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Intermediacy of Ni–Ni Species in \( sp^2 \) C–O Bond Cleavage of Aryl Esters: Relevance in Catalytic C–Si Bond Formation

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ABSTRACT: Monodentate phosphine ligands are frequently employed in the Ni-catalyzed C–O functionalization of aryl esters. However, the extensive body of preparative work on such reactions contrasts with the lack of information concerning the structure and reactivity of the relevant nickel intermediates. In fact, experimental evidence for a seemingly trivial oxidative addition into the C–O bond of aryl esters with monodentate phosphines and low-valent nickel complexes still remains elusive. Herein, we report a combined experimental and theoretical study on the Ni(0)/PCy$_3$ catalyzed silylation of aryl pivalates with CuF$_2$/CsF additives that reveals the involvement of unorthodox dinickel oxidative addition complexes in C–O bond cleavage and their relevance in C–Si bond formation. We have obtained a mechanistic picture that clarifies the role of the additives and demonstrates that dinickel complexes act as reservoirs of the propagating monomeric nickel complexes by disproportionation. We believe this study will serve as a useful entry point to unravelling the mechanistic underpinnings of other related Ni-catalyzed C–O functionalization reactions based on monodentate phosphines.

Prompted by the broad accessibility, thermal stability and cost-efficiency of phenol derivatives, C–O electrophiles have recently gained momentum as alternatives to aryl halides in cross-coupling reactions.\(^1\) Although activated aryl sulfonates have been widely adopted in the cross-coupling arena, much less attention has been devoted to much simpler aryl esters (Scheme 1). Unlike aryl sulfonates, aryl esters are not cleaved with Pd catalysts; however, aryl ester C–O bond cleavage readily occurs with cheap and Earth-abundant Ni catalysts, thus providing the opportunity to employ this functional group in orthogonal cross-coupling reactions in the presence of aryl halide partners.

**Scheme 1.** C–O electrophiles in cross-coupling reactions.

Despite the advances realized in Ni-catalyzed cross-coupling reactions of aryl esters,\(^1\) these processes are poorly understood in mechanistic terms, and progress in the field is typically based on empirical discoveries.\(^2\) At present, there seems to be consensus that \( sp^2 \) C–O activation is initiated by oxidative addition to well-defined Ni(0)L$_n$. To the best of our knowledge, Itami and co-workers isolated and characterized the first direct oxidative addition complex of an aryl ester to Ni(0)L$_n$ (Ni-1) (Scheme 2, left).\(^3\) Specifically, this reaction used bidentate dicyc (1,2-bis(dicyclohexylphosphino)-ethane) as the supporting ligand and required elevated temperatures (100 °C).\(^3\) However, experimental evidence for direct oxidative addition complexes bearing monodentate phosphine ligands (PR$_3$), the most commonly employed ligands in catalytic C–O functionalization reactions, is altogether absent in the literature (Scheme 2, right). Indeed, access to aryl–Ni(II)–OCOR species supported by PR$_3$ has only been reported via indirect pathways, rather than direct oxidative addition.\(^4\) The paucity of oxidative addition complexes supported by PR$_3$ is tentatively attributed to (a) the formation of unstable short-lived entities; (b) the less rigid coordination sphere of PR$_3$ compared to their bidentate analogues; (c) their tendency for rapid ligand dissociation to form fluxional intermediates; and/or (d) the possibility for unproductive disproportionation.
We and others have recently demonstrated that the cross-coupling of aryl esters via \(sp^2\) C–O cleavage is by no means confined to C–C bond formations, and that aminations, stannylation, silylation, and phosphorylations are within reach. In 2014, our group described a mild Ni/Cu-catalyzed C–O silylation of aryl esters using PCy\(_3\) as the ligand (Scheme 3, top). Notably, the coupling of regular arenes posed no problems, which contrasts with a number of C–O cleavage protocols that are limited to extended \(\pi\) systems. It was hypothesized that Cu was acting as a silyl transfer catalyst, and that fluoride ions from CsF/CuF\(_2\) were probably activating the Si–B bond prior to reaction with the Cu complex (Scheme 3, middle). The Ni/Cu couple has also been employed in related silylation or borylation events, among others (Scheme 3, bottom).\(^{15,16}\)

