Exploiting the trifuoroethyl group as a precatalyst ligand in nickel-catalyzed Suzuki-type alkylations†

Yi Yang, Qinghai Zhou, Junjie Cai, Teng Xue, Yingle Liu, Yan Jiang, Yumei Su, Lungwa Chung and David A. Vicic*

We report herein the exploitation of the partially fluorinated trifuoroethyl as precatalyst ligands in nickel-catalyzed Suzuki-type alkylation and fluoroalkylation coupling reactions. Compared with the [L₆Ni(aryl)(X)] precatalysts, the unique characters of bis-trifuoroethyl ligands imparted precatalyst [{bipy}Ni(CH₂CF₃)₂] with bench-top stability, good solubilities in organic media and interesting catalytic activities. Preliminary mechanistic studies reveal that an eliminative extrusion of a vinylidene difluoride (VDF, CH₂=CF₂) mask from [{bipy}Ni(CH₂CF₃)₂] is a critical step for the initiation of a catalytic reaction.

Introduction

Transition metal catalyzed cross-coupling reactions have advanced organic synthesis in the last few decades and have become powerful tools for the generation of molecular complexity. Substantial effort has been devoted to identifying general and robust transition metal catalytic systems for reaction methodology research and chemical production improvement. A prominent example is the development of Suzuki–Miyaura coupling systems, which now employ a diverse combinations of transition-metals, supporting ligands, and coupling partners to construct C(sp²)–C(sp³) bonds. Although Pd catalysts operate with much success in this arena, the development of Ni-catalyzed protocols has been of interest because of the cost efficiency and complementary reactivities. For instance, Ni-catalyzed couplings are particularly useful for constructing synthetically challenging C(sp²)–C(sp³) linkages due to the facile oxidation of low-valent nickel by C(sp³)-centered electrophiles and the suppression of undesired β-hydrogen eliminations at nickel. One of the most successful catalysts for nickel-catalyzed coupling reactions is derived from the [(bipyridine)nickel] motif which has been widely employed for both traditional cross-coupling and photoredox catalysis. However, it should be noted that the conventional [(bipyridine)nickel] systems characterized by a combination of Ni⁰ catalysts or inorganic Niᴵᴵ salts with bipyridyl ligand still suffer from some unneglectable limitations: (i) commonly used Ni⁰ sources for catalysis are expensive and air-sensitive, thus hindering their use out of glovebox for large-scale synthesis; (ii) the low solubility of inorganic Niᴵᴵ salts complicates the heteroleptic coordination of exogenous supporting ligands which could have deleterious effects on reaction outcomes.

In this context, the development of robust nickel-based precatalysts in which the metallic cores are preligated with privileged ligands is highly desirable and constitutes a viable solution to address the above-mentioned limitations. Recently, the carbon-bound nickel precatalysts have exerted powers in a variety of coupling reactions as alternatives to the conventional [L₆NiX₂] precatalysts (L = P or N ligands). Notably, many previously reported carbon-bound Ni precatalysts [L₆Ni(X)(R)] feature sterically bulky ligands (R = o-tolyl, mesityl, 1-naphthyl), or highly stabilizing motifs (R = η⁵-allyl, η⁵-Cp) for sheltering reactive organometallic nickel cores (Fig. 1-A). Considering that fluoroalkyl ligands are known to confer enhanced stability to metal complexes relative to their non-fluorinated alkyl counterparts owing to fluorine’s unique electronic and steric properties, we wondered whether the incorporation of selected fluoroalkyl moieties could support novel nickel-based precatalysts and render new catalytic activities for use in synthetic methods development (Fig. 1-B). Herein, we describe the synthesis of such a fluoroalkyl-bound nickel precatalyst and demonstrate its use in C(sp²)–C(sp³) Suzuki-type coupling reactions.

