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Regioselective Formation of Fluorinated Metallacycles from Fluoroalkenes and an Electron-Rich Ni(0) Difluorocarbene

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Supporting Information Placeholder

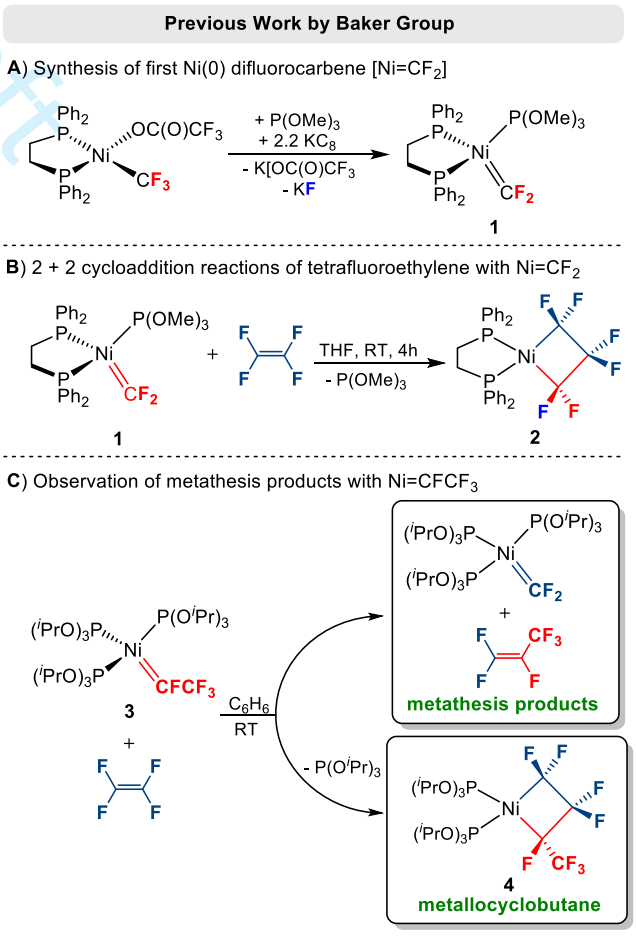
ABSTRACT: The reactivity of an electron-rich Ni-difluorocarbene complex, Ni=CF_2(dppe)[$P(OMe)_3$] (**1**), with a variety of fluorinated alkenes was investigated (dppe = 1,2-bis(diphenylphosphino)ethane). Reactions of **1** with perfluoro(methyl vinyl ether) and chlorotrifluoroethylene (CTFE) give regiospecific formation of metallacyclobutanes, in which the carbene C attacks the most electron-rich carbon of the fluoroalkene. Further reaction of the CTFE-derived metallacycle in the presence of tetrahydrofuran affords a single isomer of NiCl(σ-CF_2CF=CFH) (dppe), **8**, proposed to be formed by Ni-mediated C_α-Cl activation followed by hydride abstraction and loss of HF. While **1** also undergoes a cyclization reaction with trifluoroethylene (TrFE), instability of the presumed nickelacyclobutane affords the C3 fluoroalkene, F_2C=CH(CF_3), and subsequent formation of isomeric metallacyclopentanes from two additional TrFEs. Alternatively, reaction of **1** with hexafluoropropene forms an unexpected Ni-CF_3 σ-perfluoroallyl complex.

Introduction

Reactions involving metal alkylidenes and -carbenes are some of the most valuable and desired catalytic transformations.[1-4] While the reactivity of metal carbenes has been thoroughly studied and established, the use of metal fluorocarbenes in transition metal catalysis has only recently been investigated.[5-7] A similar statement can be made for fluorinated alkenes in comparison to their hydrocarbon counterparts.[8] The ability to activate and functionalize small fluoroalkenes could lead to development of catalytic pathways that would be invaluable towards the synthesis of a wide variety of products used in multiple industries.[9-14]

We are interested in the development of economical first-row transition metal fluorocarbene complexes for catalytic applications.[15-17] Our group has previously reported the first examples of isolable nickel difluorocarbene complexes that are formally d^{10} Ni(0).[18] The Ni-difluorocarbene complex Ni=CF_2(dppe)[$P(OMe)_3$] (**1**) is obtained by reduction of Ni(CF_3)[$OC(O)CF_3$](dppe) with KC_8 in the presence of stoichiometric $P(OMe)_3$ [**Scheme 1A;** dppe = 1,2-bis(diphenylphosphino)ethane]. Preliminary reactivity studies showed that **1** reacts with tetrafluoroethylene (TFE) efficiently at room temperature to furnish a perfluoro-metallacyclobutane product (**2**) (**Scheme 1B**). This reactivity improved upon our previous work with Co=CFR^F carbenes (R^F = F, CF_3), which required elevated temperatures and longer reaction