**Scheme 3.** Ni/Cu-catalyzed C–O silylation/borylation.

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Due to the lack of experimental evidence for a classical (PR\(_3\))Ni(0)/(II) cycle with aryl esters and the enigmatic role played by CuF\(_2\) and CsF in many cross-coupling reactions, we sought to elucidate the mechanistic details of the C–O silylation of aryl pivalates. At the outset of our investigation, it was unclear whether it would be possible to unravel the mechanistic underpinnings of this reaction. If successful, we recognized that this would be a significant step forward in the C–O functionalization arena. As part of our efforts in the field of C–O functionalization,\(^{8,9,17}\) we now report a combined experimental and computational study on the C–O silylation of aryl esters. Our work not only sheds light on the role of both Cu and fluoride ions but also demonstrates, for the first time, the role of unorthodox dinickel oxidative addition complexes in C–O cleavage. These rather stable off-cycle species evolve via disproportionation into monomeric aryl-Ni(II) intermediates that ultimately lead to C–Si bond formation. We anticipate that these results will both provide an entry point to further studies on the mechanistic intricacies of related C–O functionalizations and highlight the importance of off-cycle intermediates,\(^{18}\) which may be relevant to improving the efficiency and generality of Ni-catalyzed reactions.

**RESULTS AND DISCUSSION**

Synthesis and characterization of oxidative addition complexes of aryl pivalates to Ni/PCy\(_3\). Although oxidative addition has been invoked as the first step in the catalytic cycle of Ni(0)/PR\(_3\)-catalyzed cross-coupling reactions of aryl pivalates, the resulting putative Ar–Ni(II)–OPiv species have not been confirmed experimentally.\(^2\) With this in mind, our investigations began by reacting 1-naphthyl pivalate (1a) with [Ni(COD)]\(_2\)/PCy\(_3\) (1:2) in toluene-d\(_8\) at room temperature (Scheme 4).\(^{19}\) After 5 h, a new \(^{31}\)P NMR signal had appeared at \(\delta_{\text{ppm}} = 24.8\) ppm, and 1a had undergone 10% conversion as judged by the appearance of a new set of naphthyl signals in the H\(_1\) NMR spectrum. Specifically, the downfield signal at \(\delta_{\text{ppm}} = 10.4\) ppm paralleled that of “classical” square planar Ni(II) oxidative addition species such as \([\text{Ni(PCy}_3]_2(\sigma-1\text{-naphthyl}][\text{Cl}]\) (\(\delta_{\text{ppm}} = 10.2\), CDCl\(_3\))\(^{20}\) or \([\text{Ni(PCy}_3]_2(\sigma-1\text{-naphthyl}][\text{F}]\) (\(\delta_{\text{ppm}} = 9.9\), THF-d\(_8\)).\(^{21}\) However, the upfield signal at \(\delta_{\text{ppm}} = 5.6\) ppm also suggested that \(\eta^1\)-arene coordination to nickel was present.\(^{22}\) At first glance, one might suspect that these signals correspond to different nickel complexes; however, a \(^{1}H\)\(^{31}\)P HMBC spectrum showed correlations between the new \(^{31}\)P NMR signal at \(\delta_{\text{ppm}} = 24.8\) ppm and both \(\delta_{\text{ppm}} = 5.6\) ppm and \(\delta_{\text{ppm}} = 10.4\) ppm, indicating the presence of a single CuF\(_2\)-Ni–naphthyl fragment.

