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Activation of C–F and Ni–C Bonds of [P,S]-Ligated Nickel Perfluorometallacycles

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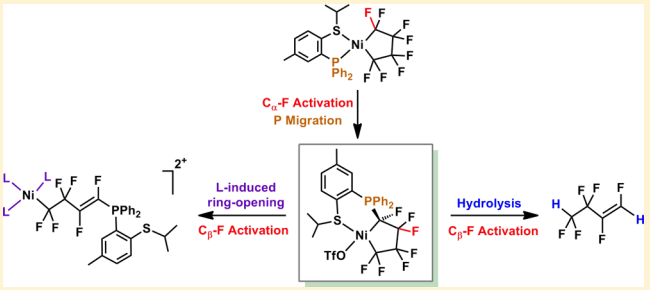
Supporting Information

ABSTRACT: The first example of a [P,S]-ligated metal perfluorocyclopentane is reported. The new metallacycle undergoes C_α–F activation in the presence of a Lewis acid, followed by chemoselective ligand migration, affording a fused metallabicyclic product. Reactivity of this product includes an unprecedented nucleophile-induced ring-opening reaction, involving loss of a β-fluoride. Additionally, hydrolysis of the metallabicyclic product affords a single isomer of hexafluoro-1-butene.

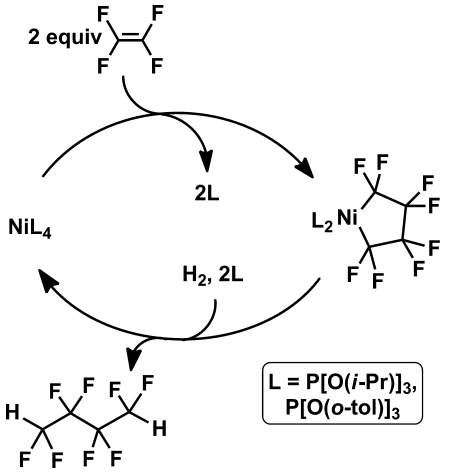


INTRODUCTION

The importance of fluorocarbons and their derivatives can be seen through their wide range of uses: small-molecule fluorocarbon derivatives are employed, for example, as refrigerants, solvents, surfactants, and pharmaceutical compounds.[1] Despite the attractive features of fluorocarbons and their derivatives (e.g., thermal and chemical/biochemical stability), their syntheses are typically energetically intensive and environmentally problematic.[2] High temperatures or large electrochemical potentials are needed, along with toxic reagents. For example, the Swarts process for synthesizing highly fluorinated organic compounds requires antimony-based catalysts with chlorocarbon and hydrofluoric acid feedstocks.[3] These harsh conditions are also incompatible with most functional groups. Our goal is to develop more sustainable routes to *functionalized* small-molecule fluorocarbons via base-metal catalysis, using fluoroalkenes obtained from waste fluoropolymers (e.g., PTFE) as feedstocks.[4] We are currently studying the stoichiometric reactions of new nickel polyfluorocyclopentane complexes, with emphasis on challenging C–F and M–R^F (R^F = fluoroalkyl) activation processes, to assess their viability for future catalytic applications.

In the 1960s, Stone and co-workers synthesized the first nickel perfluorometallacycles by reacting tetrafluoroethylene (CF_2=CF_2, TFE) with tetrakis(phosphine)- or tetrakis(phosphite)nickel(0) complexes (Scheme 1, top). Various metal systems were studied, including nickel, platinum, cobalt, and iron. It was concluded that the choice of metal and ancillary ligands dictated whether three- or five-membered metallacycles were formed.[5] Since these compounds surfaced nearly five decades ago, very few studies have focused on their reactivity and most reports have been limited to substitution of the ancillary ligands.[6] Reactions of the typically inert perfluorometallacyclic fragment are even rarer.[7] In 1988, Burch and co-workers demonstrated the activation of a C_α–F bond in $Ni(PEt_3)_2(CF_2)_4$ using BF_3; upon fluoride abstraction, one of the phosphine ligands migrated to the α-carbon, giving the phosphonium ylide $Ni(PEt_3)(BF_4)[CF(PEt_3)(CF_2)_3]$, and a transient fluorocarbene was proposed as an intermediate.[8] Baker et al. later developed a *catalytic* method for the hydrodimerization of TFE, with perfluoronickelacyclopentane and NiL_4 intermediates (Scheme 1).[9] The reaction required elevated temperatures/pressures and hydrogenolysis of the typically robust Ni–R^F bonds was only observed when π-acidic phosphite ligands were employed.[9,10] Catalysis with transition-metal perfluoroalkyl intermediates is inherently challenging due to the general stability of M–R^F (R^F = fluoroalkyl) bonds,[11,18a]

Scheme 1



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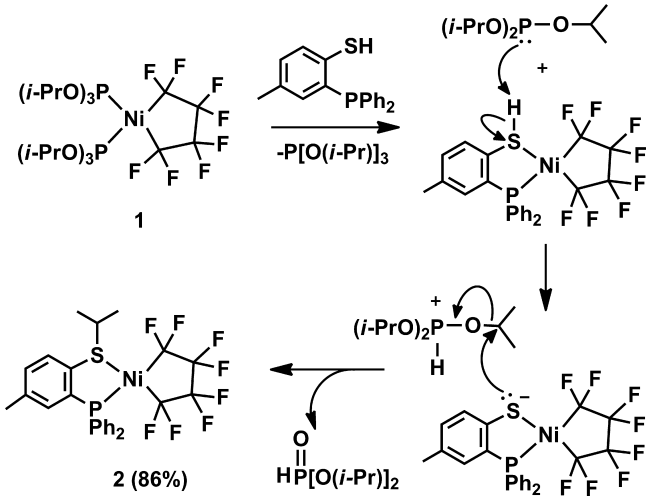
but a number of new metal-based methods for introducing R^F (predominantly CF_3) groups to organic molecules have appeared recently.[12]

RESULTS AND DISCUSSION

One approach to metal-catalyzed fluorocarbon synthesis involves metallacycle modification through C−F bond functionalization prior to hydrogenolysis. As a result, we have initiated extensive studies of fluoride abstraction as a function of metal and ancillary ligands. Herein we report the first nickel perfluorometallacycle complex with a bidentate [P,S] ligand. Most[6b] of the previously reported complexes with the perfluoronickelacyclopentane substructure have two identical monodentate ancillary ligands or a symmetrical bidentate ligand (e.g., 2,2′-bipyridine or 1,2-bis(diphenylphosphino)ethane; ideal C_{2v} symmetry for the complexes). The reactivity of the [P,S]-ligated metallacycle has been examined, and below we describe several reactions, including the activation of C_α−F and M−C bonds, as well as an unusual ring-opening reaction that appears to proceed through β-fluoride elimination.

