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# Ni-Catalyzed Carboxylation of C(sp<sup>2</sup>)-S bonds with CO<sub>2</sub>: Evidence for the Multifaceted Role of Zn

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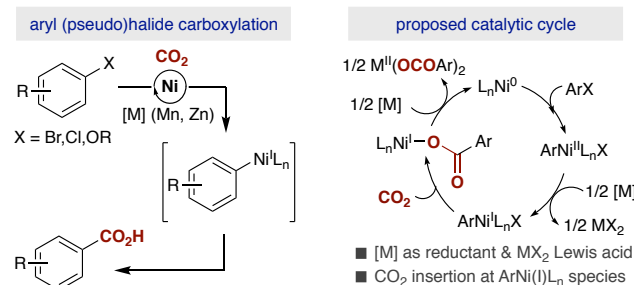
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**KEYWORDS:** Carboxylation, Nickel, C-S cleavage, Carbon dioxide, Zinc.

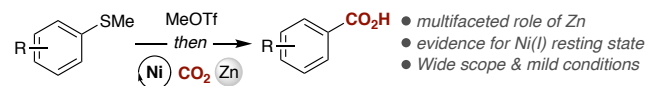
**ABSTRACT:** Nickel-catalyzed reductive carboxylation reactions of aryl electrophiles typically require the use of metallic reducing agents. At present, the prevailing perception is that these serve as both a source of electrons and as sources of Lewis acids that may aid CO<sub>2</sub> insertion into the Ni-C bond. Herein, we provide evidence for the in situ formation of organometallic species from the metallic reductant, a step that has either been ruled out or has been unexplored in catalytic carboxylation reactions with metal powder reductants. Specifically, we demonstrate that Zn(0) acts as a reductant and that Zn(II) generates arylzinc species that might play a role in the C(sp<sup>2</sup>)-S carboxylation of arylsulfonium salts. Overall, the reductive Ni-catalyzed C(sp<sup>2</sup>)-S carboxylation reaction proceeds under mild conditions in a non-amide solvent, displays a wide substrate scope, and can be applied to a formal *para* C-H carboxylation of arenes.

Nickel-catalyzed reductive carboxylation reactions of organic (pseudo)halides with CO<sub>2</sub> have recently gained considerable momentum as routes to carboxylic acids, privileged molecules in a myriad of biologically relevant scaffolds (Scheme 1).<sup>1,2</sup> Despite the advances realized, the intricacies of these reactions still remain speculative, probably due to the difficulty in accessing well-defined catalytically relevant species and the non-trivial roles exerted by the ligands and/or additives.<sup>3</sup> Although Zn(0) and Mn(0) are typically employed in these endeavors as a source of electrons in order to access Ni(0)L<sub>n</sub> and Ni(I)L<sub>n</sub> species within the catalytic cycle,<sup>2</sup> Hazari has recently shown that Mn(II) salts derived from these reductions might also play a beneficial role in the carboxylation of aryl chlorides.<sup>3d,4</sup> Overall, these observations underscore our limited mechanistic knowledge of carboxylation processes and suggest that a better understanding of the roles of the metallic reductants may in turn lay the foundation for improving these reactions.

