

Transformations of *F*-Alkyl Iodides and Bromides Induced by Nickel(0) Carbonyl†

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Adducts of primary *F*-alkyl iodides with nickel carbonyl are formed readily in donor solvents and pyrolyze at 100–150 °C to give olefinic coupling products in high yield. The mechanism proposed to account for the observed chemistry involves preferential α -elimination of fluorine with formation of a carbenoid species complex coordinated to nickel. Differences in reaction paths among several types of substrate halides are rationalized on the basis of polarization of the Ni–C bond in the adducts. Support for these proposals is provided by state-of-the-art calculations.

Introduction

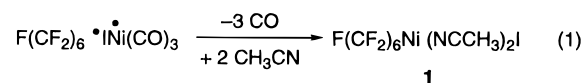
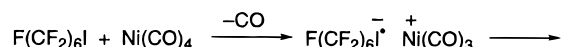
Our search for new synthetic methods in organofluorine chemistry based on readily available zero-valent metal carbonyls as reagents centered first on iron pentacarbonyl.¹ Depending upon reaction conditions, this reagent was shown to convert primary *F*-alkyl iodides into *F*-1-iodo-1-alkenes or into *F*-alkyl radicals capable of *F*-alkylating aromatic substrates. A later study² of the transformations of α -chloro fluoro ketones mediated by nickel carbonyl has now been extended to other fluoroalkyl halides as substrates. Marked differences emerge between the chemistries mediated by the iron vs the nickel reagents.

A number of stable *F*-alkylnickel(II) compounds bearing various ligands have appeared in the literature,³ so stable that, as with the iron(II) derivatives, prospects for catalytic reactions seem low.⁴ The reactions were therefore run with equimolar amounts of the metal carbonyl. Oxidative addition of a variety of fluoroalkyl halides to nickel tetracarbonyl, corresponding to one of the known general reactions producing L_2NiXR_F compounds,^{3a} was

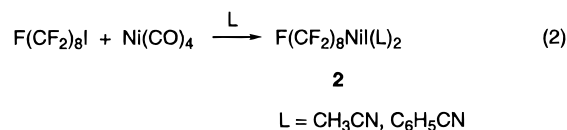
adopted as the synthetic approach. In contrast to the previous studies, the goal was to carry through to organofluorine products.

Results and Discussion

Reaction is not observed between *F*-alkyl iodides and $Ni(CO)_4$ in neat mixtures but does occur readily in donor solvents at 25–60 °C. The usual mechanistic sequence probably obtains, one in which reversible loss of CO gives $Ni(CO)_3$ having a vacant coordination site, coordination of $Ni(CO)_3$ at iodine, followed by single-electron transfer to give a charged, solvated intermediate. Subsequent transfer of iodide ion to the metal followed by radical combination leads to product. Steady loss of CO occurs during reaction, so that the final product contains two molecules of the donor solvent, generally acetonitrile in our reactions, and no carbon monoxide. Equation 1 illustrates the formation of *F*-hexylnickel derivative **1** starting from *F*-hexyl iodide.



F-Octyl iodide also adds to nickel carbonyl in acetonitrile or, more slowly, in benzonitrile media to form adducts **2**.



Proceeding from primary *F*-alkyl iodide to bromide to chloride, that is, in the direction of decreasing ease of electron transfer, gives progressively lower reactivity toward nickel carbonyl. Bromides, as exemplified by

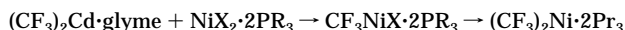
† DuPont Publication no. 7529.

Ⓢ Abstract published in *Advance ACS Abstracts*, December 1, 1997.

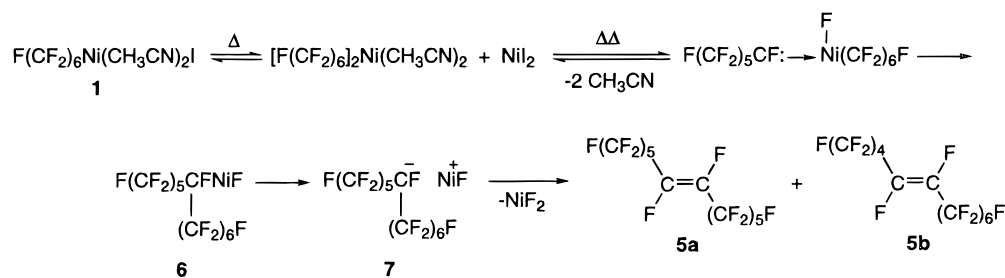
(1) Krespan, C. G. *J. Fluorine Chem.* **1988**, *40*, 129.

(2) Krespan, C. G. *J. Fluorine Chem.* **1994**, *66*, 311.

(3) (a) Oxidative substitution of various bis-ligand Ni(0) compounds with R_FI are known to give isolable derivatives of the type L_2NiIR_F ; see, for example, the following: McBride, D. W.; Stafford, S. L.; Stone, F. G. A. *J. Chem. Soc.* **1963**, 723. Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019. (b) Direct reaction of nickel metal (deposited from the vapor phase) with trifluoromethyl radicals has been used to prepare $Ni(CF_3)_2$, isolated as the stable bis(trimethylphosphine) derivative by Firsich, D. W.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1283. (c) McBride et al. (McBride, D. W.; Dudeck, E.; Stone, F. G. A. *J. Chem. Soc.* **1964**, 1752) report the synthesis of the type $\pi-C_5H_5-Ni(CO)R_F$ by oxidative cleavage of the Ni–Ni bond in $[\pi-C_5H_5Ni(CO)]_2$ with R_FI . (d) Exchange reactions can also be used to attach an R_F group to nickel; for example, Krause et al. (Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1282) carried out the following reactions:



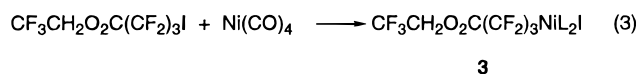
(4) (a) Hughes, R. *Adv. Organomet. Chem.* **1990**, *31*, 183. (b) See, however: Yang, Z.-Y. *J. Am. Chem. Soc.* **1996**, *118*, 8140.

Scheme 1

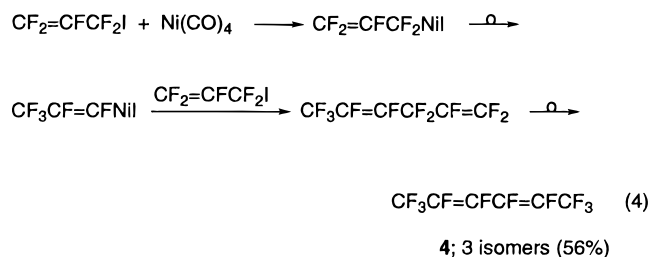
F-octyl bromide, react much more slowly than iodides, while chlorides are unreactive at moderate temperatures. The product from a fluoroalkyl bromide gives chemistry similar to that from an iodide, indicating that the (fluoroalkyl)nickel moiety tends to thermolyze independently of the halide ion present.

F-Alkylnickel(II) derivatives with appropriate ligands are known to be stable,³ as are compounds such as **1** and **2**. These crude products could be stored for weeks under nitrogen at 25 °C with little degradation.

An ester function is tolerated provided it is located some distance from the iodo substituent, as shown in eq 3.



