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Fluoroorganometallic Chemistry: Carbon–Fluorine Bond Activation in Perfluorometallacyclopentane Complexes

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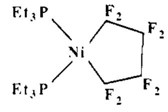
Reactions of the perfluorometallacyclopentane complex $Ni(PEt_3)_2(CF_2)_4$ with strong Lewis acids have been investigated. With 1 equiv of BF_3, the product is $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$. The reaction is believed to occur through fluoride abstraction from carbon by BF_3, phosphine migration to the resulting carbene, and BF_4^- coordination. Addition of 2 equiv of BF_3 yields a purple solid presumed to result from two fluoride abstractions and phosphine migrations. The solid reacts with bis(diphenylphosphino)ethane (DPPE) to yield $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$. The three perfluorometallacycle complexes in this series have been characterized crystallographically. $Ni(PEt_3)_2(CF_2)_4$ crystallizes in the space group *Pnn*2 with cell dimensions a = 10.155 (3), b = 10.872 (4), and c = 9.954 (3) Å. $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ crystallizes in space group $P2_1/n$ with cell dimensions a = 13.680 (5), b = 13.734 (4), c = 12.977 (5) Å, and β = 93.00 (3)°. $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$ crystallizes in space group $P2_1/c$ with cell dimensions a = 23.483 (5), b = 14.516 (8), c = 15.774 (5) Å, and β = 102.31 (3)°.

Introduction

Among the most distinctive characteristics of saturated fluorocarbons is their low reactivity,[1] a consequence of the high strength of the C–F bond.[2] As part of our exploratory effort in transition-metal organofluorine chemistry,[3] we have sought means of exploiting transition metals to effect synthetically useful transformations of fluorocarbons, a goal with a potentially large impact on the science of fluorocarbon-based polymers and specialty chemicals. Our approach has been to merge new synthetic methods in organofluorine chemistry with the known reactivity of transition-metal compounds. Herein we describe the reactivity of a perfluorometallacyclopentane complex toward strong Lewis acids giving rise to a reaction sequence comprised of extraction of fluoride ions from the coordinated perfluorometallacycle followed by quenching the transiently stable carbene species by migration of an ancillary ligand from the metal to a carbon atom of the metallacyclic ring. The result is an unprecedented substituted perfluorometallacycle with a phosphonium ylide structure.

Early work in fluoroorganometallic chemistry concerned the oxidative coupling of tetrafluoroethylene by low-valent transition-metal complexes to form perfluorometallacyclopentane compounds.[4,5] Electrophilic halogen exchange between Lewis acids and perfluoroalkyl metal carbonyl complexes proceeds through carbenoid intermediates (Scheme I, eq 1).[6] The reactivity of the readily prepared perfluorometallacyclopentane complexes toward strong Lewis acids was unexplored. Furthermore, analogous perhydrometallacyclopentane complexes are known in some cases to be in equilibrium with the corresponding bis(olefin) complex.[7] Analogous equilibria have never been demonstrated for perhalometallacyclopentane complexes (Scheme I, eq 2). Combination of these two reactions in a perfluorometallacyclopentane complex should cause chlorine to appear not only on the α-carbon atom of the metallacycle but also on the β-carbon as depicted by the sequence of eq 1–3 in Scheme I. To test this hypothesis we reacted the perfluorometallacyclopentane complex $Ni(PEt_3)_2(CF_2)_4$



with strong Lewis acids and were surprised to observe a reaction manifold different from what the literature might suggest:[6] quenching of the reactive carbenoid intermediate to yield ylide complexes of the metallacycle. This reaction sequence is described below.

Experimental Section

All experiments were performed in a nitrogen-filled drybox equipped with a built-in freezer, on a standard Schlenk line with argon source or on a vacuum line. ^{19}F NMR spectra (188 or 282

[†] Contribution no. 4599.

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(2) Carbon–fluorine bond dissociation energies range from 109 to 130 kcal/mol and are substantially stronger than analogous C–H bonds. See ref 1b.

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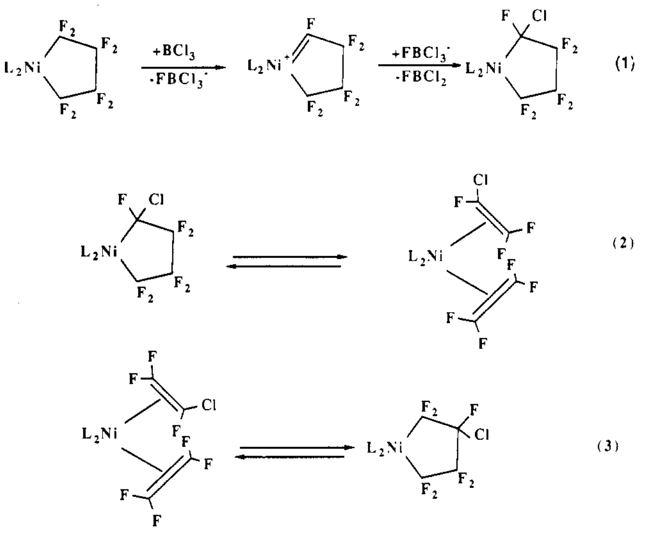
Scheme I



MHz) are reported in parts per million relative to $CFCl_3$, $^{31}P\{^1H\}$ NMR spectra (122 MHz) are reported in parts per million relative to 85% H_3PO_4, and ^1H NMR spectra (300 MHz) are reported in parts per million relative to $Si(CH_3)_4$. All coupling constants are reported in hertz. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 983 spectrophotometer. Ether, toluene, THF, and pentane were distilled from sodium benzophenone ketyl, and CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5. BF_3 and BF_3·ether were purchased from Matheson and Aldrich and used as received. DPPE was purchased from Aldrich and recrystallized from hot ethanol prior to use. The starting material $Ni(PEt_3)_2(CF_2)_4$ was prepared by the literature procedure.[5a] *Caution! C_2F_4 is potentially explosive and should be handled in well-shielded equipment with rigorous exclusion of oxygen. Heating uninhibited C_2F_4 should be avoided.*

