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Palladium-catalyzed thiocarbonylation of alkenes toward branched thioesters using CO_2 †

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Thioesters are important intermediates in natural transformations and versatile precursors in organic synthesis. Here, for the first time, thiocarbonylation of alkenes using CO_2 was developed for the preparation of a broad array of thioesters from the reactions of alkenes with different thiols under neutral conditions (40 examples, up to 94% yields, $b/l > 99/1$). Using the combination of a Pd catalyst and the N-P type carbazophosphine ligand, the reactivity and selectivity were well tuned. Experimental and DFT mechanistic studies imply that this reaction might proceed via the direct insertion of CO_2 into the Pd–C bond to generate the Pd–carboxylate species and enable the formation of Markovnikov thioester products.

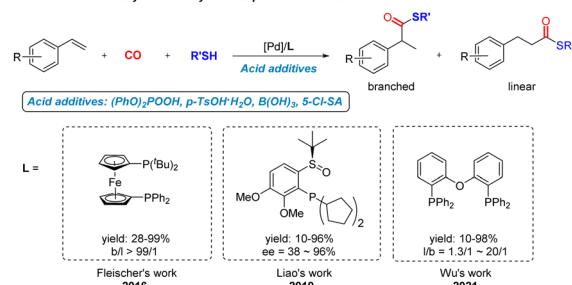
Introduction

The functionalization of alkenes is an ideal way to enable the direct synthesis of functionalized valuable chemicals. The control of selectivity, however, remains a formidable challenge in developing such transformations, which inspires the exploration of a series of catalytic systems to address this selectivity issue.¹ In this respect, suitable catalysts and ligands are key to reaction selectivity.

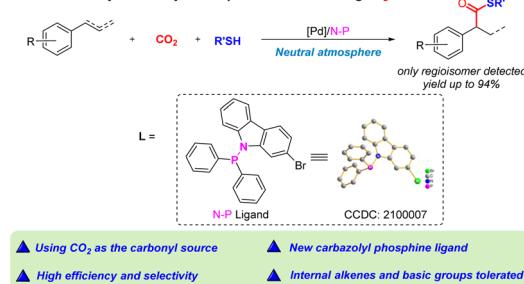
Thioesters represent an important class of molecules widely existing in natural products and are widely applied in drug synthesis.² Over the last 20 years, research on thiocarbonylation to produce thioesters was pioneered by Alper and colleagues, focusing on activated alkenes, including allenes,³ vinylcyclopropanes,⁴ allylic alcohols,⁵ conjugated enynes⁶ and 1,3-dienes.⁷ Simple alkenes were used as substrates in patents from Drent⁸ and Foley.⁹ As shown in Scheme 1A, in 2016, Fleischer and colleagues reported the palladium catalyzed thiocarbonylation of styrene derivatives.^{10a} The importance of thioesters in metal-catalyzed reactions was later reviewed by Fleischer and colleagues.^{10b} An asymmetric version was subsequently implemented by Liao and his colleagues using chiral sulfoxide-(*P*-dialkyl)-phosphine (SOP) ligands.¹¹ In 2021, Wu and colleagues reported a method to give linear products

with high selectivity.¹² However, in all these reactions toxic and dangerous carbon monoxide is used as the carbonyl source and challenging issues still remain in terms of substrate scope and catalyst efficiency due to the addition of acid additives, e.g. internal alkenes and basic substrates are not suitable reactants. Thus, it is desirable and significant to explore CO-free thiocarbonylation methods to address these issues. Moreover, thiols are widely regarded as catalyst poisons for late transition metals and the competing hydrothiolation side reaction might hinder the progress.¹³

A. Previous work: Pd-catalyzed carbonylation to produce thioesters



B. This work: Pd-catalyzed carbonylation to produce thioesters using CO_2



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Scheme 1 Palladium-catalyzed carbonylation to produce thioesters.



