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Article

Isolation and Reactivity of Arylnickel(II) Complexes in Nickel-Catalyzed Borylation of Aryl Fluorosulfates

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Cite This: JACS Au 2024, 4, 1646−1653
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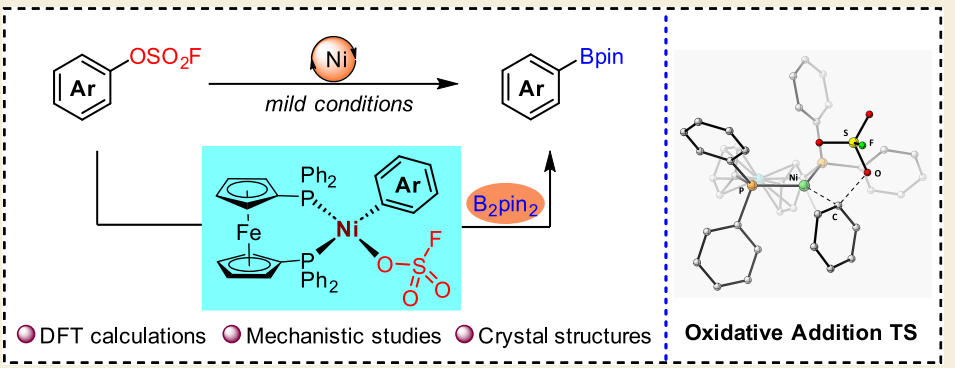


ABSTRACT: Aryl fluorosulfates have emerged as versatile SuFExable substrates, harnessing the reactivity of the S−F bond. In this study, we unveil their alternative synthetic utility in nickel-catalyzed borylation via C−O bond activation. This method highlights mild reaction conditions, a broad substrate scope, and moderate functional group tolerance, rendering it a practical and appealing approach for synthesizing a diverse array of aryl boronate esters. Furthermore, computational analysis sheds light on the reaction pathways, uncovering the participation of LNi(0) and LNi(II)ArX species. This insight is supported by the ^{31}P NMR reaction monitoring along with isolation and single-crystal X-ray structural elucidation of well-defined arylnickel(II) intermediates obtained from the oxidative addition of aryl fluorosulfates. A comprehensive investigation, merging experimental and computational approaches, deepens our understanding of the alternative reactivity of SuFExable substrates.

KEYWORDS: *aryl fluorosulfates, computational studies, intermediate isolation, nickel catalysis, organoborons*

1. INTRODUCTION

Organoborons have gained recognition as key organometallic reagents owing to their synthetic versatility, bench stability, low toxicity, and ease of handling.[1−6] Recent progress in palladium-catalyzed C−B bond formation, including the Miyaura borylation of aryl halides, has paved the way for the establishment of straightforward and reliable routes to prepare arylboron compounds.[7−10] However, comparatively less attention has been focused on elucidating the reaction pathways in nickel-catalyzed processes.[11,12] Nickel catalysts, in addition to being cost-effective, exhibit superior performance compared to palladium ones in activating less reactive electrophiles such as pseudohalides, esters, or even ethers.[13,14] Despite these advantages, nickel can exist in diverse oxidation states, and the facile interconversion between these states can pose challenges in controlling the desired reactivity.[15−19] Furthermore, the requirement of relatively high catalyst loading limits the practical application of nickel catalysis. Therefore, gaining a comprehensive understanding of the reaction mechanism, especially when it involves the activation of C−O bonds, is crucial.

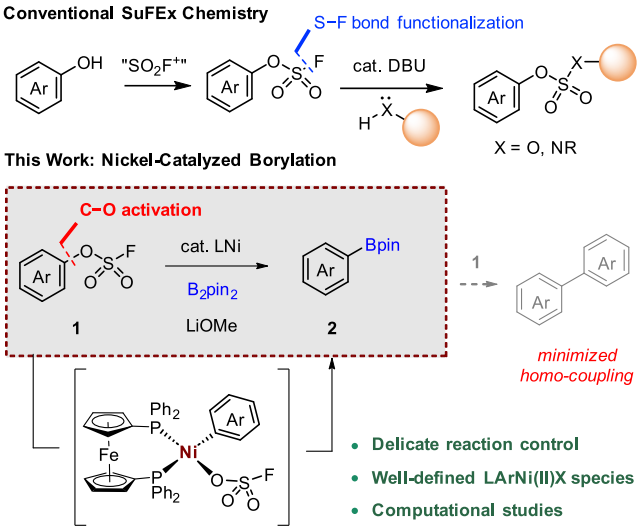
Due to the affordability and widespread availability, phenol derivatives have been employed as alternatives for aryl halides in the development of deoxygenative cross-coupling reactions.[20−23] However, a limited number of borylation reactions utilizing phenol derivatives have been reported under photoredox or first-row transition-metal catalysis.[8,24−29] This is due to the tendency of the resulting arylborons to further react with phenol derivatives, forming undesired dimerized products via cross-coupling reactions. The lack of detailed mechanistic understanding regarding key elementary reaction steps leaves room for further exploration in deoxygenative borylation using phenol derivatives.

