Rapid Intermolecular Carbon−Fluorine Bond Activation of Pentafluoropyridine at Nickel(0): Comparative Reactivity of Fluorinated Arene and Fluorinated Pyridine Derivatives

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Reaction of hexafluorobenzene with $Ni(COD)_2$ (COD = 1,5,-cyclooctadiene) in the presence of triethylphosphine or with $Ni(PEt_3)_4$ at room temperature results in very slow formation of *trans*-$Ni(PEt_3)_2(C_6F_5)F$ (**1**). The X-ray crystal structure reveals a molecular complex with approximately square-planar coordination at nickel, a Ni−F distance of 1.836(5) Å and a Ni−C distance of 1.878(7) Å. Analogous reactions with pentafluoropyridine and 2,3,5,6-tetrafluoropyridine proceed much faster. Both reactions yield C−F activation products analogous to **1** in which a single regioisomer is dominant. The crystal structure of *trans*-$Ni(PEt_3)_2(C_5HF_3N)F$ (**3**) shows that the trifluoropyridyl ligand is metalated at the 2-position. The Ni−F and Ni−C distances are 1.856(2) and 1.869(4) Å, respectively. In the structures of both **1** and **3**, the plane of the aryl ring is perpendicular to the nickel coordination plane. These structures provide the first values of nickel-fluorine distances at square-planar Ni(II). The reaction of $Ni(COD)_2$ with PEt_3 and 3,5-dichloro-2,4,6-trifluoropyridine yields exclusively *trans*-$Ni(PEt_3)_2(C_5ClF_3N)Cl$ (**4**), the product of C−Cl activation with the metal at the 3-position of the ring. The corresponding reaction with 2,3,4,5,6,-pentafluorostyrene results in rapid formation of the alkene coordination product, $Ni(PEt_3)_2(\eta^2\text{-}CH_2\text{=}CHC_6F_5)$ (**6**). The crystal structure of **6** shows the typical trigonal Ni(0) geometry with the coordinated atoms almost perfectly coplanar with the nickel. The Ni−C distances average 1.960(6) Å; the P−Ni−P angle is 115.0(1)°. Reaction with pentafluorobenzene and methoxypentafluorobenzene yield C−F activation products very slowly with little regioselectivity. The studies reported in this paper demonstrate that intermolecular C−F activation of a fluoroaromatic can take place rapidly and in good yield at a first row transition metal through the suitable choice of substrate.

Introduction

Interest in carbon−fluorine activation by transition metals has been increasing rapidly with the discovery of several systems capable of activating C−F bonds both intramolecularly and intermolecularly. Recent discoveries, summarized in two thorough reviews,[1,2] include systems capable of breaking the C−F bonds of perfluoroarenes and perfluoroalkanes. Catalytic C−F activation has also become a reality.[3,4] Industrial interest in functionalized fluorine compounds and polymers[5] suggests that it is timely to turn to the study of functionalized organofluorine compounds.

At this stage, we recognize several classes of reaction of hexafluorobenzene with transition metal complexes: (i) Nucleophilic substitution of fluoride at C_6F_6 by anionic complexes (e.g., with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$;[6] (ii) Coordination of C_6F_6 to transition metals in η^2, η^4, and η^6 modes (e.g., $Rh(\eta^5\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}C_6F_6)$, $Ir(\eta^5\text{-}C_5H_5)$-$(\eta^4\text{-}C_6F_6)$, or $W(\eta^6\text{-}C_6F_6)_2$;[7−11] (iii) Photochemical or thermal C−F oxidative addition to form complexes of the type $M(C_6F_5)F$ (e.g., $Pt(Bu^t_2PCH_2PBu^t_2)(C_6F_5)F)$;[7,12] (v) Photochemical or thermal reaction with metal dihydride complexes to form products of the type $M(C_6F_5)H$ liberating HF (e.g., $Ru(dmpe)_2(C_6F_5)H)$;[7,13,14] (vi) Combination of intermolecular C−F with intramolecular C−H activation to yield products of the type $M(C_6F_5)$ and liberate HF (e.g., with $Re(\eta^5\text{-}C_5Me_5)(CO)_3)$;[15,16] (vii) Electron transfer from transition metal complexes to C_6F_6 (e.g., with $Cr(\eta^6\text{-}C_6H_6)_2$).[17]

The reactivity adjusts to the presence of a substituent other than fluorine on the aromatic ring in different ways according to the transition metal system. For

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(1) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.
(2) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145.
(3) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674.
(4) Kiplinger, J. L.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1996**, 1115; *J. Am. Chem. Soc.* **1996**, *118*, 1805.
(5) Clark, J. H.; Wails, B.; Bastock, T. W. *Aromatic Fluorination*; CRC Press: Boca Raton, FL, 1996.
(6) King, R. B.; Binette, M. B. *J. Organomet. Chem.* **1964**, *2*, 38.