Using renewable and abundant carbon dioxide (CO_2) as an alternative carbonyl source to synthesize high value-added molecules is an important part of C1 chemistry.^{14–16} Coordination of CO_2 with a transition metal is recognized as a powerful way for CO_2 activation, commonly resulting in the formation of a metal– CO_2 complex.^{17,18} In this regard, there are two typical strategies,¹⁹ including (i) direct CO_2 insertion into the metal–carbon bond through nucleophilic attack and (ii) reactions of low valent metal complexes (mainly nickel (0) and palladium (0)) with CO_2 and unsaturated compounds, leading to the formation of five-membered metallalactones through oxidative cycloaddition. CO_2 insertion into the metal–carbon bond is the ideal straightforward way of CO_2 utilization. However, the formed metal carboxylates usually have robust C–O(M) bonds and limited reactivity and are inert to nucleophiles, such as H_2 , alcohol and amines.^{20–22} In this respect, processes such as acidification, alkylation or reductive elimination are necessary to obtain the neutral products instead of carboxylate salts.^{23–25} To the best of our knowledge, catalytic thiocarbonylation of alkenes to produce thioesters using CO_2 has not been reported yet.

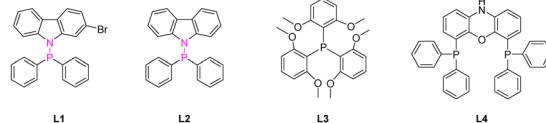
Based on our recent work on catalytic CO_2 transformation/utilization,²⁶ we envisioned that appropriate electronic and spatial properties of carbazole-derived phosphine ligands might enhance the activity of Pd-intermediates for direct preparation of high-selectivity neutral compounds from CO_2 . Phosphine ligands with a carbazolyl motif have been successfully used in many palladium-catalyzed biaryl syntheses and direct C–H bond arylation processes.²⁷ The sp^3 -hybridized *N* offers weak coordination to the palladium center whenever needed during the catalytic cycle and potentially increases the catalyst longevity, while the flattened carbazolyl bottom ring takes advantage of the extended flat-wall-like rigidity and facilitates the reductive elimination process. Herein, we developed palladium-catalyzed thiocarbonylation of alkenes for the preparation of thioesters by using CO_2 as the carbonyl source in the presence of hydrosilane as a reductant. The use of the newly designed N–P-type carbazole-derived ligand allows for high efficiency. Moreover, the reaction does not require acidic additives, which provides neutral and suitable conditions for the smooth transformation of basic substrates. Internal alkenes can also be compatible (Scheme 1B).

Results and discussion

Initially, we selected styrene **1a** and *n*BuSH **2a** as the model substrates and examined the influence of palladium salts, ligands, reductants, and additives. The reaction does not proceed without ligands (Table 1, entry 1). To our delight, when monophosphine ligand PCy_3 was added to the reaction, branched thioester product **3a** was obtained with a yield of 48% (Table 1, entry 2). When the bisphosphine ligand Xantphos was added, the reaction selectivity was reversed, and the linear thioester product **4a** was mainly obtained with a yield of 36% (Table 1, entry 3). $\text{PdCl}_2(\text{PCy}_3)_2$ was able to cata-

Table 1 Condition optimization for thiocarbonylation of styrene^a

| Entry | [Pd] | L | Reductant | Yield of | |
|-----------------|---------------------------------|----------------|---------------------------|-----------|--------------|
| | | | | 3a/% | 4a/% |
| 1 | PdCl_2 | — | PhSiH_3 | <1 | <1 |
| 2 | PdCl_2 | PCy_3 | PhSiH_3 | 48 | <1 |
| 3 | PdCl_2 | Xantphos | PhSiH_3 | 7 | 36 |
| 4 | $\text{PdCl}_2(\text{PCy}_3)_2$ | — | PhSiH_3 | 65 | <1 |
| 5 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | PhSiH₃ | 84 | <1 |
| 6 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L2 | PhSiH_3 | 70 | <1 |
| 7 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L3 | PhSiH_3 | 74 | <1 |
| 8 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L4 | PhSiH_3 | 41 | 23 |
| 9 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | Ph_2SiH_2 | 57 | <1 |
| 10 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | PMHS | 9 | 1 |
| 11 | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | Et_3SiH | <1 | 0 |
| 12 ^b | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | H_2 | 2 | <1 |
| 13 ^c | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | PhSiH_3 | 34 | 2 |
| 14 ^d | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | PhSiH_3 | 12 | 4 |
| 15 ^e | $\text{PdCl}_2(\text{PCy}_3)_2$ | L1 | PhSiH_3 | 78 | <1 |