Preparation of $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$. In a typical reaction, 0.60 g (1.21 mmol) of $Ni(PEt_3)_2(CF_2)_4$ in approximately 10 mL of CH_2Cl_2 reacted with 1.21 mmol of BF_3 in a 500-mL reaction flask. The volume of BF_3 was measured by standard vacuum line techniques. There was a near instantaneous color change from deep yellow to red-brown. The solution was stirred for 24 h at room temperature. The solution was then filtered on a fine porosity frit. Addition of approximately 3 mL of ether followed by sufficient pentane to cause cloudiness in the solution and then cooling to −35 °C resulted in formation of large maroon colored crystals suitable for X-ray crystallography. Yield: 0.480 g, 70%. Toluene was found to be a suitable alternative solvent to CH_2Cl_2 for this reaction, and $BF_3{\cdot}OEt_2$ was a suitable alternative to gaseous BF_3. Anal. Calcd for $C_{16}H_{30}F_{11}NiP_2B$: C, 34.1; H, 5.37. Found: C, 33.8; H, 5.47. IR (cm^{-1}, % T): 1418, 32; 1323, 29; 1250, 30; 1203, 28; 1128, 12; 1974, 32; 1041, 22; 997, 21; 964, 25; 925, 30; 888, 15; 820, 51; 768, 27; 738, 19; 633, 45. ^{19}F NMR (CD_2Cl_2, +25 °C): −92.5 (dd, J = 247, 21, 1 F), −100.8 (ddd, J = 247, 58, 17, 1 F), −116.3 (dd (t), J = 267, 30 (~20, 20, and 21), 1 F), −128.1 (dd, J = 267, 11, 1 F), −130.7 (dt, J = 245, 11, 1 F), −131.7 (ddd, J = 245, 20, 17, 1 F), −163 (exchange broadened, BF_4^-, 4F), and −220.0 (dd, J = 62, 30, 1 F). ^{19}F NMR (CD_2Cl_2, −80 °C): slight changes in chemical shifts; exchange process of BF_4^- halted, giving singlets at −151.1 and −151.5 ppm (3 F and 1 F). While most of the ^{19}F–^{19}F and ^{19}F–^{31}P coupling constants could be determined, it was not possible to assign the various resonances to specific nuclei. ^1H NMR (CD_2Cl_2, +25 °C): 2.00 (mult, 12 H), 1.05 (mult, 18 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): 42.6 (ddd, J = 62, 20, 11, 1 P), 16.5 (d, J = 58, 1 P).

Preparation of $[Ni(PEt_3)(H_2O)(CF(PEt_3^+)(CF_2)_3)][BF_4^-]$. A solution of $Ni(PEt_3)(BF_4)(CF(PEt_3)(CF_2)_3)$ (4.51 g, 8.0 mmol) in methylene chloride/THF (1:1, 80 mL) was treated with an excess of water (0.29 g, 16.0 mmol). The solution lightened to yellow over a period of an hour. The volume was reduced until solids started to appear, and then ether was added slowly, giving a yellow product in nearly quantitative yield. Yield: 4.59 g, 98.8%. Anal. Calcd for $C_{16}H_{32}F_{11}NiP_2OB$: C, 33.1; H, 5.55; F, 36.0. Found: C, 33.3; H, 5.86; F, 36.3. IR (cm^{-1}, % T): 3470, 23; 3413, 24; 3310, 34; 1665, 26; 1420, 24; 1377, 20; 1319, 16; 1248, 21; 1204, 16; 1144, 13; 1124, 6; 1110, 7; 1060, 7; 1016, 8; 989, 7; 955, 10; 890, 8; 825, 39; 768, 17; 740, 19; 695, 38; 631, 34; 600, 40; 525, 44; 509, 43; 484, 46; 427, 42. Changes upon D_2O substitution: 3470, 3413, and 3310 cm^{-1} shift to 2586, 2509, and 2440 cm^{-1}; 1665 cm^{-1} shifts to 1230 cm^{-1}. ^{19}F NMR (CD_2Cl_2, +25 °C): −93.2 (ddd, J = 259, 18, 9, 1 F), −102.0 (dddd, J = 259, 54, 15, 11, 1 F), −112.8 (dtt, J = 268, 20, 5, 1 F), −123.8 (dm, J = 268, 1 F), −127.9 (ddq, J = 247, 20, 10, 1 F), −130.0 (dtd, J = 247, 16, 9, 1 F), −149.3 (BF_4^-, 4F), −222.7 (ddd, J = 62, 26, 10, 1 F). ^1H NMR (CD_2Cl_2, +25 °C): 3.36 (br, 2 H), 2.36 (qd, J = 8, 4, 6 H), 1.65 (q, J = 8, 6 H), 1.53 (dt, J = 18, 8, 9 H), 1.25 (dt, J = 16, 8, 9 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): 42.2 (ddd, J = 62, 20, 11, 1 P), 17.2 (d, J = 54, 1 P).

Reaction of $Ni(PEt_3)(BF_4)(CF(PEt_3)(CF_2)_3)$ with NEt_3. A solution of $Ni(PEt_3)(BF_4)(CF(PEt_3)(CF_2)_3)$ (50 mg) in CD_2Cl_2 in an NMR tube was combined with a twofold excess of NEt_3 at 0 °C. There was no change in the NMR spectra, so the sample was warmed to room temperature. After 24 h there was still no evidence for reaction.

Preparation of $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$. $Ni(PEt_3)_2(CF_2)_4$ (1.80 g, 3.63 mmol) in approximately 30 mL CH_2Cl_2 was combined with 7.50 mmol BF_3 in a 500 mL reaction tube on a vacuum line. The quantity of BF_3 was determined by standard vacuum line techniques. There was a nearly instantaneous color change first from yellow to maroon and then ultimately (within approximately 5 min) to purple. The reaction solution was stirred for an additional 24 h at room temperature. During this time nearly all the nickel-containing materials precipitated as a purple powder that was isolated by filtration. This highly air-sensitive purple product was insoluble in all common laboratory solvents. Yield: 2.01 g, 88%. IR (cm^{-1}, % T): 1415, 47; 1323, 46; 1255, 48; 1222, 38; 1152, 22 (sh), 1131, 18; 1057, 35; 1040, 43 (sh); 1030, 48; 969, 41; 922, 38; 886, 23; 787, 48; 757, 44; 725, 28; 513, 53. The same compound was obtained when BF_3 etherate was substituted for BF_3.