## Scheme 1. Metallic reductants in carboxylation reactions.



## Scheme 2. Carboxylation of arylsulfonium salts.



Driven by the ready availability and synthetic versatility of organosulfur compounds, we wondered whether it would be possible to develop a Ni-catalyzed reductive carboxylation of arylsulfonium salts via C(sp<sup>2</sup>)-S cleavage (Scheme 2).<sup>5-8</sup> The choice of this electrophile is not arbitrary.<sup>9</sup> First, arylsulfonium salts are bench-stable compounds that are easily accessed on a large scale from simple aryl sulfides upon treatment with an appropriate electrophilic partner. Second, the neutral R<sub>2</sub>S leaving group of the sulfonium moiety should not compete for binding at the nickel center.<sup>10,11</sup> Furthermore, the electron-deficient nature of the arylsulfonium salt should facilitate oxidative addition at Ni(0)L<sub>n</sub>.<sup>12</sup> If successful, we recognized that such a reaction would not only provide an unrealized opportunity to enable a catalytic C-S functionalization/CO<sub>2</sub> fixation, but would also offer the possibility to study mechanistic aspects of the reaction, such as the role of the metal reductant in the targeted carboxylation event. As part of our ongoing interest in catalytic carboxylations<sup>13,14</sup> and C-S bond functionalization,<sup>7d,11b,f,g</sup> we report herein the successful realization of a mild catalytic carboxylation of arylsulfonium salts. Importantly, we provide evidence for the intermediacy of a Ni(I) species and the involvement of organozinc species, thus revealing a multifaceted role played by

Zn that may have implications in related reductive cross-coupling endeavors.

Our investigations began by evaluating the catalytic carboxylation of **2a**, which is readily obtained on a multigram scale from the corresponding aryl sulfide **1a** by treatment with MeOTf. After some experimentation, we found that **2a** underwent carboxylation with CO<sub>2</sub> (1 atm) in the presence of a Ni(II) precatalyst bearing **L1** and Zn powder to give **3a** in 84% isolated yield at room temperature (Table 1, entry 1). Of particular note was the use of DMSO as the solvent (entries 8 and 9): our protocol is therefore a rare example of a Ni-catalyzed reductive carboxylation that avoids toxic amide solvents such as DMF, DMA, or NMP.<sup>3d,15</sup> As anticipated, the nature of the ligand was critical to success, with phenanthroline ligands possessing substituents adjacent to the nitrogen atoms providing the best results (entries 2-6). Strikingly, Zn ( $E^\circ = -0.76$  V vs SCE)<sup>16</sup> was uniquely suited for the carboxylation of **2a** and no acid was obtained with stronger reductant Mn ( $E^\circ = -1.32$  V vs SCE, entry 11).<sup>17</sup> Likewise, the use of homogeneous reductants such as tetrakis(dimethylamino)ethylene (TDAE;  $E^\circ = -0.62$  V vs SCE)<sup>16</sup>, DMAP-OED ( $E^\circ = -1.24$  V vs SCE)<sup>18</sup>, or CoCp<sub>2</sub> ( $E^\circ = -0.87$  V vs SCE)<sup>19,20</sup> did not deliver **3a** (entries 12-14). Importantly, direct reduction of **2g** by Zn only gave a 3% yield of aryl sulfide **1g**, while reaction between DMAP-OED and **2f** gave a 60% yield of **1f**.<sup>21</sup> The use of Mn did not result in the formation of **1a**. Together, these experiments suggest that Zn does not solely act as a reductant during the catalytic cycle and that other scenarios might come into play. Control experiments revealed that both Ni and Zn were critical for success (entry 15). In particular, we observed that *p*-tolylSMe did not undergo