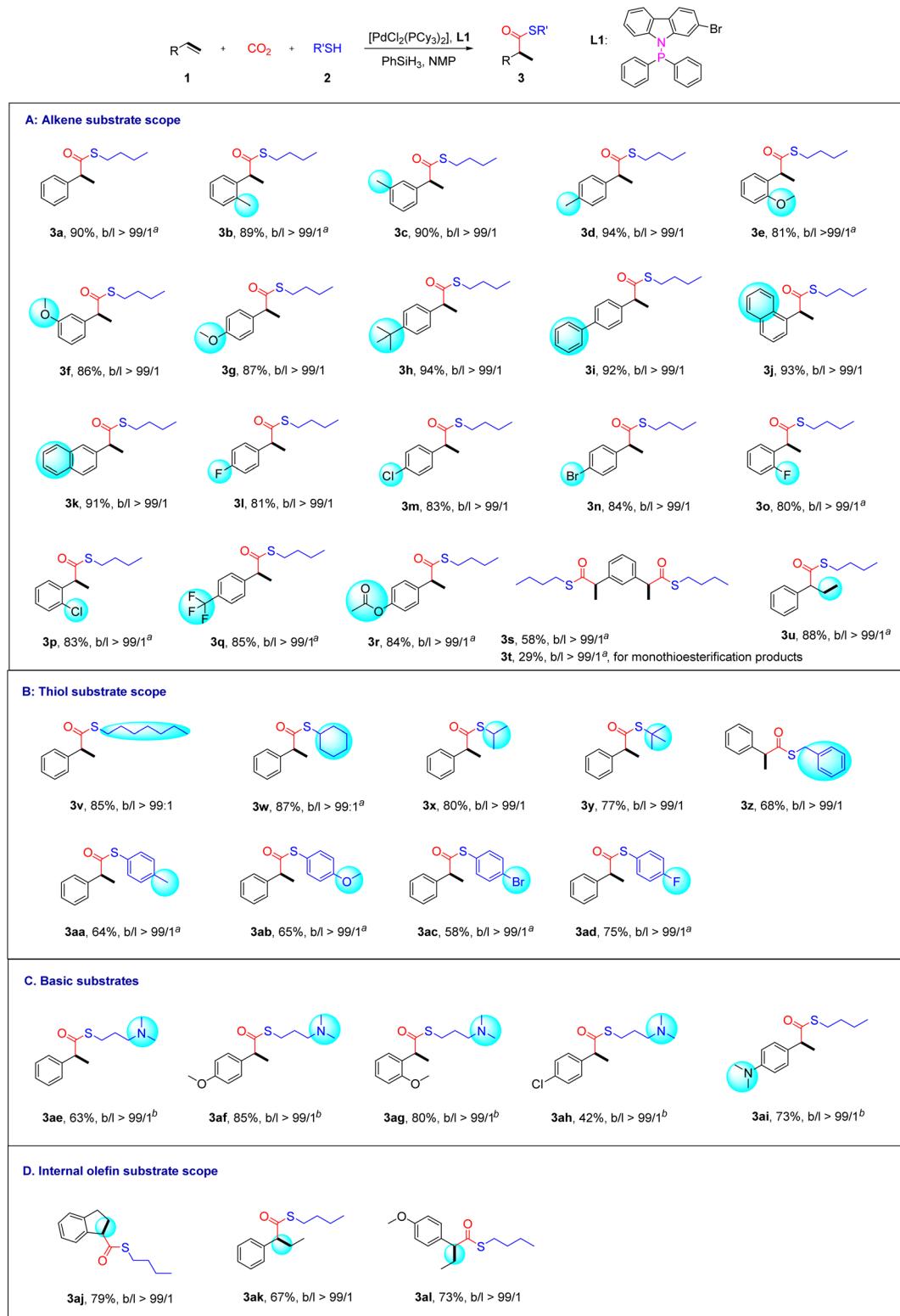


^a Reaction conditions: **1a** (0.2 mmol), **2a** (1.7 equiv.), [Pd] (5.0 mol%), monophosphine ligand (10.0 mol%), bidentate phosphine ligand (5.0 mol%), [Si–H] (1.8 equiv.), CO_2 (20 bar), 80 °C, 18 h. PMHS = polymethylhydrosilane. ^b H_2 (10 bar). ^c *p*-TsOH (20.0 mol%). ^d $\text{B}(\text{OH})_3$ (20.0 mol%). ^e $\text{PdCl}_2(\text{PCy}_3)_2$ (2.0 mol%). Yields of **3a** and **4a** were determined by GC analysis using dodecane as the internal standard.