A slurry of 0.60 g of the purple insoluble powder prepared as described above in approximately 35 mL of CH_2Cl_2 was treated dropwise with stirring over the course of approximately 2 h with a solution of 0.40 g (0.50 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, DPPE, in approximately 20 mL of CH_2Cl_2. As the phosphine solution was added, the purple insoluble powder dissolved to yield a clear orange solution. The solution was then filtered on a fine porosity frit. Equal volumes of ether and pentane were added to just induce cloudiness. Then the solution was cooled to −35 °C for 24 h to yield a crop of crystals of $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$. Yield: 0.84 g, 86%. Anal. Calcd for $C_{42}H_{54}F_{14}NiP_4B_2$: C, 49.0; H, 5.29; F, 25.9. Found: C, 49.2; H, 5.13; F, 26.3. IR (cm^{-1}, % T): 1439, 29; 1419, 48; 1309, 48; 1271, 49; 1239, 56; 1205, 47 (sh); 1194, 42; 1169, 56; 1102, 25; 1096, 27 (sh); 1056, 18; 997, 36; 929, 41; 876, 51; 823, 53; 787, 49; 776, 51; 755, 41; 733, 37; 718, 40; 698, 34; 626, 69; 615, 69; 530, 43; 485, 57 (sh); 472, 56. ^{19}F NMR (CD_2Cl_2, +25 °C): −103.4 (d, J = 248, 2 F), −104.4 (d, J = 248, 2 F), −152.2 and −152.3 (for ^{11}B and ^{10}B BF_4^-, respectively, 8 F), −184.4 (br s, 2 F). ^1H NMR (CD_2Cl_2, +25 °C): 8.2–7.5 (mult, aryl, 20 H), 2.70 (d of d, 2 H, J_1 = 9 Hz, J_2 = 50 Hz), 2.00 (mult, 4 H), 1.80 (mult, 4 H), 1.05 (d of t, J = 32 Hz for d splitting, J = 12 Hz for t splitting, 24 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): 50.4 (d, J = 67 Hz), 36.4 (d of d, $J_1 \approx J_2$ = 27 Hz).

Preparation of $Ni((i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2)(CF_2)_4$. $Ni(COD)(CF_2)_4$ was prepared by the literature method.[5a] A solution of $Ni(COD)(CF_2)_4$ (0.414 g, 1.13 mmol) in ether (30 mL) was combined with $(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$ (0.404 g, 1.54 mmol) in ether (10 mL). After about a 5-mL addition, the color went to very light yellow. Within 20 min after the addition was complete, light yellow precipitate began to form. The reaction was allowed to stir for an additional 30 min with no change. The light yellow powder was collected by vacuum filtration and dried. The filtrate was concentrated under vacuum and pentane was added yielding more light yellow precipitate that was collected and dried under vacuum. Combined yield: 0.379 g, 65%. Mp: 239 °C. Anal. Calcd for $C_{18}H_{32}F_8NiP_2$: C, 41.5; H, 6.19; P, 11.9. Found: C, 41.4; H, 5.88; P, 11.5. IR (cm^{-1}, % T): 1423, 45; 1412, 39; 1387, 17; 1374, 13; 1337, 21; 1298, 42; 1258, 26; 1240, 25 (sh); 1228, 23; 1143, 13; 1132, 16 (sh); 1076, 22; 1038, 28; 1018, 43; 983, 15 (sh); 975, 14 (sh); 955, 13; 940, 14; 902, 13; 886, 13; 861, 20; 836, 33; 798, 45;

Table I. Crystal Structure Data for the Compounds $Ni(PEt_3)_2(CF_2)_4$, $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$, and $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$

	perfluoro-metallacycle	mono(ylide)	bis(ylide)·$2CH_2Cl_2$
formula	$NiP_2F_8C_{16}H_{30}$	$NiP_2F_{11}C_{16}H_{30}B$	$NiP_4F_{14}C_{44}H_{58}Cl_4B_2$
fw	495.07	562.88	1198.99
space group	*Pnn*2, No. 34	$P2_1/n$, No. 14	$P2_1/c$, No. 14
a, Å	10.155 (3)	13.680 (5)	23.483 (5)
b, Å	10.872 (4)	13.734 (4)	14.516 (8)
c, Å	9.954	12.977 (5)	15.774 (5)
β, deg		93.00 (3)	102.31 (3)
V, $Å^3$	1099.0	2434.8	5253.4
Z	2	4	4
D(calcd), g cm^{-3}	1.496	1.535	1.516
cryst dimen, mm	0.48 × 0.45 × 0.50	0.28 × 0.15 × 0.43	0.35 × 0.35 × 0.30
temp, °C	−70	−75	−70
radiatn	Mo Kα (graphite monochromated, λ = 0.71069 Å)		
μ, cm^{-1}	10.93	10.12	7.75
2θ limits, deg	3.8–55	4.2–55	1.8–48
max *hkl*	12, 13, 14	17, 17, 16	26, 16, 18
octants	+++, −−−	+++, −++	+++, −++
scan width (ω, deg)	1.2–1.8	2.1–2.4	1.2–1.5
scan speed (deg/min)	1.8–5.0	2.5–5.0	1.5–5.0
data, $I_o \geq$ $(3\sigma(I_o)$	991	2856	4548
anomalous terms	Ni, P	Ni, P	Ni, Cl, P
final no. of variables	122	280	622
R	0.036	0.047	0.052
R_w	0.036	0.043	0.051

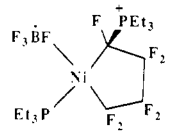
723, 57; 698, 29; 678, 35; 650, 32; 630, 36; 613, 44; 564, 50; 520, 49; 488, 53; 468, 49. ^{19}F NMR (CD_2Cl_2, +25 °C): −102.8 (t, *J* = 24, 4 F), −139.2 (s, 4 F). ^1H NMR (CD_2Cl_2, +25 °C): 2.27 (h, *J* = 7, 4 H), 1.70 (d, *J* = 11, 4 H), 1.27 (dd, *J* = 16, 7, 12 H); 1.16 (dd, *J* = 13, 7, 12 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, +25 °C): 75.7 (q, *J* = 24, 2P).

Reaction of $Ni((i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2)(CF_2)_4$ with BF_3. A sample of $Ni((i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2)(CF_2)_4$ (50 mg) in CD_2Cl_2 (1 mL) was combined with a twofold excess of BF_3·(ether) at room temperature in an NMR tube. The NMR spectra were unchanged after an hour. The sample was heated at 50 °C for an additional 2 h with no evidence of reaction.

