EtONa system is different from [Pd]-NEt_3 system.

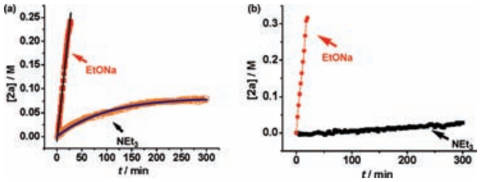
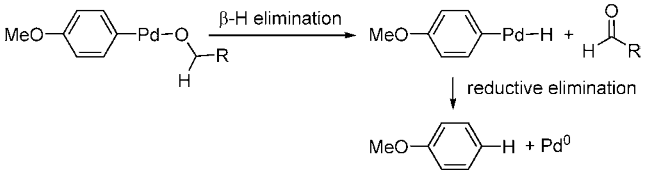


Figure 1. Kinetic plots of carbonylation of **1a** at 60 °C under balloon pressure of CO recorded by *in situ* IR. Reaction conditions: [Cat.] = 0.0067 M, [**1a**] = 0.33 M, [EtONa] = 0.44 M, [NEt_3] = 1.0 M. (a) Cat.= $PdCl_2(MeCN)_2$/**L1**; (b) Cat. = $PdCl_2(PPh_3)_2$.

Scheme 3. Proposed Pathway for the Formation of Anisole



2. Existence of Pd(II)-OR Intermediate. It has been reported that Pd(II)-alkoxide intermediate could be formed rapidly from the reaction of Pd(II)-Cl with MeONa,[24] and this intermediate has been involved in several transformations.[25−29] In addition, *β*-H elimination of metal-alkoxo complexes is known. Thus, we envisioned that the deiodinated side product anisole in the EtONa system originated from *β*-H elimination of (4-$MeOC_6H_4$)PdOEt (Scheme 3, R = Me).[25,26,30−32]

It could be deduced from Scheme 3 that along with anisole, an equal amount of aldehyde should be formed. To probe this speculation, $PdCl_2(PPh_3)_2$-catalyzed alkoxycarbonylation of **1a** with BnONa as the base in BnOH was followed by GC.[33] In 30 min, 20% of the carbonylative product benzyl-4-methoxybenzoate **3a** was obtained along with 66% of anisole and 71% of benzaldehyde. Importantly, the formation rates of anisole and benzaldehyde were virtually the same (Figure 2).

The formation of PhS^nBu, as the other competitive pathway in the butylthiocarbonylation of PhI with *n*-BuSNa in the presence of 10 atm CO, could serve as an additional evidence for the existenec of ArPdOR in above exthoxylcarbonylation of **1a** using EtONa as the base. Shown in the Table 1, competition between thiocarbonylation **4a** and directly C−S bond formation **4a′** was observed by varying the ligands. When

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(33) For the sake of generality, the following mechanistic investigation was carried out with $PdCl_2(PPh_3)_2$ as the catalyst.

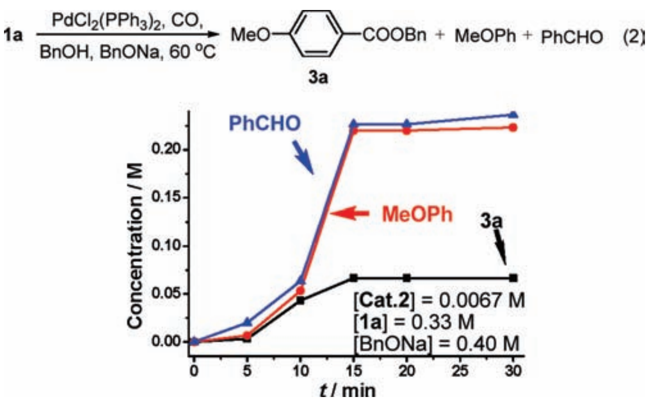
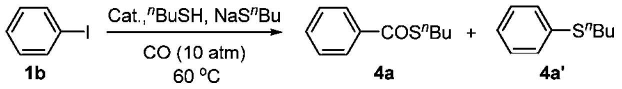


Figure 2. Kinetic plots of benzoxycarbonylation of **1a** at 60 °C under balloon pressure of CO.