lyze the reaction with high selectivity for branched thioesters, resulting in a yield of 65% (Table 1, entry 4). The best result was obtained through the use of **L1** (84% yield) (Table 1, entry 5). We found that the addition of **L1** suppressed the hydrothiolation side-reaction and increased the yield. These results show the importance of ligand effects in both reactivity and selectivity in thiocarbonylation of alkenes. The use of other mono or di-phosphines led to decreased yields or lower selectivity (Table 1, entries 6–8). In addition, the use of H_2 or other hydrosilanes instead of PhSiH_3 was not suitable (Table 1, entries 9–12). To our surprise, different from previously reported methods using CO relying on the use of Brønsted acid additives,^{10–12} the addition of *p*-TsOH or $\text{B}(\text{OH})_3$ significantly inhibited the desired reaction (Table 1, entries 13 and 14). According to literature research, acidic conditions may not be conducive to the catalytic conversion of CO_2 .²⁸ When the amount of catalyst was reduced to 2 mmol%, the yield reduced to 78% (Table 1, entry 15).

With the optimized reaction conditions in hand, we next explored the substrate scope of this methodology. First, different styrene substrates were screened (Scheme 2A). In general, various thioester products were smoothly obtained from styrene derivatives bearing either electron-withdrawing or electron-donating groups. Specifically, styrenes containing *ortho*-, *meta*- or *para*-halogen (F, Cl, or Br), alkyl (Me, ⁴Bu, or F_3C), aryl (Ph), ether (OMe), or ester (OAc) groups were compa-





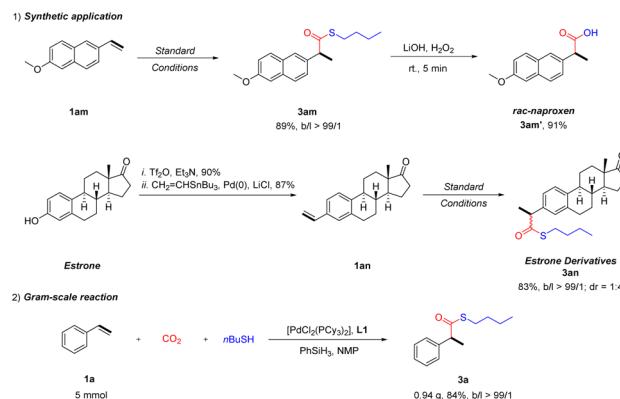
Scheme 2 Synthesis of branched thioesters by thiocarbonylation of alkenes. Reaction conditions: olefin (0.2 mmol), thiol (1.7 equiv.), $\text{PdCl}_2(\text{PCy}_3)_2$ (5.0 mol%), L1 (10.0 mol%), PhSiH₃ (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL), and stirred at 80 °C for 18 h; branched to linear ratios determined by GC-MS. ^aWith ZnI_2 (20 mol%). ^bWith DABCO (20 mol%), DABCO = 1,4-diazabicyclo [2.2.2] octane. Isolated yields of branched products.

table. These substrates were converted into branched thioesters in good yields (**3b**–**3i**, **3l**–**3r**, 80%–94%). Naphthyl alkenes also appeared to be suitable for this transformation (**3j**–**3k**). Meanwhile, we found that the addition of zinc iodide could further improve the yields. According to the literature, zinc iodide might act as a weak Lewis acid to activate the carbonyl oxygen of CO_2 .^{21b} For the diolefin substrate, the reaction can give dithioesterified products **3s** and monothioesterified products **3t**, with dithioester as the major product. The terminal non-conjugated alkene allylbenzene was exclusively converted into the branched product **3u** in good yield *via* chain walking of Pd–H.