Result and discussion

At the outset, we began the rational design of precatalyst based on the principles of utilizing short fluoroalkyl and bipyridine as supporting ligands for atomic economy and C(sp²)–C(sp³)
coupling reaction efficiency. Specifically, the short and partially fluorinated CF$_3$CH$_2$ group was selected as supporting ligand (analogue of ethyl group but end-capped with fluorines) which was anticipated to render distinctive thermostability and reactivities versus both the hydrocarbonated [(bipy)Ni(CH$_2$CH$_3$)$_2$] and perfluorinated [(bipy)Ni(CF$_2$CF$_3$)$_2$] counterparts (Fig. 1B, bipy = 2,2'-bipyridine). Gratifyingly, the reaction of [Ni(COD)$_2$], CF$_3$CH$_2$I, and 2,2-bipyridine furnished [(bipy)Ni(CH$_2$CF$_3$)$_2$] 2 in 41% isolated yield (eqn (1)) presumably via an interesting ligand redistribution$^{12-15}$ of the intermediate [(bipy)Ni(CH$_2$CF$_3$)$_2$] 1. The solubility of complex 2 in benzene facilitated its isolation from the nickel halide co-products 3. The $^{19}$F NMR spectra of 2 exhibited a triplet at $\delta = -47.98$ ppm, demonstrating the presence of CH$_2$CF$_3$ groups and their bonding to Ni core. Dark red crystals of 2 can be grown from THF/pentane and are air-stable at room temperature for several weeks.

\[
\begin{align*}
\text{Ni(COD)$_2$} + \text{bipy} & \xrightarrow{CF_3CH_2I} [\text{(bipy)Ni(CH$_2$CF$_3$)$_2$}] \\
1/2 \times (\text{bipy})\text{Ni(CH$_2$CF$_3$)$_2$} + & \xrightarrow{1/2 \times \text{bipy} \text{NiI}_2} 2 \quad 41\% \text{ isolated yield} \\
& \text{insoluble in benzene}
\end{align*}
\]

X-ray diffraction analysis of 2 confirmed the ligation of two CH$_2$CF$_3$ groups at nickel (Fig. 2). Complex 2 featured a square planar arrangement at the Ni$^{10}$ core with a rough linear trans N–Ni–C linkage (bond angle: 177.4(2) and 177.8(2)$^{\circ}$). In contrast, more striking distortions were found in the previously reported and related complexes [(bipy)Ni(CF$_2$CF$_3$)$_2$] 4 (trans N–Ni–C bond angles: 165.1(2)$^{\circ}$ and 159.7(2)$^{\circ}$) and [(bipy)Ni(CF$_2$CF$_3$)$_2$] 5 (both at 132.2$^{\circ}$)$^{14,15}$, indicating fewer steric and electronic repulsions of the CH$_2$CF$_3$ chains in 2 compared to the perfluorinated derivatives. Interestingly, Ni–C distances of 2 (1.944(5) and 1.942(4) Å) are substantially longer than those of 4 (1.872(6) and 1.883(6) Å) and 5 (1.910(6) and 1.911(6) Å). Besides, the value of C(2)–F(3) bond length [1.366(6) Å, trans coplanar to C(1)–Ni bond] was clearly larger than the others two carbon–fluorine bonds [C(2)–F(1) 1.346(5) Å; C(2)–F(2) 1.342(6) Å] which implied the possible use of β-fluorine elimination for further coupling reaction development.

Although we did not obtain the one fluoroalkyl accommodated nickel complex [(bipy)Ni(CH$_2$CF$_3$)$_2$] 1 which showed more structural similarities to the reported [(bipy)Ni(o-tolyl)Cl] precatalyst,$^{14b}$ we presumed that β-fluorine elimination$^{16}$ of [(bipy)Ni(CH$_2$CF$_3$)$_2$] 2 hinted by the C–F bond length analysis could be leveraged for the in situ generation of [(bipy)NiF(CH$_2$CF$_3$)$_2$] 2a with concurrent extrusion of vinylidenedifluoride (CH$_2$=CF$_2$). Notably, the Ni–F structural motif of intermediate 2a was supposed to facilitate the transmetalation of aryboronic acids towards nickel according to a recent example of base-free Suzuki coupling.$^{5e}$ Furthermore, the bis-trifluoroethyl structural motifs of [(bipy)Ni(CH$_2$CF$_3$)$_2$] 2 entails the bench-top stability and excellent solubility in organic solvents which is of vital importance for developing nickel-based precatalysts.$^{9,10}$