**Scheme 4.** \(^{1}H\) NMR evidence for Ni–naphthyl bonding.

Optimization of the reaction conditions allowed us to isolate a green air-sensitive solid (2a) from the reaction mixture in a 50% yield (Scheme 5, top), and crystallization from toluene/pentane at –30 ºC furnished crystals suitable for X-ray diffraction (Figure 1). The most striking feature of 2a is the presence of a Ni–Ni bond, the length of which (2.3949(9) Å) is by no means confined to C–C bond formations, and that aminations, stannylation, silylation, and phosphorylations are within reach. In 2014, our group described a mild Ni/Cu-catalyzed C–O silylation of aryl esters using PCy\(_3\) as the ligand (Scheme 3, top). Notably, the coupling of regular arenes posed no problems, which contrasts with a number of C–O cleavage protocols that are limited to extended \(\pi\) systems. It was hypothesized that Cu was acting as a silyl transfer catalyst, and that fluoride ions from CsF/CuF\(_2\) were probably activating the Si–B bond prior to reaction with the Cu complex (Scheme 3, middle). The Ni/Cu couple has also been employed in related silylation or borylation events, among others (Scheme 3, bottom).\(^{15,16}\)

Due to the lack of experimental evidence for a classical (PR\(_3\))Ni(0)/(II) cycle with aryl esters and the enigmatic role played by CuF\(_2\) and CsF in many cross-coupling reactions, we sought to elucidate the mechanistic details of the C–O silylation of aryl pivalates. At the outset of our investigation, it was unclear whether it would be possible to unravel the mechanistic underpinnings of this reaction. If successful, we recognized that this would be a significant step forward in the C–O functionalization arena. As part of our efforts in the field of C–O functionalization,\(^{8,9,17}\) we now report a combined experimental and computational study on the C–O silylation of aryl esters. Our work not only sheds light on the role of both Cu and fluoride ions but also demonstrates, for the first time, the role of unorthodox dinickel oxidative addition complexes in C–O cleavage. These rather stable off-cycle species evolve via disproportionation into monomeric aryl-Ni(II) intermediates that ultimately lead to C–Si bond formation. We anticipate that these results will both provide an entry point to further studies on the mechanistic intricacies of related C–O functionalizations and highlight the importance of off-cycle intermediates,\(^{18}\) which may be relevant to improving the efficiency and generality of Ni-catalyzed reactions.
measurements confirmed that 2a is diamagnetic with a singlet ground state, consistent with its well-resolved NMR spectra.24

NBO analysis of 2a showed a symmetrical distribution of charge at the Ni–Ni core, with the two Ni atoms bearing similar positive charges (+0.16 and +0.15) and the two oxygen atoms of the pivalate fragment bearing similar negative charges (-0.69 and -0.68). As mentioned above, the room temperature 31P NMR spectrum of 2a contained one signal (δp = 24.8 ppm), suggesting that the two distinct Ni–C interactions are rapidly exchanged between the Ni centers to place the PCy3 ligands in a single averaged environment. Indeed, lowering the temperature ultimately resulted in this signal splitting into two signals at δp = 16.3 and 32.8 ppm, with coalescence occurring at approximately -40 ºC.24

Scheme 5. Synthesis of dinickel oxidative addition complex.

The formation of 2a requires the dissociation of COD, and thus may be hindered by competing ligand substitution processes. Using [Ni(PCy3)2]2N2 as an alternative Ni(0) source, we found that 2a formed much more rapidly in the absence of COD, with full conversion to a 1:1 mixture of 2a and PCy3 obtained within 15 minutes at room temperature (Scheme 5, bottom). The facile oxidative addition of 1a was further supported when the reaction was monitored by variable temperature NMR spectroscopy, with signals for 2a appearing at 0 ºC when the reaction was warmed from -40 ºC. This result is of particular importance, as it not only shows that C–O functional groups can be oxidatively added to Ni(0) in a single averaged environment. Indeed, lowering the temperature ultimately resulted in this signal splitting into two signals at δp = 16.3 and 32.8 ppm, with coalescence occurring at approximately -40 ºC.24

Interestingly, 1,1’-binaphthalene was produced when 1a was reacted with [Ni(COD)]/[PCy3] at 100 ºC (Scheme 6).25 This homocoupled product was accompanied by dark green crystals of an air-stable compound. X-ray crystallographic analysis showed the formation of Ni(II) paddlewheel complex Ni2(μ-OPiv)(PCy3)2 (3) with a Ni–Ni distance of 2.7364(2) Å. Notably, binaphthalene and broad signals belonging to 3 were also detected by 'H NMR upon heating 2a to 100 ºC. Undesirable homocoupling pathways can negatively affect cross-coupling reactions of aryl esters that are conducted at high temperatures. Therefore, this finding suggests that preventing the formation of Ni(II) dimers such as 3 may help maintain productive catalyst activity for sp2 C–O functionalization methods based on Ni(0)/PCy3.25

Scheme 6. Formation of 1,1’-binaphthalene and Ni(II) OPiv dimer 3 at elevated temperatures.