F-Allyl iodide is unusual in that it reacts exothermically to form the rearranged coupling products, known diene isomers **4**, directly. In this case, we propose that the expected intermediate isomerizes to the *F*-propenyl derivative, which then can heterolyze to give *F*-propenyl anion capable of attack on *F*-allyl iodide to form diene. The observed product, **4**, is the result of equilibration of the diene.

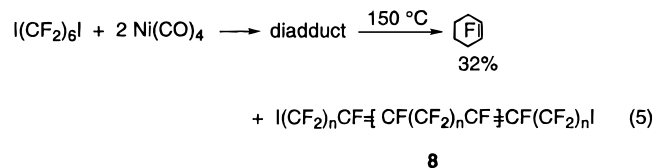


Pyrolysis of *F*-alkylnickel halides such as **1** occurs at temperatures above about 120 °C to give a mixture of two olefinic coupling products in remarkably high yield. Analyses by ¹⁹F NMR, IR, Raman, and GC/MS show an approximately 1:1 mixture of *trans*-*F*-dodecene-6 (**5a**) and *trans*-*F*-dodecene-5 (**5b**). We interpret the facts that only two closely related olefins are formed and those by a highly efficient coupling reaction to mean that formation of a carbenoid intermediate is a key step.^{5a} As indicated in Scheme 1, α-elimination of fluorine can provide a perfluorohexylene species in the inner sphere coordinated

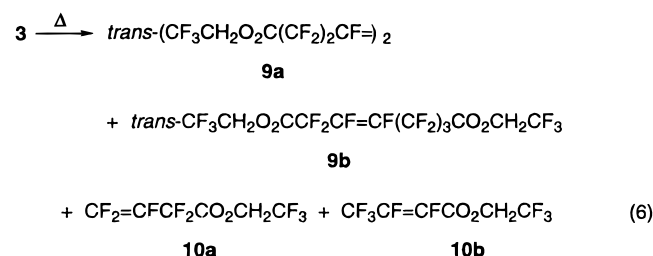
to Ni(II). Insertion of this very reactive carbenoid species into a nearby C–Ni σ-bond^{5b} proceeds cleanly to generate **6** containing a secondary perfluoroalkyl group bonded to nickel. As the evidence indicates (vide infra), heterolysis of this new C–Ni σ-bond leads to carbanion **7**, from which olefins **5** are formed by nonregioselective β-elimination of fluoride. Since β-elimination can evidently occur in two and only two directions with about equal ease to give Δ⁵ and Δ⁶ olefins, this mechanism leads to the product mix actually obtained. The isomers **5** are clearly kinetic products, since contact with an acetonitrile solution of TASF at 25 °C or CsF/diglyme at 100 °C caused the appearance of new olefin isomers in the mixture.

The fluoroalkyl–nickel bond in compounds such as **1** is not only stable for prolonged periods at 25–50 °C but also remains essentially intact at 80 °C for hours. This level of stability was demonstrated when product **1**, prepared from 0.1 mol each of F(CF₂)₆I and Ni(CO)₄, was refluxed with 100 mL of benzene for 12 h. The red solid, **1**, which was still present after removal of volatiles at 25 °C under vacuum, was pyrolyzed to give 19 g (63%) of **5**. Minor amounts of F(CF₂)₄CF=CF₂, F(CF₂)₅H, and F(CF₂)₆I were also formed, but no products from interaction with the benzene ring were detected.

An intramolecular version of the coupling reaction is observed on pyrolysis of the intermediate from interaction of *F*-1,6-diiodohexane with an excess of Ni(CO)₄. *F*-Cyclohexene is obtained in essentially one step from the diiodide. Low molecular weight iodine-containing polymer presumed to have the general structure **8** is also formed.



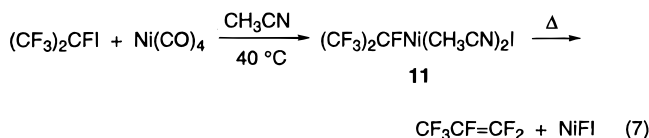
The carbomethoxy group survives the pyrolytic coupling conditions well, as indicated by the results obtained on pyrolysis of **3** to form **9a,b**.



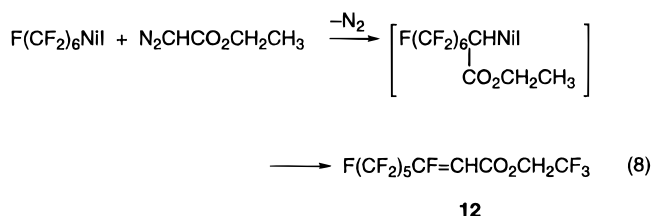
One feature of the proposed mechanism was tested by reaction of nickel carbonyl with a secondary iodide, *F*-2-

(5) (a) See ref 4b for a discussion of difluorocarbene complexes with nickel and for leading references. (b) A reviewer has pointed out that although we have found no literature on disproportionations of (perfluoroalkyl)nickel derivatives as is indicated in Scheme 1, Klabunde et al. (Klabunde, K. J.; Anderson, B. B.; Bader, M.; Radomovitch, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1313) established the formation of (C₆F₅)₂-Ni(PET₃)₂ under some conditions from reactions known to produce initially C₆F₅NiBr.

iodopropane, to attach nickel to a perfluoroalkyl group at a secondary carbon. This intermediate, **11**, could be detected by ^{19}F NMR but proved to be unstable at even moderate temperatures. Decomposition occurred with formation of *F*-propene, the expected product of β -fluoride elimination, with no sign of coupling products.



An attempt to emulate the postulated insertion of a carbenoid species into a Ni–C bond was made by addition of ethyl diazoacetate as a carbene source to *F*-hexylnickel iodide in acetonitrile at 25 °C. Rapid reaction occurred with formation of mixed coupling product **12** in 7% yield. The low yield of **12** may reflect the extent to which carbethoxycarbene is generated with access to the inner coordination sphere of nickel where the insertion could proceed.



SET to a ClCF_2 - or Cl_2CF - group is disfavored with $\text{Ni}(\text{CO})_4$, since no reaction is observed with $\text{ClCF}_2\text{CFCl}_2$. On the other hand, a Cl_3C - group does participate, as shown by the reactivity of $\text{ClCF}_2\text{CF}_2\text{CCl}_3$ toward $\text{Ni}(\text{CO})_4$ at 25 °C. Several products are formed, and as indicated in Scheme 2, it is apparent that both α - and β -elimination of halogen occur.