The bis(phosphite)nickel perfluorometallacycle **1** was synthesized according to reported methods.[3,9] Treatment of **1** with the thiol form of the ligand, 1,2,4-(HS)(Ph_2P)Me(C_6H_3) (variation of the known ligand 1,2-(HS)(Ph_2P)(C_6H_4))[13] led to unexpected migration of an isopropyl group of the phosphite ligand to the sulfur atom of the ligand, cleanly yielding complex **2** (86% isolated yield). The diisopropyl phosphonate side product was observed by $^{31}P\{^1H\}$ NMR at 1.1 ppm with an equimolar amount of free phosphite appearing at 135.8 ppm. The mechanism for the formation of **2** is speculative at this point but likely involves a transient nickel-coordinated thiol, which is deprotonated by the phosphite; the resulting phosphorus acid then transfers an alkyl group to the nickel-bound thiolate (Scheme 2).[14] This proposed mechanism is

Scheme 2



similar to the organic Michaelis−Arbuzov reaction, which involves formation of a phosphonate from a trialkyl phosphite and an alkyl halide; the potently electrophilic P-alkylated phosphite transfers another alkyl group to the halide.[15]

The ^{19}F NMR data for **2** are consistent with the loss of symmetry (apparent C_s) relative to **1** (C_{2v}) and show four unique fluorine environments. Considering that the nickel-coordinated sulfur atom is chiral and pyramidal inversion is unlikely (on the basis of previous reports of sulfonium salts and metal-coordinated thioethers),[16] we propose that the thioether group rapidly coordinates/decoordinates from the metal, resulting in the apparent equivalence of the two faces of the perfluorometallacycle. The $^{31}P\{^1H\}$ signal for **2** (44.0 ppm) is an apparent quintet due to coupling with the fluorines on the C_α atoms. Complex **2** was characterized by single-crystal X-ray diffraction (Figure 1).[17] Crystals were grown by slow

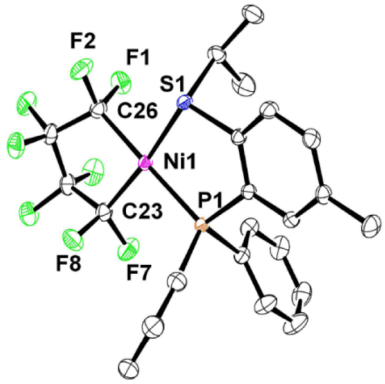


Figure 1. ORTEP representation of the molecular structure of complex **2**. Ellipsoids are set at the 40% probability level, and hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Ni1−C23 1.9204(14), Ni1−C26 1.9470(13), Ni1−S1 2.2147(3), Ni1−P1 2.2194(3), C26−F1 1.3852(17), C26−F2 1.3897(17), C23−F7 1.3743, C23−F8 1.3823(18); C23−Ni1−C26 85.82(6), C26−Ni1−S1 91.12(4), C23−Ni1−P1 93.57(4), S1−Ni1−P1 89.860(13).

evaporation of a diethyl ether solution. Bond angles are consistent with a distorted-square-planar Ni(II) center. As expected,[11] the C_α−F bonds are significantly elongated in comparison to C_β−F bonds (e.g., 1.3897(17) and 1.3507(18) Å, respectively). The Ni(1)−C(26) bond in **2** is appreciably longer than the Ni(1)−C(23) bond trans to the sulfur donor (1.9470(13) and 1.9204(14) Å, respectively), reflecting the larger trans influence of the phosphine in comparison to the thioether.

When the [P,S] perfluorometallacycle **2** was treated with the Lewis acid Me_3SiOTf (Tf = SO_2CF_3), a fluoride was abstracted from the metallacycle, presumably from one of the metal-activated C_α positions,[18] yielding the fused metallabicyclic complex **3** in 95% isolated yield (48 h, 60 °C in toluene) (Scheme 3, top). At this stage, it is not clear which of the α-fluoride atoms is activated: the C_α−F bond lengths in the solid-state structure of **2** are very similar for the carbon atoms trans to P and S and thus offer no insight into the likely site of fluoride abstraction. When BF_3−etherate was employed as the Lewis acid, the BF_4-ligated analogue of **3** was not formed and only minor, unidentified products were observed (C_6D_6, 60 °C, <10% conversion of starting material after 48 h). Complex **3** is air-stable and did not decompose upon heating (80 °C) in CD_3CN for 24 h.