Received: February 12, 2024
Revised: March 6, 2024
Accepted: March 11, 2024
Published: March 25, 2024

https://doi.org/10.1021/jacsau.4c00128
JACS Au 2024, 4, 1646−1653

After the pioneering development of the sulfur(VI) fluoride exchange (SuFEx) chemistry by Sharpless and co-workers,[30−33] aryl fluorosulfates have found extensive use in ligation or polymerization reactions (Scheme 1). Aryl fluorosulfates show excellent stability against hydrolysis and thermolysis when compared to sulfonyl halides.[30] These advantages of aryl fluorosulfates have enabled their exploration as a convenient source of electrophiles within catalytic reactions.[34−39] However, there is a lack of experimental characterization of well-defined nickel complexes within catalytic cycles. Herein, we present an efficient deoxygenative borylation of aryl fluorosulfates under mild conditions, achieved through nickel-catalyzed C−O bond activation instead of the typical S−F bond cleavage in SuFEx chemistry. To gain insights into the reaction mechanism, we employed a combined experimental and computational approach to elucidate the elementary reaction steps in this nickel catalysis.

Scheme 1. Catalytic S−F vs C−O Bond Activation of Aryl Fluorosulfates

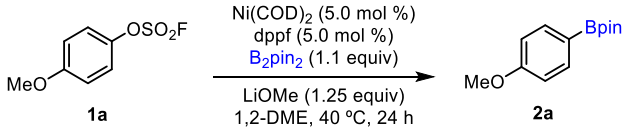


2. RESULTS AND DISCUSSION

2.1. Reaction Optmization

We began our investigation of the Ni-catalyzed borylation reaction using 4-methoxyphenyl fluorosulfate (**1a**) as a model substrate (Table 1). After rigorous optimization of the reaction parameters (see also Supporting Information, Section III-2), to our delight, the borylation proceeded efficiently under mild reaction conditions at a temperature of 40 °C. By employing 5 mol % each of $Ni(COD)_2$ and 1,1′-bis(diphenylphosphino)-ferrocene (dppf), the desired boronic ester **2a** was obtained in 82% GC yield after 24 h (Table 1, entry 1). Notably, the C−O activation of the methoxy substituent was not observed. In addition, no side products associated with the S−F activation of the fluorosulfate moiety were observed. Moreover, the reaction required near equimolar amounts of B_2pin_2 (1.1 equiv) and LiOMe (1.25 equiv) with the optimal solvent, 1,2-dimethoxy-ethane (1,2-DME). The presence of both a base and a ligand was found to be crucial for the reaction, as evidenced by the formation of only traces of the desired product **2a** in their absence (entry 2). No desired product was observed without the nickel source (entry 3). Moreover, dppf was found to be the most efficient ligand for yielding **2a**, while all other *P,P* or *N,N*-ligands were less efficient (entries 4 and 5, for more details, see also Supporting Information). Various nickel catalysts, including $NiCl_2$ glyme, $(Me_3P)_2NiCl_2$, (dcpe)Ni(COD) (**Ni1**), and $(dppf)NiCl_2$, afforded the product in moderate yields (entries 6−9). Similarly, among various solvents tested for this reaction, ethereal solvents were found to be effective and gave the desired product in high yields, while others showed poor yields (Table S1). The reaction efficiency was significantly affected by the choice of base, and except for LiOMe, other bases were found to be less effective in giving high product yields (Table S3). Notably, precomplexed catalyst (dppf)Ni(COD) (**Ni2**) afforded **2a** in higher yield (entry 10). However, when the reaction temperature was lowered to rt or the loading of **Ni2** was reduced to 2.5 mol %, the yield of **2a** was diminished to 61 and 49%, respectively (entries 11 and 12).