With [(bipy)Ni(CH$_2$CF$_3$)$_2$] 2 in hand, we initially assessed it as a precatalyst for the Suzuki-type coupling between CF$_3$CH$_2$I and aryboronic acids for C(sp$^3$)–C(sp$^3$) bonding. Based upon previously established Ni-catalyzed trifluoroethylation conditions,$^{17}$ we were pleased to find that coupling products can be obtained in excellent yields at 80 °C with 5 mol% catalyst loading using K$_3$PO$_4$ as a base and DME as a solvent (Table 1, entry 1). Use of other solvents decreased the yields, and only polar non-protic DMSO solvent was comparatively effective. Furthermore, the use of KFPO$_4$ was critical to the success of the coupling reaction and suppressing dehydrofluorination of the final products (for details, see ESI Tables S1 and S2†). The commercialized [TMEDA]Ni(o-tolyl)Cl bearing modular TMEDA was found to be less efficient (yield 35%) with using the privileged bipyridine as the leading supporting ligand (Table 1, entry 2). In contrast, the bipyridine preligated [(bipy)Ni(o-tolyl)]
bearing the privileged o-tolyl ligand improved the coupling yield to 78% but was still inferior to that of [(bipy)Ni(CH2CF3)2]. These results demonstrated the importances of supporting ligation groups of both trifluoroethyl and bipyridine in the structural motif of [(bipy)Ni(CH2CF3)2] (Table 1, entries 2–3). Even the classical [(dppf)Ni(o-tolyl)Cl] or [Ni(COD)2] did not perform as well.

**Table 1** Survey of reaction conditions

| Entry | Variation from standard conditions | Isolated yield |
|-------|------------------------------------|----------------|
| 1     | None                               | 93%            |
| 2     | [[TMEDA]Ni(o-tolyl)Cl] (5.0 mol%) and 2,2-bipyridine (5.0 mol%) instead of 2 | 35%            |
| 3     | [[bipy]Ni(o-tolyl)Cl] (5.0 mol%) instead of 2 | 78%            |
| 4     | [[dppf]Ni(o-tolyl)Cl] (5.0 mol%) instead of 2 | 25%            |
| 5     | [Ni(COD)2] (5.0 mol%) and 2,2-bipyridine (5.0 mol%) instead of 2 | 40%            |
| 6     | [bipy]NiEt2] (5.0 mol%) instead of 2 | 13%            |
| 7     | [(MeCN)2Ni(CF2CF3)2] (5.0 mol%) and 2,2-bipyridine (5.0 mol%) instead of 2 | 55%            |
| 8     | [(MeCN)2Ni(CF3)2] (5.0 mol%) and 2,2-bipyridine (5.0 mol%) instead of 2 | 51%            |
| 9     | 2.5 mol% loading of precatalyst 2 | 91% (83%)      |
| 10    | 1.0 mol% loading of precatalyst 2 | 79%            |

**Table 2** Substrate scope of (hetero)arylboronic acid partners

| (Het)Ar-B(OH)2 | CF3CH2I | Isolated yield |
|----------------|---------|----------------|
| 1              | 25 mol% of 2 | 80%            |