Table 1. Thiocarbonylation of PhI with *n*-BuSNa[a]



entry	Cat.	yield [%][b]	
		4a	4a′
1	Cat. 2	88	7
2	$PdCl_2(CH_3CN)_2$	trace	trace
3	$PdCl_2(CH_3CN)_2$/DPE phos	25	73
4	$PdCl_2(CH_3CN)_2$/dppf	30	77

[a] Pd-catalyzed thiocarbonylation of PhI with *n*-BuSNa as the base. Reaction conditions: **1b** (1.0 mmol), *n*-BuSNa (1.2 mmol), in *n*-BuSH/THF for 24 h. [b] GC yields.

PPh_3 was used as the ligand, 88% butylthiocarbonylation product was obtained (Table 1, entry 1), while the directly C−S bond formation (**4a′**) was dominated in the presence of dppf as the ligand (Table 1, entry 4). The formation of **4a′** reveals the existence of Ph-Pd(L_n)SBu, which should generate from the metathesis between Ph-Pd(L_n)I and *n*-BuSNa.

Two possibilities existed for the ArPdOR species. ArPdOR could be invovled in the catalytic cycle (Scheme 1, Path **II**). Alternatively, ArPdOR could just function in a side path to produce the deiodination side-product, and the carbonylation product was still from Path **I**. To distinguish the two possiblities, stoichiometric reactions of complex **I** were investigated. When complex **I** was treated with EtONa at −20 °C under balloon pressure of CO, ethyl benzoate was formed (eq 3 in Figure 3). However, without EtONa, complex **II** was obtained (eq 4 in Figure 3). Moreover, the rate of reaction in eq 3 was faster than that of reaction in eq 4 (Figure 3).

In kinetic studies, if a reaction is composed of multiple steps, the observed global kinetic rate should be slower than the rate of each of component steps, or at least equal to the slowest step if it exists. If eq 3 operated via Path I (Scheme 1), eq 4 should be part of the reaction pathway, and the observed rate of eq 4 should be faster or at least equal to that of eq 3. However, opposite results were gained (*vide supra* in Figure 3), which excluded aroyl Pd(II) complex **II** as an intermediate in the reaction of eq 3. Consequently, the possibility of alkoxycarbonylation in EtONa system going through Path I was disfavored, and ArPdOR should be involved in the catalytic cycle.

3. CO Insertion Step. The step following the ArPdOR formation was CO insertion, which could proceed in two plausible pathways. CO could either insert into the Pd−Ar bond (Scheme 4, Path A) or the Pd-OR bond (Scheme 4, Path B). Upon reductive elimination, both would give the desired product.

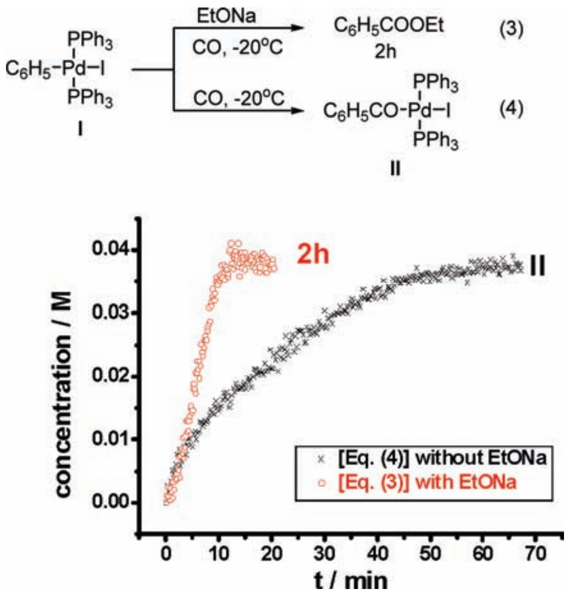
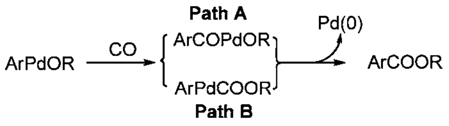


Figure 3. Stoichiometric reactions and their progress profiles under balloon CO pressure and at −20 °C.