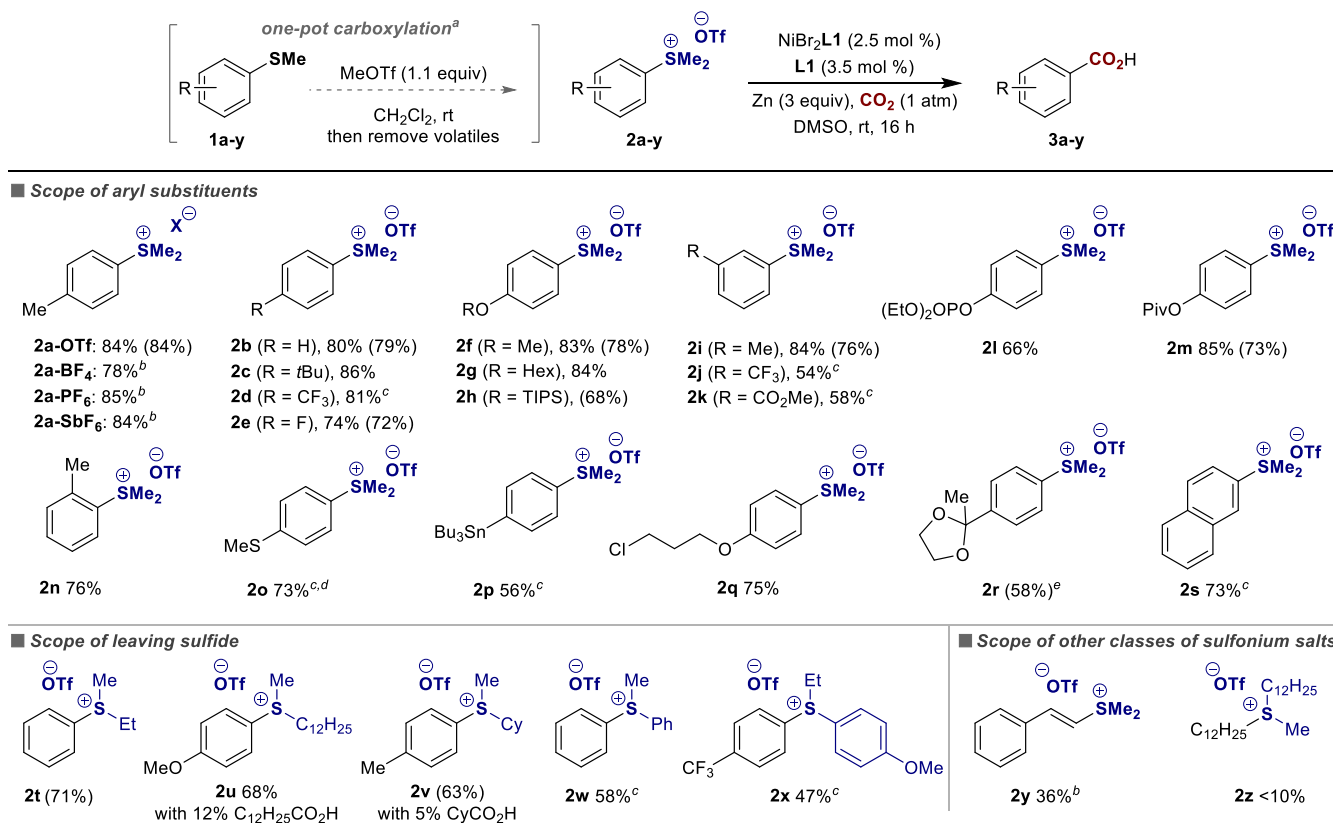
carboxylation, ruling out the requirement for aryl sulfide intermediates during the carboxylation of arylsulfonium salts.

**Table 1. Optimization of the Reaction Conditions.**

entry	deviation from standard conditions	<b>3</b> (%) <sup>b</sup>
1	none	<b>87 (84)<sup>c</sup></b>
2	<b>L2</b> instead of <b>L1</b>	48
3	<b>L3</b> instead of <b>L1</b>	33
4	<b>L4</b> instead of <b>L1</b>	56
5	<b>L5</b> instead of <b>L1</b>	47
6	NiCl <sub>2</sub> (dppf) instead of NiBr <sub>2</sub> L <sub>1</sub> /L <sub>1</sub>	3
7	Ni(COD) <sub>2</sub> /L <sub>1</sub> instead of NiBr <sub>2</sub> L <sub>1</sub>	86
8	DMA (DMF) instead of DMSO	13 (28)
9	NMP as solvent	15
10	<i>p</i> -C <sub>6</sub> H <sub>4</sub> SMe ( <b>1a</b> ) instead of <b>2a</b>	0
11	Mn instead of Zn	0
12	TDAE (3 equiv) instead of Zn	0 <sup>d</sup>
13	DMAP-OED (3 equiv) instead of Zn	0 <sup>d,e</sup>
14	CoCp <sub>2</sub> (3 equiv) instead of Zn	0
15	no Zn or no Ni/L <sub>1</sub>	0