**General conditions:** 4-biphenylboronic acid (0.3 mmol), CF3CH2I (0.2 mmol), K3PO4 (0.4 mmol), 5.0 mol% precatalyst loading of 2, DME (1.0 mL). **Gram-scale synthesis.**
bipyridine combined system gave unsatisfactory yield (25–40%) compared with the use of 2 (Table 1, entries 4–5). For further demonstrating the distinctive role of partially fluorinated trifluoroethyl ligand, we compared its catalytic performance with those surrogating [(bipy)NiEt₂]₁⁶ [(bipy)Ni(CF₂CF₃)₂]₁² and [(bipy)Ni(CF₃)₂]₁² (Table 1, entries 6–8). It was found that these fully hydrocarbonated and fluorinated counterpart complexes can not furnish comparable catalytic outcomes. Gratifyingly, the tests of decreasing the precatalyst loading and gram-scale synthesis also provided the coupling product in comparatively good yields (Table 1, entries 6–7). These results demonstrated proof-in-principle of the excellent catalytic efficiency of precatalyst 2 for the targeted Suzuki-type couplings.

Under the optimized conditions, a wide array of arylboronic acid coupling partners were found to successfully participate in the Suzuki-type trifluoroethylation catalyzed by 2 (Table 2). Both the electron-donating and electron-withdrawing groups substituted arylboronic acids were competent substrates and gave the desired product in moderate to good yield. Broad functional groups were well tolerated, including ethers (7c–7e), aldehydes (7f, 7j), enolizable ketones (7g, 7k), esters (7h, 7l) and nitriles (7i, 7m). Notably, the nitrogen-containing heterocyclic boronic acids (7o, 7p) proceeded smoothly with good yields despite the potential strong binding affinity of the nitrogen atoms with Ni. To further exhibit the synthetic practicability of our precatalyst and trifluoroethylolation protocol, the late-stage modifications of fenofibrate and clofibrate (drugs against cardiovascular disease) were accomplished (7s, 7t). Therefore, this synthetic strategy should provide important opportunities for making more diverse biologically active molecules.

Further demonstration of the privileged catalytic utilities of precatalyst [(bipy)Ni(CH₂CF₃)₂]₂ was showcased by several types of C(sp²)–C(sp³) Suzuki-type alkylations. Iodoethane (8), 3-iodooxetane (9), ethyl bromoacetate (10), allyl bromide (11), (4,4,4-trifluoro-3-iodobutyl)benzene (12a), HCF₂CH₂I (12b) and FCH₂CH₂I (12c) were found to successfully couple with a series of arylboronic acids ranging from electron-poor and electron-rich types (Table 3). The encouraging results showed

![Table 3 Versatility of precatalyst 2 for aryl–alkyl cross-coupling reactions](image)

For the complete table, please refer to the original publication.

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* General conditions: (hetero)arylboronic acid (0.6 mmol), the indicated R–X (0.4 mmol), base (0.8 mmol), 2.5 mol% precatalyst loading, DME (2.0 mL), 80 °C. Isolated yield. Yield determined by ¹H NMR spectroscopy using Cl₂CHCHCl₂ as an internal standard due to the difficulties in separation of product from deboronative byproduct. Using 5.0 mol% precatalyst loading and DMSO as the solvent instead of DME. Using 5.0 mol% precatalyst loading.
that these primary and secondary alkyl halides were readily compatible with this catalytic alkylation, regardless of the possible β-H or β-F elimination problems.49 Further, the active allyl group can be coupled with the aromatic groups without detection of the migration of double bond (13d).7