Scheme 4. Plausible Pathways for the CO Insertion Step in the Proposed Path II Mechanism of Scheme [1]



Alper et al. have reported that oxidative addition of aryl halides to [PdL], in the presence of aqueous KOH, followed by metathesis produces a series of organometallic hydroxo dimers $[L_2Ar_2Pd_2(\mu{-}OH)_2]$. Upon treatment of the dimers with CO, the corresponding arylcarboxylate anions were obtained.[34] However, the detail of CO insertion was not discussed. Campora and Palma et al. have experimentally observed the insertion of CO into a Pd−OH bond to form a hydroxycarbonyl palladium complex.[35] In stoichiometric reactions of MePd(OR) with CO, perference toward insertion into Pd−OR than into Pd−Me was observed.[24,36−40] Macgregor and Neave concluded by DFT calculations that there was an overall kinetic preference for migratory insertion of CO into the Pd−OMe bond for a series of MePd(OR)L_n isomers including trans-Pd(Me)(CO)(OMe)-(PH_3).[41]

To probe the insertion trend of CO in our system, we carried out DFT calculations with trans-PdPh(CO)(OEt)(PMe_3) as the

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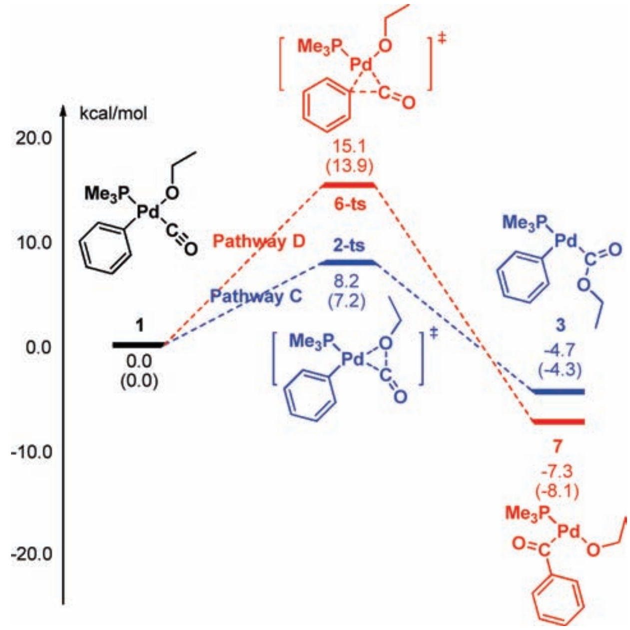
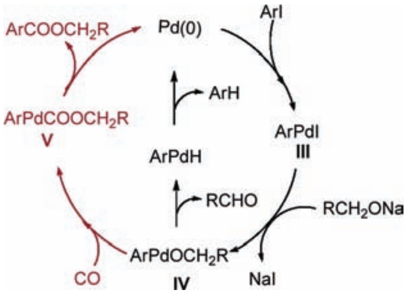


Figure 4. Reaction profiles (kcal/mol) calculated by DFT for the CO migratory insertion of Pd(Ph)(OEt)$(PMe_3)_2$ species.

Scheme 5. Plausible Mechanisms of Pd-Catalyzed Alkoxycarbon-Ylation of Aryl Iodides with Sodium Alkoxide as the Base



model (Figure 4). The energy barrier for CO insertion into the Pd-OEt via transition state **2-ts** (Path C, Figure 4) was 6.9 kcal/mol lower in energy than transition state **6-ts** which involved CO insertion into the Pd-Ph bond (Path D, Figure 4). The results were consistent with the reported theoretical result,[41] and in favor of Path B in Scheme 4.

4. Overall Catalytic Cycle for Alkoxycarbonylation of Aryl Halides in EtONa System. On the basis of the experimental and computational results above, it is reasonable to propose that when sodium alkoxide is the base, palladium catalyzed alkoxycarbonylation of aryl iodides went through a catalytic cycle different from the traditional one. As shown in Scheme 5, oxidative addition of aryl iodide to Pd^0 generated complex **III**, transmetalation with sodium alkoxide led to the key intermediate **IV**. This intermediate underwent β-H elimination and reductive elimination to produce the dehalogenated product ArH. Alternatively, CO could coordinate to **IV** and then insert into the Pd−O bond to afford **V**; reductive elimination of **V** gave ArCOOR and completes the catalytic cycle.

