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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.8b04479 • Publication Date (Web): 18 Jun 2018

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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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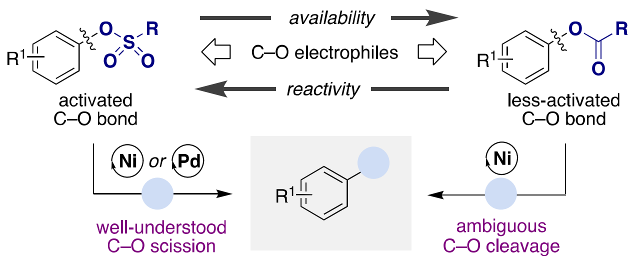
ABSTRACT: Monodentate phosphine ligands are frequently employed in the Ni-catalyzed C–O functionalization of aryl esters. However, the extensive body of preparative work on such reactions contrasts with the lack of information concerning the structure and reactivity of the relevant nickel intermediates. 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.

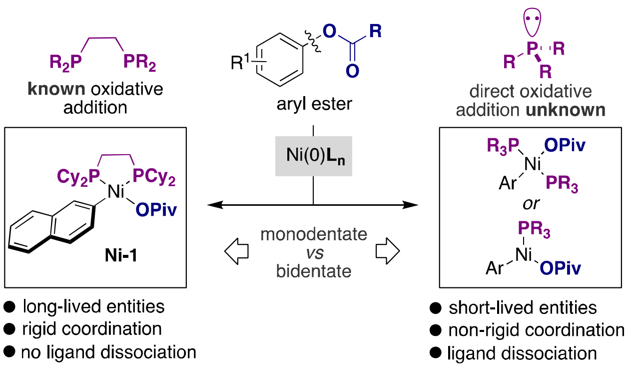
Prompted by the broad accessibility, thermal stability and cost-efficiency of phenol derivatives, C–O electrophiles have recently gained momentum as alternatives to aryl halides in cross-coupling reactions.[1] Although activated aryl sulfonates have been widely adopted in the cross-coupling arena, much 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.



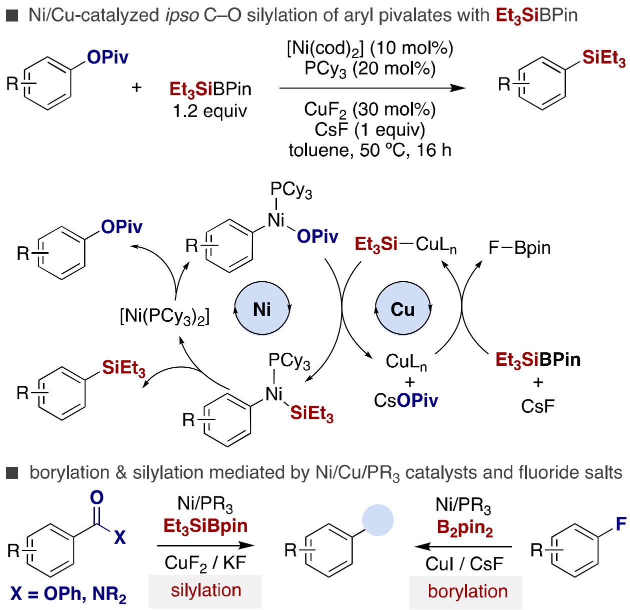
Despite the advances realized in Ni-catalyzed cross-coupling reactions of aryl esters,[1] these processes are poorly understood in mechanistic terms, and progress in the field is typically based on empirical discoveries.[2] At present, there seems to be consensus that sp^2 C–O activation is initiated 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 dcype (1,2-bis(dicyclohexylphosphino)-ethane) as the supporting ligand and required elevated temperatures (100 ºC).[3–5] 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.[6] 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.

Scheme 2. Oxidative addition into the *sp*^{2} C–O bond.



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,[7] silylation,[8] stannylation,[9] borylations[10] and phosphorylations[11] 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*).[8] Notably, the coupling of regular arenes posed no problems, which contrasts with a number of C–O cleavage protocols that are limited to extended π systems.[12,13] It was hypothesized that Cu was acting as a silyl transfer catalyst,[14] 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).