The reactivity described above is reminiscent of Burch's observation of monodentate phosphine (PEt_3) migration upon fluoride abstraction (see above).[8] Interestingly, fluoride abstraction/phosphine migration was *not* observed when excess BF_3 was combined with perfluoronickelacyclopentane bearing a bidentate [P,P] ligand {Ni[κ^2-(*i*-Pr)$_2$PCH$_2$CH$_2$P(*i*-Pr)$_2$)]-(CF_2)$_4$}, even upon heating.[8] The failure of the [P,P] complex to undergo fluoride abstraction derives presumably from the

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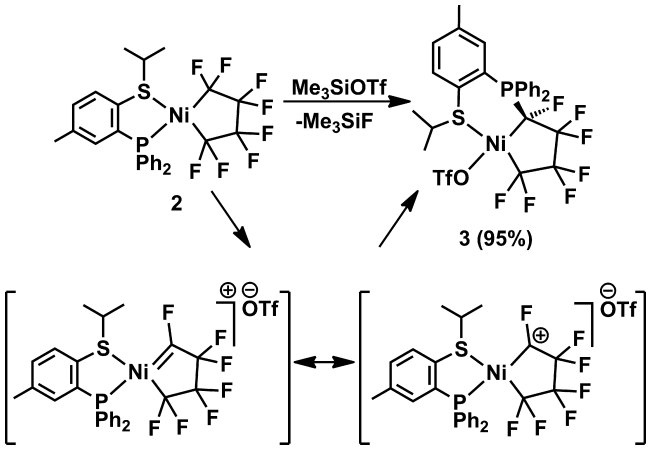
Scheme 3



increased Lewis basicity and/or size of the phosphine groups, relative to the P and S donors in **2**. However, BF_3 also failed to abstract fluoride from complex **2** (see above) and it is possible the [P,P] metallacycle could be activated using Me_3SiOTf. Burch proposed the fluoride-activation reaction proceeds through a short-lived nickel fluorocarbene.[8] In keeping with this proposal, we speculate that the reaction proceeds through one of two possible intermediates: a fluorocarbene (Scheme 3, bottom left) or a carbocation intermediate[19] (Scheme 3, bottom right). The highly electrophilic[18a,20] intermediate is attacked, chemoselectively, by the more nucleophilic phosphine group of the [P,S] ligand to give **3**.

The ^{19}F NMR spectrum of **3** shows eight unique fluorine environments (including the CF_3 from the triflate group), consistent with loss of apparent mirror-plane symmetry (C_s to C_1) and the formation of a new chiral carbon center upon phosphine migration. Again, the sulfur atom is chiral, but the ^1H NMR data show only two methyl environments for the S-bound isopropyl group, indicating either the formation of only one diastereomer or rapid racemization at sulfur (see above).[16] Geminal F−F ($^2J_{FF}$) coupling constants range between 250 and 275 Hz, and the fluorine geminal to P is shifted significantly upfield to −198.4 ppm ($^2J_{FP}$ = 69 Hz). All seven of the metallacyclic fluorine environments were assigned by ^{19}F NOESY NMR experiments (see the Supporting Information for complete details).

Single crystals of **3** were obtained by slowly cooling a benzene solution. Distorted-square-planar geometry is again observed at the Ni center. For the Ni−C−P fragment, the Ni−C bond is approximately the same length or shorter than the three Ni−CF_2R^F bonds in structures **2** and **3** (Figure 2). Presumably, the weak trans influence of the OTf ligand contributes to the short metal−carbon bond, although the effects of replacing a fluoride with a phosphine substituent are unclear at present.

We began to explore the reactivity of complex **3**, initially focusing on ligand substitution reactions with a variety of nucleophiles. Dissolving **3** in acetonitrile leads to displacement of the triflate ion with acetonitrile to yield **3**·CH_3CN (Scheme 4, left). Substitution of the triflate group was also observed when **3** was treated with 1 equiv of 2,6-dimethylphenyl isocyanide (CNAr) or sodium thiophenolate, to afford **4** and **5**, respectively (Scheme 4). Thus, the triflate ion of **3** can be displaced from nickel by a variety of nucleophiles, while the thioether group remains coordinated in the products.

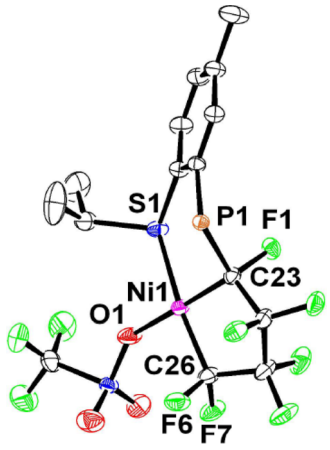
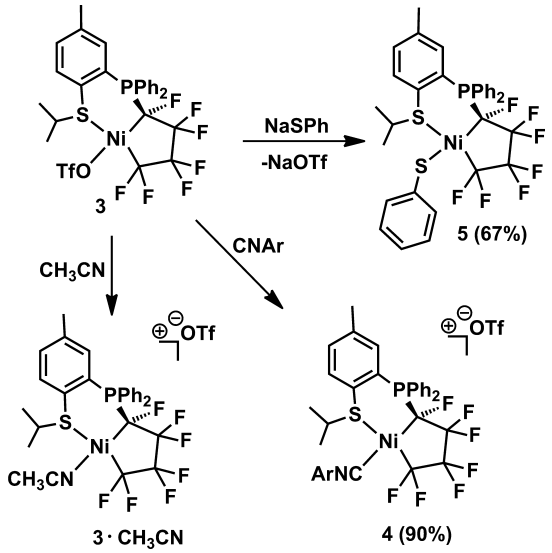


Figure 2. ORTEP representation of the molecular structure of complex **3**. Ellipsoids are set at the 40% probability level, and hydrogen atoms are omitted. Two phenyl groups are omitted from P1 for clarity. One of two orientations of the disordered OTf group is depicted. Selected bond lengths (Å) and angles (deg): Ni1−C23 1.9160(15), Ni1−C26 1.9149(15), Ni1−S1 1.2777(4), P1−C23 1.8494(14); O1−Ni1−S1 84.49(14), C23−Ni1−S1 93.58(4), O1−Ni1−C26 95.07(15), C23−Ni1−C26 86.73(6).