<sup>a</sup> **2a** (0.30 mmol), NiBr<sub>2</sub>L<sub>1</sub> (2.5 mol %), L<sub>1</sub> (3.5 mol %), Zn powder (0.90 mmol), CO<sub>2</sub> (1 atm), DMSO (1.5 mL) at rt for 16 h followed by acidic workup. <sup>b</sup> NMR yields using 1,1,2,2-tetrabromoethane as internal standard. <sup>c</sup> Isolated yield. <sup>d</sup> A similar result was found with the addition of 1 equiv Zn(OTf)<sub>2</sub>. <sup>e</sup> THF solvent.

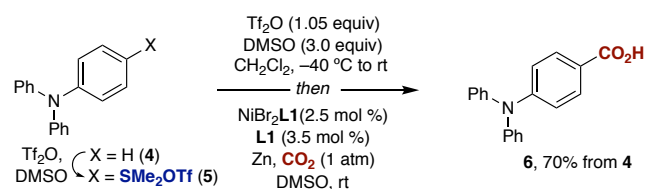
**Scheme 3. Scope of the Catalytic Carboxylation of Arylsulfonium Salts.**



<sup>a</sup> Isolated yield from arylsulfonium salts. Yields in one-pot carboxylation of aryl sulfides are shown in parentheses. <sup>b</sup> Yield was determined by NMR using 1,1,2,2-tetrabromoethane as an internal standard. <sup>c</sup> 5.0 mol % NiBr<sub>2</sub>L1 and 7.0 mol % L1 was used. <sup>d</sup> 5% of **2b** was also formed. <sup>e</sup> Obtained as 4-acetylbenzoic acid after acidic workup.

With optimized conditions in hand, we investigated the generality of the reaction (Scheme 3). Overall, electron-neutral or electron-rich arylsulfonium salts showed good-to-excellent reactivity regardless of the counterion.<sup>21,22</sup> Likewise, groups that are also reactive in Ni-catalyzed reactions – esters (**2k**, **2m**), aryl fluorides (**2e**), phosphonates (**2l**), ethers (**2f**, **2g**, **2h** and **2q**) and alkyl chlorides (**2q**) – were all well tolerated. We note that reactions of electron-deficient substrates (**2d**, **2j** and **2k**) were carried out with higher catalyst loadings due to competitive reductive demethylation by Zn.<sup>21</sup> As expected, a substrate possessing an aryl methyl sulfide group was selectively carboxylated at the sulfonium moiety (**2o**). Surprisingly, the carboxylation reaction could be conducted in the presence of an organotin group (**2p**), providing ample room for further derivatization via orthogonal Stille-Migita-Kosugi cross-coupling reactions. Unfortunately, pyridyl sulfides could not be transformed to sulfonium salts with MeOTf due to preferential N-methylation. As shown for **2n**, the use of an *ortho*-substituted arylsulfonium salts did not hinder the reaction.<sup>22</sup> Similar results were also obtained regardless of the alkyl substituents on the sulfonium moiety (**2t-2v**). Note, however, that non-negligible amounts of alkyl carboxylic acids were sometimes obtained via C(*sp*<sup>3</sup>)-S bond cleavage. Interestingly, the reaction can also be extended to diarylsulfonium salts (**2w**). For unsymmetrically substituted analogues (**2x**), carboxylation occurred preferentially at the most electron-deficient C-S bond. As demonstrated by the successful carboxylation of  $\beta$ -styrylsulfonium **2y**, C(*sp*<sup>2</sup>)-S carboxylation is not limited to arylsulfonium salts. Unfortunately, the reaction could not be extended to trialkylsulfonium salts (**2z**). Particularly noteworthy was the observation that the catalytic carboxylation of a variety of arylsulfonium salts can be carried out in a one-pot procedure from the parent aryl sulfide after simply removing volatiles upon completion of the reaction with MeOTf. The versatility and synthetic applicability of our protocol is further illustrated in Scheme 4. As shown, **6** can easily be obtained from **4** by telescoping the formation of the arylsulfonium salt **5** without isolation. Indeed, the successful preparation of **6** indicates that *sulfonium salts might be used as linchpins in formal para-C(sp<sup>2</sup>)-H carboxylation reactions.*<sup>23</sup> This is particularly important, as it might lead to new knowledge in synthetic design for incorporating CO<sub>2</sub> at remote C(*sp*<sup>2</sup>)-H bonds.