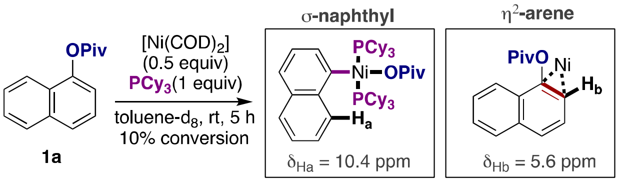


Due to the lack of experimental evidence for a classical (PR$_3$)Ni(0)/(II) cycle with aryl esters and the enigmatic role played by CuF$_2$ and CsF in many cross-coupling reactions, we sought to elucidate the mechanistic details of the C–O silylation of aryl pivalates. At the outset of our investigation, 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

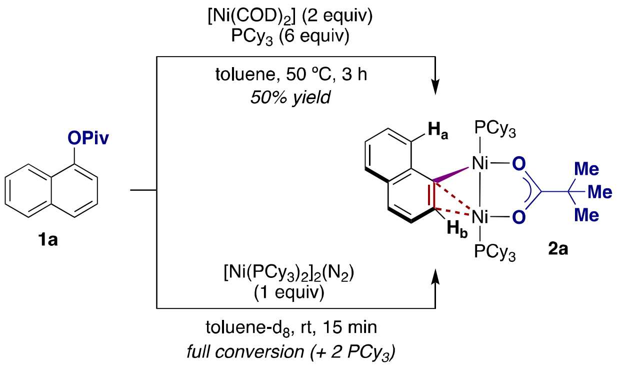
Synthesis and characterization of oxidative addition complexes of aryl pivalates to Ni/PCy$_3$. Although oxidative addition has been invoked as the first step in the catalytic cycle of Ni(0)/PR$_3$-catalyzed cross-coupling reactions of aryl pivalates, the resulting putative Ar–Ni(II)–OPiv species have 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 δ_P = 24.8 ppm, and **1a** had undergone 10% conversion as judged by the appearance of a new set of naphthyl signals in the ^{1}H NMR spectrum. Specifically, the downfield signal at δ_H = 10.4 ppm paralleled that of "classical" square planar Ni(II) oxidative addition species such as [Ni(PCy$_3$)$_2$(σ-1-naphthyl)Cl] (δ_H = 10.2, CDCl$_3$)[20] or [Ni(PCy$_3$)$_2$(σ-1-naphthyl)F] (δ_H = 9.9, THF-d$_8$).[21] However, the upfield signal at δ_H = 5.6 ppm also suggested that η^2-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 δ_P = 24.8 ppm and both δ_H = 5.6 ppm and δ_H = 10.4 ppm, indicating the presence of a single Cy$_3$P–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 consistent with related Ni–Ni complexes supported by phosphine ligands, N-heterocyclic carbenes, or a naphthyridine-diimine ligand.[23] In line with our spectroscopic data, the naphthyl fragment interacts with the Ni–Ni core via both a σ-bond to Ni2 (1.857(6) Å) and an η^2 interaction between the C1–C2 bond and Ni1. Completing the dinickel structure is a bridging pivalate ligand having identical Ni1–O1 and Ni2–O2 bond distances within 3σ (1.951(4) and 1.948(4) Å). Magnetic 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 ^{31}P NMR spectrum of **2a** contained one signal (δ_P = 24.8 ppm), suggesting that the two distinct Ni–C interactions are rapidly exchanged between the Ni centers to place the PCy_3 ligands in a single averaged environment. Indeed, lowering the temperature ultimately resulted in this signal splitting into two signals at δ_P = 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 $[Ni(PCy_3)_2]_2N_2$ 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 PCy_3 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–OPiv cleavage via oxidative addition to Ni(0)/PCy_3 is facile, but also argues against oxidative addition being rate-determining under our reaction conditions. These results are in contrast with the conditions described by Itami (100 ºC) for the synthesis of **Ni-1** via C–OPiv cleavage with otherwise related dcype (Scheme 2, *left*).[3,4] However, it is worth noting that Love[4] showed that oxidative addition complexes supported by bidentate dtbpe (1,2-bis(ditertbutylphosphino)-ethane) could also be prepared at lower temperatures to those shown by Itami.[3,5]

