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Decisive Steps of the Hydrodefluorination of Fluoroaromatics using [Ni(NHC)$_2$]

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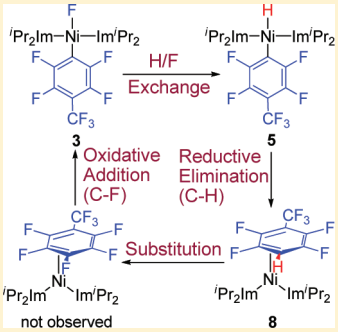
Supporting Information

ABSTRACT: The hydrodefluorination reaction of perfluorinated arenes using [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**; ^{i}Pr$_2$Im = 1,3-bis(isopropyl)imidazolin-2-ylidene) as a catalyst as well as stoichiometric transformations to elucidate the decisive steps for this reaction are reported. The reaction of hexafluorobenzene with 5 equiv of triphenylsilane in the presence of 5 mol % of **1** affords 1,2,4,5-tetrafluorobenzene after 48 h at 60 °C and 1,4-difluorobenzene after 96 h at 80 °C; the reaction of perfluorotoluene and 5 equiv of Et$_3$SiH for 4 days at 80 °C results in the selective formation of 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H. Stoichiometric transformations of the complexes *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiPh$_3$)] and *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiMePh$_2$)] with hexafluorobenzene at room temperature lead to the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) with elimination of the corresponding silane or fluorosilane. The reactions of the C−F activation products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**) with PhSiH$_3$ and Ph$_2$SiH$_2$ afford the hydride complexes *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**), which convert into the compounds *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**), *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**), and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), respectively. In the case of the rearrangement of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) the intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) was detected. Reaction of **8** with perfluorotoluene gave the C−F activation product *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**). All these experimental findings point to a mechanism for the HDF by [Ni(^{i}Pr$_2$Im)$_2$] via the "fluoride route" involving C−F activation of the polyfluoroarene, H/F exchange of the resulting nickel fluoride, reductive elimination of the polyfluoroaryl nickel hydride to an intermediate with a η^2-C,C-coordinated arene ligand, subsequent ligand exchange with the higher fluorinated polyfluoroarene, and renewed C−F activation of the polyfluoroarene. Without additional reagents, [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) rearranges to the isomers *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**; major) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**; minor) in a ratio of 80:20. DFT calculations performed on conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] **5** into the two products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] **9a** and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**) using the commonly accepted intramolecular concerted pathway via η^2-C,F-σ-bound transition states predict **9b** to be the major product. We thus propose that this reaction mechanism is not valid for the [Ni(NHC)$_2$]-mediated C−F activation of partially fluorinated arenes with special substitution patterns.



INTRODUCTION

The selective synthesis of fluoroarene compounds has become a subject of growing interest due to the prominent role such species play in many modern pharmaceuticals, agrochemicals, and other industrially important products.[1] An attractive route for the selective substitution of fluoroarenes is based on the functionalization of activated aromatic C−F bonds derived from readily available perfluoroarenes.[2] The simplest example for this process is the hydrodefluorination reaction (HDF), in which fluorine is substituted for hydrogen. Catalytic HDF of C$_6$F$_6$ and C$_6$F$_5$H to C$_6$F$_5$H and 1,2,4,5-C$_6$F$_4$H$_2$ has been reported by Milstein and Aizenberg using a silylrhodium complex.[3] Since their seminal work on the F/H exchange between hydrosilanes and fluoroarenes under mild conditions, the work on hydrodehalogenation reactions of fluorocarbons using silanes has grown consistently.[4] Holland et al.[4c] reported in 2005 on the catalytic HDF of perfluorinated aromatic compounds such as hexafluorobenzene, pentafluoropyridine, and octafluorotoluene with silanes R$_3$SiH (R = OEt, Et, Ph) using β-diketiminate iron(II) fluoride complexes as catalysts. For this system high catalyst loadings up to 20 mol % were needed and the turnover numbers observed were low due to catalyst degradation at the temperatures used. Another interesting example was reported recently by Whittlesey and co-workers.[4h,l] The HDF of C$_6$F$_6$ and C$_6$F$_5$H using a NHC-stabilized ruthenium dihydride complex resulted in the formation of C$_6$F$_5$H and 1,2,3,4-C$_6$F$_4$H$_2$. The most unusual feature of this system is the high ortho regioselectivity, which is in complete contrast to the reaction products observed for the systems of Milstein and Holland. Initially, the involvement of a tetrafluorobenzyne intermediate was postulated to account for this unusual regioselectivity, but later an alternative pathway

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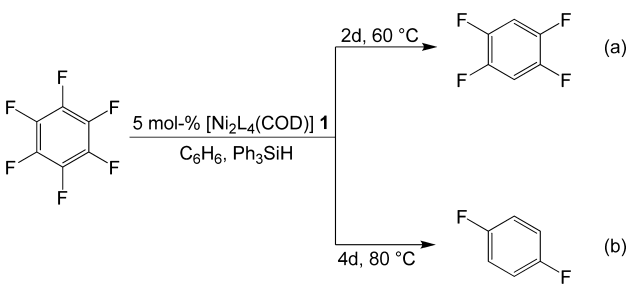
based on nucleophilic attack of a coordinated hydride ligand at C_6F_5H was established by means of DFT calculations.[4l]

Although much work has been done in the field of nickel-mediated C−F bond activation,[5] reports on applications of nickel complexes in hydrodefluorination reactions are rather scarce.[6] It is now well established that Ni^0 complexes, stabilized by phosphine, carbene, and certain nitrogen ligands, undergo C−F activation with hexafluorobenzene to yield complexes of the type *trans*-[Ni(L)$_2$(F)(C_6F_5)]. Over the past few years we have reported the facile and clean oxidative addition of hexafluorobenzene and perfluorotoluene to the NHC-stabilized complex fragment [Ni(^{i}Pr$_2$Im)$_2$][7] (^{i}Pr$_2$Im = 1,3-bis(isopropyl)-imidazolin-2-ylidene), as provided by [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**).[8] Those were the first C−F activation reactions of polyfluoroarenes at nickel performed at room temperature on a time scale reasonable for practical catalysis. The C−F activation reactions have been applied in Suzuki−Miyaura-type cross-coupling reactions of perfluorinated aromatics with boronic acids using [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) as a catalyst.[7b] In stoichiometric reactions we have shown that the fluorine atom in complexes of the type *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(Ar$_F$)] can be substituted easily.[7d] As an example, we reported the preparation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(R)(Ar$_F$)] via salt metathesis using organolithium compounds and the silaphilicity of the Ni−F bond in *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(Ar$_F$)]. The reaction of X-SiMe$_3$ with *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(Ar$_F$)] leads in many cases to the substitution product *trans*-[Ni(^{i}Pr$_2$Im)$_2$(X)(Ar$_F$)] with elimination of F−SiMe$_3$, making these fluoride complexes attractive synthetic precursors for new molecules with a variety of ligands.[7d] We recognized already at that time that the reaction of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C_6F_5)] with phenylsilanes affords the highly sensitive nickel hydride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C_6F_5)]. We wish to report here initial investigations into catalytic HDF reactions of polyfluoroaromatics using hydrosilanes as well as results concerning the isolation and characterization of intermediates of this reaction.

RESULTS AND DISCUSSION

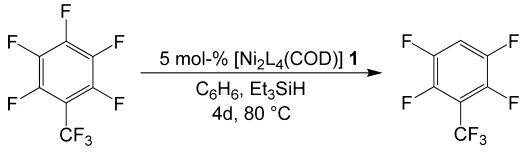
In preliminary experiments we realized that catalytic HDF reactions with silanes as the hydride source and [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) as a catalyst lead to complex reaction mixtures. Using different silanes and reaction conditions, we usually obtain mixtures of fluoroaromatics, depending on the reaction time, the temperature, and the silane employed. In some cases, however, we can also optimize the reaction conditions in a way to obtain specifically one product. The reaction of hexafluorobenzene with 5 equiv of triphenylsilane in the presence of 5 mol % of the nickel catalyst affords exclusively 1,2,4,5-tetrafluorobenzene after 48 h at 60 °C and 1,4-difluorobenzene after 96 h at 80 °C (see Scheme 1). In the case of the formation of 1,2,4,5-tetrafluorobenzene we detected pentafluorobenzene as an intermediate of the reaction. Thus, the regioselectivities observed are in accordance with earlier work reported by Milstein et al. and Holland et al. for the rhodium and iron systems mentioned above, where the HDF of pentafluorobenzene leads to the 1,2,4,5-isomer.