Table 1. Reaction Optimization[a,b]



entry	variation from initial conditions	yield (%)[a]
1	**none**	**82**
2	no base or no ligand	trace
3	no $Ni(COD)_2$	0
4	dcpe instead of dppf	27
5	xantphos instead of dppf	29
6	$NiCl_2$ glyme instead of $Ni(COD)_2$	50
7	$(Me_3P)_2NiCl_2$ as catalyst	46
8	(dcpe)Ni(COD) (**Ni1**) as catalyst	42
9	$(dppf)NiCl_2$ as catalyst	48
10	**(dppf)Ni(COD) (Ni2) as catalyst**	**88(71)**[b]
11	**Ni2** as catalyst at rt	61
12	2.5 mol % of **Ni2** used	49

[a]Reaction conditions: **1a** (0.4 mmol), B_2pin_2 (0.44 mmol, 1.1 equiv), [Ni] (5.0 mol %), ligand (5.0 mol %), base (0.5 mmol, 1.25 equiv), and 1,2-DME (1.0 mL), 40 °C, 24 h. Yields were determined by analyzing the crude reaction mixture in GC-FID using *n*-dodecane as an internal standard. [b]Isolated yield in parentheses.

2.2. Reaction Scope

With the optimized conditions in hand, we next explored the scope of the borylation reactions (Table 2). Diverse (hetero)aryl fluorosulfates and fluorosulfurylated bioactive molecules smoothly underwent the borylation reactions, affording the corresponding products **2** in moderate-to-high yields. Phenyl boronate ester **2b** was isolated in a moderate yield of 48%. *Para*-substituted electron-rich aryl fluorosulfates bearing OMe, OBn, *t*Bu, or adamantyl groups gave the respective borylated products in 61−84% isolated yields (**2a**, **2c**, **2e**, and **2k**). Substrates with electron-withdrawing groups in the *para* position, such as *p*-OPiv, *p*-CO_2Me, and *p*-$CONH_2$, afforded the corresponding boronate esters **2d**, **2h**, and **2i** in moderate-to-good yields (41−81%). Additionally, *para*-phenyl-substituted **1j** gave **2j** in a 62% isolated yield. Notably, functional groups such as *p*-F and *p*-CN were also tolerated, providing their corresponding products **2f** and **2g**, albeit in low isolated yields. Substrates bearing *o*-Me and *o*-*i*Pr groups gave the boronate esters **2l** and **2m** in 53 and 23% isolated yields, respectively, possibly due to steric hindrance.

Furthermore, disubstituted **2o** and trisubstituted **2p** were isolated in yields of 61 and 81%, respectively. Interestingly, *meta*-substituted **2n** was obtained in a high isolated yield of 84%.

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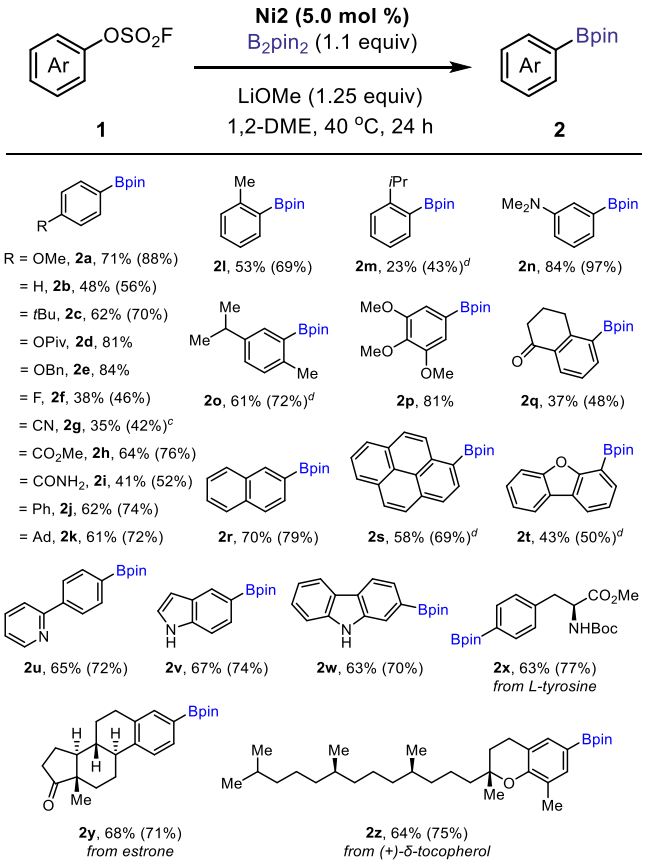
Table 2. Substrate Scope Study[a,b]



[a]Reaction conditions: **1** (0.4 mmol), B_2pin_2 (0.44 mmol, 1.1 equiv), **Ni2** (5.0 mol %), LiOMe (0.5 mmol, 1.25 equiv), and 1,2-DME (1.0 mL), 40 °C, 24 h. [b]Isolated yields are provided, with the NMR yields given in parentheses using mesitylene as an internal standard. [c]Dimerized product of **1g** was isolated in an 8% yield. [d]The reaction was extended to 36 h using 2.0 equiv of B_2pin_2 and 2.5 equiv of LiOMe.