α -Elimination of chlorine is occurring at a much lower temperature than it does with fluorine, in keeping with the lower bond strength for C–Cl. Since the resulting carbenoid species coordinated to nickel is formed while carbon monoxide is still coordinated to nickel as well (as indicated for **13**), coupling of the two carbenes in the nickel coordination sphere to form ketene **14** can occur. The ketene is not isolated as such, since it rearranges to the isomeric acid fluorides **15**.⁶

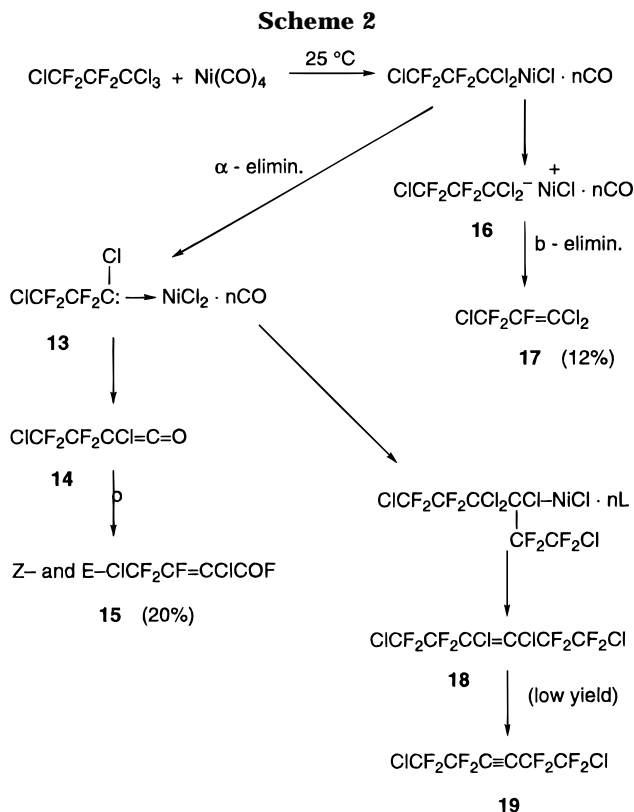
The product from insertion of carbenoid ligand in **13** into a C–Ni bond also occurs to a minor extent. The resulting (haloalkyl)nickel moiety can then ionize to give a relatively stable carbanion that preferentially eliminates a β -chlorine to afford olefin **18**.^{7a}

The competing pathway for decomposition via β -elimination of fluorine is also observed, no doubt because

(6) England et al. (England, D. C.; Solomon, L.; Krespan, C. G. *J. Fluorine Chem.* **1973**, *3*, 63) report the same observation in the synthesis of *F*-acryloyl fluoride with no indication of *F*-methylketene in equilibrium.

(7) (a) Krespan et al. (Krespan, C. G.; Harder, R. J.; Drysdale, J. J. *J. Am. Chem. Soc.* **1961**, *83*, 3424) report the preparation of this olefin by coupling of $\text{ClCF}_2\text{CF}_2\text{CCl}_3$ with copper at elevated temperature (200 °C). Synthesis of acetylene **19** by dechlorination of **18** is also reported. (b) Interestingly, Klabunde et al. (Klabunde, K. J.; Key, M. S.; Low, J. Y. F. *J. Am. Chem. Soc.* **1972**, *94*, 1000) report results with R_2ZnI that imply an ordering of reactivities similar to ours.

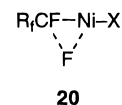
(8) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levein, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement No. 1.



heterolysis of the primary adduct gives stabilized carbanion **16** as precursor to olefin **17**.

Computational Results

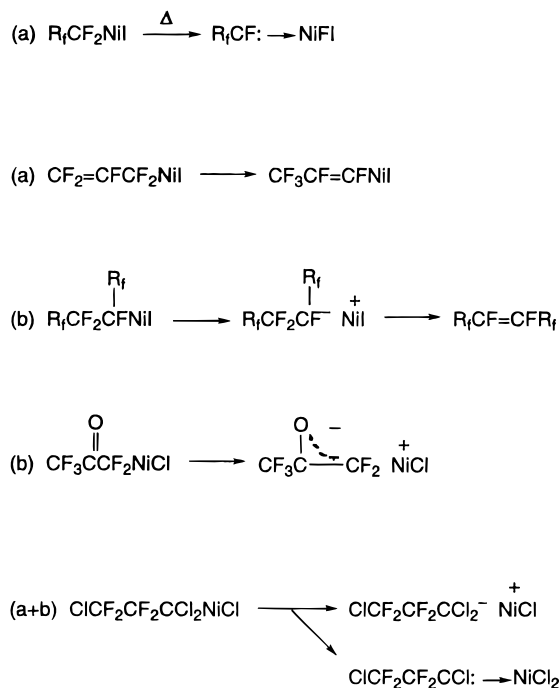
Our interpretation of the results hinges on the ease of heterolysis of the C–Ni bond in the products of oxidative addition, R_fNiX . Primary *F*-alkyl groups C_2 and higher form a stable, relatively covalent bond to nickel, so that decomposition occurs by a synchronous transfer of α -fluorine from C to Ni and formation of coordinated carbene via a three-center fluorine-bridged intermediate represented by **20**.



As the C–Ni bond becomes more polarized by the presence of an α -fluoroalkyl group and the fluoroalkyl group more effectively stabilizes a negative charge, products of β -elimination tend to predominate. Similarly, the anion-stabilizing influence of the trifluoroacetyl group and of chlorine atoms as α -substituents serves to promote heterolytic cleavage of the C–Ni bond followed by reactions characteristic of the carbanions. This transition from one mode of decomposition to another is detailed in Figure 1.^{7b}

To assess the relative stabilities of the carbanions, the gas-phase acidities of various model species were calculated.⁸ The acidity gives information about the stability of the anion relative to the strength of the C–H bond in the neutral. The acidity of AH is defined as the value of $\Delta H(298)$ for reaction 9



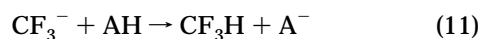
**Figure 1.** α -Elimination (type a) vs heterolysis (type b).

The acidity in kcal/mol can be calculated directly from the total energies of AH and A^- , the difference in zero point energies (a negative number) and a correction for thermal effects and to convert from ΔE to ΔH as given in eq 10.

$$\Delta H_f(9) = \Delta E_0(\text{elec}) + \Delta ZPE + 1.5 \quad (10)$$

We show the directly calculated acidity results in Table 1.

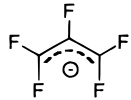
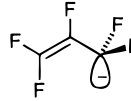
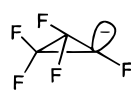




The direct calculation of gas-phase acidities can be difficult to do accurately as an anion is produced and it is more difficult to treat computationally the behavior of negative ions because of the diffuse nature of the charge distribution. Another means to calculate the acidity is to calculate the heats of formation of the neutral and the ion by some scheme and then to calculate $\Delta H(9)$ from the available ΔH_f s. The ΔH_f s of the neutrals if they are not known from experiment can be calculated from isodesmic reactions if the heats of formation of three of the four species are known. The ΔH_f s for the neutrals are shown in Table 2 together with the isodesmic reactions used to generate them. The ΔH_f s of the anions can be calculated in two ways. The first is as a proton-transfer reaction involving the CF_3^-/CF_3H couple as shown in reaction 11.



This couple was chosen because the experimental heats of formation of CF_3^- ⁸ and CF_3H ⁹ are known although the heat of formation of CF_3^- has somewhat larger error bars (± 10 kJ/mol = ± 2.4 kcal/mol) than one would like. The values of $\Delta H(11)$ are given in Table 3, and the resulting ΔH_f s are shown in Table 4. The second means is to calculate the fluoride affinity (FA) of molecule B

(9) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

Table 1. Gas-Phase Acidities (kcal/mol) of Fluorocarbons

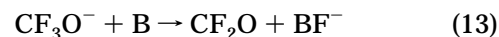
Neutral	Anion	Acidity Direct	Acidity FA	Acidity H ⁺ Transfer
CF_3H^a	CF_3^-	390	—	377 ^a
$F_2C=CF CF_2H$		409	408	396
		385	384	372
		381	381	369
CF_3CF_2H	$CF_3CF_2^-$	381	372	368
$CF_3CF_2CF_2H$	$CF_3CF_2CF_2^-$	376	370	364
HF^a	F^-	371	—	371
		372	—	360
		371	—	359
CF_3CCl_2H	$CF_3CCl_2^-$	367	362	354
CF_3CFHCF_3	$(CF_3)_2CF^-$	363	357	351
$CF_3-C(=O)-CF_2H$	$CF_2=C(O^-)-CF_3$	357	—	344

^a From experimental values.

which yields BF^- which has the same structure as A^- . The fluoride affinity is defined as $-\Delta H$ for reaction 12.