Scheme 1. Catalytic HDF of C_6F_6 to 1,2,4,5-$C_6F_4H_2$ (a) and 1,4-$C_6F_2H_4$ (b) (L = ^{i}Pr$_2$Im)



Whereas Ph_3SiH is the silane of choice for a controlled HDF reaction of C_6F_6, we have found that Et_3SiH gives the best results for a controlled HDF of C_7F_8. The HDF reaction of perfluorinated toluene is noticeably slower compared to the HDF of perfluorobenzene. Heating C_7F_8 and 5 equiv of Et_3SiH for 4 days at 80 °C leads to the selective formation of 1-(CF_3)-2,3,5,6-C_6F_4H (see Scheme 2). All the reaction products were verified by comparison of the analytical data with commercial samples.

Scheme 2. Catalytic HDF of C_7F_8 to 1-(CF_3)-2,3,5,6-C_6F_4H (L = ^{i}Pr$_2$Im)



In light of these results we were interested in the essential steps of the nickel-catalyzed HDF reaction. In the NMR spectra of the reaction mixtures we observe resonances for nickel fluoride and nickel hydride species. We reported earlier the reaction of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) with silanes such as Ph_3SiH and Ph_2MeSiH, which affords nickel silyl hydride complexes of the type *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiR$_3$)].[8i] Although formation of such species is likely in the reaction mixture of HDF catalysis, we observe in stoichiometric reactions of *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiPh$_3$)] and *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiMePh$_2$)] with hexafluorobenzene at room temperature the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C_6F_5)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)-(C_6F_5)] (**4**) with elimination of the corresponding silane or fluorosilane, respectively (vide infra). This is a clear indication that complexes of the type *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(Ar$_F$)] and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(Ar$_F$)] are more likely intermediates than complexes of the type *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiR$_3$)].

Therefore, we were interested in the reactivity of complexes of the type *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(Ar$_F$)] with silanes and the reactivity of the reaction products. The reaction of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) with stoichiometric amounts of the perfluorinated arenes C_6F_6 and (CF_3)C_6F_5 in toluene or tetrahydrofuran proceeds quickly and cleanly at room temperature. As reported previously, oxidative addition of one of the C−F bonds takes place—in the case of perfluorotoluene regioselectively in a position para to the CF_3 group—and leads to the C−F activation products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C_6F_5)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF_3)C_6F_4)] (**3**) (fluoroaryl ligands are numbered with the nickel atom in the position 1). These can be isolated in good yields.

The reactions of these C−F activation compounds with silanes such as $PhSiH_3$ and Ph_2SiH_2 lead to the formation of the corresponding hydride complexes *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)-(C_6F_5)] (**4**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (**5**) (see Scheme 3). After addition of the silane at room temperature to **2** and **3** in thf or toluene the suspension cleared up rapidly but was stirred for another 2 h before workup. These reactions are quantitative if performed on an

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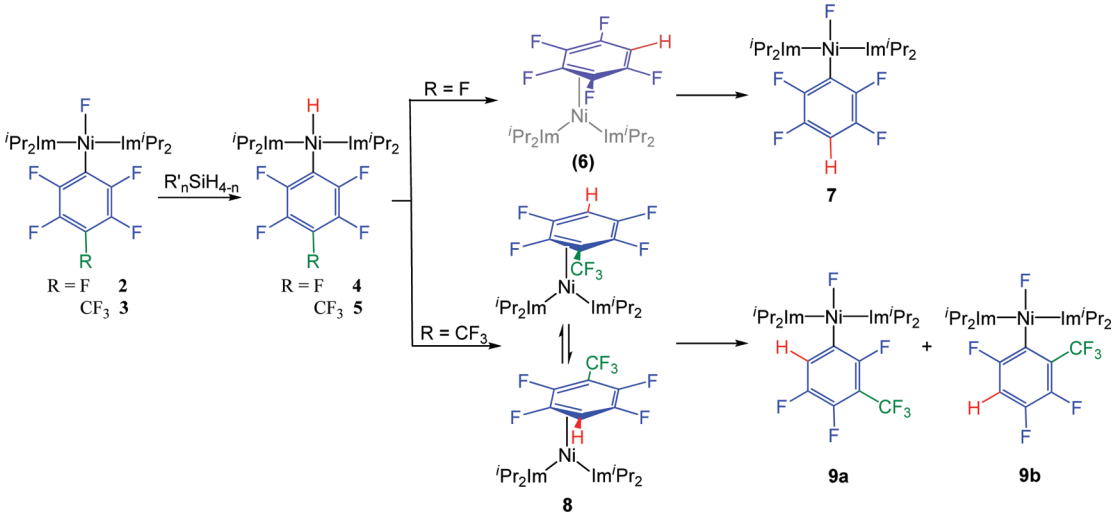
Scheme 3. Synthesis of the Hydride Complexes *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (4) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (5) and the Rearrangement of These Compounds to the Fluoride Complexes *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (7), *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (9a), and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (9b)[a]



[a]Intermediate **6** was not observed.

NMR scale, but isolation of the pure compound was hampered by an ineffective crystallization step. Both complexes were isolated in analytically pure form in rather low yields of approximately 20%. In the proton NMR spectra of both complexes the characteristic hydride resonances were detected at −13.99 ppm (**4**) and −13.68 ppm (**5**) as irregular septets due to the coupling of the hydride ligand with the fluorine nuclei of the perfluoroaryl ligand. In contrast to the C−F activation products **2** and **3**, for which we observe broadened signals for the carbene isopropyl methyl hydrogen atoms,[7c] these resonances appear in the case of the hydride compounds as sharp doublets at 1.21 (**4**) and 1.20 ppm (**5**) at room temperature. The set of ^{19}F NMR resonances for the perfluoroaryl ligand of **4** and **5** are almost identical with the resonances observed for the C−F activation products **2** and **3**.

Crystals of **5** suitable for X-ray diffraction were grown from a hexane solution at −40 °C. The crystals obtained are very sensitive toward air and moisture and decompose in ethereal and halogenated solvents, but they are stable and can be stored for a longer period of time in the solid state under an inert gas atmosphere. In toluene and thf solutions, however, the hydride complexes show rearrangement within a few days at room temperature (vide infra). Compound **5** crystallizes in the monoclinic space group *C*2/*m* with half of the molecule in the asymmetric unit (Figure 1). The hydride hydrogen atom of the complex has been refined isotropically. *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) adopts a square-planar geometry, which is significantly distorted in comparison to other complexes of the type *trans*-[Ni(^{i}Pr$_2$Im)$_2$(X)(Ar$_F$)].[7,8] Both carbene ligands are bent away from the pentafluorophenyl ligand toward the hydride ligand. The angle C(1)−Ni−C(1)′ of 163.2(2)° differs significantly from an ideal value of 180°, and the angle C(1)−Ni−H(1) of 81.69(10)° clearly reveals the distortion toward the hydride. The Ni−H(1) distance of 1.54(5) Å observed by X-ray diffraction is close to the recently published value of 1.4919 Å calculated for *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] by means of DFT (TURBOMOLE, RIDFT, BP86, TZVPP).[7d] This distance is considerably shorter compared to the Ni−F distance of 1.856(4) Å determined for

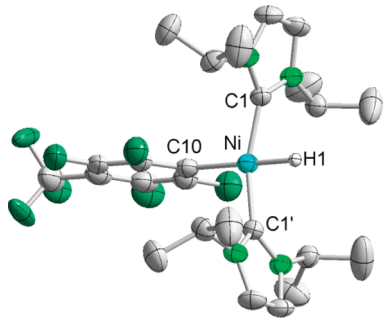


Figure 1. ORTEP diagram of the molecular structure of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) in the solid state. With the exception of the hydride ligand H(1), all other H atoms have been omitted for clarity (thermal ellipsoids shown at the 50% probability level). Selected bond lengths (Å) and angles (deg): Ni−C(1) = 1.877(3), Ni−C(10) = 1.945(5), Ni−H(1) = 1.54(5); C(1)−Ni−C(1)′ = 163.2(2); C(1)−Ni−C(10) = 98.32(10); C(1)−Ni−H(1) = 81.69(10); C(10)−Ni−H(1) = 179.2(16).

the corresponding nickel fluoride *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**).[7b]

As mentioned above, the hydride complexes **4** and **5** rearrange within a few days in solution at room temperature, but the reaction time is significantly reduced to several hours if solutions are heated to 60 °C. The product of the rearrangement of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) is the tetrafluorophenyl fluoride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**), which was prepared before from the reaction of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) and pentafluorobenzene.[7c] For the perfluorotolyl complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) we observe the formation of two isomers, *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), in a ratio of approximately 80:20 (see Scheme 3).