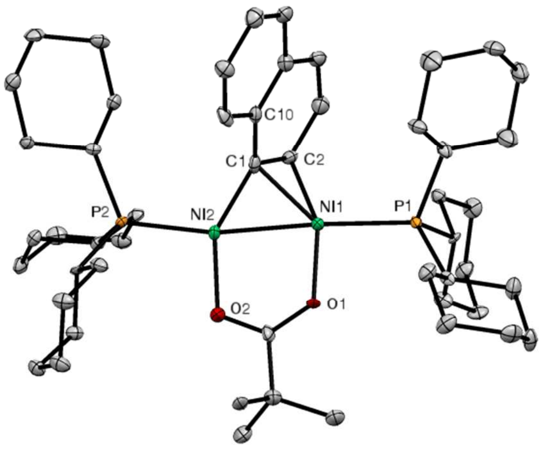
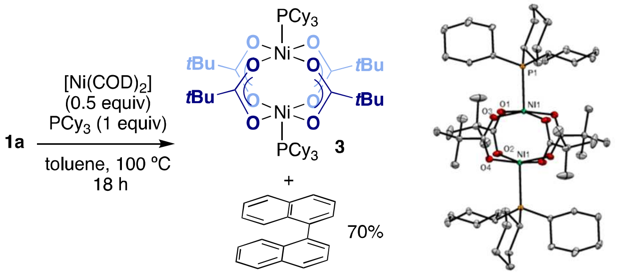


Figure 1. X-ray crystal structure of **2a** (thermal ellipsoids at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (º): Ni1–Ni2 = 2.3949(9), Ni2–C1 = 1.857(6), Ni1–C1 = 2.019(6), Ni1–C2 = 2.102(6), Ni1–O1 = 1.951(4), Ni2–O2 = 1.948(4). C10–1–Ni2 = 127.4(5), C2–C1–Ni2 = 117.6(4).

Interestingly, 1,1'-binaphthalene was produced when **1a** was reacted with [Ni(COD)$_2$]/PCy$_3$ 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 $[Ni_2(\mu\text{-OPiv})_4(PCy_3)_2]$ (**3**) with a Ni–Ni distance of 2.7364(2) Å.[25,26] Notably, binaphthalene and broad signals belonging to **3** were also detected by ^{1}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 *sp*^{2} C–O functionalization methods based on Ni(0)/PR$_3$.[27]

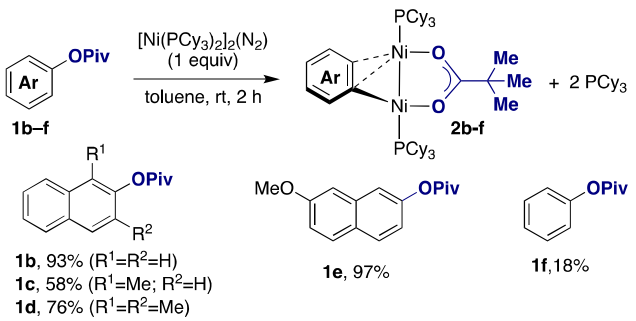
Scheme 6. Formation of 1,1'–binaphthalene and Ni(II) OPiv dimer 3 at elevated temperatures.



The formation of **2a** can be explained by invoking an oxidative addition of the aryl pivalate to Ni(0)/PCy$_3$, a pathway that was first described computationally by Liu and co-workers.[2f,28] This results in a monomeric Ni(II) species $[Ni(PCy_3)(\sigma\text{-aryl})(\kappa^2\text{-OPiv})]$ (**4**). In the presence of Ni(0)L$_n$ – likely to be formulated as [(PCy$_3$)Ni(toluene)],[29] or [Ni(0)(PCy$_3$)(ArOPiv)][30] – 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.[31] It is worth highlighting that *complex **2a** represents the first experimental and structural evidence for an oxidative addition of an aryl ester to*

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.[23,32] Considering the prevalence of PCy_3 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.

Scheme 7. Accessing dinickel species from ArOPiv.



Prompted by these results, we anticipated that the facile oxidative addition of $[Ni(PCy_3)_2]_2(N_2)$ 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-η^2-arene) core was identified by comparing the $^{13}C\{^1H\}$ NMR signals of the Ni–C environment (δ = 143–150 ppm ($^2J_{PC}$ triplet)) and the C=O signal of the bridging pivalate ligand (δ = 195–196 ppm ($^3J_{PC}$ 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 $[Ni(PCy_3)_2]_2(N_2)$ was rather sluggish when compared with naphthyl pivalates **1a**–**e**. After 2 h at room temperature, the ^{31}P NMR spectrum showed that although $[(PCy_3)Ni(toluene)]$[28] and free PCy_3 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 (**5a**). Notably, control experiments revealed that **2a** could be used as the precatalyst to afford **5a** in an almost identical yield to that obtained using $[Ni(COD)_2]/PCy_3$ or $[Ni(PCy_3)_2]_2N_2$, demonstrating its ability to participate in the silylation reaction.[24] We next monitored the silylation of **1a** by NMR spectroscopy to determine whether **2a** was present during the reaction.[34] Due to the heterogeneity introduced by CsF and CuF_2, 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 ^{31}P 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*).