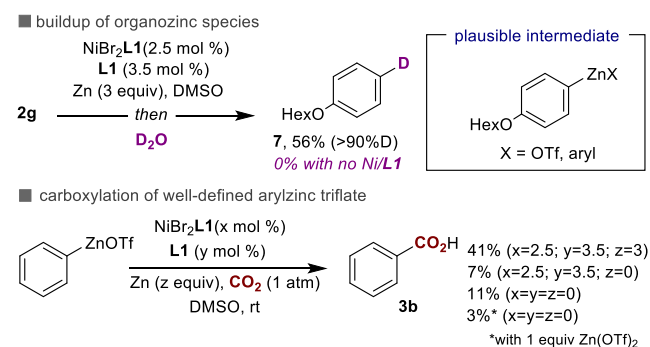
#### Scheme 4. Formal *para*-C(*sp*<sup>2</sup>)-H carboxylation of arenes.



Encouraged by the preparative aspects of our catalytic carboxylation reaction, we turned our attention to studying the mechanistic intricacies of the reaction. Interestingly, exposing **2g** to the optimized conditions *in the absence of CO<sub>2</sub>* followed by a D<sub>2</sub>O quench led to **7** in 55% yield and with >90% D incorporation (Scheme 5, *top*). This suggested a build-up of basic aryl organometallic species in solution.<sup>24</sup> Considering that *the Ni catalyst is required for the carboxylation to occur, the*

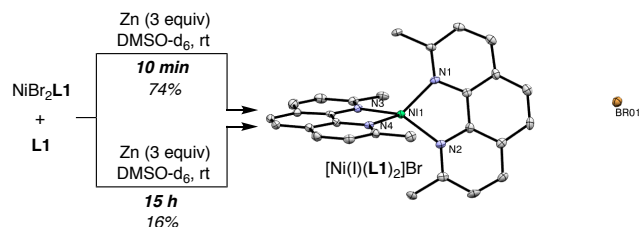
*formation of 3 suggests that a Ni-to-Zn transmetalation might occur prior to CO<sub>2</sub> insertion.*<sup>25,26</sup> This notion was investigated by attempting the carboxylation of phenylzinc triflate with CO<sub>2</sub> in order to determine whether arylzinc species were competent reaction intermediates (Scheme 5, *bottom*). Low conversions to **3b** were observed in the absence of Ni(II) or Zn(0), and a high yield was only observed in the presence of *both* the Ni catalyst and Zn(0). Although Zn(OTf)<sub>2</sub> may promote carboxylation of PhZnOTf as a Lewis acid,<sup>27</sup> its addition did not result in an increased yield of **3b**. These results provide evidence that the carboxylation event is assisted by the Ni catalyst regardless of whether or not arylzinc species are formed.<sup>15a,27</sup>