Intermediates with an η^2-C,C-coordinated perfluoroarene ligand, i.e. [Ni(^{i}Pr$_2$Im)$_2$(η^2-C,C-C$_6$F$_6$)] and [Ni(^{i}Pr$_2$Im)$_2$(η^2-C,C-C$_{10}$F$_8$)], have been detected in solution for the C−F activation of hexafluorobenzene and octafluoronaphthalene with [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**)

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or the ethylene complex [Ni(^{i}Pr$_2$Im)$_2$(η^2-C$_2$H$_4$)].[7c] For the rearrangement observed here, we anticipated a reductive elimination/oxidative addition mechanism leading to the formation of η^2-bound intermediates [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-C$_6$F$_5$H)] (**6**) and [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**).

Figure 2 displays the time-dependent ^{19}F NMR spectra for the conversion of *trans*- [Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**) at 60 °C. The signals of the perfluorophenyl ligand of the hydride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) at −114.2 and −164.8 ppm decrease with time and are completely absent after 90 min. On the other side, a new set of signals starts to develop after a few minutes at −117.7 and −143.5 ppm for the tetrafluorophenyl ligand and at −374.2 ppm for the fluoride ligand of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**). The ^{1}H NMR spectrum of **7** (not shown in Figure 2) reveals a broad singlet at 1.30 ppm for the isopropyl methyl hydrogen atoms, a septet for the isopropyl methane hydrogen atoms at 6.56 ppm, a singlet at 6.31 ppm for the carbene olefinic protons, and a multiplet between 6.23 and 6.29 ppm for the hydrogen atom located in a position para to the activated C−F bond. These resonances are in accordance with those of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] reported earlier.[7c] According to ^{19}F NMR tiny amounts of two minor products were observed in 3.6% and 0.2% yields, as judged from the integration of the nickel fluoride resonances. These are presumably the products of an activation at the ortho and para positions (relative to H), *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,4,6-C$_6$F$_4$H)] and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,4,5-C$_6$F$_4$H)]. However, these compounds could not be characterized properly—not even by ^{19}F NMR spectroscopy.

Time-dependent NMR spectra for the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**) at 60 °C are given in Figure 3. Aside from the signals of **5**, **9a**, and **9b**, we observe in the intermediate time intervals resonances of an intermediate, presumably [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**). Figure 3a displays the proton and fluorine NMR spectra in the region relevant for the nickel hydride and nickel fluoride ligands discussed here. The hydride resonance of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) at −13.68 ppm, still apparent at the beginning of the measurement, is absent after 35 min. The resonances of the fluoride ligands at −368.0 (**9a**) and −378.8 ppm (**9b**), on the other hand, start to develop after approximately 60 min. This is a clear indication that in the meantime an intermediate without Ni−H or Ni−F ligands is formed in solution. These findings are corroborated by the ^{19}F NMR spectra recorded for the aryl fluoride region, shown in Figure 3b. No signals of the hydride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] **5** at −55.2, −114.1, or −145.8 ppm (marked with a green asterisk in Figure 3) can be detected after 1 h, and a set of resonances attributed to the η^2-coordinated intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) (marked in Figure 3b with a blue asterisk) develop rapidly after the reaction starts. This intermediate is the predominant species after approximately 1 h. The ^{19}F NMR spectrum shows a sharp triplet at −49.6 ppm for the CF$_3$ group and two broad singlets at −142.8 and −155.5 ppm for the ^{19}F nuclei of the aromatic system, which are typical for this kind of coordination mode. The ^{1}H NMR spectrum of **8** reveals a broad resonance at 1.07 ppm for the isopropyl methyl hydrogen atoms at room temperature, a broad signal for the isopropyl methine hydrogen atoms at 5.06 ppm, a singlet at 6.38 ppm for the NHC backbone protons, and, most significantly, a multiplet at 5.56 ppm for the hydrogen atom located in a position para to the CF$_3$ group in an integration ratio of 24:4:4:1. Similar broadened resonances of the isopropyl ligands have been found in the ^{1}H NMR spectrum of the structurally characterized complex [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-C$_{10}$F$_8$)].[7c] Compound **8** was synthesized and characterized independently from the reaction of **1** with 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H at room temperature (with minor impurities of **9a** and **9b**) to substantiate the assignment. Despite several attempts, we were unsuccessful in growing crystals of this complex suitable for X-ray diffraction. However, having [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) in hand, we reacted this complex with perfluorotoluene to simulate the conditions of the HDF reaction (perfluorotoluene present in solution). Experimentally, we found the formation of the C−F activation product *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)-C$_6$F$_4$)] (**3**) from the reaction of **8** with perfluorotoluene at 80 °C, presumably via [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_5$)] as an intermediate (see Scheme 4).

DFT calculations predicted the η^2-C,C-bound intermediate of perfluorotoluene [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_5$)] to be energetically more stable by at least 7 kJ/mol compared to [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**). This experiment reveals that hopping of the [Ni(^{i}Pr$_2$Im)$_2$] moiety between (CF$_3$)C$_6$F$_5$ and 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H rings is more rapid than C−F bond activation. Furthermore, the introduction of C−H

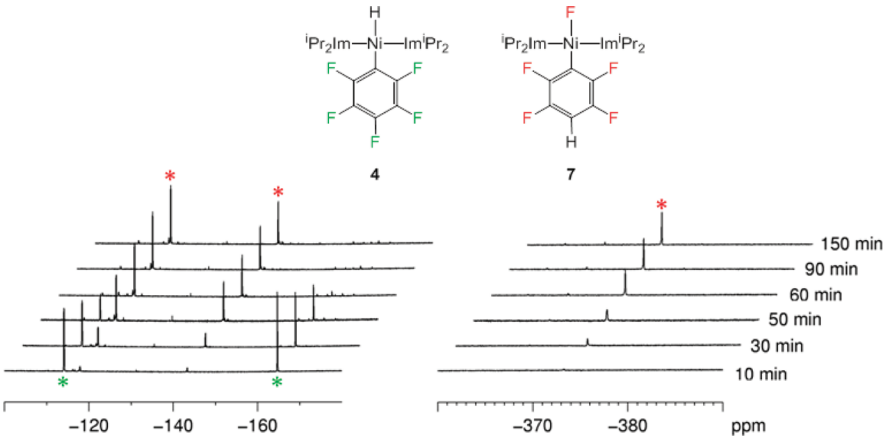

Figure 2. Time-dependent ^{19}F NMR spectra for the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**) at 60 °C. Resonances of different complexes are marked with colored asterisks: **4**, green, **7**, red.

