



Transition metal-catalyzed carbonylative coupling of aryl/alkyl halides with thiols: A straightforward synthesis of thioester derivatives

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ABSTRACT

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Thioesters are a class of highly useful compounds in synthetic chemistry, and many thioester compounds show biological and pharmacological activities. Organic halides and thiols are widely accessible chemical feedstocks and are widely used in industry as building blocks. The synthesis of thioesters from these basic chemicals is important for chemical synthesis nowadays. Over the years, many efforts have been made to access thioester derivatives through thiocarbonylation of organic halides with thiols using different carbon monoxide sources including CO, CO₂, COgen, [CpFe(CO)₂]₂, Cr(CO)₆, etc. Herein, we summarize the recent advances of these carbonylative coupling reactions.

1. Introduction

Synthesis of the biologically active compounds is very important [1-12]. Thioesters (thiocarboxylates) are one of the most important classes of organosulfur compounds found in numerous natural products [13], pharmaceutical [14] and agricultural chemicals [15]. In addition, they represent excellent building blocks to synthesize various organic functional materials such as ketones [16], aldehydes [17], esters [18], and amides [19], acylsilanes [20], dithioesters [21], 2-methylthio-1, 3-oxazoles [22], and many more [23, 24]. In light of the increasing importance of this class of organosulfur compounds, the exploration of new synthetic methodologies for their preparation is of great interest for organic synthetic chemists. Traditional approaches for their synthesis largely depend on acylation of thiols with carboxylic acids and their derivatives (e.g., acid anhydrides, acyl

chlorides) [25, 26]. Alternative methods including direct thioesterification of aldehydes with various thiol sources (e.g., thiols, disulfides, thiosulfonates, diisobutylaluminum thiolates) [27]. In the past decade, transition metal-catalyzed carbonylative coupling reaction between organic halides and thiols has emerged as a powerful and efficient synthetic method for the construction of thioester compounds. This new page of thioester synthesis offers several advantages, such as: 1) easily accessible starting materials; 2) high functional group tolerance; 3) high atom economy and many more. To the best of our knowledge, there has not been a comprehensive review of thiocarbonylation of aryl/alkyl halides with thiols. This review is an attempt to summarize the existing literature on the synthesis of the thioester derivatives through the carbonylative coupling of aryl/alkyl halides with thiols (Figure 1). Notably, we have classified these reactions into two major sections.

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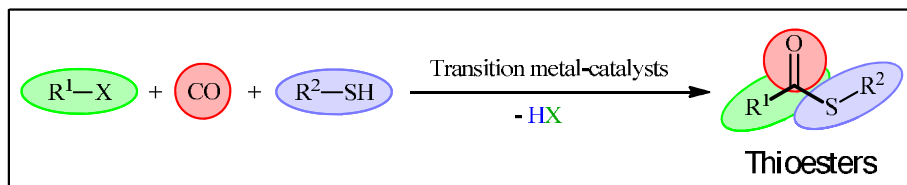


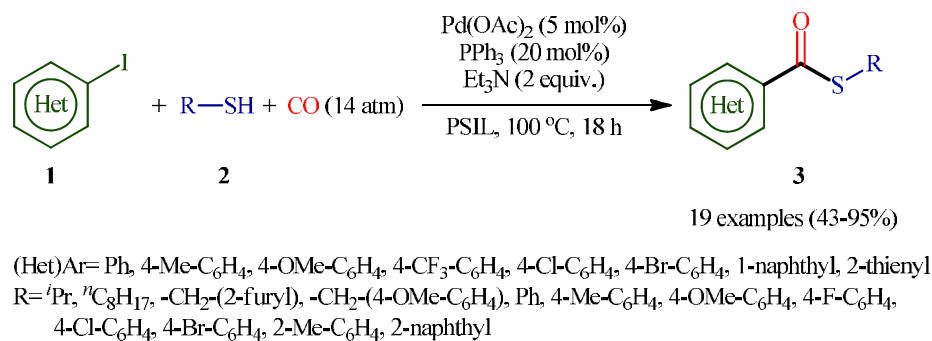
Fig. 1. Thiocarbonylation of organic halides with thiols.

The first section of this review will be focused on the synthesis of *S*-aryl thioesters from aryl halides. In the second section, methodologies for the synthesis of *S*-alkyl thioesters from alkyl halides will be discussed.

2. Thiocarbonylation of aryl halides

After seminal work by Wang and Chen on the synthesis of thioesters through Pd-catalyzed alkyl/aryl-thiocarbonylation of diaryliodonium salts [28], the first report on the synthesis of thioester derivatives *via* carbonylative coupling of aryl halides with thiols was published in 2008 by Alper and co-workers [29]. They unraveled that various (hetero)aromatic aryl iodides **1** underwent smooth carbonylative thiolation with carbon monoxide (CO) and thiols **2** in the presence of Pd(OAc)₂/PPh₃/Et₃N combination as a catalytic system in a phosphonium salt ionic liquid (PSIL), affording the corresponding