Scheme 1. Previous work: A) Synthesis of first Ni-fluorocarbene (**1**); B) Reactivity of **1** with TFE; C) Reaction of Ni=$CF(CF_3)$ with TFE to furnish metathesis products Ni=CF_2 and HFP.



times.[14] More recently, we demonstrated that treatment of the Ni fluorocarbene complex Ni=CF(CF_3)[P(O^iPr)$_3$]$_3$ (**3**) with TFE generated a mixture of both perfluorometallacyclobutane (**4**) and metathesis products (9:1 ratio; **Scheme 1C**).[19] Accompanying DFT calculations identified a tetrahedral transition state, allowing the metathesis reaction pathway to compete with formation of stable perfluorometallacyclobutanes previously shown to form via a diradical intermediate.[20] Furthermore, the metathesis products [Ni=CF_2 + hexafluoropropene (HFP)] were found to be surprisingly thermodynamically stable (-24.4 kcal/mol relative to Ni=CF(CF_3) + TFE).[19]

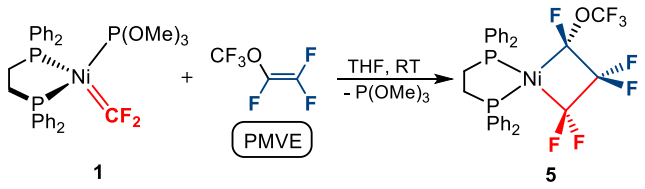
This first observation of stoichiometric fluoroalkene metathesis using base metal fluorocarbene precursors represents solid progress towards fluorinated olefin metathesis. However, the difficulty in preparing derivatives of Ni=CF(CF_3) complex **3** has so far limited further development of this system. Herein, we detail our investigation into electron-rich dppe Ni=CF_2 complex **1** as a potential metathesis precursor by expanding the currently known fluoroalkene scope to include varying degrees of fluorination and functional groups.

Results and Discussion

Before our investigation into the reactivity of **1** with an expanded fluoroalkene scope, we first optimized the synthesis of **1** to more consistently furnish an easily handled solid. Since reaction of **2** with either perfluoro(methyl vinyl ether) (PMVE) or trifluoroethylene (TrFE) gave metathesis products in more favorable ratios than TFE,[19] we began our investigations with these perfluorinated alkenes to see if **1** might demonstrate similar reactivity.

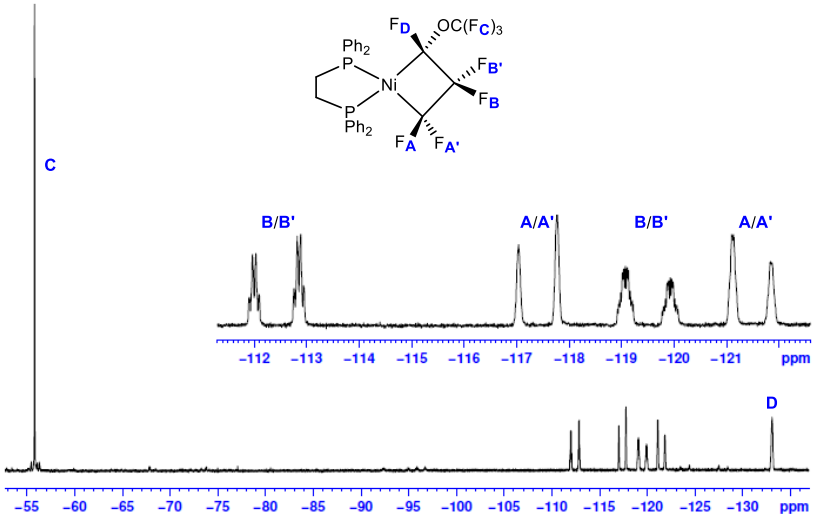
A solution of **1** in THF was charged with an excess of PMVE, giving a dark red solution. After 20 h at room temperature the reaction mixture became light-yellow. Analysis of the crude ^{19}F NMR spectrum showed complete consumption of **1** with regiospecific formation of nickelacyclobutane **5** (**Scheme 2**). The structure of **5** was confirmed from its unsymmetrical ^{19}F NMR spectrum featuring two inequivalent geminal CF_2 groups ($^2J_{FF}$ = 285 (C_α) and 280 Hz (C_β); **Figure 1**, inset). No evidence of the Ni=CF(OCF_3) carbene or fluoroalkene metathesis products was observed. Interestingly, the ^{31}P NMR spectrum consisted of a single broad resonance (Fig. S1 in Supplementary Material) due to an unusual fluxional process that we are currently investigating further.