Unfortunately, simple aliphatic olefins are prone to olefin isomerization, so they are not suitable substrates. Next, the generality of the procedure was tested on various thiol substrates (Scheme 2B). In most cases, this transformation provided the desired branched thioester products in moderate to good yields (58–87%). Among them, aliphatic primary, secondary and tertiary thiols furnished high yields of branched products **3v**–**3y**. The use of benzylthiol also resulted in product **3z** with a moderate yield of 68%. Thiophenols led to the formation of the desired thioester product with only a minor amount of linear thioether as the by-product (**3aa**–**3ad**). In general, as arylthiols are poorer nucleophiles than alkylthiols, they are more likely to go through hydrothiolation of styrenes.²⁹

To our delight, alkaline substrates with amino groups and internal alkenes are also tolerated in our system (Scheme 2C and D). The amino functional group is a very important structural fragment in organic chemistry. By fine-tuning the reaction conditions, products **3ae**–**3ai** were successfully obtained with the addition of DABCO (42%–85% yields) (Scheme 2C). The role of DABCO might be related to the increase of CO_2 concentration in the solution.²⁸ As shown in Scheme 2D, under optimized conditions, internal alkenes with steric hindrance were also transformed into the desired branched thioesters in moderate to good yields (**3aj**–**3al**, 67%–79%). We believe that this result might originate from the advantages of the neutral-Pd-mediated catalytic procedure compared to cationic palladium catalytic systems that use CO. The stronger hydridic character of Pd–H (chemical shift: *ca.* –14 ppm *vs.* *ca.* –7 ppm for cationic Pd–H in ^1H NMR) might make the insertion of olefin molecules more efficient,³⁰ and thus under neutral conditions, it allows good yields for internal olefin substrates and basic substrates. In addition, competition reactions between different substrates were carried out as well (Scheme S4†).

Furthermore, the applicability of this method was studied (Scheme 3). 2-Arylpropionic acids are related to nonsteroidal anti-inflammatory drugs (NSAIDs).³¹ Starting from 6-methoxy-2-vinylnaphthalene **1am**, naproxen **3am'** was obtained in high yield after convenient hydrolysis of thioester **3am**. Estrone is an important female hormone.³² Under standard conditions, the estrone derivative **3an** can be successfully prepared with a yield of 83%. Moreover, a gram-scale reaction proceeds well, giving the desired product with 84% yield. In addition, pre-



Scheme 3 Application study.

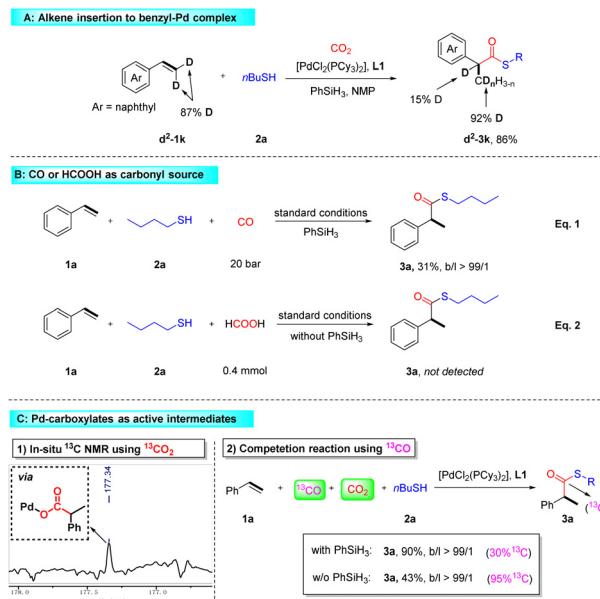
liminary attempts on the asymmetric thiocarbonylation of styrene were carried out. It was found that with the addition of the chiral ferrocene derived ligand, the *enantio*-enriched branched product can be obtained with 38% yield and 46% ee. Further exploration of this asymmetric process is underway.

Mechanistic studies were conducted to further understand the CO_2 -based thiocarbonylation system. First, to verify the source of hydride in the Pd–H species, *in situ* NMR experiments in a J. Young/valved NMR tube were carried out. As shown in Fig. S2,† by mixing $\text{PdCl}_2(\text{PCy}_3)_2$ and PhSiH_3 in C_6D_6 at 80 °C for 4 h, hydride signals were not detected (Fig. S2-A†). After adding $n\text{BuSH}$ to the above reaction solution at 80 °C for 1 h, new species at –14.36 ppm in ^1H NMR (Fig. S2-B†) and 42.10 ppm in ^{31}P NMR (Fig. S3-B†) were observed, which might correspond to the formation of *trans*-Pd(PCy_3)₂(H) (SC_4H_9).^{30a,b} Furthermore, on heating the above mixture at 80 °C for 4 h or 18 h, the strength of the hydride signal increased (Fig. S2-C and D†). These results suggested that thiols play an important role in the formation of the Pd(II)–H species.³³ It could involve a process in which phenylsilane first reduces Pd(II) to Pd(0), followed by a reaction with thiols to generate the crucial Pd(II)–H species.