The success of precatalyst 2 for the Suzuki-type alkylations further encouraged us to investigate the reaction mechanism. At the start, we intended to determine whether the activation mode of [(bipy)Ni(CH2CF3)2] was consistent with our β-fluorene elimination hypothesis. The precatalyst could undergo β-fluorene elimination to afford [(bipy)Ni(F)(CH2CF3)] 2a with extrusion of CH2=CF2, or alternatively undergo reductive elimination like the analogous [(bipy)Ni(CH2CH3)] to generate a [(bipy)Ni(0)] species and CF3CH2CH2CF3. Heating precatalyst 2 at elevated temperature indicated the clear formation of CH2=CF2 rather than CF3CH2CH2CF3 through continuous 1H and 19F NMR monitoring (for details, see ESI†). These results suggested that the formation of CH2=CF2 was less likely (Scheme 1-A).9 Additionally, the identification of CH2=CF2 and Ar-CH2CF3 (Ar = 4-biphenyl) in GC-MS and NMR analysis of the reactions in Table 3 (e.g. 14b, coupling between 4-biphenylboronic acid and 3-iodooxetane in Scheme 1B) revealed the important roles of the trifluoroethyl groups bound to nickel core (for details, see ESI Fig. S124, S125 and Table S5†). These results suggested that the first trifluoroethyl group functioned as the mask of the suggested active species [(bipy)Ni(F)(CH2CF3)] 2a via a CH2=CF2 extrusion and the second trifluoroethyl moiety contributed as coupling partner for the formation of Ar-CH2CF3. Interestingly, the finding of byproduct CH2OCH[Ar]CH2OCH3 and ArCH2OCH2CH2OCH3 (Scheme 1-B) illustrated plausible radical activation of DME through abstraction of ethereal α-hydrogens by solvent-caged alkyl radicals.49

Next, a series of radical inhibition experiments were conducted to verify the possibilities of radical intermediacy (for details, see ESI Tables S8–S10†). It was found that the radical scavenger TEMPO shut down the coupling reactions completely when using the 3-iodooxetane or CF3CH2I as the alkyl electrophiles. Instead, TEMPO-alkyl (alkyl = 3-oxetanyl or trifluoroethyl) adducts 17 and 18 were observed in the GC-MS analysis, respectively. Also, when a radical-clock cyclopropane-based substrate was used, a few ring-opening products like the CF3CH2-merged product 20 and aryl-incorporated product 21 were identified. These experimental results suggested the involvement of CF3CH2- radicals (or R radicals) as well as aryl-bound nickel intermediates in the reaction profile.

With the above clues of reaction scenarios in hand, we conducted further interrogations on whether the reactions proceeded via a NiII/Ni0 or Ni0/NiII redox shuttle. The important findings of bis-trifluoroethyl ligands of 2 serving as CH2=CF2 mask and operational ligand for producing Ar-CH2CF3 inspired us to devise a stoichiometric reaction of complex 2 with 4-biphenylboronic acid as control experiment (Scheme 2-A). The intermediate [(bipy)Ni(F)(CH2CF3)] 2a could be generated in situ under the reaction conditions which was supposed to further undergo a facile Ni–B transmetalation* to deliver [(bipy)Ni([Ar][CH2CF3])] 2b (Ar = 4-biphenyl). However, the putative [(bipy)Ni(4-biphenyl)] intermediate did not proceed through a Ni(0)/Ni(0) reductive elimination† to furnish Ar-CH2CF3. In addition, CF3CH2F and CF3CH2CH2CF3 were also not found which disfavored the scenario of Ni formation from the reductive elimination of 2a and 2. Taken together, these divalent organonickel intermediates (2, 2a and 2b) were not productive for the corresponding NiII/Ni0 reductive elimination under this current reaction system. Interestingly, the product

**Scheme 1** Control experiments for identifying the role of trifluoroethyl ligands in precatalyst 2.

**Scheme 2** Control experiments to support NiII/Ni0 redox shuttle in the catalytic cycle.
Ar–CH2CF3 was almost comparably efficiently obtained when the precatalyst 2 was replaced by the putative [(bipy)NiI(Br)] complex21 for the coupling between ArB(OH)2 and CF3CH2I (Scheme 2-B). These experimental results suggested that a NiI/NiII catalytic cycle was highly likely to be superior to NiII/NiIII counterpart in the current reaction systems.

