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Complete List of Authors:	Giffin, Kaitie; University of Ottawa, Department of Chemistry and Biomolecular Sciences and CCRI Korobkov, Ilia; University of Ottawa, Department of Chemistry and Biomolecular Sciences and CCRI Baker, R; University of Ottawa, Department of Chemistry and Biomolecular Sciences and CCRI

Brønsted Acid-Promoted C−F Bond Activation in [P,S]-Ligated Neutral and Anionic Perfluoronickelacyclopentanes†

Kaitie A. Giffin, Ilia Korobkov, and R. Tom Baker*

Treatment of $L_2Ni(CF_2)_4$ **4a-c** (L = PPh_3, PPh_2Me, pyridine) with an external Lewis acid (trimethylsilyl triflate) gives new functionalized fluoronickelacyclopentanes **5a-c**. Complexes $L_2Ni(CF_2)_4$ **4a,b** react with the thiol form of the bidentate ligand 1,2,4-(HS)(Ph_2P)Me(C_6H_3) **[P,SH]** through a unique Brønsted acid-promoted C_α−F bond activation mechanism, affording phosphine-functionalized nickelacycles bearing a phosphinothiolate ligand **6a-b.** Furthermore, substituting monodentate ligands in $L_2Ni(CF_2)_4$ **4a-c** with the deprotonated form of the bidentate ligand **[P,S$^-$]** leads to the first anionic perfluoronickelacycle **7**. The anionic metallacyle reacts with phosphonium salts [$PHPh_3$](Br) and [$PHPh_2Me$](Br) to yield HF and phosphine-functionalized nickelacycles **6a,b** that still contain the terminal thiolate moiety.

Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, University of Ottawa, 30 Marie Curie, Ottawa, ON K1N 6N5, Canada. E-mail: rbaker@uottawa.ca; Tel +1-613-562-5698

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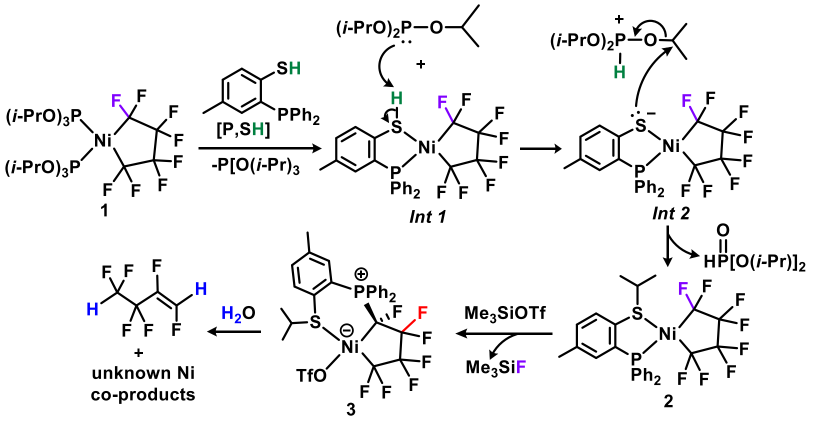
Introduction

The development of new homogeneous catalytic routes to small functionalized fluorocarbons (FCs) remains an attractive target due to the high utility of FCs in a broad range of applications.[1] Recently, there have been significant advances in homogeneously catalyzed routes for the installment of fluorine (−F)[2], trifluoromethyl (−CF_3)[3], difluoromethyl (−CHF_2)[4], and difluoromethylene (−CF_2−)[4] groups to unactivated organic substrates, typically proceeding through M−F or M−R^F (M = transition metal, R^F = fluoroalkyl) intermediates. In contrast, examples of M−R^F complexes containing a perfluoroalkyl fragment with more than one perfluoromethylene unit, as intermediates in catalysis are less common, and often require the use of halogenated FCs as precursors for M−R^F synthesis.[4,5] To circumvent this, we investigated the reactivity of perfluorometallacycle complexes synthesized by the oxidative cycloaddition of tetrafluoroethylene (TFE; obtained from waste PTFE)[6] to low-valent metal centres. Previous studies have concluded that both the metal and ancillary ligands influence whether three- or five-membered metallacycles are formed upon reacting TFE with low-valent metals.[7] To date, there are few reports on Ni−C and C−F bond reactivity studies involving perfluoronickelacyclopentanes. Among these is work patented by Baker *et al.*, wherein catalytic hydrodimerization of TFE resulting in the synthesis of octafluorobutane, a useful solvent in several industrial processes, was achieved.[5c] Additionally, work published by Burch and co-workers demonstrated the activation of a C_α−F bond of $(PEt_3)_2Ni(CF_2)_4$ in the presence of a stoichiometric amount of the fluorophilic Lewis acid BF_3.[8] Following fluoride abstraction, triethylphosphine ligand migration to the α-carbon occurred, affording $(PEt_3)(BF_4)Ni[CF(PEt_3)(CF_2)_3]$. In an effort to develop novel strategies for activation of C−F bonds and functionalization of nickel fluorocyclopentanes, we aim to assess their reactivity as a function of ancillary ligand(s) modification. Our group recently reported a new T-shaped three-coordinate perfluoronickelacyclopentane–NHC complex that undergoes an unusual fluoroalkyl group migration upon C_α−F activation by a Lewis acid. Additionally, the NHC perfluoronickelacycle reacts with carboxylic acids to afford C_α ester-functionalized metallacycles and/or Ni−C bond protonolysis products.[9]

We previously communicated the synthesis of an unsymmetrical **[P,S$^{(i\text{-Pr})}$]**-ligated nickel perfluorocyclopentane (complex **2**, Scheme 1) which displayed examples of C_α−F, C_β−F and Ni−R^F bond activation reactivity.[10] Upon treatment of $[P[O(i\text{-Pr})]_3]_2Ni(CF_2)_4$ **(1)** with 1,2,4-$(HS)(Ph_2P)Me(C_6H_3)$ **[P,SH]** an isopropyl transfer from one free phosphite to the sulfur occurred, resulting in the selective formation of the phosphinothioether-coordinated nickel complex **2**. We speculate that this reaction proceeds through a transient acidic thiol-bound intermediate (***Int 1***) that, upon deprotonation by a free phosphite, results in a short-lived thiolate-coordinated anionic nickel intermediate (***Int 2***). In a mechanism reminiscent of the organic Michaelis-Arbuzov reaction, nucleophilic attack by the nickel-coordinated thiolate on one O−*i*-Pr bond of the phosphorus acid leads to the formation of product **2**.[11] Treating **2** with the strongly Lewis acidic Me_3SiOTf (OTf = SO_2CF_3) resulted in C_α−F activation followed by chemoselective phosphine migration, resulting in the metallabicyclic product **3**. Hydrolysis of **3** with heating led to exclusive formation of the (E)-1,2,3,3,4,4-hexafluoro-1-butene as the major product, through the presumed loss of a β-fluoride.

Scheme 1



In this work, we turned our focus to other perfluoronickelacyclopentanes bearing two monodentate ancillary ligands, $L_2Ni(CF_2)_4$, where L = PPh_3 **(4a)**, PPh_2Me **(4b)**, and pyridine **(4c)**. Nickelacycles **4a** and **4b** have both been previously characterized by Stone and co-workers. Bis(pyridine)$Ni(CF_2)_4$ **(4c)** has not been reported, however Stone did characterize the analogous bis(γ-picoline)$Ni(CF_2)_4$.[7d] Complexes **4a-c** were of interest for our study as they do not offer potential alkyl transfer to the sulfur atom (see Scheme 1, ***Int 2***) as was observed with phosphite ancillary ligands containing O−*i*-Pr bonds susceptible to nucleophilic attack. The phosphinothiol ligand offers versatility as it can be employed in its acidic thiol form **[P,SH]** or in its basic thiolate form **[P,S$^-$]**. A handful of Ni(I) and Ni(II) complexes bearing the 1,2-(S^-)(Ph_2P)(C_6H_4) ligand (slight variation on the ligand used in this study) have been reported to date.[12] Most preceding examples of C_α−F activation of nickel perfluorocyclopentanes have required the use of a strong Lewis acid, where the driving force for the reaction is the formation of the stronger B−F or Si−F bond (relative to C−F). Herein, we present the reactivity of the unsymmetrical bidentate ligand **[P,SH]** in substitution reactions with $L_2Ni(CF_2)_4$ **4a-c**, where a unique ligand-assisted/Brønsted acid-promoted C_α−F activation occurs. Furthermore, the synthesis and characterization of an anionic perfluoronickelacyclopentane will be presented, along with preliminary reactivity studies.