The formation of 2a can be explained by invoking an oxidative addition of the aryl pivalate to Ni(0)/PCy3, a pathway that was first described computationally by Liu and co-workers.21,22 This results in a monomeric Ni(II) species [Ni(PCy3)2(σ-aryl)(κ2-OPiv)] (4). In the presence of Ni(0)Ln – likely to be formulated as [(PCy3)Ni(toluene)] or [Ni(0)(PCy3)(ArOPiv)] – comproportionation could occur to form a Ni(I)–Ni(I) bond. A similar comproportionation reaction at a Ni(II) center supported by a diphosphine ligand has been proposed by Balcells and Hazari.26 It is worth highlighting that complex 2a represents the first experimental and structural evidence for an oxidative addition of an aryl ester to a Ni(0) center.

Figure 1. X-ray crystal structure of 2a (thermal ellipsoids at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (º): Ni1–Ni2 = 2.3949(9), Ni2–C1 = 1.857(6), Ni1–C1 = 2.019(6), Ni1–C2 = 2.102(6), Ni1–O1 = 1.951(4), Ni2–O2 = 1.948(4). C10–1–Ni2 = 127.4(5), C2–C1–Ni2 = 117.6(4).
Ni(0) supported by a monodentate phosphine. Additionally, 2a contains a rare case of a σ-arene ligand having a π-interaction to a second metal center and is a new member of the small family of dinickel complexes exhibiting such coordination.21,32 Considering the prevalence of PCy₃ in C–O cleavage reactions, we speculate that 2a is relevant to other cross-coupling reactions of aryl ester derivatives and may offer a useful entry point to studying the mechanisms of these reactions.

Prompted by these results, we anticipated that the facile oxidative addition of [Ni(PCy₃)₂] with 1a would not be limited to the formation of 2a. As shown in Scheme 7, this turned out to be the case, and aryl pivalates 1b–f provided dinickel oxidative addition complexes 2b–f in moderate-to-excellent NMR yields after 2 h.33 Unfortunately, complexes 2b–f were considerably more soluble than 2a, and although no crystals suitable for X-ray diffraction were obtained, the dinickel(μ-η¹-arene) core was identified by comparing the ¹³C{¹H} NMR signals of the Ni–C environment (δ = 143–150 ppm ([JPC] triplet)) and the C=O signal of the bridging pivalate ligand (δ = 195–196 ppm ([JPC] triplet)) of 2b–f, with those of 2a. Given that extended π-systems are typically more reactive in C–O functionalization than regular arenes,12,13 we wondered whether a dinickel oxidative addition complex would also form with simple phenyl pivalate (1f). As anticipated, the reaction of 1f with [Ni(PCy₃)₂] resulted in no conversion when compared with naphthyl pivalates 1a–e. After 2 h at room temperature, the ³¹P NMR spectrum showed that although ([PCy₃]Ni(toluene))₃ and free PCy₃ were the major species in solution, a small signal had appeared that was consistent with a dinickel oxidative addition complex (2f, 18% yield).

Identification of dinickel complex 2a as the catalyst resting state. The data outlined above leave no doubt about the importance of dinickel complexes in the C–O cleavage of aryl esters. Therefore, we next investigated the relevance of 2a in the C–O silylation of 1-triethylsilyl)naphthalene (1a). Notably, control experiments revealed that 2a could be used as the precatalyst to afford 5a in an almost identical yield to that obtained using [Ni(COD)]PCy₃ or [Ni(PCy₃)₂]N₂, demonstrating its ability to participate in the silylation reaction.34 We next monitored the silylation of 1a by NMR spectroscopy to determine whether 2a was present during the reaction.35 Due to the heterogeneity introduced by CsF and CuF₂, we omitted these additives in our NMR monitoring studies. Although this resulted in a reduced yield of 5a, the early formation of 2a and its persistence throughout the reaction was evident in both the ³¹P and ¹H NMR spectra of the reaction (Figure 2 – ¹H NMR) suggesting that 2a is indeed relevant to the catalytic C–O silylation reaction. It is worth noting that the concentration of 2a decreased slightly throughout the course of the reaction, and that a small amount (7.5% at 16.7 h) of homocoupled 1a (1,1'-binaphthalene) was observed (Figure 2-right).