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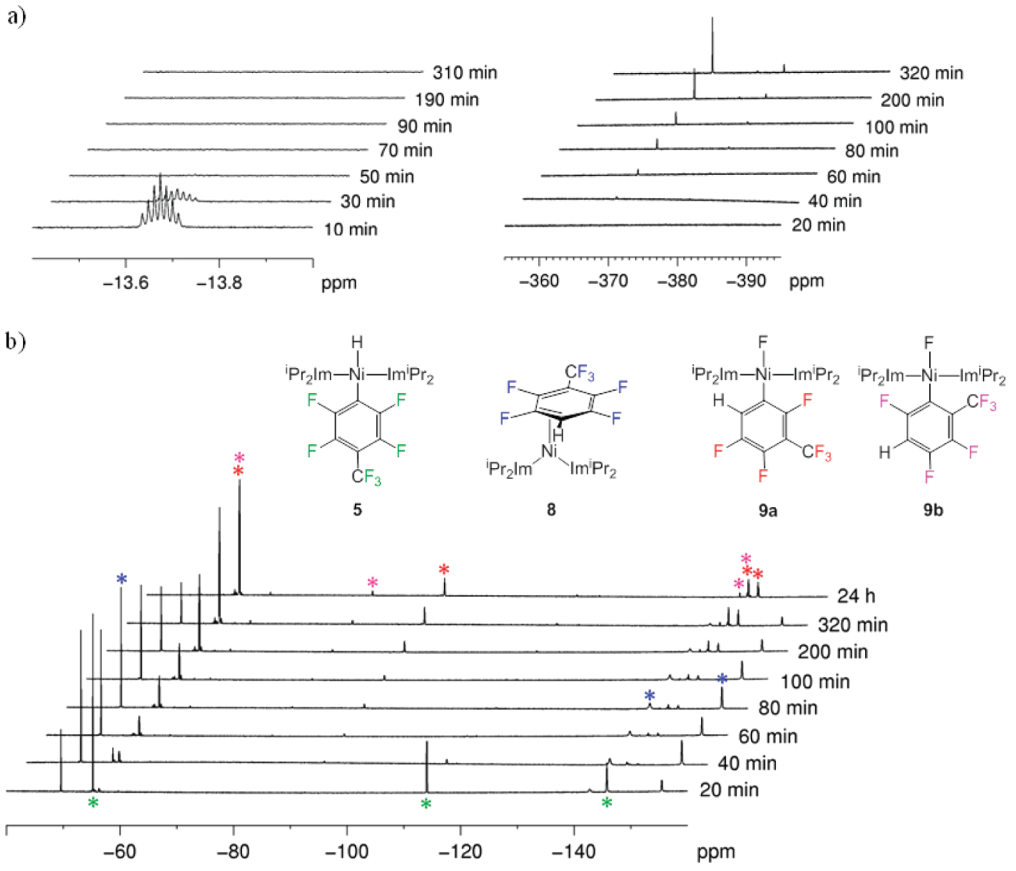
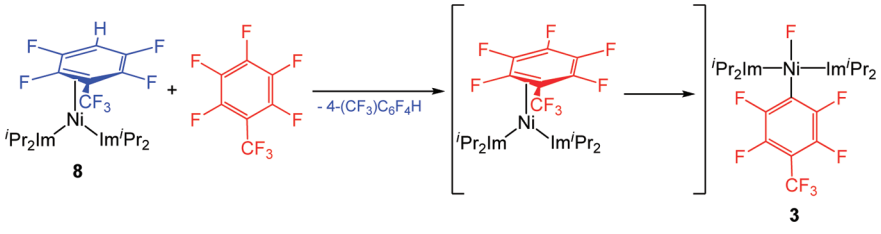


Figure 3. Time-dependent NMR spectra for the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**) at 60 °C: (a) time-dependent ^{1}H (left) and ^{19}F (right) NMR spectra in the nickel hydride and nickel fluoride region; (b) time-dependent ^{19}F NMR spectra in the aryl fluoride region. Resonances of different complexes are marked with colored asterisks: **5**, green; **8**, blue; **9a**, red; **9b**, magenta.

Scheme 4. Reaction of [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (8) with Perfluorotoluene



bonds into substrates usually slows the reaction rates of C−F activation and generates competition between the two substrates perfluorotoluene and 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H, with a much faster reaction rate for perfluorotoluene. Overall, our results presented here are in agreement with the crucial steps for the [Ni(^{i}Pr$_2$Im)$_2$] catalyzed HDF of perfluorotoluene as depicted in Scheme 5.

The mixture of perfluorotoluene, silane, and nickel complex **1** reacts to give the C−F activation product *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**). C−F activation takes place regioselectively at the position para to the CF$_3$ group. Complex **3** reacts readily with the silane R$_3$Si−H with H/F exchange to afford the fluorosilane R$_3$Si−F and the hydrido complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**). This compound eliminates 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H with formation of the η^2-*C*,*C*-coordinated intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**). At this stage substitution of the 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H ligand with perfluorotoluene occurs to give [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_5$)], a step which can also be considered as intermolecular, exothermic ring hopping of [Ni(^{i}Pr$_2$Im)$_2$] from 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H to perfluorotoluene. This compound is the precursor complex for oxidative addition of the C−F bond to yield *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**), and thus the catalytic cycle is closed.

Without additional perfluorotoluene, complex **8** rearranges to the products of C−F activation of 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H, as depicted in Figure 3. After approximately 1 h two sets of resonances start to develop for the C−F activation products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**) (marked with a red asterisk in Figure 3) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**) (marked with a magenta asterisk in Figure 3) in a ratio of approximately 80:20, on the basis of the integration of the ^{19}F NMR signals of the fluoride ligands. In other words, the product of an oxidative addition of the C−F

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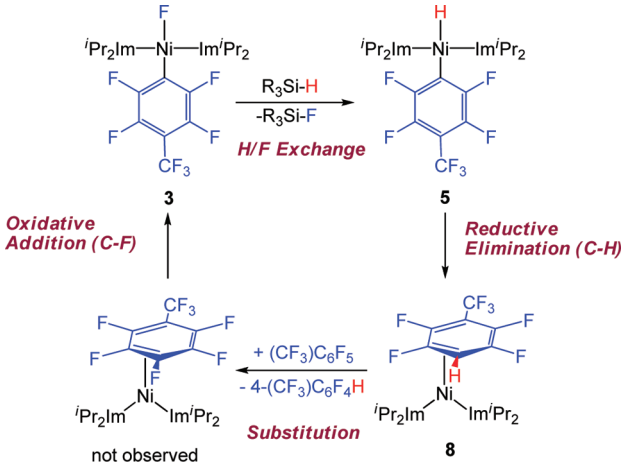
Scheme 5. Key Intermediates of the [Ni(^{i}Pr$_2$Im)$_2$] Catalyzed HDF of Perfluorotoluene



bond next to the hydrogen atom prevails over the product of an oxidative addition of the C−F bond next to the CF_3 group. This experimental result was corroborated by the reaction of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) with 1-(CF_3)-2,3,5,6-C_6F_4H at 60 °C, which leads to the same product ratio. Within experimental error, this distribution is not affected by factors such as substrate concentration and nickel complex concentration. As a general trend, transition-metal complexes often react with polyfluoroaromatics in nucleophilic replacement reactions with similar selectivity as simple nucleophiles, such as methoxide. For the methoxydefluorination reaction of 1-(CF_3)-2,3,5,6-C_6F_4H it has been found that nucleophilic replacement occurs at the position ortho to the CF_3 substituent[9] and thus a pure nucleophilic reaction pathway is unlikely in our case.

The ^{19}F NMR spectrum of **9a** reveals a doublet of doublets at −56.3 ppm for the CF_3 group with two $^4J_{FF}$ coupling constants of 21.4 and 24.7 Hz to the fluorine atoms in ortho and para positions (with respect to the Ni atom) as well as resonances in the aryl fluoride region at −92.5, −146.0, and −147.7 ppm. For the minor product **9b** we observe a doublet at −56.3 ppm with a $^4J_{FF}$ coupling constant of 18.8 Hz to the fluorine ligand in a meta position (with respect to the Ni atom) and resonances at −79.7, −144.5, and −145.8 ppm for the fluorophenyl ligand. The resonances of the fluoride ligands were detected in the region typically observed for Ni−F at −368.0 (**9a**) and −378.8 ppm (**9b**). The assignment of the two products is based on resonance positioning and coupling constant arguments observed for the signals in the polyfluoroaryl region of the ^{19}F NMR spectra. Our earlier work on partially fluorinated benzenes revealed that *o*-fluoride substituents of polyfluoroaryl ligands are detected in a range between −80 and −100 ppm in the absence of fluoride substituents in meta postions. If *m*-fluoride substituents are present, these resonances are usually detected in a range between −110 and −120 ppm. Furthermore, the signal of the main product at −92.5 ppm reveals a $^4J_{FF}$ coupling constant of 21.4 Hz to an adjacent CF_3 group and was therefore assigned to the signal set of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (**9a**). The resonance at −79.7 ppm, on the other hand, reveals coupling with the two fluorine ligands of the aromatic system ($^5J_{FF}$ = 15.6 Hz, $^4J_{FF}$ = 3.6 Hz), but no $^4J_{FF}$ coupling to a CF_3 group is observed.