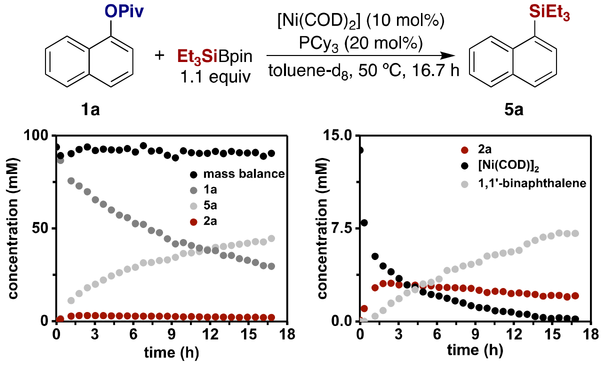
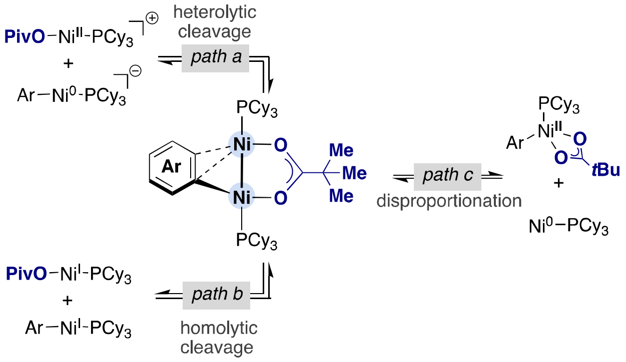


Figure 2. ^1H NMR monitoring of the CsF/CuF_2-free C–O silylation of **1a** with $Et_3SiBPin$. Spectra collected every 38 min. [**1a**]: 0.094 M.

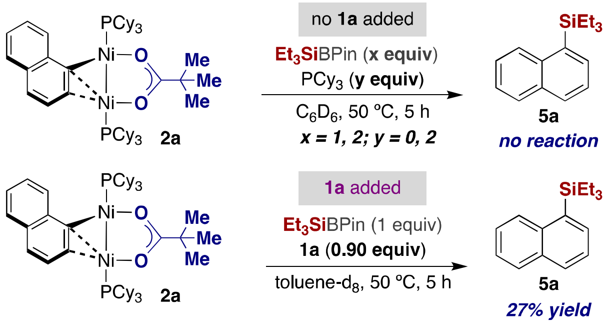
Unravelling the role of dinickel complexes as reaction intermediates. Although the above data provided compelling evidence for the formation of dinickel complex **2a** during the $Ni(0)/PCy_3$-catalyzed silylation of **1a**, it was unclear how **2a** participated in the catalytic cycle. Indeed, the Ni–Ni bond might remain intact throughout the reaction with $Et_3SiBPin$ 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*).

Scheme 8. Accessing catalytic relevant species via Ni–Ni cleavage from dinickel complexes.



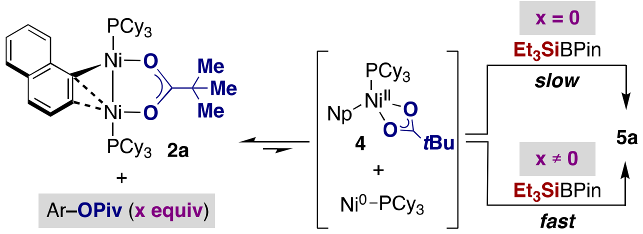
In order to clarify the role of dinickel oxidative addition complexes as reaction intermediates, we carried out stoichiometric experiments with **2a**. Importantly, reaction of **2a** with $Et_3SiBPin$ resulted in no conversion to **5a** after 5 h (Scheme 9, *top*). This suggested that silylation does not occur directly from the dinickel oxidative addition complex. Intriguingly, the addition of **1a** (0.90 equiv) gave **5a** in a 27% yield after 5 h, together with unreacted **2a** (Scheme 9, *bottom*). These results suggested that the presence of aryl pivalate facilitates C–Si bond-formation, thus arguing against a heterolytic or homolytic cleavage pathway (Scheme 8, *left pathways*). Indeed, reaction of **1a** with the monomeric Ni species derived from homolytic or heterolytic cleavage of the Ni–Ni bond would not be expected to aid formation of **5a** in the presence of $Et_3SiBPin$.[36]

Scheme 9. Reaction of dinickel complex 2a with $Et_3SiBpin$.