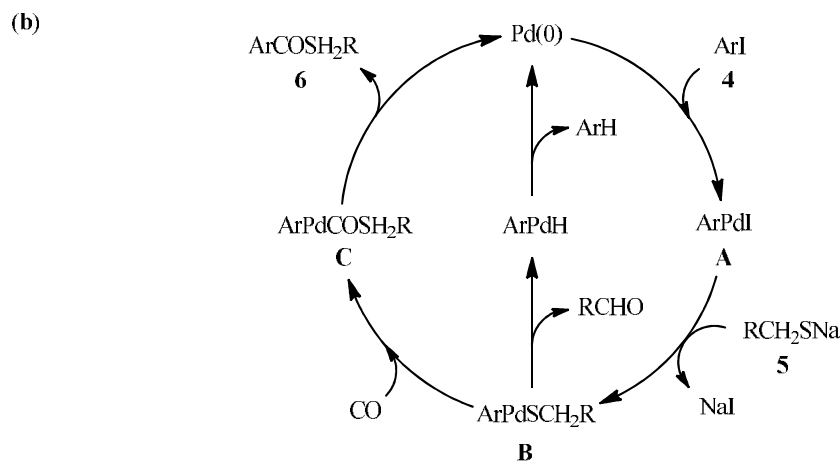
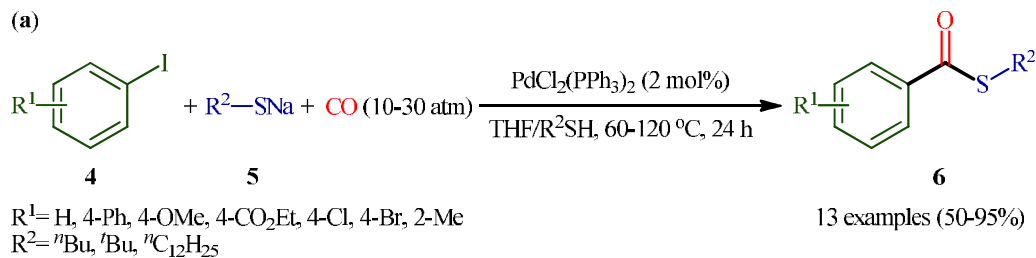
aromatic thioesters **3** in moderate to excellent yields (Scheme 1). The present protocol features wide substrate scope. Various aliphatic, benzylic, and aromatic thiols including sterically hindered substrates were compatible with the reaction. Aryl iodide substrates with electron-donating and -withdrawing groups were also tolerated in the transformation. It should be mentioned that the reaction exhibited extremely high degree of site-selectivity, in which thiocarbonylation is exclusively took place at C-I bond of bromo/chloro iodoarenes (C-I vs. C-Br and C-Cl). Therefore, this protocol could be successfully applied to iodoarenes with the chloro and bromo groups on the aromatic ring, which provided a complementary platform for further diversification through transition metal catalyzed-coupling reactions to create more complex molecules. Unfortunately, no comment was made by the authors regarding the possible mechanistic pathway of this transformation.



Scheme 1. Alper's synthesis of thioesters **3**.

Drawing inspiration from this work, Lei and co-workers reported a similar Pd-catalyzed thiocarbonylation of iodoarenes **4** with sodium thiolates **5** under ligand-free conditions in a thiol/THF solvent mixture [30]. The reactions were carried out in the presence of only 2 mol% of PdCl₂(PPh₃)₂ under CO atmosphere at 60-120 °C, and provided moderate to excellent yields of the desired *S*-alkyl thioester products **6** (Scheme 2a). Intriguingly, the protocol was able to afford sterically hindered thioesters, such as ArCOS^tBu. A plausible mechanism that explains this transformation involves the initial formation of

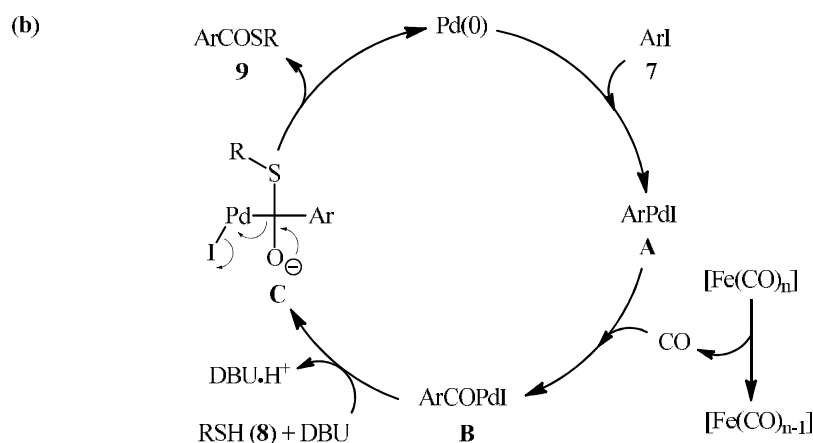
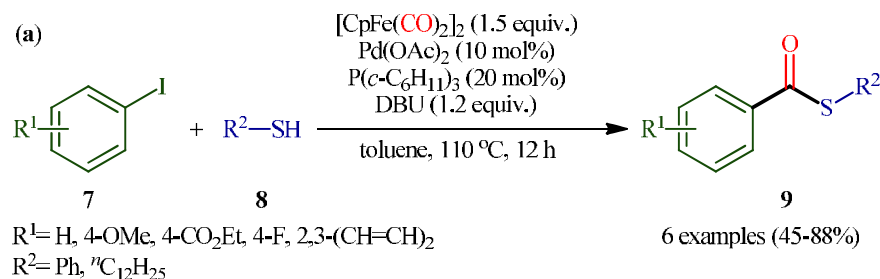
aryl-Pd-I complex **A** through the oxidative addition of aryl iodide **4** to Pd(0) catalyst, which after transmetalation with sodium thiolate **5** affords the key intermediate **B**. Subsequently, insertion of CO into the Pd-S bond of complex **B** provides aryl-Pd^{II}-CO-SR complex **C**. Finally, reductive elimination of this complex generates the target thioester **6** (Scheme 2b). Concurrently, an improved version of this reaction was applied by Tanis *et al.* as the key strategic step in synthesis of a series of biologically active 2-aryl-2-hydroxy ethylamine substituted 1*H*,7*H*-pyrido[1,2,3-*de*]quinoxaline-6-carboxamides [31].