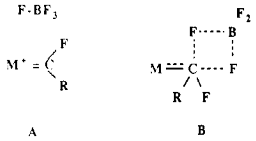
X-ray Structure Determinations. Many of the details of the crystal structures are given in Table I. Data were collected on a Enraf-Nonius CAD-4 diffractometer using the ω-scan method. The scan width was increased in the data collection for $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ because of split diffraction peaks (see Table I). In each data collection, the standards showed a 3–4% decrease in intensity; the data were adjusted appropriately. An absorption correction was applied to the data for the mono(ylide); transmission coefficients (DIFABS) varied by 46%. The structures were solved by automated Patterson techniques (PHASE). Refinements were carried out by full-matrix least squares on *F* by using scattering factors from ref 8 and included anomalous terms for the atoms indicated in Table I. The weighting scheme was proportional to $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions and isotropic thermal parameters were fixed. In $Ni(PEt_3)_2(CF_2)_4$, the largest residual density of 0.49 e/$Å^3$ was found near Ni. In $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$, the largest residual density of 0.50 e/$Å^3$ was found near carbon atoms (C23, C24) of one of the ethyl groups that was disordered. The elongated thermal ellipsoids are indicative of the disorder. In $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$, the largest residual density of 1.13 e/$Å^3$ was found near one BF_4 anion, suggesting a slight contribution from a second orientation.

Results and Discussion

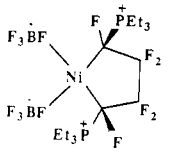
When $Ni(PEt_3)_2(CF_2)_4$ reacts with BCl_3, no evidence for electrophilic halogen exchange on the perfluorometallacycle ring is observed. Instead, the strong Lewis acids BCl_3 and BF_3 effect an irreversible transformation of the perfluorometallacycle; the precise outcome of the reaction depends on the stoichiometry. When $Ni(PEt_3)_2(CF_2)_4$ reacts with 1 equiv of BF_3, a maroon-colored material is formed. This compound was crystallized from organic solvents, yielding single crystals suitable for an X-ray diffraction study which revealed that this complex is a phosphonium ylide compound, $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$, as depicted below.



Perspective views of $Ni(PEt_3)_2(CF_2)_4$ and $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ are given in Figures 1 and 2, respectively. A detailed description of the structures follows later in this discussion. The structure of $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ reveals that an α-fluoride was in fact extracted from the perfluorometallacyclopentane ring, in accord with the literature precedent.[6] A transiently stable fluorocarbene–fluoroalkyl metal complex was presumably generated but was not detected. In a subsequent step, one of the phosphine ligands migrated to the carbene carbon generating an ylide-like structure. The coordination site vacated by the phosphine was occupied by a monodentate tetrafluoroborate ligand. The postulated reaction sequence is depicted in Scheme II. Whether the reaction is fully ionic (as in A) or is of a concerted nature (as in B) remains unclear.



The starting perfluorometallacycle, $Ni(PEt_3)_2(CF_2)_4$, reacts nearly instantaneously at room temperature with excesses (>2 equiv) of BF_3 to give an ultimate product different from the one described above. In this case, a purple insoluble powder is formed quantitatively in the reaction. The insolubility of this product precluded obtaining NMR spectra or a single-crystal X-ray diffraction study. However, the infrared spectrum suggests that BF_4^- is formed and that the purple insoluble powder still bears fluorocarbon ligands; absorptions at 1060 (s, br), 1040 (m, sh), and 1030 (w, sh) cm^{-1} are attributed to BF_4^-, and C–F absorptions were found at 1255 (w), 1227 (m), 1152 (s), and 1135 (s) cm^{-1}. Therefore, BF_3 reacts irreversibly with $Ni(PEt_3)_2(CF_2)_4$ to effect fluoride ion abstraction, leaving a new nickel fluorocarbon complex as a purple insoluble powder. On the basis of the outcome of the reaction of the perfluorometallacycle with 1 equiv of BF_3, we postulated an analogous outcome for the reaction with excesses of strong Lewis acid. The proposed structure of the purple insoluble powder is as shown below.



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[8] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

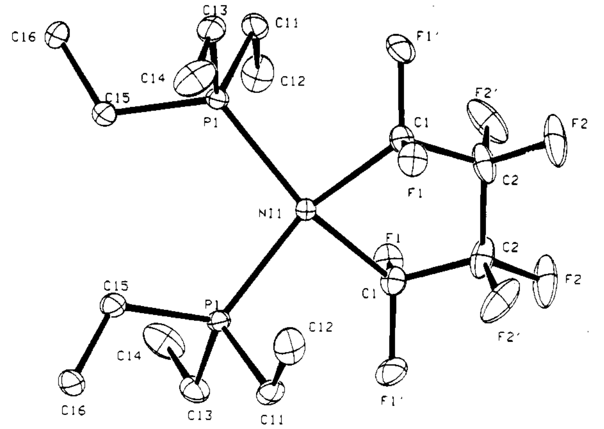


Figure 1. Perspective view of $Ni(PEt_3)_2(CF_2)_4$ displaying non-hydrogen atoms and atom-labeling scheme.

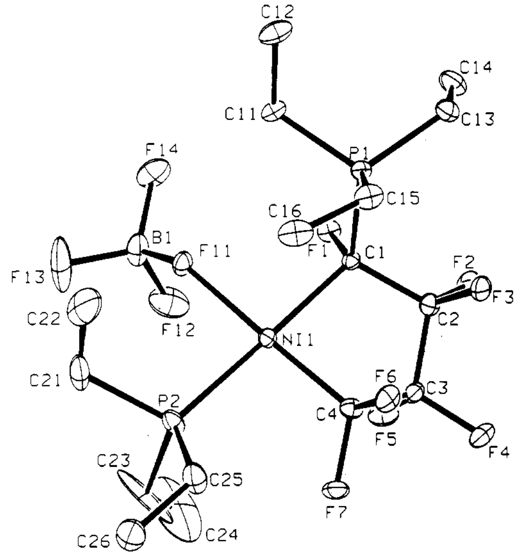
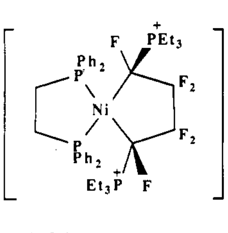


Figure 2. Perspective view of $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ displaying non-hydrogen atoms and atom-labeling scheme.

To test the assumption that the purple insoluble powder was in fact a bis(ylide) complex, it was derivatized by reaction with the chelating bis(phosphine) ligand DPPE ($(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$). The purple compound rapidly dissolves into a solution containing 1 equiv of DPPE to give an orange solution from which yellow-orange crystals suitable for a single-crystal X-ray diffraction study were isolated in high yield. Spectroscopic studies revealed that the cationic bis(ylide) was the sole product formed in this reaction. The crystal structure of this product showed that it was a bis(ylide) dicationic complex, [Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]$_2$.