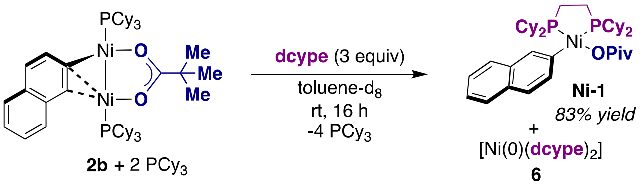
The combined data from our stoichiometric experiments suggested that a disproportionation pathway comes into play, where **2a** is in equilibrium with Ni(II) complex $[Ni(PCy_3)(\sigma\text{-naphthyl})(\kappa^2\text{-OPiv})]$ (**4**) and Ni(0) (Scheme 10). The addition of ArOPiv would then intercept 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.

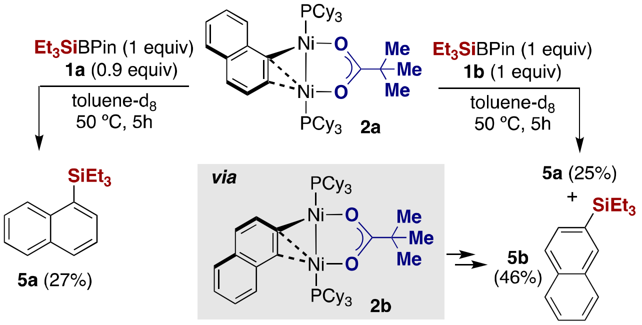


It is worth noting that disproportionation of **2a** is also the microscopic reverse of the comproportionation mechanism proposed for its formation. In line with this notion, we investigated whether disproportionation could be triggered by addition of dcype, a bidentate phosphine ligand that was shown by Itami to stabilize the mononuclear Ni(II) species [Ni(dcype)(2-naphthyl)OPiv] (**Ni-1**).[3,38] 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.[24] The presence of Ni(0) species was further assessed by reacting **2a** with 2-naphthyl pivalate (**1b**) in the presence of $Et_3SiBPin$ (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 $Et_3SiBPin$ 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 $Et_3SiBPin$ in the presence of $[Ni(PCy_3)_2]_2(N_2)$ (2.08 mM–6.25 mM) and CsF/CuF_2 at 50 ºC.[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 $t[cat]^{order}$ 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 carbenes 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.

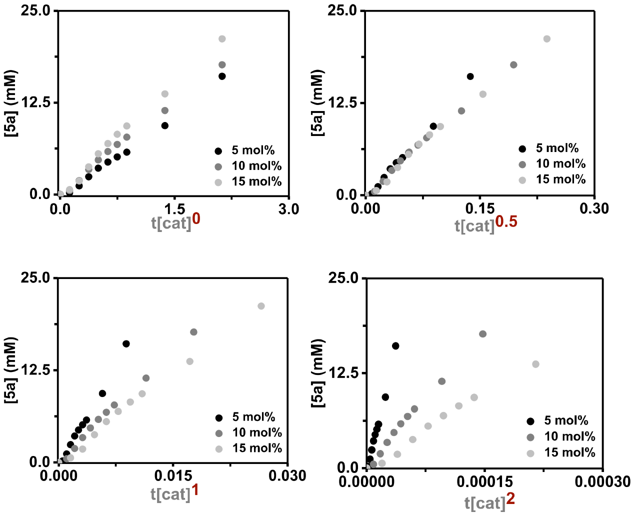


Figure 3. VTNA for order in catalyst showing the greatest overlay at 0.5 order. $[Ni(PCy_3)_2]_2(N_2)$ (2.08 mM–6.25 mM).

Additionally, the kinetic orders of **1a** and $Et_3SiBPin$ 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 $[Et_3SiBPin]$ 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]

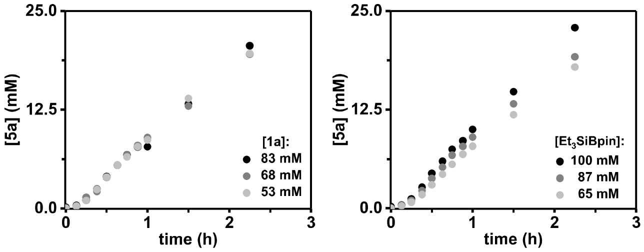
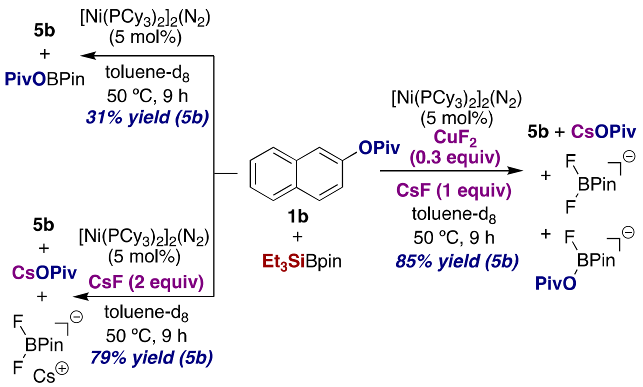


Figure 4. Kinetic study of order in **1a** (left) and $Et_3SiBpin$ (right).