5. Kinetic Studies of the Catalytic Reaction. Since this carbonylative reaction is a gas−liquid two phase system, it is necessary to investigate the gas diffusion before quantitative kinetic study of the catalytic system. If gas diffusion is a rate-determining step, the reaction rate is only related with the gas up-taking rate, which is usually affected by stirring rate, gas pressure, solvent, and reaction temperature etc. Thus, ethoxycarbonylation of **1a** was monitored by in situ IR under 10 atm CO at 50 °C. Three reactions were carried out at 300, 400, and 500 rpm/min, respectively. The kinetic profiles were shown in the Figure 6, and they were overlaid. These kinetic data revealed that the reaction rate is independent of stirring rate. Thus, gas diffusion was not rate-determining under the conditions.

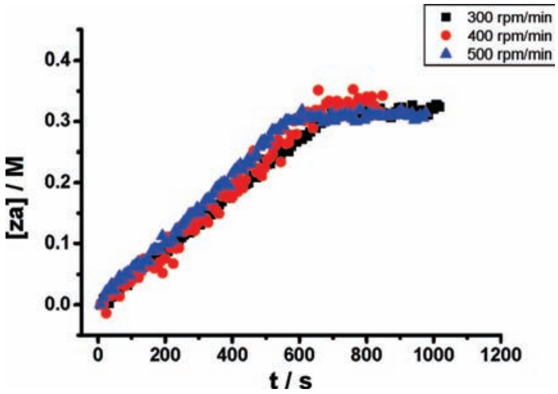


Figure 6. The kinetic plots of ethoxycarbonylation of **1a** at different stirring rates under 10 atm of CO at 50 °C.

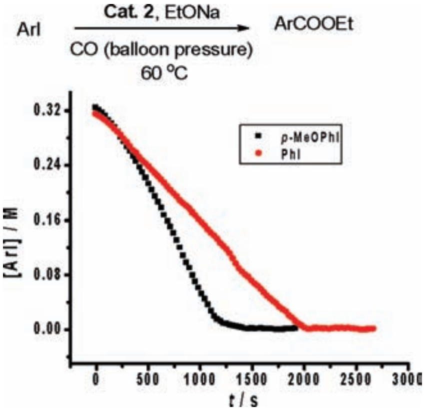


Figure 7. Kinetic plots of ethoxycarbonylation using different ArI under 1 atm of CO at 60 °C.

To further confirm that the rate limiting step was not the gas diffusion, reactions employing different ArI in the same conditions were carried out. If two reactions using different substrates, but under same reaction conditions, have different rates, then gas diffusion could be ruled out as the rate-determining step. Shown in Figure 7, the reaction employing *p*-MeOPhI as substrate at 60 °C under balloon pressure of CO was faster than the carbonylation of iodobenzene. The experiment results indicated that the gas diffusion was not the slowest step under these reaction conditions and properly suggested that electron donating group could facilitate the transformation from IV to V (Scheme 5).

Variation of the initial concentration of **1a** under 10 atm of CO displayed little influence on the reaction rates (Figure 7). Thus, the rate was zero order in both the concentrations of **1a** and sodium ethoxide under the reaction conditions, which meant that neither the formation of intermediate **III** nor that of **IV** in Scheme 5 was rate limiting (Figure 8).

The effect of CO pressures was investigated in the range of 5 to 20 atm. At any single pressure, where CO concentration in solution was constant, zero-order kinetic behavior was observed (Figure 9A). When the reaction rates were plotted vs CO

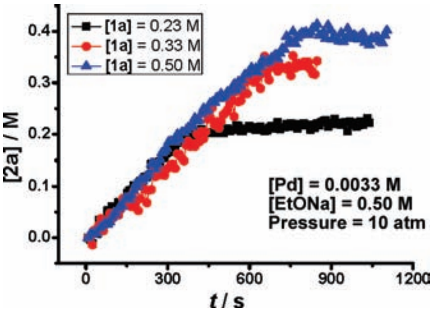
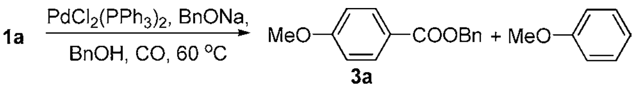


Figure 8. Kinetic plots at different initial concentrations of **1a** with $Pd(PPh_3)_2Cl_2$.