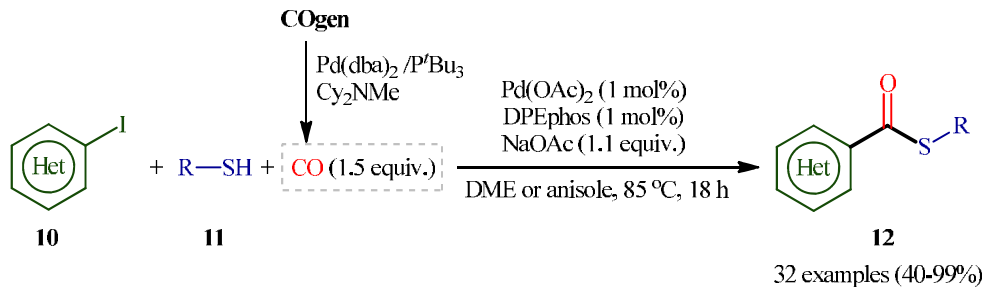
Scheme 2. (a) Lei's synthesis of thioesters **6**; (b) Proposed mechanism for the formation of thioesters **6**.

In 2011, Yorimitsu and Oshima along with their co-workers reported carbonylative coupling of aryl iodides and thiols using bis(cyclopentadienyldicarbonyliron) ($[\text{CpFe}(\text{CO})_2]_2$) as a solid source of carbon monoxide and $\text{Pd}(\text{OAc})_2$ as the catalyst [32]. In this investigation, a series of phosphine ligands [*i.e.*, PPh_3 , $\text{P}(c\text{-C}_6\text{H}_{11})_3$, DPPE] were used for a comparative study. The best result was obtained with $\text{P}(c\text{-C}_6\text{H}_{11})_3$. Furthermore, the optimization study revealed that the bicyclic amidine base DBU can be used to facilitate this coupling reaction. A library of iodoarenes **7** and a small series of thiols **8** were reacted well under the optimized reaction conditions to produce the corresponding thioesters **9** in moderate to high yields (Scheme 3a). Under the identical conditions, similar reactions with amines and phenols provided the corresponding benzamides and benzoate esters, respectively. According to the authors proposed mechanism, this reaction proceed through an oxidative addition/CO insertion/nucleophilic attack/elimination sequential process (Scheme 3b).

Two years later, Skrydstrup and colleague disclosed a mild $\text{Pd}(\text{OAc})_2$ -catalyzed thiocarbonylation of (hetero)aryl iodides **10** with thiols **11** using only a stoichiometric amount of carbon monoxide, generated *ex situ* from 9-methylfluorene-9-carbonyl chloride (COgen) in a two-chamber pressure tube (Scheme 4) [33]. The chemoselectivity of the reaction was highly dependent on the choice of metal ligand and solvent system used. A thorough solvent and ligand screening indicated that in the presence of Josiphos ($\text{PhPF-}^t\text{Bu}$), the unwanted thioether was formed exclusively even in the presence of CO, while switching the ligand to a wide bite angle diphosphine ligand DPEphos afforded the desired thioester in a reversal of chemoselectivity. Moreover, DME as a solvent worked for the carbonylation of electron-rich aryl iodides, whilst anisole proved to be the most effective solvent for the electron deficient ones. The authors elegantly showed the application of their methodology in the high yielding syntheses of an interesting amide version of the new antidepressive agent, vortioxetine, including its ^{13}C -labelled version.



Scheme 3. (a) Pd-catalyzed carbonylative coupling of aryl iodides **7** with thiols **8** using [CpFe(CO)₂]₂ as CO source; (b) mechanistic explanation of the synthesis of thioesters **9**.