Then, deuterium labeling experiments were performed (Scheme S2†). When deuterated heptanethiol **d-2v** (62% D) was subjected to the reaction, product **d²-3v** (18% D in CH and 54% D in $\text{CD}_n\text{H}_{3-n}$) was obtained in 81% yield (Scheme S2-a†). Further experiments using PhSiD_3 indicate that hydride exchange between PhSiD_3 and Pd–H might exist (Scheme S2-b†). Meanwhile, the hydropalladation reaction of palladium hydride to the alkylpalladium species was found to be reversible when **d²-1k** was used as the starting material (Scheme 4A).

Furthermore, in order to test the possibility of CO or HCOOH as the intermediate, control experiments were performed (Scheme 4B). First, we observed that *ca.* 700 ppm concentration of CO was generated under standard conditions (Scheme S3 and Fig. S4†). Then, by replacing CO_2 with CO under our standard conditions, the product **3a** was obtained in 31% yield, which suggested that CO might be an intermediate in the transformation (Scheme 4B, eqn (1)). In addition, the reduction of CO_2 by PhSiH_3 is likely to proceed through the





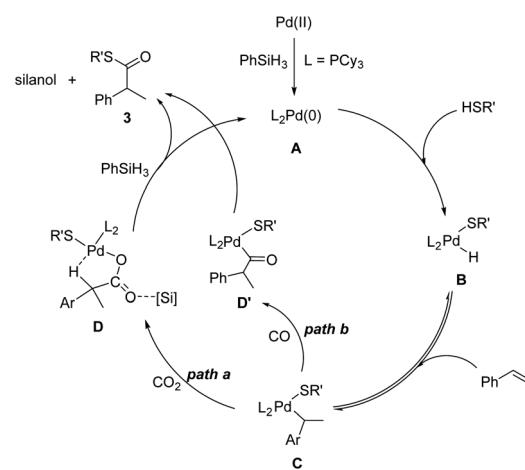
Scheme 4 Experimental studies on the mechanism. Reaction conditions: **1a**/**d²-1k** (0.2 mmol), **2a** (1.7 equiv.), $\text{PdCl}_2(\text{PCy}_3)_2$ (5.0 mol%), **L1** (10.0 mol%), PhSiH_3 (1.8 equiv.), CO_2 (20 bar), NMP (0.5 mL), and stirred at 80 °C for 18 h. Isolated yields of branched products.

formation of silyl formates $\{\text{HC}(\text{O})\text{O-SiR}_3\}$,^{1c} which would readily release CO under heating conditions.³⁴ Indeed, we detected the formation of silyl formate by NMR (Scheme S3, Fig. S5 and S6†). However, on addition of substrate styrene **1a** and *n*BuSH **2a** *in situ*, the formation of product **3a** at 80 °C for 18 h under N_2 conditions was not detected, which suggested that silyl formate might not be the major intermediate. Additionally, by employing HCOOH as the carbonylation source in the absence of PhSiH_3 , no formation of **3a** was observed (Scheme 4B, eqn (2)), which suggested that HCOOH might not be the major intermediate.

Then, *in situ* NMR experiments in a Young/valved NMR tube were carried out (Scheme 4C; left and Fig. S7†). The tube was charged with ¹³CO₂ and then heated at 80 °C for 30 min, and a peak at 177.34 ppm in ¹³C NMR was observed. This signal might correspond to the formation of the Pd-carboxylate species.^{21b,35,36} At the same time, a signal at $\delta = 200.34$ ppm was detected, demonstrating the formation of thioester ¹³C-**3a** (Fig. S7†). To further confirm whether Pd carboxylate is the active intermediate, competition experiments using CO₂ and ¹³CO were performed (Scheme 4C; right and Fig. S10 and S11†). In the presence of silane, a high yield was obtained and the enrichment of the ¹³C atom was only 30 atom%, which was determined and analyzed using HRMS. Considering the formation of only trace amounts of CO from CO₂, it means that 30% of the product is formed from ¹³CO and the other major part (70%) is from CO₂. When silane is absent, the product is almost completely ¹³C-labeled. Moreover, the hydrochloric acid quenching experiment showed the formation of the 2-phenylpropionic acid species (Fig. S8 and S9†). Therefore, we believe that the reaction may

also go through the path of direct CO₂ insertion to form the palladium carboxylate species. The free radical mechanism was excluded through the reaction with the addition of butylated hydroxytoluene (see the ESI for details†).³⁷