A perspective view of this structure can be found in Figure 3. The structure suggests that the purple insoluble compound is the product of two sequential fluoride abstractions, each followed by triethylphosphine migration to the unsaturated carbon atom. The two vacant coordination sites are occupied by the tetrafluoroborate anions. In the case of the DPPE derivative, the tetrafluoroborate ligands are displaced and the DPPE chelates the nickel atom. Boron trichloride behaves similarly, but crystalline products were not obtained. Attempted reaction of the DPPE adduct with TAS-F (tris(dimethylamino)sulfur (trimethylsilyl)difluoride), a potent source of fluoride, gave unreacted starting materials.

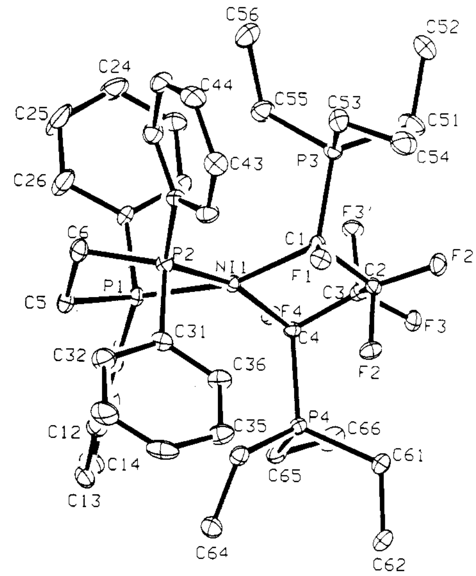
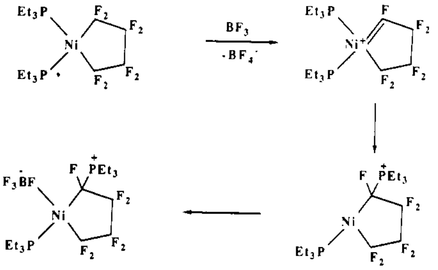


Figure 3. Perspective view of [Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]$_2$ displaying non-hydrogen atoms and atom-labeling scheme.

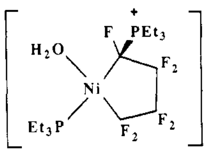
Scheme II



In contrast to the reactivity observed in the $Ni(PEt_3)_2(CF_2)_4$ system, the iron carbonyl perfluorometallacyclopentane, $Fe(CO)_4(CF_2)_4$,[4] was found to be unreactive toward BF_3 and showed no evidence for electrophilic halogen exchange in a reaction with BCl_3. This outcome illustrates the effect of the highly electron-donor phosphine ligand in stabilization of the intermediate fluorocarbene. It was found that $B(OR)_3$ and $Me_3SiO_3SCF_3$ were not sufficiently active as Lewis acids to extract a fluoride from $Ni(PEt_3)_2(CF_2)_4$.

The reaction with 1 equiv of Lewis acid was repeated by using the complex Ni(*i*-Pr)$_2$PCH$_2$CH$_2$P(*i*-Pr)$_2$)(CF_2)$_4$. This complex was chosen because the increased basicity of the alkylphosphine ligand relative to PEt_3 would promote the abstraction of fluoride from the complex, but the chelating nature of the ligand would impede the migration to the carbenium site. Surprisingly, no reaction was observed, even upon heating in the presence of an excess of BF_3·(ether). The basis for this lack of reactivity is unclear.

To test the reactivity of the mono(ylide) complex, $Ni(PEt_3)(BF_4)(CF(PEt_3)(CF_2)_3)$, with other nucleophiles, its reactivity with water was explored. Rather than displace the phosphine from the fluorocarbenium site, the water instead displaces the coordinated tetrafluoroborate anion giving the cationic complex $[Ni(PEt_3)(H_2O)(CF(PEt_3)(CF_2)_3)]^+[BF_4]^-$, as depicted below.



The fluorine NMR spectrum is virtually identical with that of its precursor except for the shift in the coordinated BF_4^- resonance, indicating that the fluorocarbon ring is essentially unchanged. The infrared spectrum contains the O–H stretching frequencies expected for an aquo complex with no hydrogen bonding, but there is also an unusually strong and sharp water deformation at 1665 cm^{-1}. Both the stretching and deformation modes shifted appropriately upon exchange of the water with D_2O, confirming their nature. Triethylamine did not react with the mono(ylide).

The fact that $Ni(PEt_3)_2(CF_2)_4$ undergoes an irreversible transformation by reaction with strong Lewis acids while the simple metal carbonyl perfluoroalkyl complexes undergo electrophilic halogen exchange by reaction with strong Lewis acids is interesting. Presumably the highly electron-donating triethylphosphine ligands serve to stabilize the fluorocarbene intermediates in the nickel phosphine complexes, and no such stabilization is available for the metal carbonyls. In the other complexes in which fluorocarbene ligands have been prepared in the presence of phosphine ligands, phosphine migration has not been observed.[6f,9] Therefore, the electrophilic halogen exchange manifold remains available to the metal carbonyl perfluoroalkyl complexes. We are presently exploring reactions to develop the ylide-like reactivity of these complexes in order to effect synthetically useful transformations.

Transition-metal phosphonium ylide complexes, $L_xM{-}CH_2PR_3$, are relatively common species.[10] In general, they are prepared by reaction of the pre-formed ylide $R_3P{=}CH_2$ with a low-valent transition-metal complex. The metallacyclic complexes described here are to our knowledge the first examples of ylide complexes derived by migration of phosphine ligand to a metal-bonded carbene in the coordination sphere of the same metal and is also a rare example of an ylide that includes a metallacyclic ring.[11,12]

Description of the Structures. Single-crystal X-ray diffraction studies have been carried out on the parent perfluorometallacyclopentane, $Ni(PEt_3)_2(CF_2)_4$ (Figure 1), the mono(ylide) complex, $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$ (Figure 2), and the bis(ylide) complex, $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2$ (Figure 3). Details of the structure determinations are given in Table I. Fractional coordinates and thermal parameters are given in Tables II–IV. The most important bond lengths and angles are given in Table V; more complete listings are given in the supplementary materials.