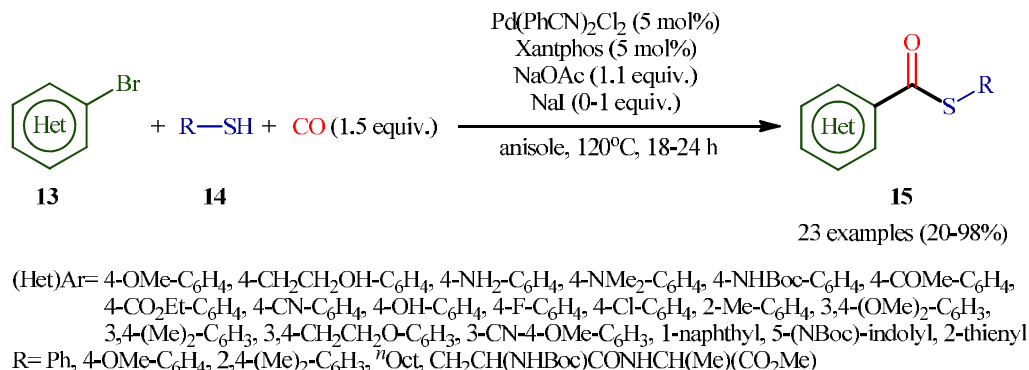
(Het)Ar= Ph, 4-Me-C₆H₄, 4-^tBu-C₆H₄, 4-OMe-C₆H₄, 4-CF₃-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 4-COMe-C₆H₄, 4-CO₂Et-C₆H₄, 4-NMe(Boc)-C₆H₄, 4-NO₂-C₆H₄, 3-Me-C₆H₄, 3-OMe-C₆H₄, 3-Cl-C₆H₄, 2-Me-C₆H₄, 2-OMe-C₆H₄, 3,4-(OMe)₂-C₆H₃, 2,4-(OMe)₂-C₆H₃, 3,4,5-(OMe)₃-C₆H₂, 1-naphthyl, 3-indolyl, 3-(NBoc)-indolyl, 2-thienyl
 R= Ph, 4-OMe-C₆H₄, 4-F-C₆H₄, 3-OMe-C₆H₄, 2,6-(Me)₂-C₆H₃, ⁿOct, CH₂CH(NHBoc)(CO₂Me), CH₂CH(NHBoc)CONHCH(Me)(CO₂Me)

Scheme 4. Skrydstrup's synthesis of thioesters **12**.

Shortly afterwards, this innovative research group further expanded the scope of this chemistry to bromoarenes using the merge of Pd(PhCN)₂Cl₂ and Xantphos with NaOAc as the catalytic system [34]. A broad range of (hetero)aryl bromides **13** could be coupled with various aliphatic and aromatic thiols **14** by this method, and effectively furnished the corresponding *S*-alkyl/aryl thioesters **15** in poor to excellent yields (Scheme 5). This protocol tolerated the

presence of a number of important functional groups, including hydroxyl, fluoro, chloro, cyano, amino, amido, ester, ether, and ketone functionalities, and promised its potential applications in the further diversification of the prepared thioester products [35]. Apart from aryl bromides, alkyl halides (bromides and chlorides) and vinyl bromides were also compatible with this scenario. Notably, this methodology was also successfully applied for the preparation of a series

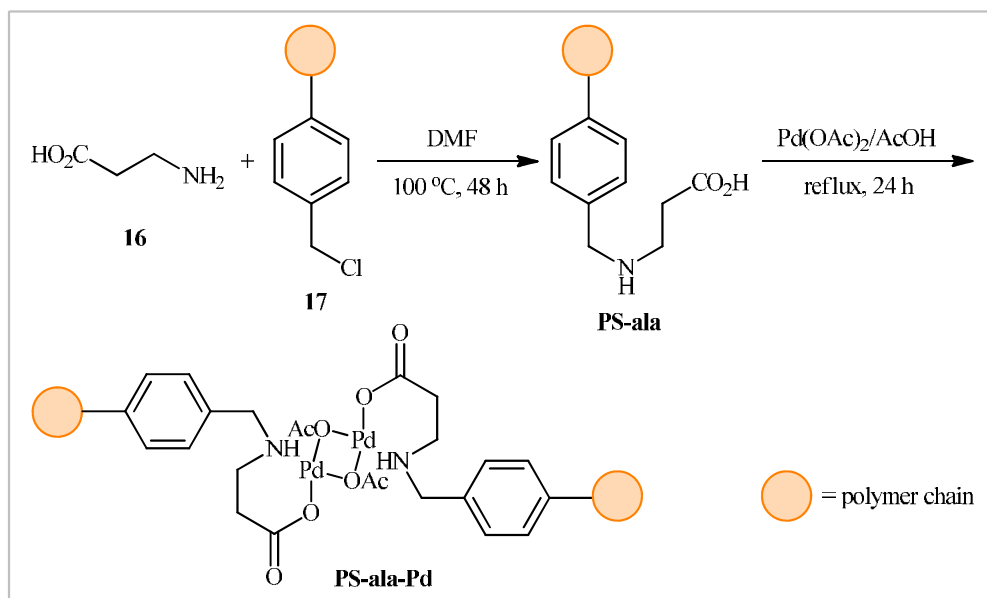
of benzothiophenes, whereby the formed thioesters were ring closed *via* a McMurry coupling.