DFT calculations have been performed to gain more information about the energetics of the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (**5**) into the two products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (**9b**). The calculations of this process along a reductive elimination/oxidative addition pathway are summarized in Figure 4 and were calibrated on the basis of the isolated hydride

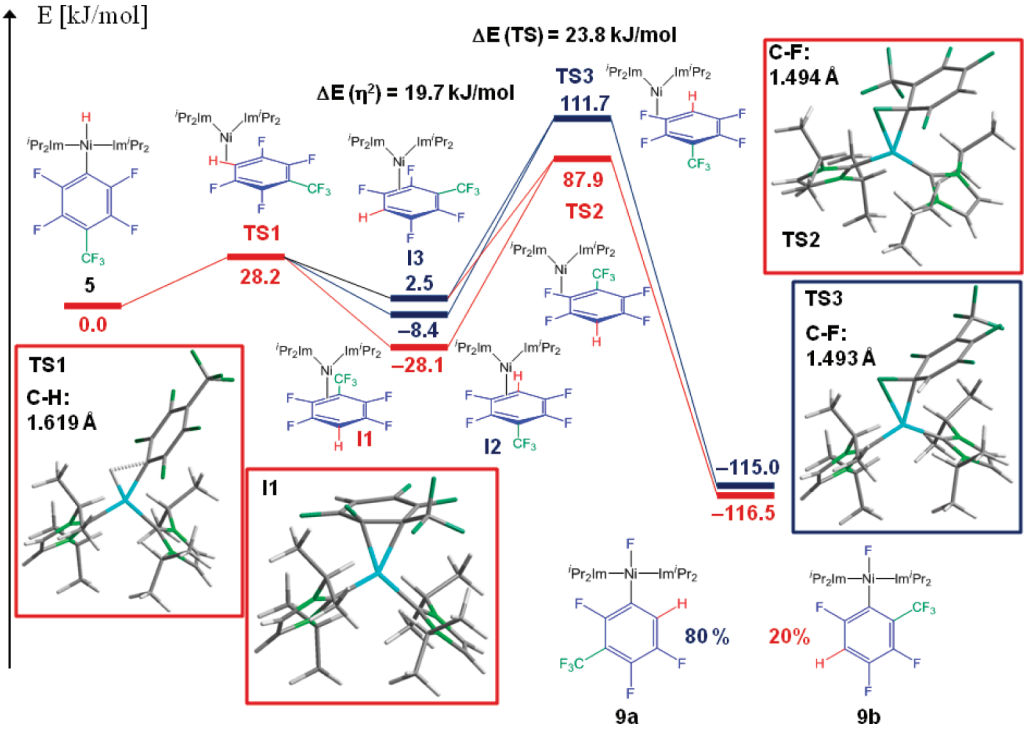


Figure 4. Calculated energetics (electronic energies) for likely intermediates and transition states of the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (**5**) into the products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (**9b**).

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complex **5**. The reductive elimination reaction starting from the *p*-perfluorotolyl nickel hydride complex to a compound with an η^2-coordinated arene ligand via an η^2-C,H-σ complex as a transition state **TS1** requires only 28.2 kJ/mol. The transition state features an η^2-C,H-σ-coordinated ligand in which the C−H bond length of 1.619 Å is significantly elongated in comparison to C_{ar}−H distances. This energetically low lying transition state is a consequence of the relatively weak Ni−H bond in comparison with Ni−F bonds in complexes such as *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**). For a similar transformation of the latter complex to a transition state with the η^2-C,F-σ-coordinated ligand in a position para to the CF$_3$ substituent, i.e. [Ni(^{i}Pr$_2$Im)$_2${η^2-*C*,*F*-4-(CF$_3$)C$_6$F$_5$)], we calculated a barrier of 216.3 kJ/mol.[7c] Lower in energy in comparison to **TS1** are all of the possible η^2-C,C-bound intermediates, denoted as **I1**−**I3** in Figure 4. A closer inspection of these η^2-C,C-bound intermediates reveal that η^2-C,C binding of the [Ni(^{i}Pr$_2$Im)$_2$] complex fragment is actually preferred at the 1,2-C−C position (**I1**): i.e. the bond of the ipso carbon atom at the CF$_3$ substituent to the ortho carbon atom. Coordination at the 3,4-C−C bond (**I2**) is disfavored by 19.7 kJ/mol with respect to **I1** and coordination at the 2,3-C−C bond by 30.6 kJ/mol. If we presume that these isomers are in equilibrium with each other, the different energies of the η^2-C,C intermediates will, according to the Curtin−Hammett principle, have no influence on the selectivity of the product formation. However, the calculations also predict that the metal atom of the energetically favored intermediate **I1** is already in the correct position to reach the energetically lowest lying transition state for C−F activation. The transition states leading to cleavage of the C−F bond are much higher in energy in comparison to the transition state for C−H activation, and C−F cleavage leads to products **9a**,**b** which are thermodynamically much more stable compared to **5**. This closely resembles the experimental data. The calculated transition states for C−F activation lie 59.7 kJ/mol (**TS2**) and 83.5 kJ/mol (**TS3**) above the transition state **TS1** for C−H activation and 116.0 kJ/mol (**TS2**) and 139.8 kJ/mol (**TS3**) above the energetically lowest lying intermediate **I1**. Assuming a concerted reaction pathway for the oxidative addition, the transition states **TS2** and **TS3** feature η^2-C,F-σ-coordinated arene ligands, in which the C−F bond lengths of 1.493 Å (**TS2**) and 1.494 Å (**TS3**) are elongated compared to C_{ar}−F distances. Both transition states are closely related to the geometries obtained for similar transition states with η^2-C,F-σ-coordinated arene ligands calculated previously.[5g,7c] For a concerted oxidative addition, the relative energies of **TS2** and **TS3** reveal a kinetic preference for the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), because the transition state corresponding to this complex is favored by 23.8 kJ/mol with respect to the transition state for the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**). From a thermodynamic point of view the products **9a**,**b** lie at almost the same energy; thus, a clear kinetic resolution is predicted by theory. However, in this case we calculate an energetically much lower lying transition state (red path in Figure 4) for the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), the isomer we experimentally observe as a minor product.