Remarkably, **1q** bearing ketone functionality was tolerated, giving the corresponding product **2q**, albeit in a low yield. Moreover, 2-naphthol-derived **1r** and pyrene derivative **1s** produced **2r** and **2s** in moderate yields. Additionally, this method demonstrated competence in the synthesis of heteroaromatic boronic esters, providing **2t**−**2w** in moderate-to-good yields. We further highlighted the synthetic utility of this nickel catalysis by conducting late-stage borylation of fluorosulfurylated derivatives of L-tyrosine (**1x**), estrone (**1y**), and (+)δ-tocopherol (**1z**). This led to the successful formation of the corresponding borylated products **2x**−**2z** in good yields (63 to 68%).

2.3. Computational Investigations

To shed light on the detailed mechanism of this catalytic reaction, we performed density functional theory (DFT) calculations for the formation of **2b** as a model reaction, as depicted in Figure 1. The catalytic cycle is initiated by the endergonic displacement of the COD ligand of **Ni2** (denoted as **NiI**) to **1b**, generating η^2-coordinated **Int-1**. Our calculation revealed that the oxidative addition proceeded through S_NAr-type TS (**TS-1**, Figure 2a), followed by rebound of OSO_2F anion (**Int-2**). The overall free-energy barrier for the oxidative addition is computed as 8.0 kcal/mol, and the formation of **Int-2** is exergonic by 20.3 kcal/mol. The experimental studies for the isolation of arylnickel(II) intermediate by the oxidative addition will be discussed vide infra (Section 2.4). While the anion exchange between the OSO_2F anion of **Int-2** and methoxide is favored by 6 kcal/mol, in our experimental observation, the corresponding **Int-2′** species could not be detected, whereas **Int-2** was readily observed. This discrepancy may be attributed to the preferential reactivity of lithium methoxide toward B_2pin_2, leading to the formation of boronate ester (B_2pin_2·LiOMe, **A**) and concurrent reduction of the effective concentration of free methoxide ions.

During our attempts to locate the transmetalation TS directly from **Int-2**, we found that the monodentate dppf ligation is required to structurally organize **A** into the proper orientation for the TS. The formation of **Int-3** from **Int-2** is slightly exergonic by 0.2 kcal/mol and the intermediate features square planar coordination, where the methoxide of **A** and the phenyl group are coordinated trans to phosphine and OSO_2F, respectively. Interestingly, OSO_2F and pinacol are bridged by the lithium cation, and Bpin is positioned at the axial position. In the transmetalation TS (**TS-2**, Figure 2b), the Bpin is transferred to the nickel center with simultaneous cleavage of the B−B bond of **A**, generating nickel boryl intermediate **Int-4**. Our calculation revealed that the transmetalation step is highly exergonic by 25.7 kcal/mol with the free-energy barrier of 15.1 kcal/mol, indicating that the transmetalation is the rate-limiting step. For the reductive elimination step, we removed $LiOSO_2F$ and (MeO)Bpin from **Int-4** because these species are weakly bound to the nickel center. During the optimization process, we observed the bond formation between the phenyl group and the Bpin group. The resulting product-coordinated species (**Int-5**) features an η^2-coordination mode, and monodentate dppf ligation and is 7.5 kcal/mol more stable than **Int-4**. The subsequent bidentate chelation of the dppf ligand is computed to be exergonic by 16.6 kcal/mol (**Int-6**), and the product displacement of **Int-6** with **1b** regenerates **Int-1**. From the reductive elimination of **Int-4** to the catalyst regeneration step, a thermodynamically downhill process of 29.1 kcal/mol was calculated. The high exergonicity of the energy profile may provide the driving force for this nickel catalysis under mild reaction conditions.

2.4. Experimental Investigations

To gain deeper insights into the reaction mechanism, we undertook efforts to prepare catalytic reaction intermediates that correspond to the proposed elementary reaction steps. Our initial attempt to capture the oxidative addition complex **Ni3′** from **1g** and **Ni1** was unsuccessful due to its instability. We reasoned that the ligand exchange, replacing fluorosulfate with pivalate, may yield a more stabilized structure.[40] Notably, complex **Ni3** was successfully isolated in a high yield using this indirect ligand exchange method (Figure 3a). The structure of **Ni3** was unequivocally confirmed by single-crystal X-ray diffraction (XRD). Its characterization was also confirmed by comparing the spectroscopic data of the complex directly prepared from **3** with **Ni1** via oxidative addition, according to the Itami group's procedure.[40,41]