Experimental Section

General. Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glove box. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, and dichloroethane (DCE) 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 chlorobenzene were dried by stirring over activated alumina (ca. 10 wt. %) overnight, followed by filtration. Acetonitrile (CH_3CN), acetonitrile-d_3 (CD_3CN), and dichloromethane (DCM) were dried by refluxing over calcium hydride under nitrogen. After distillation, CH_3CN, CD_3CN and DCM were further dried 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 (0) ($Ni(COD)_2$, Strem, 98+%), 4-methylbenzenethiol (1,4-(HS)Me(C6H4), Aldrich, 98%), and diphenylchlorophosphine (PPh_2Cl, Strem, minimum 95%). Tetrafluoroethylene was 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).[6]

Compound $[P[O(o\text{-tol})_3]_2]Ni(CF_2)_4$ was made by oxidative addition of tetrafluoroethylene to $Ni[P[O(o\text{-tol})]_3]_4$ using slightly modified literature procedures.[5c] $(PPh_3)_2Ni(CF_2)_4$ and $(PPh_2Me)_2Ni(CF_2)_4$ complexes were prepared from $Ni(COD)_2$ following reported methods.[7d,7i] ^1H, ^{19}F, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectra were recorded on a 300 MHz Bruker Avance instrument at room-temperature (21-23°C). ^1H 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; $CDCl_3$: 7.26 ppm; CD_2Cl_2: 5.32 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). ^1H NMR data for BTB: (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); (300 MHz, CD_3CN) δ 7.76-7.84 (m, 1H, Ar-H), 7.95-8.04 (m, 3H, Ar-H). $^{31}P\{^1H\}$ NMR data were referenced to external H_3PO_4 (85 % aqueous solution), set to 0.0 ppm. UV-vis spectra were recorded on a Cary 100 instrument, using sealable quartz cuvettes (1.0 cm pathlength). Electrospray ionization mass spectral data were collected using an Applied Biosystem API2000 triple-quadrupole mass spectrometer. Elemental analyses were performed by Laboratoire d'Analyse Élémentaire de l'Université de Montréal.

$(Pyr)_2Ni(C_4F_8)$ (4c). $[P[O(o\text{-tol})_3]]_2Ni(CF_2)_4$ (1.0 g, 0.00104 mol) was placed in a 100 mL round bottom Schlenk flask and dissolved in a minimal amount of pyridine (~ 10 mL). Left to stir at room temperature for ~ 16 hrs. The reaction mixture was concentrated *in vacuo* until ~ 1 mL of solution was remaining. Hexanes was added (~15 mL), precipitating out a light yellow solid. The flask was placed in a -35 °C freezer for 16 hours. The product was filtered cold and washed with pre-cooled hexanes (-35 °C, 2 x 3 mL), and dried in vacuo, affording a light beige powder. Yield: 338 mg, 0.81 mmol, 78 % based on $[P[O(o\text{-tol})_3]]_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. X-ray quality crystals were grown from a saturated solution of **4c** in toluene/hexanes/diethyl ether. ^1H NMR (300 MHz, C_6D_6) δ 6.27 (br t, 4H, H_{meta}), 6.50 (br t, 2H, H_{para}), 7.16 (solvent), 8.29 (br d, 4H, H_{ortho}). ^{19}F NMR (282 MHz, C_6D_6) δ -63.5 (s, BTB), -111.3 (s, $4F_\alpha$), -139.3 (s, $4F_\beta$). Anal. Calc. for $C_{14}H_{10}F_8NiN_2$: C, 40.33, H, 2.42, N, 6.72. Found: C, 40.59, H, 2.43, N, 6.64. See Figures S1-S3 for the ORTEP representation, ^1H, and ^{19}F spectra.

$(PPh_3)(OTf)Ni[CF(PPh_3)(CF_2)_3]$ (5a): $(PPh_3)_2Ni(CF_2)_4$ (100 mg, 0.13 mmol, 1 eq.) was dissolved in ca. 10 mL of C_6H_6 in a 50 mL Schlenk ampoule. Me_3SiOTf (25.5 µL, 0.14 mmol, 1.1 eq.) was added via 25 µL syringe. Heated to 40 °C and left to stir for 3 days. Colour change from clear dark yellow to a cloudy bright orange throughout the reaction. The reaction mixture was filtered through a 15 mL medium pore fritted funnel, collecting a light orange solid. The product was washed with cold hexanes (-35 °C, 3 x

3mL). The isolated material was dried in vacuo, affording a light orange powder. Yield: 94 mg, 0.10 mmol, 80 % based on $(PPh_3)_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. UV-vis (0.3 mM in dichloromethane): $\lambda_{max}(\varepsilon)$ = 451 nm (1095). By NMR in CD_2Cl_2, there is ~ 8 % of a minor shifted functionalized metallacycle, which we propose to be the other regioisomer (C_{α}−P *trans* to OTf). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 5.32 (solvent), 7.30-7.53 (m, 21H, Ar-H), 7.75 (d m, 3H, Ar-H), 8.02 (d d, $^{3}J_{HP}$ = 13 Hz, $^{3}J_{HH}$ = 8 Hz, 6H, Ar-H). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -63.5 (s, BTB), -79.1, (s, 3F, OTf), -94.2 (d, $^{2}J_{FF}$ = 239 Hz, 1F_{α}), -96.2 (d d m, $^{2}J_{FF}$ = 239 Hz, $^{3}J_{FP}$ = 65 Hz, 1F_{α}), -102.8 (br d, $^{2}J_{FF}$ = 265 Hz, 1F_{β}), -124.3 (d, $^{2}J_{FF}$ = 265 Hz, 1F_{β}), -128.6 (d m, $^{2}J_{FF}$ = 243 Hz, 1F_{β}), -129.8 (d m, $^{2}J_{FF}$ = 243 Hz, 1F_{β}), -206.9 (d m, $^{2}J_{FP}$ = 74 Hz, 1F_{α}). ^{31}P{^{1}H} (121 MHz, CD_2Cl_2) δ 15.6 (d m, $^{3}J_{PF}$ = 65 Hz, Ni-P), 19.1 (d d d, $^{2}J_{PF}$ = 74 Hz, $^{3}J_{PF}$ = 34 Hz, C_{α}-P). Repeated elemental analysis resulted in low % Carbon for **5a**. Anal. Calc. for $C_{41}H_{30}F_{10}NiO_3P_2S$: C, 53.92, H, 3.31, S, 3.51. Found: C, 50.44, H, 3.20, S, 3.84. See Figures S4-S6 for ^{1}H, ^{19}F and ^{31}P{^{1}H} spectra.

{$(PPh_3)(NCCH_3)Ni[CF(PPh_3)(CF_2)_3]$}$^{+}(OTf)^{-}$ (5a·CH_3CN): $(PPh_3)(OTf)Ni[CF(PPh_3)(CF_2)_3]$ **(5a)** was dissolved in deuterated acetonitrile. ^{1}H NMR (300 MHz, CD_3CN) δ 1.94 (solvent), 7.36-7.50 (m, 15 H, Ar-H), 7.70-7.79 (m, 6H, Ar-H), 7.87 (m, 3H, Ar-H), 8.22 (d d, $^{3}J_{HP}$ = 13 Hz, $^{3}J_{HH}$ = 8 Hz, 6H, Ar-H). ^{19}F NMR (282 MHz, CD_3CN) δ -63.5 (s, BTB), -79.4 (s, 3F, OTf), -97.9 (br d, $^{2}J_{FF}$ = 254 Hz, 1F_{α}), -107.4 (br d, $^{2}J_{FF}$ = 254 Hz, 1F_{α}), -110.7 (d m, $^{2}J_{FF}$ = 269 Hz, 1F_{β}), -126.1 (d t t, $^{2}J_{FF}$ = 269 Hz, $^{3}J_{FF}$ = 16 Hz, $^{3}J_{FF}$ = 2 Hz, 1F_{β}), -130.8 (d m, $^{2}J_{FF}$ = 247 Hz, 1F_{β}), -132.8 (d m, $^{2}J_{FF}$ = 247 Hz, 1F_{β}), -203.1 (d d m, $^{2}J_{FP}$ = 63 Hz, $^{3}J_{FF}$ = 29 Hz, 1F_{α}) . ^{31}P{^{1}H} (121 MHz, CD_3CN) δ 4.7 (v br s, 1P, Ni-P), 18.5 (d d d, $^{2}J_{PF}$ = 63 Hz, $^{3}J_{PF}$ = 24 Hz, $^{3}J_{PF}$ = 12 Hz, 1P, C_{α}-P). High-resolution Electrospray Ionisation; mass calculated for $C_{40}H_{30}NiF_7P_2$ (M^{+} - CH_3CN) 763.1064, found 763.1003. MS [ESI (positive mode), solvent: CH_3CN] *m/z* calcd for $C_{40}H_{30}F_7NiP_2$ (M^{+} - CH_3CN) 763.1, *m/z* found (% intensity) 763.3 (56 %); *m/z* calcd for $C_{26}H_{21}F_7N_2NiP$ (M^{+} - PPh_3 + CH_3CN) 583.1, *m/z* found 583.2 (16 %); *m/z* calcd for $C_{24}H_{18}F_7NNiP$ (M^{+} - PPh_3) 542.0, *m/z* found 542.2 (51 %); *m/z* calcd for $C_{22}H_{15}F_7NiP$ (M^{+} - CH_3CN - PPh_3) 501.0, *m/z* found 501.2 (50 %); *m/z* calcd for $C_{22}H_{15}F_5P$ ($C_4F_5PPh_3$) 405.1, *m/z* found 405.2 (100%).