We have previously been able to predict the relative FAs of organofluorine compounds with good reliability.^{10,11} Furthermore, we have shown that we can calculate¹² absolute FAs with good reliability based on the FAs of HF ¹³ and CF_2O ¹⁴ which have recently been reliably established. The fluoride affinity is calculated as a relative value based on eq 13



(10) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027.

(11) Dixon, D. A.; Farnham, W. B.; Heilemann, W.; Mews, R.; Noltemeyer, M. *Heteroatom* **1993**, *4*, 287.

(12) Krespan, C. G.; Dixon, D. A. *J. Fluorine Chem.* **1996**, *77*, 117.

(13) Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.* **1995**, *99*, 2002.

(14) (a) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944. (b) McMahon, T. B., private communication.

Table 2. Heats of Formation (kcal/mol) of Neutrals and Appropriate Isodesmic Reactions

Reaction		ΔH_f (kcal/mol)
		13.1
		2.4
		-2.1
		-2.5
		-9.7

Molecule	ΔH_f	Molecule	ΔH_f
CF ₃ H	-166.2 ^a		-215.2
CF ₃ CF ₂ H	-236.6 ^a		-226.3
CF ₃ CFHCF ₃	-371.1		-228.5
CF ₃ CF ₂ CF ₂ H	-364.1		
	-282.1		
CF ₃ CCl ₂ H	-176.1		
HF	-65.1 ^a		

^a Experimental values. See refs 8 and 9.

and then corrected to an absolute value by adding the above energy difference to the absolute value of $FA(CF_2O) = 49.9$ kcal/mol. Given ΔH_f of B, one can then calculate $\Delta H_f(BF^-)$ from eq 12. The values of the absolute fluoride affinities are given in Table 5, and the resulting ΔH_s are shown in Table 4. Given the heats of formation of the species in reaction 9 and that of the proton, the acidities can also be calculated and these are given in Table 1.

The heats of formation of the anions from the two methods do not agree with each other as well as one would like. The values calculated from the proton transfer reactions are uniformly more negative than those calculated from fluoride affinities. The best agreement is found for $CF_3CF_2^-$ which has the structure most similar to that of CF_3^- . The difference here is about 3 kcal/mol, and the difference approximately doubles for $CF_3CF_2CF_2^-$ and $(CF_3)_2CF^-$. These differences are probably due to the fact that CF_3^- is a small anion, and our basis set does not describe it as well as the larger ones. A larger difference of about 12 kcal/mol is predicted for the anions derived from perfluoroallyl anion. This arises from the basis size effect described above and to a possible difficulty in describing the addition of F^- to perfluoroallene or to an error in the predicted heat of formation of $CF_2=C=CF_2$.¹⁵

The direct calculation of the acidity shows good agreement with the acidities derived from fluoride affinities

Table 3. Proton Transfer Reaction Energies

Reaction	ΔH (kcal/mol)
$CF_3^- + CF_3CF_2H \rightarrow CF_3CF_2^- + CF_3H$	-8.5
$CF_3^- + CF_3CCl_2H \rightarrow CF_3CCl_2^- + CF_3H$	-23.0
$CF_3^- + CF_3CF_2CF_2H \rightarrow CF_3CF_2CF_2^- + CF_3H$	-13.6
$CF_3^- + CF_3CFHCF_3 \rightarrow (CF_3)_2CF^- + CF_3H$	-26.3
$CF_3^- + \text{CF}_3\text{C(=O)CF}_2\text{H} \rightarrow \text{CF}_2=\text{C}(\text{CF}_3)\text{O}^- + \text{CF}_3\text{H}$	-33.0
$CF_3^- + \text{CF}_3\text{C(F)=CF}_2\text{H} \rightarrow \text{CF}_3\text{C(F)=CF}_2^- + \text{CF}_3\text{H}$	19.4
$CF_3^- + \text{CF}_3\text{C(F)=CF}_2\text{H} \rightarrow \text{CF}_3\text{C(F)=CF}_2^- + \text{CF}_3\text{H}$	-5.0
$CF_3^- + \text{CF}_3\text{C(F)=CF}_2\text{H} \rightarrow \text{CF}_3\text{C(F)=CF}_2^- + \text{CF}_3\text{H}$	-8.4
$CF_3^- + \text{CF}_3\text{C(F)=CF}_2\text{H} \rightarrow \text{CF}_3\text{C(F)=CF}_2^- + \text{CF}_3\text{H}$	-17.6
$CF_3^- + \text{CF}_3\text{C(F)=CF}_2\text{H} \rightarrow \text{CF}_3\text{C(F)=CF}_2^- + \text{CF}_3\text{H}$	-18.6

for the anions derived from perfluoroallyl anion. The differences are larger for the other compounds, but the agreement for the direct calculation of the acidity is always better with the fluoride affinity values. However, the acidity scale does not really depend on the type of calculation except where HF lies on the scale as this is an experimental value. The acidity trends in Table 1 show that the least stable acid is CF_3H followed by CF_3CF_2H and $CF_2=CFCF_2H$ with the latter two compounds having comparable acidities except on the fluoride affinity scale. Note, however, that the latter acid would form either $CF_2=CFCF_2^-$ (no allylic delocalization) or the perfluorocyclopropyl anion. The next weakest acid is the one derived from elongation of the alkane chain, $CF_3CF_2CF_2H$. Its isomer, CF_3CFHCF_3 has a significantly higher acidity (easier loss of a proton). The acid CF_3CCl_2H is a stronger acid than CF_3CF_2H by almost 20 kcal/mol, showing the significant stabilization by the Cl atoms α to the carbanion center as compared to F atoms. The strongest acid is that derived from the fluorocarbonyl derivative. The ordering of the acidities correlates well with the two pathways that are observed. The stronger acids (more stable carbanions) give type b reactions which are dominated by preliminary heterolysis. The weaker acids favor the α -elimination type a pathways.

Conclusions

The pyrolytic behavior of primary (perfluoroalkyl)-nickel(II) halides involves transfer of α -fluorine to nickel followed by reactions of the carbenoid species so produced. The olefinic coupling products are formed in 56–90% overall yield, providing a convenient one-pot route

Table 4. Anion Heats of Formation (kcal/mol)

Anion	ΔH_f (FA) ^a	ΔH_f (H ⁺ -transfer) ^b
	-172.6	-184.5
	-196.8	-208.6
	-200.1	-212.0
CF ₃ ⁻	-257.7	-260.8
CF ₃ CF ₂ ⁻	-154.8 ± 2.4 ^c	-154.8 ± 2.4 ^c
CF ₃ CF ₂ CF ₂ ⁻	-359.9	-366.3
(CF ₃) ₂ CF ⁻	-379.8	-386.1
CF ₂ =C(O ⁻)CF ₃	-	-303.8
CF ₃ CCl ₂ ⁻	-180.1	-187.9
F ⁻	-59.6 ^c	-59.6 ^c
	-	-232.5
	-	-235.6

^a ΔH_f from fluoride affinities (Table 5). ^b ΔH_f from proton transfer reactions (Table 3). ^c Experimental values from refs 8 and 9.

to such materials. Versatility of the synthesis is enhanced by tolerance of the presence of at least the ester functionality.