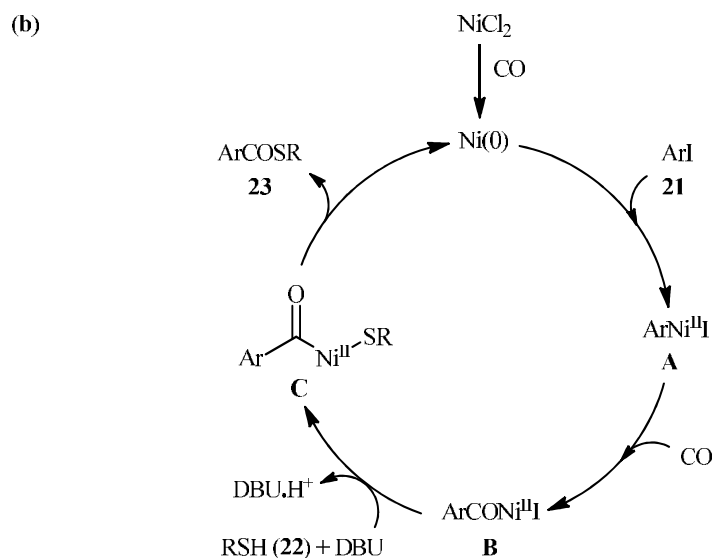
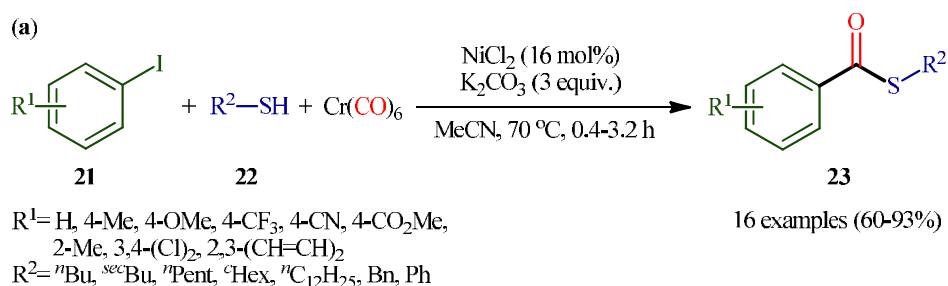


Scheme 5. Pd-catalyzed carbonylative coupling of aryl bromides **13** with thiols **14**.

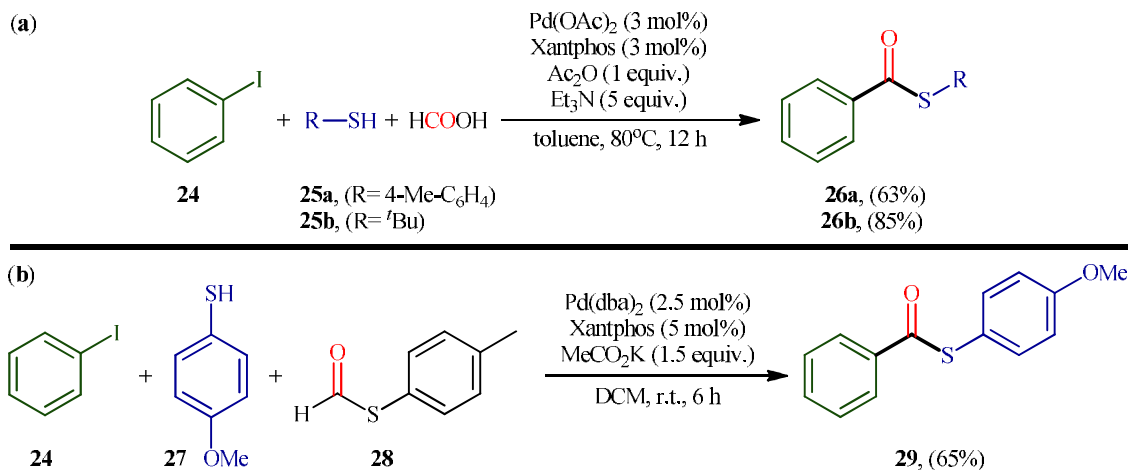
Concurrently, Islam and co-workers designed and synthesized a new polymer supported phosphine free Pd(II) complex (PS-ala-Pd) through a simple procedure *via* *N*-alkylation of β -alanine **16** with chloromethylated polystyrene **17** in DMF at 100 °C followed by reaction with Pd(OAc)₂ in refluxing acetic acid for 24 h (Scheme 6) [36]. The prepared polymer supported Pd catalyst has been characterized by using various analyses such as SEM-EDX, TGA, IR and solid UV-vis spectroscopy [37]. Palladium content in the catalyst determined by AAS suggests 9.08 wt% Pd in the catalyst. This polymer supported Pd(II) complex was applied as an efficient catalyst for synthesis of a panel of 23 thioesters **20** through carbonylative coupling of (hetero)aryl iodides **18**

with thiophenols **19** under CO atmosphere using NaOAc as a base. As shown in Scheme 7, the protocol well tolerated diverse electronic and steric substituents of the iodoarenes, as well as heterocyclic substrates, all resulting in moderate to excellent yields. However, neither aryl bromides nor aryl chlorides were reacted under the conditions employed. The reaction, moreover, appears to be limited to only electron-rich thiophenols. Unfortunately, the applicability of aliphatic thiols was not investigated in this study. Noteworthy, the catalyst can be easily recovered from the reaction mixture by a simple filtration and reused up to six reaction cycles without a significant decrease in activity.