Unravelling the role of dinickel complexes as reaction intermediates. Although the above data provided compelling evidence for the formation of dinickel complex 2a during the Ni(0)/PCy₃-catalyzed silylation of 1a, it was unclear how 2a participated in the catalytic cycle. Indeed, the Ni–Ni bond might remain intact throughout the reaction with Et₃SiPb or might be cleaved to release mononickel species in solution (Scheme 8).35 In the latter case, three scenarios are conceivable for Ni–Ni cleavage: (a) heterolytic cleavage, in which a two-electron transfer from one nickel atom results in the formation of a pair of charged nickel species (path a, Scheme 8); (b) homolysis of the Ni–Ni bond, leading to a pair of neutral Ni(I) species (path b); or (c) disproportionation of the Ni–Ni bond to generate a Ni(0) and a Ni(II) species (path c).
lytic or heterolytic cleavage of the Ni–Ni bond would not be expected to aid formation of 5a in the presence of Et$_3$SiBPin.$^{36}$

**Scheme 9. Reaction of dinickel complex 2a with Et$_3$SiBPin.**

The combined data from our stoichiometric experiments suggested that a disproportionation pathway comes into play, where 2a is in equilibrium with Ni(II) complex [Ni(PCy$_3$)$_2$(µ-c$_2$-naphthyl)OPiv] (4) and Ni(0) (Scheme 10). The addition of ArOPiv would then intercept the Ni(0) and in doing so, increase the concentration of 4. Indeed, disproportionation reactions for group 10 metal–metal dimers have been reported, providing precedent for the viability of Scheme 8 (path c) with intermediates such as 2a.$^{35}$ For example, Pfaltz observed Pd–Pd dimers and their corresponding Pd(0) and Pd(II) disproportionation products by ESI-mass spectroscopy.$^{37}$

**Scheme 10: Perturbation of disproportionation equilibrium of 2a in the presence of ArOPiv.**

It is worth noting that disproportionation of 2a is also the microscopic reverse of the comproportionation mechanism proposed for its formation. In line with this notion, we investigated whether disproportionation could be triggered by addition of dcype, a bidentate phosphine ligand that was shown by Itami to stabilize the mononuclear Ni(II) species [Ni(dcype)(2-cnaphthyl)OPiv] (Ni-1).$^{33,38}$ Indeed, exposure of 2b to dcype (3 equivalents) at room temperature resulted in the formation of Ni-1 and [Ni(0)(dcype)$_2$] (6) (Scheme 11). As expected, repeating the experiment with 2a gave rise to 6 and [Ni(dcype)(1-naphthyl)OPiv] (Ni-2), the structure of which was confirmed by NMR and X-ray crystallography.$^{34}$ The presence of Ni(0) species was further assessed by reacting 2a with 2-naphthyl pivalate (1b) in the presence of Et$_3$SiBPin (Scheme 12). We hypothesized that if Ni(0) is generated in situ, then isomeric oxidative addition products – dinickel complex 2b and silylated 5b – would be detected alongside 5a. As shown in Scheme 12, this was indeed the case, with both 5a and 5b observed in 25% and 46% yields, respectively.