(7) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.
(8) Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911.
(9) Higgitt, C. L.; Klahn, A. H.; Moore, M. H.; Oelckers, B.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **1997**, 1269.
(10) Barker, J. J.; Orpen, A. G.; Seeley, A. J.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1993**, 3097.
(11) Martin, A.; Orpen, A. G.; Seeley, A. J.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1994**, 2251.
(12) Hofmann, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659.
(13) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 787.
(14) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187.
(15) Klahn, A. H.; Moore M. H.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1992**, 1699.
(16) Ballhorn, M.; Partridge, M. G.; Perutz, R. N.; Whittlesey, M. K. *J. Chem. Soc., Chem. Commun.* **1996**, 961.
(17) Aspley, C.; Higgitt, C. L.; Long, C.; Perutz, R. N. Unpublished results.

Scheme 1. Reactions of Ni(COD)$_2$ with Fluoroarenes, Fluoropyridines, and Triethylphosphine
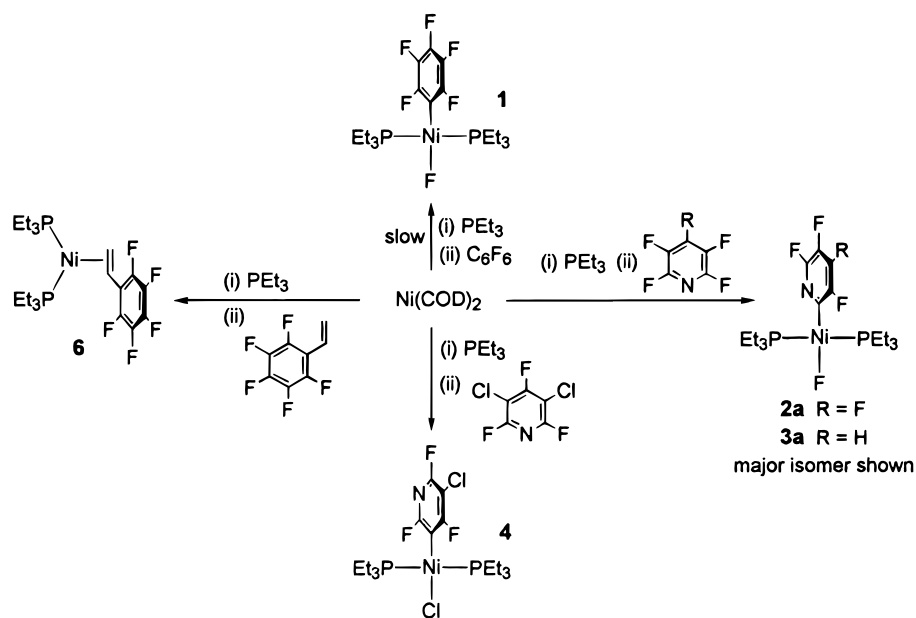
instance, hexafluorobenzene undergoes C−F oxidative addition at the Rh(η^5-C$_5$Me$_5$)(PMe$_3$) fragment,[7] but pentafluorobenzene undergoes only C−H bond activation.[18] In contrast, Ru(dmpe)$_2$H$_2$ yields products of C−F bond activation with both hexafluorobenzene and pentafluorobenzene:[13] i.e., Rh(η^5-C$_5$Me$_5$)(PMe$_3$) is selective for C−H over C−F activation, while Ru(dmpe)$_2$H$_2$ is selective for C−F over C−H insertion. The presence of a methoxy substituent is also influential. With hexafluorobenzene, Rh(η^5-C$_5$H$_5$)(PMe$_3$)(C$_2$H$_4$) reacts photochemically to form Rh(η^5-C$_5$H$_5$)(PMe$_3$)(η^2-C$_6$F$_6$) but the C−F oxidative-addition product is observed only in low-temperature matrices.[7] In contrast, the corresponding reaction with C$_6$F$_5$OMe yields Rh(η^5-C$_5$H$_5$)(PMe$_3$)(η^2-C$_6$F$_5$OMe), which converts to the metallacycle Rh(η^5-C$_5$H$_5$)(PMe$_3$)(C$_6$F$_4$OCH$_2$) with liberation of HF.[16] A methoxy substituent, however, has little effect on the reactivity of Ru(dmpe)$_2$H$_2$.[13]