#### Scheme 5. Intermediacy of Arylzinc Species.



Aiming at shedding light on the origin of C(*sp*<sup>2</sup>)-S cleavage, we next turned our attention to investigating the formation of Ni(0)L<sub>n</sub> from Ni(II)L<sub>n</sub> prior to oxidative addition. In order to mimic the optimized catalytic carboxylation conditions, we monitored the reduction of NiBr<sub>2</sub>L1 with Zn(0) using <sup>1</sup>H NMR spectroscopy. The formation of DMSO-ligated Ni(II) species was observed upon dissolving NiBr<sub>2</sub>L1 in DMSO-*d*<sub>6</sub> and the formation of a DMSO adduct was confirmed by X-ray crystallography.<sup>28</sup> In the presence of Zn(0), NiBr<sub>2</sub>L1 was transformed within 10 minutes into a deep blue paramagnetic Ni(I) complex in 74% yield (Scheme 6). X-ray crystallography identified this complex as [Ni(I)(L1)<sub>2</sub>]Br, with the halide anion being outer-sphere.<sup>29,30</sup> After longer reaction times, we observed that the yield [Ni(I)(L1)<sub>2</sub>]Br had reduced to only 16%, suggesting the formation of further reduced Ni(0)L1 species. Unfortunately, these Ni(0) species could not be quantified, probably due to the very poor solubility of Ni(L1)<sub>2</sub> in DMSO.<sup>31</sup> However, evidence for the presence of Ni(0) was obtained by addition of Ph<sub>2</sub>S<sub>2</sub> or 1,5-cyclooctadiene to the reaction mixture, leading to the observation of oxidized products and COD-bearing complexes, respectively.<sup>32</sup> These experiments provided indirect evidence for the formation of Ni(0) species from the overall reaction between NiBr<sub>2</sub>L1 and Zn. This contrasts with a recent report by Diaio where the formation of Ni(0) from a related Ni(bipyridine)/Zn system was ruled out.<sup>33</sup>

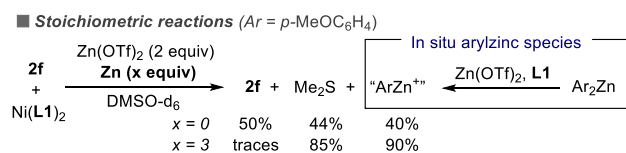
#### Scheme 6. Formation of a Ni(I) Complex.



Prompted by the results shown in Scheme 6, we investigated the catalytic relevance of  $[\text{Ni}(\text{I})(\text{L}1)_2]^+$  complexes in the carboxylation of arylsulfonium salts. Indeed, analyzing the catalytic carboxylation of **2f** by both NMR and EPR spectroscopy allowed us to detect the presence of  $[\text{Ni}(\text{I})(\text{L}1)_2]\text{OTf}$  during catalysis. An aliquot removed after 1 h of reaction showed that of the initial catalyst loading (5 mol %), 60% of the Ni existed as  $[\text{Ni}(\text{I})(\text{L}1)_2]\text{OTf}$ . After 3.5 h this was 44%.<sup>30</sup> This finding is particularly relevant as it suggests that  $[\text{Ni}(\text{L}1)_2]\text{OTf}$  may be a catalyst resting state. With evidence for both Ni(I) and Ni(0) intermediates in hand, stoichiometric experiments were carried out with  $\text{Ni}(\text{L}1)_2$  in order to study oxidative addition of the  $\text{C}(\text{sp}^2)\text{-S}$  bond (Scheme 7). First, reaction of **2f** with  $\text{Ni}(\text{L}1)_2$  and  $\text{Zn}(\text{OTf})_2$  – produced during every turnover of the catalyst – resulted in 50% conversion of **2f** and a 44% yield of  $\text{Me}_2\text{S}$ , with  $[\text{Ni}(\text{L}1)_2]\text{OTf}$  (70%) being the only Ni species detected by  $^1\text{H}$  NMR spectroscopy.<sup>34</sup> Interestingly, the presence of  $\text{Zn}(0)$  led to full conversion of **2f** and an 80% yield of  $\text{Me}_2\text{S}$ , indicating that Zn could generate Ni(0) species from  $[\text{Ni}(\text{L}1)_2]\text{OTf}$ .