Based on the above-mentioned experimental results and relevant previous reports,5,6,11,13 a plausible mechanism was proposed for these current cross-couplings (Scheme 3). The catalysis commences with an eliminative liberation of a CH2==CF2 mask and 2a. Intermediate 2a is proposed to undergo transmetalation and subsequent abstraction of halogen atom from R–X to afford (bipy)NiII[(Ar)(CH2CF3)](X) A. Reductive elimination of A has been fingerprinted by the formation of Ar–CH2CF3 and delivered a key catalytic species (bipy)NiI(X) B. Upon the participation of B into the conventional NiI/NiII/NiIII catalytic cycle, the shuttles via transmetalation/oxidative addition/reductive elimination provided efficient platform for the above described Suzuki-type C(sp2)–C(sp3) alkyl coupling reactions.14

Conclusions

In conclusion, we demonstrated that the nickel-based precatalyst 2 [(bipy)Ni(2-iodo-1,1,1-trifluoroethane)12a–12c] can be employed in Suzuki-type coupling reactions between (hetero)arylborationics and a variety of alkyl halides including several typical partially fluorinated alkyl halides bearing susceptible β-fluorine atoms (2-iodo-1,1,1-trifluoroethane and 12a–12c), leading to new C(sp2)–C(sp3) linkages. Catalytic performance tests demonstrated the advantages of the trifluoroethyl ligand motifs in the precatalyst [(bipy)Ni(CH2CF3)2] versus several sibling perfluorinated and hydrocarbonated counterparts.24 The critical roles of trifluoroethyl groups of precatalyst 2 as both CH2==CF2 mask and triggering coupling-ligand in these nickel-catalyzed Suzuki-type alkylations were elucidated through mechanistic investigations. We believe that the initial success outlined here could prompt the utilization of more fluoroalkyl binding moieties for the development of new metal-based precatalysts with tailored activities. Further studies towards this endeavor and mechanistic details are underway in our laboratory, and the results will be reported in due course.

Conflicts of interest

We authors announce that there are no conflicts to declare.

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18 Although \([\text{bip} \text{pyNi(CH}_2\text{CF}_3)_2]\) could be generated in situ within the [Ni(COD)]_2/bipyridine trifluoroethylation systems, the deleterious effect of 1,5-cyclooctadiene (COD) on the current coupling can not be neglected. Please see related ref. 10a, ej. D. Shields, D. T. Ahneman, T. J. A. Graham and A. G. Doyle, \textit{Org. Lett.}, 2014, \textit{16}, 142, and .

19 The reductive eliminations of difluoroalkynickel species were also proved to be challenging in the ref. 12e and 13c.

20 When using CF\(_3\)CH\(_2\)I or BrCH\(_2\)CO\(_2\)Et as electrophiles, we also found the formation of by product R−H (R = CF\(_3\)CH\(_2\)- or EtOOCCH\(_2\)-) which could be ascribed to the abstraction of ethereal \(\alpha\)-hydrogen in the DME solvent cages (for details, see ESI Tables S6 and S7\(^{\dag}\)). For related references for radical reactions in solvent cage: (a) D. A. Braden, E. E. Parrack and D. R. Tyler, \textit{Coord. Chem. Rev.}, 2001, \textit{211}, 279; (b) K. Michio, G. Michiko and Y. Masato, \textit{Bull. Chem. Soc. Jpn.}, 1987, \textit{60}, 295; (c) R. A. Sheldon and J. K. Kochi, \textit{J. Am. Chem. Soc.}, 1970, \textit{92}, 4395.

21 \([\text{bipyNiI}}\text{Br}]]\) was prepared according to the synthetic method of \([\text{dipfNiI}}\text{Cl}]]\): (a) L. M. Guard, M. Mohadjer Beromi, G. W. Brudvig, N. Hazari and D. J. Vinyard, \textit{Angew. Chem., Int. Ed.}, 2015, \textit{54}, 13352. It was characterized by IR and XPS due to its bad solubility for single crystal formation (for details, see ESI\(^{\dag}\)). Very recently, Hazari group disclosed the synthesis of \([\text{neocuproineNiI}}\text{Cl}]](\text{Cl})\) which had a similar skeleton: (b) M. Mohadjer Beromi, G. W. Brudvig, N. Hazari, H. M. C. Lant and B. Q. Mercado, \textit{Angew. Chem., Int. Ed.}, 2019, DOI: 10.1002/anie.201901866.