The most interesting feature of the calculations presented here is the mismatch between experiment and theory. The mechanism of C−F oxidative addition of hexafluorobenzene at Ni^0 is usually thought to involve precoordination of the fluoroarene followed by concerted oxidative cleavage of the C−F bond. The η^2-C,C-fluoroarene intermediates were isolated, and the conversion to nickel fluoride was followed directly in some cases.[2g,5e,n,q,7c] Computational studies of the reaction pathways also support this mechanism, but there is compelling evidence that the reaction mechanisms differ individually in the dependence of the metal atom and the ligand environment employed. For the nickel phosphine system, for example, a phosphine-assisted mechanism was recently established for C−F activation reactions of pentafluoropyridine.[5o] The Johnson group has shown lately that the introduction of C−H bonds into substrates often changes reaction mechanisms and generates competition between C−F and C−H activation at nickel.[5l,n,q] In the case of C$_6$F$_5$H, 1,2,4,5-C$_6$F$_4$H$_2$, and 1,2,3,5-C$_6$F$_4$H$_2$ C−H activated species are formed reversibly as kinetic products of their reaction with [Ni(PEt$_3$)$_2$].[5n,q] Moreover, Johnson et al. have isolated the dinuclear complexes [{(Et$_3$P)$_2$Ni}$_2$(μ-η^2:η^2-*C*,*C*-C$_6$F$_5$X)] (X = H, F), in which a hexafluoro- or pentafluorobenzene ligand bridges two [Ni(PEt$_3$)$_2$] complex fragments. In the case of [{(Et$_3$P)$_2$Ni}$_2$(μ-η^2:η^2-*C*,*C*-C$_6$F$_5$H)] it was shown that the addition of C$_6$F$_5$H to solutions of this dinuclear complex provided equilibrium amounts of the mononuclear compound [Ni(PEt$_3$)$_2$(η^2-*C*,*C*-C$_6$F$_5$H)] and the C−H activation product *trans*-[Ni(PEt$_3$)$_2$(H)(C$_6$F$_5$)] as intermediates. Solutions of [{(PEt$_3$)$_2$Ni}$_2$(μ-η^2:η^2-*C*,*C*-C$_6$F$_5$H)] with added C$_6$F$_5$H, however, convert with high selectivity to the *o*-C−F activated compound *trans*-[Ni(PEt$_3$)$_2$(F)(2,3,4,5-C$_6$F$_4$H)]. The mechanism of this conversion is not yet clear, but all the complexes [{(PEt$_3$)$_2$Ni}$_2$(μ-η^2:η^2-*C*,*C*-C$_6$F$_5$H)], [Ni(PEt$_3$)$_2$(η^2-*C*,*C*-C$_6$F$_5$H)], and *trans*-[Ni(PEt$_3$)$_2$(H)(C$_6$F$_5$)] are likely intermediates.[5n,q] In the case presented here we could not observe dinuclear intermediates in solution (judged by the integration of the proton NMR spectrum). Similar to the work of Johnson et al. mentioned above, we demonstrated that conversion of [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) to the C−F activation product **9a** occurs with an ortho selectivity (ortho to the hydrogen substituent) much higher than predicted using a concerted reaction model. This is also in line with results obtained earlier for the C−F activation of 1,2,3-trifluorobenzene by [Ni(^{i}Pr$_2$Im)$_2$].[7c] We reported that the reaction of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) with 1,2,3-trifluorobenzene leads to a mixture of the isomers *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3-C$_6$F$_2$H$_3$)] and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,6-C$_6$F$_2$H$_3$)]. The activation product of the statistically more favored C−F bonds at position 1 leads to the major isomer (approximately 90% judged by ^{19}F NMR spectroscopy) and minor amounts (approximately 10%) of the second isomer resulting from an activation of the 2-position. This distribution closely resembles the product distribution obtained for the nucleophilic replacement with methoxide reacted with a 4:1 preference for the 1-site with 1,2,3-trifluorobenzene.[10] However, DFT calculations of the η^2-C,F-transition states clearly render [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*F*-2-1,2,3-C$_6$F$_3$H$_3$)], i.e. the transition state leading to the minor isomer *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,6-C$_6$F$_2$H$_3$)], as energetically more favorable by approximately 12 kJ/mol compared to [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*F*-1-1,2,3-C$_6$F$_3$H$_3$)] (unpublished results). Furthermore, the DFT calculations predict the minor isomer *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,6-C$_6$F$_2$H$_3$)] to be the thermodynamically more stable complex. Thus, a mechanism for the activation of 1,2,3-trifluorobenzene via a concerted reaction mechanism seems to be either unlikely or is at least superimposed by other pathways. All these findings lead to the conclusion that for C−F activation of partially fluorinated aromatics at Ni^0 reaction mechanisms different from the commonly accepted intramolecular (concerted) pathways are likely to predominate for certain cases, depending on the substrate employed. These include a mechanism via nucleophilic attack of the metal base,

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radical pathways, or pathways that include NHC assistance. Future work will focus on mechanistic studies of the C−F activation of partially fluorinated aromatics using [Ni(^{i}Pr$_2$Im)$_2$].

CONCLUSIONS

[Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) is an active catalyst for the hydrodefluorination (HDF) of polyfluorinated arenes using hydrosilanes as the hydrogen source. The reaction of hexafluorobenzene with 5 equiv of triphenylsilane in the presence of 5 mol % of **1** affords 1,2,4,5-tetrafluorobenzene after 48 h at 60 °C and 1,4-difluorobenzene after 96 h at 80 °C. Similarly, the reaction of perfluorotoluene and 5 equiv of Et$_3$SiH for 4 days at 80 °C in the presence of 5 mol % of **1** leads to the selective formation of 1-(CF$_3$)-2,3,5,6-C$_6$F$_4$H. Conceivable reaction sequences for the HDF at nickel are (i) the activation of the silyl hydride and subsequent reaction with the fluoroarene ("silane route") and (ii) C−F activation of the fluoroarene and subsequent reaction of the resulting nickel fluoride with the silane ("fluoride route"). Stoichiometric transformations of the complexes *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiPh$_3$)] and *cis*-[Ni(^{i}Pr$_2$Im)$_2$(H)(SiMePh$_2$)] with hexafluorobenzene at room temperature lead to the formation of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) with elimination of the corresponding silane or fluorosilane. The reactions of C−F activation products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**2**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**) with PhSiH$_3$ and Ph$_2$SiH$_2$ result in the formation of the hydride complexes *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (**4**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**), which convert into the compounds *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C$_6$F$_4$H)] (**7**), *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**), and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), respectively. In the case of the rearrangement of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) the intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**) was detected in solution. This intermediate is prone to substitution of the arene ligand with perfluorotoluene under the conditions of HDF catalysis to give the C−F activation product *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**), presumably via another intermediate with η^2-C,C-coordinated perfluorotoluene: i.e., [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_5$)]. All these experimental findings point to a mechanism for the catalytic HDF by [Ni(^{i}Pr$_2$Im)$_2$] along the "fluoride route", which involves C−F activation of the polyfluoroarene, H/F exchange of the resulting nickel fluoride ligand, reductive elimination of the polyfluoroaryl nickel hydride to an intermediate with an η^2-C,C-coordinated arene ligand, and subsequent ligand exchange with the higher fluorinated polyfluoroarene, which is the precursor for the C−F activation step to close the catalytic cycle (see Scheme 5).

Furthermore, DFT calculations performed on the conversion of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (**5**) into the two products *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**) along a reductive elimination/oxidative addition pathway via η^2-C,H- and η^2-C,F-σ-complexes as transition states are in disagreement with the data obtained experimentally. The rate and product contribution determining transition states are those of the C−F activation step. Starting from the η^2-C,C intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF$_3$)C$_6$F$_4$H)] (**8**), we calculate a low-lying η^2-C,F transition state which leads to the minor isomer *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF$_3$)-3,4,6-C$_6$F$_3$H)] (**9b**), if we assume a concerted mechanism. The major isomer observed experimentally is *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF$_3$)-2,4,5-C$_6$F$_3$H)] (**9a**), the product in which C−F activation takes place at the position ortho to the hydrogen substituent. The methoxydefluorination reaction of **1**-(CF$_3$)-2,3,5,6-C$_6$F$_4$H takes place exclusively at the position ortho to the CF$_3$ substituent,[9] and thus a pure nucleophilic reaction pathway is unlikely here. High selectivity for *o*-C−F activation has been previously reported for specific examples: e.g., for the nickel phosphine system by Johnson et al.[5n,q] and for our nickel carbene system.[7c] We assume therefore that in certain cases of the [NiL$_2$]-mediated C−F activation of partially fluorinated arenes neither the commonly accepted intramolecular concerted pathway nor a mechanism via nucleophilic attack of the metal base are valid.

EXPERIMENTAL SECTION

General Considerations. All reactions and subsequent manipulations involving organometallic reagents were performed under a nitrogen or argon atmosphere using standard Schlenk techniques as reported previously.[11] Elemental analyses were performed in the microanalytical laboratory of the authors' department. EI mass spectra were recorded on a Varian MAT 3830 instrument (70 eV). NMR spectra were recorded on a Bruker AV 400 at 333 K or a Bruker Avance 200 at 296 K unless otherwise stated. ^{13}C NMR spectra are broad-band proton-decoupled ^{13}C{^{1}H}. NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H and ^{13}C) and CFCl$_3$ (^{19}F). Coupling constants are quoted in hertz (Hz). Spectra are referenced internally to residual protio solvent resonances (^{1}H, C$_6$D$_5$H 7.16 ppm) or natural-abundance carbon resonances (^{13}C, C$_6$D$_6$, 128.02 ppm). The ^{19}F NMR spectra were referenced to external C$_6$F$_6$ at δ −162.9 ppm. Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 instrument and are reported in cm^{-1}. [Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)][7a] and [Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)][7b] were prepared according to literature procedures. PhSiH$_3$ and C$_6$F$_6$ were purchased from ABCR and used without further purification.