Scheme 2. Reaction of **1** with PMVE to form **5**.



Since **2** was previously shown to also form metathesis products upon reaction with TrFE (albeit with multiple by-products),[19] this substrate was investigated next. After 2 h, the reaction mixture containing **1** and excess TrFE changed colour from dark red to orange. The crude ^{19}F NMR spectrum displayed unreacted **1** and several small signals. After 19 h, multiplet resonances at -58.8, -73.5, and -78.0 ppm were observed and assigned to the fluoroalkene F_2C=CH(CF_3). After 48 h, the colour of the reaction mixture was yellow and new NMR resonances had appeared. Finally, after 5 d the ^{19}F NMR spectrum displayed new sets of resonances corresponding to the formation of three new products. Multiplet resonances at -87.5, -98.9, and -213.0 ppm in a 1:1:1 ratio, are assigned to the $C_\alpha F_2$ ($^3J_{FF}$ = 270 Hz) and C_βFH ($^2J_{FH}$ = 55 Hz) groups of C2 symmetrical *trans* head-to-head nickelacyclopentane isomer **6-*t*-hh** (**Scheme 3**), as corroborated by a 2D-^{19}F-COSY NMR experiment (Fig. S5). The other resonances are assigned to *cis*- and *trans*-head-to-tail nickelacyclopentanes, **6*c,t*-ht**; analogues of which (containing 2 $PMePh_2$ ligands) have been characterized previously by our group.[16] The observed regioselectivity

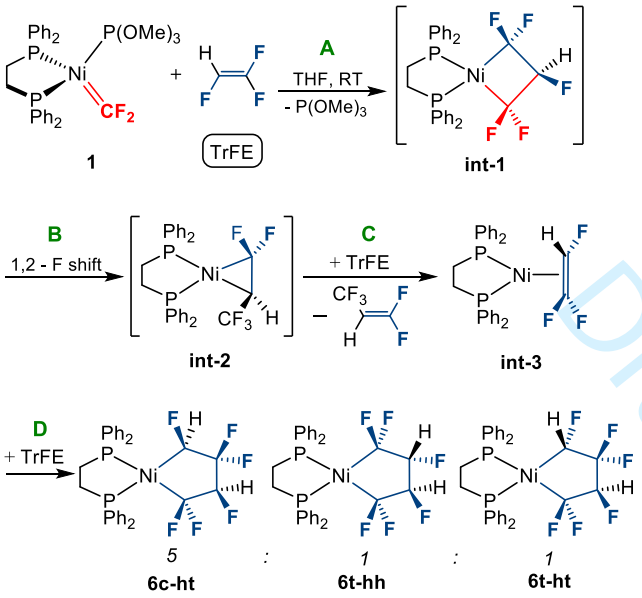
Figure 1. ^{19}F NMR spectrum of **5** in THF.



(***c*-ht**:***t*-ht**:***t*-hh** = 5:1:1) can be compared to that observed for the $PMePh_2$ analog (ca. 2.5:1:1).[16]

A proposed reaction pathway for the formation of this complex product mixture is shown in **Scheme 3**. In step A, reaction of **1** with TrFE proceeds regiospecifically through unobserved intermediate metallacyclobutane (**int-1**) that subsequently undergoes a 1,2-fluoride shift (step B) to form unobserved pentafluoropropene complex **int-2**. Similar reactivity, driven by formation of the stable CF_3 group, was observed in the reaction of **2** with TrFE.[19] In step C a second equivalent of TrFE rapidly liberates the observed pentafluoropropene, forming unobserved Ni-TrFE complex **int-3**. Finally, in Step D a third equiv of TrFE coordinates to Ni and undergoes coupling to furnish the three isomers of **6**.