Scheme 4



When **3** is treated with >1 equiv of CNAr, a surprising ligand−induced ring-opening reaction occurs, in which Ni−S, Ni−C, and C_β−F bonds are cleaved and P−F/C−C bonds are formed. Treatment of **3** with 3 equiv of CNAr yields complex **6** (room temperature, 1 h, C_6D_6) (Scheme 5, top right), which was observed using multinuclear NMR.[21,22] Evidence for the P−F group is provided by ^{19}F and ^{31}P NMR: the large coupling constant of 660 Hz is strongly indicative of one-bond P−F coupling and the downfield ^{19}F shift of +16.5 ppm also supports a fluorine−phosphorus bond. The $^{31}P\{^1H\}$ NMR resonance for **6** is found significantly upfield at −73.8 ppm, suggestive of a five-coordinate phosphorus atom.[23] For the alkenyl fluorine atoms, $^3J_{FF}$ = 135 Hz, pointing to exclusive formation of the F,F-*trans* (*E*) double-bond isomer. Attempts to isolate **6** led to decomposition; we obtained the more stable compound **7** (91% isolated yield) by fluoride abstraction from the phosphorus center of **6**, using Me_3SiOTf (Scheme 5).

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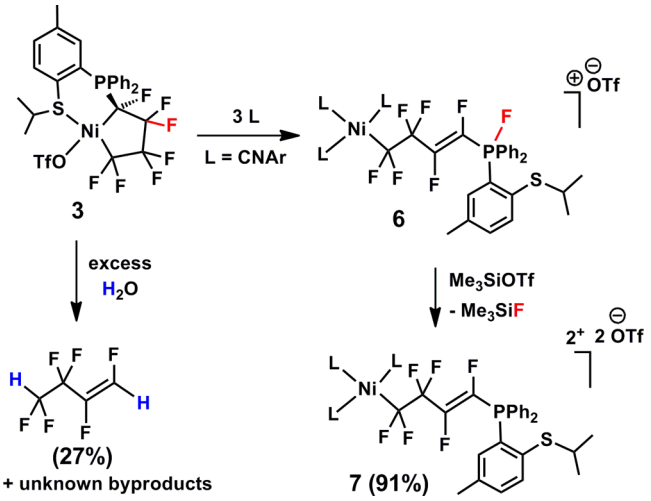
Scheme 5



Complex **7** was characterized by ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR, UV−vis, and ESI-MS.

Upon hydrolysis, **3** releases exclusively the F,F-*trans* (*E*) double-bond isomer fluoroalkene shown in Scheme 5 (bottom) and as yet uncharacterized byproducts.[24] This is the first example of a transition-metal-mediated process for the selective formation of (*E*)-1,2,3,3,4,4-hexafluoro-1-butene.[25] An experiment with D_2O confirms that the hydrogens of the product originate from water. We suspect the obtained NMR yield of the hydrofluoroalkene (27% based on three trials) is artificially low due to liquid−gas phase partitioning and/or supersaturation of the benzene solvent. The crude ^{19}F NMR spectrum for the hydrolysis reaction showed only minor impurities and (*E*)-1,2,3,3,4,4-hexafluoro-1-butene as the only major product (see the Supporting Information, Figures S29 and S30).

Treating complex **7** with water *does not* generate (*E*)-1,2,3,3,4,4-hexafluoro-1-butene. ^{19}F and ^{31}P{^{1}H} NMR data indicate that an intact P−C(F) bond is present among the unknown hydrolysis products, on the basis of geminal coupling between the phosphorus and one fluorine atom (see the Supporting Information for additional details).

CONCLUSIONS

In summary, the synthesis of a new nickel perfluorometallacycle (**2**), with a hemilabile phosphine/thioether ligand, has been described. Fluoride abstraction from this complex yielded a phosphine migration product (**3**), featuring weakly bound thioether and triflate groups on the nickel atom. Ligand substitution studies revealed that the triflate ligand may be displaced from the metal, producing neutral or cationic complexes by employing different nucleophiles. The reaction of **3** with CNAr (≥3 equiv) produced an unexpected ring-opened product via Ni−C and C−F activation pathways. Finally, hydrolysis of **3** afforded a single isomer of hexafluoro-1-butene, thus demonstrating the potential of metallacycle modification for selective production of unsaturated hydrofluorocarbons. A combined experimental and computational study is underway to elucidate the mechanism for this unprecedented ring-opening reaction. The stoichiometric systems reported here will be studied more extensively with the goal of designing *catalytic* systems for the synthesis of functionalized fluorocarbons.

EXPERIMENTAL SECTION

General Considerations. Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glovebox. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether (DEE), and tetrahydrofuran (THF) were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system. Benzene-d_6 (C_6D_6) and dichloromethane (DCM) were dried by stirring over activated alumina (ca. 10 wt %) overnight, followed by filtration. Acetonitrile (MeCN) and acetonitrile-d_3 (CD_3CN) were dried by refluxing over calcium hydride under nitrogen. After distillation, they were dried further by stirring over activated alumina (ca. 5 wt %) overnight, followed by filtration. All solvents were stored over activated (heated at ca. 250 °C for >10 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 150 °C for >2 h. The following chemicals were obtained commercially, as indicated: trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf, Aldrich, 99%), bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$, Strem, 98+%), triisopropyl phosphite ($P(O\text{-}i\text{-}Pr)_3$, Aldrich, 95%), 4-methylbenzenethiol (1,4-(HS)Me(C_6H_4), Aldrich, 98%), diphenylchlorophosphine (PPh_2Cl, Strem, minimum 95%), 2,6-dimethylphenyl isocyanide (1,2,6-(CN)Me_2(C_6H_3), Aldrich, 96%), sodium thiophenolate (NaSPh, Aldrich, ≥96.5%). Tetrafluoroethylene was purchased from ABCR (99%) or made by pyrolysis of polytetrafluoroethylene (Scientific Polymer Products, powdered) under vacuum, using a slightly modified literature procedure (10−20 mTorr, 650 °C, 30 g scale, product stabilized with (*R*)-(+)-limonene (Aldrich, 97%), giving TFE of ca. 97% purity).[26] $Ni[P(O\text{-}i\text{-}Pr)_3]_2(C_4F_8)$ was made by oxidative addition of tetrafluoroethylene to $Ni[P(O\text{-}i\text{-}Pr)_3]_4$ using a slightly modified literature procedure.[3,9] $Ni[P(O\text{-}i\text{-}Pr)_3]_4$ was prepared from $Ni(COD)_2$ following reported methods. ^{31}H, ^{19}F, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a 300 MHz Bruker Avance instrument at room temperature (21−23 °C). ^{1}H NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (C_6D_6, 7.16 ppm; CD_3CN, 1.94 ppm). ^{19}F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to −63.5 ppm. Note: for NMR solutions containing both BTB and hexafluorobenzene (C_6F_6) (Aldrich, 99%), the chemical shift of C_6F_6 appears at −163.6 or −164.5 ppm, in C_6D_6 and CD_3CN, respectively (with BTB at −63.5 ppm). ^{1}H NMR data for BTB: at 300 MHz, C_6D_6, δ 6.60 (m, 1H, Ar-5-H), 7.12 (m, 2H, Ar-4,6-H), 7.76 (m, 1H, Ar-2-H); at 300 MHz, CD_3CN, δ 7.76−7.84 (m, 1H, Ar-H), 7.95−8.04 (ov m, 3H, Ar-H). We chose BTB as an internal ^{19}F NMR standard over C_6F_6 because we expected it to be less reactive with any of the reported Ni complexes or reactive intermediates. ^{31}P{^{1}H} NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. Electrospray ionization mass spectral data were collected using an Applied Biosystem API2000 triple-quadrupole mass spectrometer. UV−vis spectra were recorded on a Cary 100 instrument, using sealable quartz cuvettes (1.0 cm path length). Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, British Columbia, Canada).