$(PPh_2Me)(OTf)Ni[CF(PPh_2Me)(CF_2)_3]$ (5b): $(PPh_2Me)_2Ni(CF_2)_4$ (100 mg, 0.15 mmol, 1 eq.) was dissolved in ca. 10 mL of DCM in a 100 mL Schlenk ampoule. Me_3SiOTf (30.2 µL, 0.17 mmol, 1.1 eq.) was added via 100 µL syringe. Heated to 40 °C and left to stir for 4 days. Colour change from clear yellow to a darker clear orange throughout the reaction. The reaction mixture was transferred to a 50 mL RB Schlenk flask, solvent volume was reduced in vacuo to ca. 2 mL and hexanes was added, precipitating out a dark yellow solid. The flask was placed in a -35 °C for 16 hours. The product was filtered cold and washed with cold hexanes (-35 °C, 3 x 3mL). The isolated material was dried in vacuo, affording a bright yellow powder. Yield: 86 mg, 0.11 mmol, 73 % based on $(PPh_2Me)_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. X-ray quality crystals were grown by slow diffusion of hexanes into a supersaturated solution of **5b** in dichloroethane. UV-vis (0.7 mM in dichloromethane): $\lambda_{max}(\varepsilon)$ = 419 nm (911). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (d, $^2J_{HP}$ = 9 Hz, 3H, CH_3), 2.47 (d d, $^2J_{HP}$ = 13 Hz, $^3J_{HH}$ = 3 Hz, 3H, CH_3), 7.26 (solvent), 7.27-7.55 (ov m, 14H, Ar-H), 7.64 (m, 1H, Ar-H), 8.00 (m, 2H, Ar-H), 8.10 (m, 1H, Ar-H), 8.50 (d d, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, 2H, Ar-H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.5 (s, BTB), -77.9 (d, $^6J_{FF}$ = 9 Hz, 3F, OTf), -93.5 (d m, $^2J_{FF}$ = 258 Hz, 1F$_\alpha$), -100.8 (d d t, $^2J_{FF}$ = 258 Hz, $^3J_{FF}$ = 15 Hz, $^3J_{FP}$ = 67 Hz, 1F$_\alpha$), -114.0 (d m, $^2J_{FF}$ = 274 Hz, 1F$_\beta$), -130.0 (d d d, $^2J_{FF}$ = 274 Hz, 3J$_{FF}$ = 28 Hz, $^3J_{FF}$ = 15 Hz, 1F$_\beta$), -131.9 (app s, 2F$_\beta$), -207.1 (br d d m, $^2J_{FP}$ = 74 Hz, $^3J_{FF}$ = 31 Hz, 1F$_\alpha$). ^{31}P{^{1}H} (121 MHz, $CDCl_3$) δ 4.8 (d t, $^3J_{PF}$ = 67 Hz, 1P, Ni-P), 21.2 (d d, $^2J_{PF}$ = 74 Hz, $^3J_{PF}$ = 22 Hz, 1P, C$_\alpha$-P). See Figures S7-S9 for ^{1}H, ^{19}F and ^{31}P{^{1}H} spectra.

{(PPh$_2$Me)(NCCH$_3$)Ni[CF(PPh$_2$Me)(CF$_2$)$_3$]}$^+$(OTf)$^-$ (5b·CH$_3$CN): (PPh$_2$Me)(OTf)Ni[CF(PPh$_2$Me)(CF$_2$)$_3$] **(5b)** was dissolved in deuterated acetonitrile. ^{1}H NMR (300 MHz, CD_3CN) δ 1.94 (solvent), 2.03 (br d, $^2J_{HP}$ = 7 Hz, 3H, CH_3), 2.72 (d, $^2J_{HP}$ = 13 Hz, 3H, CH_3), 7.45-7.89 (m, 15 H, Ar-H), 7.93-8.04 (m, 3H, Ar-H), 8.10 (d d, $^2J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, 2H, Ar-H). ^{19}F NMR (282 MHz, CD_3CN) δ -63.5 (s, BTB), -79.3 (s, 3F, OTf), -96.6 (d m, $^2J_{FF}$ = 270 Hz, 1F$_\alpha$), -104.1 (d m, $^2J_{FF}$ = 270 Hz, 1F$_\alpha$), -112.2 (d m, $^2J_{FF}$ = 272 Hz, 1F$_\beta$), -128.3 (d t, $^2J_{FF}$ = 272 Hz, $^3J_{FF}$ = 15 Hz, 1F$_\beta$), -131.3 (ov d d, $^2J_{FF}$ = ~ 267 Hz, 2F$_\beta$), -207.5 (d d, $^2J_{FP}$ = 65 Hz, $^3J_{FF}$ = 29 Hz, 1F$_\alpha$) . ^{31}P{^{1}H} (121 MHz, CD_3CN) δ 12.2 (br s, 1P, Ni-P), 19.6 (d d d, $^2J_{PF}$ = 65 Hz, $^3J_{PF}$ = 30 Hz, $^3J_{PF}$ = 9 Hz, 1P, C$_\alpha$-P). High-resolution Electrospray Ionisation; mass calculated for $C_{32}H_{29}NNiP_2$ (M$^+$) 680.1017, found 680.0950. MS [ESI (positive mode), solvent: CH_3CN] *m/z* calcd for $C_{32}H_{29}F_7NNiP_2$ (M$^+$) 680.1, *m/z* found (% intensity) 680.3 (7 %); *m/z* calcd for $C_{30}H_{26}F_7NiP_2$ (M$^+$ - CH_3CN) 639.1, *m/z* found 639.3 (43 %); *m/z* calcd for $C_{19}H_{16}F_7NNiP$ (M$^+$ - PPh$_2$Me) 480.0, *m/z* found 480.2 (24 %); *m/z* calcd for $C_{17}H_{13}F_7NiP$ (M$^+$ - CH_3CN - PPh$_2$Me) 439.0, *m/z* found 439.1 (18 %). See Figure S26 for ESI-MS spectrum.