Furthermore, the reaction progress between **1g** and **Ni1** in the presence of CsOPiv was monitored by ^{31}P NMR analysis (Figure 3b). Within 10 min of the reaction, two sets of clear doublets evolved as indicated in the ^{31}P NMR spectra along with the characteristic singlet from unreacted **Ni1**. One set of doublets at chemical shifts of 70.9 and 57.5 ppm, assigned to the

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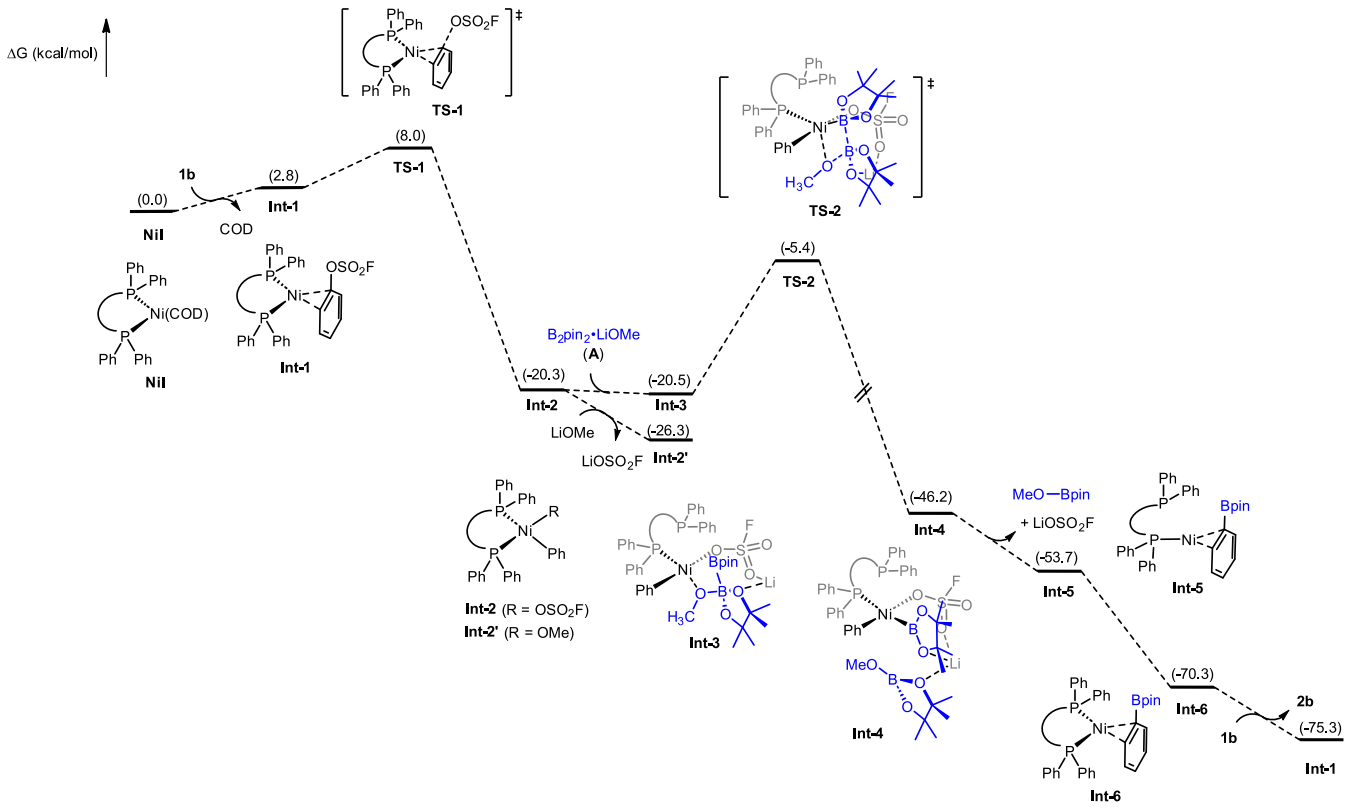

Figure 1. Calculated free-energy profile for the nickel-catalyzed borylation of aryl fluorosulfate **1b**. All calculations were performed at the SMD(DME)/M06/SDD(Ni, Fe)/6-311++G**//B3LYP-D3/LANL2DZ(Ni, Fe)/6-31G* level of theory. Energies are given in kcal/mol.