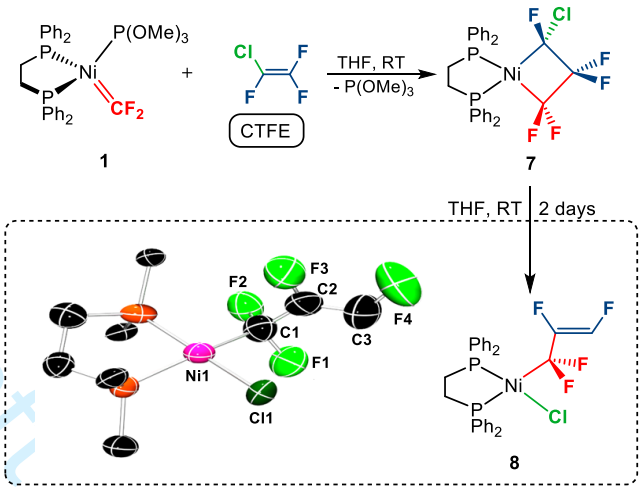
Scheme 3. Proposed reaction pathway for **1** with TrFE.



As reactions of **1** with both PMVE and TrFE did not yield any metathesis products, we continued to investigate different fluoroalkenes to further probe its reactivity. Chlorotrifluoroethylene (CTFE) is another readily available fluoroalkene for which the effects of heavier halogen substitution on metallacyclobutane formation and reactivity can be probed. A solution of **1** was charged with an excess of CTFE giving a dark red solution, and after 14 h at room temperature a colour change to light orange was observed. The ^{19}F NMR spectrum was consistent with regioselective formation of the expected metallacyclobutane **7** (**Scheme 4**). As for **5**, a single ^{31}P NMR resonance was observed, due to a fluxional process. To the best of our knowledge, this is the first report of a fluorometallacycle with a Cl substituent on C_α.

Further observation of the reaction mixture two days later showed conversion of **7** to a new product (**8**), with ^{19}F NMR resonances at -82.4, -145.5, and -174.1 ppm in a 2:1:1 ratio which can be assigned to a Ni σ-tetrafluoroallyl complex. The CF_2 resonance at -82.4 ppm is an apparent triplet of doublets ($^3J_{FP}$ = ca. 36 and $^3J_{FF}$ = 21 Hz) from coupling to the inequivalent Ps of the ancillary dppe ligand and β-fluorine. The signal at -145.5 ppm is an authentic triplet of doublets ($^3J_{FF}$ = 21 and $^3J_{FF}$ = 14 Hz), resulting from coupling to the two α-fluorines and the *cis* γ-fluorine. Finally, the γ-fluorine resonance at -174.1 ppm is a doublet of doublets ($^3J_{FH}$ = 75 and $^3J_{FF}$ = 14 Hz), from coupling to the adjacent proton and the *cis* β-fluorine. Surprisingly, replacement of a γ-fluorine by hydrogen was observed, constituting an unusual mechanistic step in the formation of **8**. The reaction was scaled up to isolate **8** and although the solid-state molecular structure obtained by single crystal X-ray diffraction was of poor quality, it confirmed that derived from the solution NMR (**Scheme 4**).

Scheme 4. Reaction of **1** with CTFE to form **7** and resultant conversion to **8**. The solid-state molecular structure of **8** has phenyls and hydrogens omitted for clarity.