Scheme 6. Benzoxycarbonylation of **1a** under Different Pressures of CO



3a

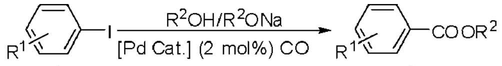
CO:	3a	:	
CO: balloon pressure	23	:	77
10 atm	99	:	1

pressure, a linear correlation was observed (Figure 9B), supporting that the step involving CO from intermediate **IV** to **V** was the rate-determining step.

The influence of CO pressure upon the reaction was further evaluated by comparing the benzoxycarbonylation of **1a** under balloon pressure of CO with that under 10 atm CO. The selectivity of the desired product **3a** vs anisole was improved from 23:77 to 99:1 (determined by GC) (Scheme 6). These results were consistent with the kinetic data and supported that the step from **IV** to **V** in Scheme 5 was the key step in the whole catalytic cycle.

6. Carbonylation of Aryl Iodides with NaOR and NaSR. According to the traditional mechanism (Scheme 1, Path I), alcoholysis is rate determining, which means that the steric and electronic properties of the alcohol will greatly affect the reaction. Consequently, few examples of successful production of *t*-butyl esters through carbonylation have been reported.[14] However, our studies revealed that the rate-determining step was associated with the reaction of CO with the ArPdOR intermediate **IV**, and the introduction of RO^- into Pd-center was now a facile step. Thus, this new mechanism provided a better opportunity to synthesize esters through carbonylation including the most challenging, sterically hindered *t*-butyl esters. As shown in Table 1, initially we observed that $PdCl_2(PPh_3)_2$ catalyzed *t*-butoxylation with *t*BuONa as the base only gave moderate yields (46−67%, Table 2, entries 1−3). Pleasantly, switching to $PdCl_2(MeCN)_2$/**L1** resulted in much better yields (73−87%, Table 2, entries 4−6). Moreover, *iso*-propyl esters were prepared in yields of 82−94% (Table 2, entries 7−10) and ethyl esters were prepared under mild conditions (room temperature, balloon pressure of CO) in yields of 73−90% (Table 2, entries 11−19).

Table 2. Carbonylation of Aryl Iodides with NaOR[a]



1 **2**

entry	R^1	R^2	[Pd Cat.]	P_{CO} (atm)	*T*, °C	yield [%][b]
1	**1a**	^{t}Bu	Cat.2	10	95	46[c] (**2p**)
2	H (**1b**)	^{t}Bu	Cat.2	10	95	60[c] (**2b**)
3	4-Ph (**1c**)	^{t}Bu	Cat.2	10	95	67[c] (**2c**)
4	**1a**	^{t}Bu	Cat.1	10	95	87 (**4a**)
5	**1b**	^{t}Bu	Cat.1	10	95	84[c] (**2b**)
6	**1c**	^{t}Bu	Cat.1	10	95	73 (**2c**)
7	**1a**	^{i}Pr	Cat.2	10	80	88 (**2d**)
8	**1b**	^{i}Pr	Cat.2	10	80	86 (**2e**)
9	**1c**	^{i}Pr	Cat.2	10	80	94 (**2f**)
10	2-OMe(**1d**)	^{i}Pr	Cat.2	10	80	82 (**2g**)
11	**1a**	Et	Cat.2	1	r.t	84 (**2a**)
12	**1b**	Et	Cat.2	1	r.t	84 (**2h**)
13	**1d**	Et	Cat.2	1	r.t	84 (**2i**)
14	4-COOEt (**1e**)	Et	Cat.2	1	r.t	90 (**2j**)
15	2-COOEt (**1f**)	Et	Cat.2	1	r.t	90 (**2k**)
16	4-Me (**1g**)	Et	Cat.2	1	r.t	73 (**2l**)
17	4-Cl (**1h**)	Et	Cat.2	1	r.t	75 (2m)
18	4-Br (**1i**)	Et	Cat.2	1	r.t	80 (**2n**)
19	2-Br (**1j**)	Et	Cat.2	1	r.t	81 (**2o**)

[a] Pd-catalyzed carbonylation of aryl iodides with R^2ONa as the base. Reaction conditions: **1** (1.0 mmol), R^2ONa (1.2 equiv), in $R^2OH$for 24 h. [b] Isolated yields. [c] GC yields.