(Pyr)(OTf)Ni[CF(Pyr)(CF$_2$)$_3$] (5c): (Pyr)$_2$Ni(CF$_2$)$_4$ (117 mg, 0.28 mmol, 1 eq.) was dissolved in ca. 8 mL of DCE in a 50 mL Schlenk ampoule. Me$_3$SiOTf (66.1 μL, 0.37 mmol, 1.3 eq.) was added via 100 μL syringe. The reaction mixture was heated to 60 °C and left to stir for 24 hours. Colour change from clear beige to a cloudy yellow throughout the course of the reaction. The reaction mixture was transferred to a 50 mL RB Schlenk flask, solvent volume was reduced in vacuo to ca. 2 mL and hexanes was added, precipitating out a bright yellow solid. The flask was placed in a -35 °C for 16 hours. The product was filtered cold and washed with cold hexanes (-35 °C, 3 x 2 mL). The isolated material was dried in vacuo, affording a bright yellow powder. Yield: 130 mg, 0.24 mmol, 84 % based on (Pyr)$_2$Ni(CF$_2$)$_4$. The isolated material was stored at room temperature under nitrogen. X-ray quality crystals were grown by slow evaporation of dichloromethane. UV-vis (0.7 mM in dichloromethane): $\lambda_{max}(\varepsilon)$ = 398 nm (627). ^{19}F NMR

(282 MHz, CH_2Cl_2/C_6D_6 lock) δ -63.5 (s, BTB), - 79.8 (br s, 3F, OTf), -99.0 (d t, $^2J_{FF}$ = 253 Hz, $^3J_{FF}$ = 11 Hz, $1F_\alpha$), -113.9 (d d d, $^2J_{FF}$ = 253 Hz, $^3J_{FF}$ = 15 Hz, $^3J_{FF}$ = 6 Hz, $1F_\alpha$), -126.1 (d m, $^2J_{FF}$ = 254 Hz, $1F_\beta$), -130.1 (d m, $^2J_{FF}$ = 252 Hz, $1F_\beta$), -141.1 (d m, $^2J_{FF}$ = 252 Hz, $1F_\beta$), -144.4 (d t, $^2J_{FF}$ = 254 Hz, $^3J_{FF}$ = 13 Hz, $1F_\beta$), -153.0 (app t, $^3J_{FF}$ = ~ 14 Hz, $1F_\alpha$). Anal. Calc. for $C_{15}H_{10}F_{10}N_2NiO_3S$: C, 32.94, H, 1.84, N, 5.12, S, 5.86. Found: C, 32.69, H, 2.00, N, 5.01, S, 5.72.

{(Pyr)($NCCH_3$)Ni[CF(Pyr)(CF_2)$_3$]}$^+$(OTf)$^-$ (5c·CH_3CN): (Pyr)(OTf)Ni[CF(Pyr)(CF_2)$_3$] **(5c)** was dissolved in deuterated acetonitrile. ^{1}H NMR (300 MHz, CD_3CN) δ 1.94 (solvent), 7.49 (br t, $^3J_{HH}$ = 6 Hz, 2H), 7.91 (t, $^3J_{HH}$ = 7 Hz, 1H), 8.13 (t, $^3J_{HH}$ = 7 Hz, 2H), 8.60 (t, $^3J_{HH}$ = 8 Hz, 1H), 8.91 (br d, 2H), 9.59 (d, $^3J_{HH}$ = 6 Hz, 2H). ^{19}F NMR (282 MHz, CD_3CN) δ -63.5 (s, BTB), -79.3 (s, 3F, OTf), -103.5 (br d, $^2J_{FF}$ = ~ 263 Hz, $1F_\alpha$), -114.8 (br d, $^2J_{FF}$ = ~ 263 Hz, $1F_\alpha$), -126.8 (app d q, $^2J_{FF}$ = 256 Hz, $^3J_{FF}$ = 30 Hz ,$^3J_{FF}$ = 15 Hz, $1F_\beta$), -131.6 (d m, $^2J_{FF}$ = 253 Hz, $1F_\beta$), -140.8 (br d, $^2J_{FF}$ = 253 Hz, $1F_\beta$), -142.6 (d m, $^2J_{FP}$ = 256 Hz, $1F_\beta$), -150.7 (v br s, $1F_\alpha$). $^{13}C\{^1H\}$ (75 MHz, CD_3CN) δ 1.3 (solvent), 118.3 (solvent), 126.5 (s, 2C, pyr), 128.8 (d, J_{CF} = 2 Hz, 2C, pyr), 140.2 (s, 1C, pyr), 143.3 (d, J_{CF} = 9 Hz, 2C, pyr), 148.8 (s, 1C, pyr), 150.7 (s, 2C, pyr). See Figures S10-S11 for ^{1}H and ^{19}F spectra.). High-resolution Electrospray Ionisation; mass calculated for $C_{16}H_{13}NiF_7N_3$ (M^+) 438.0351, found 438.0365. MS [ESI (positive mode), solvent: CH_3CN] *m/z* calcd for $C_{16}H_{13}F_7N_3Ni$ (M^+) 438.0, *m/z* found (% intensity) 438.1 (76 %); *m/z* calcd for $C_{13}H_{11}F_7N_3Ni$ (M^+ - Pyr + CH_3CN) 400.0, *m/z* found 400.1 (100 %); *m/z* calcd for $C_{11}H_8F_7N_2Ni$ (M^+ - Pyr) 359.0, *m/z* found 359.0 (23 %). See Figure S27 for ESI-MS spectrum.

[1,2,4-(S),(Ph_2P),Me(C_6H_3)]Ni[CF(PPh_3)(CF_2)$_3$] (6a):

NMR scale 6a: (PPh_3)$_2$Ni(CF_2)$_4$ (**4a**) (20 mg, 0.03 mmol) was dissolved in a 1:1 mixture of C_6D_6/C_6H_6 (total volume ~ 2 mL). To the solution was added a solution of [1,2,4-(HS),(Ph_2P),Me(C_6H_3)] (dissolved in ~ 2 mL C_6H_6). Left to stir at RT for 3 hours. A ^{19}F NMR yield (by integration of product F peaks relative to BTB) indicated an 89 % yield of **6a**.

Isolation of 6a: (PPh_3)$_2$Ni(CF_2)$_4$ (**4a**) (224 mg, 0.29 mmol) was placed in a 100 mL round bottom Schlenk flask and dissolved in chlorobenzene (~ 20 mL). 1,2,4-(HS),(Ph_2P),Me(C_6H_3)] (88 mg, 0.29 mmol) was dissolved in ~ 10 mL of chlorobenzene and added to the (PPh_3)$_2$Ni(CF_2)$_4$/chlorobenzene mixture. A gradual colour change (over ~ 30 min.) from clear yellow to clear bright orange occurred. The reaction mixture was left to stir at room temperature for 14 hours. The clear orange reaction mixture was concentrated in vacuo until ~ 5 mL solution remaining in flask (cloudy orange). Around 10 mL of hexanes was then added to the round bottom flask, precipitating a light orange powder. The flask was placed in a -35 °C freezer for 16 hours. The product was filtered cold (15 mL medium pore fritted funnel), and washed with 2 x 2 mL pre-cooled acetonitrile/ 2 x 2 mL pre-cooled hexanes, and dried in vacuo, affording a light orange powder. Yield: 140 mg, 0.17 mmol, 61 % based on $(PPh_3)_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. X-ray quality crystals were grown by slow evaporation of a saturated solution of **6a** in benzene. UV-vis (0.7 mM in dichloromethane): $\lambda_{max}(\varepsilon)$ = 377 nm (2814). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H, CH_3), 6.60 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar-H), 6.74 (m, 2H, Ar-H), 7.26 (solvent), 7.29-7.67 (m, 17H, Ar-H), 7.90 (d d d, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz, 2H, Ar-H), 8.13 (d d, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, 6H, Ar-H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.5 (s, BTB), -94.7 (d m, $^2J_{FF}$ = 282 Hz, $1F_\alpha$), -108.3 (d d d d, $^2J_{FF}$ = 282 Hz, $^3J_{FP}$ = 57 Hz, $^3J_{FF}$ = 22 Hz, $1F_\alpha$), -109.3 (d m, $^2J_{FF}$ = 267 Hz, $1F_\beta$), -126.1 (d m, $^2J_{FF}$ = 267 Hz, $1F_\beta$), -129.0 (d m, $^2J_{FF}$ = 245 Hz, $1F_\beta$), -136.3 (d m, $^2J_{FF}$ = 245 Hz, $1F_\beta$), -203.1 (d d d, $^2J_{FP}$ = 65 Hz, $^3J_{FF}$ = 36 Hz, $1F_\alpha$).). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$) δ 17.3 (d m, $^2J_{PF}$ = 65 Hz, 1P, C_α-P), 54.3 (d m, $^3J_{PF}$ = 57 Hz, 1P, Ni-P). Repeated elemental analysis resulted in low % Carbon for **6a**. Anal. Calc. for $C_{41}H_{31}F_7NiP_2S$: C, 60.84, H, 3.86, S, 3.96. Found: C, 59.65, H, 3.90, S, 3.94. High-resolution Electrospray Ionisation; mass calculated for $C_{41}H_{32}SNiP_2F_7$ (M + H^+) 809.0942, found 809.0920. MS [ESI (positive mode), solvent: CH_3CN] *m/z* calcd for $C_{41}H_{31}SNiP_2F_7K$ (M + K^+) 847.1, *m/z* found (% intensity) 847.2 (32 %); *m/z* calcd for $C_{41}H_{31}SNiP_2F_6$ $(M – F)^+$ 789.1, *m/z* found 789.3 (34 %). See Figures S12-S14 for the ^{1}H, ^{19}F and $^{31}P\{^1H\}$ spectra.