Introduction of groups at the α -position to provide better stabilization of negative charge promotes formation of products of heterolysis of the C–Ni bond. Our computational results support these conclusions in that the ordering of anion stabilities correlates well with the observed change in mechanism with fluoride ion standing at the approximate dividing line between the two types of pyrolytic cleavage.

Experimental Details

Boiling points are uncorrected. Unless otherwise specified, ¹⁹F NMR spectra were taken at 188.2 MHz on 20% solutions in CDCl₃ with CFCl₃ as internal standard, and ¹H NMR spectra were taken at 300.2 MHz on similar solutions with Si(CH₃)₄ as internal standard.

CAUTION! Care must be exercised when using Ni(CO)₄, a volatile, highly toxic material. All runs with it were carried out under nitrogen in systems vented through a –80 °C cold trap. Equipment and cold trap contents were decontaminated by treatment with Br₂ or aqueous NaOCl before removal from the hood.

Formation and Pyrolysis of *F*-Hexylnickel Iodide Bis-(acetonitrile) Complex (1) to *F*-Dodecenes 5a,b. (a) A mixture of 44.6 g (0.10 mol) of *F*-hexyl iodide, 17.1 g (13 mL, 0.10 mol) of nickel carbonyl, and 100 mL of acetonitrile (purified by distillation from P₂O₅, degassed with N₂, and

Table 5. Absolute Fluoride Affinities

Neutral	Anion	FA
CF ₂ =C=CF ₂		-8.1
		16.3
		19.7
CF ₂ =CF ₂	CF ₃ CF ₂ ⁻	40.7
	CF ₃ CF ₂ CF ₂ ⁻	30.6
	(CF ₃) ₂ CF ⁻	50.7
CF ₂ =CCl ₂	CF ₃ Cl ₂ ⁻	43.0

stored over 4 Å molecular sieves) was stirred under N₂ at 50 °C for 6.5 h, at which point CO evolution had practically ceased and appreciable crystalline red precipitate was present. The dark red crystals, which readily turned green in moist air, were filtered under nitrogen, rinsed with a little acetonitrile, and dried under vacuum to afford 6.3 g of dark red crystals. IR (Nujol): 2310 and 2280 (complexed CN), traces only of CF absorption near 1200 cm⁻¹, and indications of H₂ at 3330 and 1630 cm⁻¹.

Anal. Calcd for C₄H₆I₂N₂Ni: C, 12.17; H, 1.53; N, 7.10; Ni, 14.88. Found: C, 12.82; H, 2.40; N, 6.93; Ni, 13.69.

The insoluble solid was impure NiI₂·2CH₃CN containing a very small amount of **1** and appeared to be slightly hydrated.

The dark red filtrate was evaporated to dryness at 0.2 mm overnight to give 41.6 g of a red-black soft solid. IR (Nujol): 2340, 2310, 2290 (complexed CN), 1250–1100 cm⁻¹ (str, CF). NMR (CD₃CN): ¹⁹F ϕ –80.7 (s, 3F, CF₃), –96.7 (s, 2F, CF₂⁻Ni), –113.9 (s, 2F, CF₂), –121.7 (s, 2F, CF₂), –122.3 (s, 2F, CF₂), –125.87 (s, 2F, CF₂). Weak bands for starting iodide were also present.

Anal. Calcd for C₁₀H₆F₁₃IN₂Ni: C, 20.47; H, 1.03; F, 42.09; N, 4.77; Ni, 10.01. Found: C, 20.52; H, 0.96; F, 43.99, 43.73; N, 4.01, 3.98; Ni, 9.08, 9.06.

Well-defined crystals were not obtained, but the data indicate the soluble product to be mainly structure **1**.

(b) A reaction similar to that above was carried out over 7 h. GC analysis indicated the presence of residual iodide, so 7.9 g (6.0 mL, 0.046 mol) of additional nickel carbonyl was added, and the reaction was continued at 50 °C for 2 h. Only a trace of iodide remained. Volatiles were removed from the red suspension at 25 °C (0.2 mm) to give a dark red residue which was pyrolyzed at 100–170 °C (1–0.1 mm). The pyrolysate collected in a –80 °C trap consisted of an upper layer of acetonitrile and 28.6 g of a lower layer composed of 95% **5a** + **5b** with traces of F(CF₂)₄CF=CF₂, F(CF₂)₆I, and other impurities. The yield of isomers **5** is therefore 27.2 g (90%).

Pure **5** was isolated by fractionation as an approximately 1:1 mixture of *trans* olefins **5a** and **5b**, bp 74–75 °C (20 mm). GC (fluorosilicone packed column): single component. Capillary GC (methylsilicone column): 60/40 mixture of two computer-resolved components. IR (neat): 1250–1150 cm⁻¹ (CF). Raman: 1724.3 cm⁻¹ (*trans*-R_FCF=CFR_F). NMR (CFCl₃): ¹H none; ¹⁹F (94.1 MHz) ϕ –81.6 (t of t, *J*_{FF} = 9.8, 2.5 Hz, 6F from **5a** and 3F from **5b**, CF₃), –81.8 (t of t, *J*_{FF} = 10, 2.2 Hz, 3F from **5b**, CF₃), –118.6 (m, 8F, CF₂C=), –122.4 (m, 2F from **5b** CF₂), –123.3 (m, 4F from **5a** and 2F from **5b**, CF₂), –124.1

(m, 4F from **5a** and 2F from **4b**, CF_2), -125.0 (m, 2F from **5b**, CF_2), -126.7 (m, 8F, CF_2), -154.0 (m, 4F, =CF). A ^{19}F NMR spectrum taken at 376.5 MHz ($CFCl_3$) clearly showed a 53/47 mixture of **5a** and **5b**. For **5a**: ^{19}F ϕ -81.6 (t of t, $J_{FF} = 10.0$, 2.5 Hz, 6F, CF_3), -118.7 (m, 4F, $CF_2C=$), -123.5 (m, 4F, CF_2), -124.4 (s, 4F, CF_2), -126.8 (m, 4F, CF_2), -154.0 (m, 2F, =CF). For **5b**, with some of the resonances still coincidental with those of **5a**: -81.6 (t of t, $J_{FF} = 10.0$, 2.5 Hz, 3F, CF_3), -81.7 (t of t, $J_{FF} = 9.9$, 2.2 Hz, 3F, CF_3), -118.7 (m, 2F, $CF_2C=$), -118.9 (m, 2F, $CF_2C=$), -122.7 (m, 2F, CF_2), -123.3 (m, 2F, CF_2), -124.1 (m, 2F, CF_2), -125.1 (m, 2F, CF_2), -126.8 (m, 2F, CF_2), -126.9 (s, 2F, CF_2), -154.0 (m, 2F, =CF).

Anal. Calcd for $C_{12}F_{24}$: C, 24.02. Found: 24.23.