**Scheme 11. Disproportionation with dcype.**

**Scheme 12. Reactivity of 2a with Et$_3$SiBPin and ArOPiv.**

In order to validate the conclusions extracted from the stoichiometric studies, kinetic studies were performed. First, the kinetic order in catalyst was determined. If an equilibrium with 2a to form active monomeric species affects the reaction rate, a half order in [Ni] may be expected. Therefore, 1a was reacted with Et$_3$SiBPin in the presence of [Ni(PCy$_3$)$_2$]$_2$(N$_2$) (2.08 mM–6.25 mM) and CsF/CuF$_2$ at 50 °C.$^{39}$ Due to the stirring difficulties that occur after 90 minutes (vide infra), kinetic orders were obtained using data collected from the first 90 minutes of the reactions. The order in catalyst was extracted from the resulting data by variable time normalization analysis (VTNA) – a method that uses reaction profiles (integral data) to determine the kinetic orders of reaction components (Figure 3).$^{40}$ In this analysis, the time axes of the concentration profiles were normalized to remove the effect of the catalyst on the catalytic profile. Specifically, normalizing by t[cat]$^{0.5}$ allowed us to determine that the three profiles best overlay at t[cat]$^{0.5}$. A half-order dependence is consistent with the presence of an off-cycle equilibrium lying towards the catalytically inactive species 2a. This conclusion contrasts with a recent disclosure, which suggested that similar µ-η$^2$-arene dinickel complexes supported by N-heterocyclic carbones remain intact during the cross-coupling of an aryl halide with a Grignard reagent.$^{32a}$ To what extent the nature of the supporting ligand is responsible for this behavior remains to be elucidated.
Figure 3. VTNA for order in catalyst showing the greatest overlay at 0.5 order. [Ni(PCy$_3$)$_2$(N$_2$)] (2.08 mM–6.25 mM).

Additionally, the kinetic orders of 1a and Et$_3$SiBPin were determined. As shown in Figure 4, the reaction exhibited zero-order dependence in 1a, suggesting that oxidative addition is not rate determining. In contrast, a positive order dependence on [Et$_3$SiBPin] was determined, with VTNA analysis giving a range of orders between 0.4 and 1, providing evidence for the participation of this species in a rate-determining step of the reaction.$^{41}$

Figure 4. Kinetic study of order in 1a (left) and Et$_3$SiBPin (right).

**Role of the CuF$_2$ and CsF.** To summarize, we have determined that oxidative addition of aryl pivalates to Ni(0)/PCy$_3$ readily forms dinickel complexes. These release mononickel complexes that participate in the rate-determining transmetalation with Et$_3$SiBPin. Still, however, the role of CuF$_2$ and CsF remained unclear. Specifically, control experiments revealed a three-fold increase in yield for the silylation of 1b when both CsF and CuF$_2$ were present, affording 5b in 90% isolated yield after 16 h at 50 °C. Prompted by these results, we next turned our attention to studying the influence of CuF$_2$ and CsF (Scheme 13). In the absence of both CsF and CuF$_2$, the formation of PivOBpin was observed by $^{13}$B NMR spectroscopy ($\delta_B = 23$ ppm, toluene-d$_8$, 50 °C), and the reaction mixture remained homogeneous (Scheme 13, top left); however, the addition of CsF, with or without CuF$_2$, resulted in the formation of insoluble byproducts. In particular, different insoluble compounds were obtained depending on whether excess CsF (2 equiv) or a combination of CsF (1 equiv) and CuF$_2$ (0.3 equiv) was utilized. In the former, we obtained a 79% yield of 5b after 9 h, demonstrating that removing the Cu source entirely and replacing it with an extra equivalent of CsF gives a comparable yield to the standard conditions (85%, see Figure 5-left for a comparison of the reaction profiles). In this case, we isolated CsOPiv and Cs[F$_2$Bpin] from the reaction mixture (Scheme 13, bottom left). The CsOPiv was identified by $^1$H NMR, and the fluoroborate by a well-resolved triplet in the $^{19}$F NMR spectrum ($\delta_F = 4.78$ ppm ($J_{BF} = 21$ Hz) and a multiplet in the $^{11}$B NMR spectrum ($\delta_B = -138.9$ ppm ($J_{BF} = 20.5$ Hz)). If both CsF and CuF$_2$ were employed, Cs[F$_2$Bpin] was accompanied by a new set of fluoroborate signals ($\delta_F = 5.34$ ppm, $\delta_B = -138.3$ ppm) (Scheme 13, right). These signals presumably correspond to [F(PivO)Bpin], as only 1.6 equivalents of fluoride are available under these conditions, thus preventing the complete formation of [F$_2$Bpin].