[1,2,4-(S),(Ph$_2$P),Me(C$_6$H$_3$)]Ni[CF(PPh$_2$Me)(CF$_2$)$_3$] (6b):

NMR scale 6b: $(PPh_2Me)_2Ni(CF_2)_4$ (**4b**) (15 mg, 0.023 mmol) was dissolved in a minimum amount (~ 3 mL) of chlorobenzene. [1,2,4-(HS),(Ph$_2$P),Me(C$_6$H$_3$)] (8 mg, 0.025 mmol) was dissolved in ~ 4 mL of cholorobenzene and transferred to the vial containing the $(PPh_2Me)_2Ni(CF_2)_4$/chlorobenzene mixture. Stirred at room temperature for 15 hours. Colour had changed from bright clear yellow to clear orange-yellow. A ^{19}F NMR yield (by integration of product F peaks relative to BTB) indicated 92 % yield of **6b**.

Isolation of 6b: $(PPh_2Me)_2Ni(CF_2)_4$ (**4b**) (250 mg, 0.38 mmol) was placed in a 100 mL round bottom Schlenk flask and dissolved in chlorobenzene (~ 20 mL). 1,2,4-(HS),(Ph$_2$P),Me(C$_6$H$_3$)] (123 mg, 0.40 mmol) was dissolved in ~ 15 mL of chlorobenzene and added to the $(PPh_2Me)_2Ni(CF_2)_4$/chlorobenzene mixture. A gradual colour change (over ~ 30 min.) from clear yellow to cloudy bright yellow occurred. The reaction mixture was left to stir at room temperature for ~ 14 hours. The clear deep orange reaction mixture was concentrated and dried in vacuo for 2 hours, leaving a yellow solid. The product was dissolved/suspended in ~ 5 mL of acetonitrile. The flask was placed in a -35 °C freezer for 16 hours. The product was filtered cold (15 mL medium pore fritted funnel), and washed with 3 x 3 mL pre-cooled hexanes, and dried in vacuo, affording a dark yellow powder. Yield: 165 mg, 0.22 mmol, 58 % based on $(PPh_2Me)_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. X-ray quality crystals were grown by gradual cooling of a supersaturated solution of **6b** in dichloromethane. UV-vis (0.7 mM in chloromethane): $\lambda_{max}(\varepsilon)$ = 374 nm (1332). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H, CH_3), 2.78 (d d, $^3J_{HP}$ = 14 Hz, $^3J_{HH}$ = 2 Hz, 3H, CH_3), 6.64 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar-H), 6.84 (d m, $^3J_{HH}$ = 8 Hz, 1H, Ar-H), 7.15 (d d, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 3 Hz, 1H, Ar-H), 7.25-7.68 (ov m, 16H, Ar-H/solvent), 7.89 (d d, 2H, Ar-H), 8.18 (d d, $^3J_{HP}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, 2H, Ar-H). ^{19}F NMR (282 MHz, CD_3CN) δ -63.5 (s, BTB), -94.1 (d m, $^2J_{FF}$ = 283 Hz, $1F_\alpha$), -107.5 (d d d d, $^2J_{FF}$ = 283 Hz, $^3J_{FP}$ = 55 Hz, $^3J_{FF}$ = 21 Hz, $1F_\alpha$), -111.3 (d m, $^2J_{FF}$ = 272 Hz, $1F_\beta$), -128.1 (d m, $^2J_{FF}$ = 272 Hz, $1F_\beta$), -130.0 (d m, $^2J_{FF}$ = 245 Hz, $1F_\beta$), -135.9 (d m, $^2J_{FF}$ = 245 Hz, $1F_\beta$), -202.0 (d d d, $^2J_{FP}$ = 75 Hz, $^3J_{FF}$ = 36 Hz, $^3J_{FF}$ = 12 Hz, $1F_\alpha$). $^{31}P\{^1H\}$ (121 MHz, CD_3CN) δ 23.0 (d d d, $^2J_{PF}$ = 75 Hz, $^3J_{PF}$ = 28 Hz, $^3J_{PF}$ = 10 Hz, 1P, C_α-P), 53.5 (d m, $^3J_{PF}$ = 55 Hz, 1P, Ni-P). Anal. Calc. for $C_{36}H_{29}F_7NiP_2S$: C, 57.86, H, 3.91, S, 4.29. Found: C, 57.84, H, 3.98, S, 4.00. See Figures S15-S17 for the ^1H, ^{19}F and $^{31}P\{^1H\}$ spectra.

[1,2,4-(S^-),(Ph_2P),Me(C_6H_3)]Ni(CF_2)$_4$(Na)(18-Crown-6) (7). [1,2,4-(HS),(Ph_2P),Me(C_6H_3)] (130 mg, 0.42 mmol) was placed in a 100 mL round bottom flask and dissolved in THF (~ 10 mL). NaO^tBu (40 mg, 0.42 mmol) was added to the [1,2,4(HS),(Ph_2P),Me(C_6H_3)]/THF mixture. An immediate colour change from clear to a very pale yellow occurred. After ~ 15 minutes of stirring at room temperature, [$(PPh_3)_2Ni(CF_2)_4$] (330 mg, 0.42 mmol) was added to the mixture. An immediate colour change to clear bright yellow was observed. Immediately after, one equivalent of 18-Crown-6 was added to the flask (111 mg, 0.42 mmol). The reaction mixture was left to stir at room temperature for ~ 18 hours. The yellow-green reaction mixture was concentrated in vacuo until ~ 10 mL solution remaining in flask (precipitate already beginning to form). Around 10 mL of hexanes was then added to the round bottom flask, precipitating a bright yellow powder. The flask was placed in a -35 °C freezer for 4 hours. The product was filtered cold (30 mL medium pore fritted funnel), and washed with pre-cooled hexanes (-35 °C , 3 x 3 mL), and dried in vacuo, affording a bright yellow powder. Yield: 319 mg, 0.37 mmol, 89% based on $(PPh_3)_2Ni(CF_2)_4$. The isolated material was stored at room temperature under nitrogen. UV-vis (0.7 mM in dichloromethane): $\lambda_{max}(\varepsilon)$ = 386 nm (1176) (shoulder on off-scale signals in the UV range). ^1H NMR (300 MHz, CD_3CN) δ 1.94 (solvent), 2.08 (s, 3H, Me), 3.57 (s, 24H, 18-Crown-6), 6.74 (br d, J_{HP} = 7 Hz, 1H, Ar-H), 6.90 (br d, J_{HH} = 8 Hz, 1H, Ar-H), 7.22 (br dd, J_{HH} = 8 Hz, J_{HP} = 3 Hz, 1H, Ar-H), 7.37-7.52 (m, 6H, Ar-H), 7.64-7.74 (m, 4H, Ar-H). ^{19}F NMR (282 MHz, CD_3CN) δ –63.5 (s, BTB), -100.0 (d, $^3J_{FP}$ = 27 Hz, 2F), -107.3 (d, $^3J_{FP}$ = 25 Hz, 2F), -138.6 (m, 4F). $^{31}P\{^1H\}$ (121 MHz, CD_3CN) δ 48.7 (m, J_{PF} = 27 Hz, 25 Hz, 1P). Anal. Calc. for $C_{35}H_{40}F_8NaNiO_6PS$: C, 49.26, H, 4.72, S, 3.76. Found: C, 49.27, H, 4.78, S, 3.91. See Figures S18-S20 for the ^1H, ^{19}F, and $^{31}P\{^1H\}$ spectra.

NMR scale reaction of 7 with [$HPPh_3$](Br): [1,2,4-(S),(Ph_2P),Me(C_6H_3)]Ni(CF_2)$_4$(Na)(18-Crown-6) (25 mg, 0.029 mmol) **(7)** dissolved in ~ 1 mL dichloromethane and transferred to a vial containing [$HPPh_3$](Br) (10 mg, 0.029 mmol) dissolved /suspended in ~ 1 mL dichloromethane. Initial colour of reaction mixture was a clear bright yellow. Stirred at RT for 4 hours. Colour had changed to clear orange-yellow. A ^{19}F NMR yield (by integration of product F peaks relative to BTB) indicated 91 % yield of **6a** (^{19}F NMR indicates ~ 8 % of what we propose to be the other regioisomer, with C_α−P *trans* to S).