Formation and Pyrolysis of Adduct 2. Addition of 27.2 g (0.050 mol) of *F*-*n*-octyl iodide to 8.55 g (6.5 mL, 0.05 mol) of nickel carbonyl gave a homogeneous mixture but no detectable reaction. Reaction commenced with the addition of 21 mL of benzonitrile; the mixture was stirred at 25 °C for 6 days while slow evolution of gas (CO) and eventual precipitation of a red solid occurred. The solution was purged with dry N_2 and then filtered under N_2 . The red solid (about 4 g) was rinsed with ether, dried in a stream of N_2 , and dissolved in CD_3CN . 1H NMR showed a nine-line pattern for C_6H_5CN , but ^{19}F NMR showed no F, indicating the solid to be NiI_2 with complexed benzonitrile.

Distillation of the filtrate gave 13.0 g (48%) of recovered $F(CF_2)_8I$, bp 30–35 °C (2 mm), followed by benzonitrile, and then 3.6 g of crystalline product which collected in the stillhead as the pot temperature rose to 190 °C. Sublimation of the solid at 35 °C (0.2 mm) afforded 2.8 g (14% conv) of product fluoroolefins, mp 36–38 °C. IR (melt): 1300–1100 cm^{-1} (CF). Raman: 1729.7 cm^{-1} (sym C=C). ^{19}F NMR at 94.1 MHz did not distinguish between the two olefins believed to be present, although broadening of some peaks was noted. NMR ($CFCl_3$): 1H none; ^{19}F -81.7 (t of t, $J_{FF} = 9.9$, 2.3 Hz, 6F, CF_3), -118.5 (m, 4F, $CF_2C=$), -122.1 (m, 8F, CF_2), -123.0 (m, 4F, CF_2), -123.7 (m, 4F, CF_2), -126.5 (m, 4F, CF_2), -153.9 (m, 2F, =CF).

Addition of *F*-Octyl Bromide to $Ni(CO)_4$. A two-phase mixture of 25.0 g (0.05 mol) of *F*-*n*-octyl bromide, 50 mL of acetonitrile, and 11.8 g (9.0 mL, 0.07 mol) of $Ni(CO)_4$ was stirred at 25 °C for 20 days while CO was very slowly evolved, the lower phase was diminished, and a light-colored solid eventually precipitated. Volatiles removed at 60 mm were discarded; volatiles removed at 25 °C (0.1 mm) were found to be acetonitrile and 8.0 g (32%) of recovered bromide as separate layers. The pale green, moist, solid residue was heated at 100–200 °C (0.1–0.5 mm) while product olefin (4.5 g, 23%) distilled and solidified. A sample of the crystallized distillate, mp 40–42 °C, gave with olefin derived from $F(CF_2)_8I$ a mixed mp 37–38.5 °C. GC showed the same single peak for both samples.

Preparation of 2,2,2-Trifluoroethyl 4-Iodohexafluorobutyrate and Reaction with $Ni(CO)_4$. (a) A mixture of 63.8 g (0.20 mol) of $ICF_2CF_2CF_2COF$, 22.0 g (0.22 mol) of 2,2,2-trifluoroethanol, 17.0 g (0.40 mol) of NaF, and 50 mL of ether was stirred overnight, filtered, and distilled to give 54.7 g (68%) of 2,2,2-trifluoroethyl 4-iodohexafluorobutyrate, bp 64–66 °C (25 mm). IR (neat): 2980 (satd CH), 1800 (C=O), 1250–1100 cm^{-1} (CF). NMR ($CDCl_3$): 1H δ 4.59 ($J_{HF} = 8$ Hz, CH_2CF_3); ^{19}F ϕ -59.9 (m, 2F, CF_2I), -74.5 (t, $J_{HF} = 8$ Hz, 3F, CH_2CF_3), -114.8 (s, 2F, CF_2), -117.7 (t, $J_{FF} = 11.5$ Hz, 2F, CF_2).

(b) A mixture of 54.0 g (0.134 mol) of the ester, 150 mL of purified acetonitrile, and 26.2 g (20.0 mL, 0.15 mol) of nickel carbonyl was stirred under N_2 at 50 °C for 7 h. GC indicated a trace only of unreacted ester. Volatiles were removed from the mixture under vacuum to leave a dark red solid, assumed to be mainly **3**. This residue was heated at 100–170 °C (1–0.1 mm) over a 4-h period. Volatiles collected in a -80 °C trap were mainly acetonitrile and 2.0 g (6%) of combined olefins **10a,b**, along with lesser amounts of recovered iodo ester and coupling products **9a,b**. For **10a**, GC/MS: *m/e* 258 (M^+), 239 ($M^+ - F$), 230 ($M^+ - CO$), 159 ($CF_2=CFCF_2CO^+$, weak), 131 ($CF_2=CFCF_2^+$), 127 ($CF_3CH_2O_2C^+$), 112 ($C_3F_4^+$), 93 ($C_3F_3^+$), 83 ($CF_3CH_2^+$), 69 (CF_3^+), 64 ($CF_2=CH_2^+$), 63 ($C_2F_2H^+$), 62 ($C_2F_2^+$),

51 (CHF_2^+), 50 (CF_2^+), 44 (CO_2^+). Isomers of **10b** were present as very minor components. For *cis*-**10b**, GC/MS: *m/e* 258 (M^+), 239 ($M^+ - F$), 189 ($M^+ - CF_3$), 159 ($CF_3CF=CFCO^+$, 100% peak), 131 ($C_3F_5^+$), 112 ($C_3F_4^+$), 93 ($C_3F_3^+$), 83 ($CF_3CH_2^+$), 69 (CF_3^+), 64 ($CF_2=CH_2^+$); essentially no $M^+ - CO$ (230) peak. For *trans*-**10b**, GC/MS: *m/e* 258 (M^+), 239 ($M^+ - F$), 189 ($M^+ - CF_3$), 159 ($CF_3CF=CFCO^+$, 100% peak), 131 ($C_3F_5^+$), 112 ($C_3F_4^+$), 93 ($C_3F_3^+$), 83 ($CF_3CH_2^+$), 69 (CF_3^+).

Distillate collected during the pyrolysis was 24.5 g of nearly pure **9a,b**. GC/MS: *m/e* 516 (M^+), 497 ($M^+ - F$), 389 ($M^+ - CF_3CH_2O_2C$), 361 ($M^+ - CF_3CH_2O_2C - CO$), 339 ($M^+ - CF_3 - CH_2O_2CCF_2$), 311 ($M^+ - CF_3CH_2O_2C - CF_2CO$), 261 ($M^+ - CF_3CH_2O_2C - CF_2CF_2CO$), 212 ($C_5F_8^+$), 193 ($C_5F_7^+$), 181 ($C_4F_7^+$), 162 ($CF_2=CFCF=CF_2^+$), 149 ($CF_3CH_2OCF_2^+$), 143 ($C_4F_5^+$), 131 ($CF_2=CFCF_2^+$), 127 ($CF_3CH_2O_2C^+$), 124 ($C_4F_4^+$), 112 ($C_3F_4^+$), 100 ($C_2F_4^+$), 93 ($C_3F_3^+$), 83 ($CF_3CH_2^+$), 69 (CF_3^+), 64 ($CF_2=CH_2^+$), 63 ($C_2F_2H^+$). A mass spectrum taken late in the peak had a negligible 339 peak for $CF_3CH_2O_2CCF_2^+$ and so was presumed to be mainly **9b**.