Based on the experimental results and previous reports, we propose a plausible reaction mechanism for the thiocarbonylation of alkenes using CO₂ (Scheme 5).^{10–12,38,39} First, Pd(0) species is formed from the reduction of the Pd(II) precursor by PhSiH_3 . The active Pd–H species **B** is generated from the oxidative addition of thiol to the Pd(0) species.^{10a} After insertion of alkenes, the benzyl-Pd complex **C** is generated,⁴⁰ which is then transformed into the carboxylate Pd species **R(CO₂)Pd D** upon insertion of CO₂ into the Pd–C bond (*path a*). According to DFT calculations (Fig. S12†), the palladium carboxylate species **D** is stabilized in the form of a five-membered ring structure. Then, the carboxylate Pd species **D** reacts with PhSiH_3 and thiols to produce the desired product **3** with the regeneration of the Pd(0)/Pd–H species. The formation of silyl ester intermediates might be involved, even though their formation was not detected by *in situ* NMR.^{35a} The carboxylate Pd species **D** reacts with PhSiH_3 to produce silyl ester intermediates, which are subsequently attacked by thiolate ions to yield the desired product **3** and silanol. According to the literature, the ligand effect is crucial and it can determine the rate of CO₂ insertion into the Pd–C bond.^{35a} Ligands such as the N–P ligand with higher nucleophilicity or steric hindrance properties may be beneficial in our system. The reaction of aliphatic alkene substrates only gave isomerized alkene products, which indicates that the route from **B** to **C** is favorable and reversible for both aromatic and aliphatic alkene substrates. However, the formation of the thermodynamically more stable benzyl palladium intermediate **C** is believed to be crucial for the slow CO₂ insertion step.⁴¹ This explains why aliphatic alkenes are not suitable substrates. At the moment, CO produced from the reaction between CO₂ and silanes also participates in the reaction cycle through *path b* to generate the acyl palladium species **D'**, which is subsequently attacked by thiol directly, resulting in the formation of the Pd–H species **B**.



Scheme 5 Plausible reaction pathways for thiocarbonylation using CO₂.



or undergoing reductive elimination to produce thioester product 3.

Furthermore, the stability of the key intermediate Pd carboxylates was evaluated by computational calculations (Fig. S12†). The vibrational frequencies and the changes in Gibbs free energy (ΔG) values at 298 K were both calculated. And no imaginary frequency appears (see the ESI for the data of the vibrational frequency†), which indicates that D is a stable intermediate. Meanwhile, the conversion of C to D is exothermic by 5.6 kcal mol⁻¹ and thermodynamically advantageous, which indicates that the intermediate D is favored at 298 K. Therefore, based on the computational calculations, we can conclude that intermediate D with a five-membered ring structure is stable.

Conclusions

In summary, highly regioselective and efficient thiocarbonylation of alkenes using CO₂ as a source of the carbonyl group has been developed for the first time. This versatile protocol provides a straightforward and CO-free route to an array of valuable thioesters in moderate to good yields. The success of this thiocarbonylation reaction is attributed to the careful selection of Pd catalysts and the novel N-P-type carbazolyl phosphine ligands. Good functional group tolerance with a broad substrate scope was achieved. We speculate this reaction proceeded *via* the Pd carboxylate intermediate, and the CO pathway cannot be excluded. This method demonstrates the benefits of using CO₂ for the synthesis of carbonyl compounds from internal alkenes and basic reactants, providing promising potential in the synthesis of bio-relevant molecules.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

Y. L. directed and coordinated the project. H. W., C. L., Y. L. and J. C. performed the experiments, analysed the data and prepared the ESI.† Y. L., H. W. and S. L. wrote the paper. S. L. contributed to DFT mechanistic studies.

Conflicts of interest

The authors declare no conflict of interest.

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