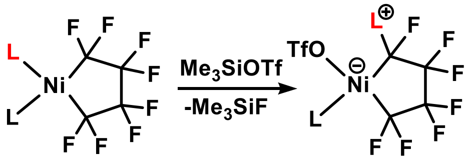
NMR scale reaction of 7 with [HPPh$_2$Me](Br): [1,2,4-(S),(Ph$_2$P),Me(C$_6$H$_3$)]Ni(CF$_2$)$_4$(Na)(18-Crown-6) (27 mg, 0.032 mmol) **(7)** was dissolved in ~ 1 mL dichloromethane and transferred to a vial containing [HPPh$_2$Me](Br) (9 mg, 0.032 mmol) dissolved /suspended in ~ 1 mL dichloromethane. Initial colour of reaction mixture was a clear yellow. Stirred at RT for 16 hours. Colour had changed to clear orange-yellow. A ^{19}F NMR yield (by integration of product F peaks relative to BTB) indicated 78 % yield of **6b** (^{19}F NMR indicates ~ 15 % of what we propose to be the other regioisomer, with C_α−P *trans* to S).

Reaction of 4c with [P,SH]: (Pyr)$_2$Ni(CF$_2$)$_4$ (80 mg, 0.19 mmol) **(4c)** was dissolved in ~ 6 mL chlorobenzene and transferred to a 50 mL RB Schlenk flask containing [1,2,4-(HS),(Ph$_2$P),Me(C$_6$H$_3$)] (118 mg, 0.38 mmol) dissolved in ~ 6 mL chlorobenzene. Immediate colour change to bright clear yellow followed by a gradual colour change over ~ 5 minutes to a deep clear red-orange. Stirred at RT for ~ 6 hours. A ^{19}F NMR yield (by integration of product F peaks relative to BTB, average of three separate experiments) indicated a 48 % yield of **8a** based on (Pyr)$_2$Ni(CF$_2$)$_4$ as well as the presence of **8b** by ^{31}P{^{1}H} NMR. **8a** was not isolated but was characterized by its ^{19}F and ^{31}P{^{1}H} spectra: ^{19}F NMR (282 MHz, C$_6$H$_5$Cl with C$_6$D$_6$ capillary) δ -63.5 (s, BTB), -94.3 (d m, $^2J_{FF}$ = 288 Hz, 1F$_\alpha$), - 107.6 (d d d, $^2J_{FF}$ = 288 Hz, $^3J_{FP}$ = 46 Hz, $^3J_{FF}$ = 19 Hz, 1F$_\alpha$), -124.4 (d m, $^2J_{FF}$ = 251 Hz, $^3J_{FF}$ = 18 Hz, 1F$_\beta$), -128.5 (d m, $^2J_{FF}$ = 250 Hz, 1F$_\beta$), -141.4 (d m, $^2J_{FF}$ = 251 Hz, 1F$_\beta$), -143.1 (ov m, 1F$_\beta$, 1F$_\alpha$). ^{31}P{^{1}H} (121 MHz, C$_6$H$_5$Cl with C$_6$D$_6$ capillary) δ 54.0 (d, $^3J_{PF}$ = 46 Hz, 1P, Ni-P). Cooling an acetonitrile solution resulted in precipitation of X-ray quality crystals of **8b**, isolated as green cubic crystals. ^{31}P{^{1}H} (121 MHz, C$_6$D$_6$) δ 52.9 (s, 2P). See Figure S21 for ORTEP representation of **8b**.

Results and Discussion

Consistent with previous results from our group and Burch *et al.*[8], C_α−F activation of **4a-c** occurs when an equimolar amount of external Lewis acid is added. This result is also congruous with precedent for the weakening of C_α−F versus C_β−F bonds in M−R^F (M = Rh, Ir, Pt, Fe, Ni) complexes.[13] The postulated short-lived electrophilic intermediate then undergoes a nucleophilic attack by one L, resulting in the zwitterionic functionalized metallacycles **5a-c**. Dissolving **5a-c** in CD$_3$CN results in displacement of the (OTf)$^-$ ligand with one molecule of acetonitrile, affording a cationic Ni centre with an outer sphere OTf anion.

Scheme 2



4a: L = PPh$_3$
4b: L = PPh$_2$Me
4c: L = pyridine

5a (80 %)
5b (73 %)
5c (84 %)

Notably, C$_\alpha$−N bond formation to give the pyridinium-functionalized nickel fluorometallacycle **5c** is the first example of N-donor migration to the C$_\alpha$ position. X-ray quality crystals of **5b** and **5c** were grown by slow diffusion of hexanes into a dichloroethane solution and slow evaporation from a dichloromethane solution respectively (Figure 1). No significant Ni−C$_\alpha$ elongation in comparison to Ni−C$_\alpha$ bonds of **4c** (See SI, Figure S1 for ORTEP representation) is observed upon substituting a fluoride with a pyridine group at C$_\alpha$. In contrast, a quite significant increase in Ni−C$_\alpha$ bond length in **5b** is observed for the C$_\alpha$−P functionalized carbon in comparison to perfluorinated C$_\alpha$ *trans* to OTf (1.994(5) Å and 1.864(6) Å respectively).

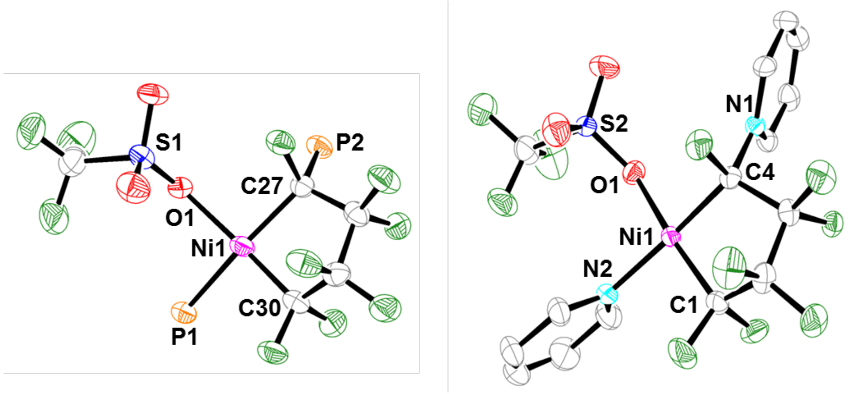
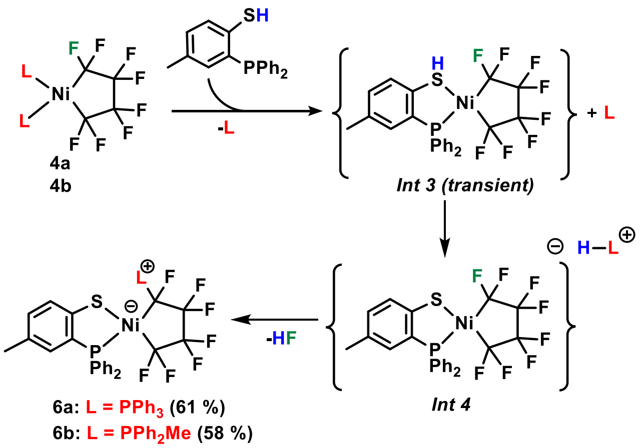


Figure 1. ORTEP representation of the molecular structures of complexes **5b** (left) and **5c** (right). Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms and phenyl/methyl groups of **P1** and **P2** (left structure) are omitted for clarity. Selected bond lengths (Å) and angles (deg): **5b :** Ni1−P1 2.2398(16), Ni1−O1 1.988(4), Ni1−C27 1.994(5), Ni1−C30 1.864(6), C27−P2 1.845(5); C30−Ni1−C27 86.4(2), C30−Ni1−P1 93.40(17), C27−Ni1−O1 93.44(19), P1−Ni1−O1 88.76(11). **5c :** Ni1−N2 1.9213(17), Ni1−O1 1.9733(15), Ni1−C1 1.879(2), Ni1−C4 1.921(2), C4−N1 1.499(3); C1−Ni1−C4 87.09(9), C1−Ni1−N2 91.35(9), C4−Ni1−O1 93.07(8), N2−Ni1−O1 89.87(7).