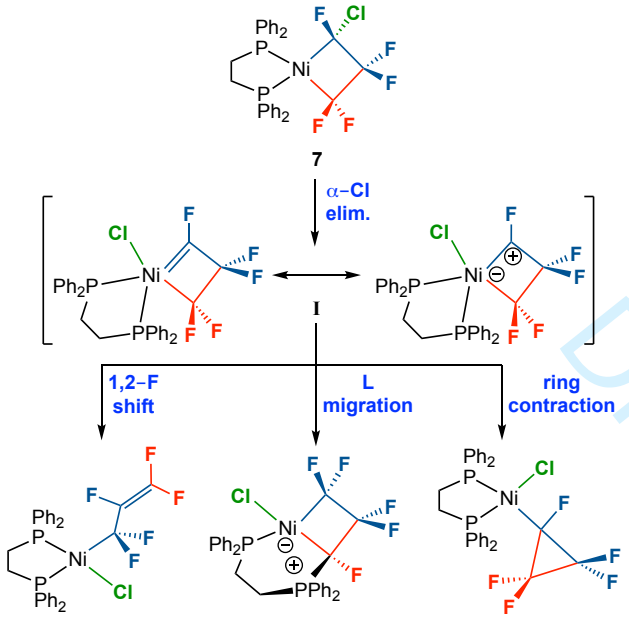


Several experiments were performed to gain further insight into the formation of unusual product **8**. A THF solution of **1** was charged to a vial with a Teflon-lined cap featuring a septum. Approximately 10 mL of CTFE was charged to the vial and the reaction mixture was stirred for 14 h, resulting in a colour change from dark red to light orange. The reaction mixture was evaporated *in vacuo* and a ^{19}F NMR spectrum of the crude solid showed **7**, and also the beginning of conversion to **8**. To determine if the presence of excess CTFE in solution was needed to form **8**, the solid was redissolved in THF and monitored. After two days the resulting ^{19}F NMR spectrum indeed showed increased formation of **8** with noticeable decrease of **7**, indicating that this transformation does not require excess CTFE.

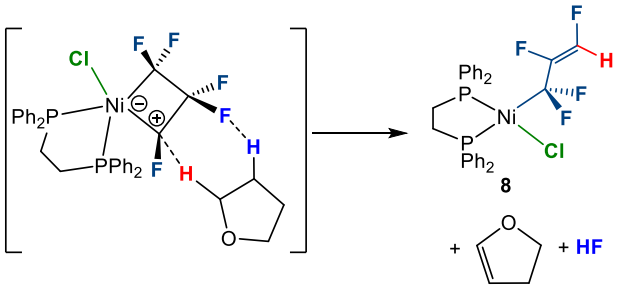
Formation of a Ni–Cl bond is presumably the result of α-Cl elimination, subsequently forming an α-carbenium ion or Ni perfluorocarbene, **I** (**Scheme 5**). This is in stark contrast to previously observed reactivity with fluorinated nickelacyclobutanes in which β-elimination is the preferred reaction pathway.[18] Based on nickelacyclopentane reactivity, subsequent steps could involve phosphine migration to $C\alpha$,[21] ring contraction to a Ni-cyclopropyl[22] or a 1,2-F shift to give the pentafluoroallyl

complex,[16] but neither can account for incorporation of the hydrogen and elimination of fluoride. Moreover, when the experiment was repeated in rigorously dried THF, the same product was observed, ruling out adventitious moisture. When the experiment was conducted in either acetonitrile or benzene, formation of **8** was not observed, suggesting a more fundamental role for THF. Given the electrophilic nature of intermediate **I**, an alternative pathway may involve hydride abstraction from THF followed by HF loss to give **8** and 2,3-dihydrofuran (**Scheme 6**). Note that this pathway also accounts for the stereospecific formation of the alkene in **8**. Although we were unable to confirm the small amount of dihydrofuran presumably formed,

Scheme 5. Three potential reaction pathways following α-Cl elimination.



Scheme 6. Proposed formation of **8** by hydride abstraction.



further reaction of **7** in benzene containing isopropanol also afforded **8** (along with other products; Fig. S8), supporting a hydride abstraction pathway.

Further unprecedented reactivity was observed in the reaction of **1** with HFP which afforded a yellow solution after 6 h. The unexpected ^{19}F NMR spectrum revealed 4 major resonances in a 3:3:1:1 ratio assigned as Ni(CF$_3$)[σ-CF=CF(CF$_3$)](dppe) (**9**; **Scheme 7**). Multiplets at -146.2 and -176.4 ppm displayed a large doublet splitting ($^3J_{FF}$ = 132 Hz) typical of *trans* vinylic fluorines. Closer analysis of the crude ^{19}F NMR spectrum provided evidence for a second isomer in which the vinylic fluorines are in a *cis* arrangement (*trans:cis* = 4:1; **Figure 2**). Furthermore, the ^{31}P{^{1}H} NMR spectrum shows two major resonances each attributed to a phosphorous either *trans* or *cis* to the CF$_3$ moiety (Fig. S10). The reaction pathway to **9** is proposed to involve a formal fluoride transfer from HFP to the Ni=CF$_2$ carbon through subsequent coordination of the resulting perfluoropropenyl cation to nickel (**int-4**). HFP is also known to react with nucleophilic carbonylmetallate anions to yield fluoride and metal σ-alkenyl complexes *via* a single-electron transfer pathway.[23] A similar pathway could be involved here, followed by fluoride capture by the electrophilic Ni^{II}-fluorocarbene carbon.

Scheme 7. Reaction of **1** with HFP to form **9**.