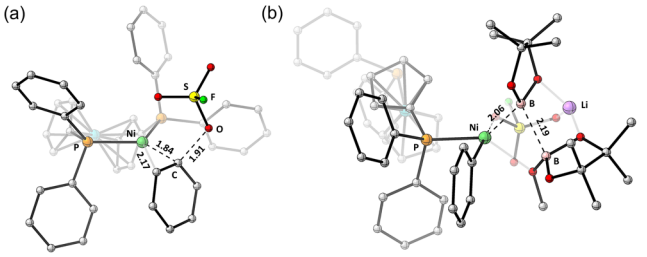

Figure 2. Optimized structures of selected TSs in Figure 1: (a) **TS-1** and (b) **TS-2**.

oxidative addition complex **Ni3′**, underwent disappearance within approximately 3 h to give **Ni3** via the ligand exchange by pivalate.

In order to obtain the isolable LArNi(OSO_2F) complex, we postulated that the introduction of substituents on the aryl fluorosulfate **4** might confer enhanced stability, as exemplified by the work of the Diao group.[42,43] To our delight, oxidative addition complexes **Ni4a** and **Ni4b** were successfully prepared by reacting aryl fluorosulfates **4a** and **4b** with **Ni2** (Figure 4a). It is noteworthy that oxidative addition across the C−O bond of aryl fluorosulfates **4a** and **4b** proceeded smoothly, reaching full conversion within 1 h of reaction time, affording the corresponding complexes **Ni4a** or **Ni4b** in 92 and 95% isolated yield, respectively. These complexes were fully characterized by spectroscopic analysis, revealing distinct features in the ^{31}P NMR spectra. Specifically, well-defined doublet signals were observed, indicative of a square planar d^8 nickel complex.[40,44] Moreover, a single-crystal X-ray structure was successfully determined for the complex **Ni4b′**, where the anionic OSO_2F group was displaced by an acetonitrile molecule during the crystal growth process.[45] These experimental results provide direct evidence of oxidative addition across the C−OSO_2F bond of aryl fluorosulfate **4b** by LNi(0), which aligns with the computational data mentioned earlier.

Then, our attention was shifted to the reactivity of the oxidative addition complexes. However, stoichiometric borylation with complex **Ni4** yielded only a trace amount of desired product **5** (Figure 4b). Instead of stoichiometric reactivity of **Ni4**, we evaluated the performance of **Ni4** in catalytic borylation of **1a** (Figure 4c), on the basis of Jamison and Doyle's previous studies that utilize the oxidative addition Ni(II) complexes as precatalysts.[46,47] Notably, these reactions gave borylated product **2a** in moderate yields under standard conditions.

In our subsequent experiments utilizing **Ni2** and aryl fluorosulfate **1a**, our aim was to investigate the role of the lithium ion in this borylation reaction. Control experiments were performed by adjusting the equivalents of 12-crown-4, a known lithium-ion capture agent. As depicted in Scheme 2, the graph shows that as the quantity of 12-crown-4 relative to LiOMe increases, the yield of **2a** decreases. This observation implies that the lithium ions are crucial for stabilizing the **TS-2** in accordance with findings from DFT studies.[42,43] Additionally, we observed that substituting LiOMe with NaOMe or KOMe (see also the Supporting Information, Table S3) led to the diminished reaction yields.

Based on the combined DFT experimental studies and the literature reports,[48−52] we propose a plausible reaction mechanism for this Ni-catalyzed borylation of aryl fluorosulfates. The initial step of the catalytic cycle involves the oxidative addition step of LNi(0) across the C−O bond of aryl fluorosulfate to give LArNi(OSO_2F). This enables an alternative reactivity of SuFExable substrates, which were previously

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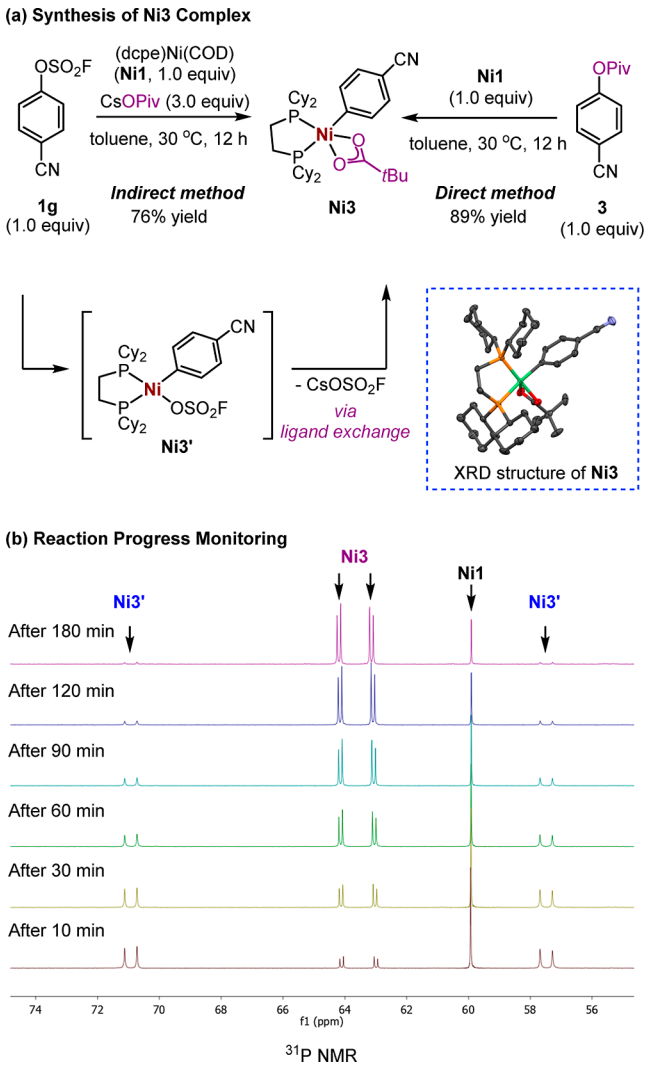