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 $Et_3SiBPin$. 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 ºC. 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 ^{11}B NMR spectroscopy (δ_B = 23 ppm, toluene-d_8, 50 ºC), 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 $Cs[F_2Bpin]$ from the reaction mixture (Scheme 13, *bottom left*). The CsOPiv was identified by ^1H NMR, and the fluoroborate by a well-resolved triplet in the ^{11}B NMR spectrum (δ_B = 4.78 ppm ($^1J_{B–F}$ = 21 Hz)) and a multiplet in the ^{19}F NMR spectrum (δ_F = -138.9 ppm ($^1J_{B-F}$ = 20.5 Hz)). If both CsF and CuF_2 were employed, $Cs[F_2Bpin]$ was accompanied by a new set of fluoroborate signals (δ_B = 5.34 ppm, δ_F = -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 $[F_2Bpin]^-$.

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 $[Ni(PCy_3)_2]_2(N_2)$ (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 CuSiEt$_3$ species. Whether a similar conclusion can be drawn for recent C–O functionalization scenarios based on CuF$_2$ remains to be investigated.

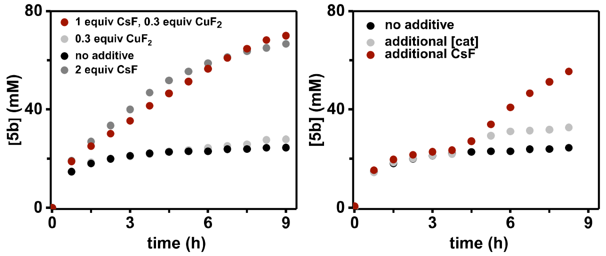
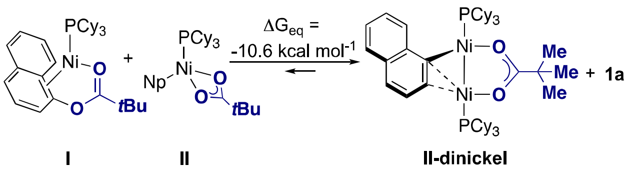


Figure 5. *Left*: Effect of additives on the silylation of **1b** over 9 h. *Right*: Effect of adding [Ni(PCy$_3$)$_2$]$_2$(N$_2$) (5 mol%) (*grey*), or CsF (2 equiv) (*red*) to the additive-free silylation of **1b**. Addition took place at 3.75 h. Aliquots were removed from the reactions every 45 minutes 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.[43] 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,[44] with the inclusion of a solvent model system (IEFPCM, dichloromethane, toluene).[45] We used Me$_3$SiBPin in place of Et$_3$SiBPin 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)PCy$_3$, followed by transmetalation with Et$_3$SiBpin 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 arene to the Ni(0) center is triggered by dissociation of PCy$_3$ from either Ni(PCy$_3$)$_2$ or [(PCy$_3$)Ni(toluene)],[28] and leads to a facile oxidative addition that gives rise to [Ni(PCy$_3$)(σ-naphthyl)(κ^2-OPiv)] (**II**) with a low activation Gibbs free energy of 14.7 kcal mol^{-1} (**TS$_{\text{I-II}}$**). The reaction further evolves to **III,** from which transmetalation with Me$_3$SiBPin leads to [Ni(PCy$_3$)(σ-naphthyl)(SiMe$_3$)] (**IV**) through a six-membered transition state (**TS$_{\text{III-IV}}$**) 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 (**TS$_{\text{V-VI}}$**, ΔG‡ = 3.2 kcal mol^{-1}). This is followed by ligand exchange with **1a** 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-TS$_{\text{III-V}}$** = 22.4 kcal mol^{-1}). This observation is consistent with the zero-order dependence in **1a** and the positive-order dependence in Et$_3$SiBPin.[24] 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