**Scheme 13. Effect of additive on byproduct identity.**

Puzzled by the reduced yields of 5a and 5b obtained in the absence of additives, the formation of 5b under CsF/CuF$_2$-free conditions was monitored and compared to the standard protocol employing CsF/CuF$_2$. As shown in Figure 5-left, similar behavior was observed for both reactions during the first 45 minutes. However, in the absence of additives, the formation of 5b slowed dramatically after this time. This disparity could be due to catalyst deactivation in the absence of additives, and/or a mechanism based on Cu–SiEt$_3$ intermediates becoming operative at later stages. However, it is important to note that, as shown in Figure 5-left, CuF$_2$ alone did not significantly increase the yield of 5b, and its replacement with an extra equivalent of CsF furnished 5b in an almost identical yield to that obtained with CsF/CuF$_2$ (83% vs 89%, red vs dark grey). The addition of [Ni(PCy$_3$)$_2$(N$_2$)] (5 mol%) to the additive-free reaction after product formation had stalled (3.75 h) resulted in a slight increase in 5b (Figure 5-right). Strikingly, when 1 equivalent of CsF was added at this time, product formation resumed without the need for extra Ni(0) (Figure 5-right). Therefore, we propose that the generation of PivOBpin in the additive-free reaction might inhibit the reaction.$^{42}$ The presence of fluoride ions allows catalytic activity to be restored by removing PivOBpin from solution as fluoroborate salts.

Taken together, these experiments indicated that our initial assumption of cooperative Ni/Cu catalysis was premature. In light of our experimental data, we currently support a mechanism in which fluoride anions provided by CsF and CuF$_2$ help to prevent catalyst deactivation by sequestering the boron-containing byproducts as fluoroborates. At present, we have
not obtained evidence that supports the intermediacy of a CuSiEt₃ species. Whether a similar conclusion can be drawn for recent C–O functionalization scenarios based on CuF₂ remains to be investigated.

**Figure 5.** Left: Effect of additives on the silylation of 1b over 9 h. Right: Effect of adding [Ni(PCy₃)₂]₂(N₂) (5 mol%) (grey), or CsF (2 equiv) (red) to the additive-free silylation of 1b. Addition took place at 3.75 h. Aliquots were removed from the reactions every 45 minutes and analyzed by GC-FID.

**DFT calculations:** Although our experimental data provided empirical evidence for the formation of dinickel complexes and for their role within the catalytic cycle of the C–O silylation of aryl esters, we turned our attention to DFT in order to gather indirect evidence about other elementary steps within the catalytic cycle. We performed DFT calculations with the Gaussian 09 suite of programs. Optimizations were carried out using 6-31G(d,p) basis sets for C, H, O, P, B, Si and the Stuttgart Dresden (SDD) basis including an effective core potential for nickel. The energies were refined by single-point calculations at the M06/def2tzvpp level, with the inclusion of a solvent model system (IEFPCM, dichloromethane, toluene). We used Me₃SiBPin in place of Et₃SiBPin to avoid the conformational complexity of the latter.