X-ray Crystallography. For **2** and **3**, samples were mounted on thin glass fibers using paraffin oil and were cooled to 200 K prior to data collection. Data were collected on a Bruker AXS KAPPA single-crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with the APEX II software package from BRUKER AXS.[27] Diffraction data were collected with a sequence of 0.5° ω scans at 0, 90, 180, and 270° in ϕ. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data set and unit-cell parameters were consistent with triclinic systems. Solutions in centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares

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procedures based on *F*.[27] In the structure, compound molecules are situated in the general position. All non-hydrogen atoms were refined anisotropically with satisfactory thermal parameter values. Additional crystallographic data and selected data collection parameters are reported below. The CIF files for **2** and **3** are available as Supporting Information.

Synthesis of [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_8$) (2). [(P(O-*i*-Pr)$_3$)$_2$Ni(C$_4$F$_8$)] (**1**; 1.00 g, 1.48 mmol) was placed in a 100 mL round-bottom flask and dissolved in ∼10 mL of toluene. [1,2,4-(HS)(Ph$_2$P)Me(C$_6$H$_3$)] (480 mg, 1.56 mmol) was added to the stirred [(P(O*i*-Pr)$_3$)$_2$Ni(C$_4$F$_8$)]/toluene mixture, and stirring was continued at room temperature for ∼12 h. The cloudy yellow-orange reaction mixture was concentrated in vacuo until ∼2 mL of yellow paste remained. Around 20 mL of hexanes was then added to the round-bottom flask, precipitating a light yellow powder. The flask was placed in a −35 °C freezer for 24 h. The product was filtered cold (30 mL medium pore fritted funnel), washed with precooled hexanes (−35 °C, 2 × 3 mL), and dried in vacuo, affording a light yellow powder. Yield: 776 mg, 1.27 mmol, 86% based on **1**. The isolated material was stored at room temperature under nitrogen. UV−vis (0.7 mM in diethyl ether): λ_{max} (ε) 332 nm (2082). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.96 (d, $J \approx 7$ Hz, 6H, 2 *i*-Pr Me), 1.64 (s, 3H, Me), 3.58 (sept, 1H, *i*-Pr H), 6.60 (d m, 1H, Ar-H), 6.98 (ov m, 8H, Ar-H), 7.60 (ov m, 4H, Ar-H). ^{19}F NMR (282 MHz, C$_6$D$_6$): δ −96.3 (d m, 2F$_\alpha$, $^3J_{FP}$ = 32 Hz), −104.7 (d m, 2F$_\alpha$, $^3J_{FP}$ = 27 Hz), −137.8 (m, 2F$_\beta$), −138.6 (m, 2F$_\beta$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): δ 44.0 (tr tr, $^3J_{PF}$ = 27, 32 Hz). Anal. Calcd for C$_{26}$H$_{23}$F$_8$NiPS: C, 51.26, H, 3.81. Found: C, 51.48, H, 3.65. See Figures S1−S3 (Supporting Information) for the ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra.

Synthesis of [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (3). [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_8$) (**2**; 831 mg, 1.36 mmol) was dissolved in ∼20 mL of toluene and transferred to a 100 mL Schlenk bomb (i.e., a tubular flask, sealed with a single polytetrafluoroethylene (PTFE) valve). To the **2**/toluene solution was added trimethylsilyl trifluoromethanesulfonate (296 μL, 1.64 mmol). The bomb was sealed and placed in a 60 °C oil bath for 48 h. A dark yellow precipitate was formed over the course of the reaction time. The product was filtered through a 30 mL medium pore fritted funnel under nitrogen. The collected dark yellow powder was washed with hexanes (2 × 3 mL) and dried in vacuo. Yield: 958 mg, 1.30 mmol, 95% based on **2**. The isolated material was stored at room temperature under nitrogen. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.59, 1.74 (d, J = 7 Hz, 3H, *i*-Pr Me), 2.33 (s, 3H, Me), 3.81 (sept, J = 7 Hz, 1H, *i*-Pr H), 7.06 (d, J_{HP} = 14 Hz, 1H, Ar-H), 7.47−8.00 (ov m, 10H, Ar-H), 8.39 (ov d m, 2H, Ar-H). ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −78.5 (s, 3F, OTf), −99.2 (d tr, $^2J_{FF}$ = 242 Hz, $^3J_{FF}$ = 12 Hz, 1F$_\alpha$), −115.6 (d d, $^2J_{FF}$ = 242 Hz, $^3J_{FF}$ = 17 Hz, 1F$_\alpha$), −117.8 (d m, $^2J_{FF}$ = 272 Hz, 1F$_\beta$), −129.9 (d m, $^2J_{FF}$ = 272 Hz, 1F$_\beta$), −132.5 (d d d, $^2J_{FF}$ = 245 Hz, $^3J_{FF}$ = 35, 16 Hz, 1F$_\beta$), −137.3 (d m, $^2J_{FF}$ = 245 Hz, 1F$_\beta$), −196.2 (d d d, $^2J_{FP}$ = 75 Hz, $^3J_{FF}$ = 31, 7 Hz, 1F$_\alpha$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$): δ 14.8 (d tr, $^2J_{PF}$ = 75, $^3J_{PF}$ = 14 Hz). Anal. Calcd for C$_{27}$H$_{23}$F$_{10}$NiO$_3$PS$_2$: C, 43.87, H, 3.14. Found: C, 43.73, H, 2.95. See Figures S4−S6 (Supporting Information) for the ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra.