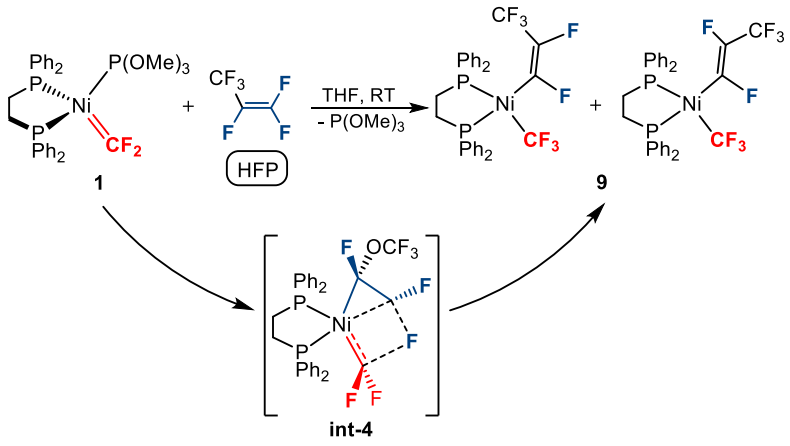
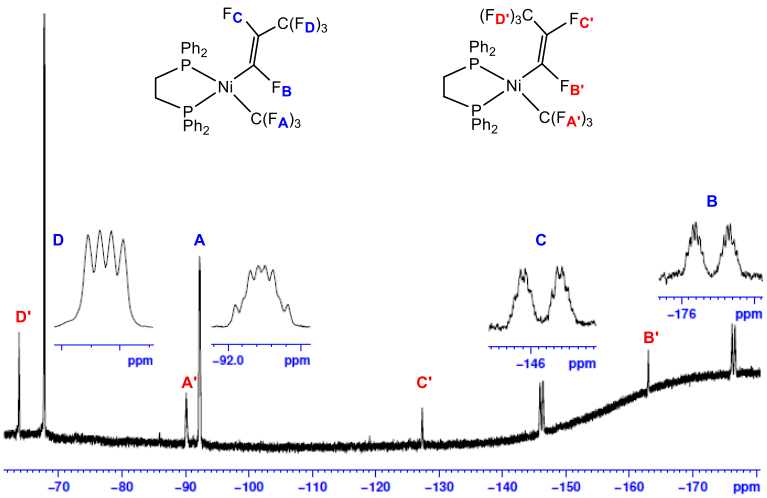


Figure 2. ^{19}F NMR spectrum showing *cis* and *trans* isomers of **9.**



Conclusions

While the ultimate objective of fluorinated alkene metathesis remains a future goal, much progress in the understanding and optimization of such systems is being made. We assessed the potential of the electron-rich dppe Ni=CF_2 complex **1** to react with a broader scope of fluoroalkenes to both stabilize the metallacycle products for future study and observe metathesis products. It was shown that **1** demonstrates great affinity for the expected cycloaddition reactions in which the =CF_2 fragment selectively attacks the most electron-rich carbon to furnish a variety of perfluorometallacycles. Furthermore, several of the resulting complexes undergo further reactions.

In previous work, the reaction of **2** with PMVE afforded three different metallacyclobutane isomers, two of which occur with the OCF_3 moiety on Cβ.[19b] In contrast, that with electron-rich **1** gave only **5**, with the OCF_3 moiety on Cα. Similar regioselective addition of TrFE to **1** reaffirmed the instability of the CHF unit in fluoronickelacyclobutanes reported previously.[19] A 1,2-F shift affords the pentafluoropropene complex that is subsequently replaced by a second equiv of TrFE, and finally a third to give isomeric metallacyclopentanes[24] **6**. Reaction of **1** with CTFE also gave the expected metallacyclobutane **7** with Cl exclusively on Cα. Unexpected further reactivity, however, led to α-Cl elimination to furnish **8** featuring a Ni–Cl bond and a σ-tetrafluoroallyl complex that underwent an unusual F substitution by H at the end of the chain, proposed to involve hydride abstraction from the THF solvent with loss of HF.

Although reactions of **1** with these fluoroalkenes failed to generate metathesis products, that with HFP cleanly generated the first example of a first-row perfluoroalkylmetal σ-perfluoroallyl complex **9**. Taken together, the distinctive reactions of this electron-rich Ni fluorocarbene shed light on the electronic properties of these fluoroalkenes and their corresponding fluoronickelacycles. Several of these complexes are currently being pursued for further reactivity investigations.