Fractionation of the distillate afforded 21.2 g (61%) of mixed isomers **9a,b**, bp 50–51 °C (0.2 mm). IR (neat): 2990 (satd CH), 1800 (C=O), 1300–1100 cm^{-1} (CF, C–O), with a weak band at 1720 (C=C). The NMR spectrum indicated a 2:5 mixture of **a/b**. For **9a**, NMR ($CDCl_3$): 1H δ 4.61 (q, $J_{HF} = 7.5$ Hz, CH_2CF_3); ^{19}F ϕ -74.6 (t, $J_{HF} = 7.5$ Hz, 6F, CH_2CF_3), -119.1 (m, 4F, CF_2), -120.3 (m, 4F, CF_2), -154.7 (m, 2F, =CF). For **9b**, NMR ($CDCl_3$): 1H δ 4.61 (q, $J_{HF} = 7.5$ Hz, 2H, CH_2CF_3), 4.57 (q, $J_{HF} = 7.5$ Hz, 2H, CH_2CF_3); ^{19}F ϕ -74.6 (t, $J_{HF} = 7.5$ Hz, 3F, CH_2CF_3), -74.7 (t, $J_{HF} = 7.5$ Hz, 3F, CH_2CF_3), -110.2 (d of d of t, $J_{FF} = 17$, 12.5, 1.5 Hz, 2F, C=CCF₂C=O), -118.6 (m, 2F, $CF_2C=C$), -119.1 (t, $J_{FF} = 10$ Hz, 2F, $CF_2C=O$), -125.1 (s, 2F, CF_2), -155.8 (A branch d of m, $J_{FF} = 139$ Hz, 1F, =CF), -158.0 (B branch d of m, $J_{FF} = 139$ Hz, 1F, =CF).

Anal. Calcd for $C_{12}H_4F_{16}O_4$: C, 27.93; H, 0.78; F, 58.89. Found: C, 27.71; H, 0.82; F, 58.65.

***F*-Cyclohexene from *F*-1,6-Diiodohexane.** A mixture of 55.4 g (0.10 mol) of *F*-1,6-diiodohexane, 100 mL of acetonitrile, and 17.1 g (13.0 mL, 0.10 mol) of $Ni(CO)_4$ was stirred for 2 days at 25 °C. Another 17.1 g (0.10 mol) of $Ni(CO)_4$ was added, and the mixture was stirred for 2 days more. Then 8.55 g (0.05 mol) of $Ni(CO)_4$ was added and the reaction continued for 3 days. The total of 10.5 mL of $Ni(CO)_4$ which had collected in the -80 °C trap was returned to the pot, and the reaction was continued for another 11 days. Unreacted $Ni(CO)_4$ and some acetonitrile were removed by evacuation to 25 °C (20 mm); then the remaining volatiles were transferred at 25 °C (0.1 mm) to give a moist, red solid residue. Pyrolysis was conducted at 130–150 °C under vacuum over 3 h. Heating the residue slowly to 205 °C (0.1 mm) allowed distillation of 6.0 g of a viscous oil (**8**) with a broad boiling point range and from which free iodine was being liberated at the higher temperatures. IR (neat): 1300–1100 cm^{-1} (st, CF) with very weak bands for unsaturation at 1785 and 1715 cm^{-1} . Extraction of the distillation residue with 100 mL of $CFCl_2CF_2Cl$ and evaporation of solvent gave 4.5 g of higher molecular weight **8** as a thick oil. IR (neat): 1300–1100 cm^{-1} (st, CF) with a weak band at 1715 cm^{-1} (C=C). Attempted distillation of this material caused further liberation of free iodine. The residue was finally warmed with 3 \times 500 mL of water to leave 8.3 g of rubbery dark tar which exhibited a similar IR spectrum and also liberated iodine on heating.

Volatile products collected in cold traps during the pyrolysis were washed with water, dried over $CaSO_4$, and distilled to afford 8.3 g (32%) of *F*-cyclohexene, bp 50–52 °C, identified by comparison of GC and IR traces with those of an authentic sample.

***F*-Hexadiene-2,4 from *F*-Allyl Iodide.** A mixture of 78.3 g (0.30 mol) of *F*-allyl iodide and 100 mL of acetonitrile was stirred while 56.3 g (0.33 mol) of $Ni(CO)_4$ was added dropwise over an 8-h period. Rapid evolution of CO occurred during the addition while the solution first decolorized (scavenging of free iodine), then became dark red, and finally produced a red crystalline precipitate. After having been stirred overnight, the mixture was evacuated at 20 °C (40 mm) until 68 mL had collected in the -80 °C trap. Treatment of the trap

contents with 65.8 g (0.26 mol) of I₂ in 200 mL of acetonitrile until Ni(CO)₄ was removed and transfer of volatiles at 20 °C (40 mm) gave 21.9 g (56%) of a lower layer of **4**; GC indicated a 34:51:15 ratio of *cis,cis* to *cis,trans* to *trans,trans* isomers. Distillation afforded 19.2 g (49%) of fractions rich in each isomer with a range of bp 39–58 °C. For the fraction bp 39–40 °C and 85:15 of *cis,cis* to *cis,trans*, IR (CCl₄): 1750 (w) and 1710 (m) (conj. C=C), 1250–1150 cm⁻¹ (CF). The *cis,cis* isomer had NMR (CCl₄): ¹⁹F ϕ 69.9 (d of t, $J_{\text{FF}} = 10.8, 5.3$ Hz, 6F, CF₃), -127.1 (s, $J_{\text{FF}} = 5.3$ Hz, 2F, central =CF), -139.4 (q, $J_{\text{FF}} = 10.8$ Hz, 2F, CF₃CF). For the fraction bp 50–56 °C and 89% *cis,trans*, IR (CCl₄): 1740 (w) and 1705 (w) (conj. C=C), 1300–1150 cm⁻¹ (CF). The *cis,trans* isomer had NMR (CCl₄): ¹⁹F ϕ -69.6 (d of d of d, $J_{\text{FF}} = 21, 9.5, 3$ Hz, 3F, CF₃), -70.7 (m, 3F, CF₃), -135.3 (d of m, $J_{\text{FF}} = 38$ Hz, 1F, =CF), -140.8 (m, 1F, =CF), -148.0 (A branch d of d of q of m, $J_{\text{FF}} = 144, 38, 21$ Hz, 1F, *trans*=CF), -154.0 (B branch d of m, $J_{\text{FF}} = 144$ Hz, 1F, *trans*=CF). For the fraction bp 56–58 °C and 17:83 *cis,trans* to *trans,trans*, IR (CCl₄): 1770 and 1705 (both extremely weak, conj. C=C), 1300–1100 cm⁻¹ (CF). UV: λ_{225} nm CH₃CN 15 800. The *trans,trans* isomer had NMR (CCl₄): ¹⁹F ϕ -69.2 (m, 6F, CF₃), -153.5 (A branch d of m, $J_{\text{FF}} = 129$ Hz, 2F, *trans*=CF), -157.0 (B branch d of m, $J_{\text{FF}} = 129$ Hz, 2F, *trans*=CF).

The reaction of *F*-allyl iodide with Ni(CO)₄ gives close to the thermodynamic mixture of diene isomers. When a 39:43:18 mixture of isomers of **4** was heated with CsF catalyst at 100 °C for 6 h, the product was the same three isomers in a 33:44:20 ratio (GC result). Treatment with CsF at 150 °C for 20 h gave a 36:43:19 mixture. The presence of a short retention time peak in 1–2% amounts may be due to the formation of a small amount of a *F*-hexyne; in contrast, *F*-butadiene is isomerized readily to hexafluoro-2-butyne, since two relatively high energy terminal double bonds are lost in the process.