{[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)](CD$_3$CN)Ni(C$_4$F$_7$)}$^+$(OTf)$^-$ (3·CD$_3$CN). [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (**3**; 10 mg, 0.0135 mmol) was dissolved in deuterated acetonitrile. UV−vis (0.7 mM in acetonitrile): λ_{max} (ε) 396 nm (907). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.18 (d d, $J \approx 7$, 1 Hz, 3H, *i*-Pr Me), 1.38 (d, $J \approx 7$ Hz, 3H, *i*-Pr Me), 2.34 (s, 3H, Me), 3.43 (sept, 1H, *i*-Pr H), 7.29 (d d m, 1H, Ar-H), 7.5−8.1 (ov m, 10H, Ar-H), 8.35 (ov d m, 2H, Ar-H). ^{19}F NMR (282 MHz, CD$_3$CN): δ −79.4 (s, 3F, OTf), −96.8 (d tr m, $^2J_{FF}$ = 250 Hz, $^3J_{FF}$ = 12 Hz, 1F$_\alpha$), −109.2 (d d, $^2J_{FF}$ = 250 Hz, $^3J_{FF}$ = 16 Hz, 1F$_\alpha$), −118.5 (d m, $^2J_{FF}$ = 273 Hz, 1F$_\beta$), −130.0 (d tr m, $^2J_{FF}$ = 273 Hz, $^3J_{FF}$ = 15 Hz, 1F$_\beta$), −132.4 (d m, $^2J_{FF}$ = 248 Hz, 1F$_\beta$), −135.8 (d m, $^2J_{FF}$ = 248 Hz, 1F$_\beta$), −198.4 (d d m, $^2J_{FP}$ = 69 Hz, $^3J_{FF}$ = 30 Hz, 1F$_\alpha$). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN): δ 15.8 (d tr, $^2J_{PF}$ = 69, $^3J_{PF}$ = 13 Hz). See Figures S7−S10 (Supporting Information) for the ^{1}H, ^{19}F, ^{31}P{^{1}H}, and ^{19}F−^{19}F NOESY spectra.

Synthesis of {[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)](CNAr)Ni(C$_4$F$_7$)}$^+$(OTf)$^-$ (4). [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (**3**; 50 mg, 0.068 mmol) was dissolved in ∼8 mL of dichloromethane (DCM) and transferred to a 50 mL round-bottom flask. To the **3**/DCM solution was added 1 equiv of 2,6-dimethylphenyl isocyanide (CNAr; 9 mg, 0.068 mmol). No significant color change was observed. The reaction mixture was stirred at room temperature for 12 h. The product was concentrated, dried in vacuo, and stored at room temperature under nitrogen. Yield: 53 mg, 0.061 mmol, 90% based on **3**. UV−vis (0.7 mM in dichloromethane): λ_{max} (ε) 352 nm (1118). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.52, 1.55 (d, J = 7 Hz, 3H, *i*-Pr Me), 2.31 (s, 6H, CNAr Me), 2.39 (s, 3H, Me), 3.75 (sept, 1H, *i*-Pr H), 7.06 (d, $^2J_{PH}$ = 14 Hz, 1H, Ar-H), 7.2 (d, 2H), 7.34 (m, 1H, Ar-H), 7.51−8.08 (ov m, 12H, Ar-H). ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −79.0 (s, 3F, OTf), −87.5 (br d, $^2J_{FF}$ = 257 Hz, 1F$_\alpha$), −94.2 (d tr, $^2J_{FF}$ = 257 Hz, J_{FF} = 10 Hz, 1F$_\alpha$), −116.9 (d m, $^2J_{FF}$ = 275 Hz, 1F$_\beta$), −128.8 (d m, $^2J_{FF}$ = 275 Hz, 1F$_\beta$), −132.5 (br AB doublets, $^2J_{FF} \approx$ 262 Hz, 2F$_\beta$), −199.0 (d d, $^3J_{FF}$ = 31 Hz, $^2J_{FP}$ = 67 Hz, 1F$_\alpha$). ^{31}P{^{1}H} NMR (121 MHz,CD$_2$Cl$_2$): δ 17.2 (d d d, $^2J_{PF}$ = 67, $^3J_{PF}$ = 17, 10 Hz). See Figures S11−S13 (Supporting Information) for the ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra. MS-ESI (positive mode, solvent CH$_3$OH): *m*/*z* calcd for {[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)](CNAr)Ni(C$_4$F$_7$)}$^+$ (% intensity), 720.1 (100), 722.1 (51), 721.1 (39), 723.1 (20); *m*/*z* found, 720.2 (100), 722.3 (51), 721.3 (39), 723.4 (22).