In 1977, Fahey and Mahan reported that carbon−halogen oxidative addition occurred on reaction of haloaromatics with Ni(COD)$_2$ (COD = 1, 5-cyclooctadiene) in the presence of PEt$_3$, yielding products of the type *trans*-Ni(PEt$_3$)$_2$(aryl)X (X = halogen).[19] The initial reaction with PEt$_3$ was reported to yield Ni(COD)-(PEt$_3$)$_2$, which subsequently reacted with the haloarene. Isolated Ni(PEt$_3$)$_4$ was sometimes used as a more reactive precursor: Ni(PEt$_3$)$_4$ (colorless) is at equilibrium in solution with Ni(PEt$_3$)$_3$ (purple) with an equilibrium constant of ca. 10^{-2}. Later, Tsou and Kochi showed that the reactions of Ni(PEt$_3$)$_4$ with haloarenes also yield paramagnetic Ni(I) complexes, Ni(X)(PEt$_3$)$_3$, as competing products, and that the ratio of the Ni(I) to the Ni(II) product is affected by the halogen (Cl, Br, I), the solvent polarity, and the aryl group.[20] They showed that the kinetically active species is Ni(PEt$_3$)$_3$ and argued that both types of product are formed via a common intermediate identified as a tight ion pair, {Ni(PEt$_3$)$_3^+$·ArX$^-$}.

Among the reactions reported by Fahey and Mahan was that with hexafluorobenzene, probably the first report of C−F oxidative addition.[19] However, the reaction was slow with a yield of only 7%, and characterization of the product as *trans*-Ni(PEt$_3$)$_2$(C$_6$F$_5$)F was limited to elemental analysis and IR spectroscopy. This result contrasted with early work by Stone et al. which showed Ni(0) reacting with perfluoroalkenes to form either Ni(η^2-perfluoroalkene) complexes or Ni(II) metallacycles.[21] Since then, three other relevant C−F activation reactions have been reported at nickel. Firstly, Ni(COD)$_2$ reacts with (C$_6$F$_5$)CH=NC$_6$H$_4$(NMe$_2$) to form a C−F activated product.[22] Secondly, Ni(dtbpe)-(η^2-C$_6$H$_6$) (dtbpe = ^{t}Bu$_2$PCH$_2$CH$_2$P^{t}Bu$_2$) reacts with C$_6$F$_6$ to form Ni(dtbpe)(η^2-C$_6$F$_6$).[23a] This isolable complex reacts over days at room temperature to form Ni(dtbpe)-(C$_6$F$_5$)F. The formation of the oxidative-addition product provides direct evidence for the thermal conversion of an (η^2-C$_6$F$_6$) complex to the pentafluorophenyl fluoride. Thirdly, Ni(bpy)Et$_2$ has been shown to react with C$_6$F$_6$ to give Ni(bpy)(C$_6$F$_5$)$_2$.[23b] Evidence for precoordination of electron-withdrawing arenes to Ni(bpy)Et$_2$ was obtained in low-temperature experiments.

In this paper, we report the full characterization of the product of the reaction of Ni(COD)$_2$ with PEt$_3$ and C$_6$F$_6$, confirming its identity as *trans*-Ni(PEt$_3$)$_2$(C$_6$F$_5$)F. We also investigate the reactivity of Ni(0) complexes toward three different functionalized analogues of hexafluorobenzene: C$_6$F$_5$(CH=CH$_2$), C$_6$F$_5$OMe, and C$_6$F$_5$H. Most importantly, we show that the corresponding reaction with fluorinated pyridines is orders of magnitude more rapid and is selective for C−F over C−H oxidative addition.

(18) Selmeczy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, *12*, 522.
(19) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501.
(20) Tsou, T. T.; Kochi, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

(21) Cundy, C. S.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 1647.
(22) Osterberg, C. E.; Richmond, T. G. In *Inorganic Fluorine Chemistry toward the 21st Century*; Thrasher J. S., Strauss, S. H., Eds.; ACS Symposium Series 555; American Chemical Society: Washington, DC, 1994; pp 392−404.
(23) (a) Bach, I.; Pörschke, K.-R.; Goddard, R.; Kopiske, C.; Krüger, C.; Rufinska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959. (b) Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209.