Materials and Methods

Unless otherwise stated, all reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene–d_6 was degassed by three freeze-pump-thaw cycles, and subsequently dried by passing through a column of activated alumina. Hexanes, diethyl ether, and THF were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system and stored over activated 4 Å molecular sieves. ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded on either a Bruker Avance or AvanceII Spectrometer operating at 300 MHz with respect to proton nuclei. ^{1}H NMR spectra were referenced to residual protons (C_6D_6, δ 7.15) with respect to tetramethylsilane at δ 0.00. ^{19}F and ^{31}P NMR chemical shifts were referenced to external $CFCl_3$ and H_3PO_4 at 0 ppm. All fluoroalkenes were used as purchased from Synquest. Precursor to complex **1**, Ni(CF_3)[OC(O)CF_3](dppe),[25] and KC_8[26] were prepared using modifications[18] of the literature procedures.

Optimized Synthesis of Ni=CF_2[P(OMe_3)](dppe) (1). In a 100 mL round-bottom Schlenk flask equipped with a magnetic stir bar, Ni(CF_3)[OC(O)CF_3](dppe) (1.0 g, 1.57 mmol) was dissolved in 30 mL of super-dry THF (run through a column of activated alumina) resulting in a dark orange solution. While stirring, P(OMe)$_3$ (185 µL, 1.57 mmol) was added, causing a colour change to a dark reddish-orange solution. A solid addition funnel was charged with KC_8 (592 mg, 4.38 mmol, 2.8 equiv.) and attached to the Schlenk flask. The reaction vessel was removed from the glovebox, placed in a pre-prepared dry ice-acetone bath, and attached to the Schlenk line. The solution was allowed to cool at -78 °C for 30 min. While stirring, the KC_8 was added slowly over the course of 10 min, resulting in a colour change to a brownish-yellow solution. After addition, the solution was left to stir at -78 °C for a further 30 min. The dry ice-acetone bath was removed to allow the temperature of the solution to rise. After approximately 10 min of warming, the solution was evaporated *in vacuo*, affording a brown solid. The reaction vessel was shipped back into the glovebox and the brown solid was extracted with diethyl ether (5x5 mL) and filtered through Celite to yield a red solution. The

solution was transferred to a 100 mL round bottom Schlenk flask, concentrated to approximately 5 mL, charged with 40 mL of hexane and placed in the freezer at -35 °C overnight. While cold, the solution was filtered through a frit and the resultant precipitate was washed with hexane. The solid was dried to give 701 mg of a red solid (71% yield). Characterization data matched that from the literature.[17]

Reaction of 1 with perfluoro(methyl vinyl ether) [PMVE; CF_2=CF(OCF_3)]. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with PMVE using a gas-tight syringe (3 mL, 0.12 mmol, excess). After 20 h at room temperature the reaction solution changed to a bright yellow colour. Analysis of the crude ^{19}F NMR spectrum showed complete consumption of **1** and exclusive formation of **5**. ^{19}F NMR (THF, Fig. 1) -55.8 (s, 3H, OCF_3); -112.4 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 241 Hz); -117.4 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 206.5 Hz); -119.5 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 241 Hz); -121.5 (d mult, 1F, α-*F*, $^2J_{FF}$ = 206.5 Hz); -133.0 ppm (mult, 1F, α-C*F*OCF_3). ^{31}P{^{1}H} NMR (THF, Fig. S1) 44.8 ppm (br ov mult, 2P, $\Delta\upsilon_{1/2}$ = 79 Hz).

Reaction of 1 with trifluoroethylene [TrFE; CF_2=CHF]. A solution of **1** (15 g, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with TrFE using a gas-tight syringe (3 mL, 0.12 mmol, excess). The reaction was left at room temperature for 4 h resulting in the observation of the free alkene, F_2C=CH(CF_3) (Fig. S2). After 24 h additional resonances grew in, which were assigned to the *cis*-head-to-tail (**6*c*-ht**), *trans*-head-to-tail (**6*t*-ht**) and *trans*-head-to-head (**6*t*-hh**) metallacyclopentane isomers (Fig. S3). ^{31}P NMR of the isomeric mixture (THF, Fig. S4): 48.0, 45.4 (ov mult), 38.2 ppm (mult). *Ni[CF_2CFHCF_2CFH-][dppe]* (**6*c*-ht**): ^{19}F NMR (THF, Fig. S3) -85.6 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 270, $^3J_{FP}$ = ca. 41 Hz); -107.0 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 270, $^3J_{FP}$ = ca. 41 Hz); -110.0 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 220 Hz); -129.6 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 220 Hz); -221.2 (mult, 1F, α-C*F*H); -226.1 ppm (d mult, 1F, β-C*F*H, $^2J_{FH}$ = 48 Hz).