Synthesis of [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)](SPh)Ni(C$_4$F$_7$) (5). [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (**3**; 70 mg, 0.095 mmol) was dissolved in ∼6 mL of acetonitrile and transferred to a 50 mL round-bottom flask. To the above solution was added sodium thiophenolate (13 mg, 0.099 mmol). An immediate color change from light orange to bright red was observed. The reaction mixture was stirred at room temperature for 12 h. The solution was concentrated in vacuo, and the product was extracted with dichloromethane, precipitating out the sodium triflate salt. The dichloromethane solution was filtered through a Celite Pasteur pipet and concentrated in vacuo in a round-bottom flask. Hexanes was added (∼20 mL), precipitating out a light orange solid. The flask was placed in a −35 °C freezer for 12 h. The product was filtered cold (15 mL medium pore fritted funnel) and washed with ∼3 mL of hexanes. The light orange powder was dried in vacuo and stored at room temperature under nitrogen. Yield: 44 mg, 0.063 mmol, 67% based on **3**. UV−vis (0.7 mM in acetonitrile): λ_{max} (ε) 310 (5886) (shoulder on off-scale signals in the UV range), 353 (2551) (shoulder/tail), 515 nm (322). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.33, 1.38 (d, $J \approx 7$ Hz, 3H, *i*-Pr Me), 2.28 (s, 3H, Me), 4.15 (sept, $J \approx 7$ Hz, 1H, *i*-Pr H), 6.82 (ov m, 3H, Ar-H), 6.93 (ov m, 2H, Ar-H), 7.17 (d, $J_{HP} \approx$ 14 Hz, 1H, Ar-H), 7.46−7.69 (ov m, 6H, Ar-H), 7.86 (ov m, 3H, Ar-H), 8.00 (m, 1H, Ar-H), 8.32 (ov d, 2H, Ar-H). ^{19}F NMR (282 MHz, CD$_3$CN): δ −93.0 (d m, $^2J_{FF}$ = 269 Hz, 1F$_\alpha$), −114.6 (d d d, $^2J_{FF}$ = 269 Hz, $^3J_{FF}$ = 20, 5 Hz, 1F$_\alpha$), −117.3 (d m, $^2J_{FF}$ = 270 Hz, 1F$_\beta$), −130.4 (d m, $^2J_{FF}$ = 270 Hz, 1F$_\beta$), −130.9 (d m, $^2J_{FF}$ = 244 Hz, 1F$_\beta$), −135.9 (d m, $^2J_{FF}$ = 244 Hz, 1F$_\beta$), −198.8 (d d, $^2J_{FP}$ = 73 Hz, $^3J_{FF}$ = 36 Hz, 1F$_\alpha$). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN): δ 13.5 (d tr, $^2J_{PF}$ = 73, $^3J_{PF}$ = 15 Hz). See Figures S14−S16 (Supporting Information) for the ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra. MS (ESI (positive mode), solvent CH$_3$CN): *m*/*z* calcd for {[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)$^+$} (% intensity), 589.0 (100), 591.0 (43), 590.1 (28); *m*/*z* found, 589.8 (100), 591.7 (48), 590.8 (43).

Observation of 6. [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf)) (**3**; 20 mg, 0.027 mmol) was dissolved in deuterated benzene (∼1 mL) in a medium screw cap vial, and 2,6-dimethylphenyl isocyanide (CNAr) (12 mg, 0.095 mmol) was added. The color changed immediately from opaque yellow to clear orange. The reaction mixture was stirred at room temperature for 30 min and then transferred to a J. Young NMR tube to obtain NMR spectra of compound **6**. See Figures S18−S20 (Supporting Information) for ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra. NMR data in benzene-*d*$_6$ are as follows. (broad peaks in fluorine and proton spectra associated with intermediate(s) en route to **6** are not reported; integrations for proton peaks are not reported due to overlap between product peaks from **6** and broad intermediate peaks). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.95 (d, J = 7 Hz, *i*-Pr Me), 2.15 (s, Me), 2.22 (s, CNAr Me), 3.11 (sept, *i*-Pr H), 6.62−6.69 (ov m, Ar-H), 6.77−6.83 (m, Ar-H), 7.66−

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7.78 (ov m, Ar-H). ^{19}F NMR (282 MHz, C_6D_6): δ 14.5 (br d, J_{FP} = 660 Hz, 1F), −55.9 (br s, 2F$_\alpha$), −78.3 (s, 3F, OTf), −105.0 (d d, $^4J_{FF}$ = 27, $^3J_{FF}$ = 11 Hz, 2F$_\beta$), −128.2 (br d, $^3J_{FF(trans)}$ = 135 Hz, 1F), −151.2 (br d, $^3J_{FF(trans)}$ = 135 Hz, 1F). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ −73.3 (br d, J_{PF} = 660 Hz). See Figures S17−S19 (Supporting Information) for ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra.