Formation and Thermolysis of Adduct 11. Postulated intermediate **6** is assumed to pyrolyze cleanly to olefin mixture **5a,b**. On that basis, a secondary (fluoroalkyl)nickel derivative such as **11** would also be expected to form uncoupled olefin. A mixture of 29.6 g (0.10 mol) of *F*-isopropyl iodide, 20 g (16 mL, 0.12 mol) of nickel carbonyl, and 100 mL of acetonitrile was stirred at 40 °C for 6.5 h. GC analysis indicated the iodide was all reacted. Volatiles (15 mL) were partially removed at 25 mm, and the residual red solution was indicated by NMR to contain (CF₃)₂CFNiI. NMR (CD₃CN/CH₃CN): ¹⁹F ϕ -67.5 (broad s, 6F, CF₃), -75.4 (broad s, 1F, CF-Ni), with only traces of fluorinated impurities.

The remainder of the volatiles was removed under vacuum, and the residue was pyrolyzed at 80–160 °C (0.5 mm). Volatile products were identified by IR as hexafluoropropene with a very minor amount of 2-H-heptafluoropropane; liquid product was acetonitrile containing a trace of heptafluoroisopropyl iodide. No coupling product was detected.

Reaction of Adduct 1 with Ethyl Diazoacetate. A mixture of 22.3 g (0.05 mol) of F(CF₂)₆I, 100 mL of purified acetonitrile, and 10 mL (13.1 g, 0.077 mol) of nickel carbonyl was stirred under N₂ at 50 °C for 6 h. The mixture was stirred for 10 days while red crystals precipitated; GC indicated only traces of starting materials left. When 5.7 g (0.05 mol) of ethyl diazoacetate was added, immediate gas evolution and an exotherm with dissolution of red solid occurred. Volatiles removed under vacuum at 25 °C were almost entirely acetonitrile. Pyrolysis of the residue at 100–180 °C (0.3 mm) gave two main products along with additional acetonitrile. The first was 10.6 g (71%) of isomeric *F*-dodecenes and 1.4 g (7%) of ester **12**, as indicated by the mass spectrum. GC/MS: *m/e* 359 (M⁺ - C₂H₃), 342 (M⁺ - C₂H₄O), 341 (M⁺ - C₂H₅O), 172 (CF₂-CF₂CF=CHC=O⁺), 153 (CF₂=CFCF=CHC=O⁺), 122 (CF₂-CF=CHC=O⁺), 119 (CF₃CF₂⁺), 117 (CF=CHCO₂CH₂CH₃⁺), 94 (CF₂CF=O⁺), 75 (C₃F₂H⁺), 69 (CF₃⁺).

Addition of 1,1,1,3-Tetrachlorotetrafluoropropane to Ni(CO)₄. A mixture of 25.4 g (0.10 mol) of 1,1,1,3-tetrachlorotetrafluoropropane and 50 mL of acetonitrile was stirred under N₂ at 25 °C while 17.1 g (13 mL, 0.10 mol) of nickel carbonyl was added dropwise. Evolution of gas and precipita-

tion of solid occurred while the mixture was stirred for 2 days. Volatiles were transferred under vacuum and fractionated to give a series of cuts, bp 67–81 °C. GC and NMR indicated low yields of coupling products **18** and **19** present in the highest and lowest boiling fractions, respectively.

In a fraction, bp 70–72 °C, the major components were **17** and **Z-15**. For **17**, IR (CCl₄): 1650 cm⁻¹ (C=C). NMR (CDCl₃): ¹H CH₃CN singlet only; ¹⁹F ϕ -54.9 (d, $J_{\text{FF}} = 12$ Hz, 2F, =CCF₂Cl), -113.5 (t, $J_{\text{FF}} = 12$ Hz, 1F, =CF). GC/MS: *m/e* 198 + 200 + 202 (M⁺), 163 + 165 + 167 (M⁺ - Cl), 109 + 111 (C₃F₂Cl⁺), 93 (C₃F₃⁺), 85 + 87 (CICF₂⁺), 78 + 80 (C₂FCl⁺). For **Z-15**, IR (CCl₄): 1840 (conj. COF), 1650 cm⁻¹ (C=C). NMR (CDCl₃): ¹⁹F ϕ 40.1 (d of t, $J_{\text{FF}} = 17, 12$ Hz, 1F, COF), -57.4 (t, $J_{\text{FF}} = 12$ Hz, 2F, =CCF₂Cl), -99.3 (d of t, $J_{\text{FF}} = 17, 12$ Hz, 1F, =CF). GC/MS: *m/e* 210 + 212 + 214 (M⁺), 175 + 177 (M⁺ - Cl), 163 + 165 + 167 (M⁺ - COF), 147 + 149 (M⁺ - Cl - CO), 125 + 127 (M⁺ - CF₂Cl), 109 + 111 (C₃F₂Cl⁺), 93 (C₃F₃⁺), 85 + 87 (CICF₂⁺).

In a fraction, bp 81 °C, only acetonitrile and *E-15* were present. For *E-15*, IR (CH₃CN): 1830 (conj. COF), 1640 (C=C). NMR (CDCl₃/CH₃CN): ¹⁹F ϕ 31.3 (d, $J_{\text{FF}} = 65.5$ Hz, 1F, COF), -58.4 (d, $J_{\text{FF}} = 8$ Hz, 2F, =CCF₂Cl), -98.1 (d of t, $J_{\text{FF}} = 65.5, 8$ Hz, 1F, =CF). GC/MS: spectrum contains the same masses as for **Z-26**, but in slightly different proportions.

Yields based on GC analyses were 2.4 g (12%) of **17** and 4.2 g (20%) of mixed *E/Z-15*.

For **18** (ref 7), GC/MS: *m/e* 364 + 366 + 368 (M⁺), 329 + 331 + 333 (M⁺ - Cl), 279 + 281 + 283 (M⁺ - CF₂Cl), 229 + 231 + 233 (M⁺ - CF₂CF₂Cl), 109 + 111 (C₃F₂Cl⁺), 85 + 87 (CICF₂⁺).

Computational Details

Geometries were gradient optimized¹⁶ with a double- ζ basis set augmented by polarization functions on C.¹⁷ This basis set has been shown to give good results for the structures of a wide range of fluorocarbons.¹⁸ Frequencies were calculated analytically¹⁹ at this level and scaled by 0.9 for use in calculating the zero-point corrections to the reaction energies. Final energies were obtained at the MP2/DZP//HF/DZ+D_C level.²⁰ All calculations were done with the programs GRAD-SCF²¹ on Cray computer systems and with Gaussian94²² on Silicon Graphics computer systems.

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(16) (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595. (b) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 202. (c) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153.

(17) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1.

(18) Dixon, D. A. *J. Phys. Chem.* **1988**, *92*, 86.

(19) (a) King, H. F.; Komornicki, A. *J. Chem. Phys.* **1986**, *84*, 5465. (b) King, H. F.; Komornicki, A. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jorgenson, P., Simons, J., Eds.; NATO ASI Series C., Vol. 166, D. Reidel: Dordrecht, 1986; p 207.

(20) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(21) GRADSCF is an ab initio program system designed and written by A. Komornicki at Polyatomics Research.

(22) Gaussian94, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.