Ni[CF_2CFHCF_2CFH-][dppe] (**6*t*-ht**): ^{19}F NMR (THF, Fig. S3) -84.2 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 283, $^3J_{FP}$ = ca. 35 Hz); -94.2 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 283, $^3J_{FP}$ = ca. 31 Hz); -111.8 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 239 Hz); -119.6 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 239 Hz); -206.0 (d mult, 1F, β-C*F*H), $^2J_{FH}$ = 51 Hz); -212.3 ppm (mult, 1F, α-C*F*H).

Ni[CF_2CFHCFHCF_2-][dppe] (**6*t*-hh**): ^{19}F NMR (THF, Fig. S3) -87.5 (d mult, 2F, CF_2, $^2J_{FF}$ = 270, $^3J_{FP}$ = ca. 43 Hz); -98.8 (d mult, 2F, CF_2, $^2J_{FF}$ = 270 Hz); -213.0 ppm (d mult, 2F, CH*F*, $^2J_{FH}$ = 57 Hz).

Reaction of 1 with chlorotrifluoroethylene [CTFE; CF_2=CFCl]. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with CTFE using a gas-tight syringe (3 mL, 0.12 mmol, excess). The reaction was left at room temperature for 8 h resulting in the formation of **7**. Crude ^{19}F NMR showed conversion to another product **8** in small amounts. After an additional 24 h conversion of **7** to **8** was complete.

Ni[CF_2CF_2CFCl-][dppe] (**7**): ^{19}F NMR (THF, Fig. S6) –102.9 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 196.5 Hz); -107.2 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 243 Hz); -119.0 (d mult, 1F, β-C*F*, $^2J_{FF}$ = 243 Hz); -121.4 (d mult, 1F, α-C*F*, $^2J_{FF}$ = 196.5 Hz); -140.4 ppm (mult, 1F, α-C*F*Cl). ^{31}P{^{1}H} NMR (THF, Fig. S7) 47.2 ppm (br mult).

NiCl[σ-CF_2CF=CFH][dppe] (**8**): ^{19}F NMR (THF, Fig. S8) -82.4 (t d, 2F, Ni–CF_2, $^3J_{FP}$ = ca. 35.5, $^3J_{FF}$ = 20.5 Hz); -145.5 (dt, 1F, Ni–CF_2C*F*, $^3J_{FF}$ = 20.5, $^3J_{FF}$ = 14.5 Hz); -174.1 ppm (dd, 1F, Ni–CF_2CF=C*F*, $^2J_{FH}$ = 75, $^3J_{FF}$ = 14.5 Hz). ^{31}P{^{1}H} NMR (THF, Fig. S7) 39.7, 58.9 ppm (br mult).

Reaction of 7 with isopropanol in benzene. Complex **7** was prepared as above using C_6D_6 solvent instead of THF. ^{19}F NMR spectra were obtained before and after addition of two drops isopropanol (4 h reaction time; Fig. S9).

Reaction of 1 with hexafluoropropene [HFP; CF_2=CF(CF_3)]. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with HFP using a gas-tight syringe (3 mL, 0.12 mmol, excess). After 20 h at room temperature the reaction solution changed to a bright yellow colour. Analysis of the crude ^{19}F NMR showed complete consumption of **1** and exclusive formation of **9** (two isomers). ^{19}F NMR (THF, Fig. 2) *Trans*-isomer*:* -67.7 (dd, 3F, CF_3, $^3J_{FF}$ = 23.5, $^4J_{FF}$ = 12 Hz); -92.2 (mult, 3F, CF_3); -146.2 (d mult, 1F, C*F*, $^2J_{FF}$ = 133 Hz); -176.4 ppm (d mult, 1F, C*F*, $^2J_{FF}$ = 133 Hz). *Cis*-isomer: -63.7 (mult, 3F, CF_3); -90.0 (mult, 3F, CF_3); -127.2 (mult, 1F, C*F*); -163.0 ppm (mult, 1F, C*F*). ^{31}P{^{1}H} NMR (THF, Fig. S10) *Trans*-isomer*:* 55.3, 30.2 ppm (ov mult, 1P). *Cis*-isomer: 55.3, 30.2 ppm (ov mult, 1P).

Supplementary Material

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi Contents include NMR spectra and X-ray crystallographic details.

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