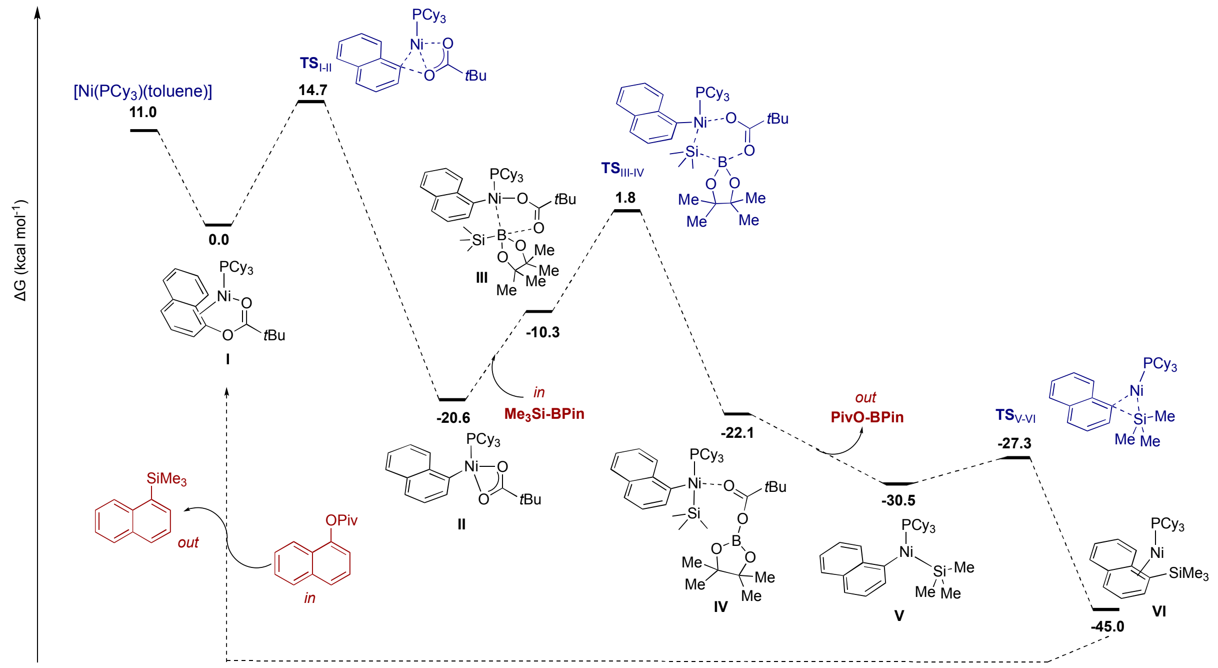
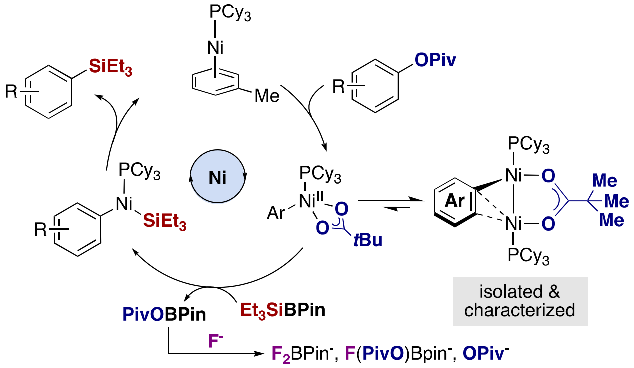


Figure 6. Free energy profile for C–O silylation via a mononickel pathway. Energies are in kcal mol^{-1} and are calculated at the M06/def2tzvpp level with the inclusion of a solvent model system (IEFPCM, dichloromethane, toluene).

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 $Et_3SiBPin$ 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.[24]

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 *sp*^{2} C–O functionalization of aryl esters generally stands in contrast with the dearth of experimental evidence available for the *sp*^{2} 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 *sp*^{2} C–O bond with monodentate phosphines was elusive. Our study of the Ni/PCy_3-catalyzed silylation of aryl esters via *sp*^{2} C–O cleavage provides compelling evidence for a mechanism containing an unusual dinickel(μ-η^2-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 dimetallic complexes might be applicable to other *sp*^{2} C–O functionalizations. Spectroscopic data, stoichiometric experiments and VTNA 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 dcype. 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 *sp*^{2} 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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Funding Sources

The authors declare no competing financial interest.