Table II. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters of Non-Hydrogen Atoms for the Structure of $Ni(PEt_3)_2(CF_2)_4$

atom	x	y	z	B_{iso},[a] Å^2
Ni(1)	5000	5000	4932	2.2 (1)
P(1)	3486 (1)	5740 (1)	6320 (2)	2.5 (1)
F(1)	5423 (3)	6969 (3)	3433 (4)	4.0 (1)
F(1′)	3311 (3)	6810 (3)	3506 (4)	4.8 (1)
F(2)	4575 (6)	6247 (4)	1074 (4)	7.7 (2)
F(2′)	3285 (6)	4888 (4)	1963 (5)	7.0 (2)
C(1)	4449 (6)	6081 (5)	3477 (7)	3.3 (2)
C(2)	4458 (8)	5469 (6)	2131 (6)	4.5 (2)
C(11)	1887 (5)	5310 (6)	5612 (6)	3.9 (2)
C(12)	1771 (6)	3919 (7)	5442 (7)	5.2 (2)
C(13)	3382 (7)	7399 (5)	6554 (7)	4.0 (2)
C(14)	4665 (7)	7983 (6)	6929 (9)	6.0 (2)
C(15)	3351 (7)	5135 (6)	8038 (6)	3.4 (2)
C(16)	2035 (6)	5283 (6)	8740 (6)	4.0 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters of Non-Hydrogen Atoms for the Structure of $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$

atom	x	y	z	B_{iso},[a] Å^2
Ni(1)	1671.6 (4)	2936.9 (5)	5421.9 (5)	2.0 (1)
P(1)	1881 (1)	3624 (1)	7809 (1)	2.2 (1)
P(2)	1922 (1)	3306 (1)	3773 (1)	3.0 (1)
F(1)	2034 (2)	1833 (2)	7210 (2)	2.5 (1)
F(2)	−116 (2)	3128 (2)	7447 (2)	4.0 (1)
F(3)	282 (2)	1601 (3)	7658 (2)	4.2 (1)
F(4)	−1074 (2)	2161 (2)	5986 (2)	4.1 (1)
F(5)	203 (2)	1292 (2)	5659 (2)	3.6 (1)
F(6)	−117 (2)	3821 (2)	5454 (2)	3.4 (1)
F(7)	−109 (2)	2701 (2)	4266 (2)	3.4 (1)
F(11)	3100 (2)	2748 (2)	5672 (2)	2.9 (1)
F(12)	3203 (3)	1109 (3)	5415 (3)	6.3 (1)
F(13)	4401 (3)	2087 (4)	4920 (3)	9.4 (2)
F(14)	4207 (2)	1824 (2)	6612 (3)	4.8 (1)
C(1)	1462 (3)	2663 (3)	6909 (4)	1.9 (1)
C(2)	395 (4)	2377 (4)	7024 (4)	2.7 (1)
C(3)	−81 (3)	2192 (4)	5971 (4)	2.5 (1)
C(4)	311 (3)	2935 (4)	5236 (4)	2.5 (1)
C(11)	3191 (3)	3631 (4)	7840 (4)	2.7 (1)
C(12)	3638 (4)	4400 (4)	8579 (5)	4.0 (2)
C(13)	1494 (4)	3455 (4)	9103 (4)	3.2 (2)
C(14)	1800 (4)	2481 (5)	9598 (4)	4.3 (2)
C(15)	1425 (4)	4786 (4)	7385 (4)	3.4 (2)
C(16)	1819 (4)	5188 (4)	6406 (5)	4.2 (2)
C(21)	3152 (5)	3753 (6)	3590 (5)	5.9 (2)
C(22)	3456 (6)	4616 (8)	4204 (7)	9.8 (4)
C(23)	1807 (11)	2262 (7)	2924 (6)	13.1 (5)
C(24)	1539 (12)	1440 (10)	3129 (10)	18.1 (7)
C(25)	1144 (4)	4223 (5)	3155 (4)	4.4 (2)
C(26)	1313 (5)	4473 (5)	2044 (5)	5.5 (2)
B(1)	3782 (5)	1910 (6)	5647 (6)	4.0 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The derivatives of the parent perfluorometallacyclopentane complexes prepared from the reaction with BF_3 show the successive replacement of a fluorine on the carbon alpha to the nickel atom with a PEt_3 group first on only one of the α-carbon atoms and then, for the bis(ylide) structure, on both of the α-carbon atoms. The nickel complexes all retain their approximate square-planar coordination geometry with a considerable tetrahedral distortion resulting in a twist between the vector formed by

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(9) (a) Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9–C12. (b) Hoskins, S. V.; Pauptit, R. A.; Roper, W. R.; Waters, J. M. *J. Organomet. Chem.* **1984**, *269*, C55–C57. (c) Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719–21. See also ref 6f.

(10) Schmidbaur, H. In *Phosphorus Chemistry* ACS Symposium Series 171; Quin, L. D., Verkade, J. G., Eds.; American Chemical Society: Washington, DC, 1981; Chapter 6.

(11) We note that examples of migration of a metal-bonded phosphine to a ligand to yield an ylide structure are known. However, these do not involve a carbene intermediate. See, for example: (a) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Yu. A.; Kaverin, V. V.; Koneva, N. Yu. *J. Organomet. Chem.* **1985**, *288*, 114–29. (b) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchias, J. E.; L'Naridon, P. *Organometallics* **1983**, *2*, 1681–7.

(12) We note that intermolecular attack of PR_3 on a perfluoroallyl ligand is known: Carl, R. T.; Hughes, R. P.; Johnson, J. A.; Davis, R. E.; Kashyap, R. P. *J. Am. Chem. Soc.* **1987**, *109*, 6875–6. In this case, the product is a perfluorinated metallacyclobutane with a phosphine bonded to the β-carbon atom.