Upon substitution of (PR$_3$)$_2$Ni(CF$_2$)$_4$ metallacycles **4a** and **4b** with the thiol form **[P,SH]** of the bidentate ligand, an unexpected C$_\alpha$−F bond activation occurs, where a displaced free phosphine is selectively installed in the C$_\alpha$ position of the final product **6,** proceeding through HF elimination. Monitoring the reaction between **4a** and **[P,SH]** in C$_6$D$_6$ at room temperature using ^{19}F NMR shows immediate consumption of (PPh$_3$)$_2$Ni(CF$_2$)$_4$ and the presence of **6** as well as an intermediate with four distinct fluorine environments: two C$_\alpha$F$_2$ peaks at δ_F = -97.4 (d, J_{FP} = 27 Hz) and -102.2 (d, J_{FP} = 24 Hz), Scheme 3



and two $C_{\beta}F_2$ peaks at -137.9 and -138.2 (see SI, Figure S22). The $^{31}P\{^1H\}$ NMR spectrum reveals two phosphorus peaks assignable to complex **6** at δ_P = 54.0 (d, J_{PF} = 57 Hz, Ni−P) and 17.6 (dm, J_{PF} = 65 Hz, C_{α}−P). The phosphorus resonances associated with the intermediate include one apparent quintet at δ_P = 46.4 (1P), and a singlet at -7.8 (2P). After 3 hours, the ^{19}F and $^{31}P\{^1H\}$NMR spectra indicate complete consumption of the intermediate, with only seven unique fluorine peaks associated with **6** remaining. Carrying out the reaction between **[P,SH]** and **4a** in THF at -40 °C reveals the formation of the same intermediate mentioned above, however no conversion to product **6** at this temperature is observed. When the reaction between **[P,SH]** and **4b** is performed in THF at room temperature, product **6** is formed along with the observation of a distinct HF peak at δ_F = -195.7 ppm (J_{FH} = 453 Hz; see SI, Figure S23). The ^{19}F NMR data for the intermediate is consistent with an unsymmetrically substituted perfluorometallacycle.[10] We reasoned that the intermediate observable by NMR either resembles the thiol-coordinated ***Int 3*** proposed in Scheme 3, or a thiolate-coordinated intermediate (***Int 4***, Scheme 3). A variable temperature multinuclear NMR experiment between **[P,SH]** and **4b** in $CDCl_3$ supports a thiolate-coordinated anionic nickel complex as the intermediate (***Int 4***, Scheme 3) based on the following observations: a) Initially, the $^{31}P\{^1H\}$ NMR spectrum at room temperature shows one apparent quintet at δ_P = 51 and a broad singlet at δ_P = -16 ($\Delta\nu_{1/2}$ = 200 Hz); b) The broad singlet at -16 ppm splits into two separate singlets at δ_P = -4 and -27 respectively upon cooling to -40 °C, revealing a chemical exchange process between two phosphorus atoms;[14] c) Performing a gated decoupled ^{31}P NMR experiment at -40 °C shows splitting from a singlet to a doublet peak at -4 ppm with a large $^1J_{PH}$ coupling constant of 522 Hz, strongly suggestive of one bond P−H coupling; d) At -40 °C, the proton with a consistent $^1J_{HP}$ = 522 Hz coupling is assigned at δ_H = 10.0 ppm. The one bond P−H coupling constant in addition to the observation of a significantly downfield chemical shift for the associated proton are in agreement with an outer sphere phosphonium cation as shown in Scheme 3, ***Int 4*** (see SI, Figures S24-S25).[15] We propose that a transient nickel-coordinated thiol intermediate ***(Int 3)*** should initially form in order to generate a sufficiently acidic proton for deprotonation by free phosphine.[16] These results provide experimental support for the intermediates we originally presented in the proposed mechanism for the synthesis of **2** (see Scheme 1). It is likely that the acidity of the generated secondary phosphonium cation in conjunction with the basicity of the anionic nickel counter ion contribute to the instability of ***Int 4***, leading to C_α−F abstraction and formation of the stable Ni(II) product **6**. Following HF elimination, a transient electrophilic carbocationic or fluorocarbene intermediate presumably precedes nucleophilic attack by free phosphine, although this intermediate is not observable by NMR even at low temperatures. Interestingly, exclusive formation of the triphenylphosphine (**6a**) and methyldiphenylphosphine (**6b**) functionalized metallacycles is observed with no evidence of **[P,S$^-$]** phosphine migration to the C_α as observed previously upon C_α−F activation of **2** using an external Lewis acid (*vide supra*). Moreover, the reaction is regioselective for a C_α−F bond *trans* to the phosphine group of the **[P,S$^-$]** ligand. Complexes **6a** and **6b** were fully characterized using multinuclear NMR, UV-Vis spectroscopy, X-ray diffraction, and elemental analysis.

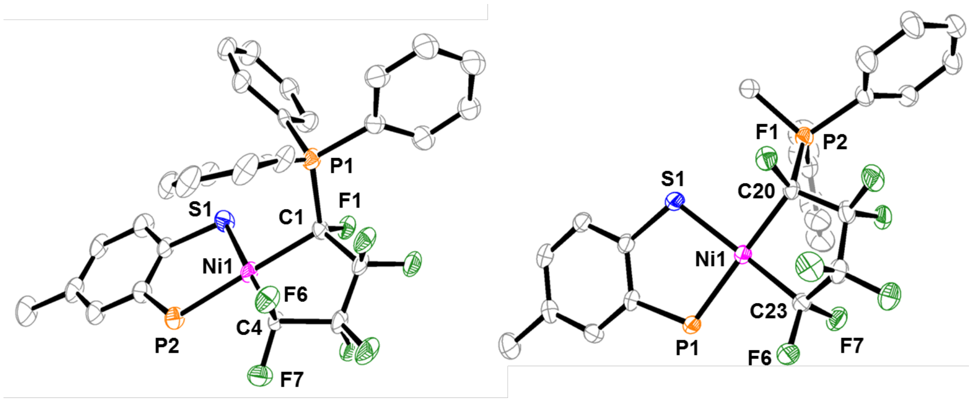
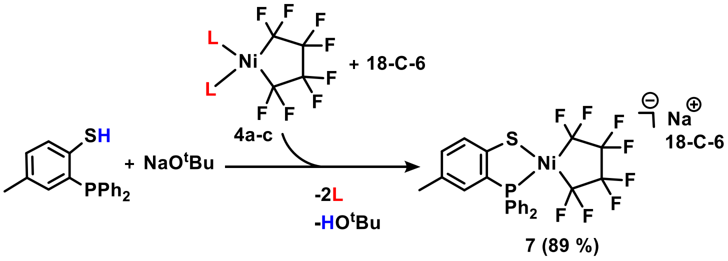


Figure 2. ORTEP representation of the molecular structures of complexes **6a** (left) and **6b** (right). Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms and phenyl rings of **P2** (left structure) and **P1** (right structure) are omitted for clarity. Selected bond lengths (Å) and angles (deg): **6a**: Ni1−C1 2.044(11), Ni1−C4 1.947(8), Ni1−P2 2.182(3), Ni1−S1 2.198(2), C1−P1 1.832(9), C1−F1 1.443(10), C4−F6 1.383(9), C4−F7 1.363(10); C4−Ni1−C1 86.7(4), C4−Ni1−P2 93.2(3), P2−Ni1−S1 88.04(11), C1−Ni1−S1 92.0(2). **6b**: Ni1−C20 2.016(3), Ni1−C23 1.926(3), Ni1−P1 2.1608(9), Ni1−S1 2.1929(10), C20−P2 1.849(4), C20−F1 1.422(3), C23−F6 1.401(4), C23−F7 1.392(4); C23−Ni1−C20 87.72(13), C23−Ni1−P1 90.97(10), P1−Ni1−S1 88.50(3), C20−Ni1−S1 92.72(10).

X-ray quality crystals of **6a** and **6b** were grown by slow evaporation of a benzene solution (Figure 2, left) and by gradual cooling of a saturated dichloromethane solution (Figure 2, right), respectively. Bond angles in the molecular structures of **6a** and **6b** confirm a distorted-square-planar geometry about the Ni(II) centres (359.9° and 359.9°, respectively). For the Ni−C−P fragment, both structures reveal a significant elongation of the metal-carbon bond upon replacement of one fluoride with a phosphine substituent. The Ni−C_α bond length associated with the phosphonium-functionalized C_α is significantly longer in comparison to the Ni−C_α bond of the perfluorinated C_α *trans* to sulfur (*e.g.,* 2.044(11) Å and 1.947(8) Å respectively for **6a**). A similar Ni−C_α bond elongation was noted above for the structure of **5b**, however was not observed in the previously reported phosphonium functionalized metallacycles presumably due to the minor *trans* influence of the weakly coordinating triflate group in **3** and the fluoride-bridging tetrafluoroborate group in $(PEt_3)(BF_4)Ni[CF(PEt_3)(CF_2)_3]$ reported by Burch and co-workers.[8,10] Treatment of $(PR_3)_2Ni(CF_2)_4$ (**4a, 4b**) with the anionic form **[P,S$^-$]** of the bidentate ligand (free ligand deprotonated *in situ* using an equimolar amount of sodium *tert*-butoxide) and one equivalent of 18-Crown-6 (18-C-6)[17] led to quantitative formation of an anionic phosphinothiolate-coordinated nickel perfluorometallacycle **7**, isolated as a bright yellow powder. To the best of our knowledge, there have been no previously reported stable anionic Ni(II) metallacycles.