22 For selected example of radical-rebound oxidative addition of alkyl halide: (a) Z. Ruan, S. Lackner and L. Ackermann, \textit{Angew. Chem., Int. Ed.}, 2016, \textit{55}, 3153. If the radical-chain mechanism was operative, the cage-escaped radicals should dimerize via radical recombination. Also, we did not detect any radical dimerization products (R−R) in these experiments which could support a fast cage-rebound other than cage-escape process. For our recent report about the radical-rebound oxidative addition step in the nickel-catalyzed Suzuki-type fluoroethylation: (b) Y. Yang, J. Cai, G. Luo, Y. Jiang, Y. Su, Y. Su, C. Li, Y. Zheng, J. Zeng and Y. Liu, \textit{Org. Chem. Front.}, 2019, DOI: 10.1039/c9qo00066f. For some seminal literatures for elucidating cage-rebound or cage-escape modes: ref. 15b and (c) J. Breitenfeld, J. Ruiz, M. D. Wodrich and X. Hu, \textit{J. Am. Chem. Soc.}, 2013, \textit{135}, 12004.

23 According to the recent reports about the catalytic activities of \([\text{L}_3\text{NiAr}]]\), the catalytic shuttle started from the species \([\text{L}_3\text{NiAr}]]\) \(B\) via a transmetalation/oxidative addition/reductive elimination sequence other than oxidative addition/transmetalation/reductive elimination order should be plausible. The observed inertness of \([\text{bipyNiI}}\text{Br}]]\) towards CF\(_3\)CH\(_2\)I seemed to rule out the oxidative addition/transmetalation/reductive elimination sequence. For some references about related \([\text{L}_3\text{NiAr}]]\) complexes: (a) J. B. Diecianni, J. Katiigbak, C. Hu and T. Diao, \textit{J. Am. Chem. Soc.}, 2019, \textit{141}, 1788; ref. 10i. More corroborative computational studies can be found in these references: (b) Z. Li, Y.-Y. Jiang and Y. Fu, \textit{Chem.–Eur. J.}, 2012, \textit{18}, 4345; (c) X. Lin and D. L. Phillips, \textit{J. Org. Chem.}, 2008, \textit{73}, 3680. For selected references that support Ni\(^{\text{II}}\)/Ni\(^{\text{III}}\) catalytic shuttle: ref. 13c and d (d) G. D. Jones, J. L. Martin, C. McFarland, O. R. Allen, R. E. Hall, A. D. Haley, R. J. Brandon, T. Konovalova, P. J. Desrochers, P. Pulya and D. A. Vicic, \textit{J. Am. Chem. Soc.}, 2006, \textit{128}, 13175; (e) B. Zheng, F. Tang, J. Luo, J. W. Schultz, N. P. Rath and L. M. Mirica, \textit{J. Am. Chem. Soc.}, 2014, \textit{136}, 6499.

24 GC-MS analysis of the reaction mixtures (Table 1, entries 7–8) revealed no formation of Ar-CF\(_3\)CF\(_3\) or Ar-CF\(_3\), respectively. These results demonstrated quite different catalytic profiles in which CF\(_3\)CF\(_3\) and CF\(_3\) did not serve as coupling ligands. Unlike the CF\(_3\)CH\(_2\) counterpart, their reluctance to contribute as triggering coupling-ligand might be explained by the challenging Ar-R\(_q\) (R\(_q\) = perfluoroalkyl) reductive elimination. For related reference: G. G. Dubinina, W. W. Brennessel, J. L. Miller and D. A. Vicic, \textit{Organometallics}, 2008, \textit{27}, 3933.