Table IV. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters of Non-Hydrogen Atoms for the Structure of $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2 \bullet 2CH_2Cl_2$

atom	x	y	z	B_{iso},[a] Å^2
Ni(1)	2503.6 (4)	532.0 (6)	3921.7 (5)	1.6 (1)
Cl(1)	4373 (1)	5215 (2)	3775 (2)	5.8 (1)
Cl(2)	3212 (1)	5974 (2)	3518 (2)	7.5 (1)
Cl(3)	858 (2)	4807 (3)	3279 (3)	10.9 (2)
Cl(4)	1926 (2)	5574 (4)	4285 (3)	15.0 (2)
P(1)	2555 (1)	−333 (1)	2760 (1)	1.9 (1)
P(2)	2429 (1)	−818 (1)	4581 (1)	2.0 (1)
P(3)	1405 (1)	1449 (1)	4718 (1)	2.1 (1)
P(4)	3633 (1)	1829 (1)	3639 (1)	1.8 (1)
F(1)	2414 (2)	967 (2)	5674 (2)	2.3 (1)
F(2)	3106 (2)	2066 (3)	5178 (2)	2.5 (1)
F(2′)	2359 (2)	2922 (2)	5233 (2)	2.7 (1)
F(3)	2712 (2)	3325 (2)	3763 (2)	2.4 (1)
F(3′)	1943 (1)	2470 (3)	3424 (2)	2.4 (1)
F(4)	2625 (1)	1793 (2)	2550 (2)	2.0 (1)
F(11)	4578 (2)	3527 (3)	974 (3)	4.6 (1)
F(12)	4842 (2)	2111 (3)	1472 (3)	4.9 (2)
F(13)	5525 (2)	3148 (3)	1314 (3)	4.7 (2)
F(14)	5023 (2)	3320 (4)	2366 (3)	5.8 (2)
F(21)	−205 (4)	7242 (6)	2543 (4)	14.3 (4)
F(22)	−8 (3)	8334 (5)	3569 (5)	10.4 (3)
F(23)	207 (3)	6977 (6)	3850 (4)	10.1 (3)
F(24)	687 (3)	7774 (5)	2993 (4)	8.6 (3)
C(1)	2214 (3)	1307 (4)	4814 (4)	1.8 (2)
C(2)	2536 (3)	2208 (4)	4789 (4)	1.8 (2)
C(3)	2511 (3)	2448 (4)	3845 (4)	1.9 (2)
C(4)	2818 (3)	1690 (4)	3471 (4)	1.7 (2)
C(5)	2663 (3)	−1537 (4)	3104 (4)	2.4 (2)
C(6)	2286 (3)	−1723 (5)	3763 (4)	2.7 (2)
C(11)	3046 (3)	−186 (4)	2021 (4)	1.9 (2)
C(12)	3615 (3)	−498 (5)	2245 (4)	2.5 (2)
C(13)	3994 (3)	−346 (5)	1696 (5)	3.1 (2)
C(14)	3800 (3)	109 (5)	916 (5)	3.4 (2)
C(15)	3235 (3)	386 (5)	677 (4)	3.1 (2)
C(16)	2855 (3)	258 (4)	1227 (4)	2.5 (2)
C(21)	1822 (3)	−285 (4)	2086 (4)	2.1 (2)
C(22)	1525 (3)	556 (5)	1967 (4)	2.8 (2)
C(23)	965 (3)	601 (5)	1491 (5)	3.3 (2)
C(24)	684 (3)	−173 (6)	1126 (5)	4.5 (3)
C(25)	972 (4)	−992 (6)	1220 (7)	6.2 (3)
C(26)	1537 (4)	−1070 (5)	1702 (6)	4.7 (3)
C(31)	3137 (3)	−1087 (5)	5267 (4)	2.4 (2)
C(32)	3327 (3)	−1990 (5)	5416 (5)	3.6 (2)
C(33)	3830 (4)	−2180 (6)	6005 (6)	4.4 (3)
C(34)	4148 (3)	−1488 (6)	6462 (5)	4.0 (3)
C(35)	3979 (3)	−584 (5)	6325 (5)	3.4 (2)
C(36)	3473 (3)	−385 (5)	5724 (4)	2.7 (2)
C(41)	1937 (3)	−1089 (4)	5300 (4)	1.9 (2)
C(42)	2126 (3)	−1029 (5)	6198 (5)	2.9 (2)
C(43)	1753 (3)	−1229 (5)	6739 (5)	3.2 (2)
C(44)	1182 (3)	−1492 (5)	6389 (5)	3.4 (2)
C(45)	999 (3)	−1567 (5)	5512 (5)	3.4 (2)
C(46)	1368 (3)	−1363 (5)	4971 (4)	2.9 (2)
C(51)	1140 (3)	2626 (5)	4604 (5)	3.9 (3)
C(52)	499 (3)	2729 (5)	4571 (5)	3.4 (2)
C(53)	1240 (3)	1021 (5)	5706 (4)	2.8 (2)
C(54)	1469 (3)	1624 (6)	6516 (5)	4.1 (3)
C(55)	1030 (3)	785 (5)	3808 (5)	3.3 (2)
C(56)	425 (3)	438 (6)	3833 (5)	4.4 (3)
C(61)	3967 (3)	2778 (5)	4318 (4)	2.4 (2)
C(62)	4607 (3)	2922 (5)	4295 (4)	2.7 (2)
C(63)	3952 (3)	774 (5)	4109 (4)	2.4 (2)
C(64)	4555 (3)	530 (5)	3969 (5)	3.3 (2)
C(65)	3786 (3)	2044 (5)	2593 (4)	2.4 (2)
C(66)	3598 (3)	3003 (5)	2236 (4)	3.3 (2)
C(71)	3956 (4)	6192 (6)	3740 (6)	5.8 (3)
C(81)	1199 (6)	5684 (11)	3970 (9)	11.4 (6)
B(1)	4992 (4)	3040 (6)	1533 (6)	3.0 (3)
B(2)	132 (7)	7669 (10)	3085 (11)	7.9 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

the two α-carbon atoms and the vector formed by the two phosphorus atoms. For the mono(ylide) structure, we consider the angle between the vector formed by the nickel-ligated phosphorus atom and the ligated fluorine atom that is twisted with respect to the vector formed by the two α-carbon atoms. These twist angles are 37° for the parent compound, 8.3° for the mono(ylide), and 23.6° for the bis(ylide). This twist is readily apparent in Figures 1, 2, and 3.

Several effects of ylide substitution at the α-carbon atoms of the perfluorometallacyclopentane are evident from the comparative bond distance information shown in Table V. It has been well-documented that carbon–fluorine bond lengths are elongated when the carbon is directly bonded to a transition metal relative to the case in which the carbon–fluorine bond is more distal to a metal atom.[13] This weakening of the α-C–F bond is also reflected in reduced infrared stretching frequencies.[14] Phosphonium ylide substitution on the α-carbon atoms exaggerates this effect, although whether the basis for the effect is steric or electronic in origin is unclear. For example, the α-carbon–fluorine bond distances are 1.383 and 1.401 Å in the parent complex and increase to 1.425 Å in the mono(ylide) and 1.425 and 1.434 Å in the bis(ylide) complex (Table V). The unsubstituted α-carbon atom in the mono(ylide) structure also has somewhat elongated carbon–fluorine bond distances (1.386 and 1.393 Å versus 1.365 Å average for the β-carbon–fluorine bond distances). The carbon–carbon bond distances within the metallacyclic ring (Table V) are longer with phosphonium ylide substitution as well.