Synthesis of {[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)][1,2,6-(CN)-(Me)$_2$(C$_6$H$_3$)]$_3$Ni(C$_4$F$_6$)}$^{2+}$(OTf)$^-_2$ (7). [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me-(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (**3**; 70 mg, 0.095 mmol) was dissolved in ∼10 mL of C_6H_6 in a 50 mL round-bottom flask. A 3.5 equiv portion of 2,6-dimethylphenyl isocyanide (CNAr) (44 mg, 0.333 mmol) was added, and the reaction mixture was stirred for 20 min at room temperature. To the **3**/CNAr benzene solution was added trimethylsilyl trifluoromethanesulfonate (18.9 μL, 0.104 mmol). The reaction mixture was stirred at room temperature for 14 h. The product was concentrated in vacuo and washed with 2 × 3 mL of benzene, affording a yellow-gold solid. Yield: 109 mg, 0.086 mmol, 91% based on **3**. UV−vis (0.7 mM in acetonitrile): λ_{max} (ε) 369 (2233) (shoulder on off-scale signals in UV range), 453 nm (1018). ^{1}H NMR (300 MHz, CD_3CN): δ 0.93 (d, J = 7 Hz, 6H, *i*-Pr Me), 2.32 (s, 3H, Me), 2.41 (ov s, 18H, CNAr Me), 3.17 (sept, 1H, *i*-Pr H), 7.23 (ov m, 6H, Ar-H), 7.36 (ov m, 5H, Ar-H), 7.75 (ov m, 9H, Ar-H), 7.94 (ov m, 2H, Ar-H). ^{19}F NMR (282 MHz, CD_3CN): δ −58.7 (br s, 2F$_\alpha$), −79.4 (s, 6F, OTf), −107.3 (d d, $^4J_{FF}$ = 23, $^3J_{FF}$ = 11 Hz, 2F$_\beta$), −133.9 (d m, $^3J_{FF(trans)}$ = 144, $^4J_{FF}$ = 11 Hz, 1F), −151.0 (d t t, $^3J_{FF(trans)}$ = 144 Hz, $^2J_{FP}$ = 60 Hz, J_{FF} = 23, $^3J_{FF}$ = 8 Hz, 1F). ^{31}P{^{1}H} NMR (121 MHz, CD_3CN): δ 15.6 (d d, $^2J_{PF}$ = 60, $^3J_{PF}$ = 7 Hz). See Figures S20−S22 (Supporting Information) for the ^{1}H, ^{19}F, and ^{31}P{^{1}H} spectra. MS (ESI (positive mode), solvent CH_3CN): *m*/*z* calcd for [{[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)][1,2,6-(CN)-(Me)$_2$(C$_6$H$_3$)]$_3$Ni(C$_4$F$_6$)}$^{2+}$(OTf)$^-$ − H + K$^+$], 1150.2; *m*/*z* found, 1150.5; *m*/*z* calcd for [{[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)][1,2,6-(CN)-(Me)$_2$(C$_6$H$_3$)](CH$_3$CN)$_2$Ni(C$_4$F$_6$)}$^{2+}$], 783.2; *m*/*z* found, 782.9; *m*/*z* calcd for [{[1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)][1,2,6-(CN)-(Me)$_2$(C$_6$H$_3$)](CH$_3$CN)$_2$Ni(C$_4$F$_6$)}$^{2+}$ + K$^+$], 822.1, *m*/*z* found, 821.9; *m*/*z* calcd for [{1,2,4-(*i*-Pr-S)(Ph$_2$P)Me-(C$_6$H$_3$)][1,2,6-(CN)-(Me)$_2$(C$_6$H$_3$)} + H$^+$], 133.1; *m*/*z* found, 133.3; *m*/*z* calcd for [{1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)][1,2,6-(CN)(Me)$_2$(C$_6$H$_3$)} − 2CH$_3$], 102.0, *m*/*z* found, 102.1.

Hydrolysis of [1,2,4-(*i*-Pr-S)(Ph$_2$P)Me(C$_6$H$_3$)]Ni(C$_4$F$_7$)(OTf) (3). **3** (60 mg, 0.081 mmol) was transferred to a 50 mL Schlenk bomb (with a side arm) in a minimal amount of deuterated benzene (∼2 mL). To the **3**/benzene solution was added 0.2 mL of water. The flask was sealed, and the contents were stirred at 75 °C for 72 h. The reaction mixture was cooled to room temperature, and the flask was connected directly to the Schlenk line. Three freeze−pump−thaw cycles were performed on the flask. J. Young NMR tube was then evacuated and cooled to −196 °C. With the bomb and J. Young tube both under vacuum, ∼0.5 mL of the reaction mixture was transferred to the J. Young tube under static vacuum, isolating (*E*)-1,2,3,3,4,4-hexafluoro-1-butene from the nickel-containing and other nonvolatile byproducts. An ^{19}F NMR yield (by integration of product CF_2 peaks relative to an internal standard) of 27% based on three trials was calculated. Note: no reaction occurred upon addition of an excess of water to **2** with heating. NMR data in benzene-d_6 (a crude ^{1}H NMR spectrum taken before vacuum transfer is shown in Figure S23 (Supporting Information)) are as follows. ^{1}H NMR (300 MHz, C_6D_6): δ 0.44 (s, H_2O), 5.06 (tr tr m, $^2J_{HF}$ = 53, $^3J_{HF}$ = 3 Hz, 1H), 6.19 (d d m, J_{HF} = 71, 4 Hz, 1H). ^{19}F NMR (282 MHz, C_6D_6): δ −122.1 (m, J_{FH} = 3 Hz, 2F), −137.3 (d m, $^2J_{FH}$ = 53 Hz, 2F), −166.8 (d d tr tr, $^3J_{FH(gem)}$ = 71 Hz, $^3J_{FF(trans)}$ = 135 Hz, J_{FF} = 21, 4 Hz, 1F), −178.5 (d m, $^3J_{FH(cis)}$ = 4 Hz, $^3J_{FF(trans)}$ = 135 Hz, 1F). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): δ −122.1 (m, 2F), −137.3 (m, 2F), −166.8 (d tr tr, $^3J_{FF(trans)}$ = 135 Hz, J_{FF} = 21, 4 Hz, 1F), −178.5 (d tr tr, $J_{FF(trans)}$ = 135 Hz, 1F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 109.2 (tr tr d, J_{CF} = 251 Hz, $^2J_{CF}$ = 38 Hz, $^3J_{CF}$ = 3 Hz, 1C), 142.9 (d d, J_{CF} = 244 Hz, $^2J_{CF(trans)}$ = 33 Hz, 1C), 144.8 (d d tr, J_{CF} = 264 Hz, $^2J_{CF(trans)}$ = 59 Hz, $^3J_{CF}$ = 3 Hz, 1C). See Figures S23−S30 (Supporting Information) for ^{1}H, ^{19}F, ^{19}F{^{1}H}, and ^{13}C{^{1}H} spectra. MS (ESI (positive mode), solvent CH_3CN): *m*/*z* calcd for [M + H$^+$], 165.0; *m*/*z* found, 165.4.

■ ASSOCIATED CONTENT

Supporting Information

CIF files for **2** and **3** giving crystallographic data, a table giving structure refinement details, text giving experimental details for the reaction of **3** with D_2O, and Figures S1−S33 containing NMR spectra of all reported products. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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