Scheme 4



Single crystals of **7** were grown by gradual cooling of a saturated THF solution (see Figure 3). The sum of the angles about the Ni(II) centre in the molecular structure of **7** demonstrate distorted-square-planar geometry (360.1°). The nickel-thiolate bond length of the anionic complex **7** (2.1903(15) Å) is similar in comparison to the Ni−S bonds of the neutral complexes **6a** and **6b** (2.198(2) Å and 2.1929(10) Å respectively). The Ni−C_α bond length *trans* to phosphine is significantly shorter in relation to the Ni−C_α bonds of the phosphonium-functionalized metallacycles **6a** and **6b** (*e.g.,* 1.943(5) Å for **7** and 2.044(11) Å for **6a**). The sodium cation is bound by two THF molecules in addition to the six oxygen atoms of 18-Crown-6, making it an octacoordinate metal centre.[18] Owing to the imparted electron density from the thiolate group and the basic nature of **7**, we directed our attention to its reactivity with a range of different acids, aiming to develop new strategies for C−F bond functionalization. Of particular interest were Brønsted acids, as these have previously demonstrated reactivity with cobalt perfluorocyclobutanes[19], nickel hexafluoropropene complexes[20], and more recently with a three-coordinate perfluoronickelacyclopentane–NHC complex.[9] Indeed, reacting **7** with the phosphonium salts $[HPPh_3](Br)$ and $[HPPh_2Me](Br)$ affords zwitterionic products **6a** and **6b**, concomitantly eliminating NaBr and HF (Scheme 5). At room temperature, full conversion of **7** to **6a** and **6b** is observed within 4 hours (91%) and 16 hours (78%), respectively (yields

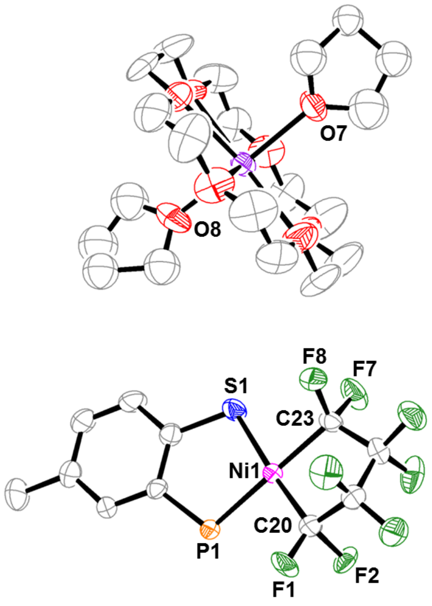
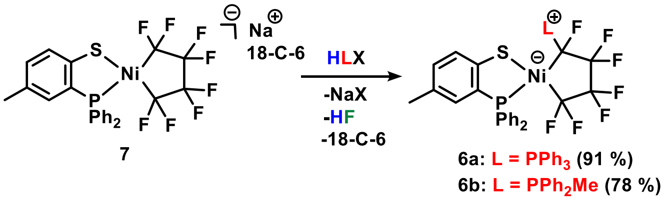


Figure 3. ORTEP representation of the molecular structure of [1,2,4-(S),(Ph$_2$P),Me(C$_6$H$_3$)]Ni(CF$_2$)$_4$[Na(18-Crown-6)(THF)$_2$] **(7·2 THF)**. Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms, two phenyl rings of **P1**, and two outer sphere THF molecules are omitted for clarity. One of two orientations of the disordered F atoms of C20 is depicted and one of two orientations for the two disordered Na$^+$ bound THF molecules. Selected bond lengths (Å) and angles (deg): Ni1−C23 1.943(5), Ni1−C20 1.925(6), Ni1−P1 2.1890(14), Ni1−S1 2.1903(15), C23−F7 1.381(6), C23−F8 1.379(6), C20−F1 1.238(16), C20−F2 1.543(18); C20−Ni1−C23 86.2(2), C20−Ni1−P1 96.75(18), P1−Ni1−S1 87.92(5), C23−Ni1−S1 89.24(16).

were determined using ^{19}F NMR spectroscopy and a quantitative amount of internal standard). Treating **7** with the more strongly Brønsted acidic trifluoroacetic acid resulted in a complex mixture of products by ^{19}F and ^{31}P{^{1}H} NMR spectroscopy.

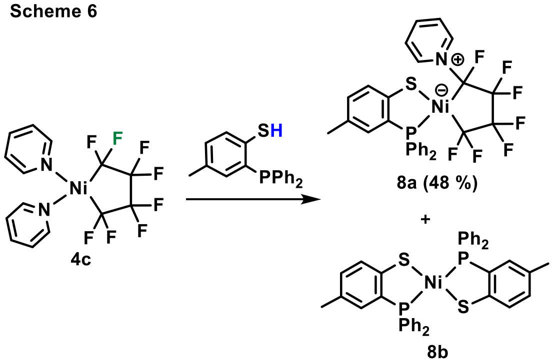
Scheme 5



In the presence of an equimolar amount of pyridinium bromide, complex **7** afforded a mixture of products with only a minor amount of C$_\alpha$−F activated pyridinium-functionalized product **8a** observed by multinuclear NMR. Unlike the (PR$_3$)$_2$Ni(CF$_2$)$_4$ perfluorometallacycles, treatment of (Pyr)$_2$Ni(CF$_2$)$_4$ **4c** with 2 equiv. of **[P,SH]** gave a mixture of Ni(II) pyridinium-functionalized metallacycle **8a** (48% yield by quantitative ^{19}F NMR), bis(chelate) [NiS$_2$P$_2$] product **8b** and other uncharacterized by-products (Scheme

6). Similar [NiS_2P_2] complexes related to **8b** have been reported previously.[12] The *trans* geometry of **8b** was determined by X-ray analysis (see Figure S21) and a characteristic singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta_P = 52.9$ ppm in C_6D_6.

Scheme 6



Conclusions

This work expands our knowledge of C−F bond activation in fluorometallacycles. Lewis acid activation of a C_α−F bond in $L_2Ni(CF_2)_4$ complexes to give zwitterionic functionalized fluoronickelacyclopentanes was extended beyond L = P donors to include the N-donor pyridine. In contrast, treatment of $(PR_3)_2Ni(CF_2)_4$ **4a-b** with an equimolar amount of protonated bidentate ligand **[P,SH]** led to a unique ligand-assisted/Brønsted acid-promoted C_α−F activation, affording phosphine-functionalized nickelacycles bearing the phosphinothiolate ligand **6a-b.** A variable temperature NMR study confirmed the presence of an intermediate consisting of an anionic nickel centre with an outer sphere phosphonium counter ion (***Int 4***) in the formation of **6a-b**. Finally, substituting the monodentate phosphines in **4a-b** with the deprotonated chelate **[P,S$^-$]** afforded an anionic phophinothiolate-cooordinated nickelacycle **7**. Treatment of **7** with weakly acidic tertiary phosphonium salts reformed **6a,b** without protonation of the thiolate sulphur. This study has revealed the versatile nature of the **[P,SH]** ligand, and corroborated previous studies that demonstrated the significant influence that ancillary ligand(s) can impart on perfluorometallacycle reactivity. Additional in-depth studies assessing the effects of the basic **[P,S$^-$]** ligand on the reactivity of perfluoronickelacyclopentanes and their functionalized derivatives is currently underway.

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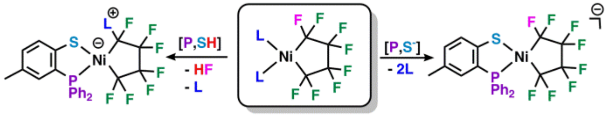

Bidentate phosphinothiol ligand induces C-F bond functionalization in perfluoronickelacycles.