Scheme 8. (a) Iranpoor-Firouzabadi's synthesis of *S*-aryl/alkyl thioesters **23**; (b) The proposed mechanism of Ni-catalyzed carbonylative coupling between aryl iodides **21** and thiols **22**.



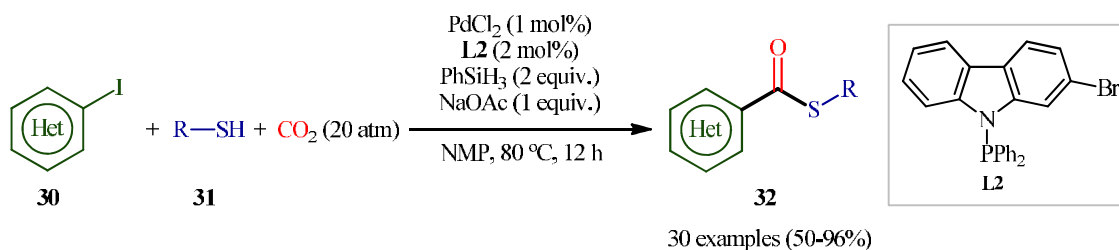
Scheme 9. (a) Wu's synthesis of thioesters **26**; (b) Zhang-Gao's synthesis of *S*-(4-methoxyphenyl) benzothioate **29**.

Very recently, Li and colleagues reported a general and practical Pd-catalyzed carbonylative coupling of a variety of (hetero)aryl iodides **30** with alkyl/aryl thiols **31** employing carbon dioxide (CO₂) as a green CO source [43]. The reaction proceeded in the presence of PdCl₂/L2/PhSiH₃/NaOAc combination as a catalytic system in *N*-methyl-2-

pyrrolidone (NMP) at 80 °C to give the corresponding thioesters **32** in moderate to excellent yields (Scheme 10). The choice of metal, ligands, and reductant were crucial for high efficiency and chemoselectivity. No reaction occurred without PdCl₂, ligand, or reductant. The optimization study using iodobenzene and *n*BuSH as the model

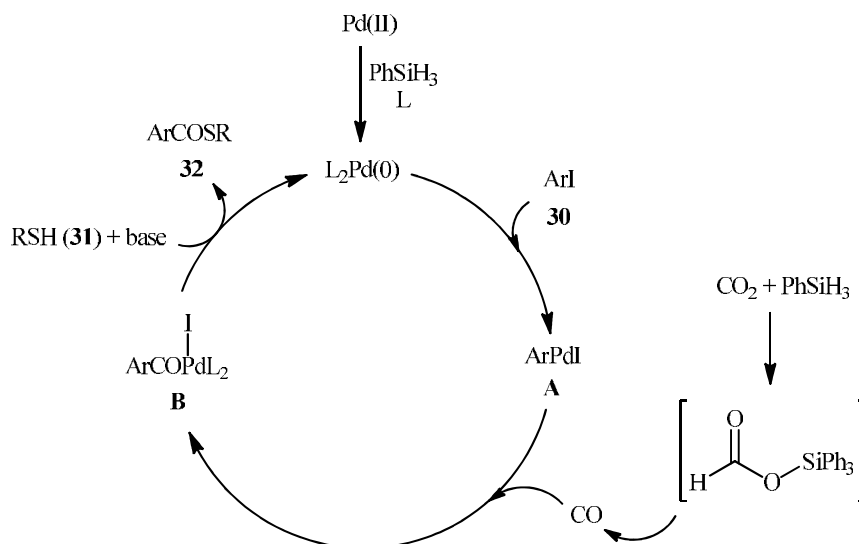
reactants indicated that commercially available monophosphine or bisphosphine ligands such as PPh₃, Xantphos, and newly designed carbazole-derived ligand (**L3** and **L4**) led to low reactivity. By contrast, when using the carbazole-derived ligand containing the P atom covalently linked to the N atom (**L1** and **L2**), good reactivity was observed under the identical reaction conditions. In addition, the usage of other hydrosilanes instead of PhSiH₃ was found to be not suitable. Under the optimized conditions 30 S-aryl/alkyl thioesters **32** were synthesized in yield ranging from 50% to 96%. The

results showed that the electronic nature of the substituents on the aryl iodides had little impact on the facility of the reaction. However, the process strongly depended on the steric effects of the substrates. The results also indicated that the relative reaction rates of thiols followed the order: primary aliphatic thiols > secondary aliphatic thiols ≈ aromatic thiols > benzylic thiols > tertiary aliphatic thiols. The possible mechanistic cycle proposed by the authors for this transformation is illustrated in Scheme 11.



(Het)Ar= Ph, 4-Me-C₆H₄, 4-Et-C₆H₄, 4-ⁱPr-C₆H₄, 4-^tBu-C₆H₄, 4-Ph-C₆H₄, 4-NMe₂-C₆H₄, 4-OMe-C₆H₄, 4-COMe-C₆H₄, 4-F-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 3-Ph-C₆H₄, 3-OMe-C₆H₄, 3-Br-C₆H₄, 2-OMe-C₆H₄, 3,4-OCH₂CH₂O-C₆H₃, 3,5-(OMe)₂-C₆H₃, 3,5-(Me)₂-C₆H₃, 3,4-(Me)₂-C₆H₃, 1-naphthyl, 2-dibenzofuryl, 3-9,9-(Me)₂-fluorenyl, 5-indolyl
R= ⁱPr, ⁿBu, ^tBu, ^cHex, ⁿC₇H₁₅, Bn, 4-OMe-C₆H₄

Scheme 10. Li's synthesis of thioesters **32**.