Figure 3. Synthesis of (dcpe)ArNiX complexes. (a) Synthesis of **Ni3** by direct and indirect methods. (b) Monitoring the reaction progress between **Ni1** and **1g** in the presence of CsOPiv by ^{31}P NMR (162 MHz, toluene-d_8).

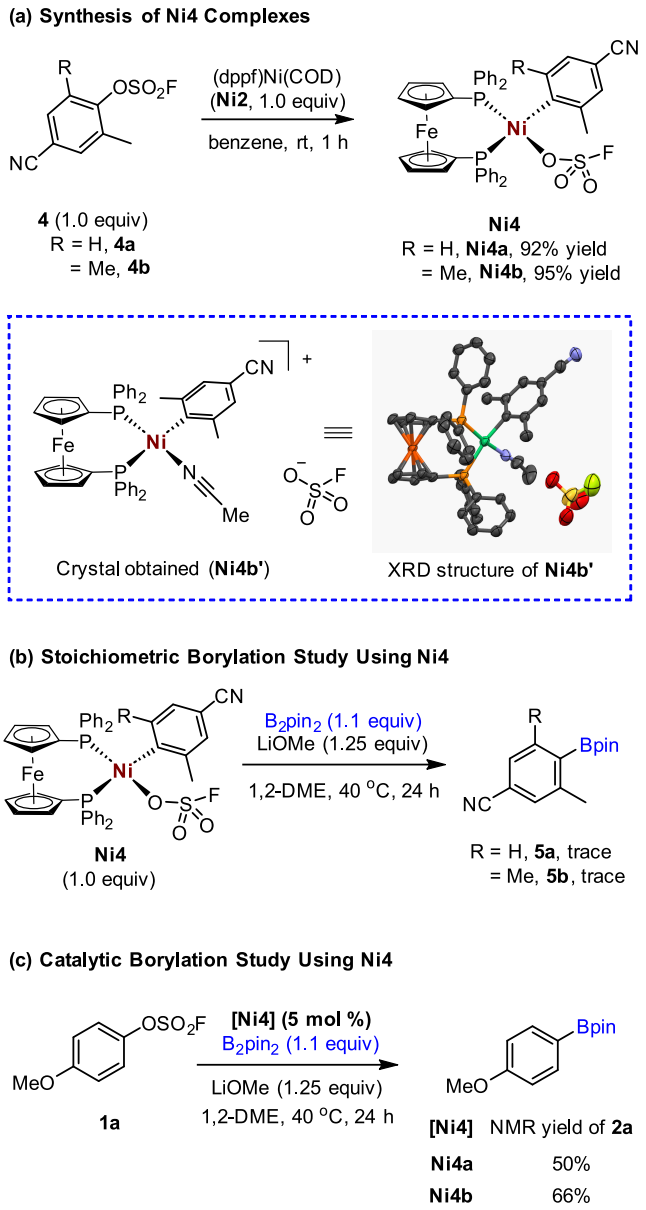

Figure 4. Synthesis of (dppf)ArNiX complexes and reactivity studies. (a) Synthesis of (dppf)ArNi(OSO$_2$F) **Ni4** by reacting **Ni2** and **4**. (b) Stoichiometric borylation reaction of **Ni4**. (c) Catalytic reactivity of **Ni4** in the borylation reaction. NMR yields were obtained by using mesitylene as an internal standard.

primarily focused on S−F bond functionalization. Following the oxidative addition step, the transmetalation step occurs where an activated B_2pin_2·LiOMe adduct transfers a boryl group to the LArNi(OSO$_2$F) complex, generating a LArNi(Bpin) complex. Finally, the reductive elimination of the complex yields the aryl boronate ester, while regenerating the Ni(0) active catalyst.