Thioester, as an important synthetic building block, is seldom reported to be prepared from the thiocarbonylation of ArX with CO in the presence of transition metals. Alper et al. had reported the first example in 2008, in which ArSH were employed as the major nucleophiles (only two examples using *i*-PrSH and *n*-$C_6H_{13}SH$) for the thiocarbonylation.[42] There is no example in the literature for the direct synthesis of sterically hindered thioesters, such as ArCOS^{t}Bu, from the thiocarbonylation of ArX with CO. Inspired by the kinetic investigation of the novel catalytic carbonylation induced by NaOR, we further examined the thiocarbonylation of ArI in the presence of NaSR. We are pleased to note that the thiocarbonylations with varied NaSR and ArI could smoothly took place, and the results were summarized in the Table 3. Although the thiocarbonylation of electron-rich **1a** with NaS^{t}Bu was sluggish under 10 atm CO pressure and 70 °C (Table 3, entry 1), the reaction was smooth

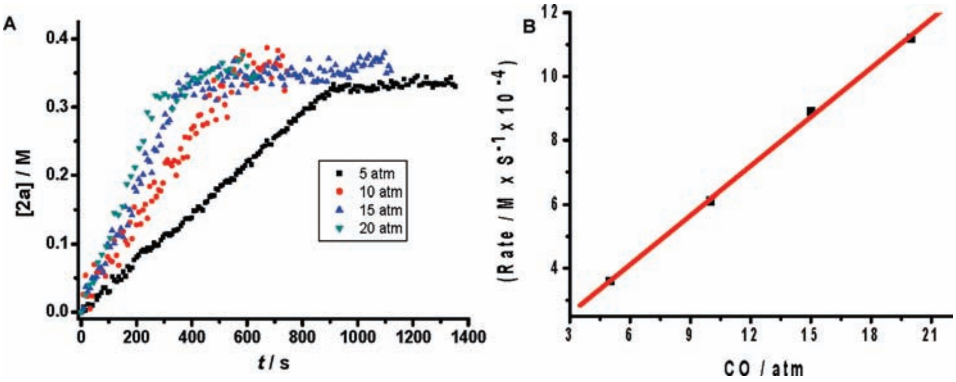
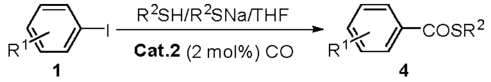


Figure 9. Kinetic profiles when different CO pressure were employed and the linear relationship of rate vs CO pressure.

Table 3. Carbonylation of Aryl Iodides with NaSR[a]



entry	R^1	R^2	P_{CO} (atm)	*T*, °C.	yield [%][b]
1	**1a**	^{t} Bu	10	70	trace (**4d**)
2	**1a**	^{t}Bu	30	120	74[c] (**4d**)
3	**1b**	^{t}Bu	10	70	95 (**4e**)
4	**1e**	^{t}Bu	10	70	50 (**4f**)
5	**1h**	^{t}Bu	10	70	76 (**4g**)
6	**1j**	^{t}Bu	10	70	75 (**4h**)
7	**1a**	$C_{12}H_{25}$	10	60	88 (**4i**)
8	**1b**	$C_{12}H_{25}$	10	60	78 (**4j**)
9	**1c**	$C_{12}H_{25}$	10	60	90 (**4k**)
10	**1h**	$C_{12}H_{25}$	10	60	54 (**4l**)
11	2-Me(**1k**)	$C_{12}H_{25}$	10	60	79 (**4m**)
12	**1a**	^{n}Bu	10	60	86 (**4a**)
13	**1b**	^{n}Bu	10	60	88[d] (**4b**)
14	**1c**	^{n}Bu	10	60	78 (**4c**)

[a] Pd-catalyzed carbonylation of aryl iodides with R^2SNa as the base. Reaction conditions: **1** (1.0 mmol), R^2SNa (1.2 equiv), in R^2SH/THF (volumn ratio = 1: 6) for 24 h. [b] Isolated yields. [c] The isolated yield was obtained in 12 h. [d] GC yield.

in 30 atm of CO, and 120 °C, and gave desired *t*-butyl thioester in 74% yield (Table 3, entry 2). PhI and other electron-deficient ArI gave *t*-butyl thioesters in moderate to excellent isolated yields (Table 3, entries 3−6). When *n*-$C_{12}H_{25}SNa$ and *n*-BuSNa were employed as the nucleophiles, corresponding thioesters were obtained in moderate to good isolated yields (Table 3, entries 7−14).