Scheme 11. Proposed mechanism for the reaction in Scheme 10.

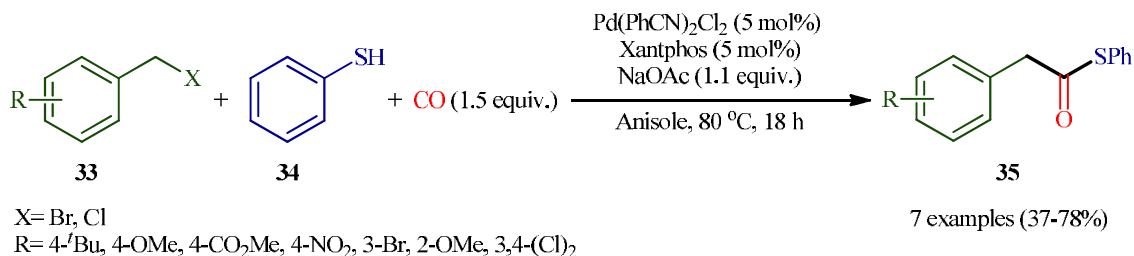
3. Thiocarbonylation of alkyl halides

Compared to carbonylative coupling of aryl halides with thiols, the synthesis of linear thioesters through thiocarbonylation of alkyl halides with thiols is much less explored and examples of such a coupling reaction are quite rare. In fact, to the best of our knowledge, only three examples of carbonylative coupling of alkyl

halides with thiols were reported in literature thus far. In 2014, in the same study describing Pd-catalyzed thiocarbonylation of aryl bromides, Skrydstrup's research group reported the synthesis of a series of *S*-phenyl 2-arylethanethioates **35** through Pd-catalyzed carbonylative coupling of respective benzyl halides **33** with thiophenol **34** in the presence of only a slight stoichiometric excess of CO under relatively mild conditions [44]. As

shown in Scheme 12, both electron-rich and electron-deficient benzyl halides (bromides and chlorides) worked well in this reaction and gave expected products in synthetically useful yields. However, only one thiol substrate was used, without any substrate scope exploration. Furthermore, the applicability of secondary and

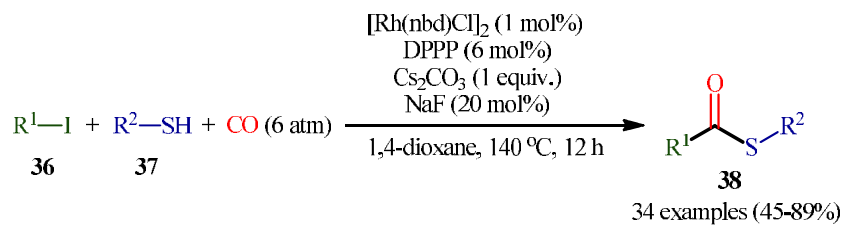
tertiary alkyl halides was not investigated in this preliminary work. Notably, the identical reaction conditions were also applied for thiocarbonylation of vinyl bromides to give the corresponding α,β -unsaturated thioesters in moderate yields (3 examples, 38–62% yield).



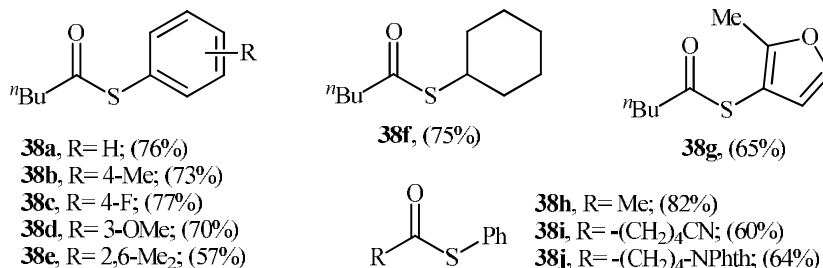
Scheme 12. Skrydstrup's synthesis of *S*-phenyl 2-arylethanethioates **35**.