We initially focused our attention on computing a mononickel mechanism consisting of an initial oxidative addition of 1a to Ni(0)PCy₃, followed by transmetalation with Et₃SiBPin and C–Si bond reductive elimination (Figure 6). The calculations were performed in the absence of fluoride sources due to the fact that (a) the first 45 minutes of the reaction profiles were similar regardless of whether fluoride sources were present or not, and (b) the observation that fluoride sources play a role in preventing catalyst deactivation by sequestering off-cycle intermediates. As expected, initial π-coordination of the arenene to the Ni(0) center is triggered by dissociation of PCy₃ from either Ni(PCy₃)₂ or [(PCy₃)Ni(toluene)]. and leads to a facile oxidative addition that gives rise to [Ni(PCy₃)(σ-naphthyl)(κ²-OPiv)] (II) with a low activation Gibbs free energy of 14.7 kcal mol⁻¹ (TS⁻⁻⁻⁻). The reaction further evolves to III, from which transmetalation with Me₃SiBPin leads to [Ni(PCy₃)(σ-naphthyl)(SiMe₃)] (IV) through a six-membered transition state (TSIII⁻⁻) with ΔG‡ = 22.4 kcal mol⁻¹. Subsequently, an energetically downhill dissociation of PivOBPin sets the scene for an effectively barrierless C–Si bond reductive elimination (TSIV⁻⁻⁻⁻⁻) that releases 2a and recovers I. As a result, it becomes apparent that the transmetalation process with the Si–B species is turnover-limiting (II–TSIII⁻⁻⁻⁻⁻). This observation is consistent with the zero-order dependence in 1a and the positive-order dependence in Et₃SiBPin. Our experimental data, however, showed that the mononickel oxidative addition complex is in equilibrium with dinickel 2a. Gratifyingly, the thermodynamic stability of 2a compared with the mononickel complex was corroborated by calculations, with the equilibrium Gibbs free energy found to be –10.6 kcal mol⁻¹ in favor of 2a (Scheme 14).

**Scheme 14. Calculated equilibrium**
This result reinforces the role of 2a as an off-cycle species and is consistent with the experimental half-order dependence on 2a. In line with our observation that silylated product 5a is not formed from 2a upon exposure to Et₂SiBPin in the absence of 1a, we were unable to locate a transition state for direct transmetalation of 2a with the corresponding Si–B species. It is worth highlighting that we computed the mechanism in the presence of CsF, confirming that similar conclusions can be drawn to those without CsF. 28

**Scheme 15. Final mechanistic proposal.**

Overall, our experimental and computational data support a mechanism where oxidative addition forms an off-cycle dinickel complex that is in equilibrium with a mononickel Ni(II) complex and Ni(0) (Scheme 15). Transmetalation occurs from the mononickel complex and forms PivOBpin as a byproduct, which is intercepted by fluoride ions to form very strong B–F bonds and insoluble fluoroborates, thus ensuring catalyst turnover.

**CONCLUSION**

The preparative potential of the Ni-catalyzed sp² C–O functionalization of aryl esters generally stands in contrast with the dearth of experimental evidence available for the sp² C–O cleavage step or for the roles of the reaction intermediates within the catalytic cycle. This is particularly evident when monodentate phosphines are employed, an observation that is typically associated with the formation of low-coordinated entities that are prone to ligand dissociation. Indeed, experimental evidence for a seemingly trivial oxidative addition into the sp² C–O bond with monodentate phosphines was elusive. Our study of the Ni(PCy₃)₂-catalyzed silylation of aryl esters via sp² C–O cleavage provides compelling evidence for a mechanism containing an unusual dinickel(μ-η²-arene) oxidative addition complex. We have shown that decomposition pathways come into play upon heating, leading to a dinickel pivalate-bridged species and homocoupling products, and suggesting that such dinickel complexes might be applicable to other sp² C–O functionalizations. Spectroscopic data, stoichiometric experiments and VTNM kinetic studies provide a detailed picture of dinickel complexes as off-cycle reservoirs of the active mononickel oxidative addition complex via disproportionation. The products of disproportionation were trapped by reacting isolated dinickel complex with bidentate dicycyle. We have also revealed the importance of fluoride ions in maintaining active catalysis.

Taking into consideration that monodentate phosphines are frequently utilized as ligands in a wide variety of C–O functionalization reactions, it is tempting to speculate that dinickel complexes play an important role in these processes. More importantly, we believe our study provides long-awaited insights into the mechanistic aspects of sp² C–O functionalization in aryl esters and will serve as a useful entry point to unravelling the mechanistic intricacies of related, yet not fully understood, Ni-catalyzed cross-coupling reactions.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectral and crystallographic data (PDF).

Computational details and Cartesian coordinates (PDF)

Data for 3 (CCDC-1839593) (CIF)

Data for 2a (CCDC-1839592) (CIF)

Data for Ni-2 (CCDC-1839591) (CIF)

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The role of CsF, CuF₂ additives

NiPC₃ catalyst

Ni-Ni intermediate

$\text{SiEt}_3$