Overall, these experiments provide further evidence that the targeted  $\text{C}(\text{sp}^2)\text{-S}$  bond cleavage occurs at Ni(0). Although the isolation of an oxidative addition complex of an arylsulfonium salt to  $\text{Ni}(\text{L}1)_2$  proved to be elusive, we were able to track the fate of the aryl group after  $\text{C}(\text{sp}^2)\text{-S}$  cleavage. Specifically, reactions between **2f** and  $\text{Ni}(\text{L}1)_2$  carried out in the presence of  $\text{Zn}(\text{OTf})_2$  revealed new  $^1\text{H}$  NMR signals that were assigned to arylzinc species based on the identical  $^1\text{H}$  NMR data obtained upon reaction of  $\text{ZnAr}_2$  with  $\text{Zn}(\text{OTf})_2/\text{L}1$  (Scheme 7).<sup>35</sup> Putting everything into perspective, we believe these experiments provide a strong argument for the formation of arylzinc species after  $\text{C}(\text{sp}^2)\text{-S}$  cleavage by  $\text{Ni}(0)\text{L}_n$ .<sup>26</sup>

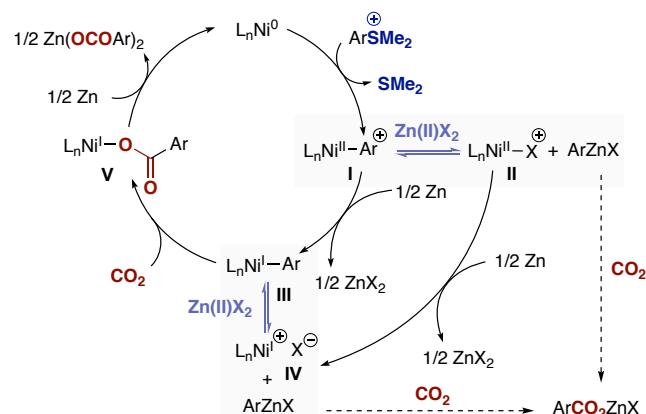
### Scheme 7. Stoichiometric Experiments with $\text{Ni}(\text{L}1)_2$ .



In light of our results, we propose the mechanistic scenario depicted in Scheme 8, which includes *Ni-to-Zn* transmetalation steps. At this stage, it is unclear whether the product of  $\text{C}(\text{sp}^2)\text{-SMe}_2^+$  oxidative addition (**I**) undergoes transmetalation with  $\text{Zn}(\text{II})$  to give Ni(II) complex **II** or whether **I** is first reduced to  $\text{Ar-Ni}(\text{I})$  species **III** prior to transmetalation en route to **IV** and  $\text{ArZnX}$ . The latter may be more feasible when comparing the nucleophilicities of the nickel centers of **I** and **III**.<sup>3a,35</sup> Whether **IV** indeed corresponds to  $[\text{Ni}(\text{L}1)_2]\text{OTf}$  – identified in the catalytic carboxylation reaction – requires further investigations.<sup>36,37</sup> After  $\text{CO}_2$  insertion to  $\text{Ar-Ni}(\text{I})$  species **III**, the resulting carboxylate complex **V** is either directly reduced to  $\text{Ni}(0)\text{L}_n$  or undergoes anion exchange with  $\text{ZnX}_2$  to form **IV** prior to reduction.<sup>3d,25</sup> Given that carboxylation of  $\text{PhZnOTf}$  required the presence of both Ni and Zn for yields to surpass ca. 10%, we

suggest that  $\text{ArZnX}$  species may serve as a reservoir of the aryl group rather than as species at which significant amounts of carboxylation occurs. This observation is particularly relevant in the context of Ni-catalyzed cross-electrophile coupling reactions mediated by Zn, because these results contribute to the perception that the role of the metallic reductant in these endeavors might not be as straightforward as one might initially anticipate and that further investigations might be required to unravel the intricacies of these processes.<sup>38</sup>

### Scheme 8. Proposed Mechanistic Rationale.



In conclusion, we have developed a mild Ni-catalyzed reductive carboxylation of arylsulfonium salts that is mediated by Zn and offers reactivity complementary to that observed with aryl (pseudo)halides. Our studies have provided evidence for the formation of organozinc intermediates during the reaction, suggesting that Ni-to-Zn transmetalation is plausible and that a greater variety of mechanistic pathways may need to be studied depending on the aryl electrophile.

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### Note

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### Supporting Information

Experimental procedures, crystallographic data and spectral data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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