The phosphorus–carbon bond distances between the ylide–phosphorus atoms and the carbon atom of the metallacyclic ring are longer than the distances to the methylene carbon atoms of the ethyl group for both of the ylide structures. This observation suggests that the phosphorus atoms are weakly bonded to the metallacyclic ring. This relatively weak P–C bonding is in contrast to that observed in previous structures of coordinated ylides[15] and indicates that the structure may be better described as a phosphine-stabilized carbenium complex rather than a phosphonium ylide complex. This description not only describes the structure observed but also reflects the origins of the compounds.

The nickel–ligand bond distances show trends through this structural series. From data in Table V, it is clear that both the nickel–phosphorus bond distances and the nickel–carbon bond distances are elongated in going from the parent perfluorometallacyclopentane complex to the mono(ylide) complex and the bis(ylide) complex. The bond angles show trends as well. In the parent perfluorometallacyclopentane $Ni(PEt_3)_2(CF_2)_4$, the P–Ni–P angle is 102.97° and the C–Ni–C angle is 83.9°. The P–Ni–P angle closes to 89.3° and 85.0° for the mono(ylide) and bis(ylide) structures, respectively. (For the mono(ylide), we consider the P–Ni–F angle for this comparison.) The C–Ni–C angle opens somewhat to 86.1° and 89.1° for the mono(ylide) and bis(ylide) structures, respectively. In

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(13) (a) Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1965**, 182–3. (b) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734–9. (c) Churchill, M. R. *Inorg. Chem.* **1967**, *6*, 185–90. (d) Churchill, M. R.; Fennessey, J. R. *Inorg. Chem.* **1967**, *6*, 1213–20.

(14) (a) Pitcher, E.; Stone, F. G. A. *Spectrochim. Acta* **1962**, *18*, 585–94. (b) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15–37. (c) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315–21. (d) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–75.

(15) (a) Erker, G.; Czisch, P.; Kruger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (b) Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Kruger, C. *Organometallics* **1985**, *4*, 1310.

Table V. Important Bond Distances (Å) and Angles (deg) in the Structures of $Ni(PEt_3)_2(CF_2)_4$, $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$, and $[Ni(DPPE)(CF(PEt_3^+)CF_2CF_2CF(PEt_3^+))][BF_4^-]_2 \bullet 2CH_2Cl_2$

	perfluorometallacycle	mono(ylide)	bis(ylide)
Ni–P	2.218 (2)	2.243 (2)	2.246 (2)
	2.218 (2)		2.243 (2)
Ni–C	1.948 (6)	2.002 (5) (ylide)	2.029 (6)
	1.948 (6)	1.864 (5)	2.025 (6)
C_α–F	1.383 (6), 1.401 (7)[a]	1.386 (5), 1.393 (5)[a]	
	1.383 (6), 1.401 (7)[a]		
C_α–F(ylide)		1.425 (5)	1.425 (7)
			1.434 (6)
C_β–F	1.354 (7), 1.359 (8)[a]	1.376 (6), 1.360 (6)[a]	1.363 (7), 1.364 (7)[a]
	1.354 (7), 1.359 (8)[a]	1.361 (5), 1.364 (6)[a]	1.373 (7), 1.358 (7)[a]
P–C(ethyl)(av)	1.830	1.813	1.801
		1.794 (ylide)	1.800
P–CF		1.834 (5)	1.887 (7), 1.887 (6)[a]
C_α–C_β	1.496 (9)	1.527 (6) (ylide)	1.514 (8)
	1.496 (9)	1.513 (7)	1.504 (8)
C_β–$C_{\beta'}$	1.501 (14)	1.505 (6)	1.518 (8)
B–F(av)		1.354	1.364
B–F_μ		1.482 (7)	
Ni–F_μ		1.981 (3)	
P–Ni–P	102.97 (9)	89.3 (1) (PNiF)	85.01 (8)
C–Ni–C	83.9 (4)	86.1 (2)	89.1 (2)
C–Ni–P	92.6 (2)	94.5 (2)	95.2 (2)
	92.6 (2)	90.4 (2) (CNiF)	95.3 (2)
Ni–F–B		135.6 (4)	

[a] C_α and C_β designate carbon atoms in the metallacycle ring that are α and β to the nickel atom, respectively.

the mono(ylide) structure, the C–Ni–F angle is 90.4° and the smaller of the two C–Ni–P angles is 94.5°. For the bis(ylide) structure and also for the parent perfluorometallacyclopentane complex, the comparable interligand bond angles are symmetric (Table V). The basis for these observed effects may be either electronic or steric.

The tetrafluoroborate anion is generally considered to be noncoordinating, but it,[16] along with other classically noncoordinating anions,[17] occasionally will occupy vacant coordination sites in extremely ligand-deficient systems. Monodentate coordination of BF_4^- is relatively rare. In $Ni(PEt_3)(BF_4^-)(CF(PEt_3^+)(CF_2)_3)$, the Ni–F distance is 1.981 (3) Å and the Ni–F–B angle is 135.6 (4)°. In the other examples of monodentate BF_4^- ligands, these values are 2.122 Å and 131° in another nickel tetrafluoroborate complex,[16f] 2.355 Å and 142° in a palladium complex,[16m] 2.272 Å and 126° in an iridium complex,[16n] and 2.31 Å and 180° in a copper complex.[16h] Coordination of the tetrafluoroborate anion in the mono(ylide) causes the boron–fluorine bond to the bridging fluoride to be elongated and the other boron fluorine bonds to be shortened relative to the average boron fluorine bond distance in the noncoordinated tetrafluoroborate anions of the bis(ylide) structure. A caveat here is that the deviation from the average in the noncoordinated tetrafluoroborate anions of the bis(ylide) structure is quite large. The nickel fluorine bond length of 1.981 Å is shorter than that observed in a macrocyclic nickel(II) complex[18] bearing trans fluoride ligands (Ni–F(av) = 2.087 Å) and comparable to the Ni–F distances in NiF_2 (1.98 and 2.04 Å).[19] An alternative valence bond representation of this structure is as a BF_3 adduct to a nickel fluoride complex, $FNi[PEt_3][CF(PEt_3)(CF_2)_3]$, a representation consistent with the very short Ni–F bond distance.

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Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond distances and angles (12 pages); tables of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page. Inquiries for copies of these materials may also be directed to the indicated author.

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