ACKNOWLEDGMENT

R.J.S and R.M. thank ICIQ, MINECO (CTQ2015-65496-R), & Severo Ochoa Accreditation SEV-2013-0319 for support. We also thank the ICIQ X-Ray Diffraction Unit and the ICIQ Mass Spectrometry unit. We sincerely thank Dr C. Sáenz and Prof J. R. Galán-Mascarós for the magnetic susceptibility analysis of **2a** and **3**. R. J. S. thanks "La Caixa" Severo Ochoa programme for a predoctoral fellowship. L. V. A. H. acknowledges financial support through the Global Engagement of Doctoral Education Program funded by Rackham Graduate School. We also acknowledge insightful discussions with Drs. M. Pérez-Temprano and F. Miloserdov. E.G-B. thanks MINECO (CTQ2016-78083-P) and IZO-SGI SGIker of UPV-EHU for human and technical support.

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24) See Supporting Information for details.

25) This finding parallels the result of Itami et al. (see ref. 3) when the conditions for the synthesis of **Ni-1** were employed with PCy$_3$. The balanced equation for the formation of **3** from [Ni(COD)$_2$] is 2[Ni(COD)$_2$] + 2PCy$_3$ + 4 **1a** → 2 (1,1'-binaphthalene) + [Ni$_2$(PCy$_3$)$_2$(μ-OPiv)$_4$] + 4 COD.

26) For a related carboxylate-bridged structure, see Cortijo, M.; Delgado-Martinez, P.; Gonzalez-Prieto, R.; Herrero, S.; Jimenez-Aparicio, R.; Perles, J.; Priego, J. L.; Torres, M. R. Microwave and Solvothermal Methods for the Synthesis of Nickel and Ruthenium Complexes with 9-Anthracene Carboxylate Ligand. *Inorganica Chim. Acta* **2015**, *424*, 176–185. and references therein.

27) 18% yield of **5a** was observed when **3** was used as a precatalyst (10 mol% Ni). See Supporting Information for details.

28) Under catalytic conditions, a dinuclear oxidative addition scenario would be kinetically indistinguishable from that of a mononuclear oxidative addition followed by formation of **2a**. However, the transition state for the oxidative addition involving dimeric nickel species was never located. For an example of a carboxylate ligand aiding dinuclear oxidative addition: Powers, D. C.; Ritter, T. A Transition State Analogue for the Oxidation of Binuclear palladium(II) to Binuclear palladium(III) Complexes. *Organometallics* **2013**, *32* (7), 2042–2045.

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33) Previously unreported aryl pivalates **1c** and **1d** can be silylated under the standard silylation conditions (see supporting information for details).

34) The isomeric complex **2b** was observed by ^{31}P NMR when 2-naphthyl pivalate **1b** underwent additive-free silylation. However, integration was not possible due to overlapping signals. See Supporting Information for details.

35) For selected reviews of metal-metal bonds in similar systems, see: (a) Inatomi, T.; Koga, Y.; Matsubara, K. Dinuclear Nickel (I) and Palladium (I) Complexes for Highly Active Transformations of Organic Compounds. *Molecules* **2018**, *23*, 140. (b) Powers, I. G.; Uyeda, C. Metal-Metal Bonds in Catalysis. *ACS Catal*. **2017**, *7*, 936–958.

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41) Although speculative, this range of normalization factors is probably due to the formation of insoluble fluoroborates during the reaction (vide infra), which result in stirring difficulties and may both affect the concentration of additives and influence processes that are sensitive to the concentration of $Et_3SiBpin$. See Supporting information for further details.

42) Upon carrying out the CsF/CuF_2-free silylation of **1b** in the presence of 10 mol% PivOBpin, a decrease in the yield of **5b** was obtained. See Supporting Information for details. These results suggest that PivOBPin might react with Ni(0) to prevent catalyst turnover.

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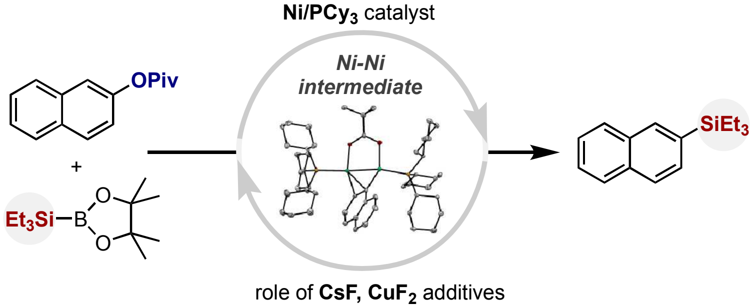
Ni/PCy3 catalyst
Ni-Ni
intermediate
OPiv
+
Et3Si
B
O
O
SiEt3
role of CsF, CuF2 additives