General Procedure for the HDF Reactions. A 1.25 mmol amount of the silane (Et$_3$SiH, 199 μL; Ph$_3$SiH, 326 mg) was added to a suspension of 10 mg (0.013 mmol) of [Ni$_2$(^{i}Pr$_2$Im)$_4$(COD)] (**1**) and 0.25 mmol of perfluoroarene (C$_6$F$_6$, 29 μL; C$_7$F$_8$, 35 μL) in 3 mL of benzene. The reaction mixtures were stirred for several days at 60 or 80 °C. The products were analyzed by ^{19}F NMR spectroscopy. The identification of the compounds was confirmed by comparison of the data with those of commercial samples.

Synthesis of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C$_6$F$_5$)] (4). PhSiH$_3$ (65.0 μL, 0.50 mmol) was added to a solution of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(C$_6$F$_5$)] (**2**; 275 mg, 0.50 mmol) in 10 mL of toluene, and the mixture was stirred at room temperature for 2 h. The solution was filtered over a pad of Celite, all volatiles of the filtrate were removed in vacuo, and the remaining solid was dissolved in 15 mL of pentane. The product was crystallized at −40 °C, filtered off, and dried in vacuo to give 60.0 mg (0.11 mmol, 22%) of pale yellow crystals. Anal. Calcd (found) for C$_{24}$H$_{33}$F$_5$N$_4$Ni [530.20 g/mol]: C, 54.26 (54.34); H, 6.26 (6.21); N, 10.55 (10.47). EI/MS *m*/*z* (%): 530 (85) [M]$^+$, 510 (93) [M − HF]$^+$, 361 (90) [Ni(^{i}Pr$_2$Im)$_2$]$^+$. IR (KBr [cm^{-1}]): 527 (w), 577 (w), 611 (vw), 628 (vw), 673 (m), 692 (s), 706 (m), 749 (m), 809 (vw), 881 (w), 939 (s), 999 (m), 1037 (s), 1056 (m), 1081 (w), 1134 (m), 1170 (vw), 1214 (s), 1280 (vw), 1302 (s), 1368 (s), 1431 (vs), 1488 (s), 1601 (w), 1627 (w), 1808 (s, br, ν_{Ni-H}), 2875 (m), 2939 (m), 2979 (s), 3145 (w), 3181 (w). ^{1}H NMR (400 MHz, C$_6$D$_6$, 333 K): δ −13.99 (m, 1 H, Ni−*H*), 1.21 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, C*H*$_3$), 5.87 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 6.37 (s, 4H, NC*HCH*N). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 333 K): δ 23.49 (CH$_3$), 52.55 (*i*Pr CH), 116.32 (NCCN), 187.41 (NCN). ^{19}F NMR (376.4 MHz, C$_6$D$_6$, 333 K): δ −114.2 (m, 2 F, aryl *F*$_o$), −164.8 (m, 3 F, aryl *F*$_{m+p}$).

Synthesis of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF$_3$)C$_6$F$_4$)] (5). PhSiH$_3$ (65.0 μL, 0.50 mmol) was added to a solution of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(4-(CF$_3$)C$_6$F$_4$)] (**3**; 300 mg, 0.50 mmol) in 10 mL of toluene and stirred at room temperature for 2 h. All volatiles were removed in vacuo, and the remaining solid was dissolved in 15 mL of pentane and filtered over a pad of Celite. The product was crystallized at −40 °C, filtered off, and dried in vacuo to give 50.0 mg (0.09 mmol, 18%)

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of pale yellow crystals. Anal. Calcd (found) for $C_{25}H_{33}F_7N_4Ni$ [580.19 g/mol]: C, 51.66 (51.96); H, 5.72 (6.02); N, 9.64 (8.70). EI/MS *m/z* (%): 580 (25) $[M]^+$, 560 (34) $[M - HF]^+$, 361 (93) $[Ni(^iPr_2Im)_2]^+$. ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ −13,68 (m, 1 H, Ni-*H*), 1.20 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 5.84 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 6.35 (s, 4H, NC*H*C*H*N). ^{13}C NMR (100 MHz, C_6D_6, 333 K): δ 23.5 (^{i}Pr CH_3), 52.6 (^{i}Pr CH), 116.5 (NCCN), 186.3 (NCN). ^{19}F NMR (376.4 MHz, C_6D_6, 333 K): δ −55.2 (t, 3 F, $^4J_{FF}$ = 21.2 Hz, CF_3), −114.1 (m, 2 F, aryl F_o), −145.8 (m, 2 F, aryl F_m).

Rearrangement of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C_6F_5)] (4) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2,3,5,6-C_6F_4H)] (7). A 5.00 mg amount (0.01 mmol) of the hydride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(C_6F_5)] (**4**) was dissolved in 0.70 mL of C_6D_6, heated to 60 °C. The reaction, which was completed after 90 min, was monitored using ^{1}H and ^{19}F NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ 1.30 (bs, 24 H, CH_3), 6.23−6.29 (m, 1 H, aryl *H*), 6.31 (s, 4H, NC*H*C*H*N), 6.56 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*). ^{19}F NMR (376.4 MHz, C_6D_6, 333 K): δ −117.8 (m, 2 F, aryl F_o), −143.5 (dd, 2 F, $^3J_{FF}$ = 16.0 Hz, $^5J_{FF}$ = 14.0 Hz, aryl F_m), −374.2 (s, 1 F, Ni−*F*).

Rearrangement of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (5) to *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (9a) and *trans*-[Ni-(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (9b). A 5.00 mg amount (0.01 mmol) of the hydride complex *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (**5**) was dissolved in 0.70 mL of C_6D_6, heated to 60 °C. The reaction, which was completed after 24 h, was monitored using ^{1}H and ^{19}F NMR spectroscopy. After 24 h we obtained two sets of signals in a ratio of approximately 80:20, as judged by ^{19}F NMR spectroscopy. The isomer with the hydrogen atom adjacent to the activated C−F bond and the CF_3 group at the 5-position, *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (**9a**), is the major reaction product.

trans-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (9a). ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ 1.26 (bd, 24 H, CH_3), 6.29 (s, 4 H, NC*H*C*H*N), 6.38 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 7.43 (bt, 1 H, aryl *H*). ^{19}F NMR (376.4 MHz, C_6D_6, 333 K): δ −56.3 (dd, 3 F, $^4J_{FF}$ = 21.4 Hz, $^4J_{FF}$ = 24.7 Hz, CF_3), −92.5 (ddq, 1 F, $^5J_{FF}$ = 16.6 Hz, $^4J_{FF}$ = 3.4 Hz, $^4J_{FF}$ = 21.4 Hz, aryl F_o), −146.0 (dd, 1 F, $^3J_{FF}$ = 20.3 Hz, $^5J_{FF}$ = 16.1 Hz, aryl F_m), −147.7 (ddq, 1 F, $^4J_{FF}$ = 3.6 Hz, $^3J_{FF}$ = 20.4 Hz, $^4J_{FF}$ = 24.4 Hz, aryl F_p), −368.0 (s, 1 F, Ni−*F*).

trans-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (9b). Byproduct with the CF_3 group at the 2-position and the hydrogen at the 5-position. ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ 1.20 (bd, 24 H, CH_3), 6.34 (s, 4H, NC*H*C*H*N), 6.45 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 6.65 (m, 1 H, aryl *H*). ^{19}F NMR (376.4 MHz, C_6D_6, 333 K): δ −56.3 (d, 3 F, $^4J_{FF}$ = 18.8 Hz, CF_3), −79.7 (dd, 1 F, $^5J_{FF}$ = 15.6 Hz, $^4J_{FF}$ = 3.6 Hz, aryl F_o), −144.5 (dd, 1 F, $^3J_{FF}$ = 19.9 Hz, $^4J_{FF}$ = 3.5 Hz, aryl F_p), −145.8 (ddq, 1 F, $^3J_{FF}$ = 20.0 Hz, $^5J_{FF}$ = 15.3 Hz, $^4J_{FF}$ = 18.8 Hz, aryl F_m), −378.8 (s, 1 F, Ni-*F*).

[Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF_3)C_6F_4H)] (8). After approximately 1 h of the reaction the following resonances were detected. These are attributed to the intermediate [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF_3)C_6F_4H)] (**8**). ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ 1.07 (bs, 24 H, CH_3), 5.06 (bsept, 4H, $^3J_{HH}$ = 6.4 Hz, ^{i}PrC*H*), 5.56 (m, 1H, aryl *H*) 6.38 (bs, 4H, NC*H*C*H*N). ^{19}F NMR (376.4 MHz, C_6D_6, 333 K): δ −49.6 (t, 3 F, $^4J_{FF}$ = 12.3 Hz, CF_3), −142.8 (bs, 2 F, aryl F_o), −155.5 (bs, 2 F, aryl F_m).

Synthesis of [Ni(^{i}Pr$_2$Im)$_2$(η^2-*C*,*C*-(CF_3)C_6F_4H)] (8). 1-(Trifluoromethyl)-2,3,5,6-tetrafluorobenzene (68.0 μL, 0.50 mmol) was added to a solution of [Ni_2(^{i}Pr$_2$Im)$_4$(COD)] (**1**; 210 mg, 0.25 mmol) in 15 mL of toluene and stirred at room temperature for 75 min. All volatiles were removed in vacuo, and the remaining solid was suspended in 10 mL of hexane. The product was filtered off and dried in vacuo to give 140 mg (0.24 mmol, 48%) of a yellow, pyrophoric powder. Anal. Calcd (found) for $C_{25}H_{33}F_7N_4Ni$ [580.19 g/mol]: C, 51.66 (51.72); H, 5.72 (6.11); N, 9.64 (9.51). ^{1}H NMR (200 MHz, C_6D_6, 296 K): δ 1.04 (bs, 24 H, CH_3), 5.04 (bsept, 4H, ^{i}PrC*H*), 5.62 (m, 1H, aryl *H*), 6.31 (s, 4H, NC*H*C*H*N). ^{19}F NMR (188.3 MHz, C_6D_6, 296 K): δ −49.3 (t, 3 F, $^4J_{FF}$ = 11.9 Hz, CF_3), −142.6 (bs, 2 F, aryl F_o), −155.6 (bs, 2 F, aryl F_m).

Synthesis of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (9a) and *trans*-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (9b) Starting from [Ni_2(^{i}Pr$_2$Im)$_4$(COD)] (1) and 1-(CF_3)-2,3,5,6-C_6F_4H. 1-(Trifluoromethyl)-2,3,5,6-tetrafluorobenzene (68.0 μL, 0.50 mmol) was added to a solution of [Ni_2(^{i}Pr$_2$Im)$_4$(COD)] (**1**; 210 mg, 0.25 mmol) in 15 mL of toluene and stirred at 60 °C for 64 h. All volatiles were removed in vacuo, and the remaining solid was suspended in 15 mL of hexane. The product was filtered off and dried in vacuo to give 120 mg (0.21 mmol, 42%) of a yellow powder.

trans-[Ni(^{i}Pr$_2$Im)$_2$(F)(3-(CF_3)-2,4,5-C_6F_3H)] (9a). ^{1}H NMR (200 MHz, C_6D_6, 296 K): δ 1.24 (bs, 24 H, CH_3), 6.21 (s, 4 H, NC*H*C*H*N), 6.40 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 7.49 (bt, 1 H, aryl *H*). ^{19}F NMR (188.3 MHz, C_6D_6, 296 K): δ −56.2 (dd, 3 F, $^4J_{FF}$ = 21.6 Hz, $^4J_{FF}$ = 24.6 Hz, CF_3), −92.7 (ddq, 1 F, $^5J_{FF}$ = 16.9 Hz, $^4J_{FF}$ = 4.5 Hz, $^4J_{FF}$ = 21.6 Hz, aryl F_o), −145.6 (dd, 1 F, $^3J_{FF}$ = 20.3 Hz, $^5J_{FF}$ = 16.1 Hz, aryl F_m), −147.7 (ddq, 1 F, $^4J_{FF}$ = 4.0 Hz, $^3J_{FF}$ = 20.7 Hz, $^4J_{FF}$ = 24.7 Hz, aryl F_p), −364.8 (s, 1 F, Ni−*F*).

trans-[Ni(^{i}Pr$_2$Im)$_2$(F)(2-(CF_3)-3,4,6-C_6F_3H)] (9b). ^{1}H NMR (200 MHz, C_6D_6, 296 K): δ 1.24 (bs, 24 H, CH_3), 6.17 (s, 4H, NC*H*C*H*N), 6.46 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, ^{i}PrC*H*), 6.67 (m, 1 H, aryl *H*). ^{19}F NMR (188.3 MHz, C_6D_6, 296 K): δ −55.7 (d, 3 F, $^4J_{FF}$ = 18.8 Hz, CF_3), −79.7 (m, 1 F, aryl F_o), −144.3 (dd, 1 F, $^3J_{FF}$ = 20.1 Hz, $^4J_{FF}$ = 3.2 Hz, aryl F_p), −146.1 (ddq, 1 F, $^3J_{FF}$ = 19.7 Hz, $^5J_{FF}$ = 15.6 Hz, $^4J_{FF}$ = 18.2 Hz, aryl F_m), −372.1 (s, 1 F, Ni-*F*).

Crystal Structure Determination of *trans*-[Ni(^{i}Pr$_2$Im)$_2$(H)(4-(CF_3)C_6F_4)] (5). Crystal data: $C_{25}H_{35}F_7N_4Ni$, M_r = 583.26 g mol^{-1}, yellow prism, size 0.30 × 0.20 × 0.15 mm^3, monoclinic, space group *C2/m*, *a* = 20.229(3) Å, *b* = 14.609(2) Å, *c* = 11.919(2) Å, β = 119.72(3)°, *V* = 3059.0(12) Å^3, *T* = 203 K, *Z* = 4, ρ_{calcd} = 1.266 g cm^{-3}, μ (Mo Kα) = 0.695 cm^{-1}, *F*(000) = 1216, 12 366 reflections in *h* (−25 to +16), *k* (−18 to +16), *l* (−13 to +14), measured in the range 3.44° < θ < 27.77°, completeness θ_{max} = 98.2%, 3688 independent reflections, R_{int} = 0.1004, 2624 reflections with $F_o > 2\sigma(F_o)$, 208 parameters, 0 restraints, $R1_{obs}$ = 0.0706, $wR2_{obs}$ = 0.1642, $R1_{all}$ = 0.1056, $wR2_{all}$ = 0.1861, GOF = 1.097, largest difference peak and hole 0.403/−0.417 e Å^{-3}.

Crystals were immersed in a film of perfluorpolyether oil on a glass fiber and transferred to a STOE-IPDS 1 image plate diffractometer (Mo Kα radiation) equipped with a FT AirJet low-temperature device. Data were collected at 200 K; equivalent reflections were merged, and the images were processed with the STOE IPDS software package. Corrections for Lorentz−polarization effects and adsorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all non-hydrogen atoms, and hydrogen atoms were included in all calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.[12]

Computational Details. All calculations were carried out with the DFT implementation of the TURBOMOLE program package, Version 5.7.[13] For the DFT calculations we used the BP86 functional,[14] SV(P) basis sets, and the RI-J approximation.[15−17] The equilibrium structures and transition states of the complexes were optimized at the RIDFT level using a SV(P) basis. Analytic second derivatives were calculated with the program AOFORCE using the RI-J approximation. All energies given are ZPE corrected.

The method employed here for the calculations has been chosen to give a qualitative understanding of the system. Truncation of the complexes under consideration, i.e. substitution of the NHC ^{i}Pr groups by hydrogen atoms, led to unreliable results, since hydrogen bonds between the N−H groups and the fluorine substituents override the steric and electronic effects in the complexes. Although the SV(P) basis set is possibly a little inflexible and the BP86 functional tends to underestimates barriers, a recent benchmark study by Bickelhaupt et al.[18] on C−F activation at Pd(0) shows that BP86 correctly reproduces all qualitative trends for the oxidative addition of C−F to Pd(0).

■ ASSOCIATED CONTENT

Supporting Information

A CIF file giving X-ray crystal data and tables giving computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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