At the outset of 2021, Wu and co-workers discovered that a combination of $[\text{Rh}(\text{nbd})\text{Cl}]_2$, bidentate ligand 1,3-bis(diphenylphosphino)propane (DPPP), inorganic base Cs_2CO_3 and NaF enabled three-component reaction between primary alkyl iodides **36**, (hetero)aromatic/aliphatic thiols **37** and CO gas, giving the corresponding thioesters **38** in moderate to high yields, ranging from 45% to 89% (Scheme 13) [44]. A quite broad scope of short- and long-chain alkyl iodides proved amenable substrates. Excellent functional group compatibility was observed, such as cyanide, imide, trifluoromethyl, ketone, ether, and indole, offering potential opportunities for further structure modifications. [45]. Unfortunately, no desired thioester was obtained when tertiary alkyl iodides were employed under these reaction conditions and only the corresponding thioethers were isolated as unwanted side-products. Secondary alkyl iodides were viable substrates, but with <10% yields owing to their relative high activity. The less reactive primary alkyl bromides remained competent in the

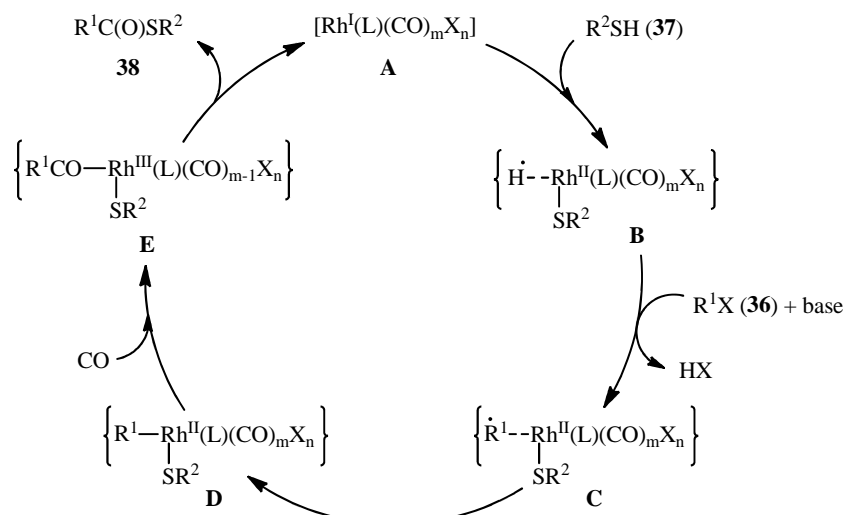
presence of stoichiometric amounts of NaI , suggesting the *in situ* formation of alkyl iodides as reactive electrophiles. Notably, this synthetic strategy was highly sensitive to water, delivering no thioester upon the addition of 1.0 equiv. water. Based on a series of mechanistic studies (radical trapping, radical clock, and EPR experiments), the authors suggested a plausible mechanistic pathway for this carbonylative coupling reaction, as depicted in Scheme 14. The reaction begins with the reaction of rhodium(I) complex **A** with thiol **37** to generate the rhodium(II) tightly associated radical complex **B** which, upon a radical transfer process in the presence of base affords the carbon-centered radical intermediate **C**. Subsequently, combination of the carbon-centered radical and the rhodium(II) complex leads to the alkylrhodium(III) species **D**, that after migratory insertion of carbon monoxide forms the acylrhodium complex **E**. Finally, reductive elimination of this complex [46] produces the desired thioester **38** and meanwhile releases Rh(I) complex for the next catalytic cycle.



selected examples:



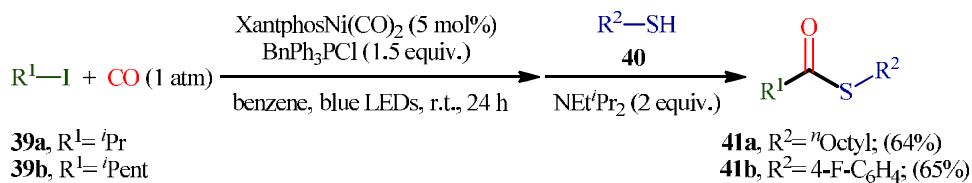
Scheme 13. Rh-catalyzed carbonylative coupling of alkyl iodides **36** with thiols **37**.



Scheme 14. Plausible reaction mechanism for the formation of thioesters **38**.

Recently, Arndtsen's research group developed a visible light driven nickel-catalyzed carbonylation of alkyl halides (primary, secondary, tertiary alkyl iodides/bromides) with CO in the presence of Ph₃BnPCl for the synthesis of acyl chlorides [47]. The combination of the large bite-angle Xantphos ligand with nickel(0) generated a catalyst capable of activating alkyl halides toward carbonylation at ambient temperature under

irradiation of blue LED light (40 W). The authors nicely demonstrated that the coupling of corresponding *in situ* generated acyl chlorides with various nucleophiles can enable the synthesis of a range of carbonylation products. Using this strategy, two thioester derivatives **41** were prepared in good yields from the corresponding alkyl iodides **39** and thiols **40** (Scheme 15).



Scheme 15. Arndtsen's synthesis of thioesters **41**.

4. Conclusion

In this review, we have briefly discussed about transition metal-catalyzed thiocarbonylation of aryl and alkyl halides with thiols employing different carbon monoxide sources (CO, CO₂, COgen, [CpFe(CO)₂]₂, Cr(CO)₆, HCOOH). These novel protocols provided efficient synthetic paths for development of *S*-alkyl/aryl thioesters with high atom- and step-economy. Although tremendous progress has been achieved during past 16 years in this field, some limitations still exist. For example, the extensive use of expensive and toxic palladium catalysts makes it urgent to find suitable inexpensive first row transition metals as substitute catalysts, and (2) the substrates applied are still dominated by expensive alkyl and aryl iodides. Therefore, future research in this area is expected to overcome the limitations of this thiocarbonylation process of organic halogen compounds.

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