Conclusion

In conclusion, a novel mechanism was proposed for the alkoxycarbonylation of aryl iodides with sodium alkoxide as the base. The catalytic cycle consisted of oxidative addition, subsequent ArPdOR formation, CO insertion to Pd−OR, and final reductive elimination of ArPdCOOR to produce ArCOOR. The kinetic simultaneity of the formation of deiodinated side product from the aryl iodide and aldehyde from corresponding alcohol and the formation of thioether as a competitive product in thiocarbonylation provided strong evidence for the existence of ArPdOR species. Kinetic studies revealed that neither oxidative addition nor reductive elimination was rate limiting and the rate determining step was associated with the reaction of CO with the ArPdOR intermediate. DFT calculations suggested a kinetic preference for CO insertion into Pd-OR bond. Understanding this mechanism allowed alkoxycarbonylation and thiocarbonylation of aryl iodides to proceed smoothly including the formation of *t*-butyl esters and thioesters which are usually difficult under classic mechanistic pathway.

Experimental Procedures

General Procedure for Carbonylation of Aryl Iodides under Balloon Pressure. $Pd(PPh_3)_2Cl_2$ (2 mol %) and the selected aryl iodide (1 mmol) were added into a oven-dried Schlenk tube under N_2 atmosphere. Then the system was evacuated and filled with CO (balloon) for 3 times, and corresponding base (1.2 equiv) and EtOH were added. The reaction mixture was stirred at room temperature for 24 h and quenched NH_4Cl (aq) after dilution with ether (10 mL). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by a flash chromatography (PE/EtOAc = 30/1) on silica gel to afford the product.

General Procedure for Carbonylation of Aryl Iodides under 10 atm CO. Pd catalyst (2 mol %), aryl iodide (1 mmol) and base (1.2 equiv) were added together with 3 mL alcohol solvent to an autoclave. The system was evacuated and refilled with CO for 3 times and the system pressure was retained at 10 atm. The reaction mixture was stirred at 80, 95 or 60 °C for 24 h, and the autoclave was cooled to room temperature and depressurized. The reaction mixture was diluted with ether (10 mL) and quenched with NH_4Cl (aq.). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by a flash chromatography (PE/EtOAc = 30/1) on silica gel to afford the product.

Procedure for the Kinetic Experiments. Pd catalysts and biphenyl (internal standard) were added to an oven-dried Schlenk tube under N_2 atmosphere, and the system was evacuated and refilled with CO (balloon) for 3 times. Then base was added by syringe, and the reaction mixture was stirred at 60 °C during the investigation process. Aliquots were taken at specific time for determination of component concentrations by GC.

Synthesis of *trans*-$[C_6H_5PdI(PPh_3)_2]$:[14] $Pd(dba)_2$ (2.0 g, 3.5 mmol), PPh_3 (2.3 g, 8.7 mmol) and toluene (15 mL) were added to an oven-dried Schlenk tube under N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min followed by addition of iodobenzene (1.1 g, 5.3 mmol). After stirring at room temperature for 6 h, the solvent was removed under vacuum to give a green, powdered solid. Recrystallization from CH_2Cl_2/hexane gave 1.2 g (41% yield) crystals of *trans*-$[C_6H_5PdI (PPh_3)_2]$. ^1H NMR (300 MHz, $CDCl_3$) δ 6.24−6.36 (m, 3 H), 6.63 (d, J = 5.7 Hz, 1H), 7.26−7.34 (m, 18H), 7.52−7.54 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.00, 127.93, 129.87, 132.13, 132.29, 132.44, 135.01, 136.10.

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Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem.* **2008**, *73*, 3530–3534.