3. SUMMARY AND CONCLUSIONS

In this work, we successfully demonstrated a catalytic approach for transforming aryl fluorosulfates into aryl boronate esters. The reaction conditions are mild and require a low catalyst loading. Well-defined arylnickel(II) species, obtained from the oxidative addition of aryl fluorosulfates, were isolated for the first time, and their catalytic activities were examined. DFT calculations indicate that the direct transfer of the Bpin moiety from the activated boronate ester to the arylnickel(II) intermediate is operative via the unique lithium-bridged transition state. We anticipate that the combined experimental and computational studies will enhance our understanding of catalytic intermediates. These findings can serve as the foundation for rational catalytic system design associated with organic synthesis, particularly for less explored substrates.

4. METHODS

4.1. General Borylation Procedure

In a N_2-filled glovebox, a 4 mL vial equipped with a magnetic stir bar was charged with (dppf)Ni(COD) (**Ni2**) (5 mol %), bis(pinacolato)-diboron (1.1 equiv), and LiOMe (1.25 equiv), followed by 1,2-DME. The mixture was then stirred at 40 °C for 15 min on a preheated metallic block. Subsequently, aryl fluorosulfate (1.0 equiv) was added. After stirring for 24 h at 40 °C, the reaction mixture was transferred to a 50 mL round-bottomed flask containing 20 mL of diethyl ether. After stirring for an additional 15 min at rt, the mixture was filtered through a short pad of Celite and washed thoroughly with diethyl ether (10 mL × 2). The combined filtrate was concentrated in vacuo. The corresponding aryl boronic ester was isolated by flash column

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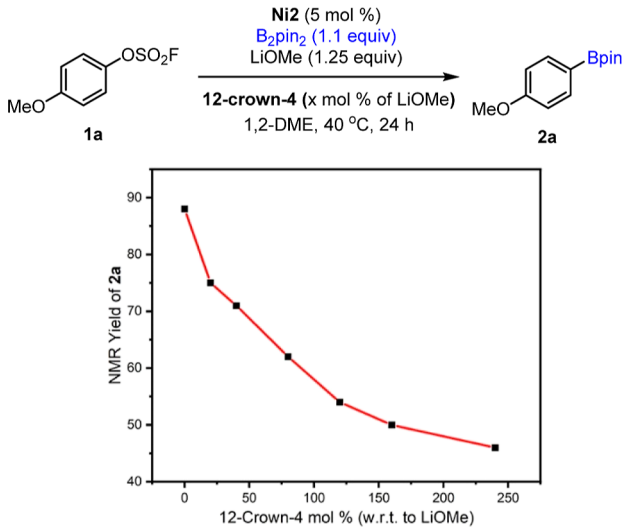
Scheme 2. Role of Lithium Ions in the Catalytic Activity



chromatography using boric acid-impregnated silica gel to obtain the desired product.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.4c00128.

Experimental procedures, experimental and computational details, characterization data, spectra for all new compounds, crystallographic data, and Cartesian coordinates of all-computed structures (PDF)

Crystallographic data for **Ni3** (CIF)

Crystallographic data for **Ni4b′** (CIF)

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Author Contributions

M.K.S., B.J., J.K., and S.Y.H. conceived the project. M.K.S. and J.W.L. conducted the experiments. S.L. and W.C. obtained and analyzed the single-crystal XRD structure data. J.K. carried out the DFT calculations. All authors analyzed and interpreted the results. The manuscript was written through the contributions of all authors. All authors have given their approval to the final version of the manuscript. CRediT: **Manoj Kumar Sahoo** conceptualization, formal analysis, investigation, methodology, writing-original draft, writing-review & editing; **Jeong Woo Lee** data curation, formal analysis, writing-review & editing; **Soochan Lee** formal analysis, investigation, writing-original draft, writing-review & editing; **Wonyoung Choe** data curation, formal analysis, investigation, writing-original draft, writing-review & editing; **Byunghyuck Jung** conceptualization, data curation, formal analysis, investigation, writing-original draft, writing-review & editing; **Jaesung Kwak** conceptualization, data curation, formal analysis, funding acquisition, software, validation, writing-original draft, writing-review & editing; **Sung You Hong** conceptualization, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, writing-original draft, writing-review & editing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Professor Joong-Hyun Chun for discussions and valuable suggestions. This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2023R1A2C1004563, NRF-2020M3H4A3081883, and NRF-2020R1A5A1019631) and R&D research program of the Institutional Research Program of KRICT (KK2432-10). Single-crystal XRD experiments with synchrotron radiation were performed at the BL2D-SMC in the Pohang Accelerator Laboratory.

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