Table 1. NMR Data at 298 K[a]

| complex	^{1}H	^{31}P{^{1}H}	^{19}F	^{13}C{^{1}H}
1 (C_6D_6)	0.97 (m, 18H, CH$_3$), 1.08 (m, 12H, CH$_2$)	12.24 (d, $J_{PF} = 46$)	-390.33 (tt, $J_{PF} = 48$, $J_{FF} = 9$, NiF), -163.75 (tm, $J = 21$, 2F, F$_{meta}$), -161.05 (t, $J = 20$, 1F, F$_{para}$), -115.39 (d, $J = 32$, 2F, F$_{ortho}$)	7.78 (s, CH$_3$), 13.3 (td, $J_{PC} = 20$,[e] $J_{FC} = 5$, CH$_2$), 113.6 (m, C$_{ipso}$),[b] 135.9 (dm, $J = 255$, CF), 147.0 (dm, $J = 240$, CF)
2a (THF-d_8)	1.29 (m, 18H, CH$_3$), 1.46 (m, 12H, CH$_2$)	14.19 (d, $J_{PF} = 47$)	-371.35 (td, $J_{PF} = 47$, $J_{FF} = 6$, 1F, NiF), -173.38 (m, 1F, F^5), -150.75 (m, 1F, F^4), -131.33 (t, $J = 27$, 1F, F^3), -84.70 (m, 1F, F^6)	6.91 (s, CH$_3$), 12.6 (td, $J_{PC} = 12$,[e] $J_{FC} = 3$, CH$_2$), 129.8 (dm, $J = 199$, CF), 143.5 (dm, $J = 266$, CF), 146.6 (dm, $J = 228$, CF), 148.7 (dm, $J = 231$, CF), 163.6 (m, C$_{ipso}$)
2b, 2c (THF-d_8)		13.55 (d, $J_{PF} = 48$), 13.62 (d, $J_{PF} = 49$)	-368.54 (t, $J = 48$, NiF), -368.26 (t, $J = 50$, NiF)	
3a (THF-d_8)	1.28 (m, 18H, CH$_3$), 1.44 (m, 12H, CH$_2$), 6.98 (m, 1H, CH)	9.89 (d, $J_{PF} = 48$)	-370.31 (t, $J = 48$, NiF), -152.83 (dm, $J = 31$, 1F, CF), -111.25 (d, $J = 31$, 1F, CF), -92.23 (td, $J = 32$, 8, 1F, CF)	8.05 (s, CH$_3$), 13.78 (t, $J_{PC} = 11$,[e] CH$_2$), 109.5 (dd, $J = 31$, 18, CH), 140.2 (dm, $J = 253$, CF), 147.5 (dm, $J = 217$, CF), 160.4 (dm, $J = 234$, CF), 160.5 (m, C$_{ipso}$)
3b (THF-d_8)		9.34 (d, $J_{PF} = 49$)	-367.16 (t, $J = 45$, NiF)	
4 (C_6D_6)	0.88 (m, 18H, CH$_3$), 1.14 (m, 12H, CH$_2$)	15.4 (s)	-82.35 (m, 1F, CF), -75.22 (m, 1F, CF), -47.97 (m, 1F, CF)	7.88 (s, CH$_3$), 14.3 (t, $J_{PC} = 13$,[e] CH$_2$), 100.5 (m, C$_{ipso}$), 111.5 (m, CCl), 157.0 (dm, $J = 248$, CF), 161.6 (dm, $J = 228$, CF), 169.2 (dm, $J = 222$, CF)
5 (C_6D_6)	1.07 (m, 18H, CH$_3$), 1.32 (m, 12H, CH$_2$)	14.97 (s)	-162.89 (m, 2F, F$_{meta}$), -160.38 (t, $J = 20$, 1F, F$_{para}$), -114.53 (m, 2F, F$_{ortho}$)	
6[d] (THF-d_8)	1.03 (dt, $J_{PH} = 14.5$, $J_{HH} = 7.6$, 9H, CH$_3$), 1.19 (dt, $J_{PH} = 14.4$, $J_{HH} = 7.5$, 9H, CH$_3$), 1.39 (ps-septet, $J = 7.2$, 3H, CH$_2$), 1.54 (ps-septet, $J = 7.2$, 3H, CH$_2$), 1.74 (ps-quin, $J = 7.4$, 7H, CH$_2$ and H$_\gamma$ or H$_\beta$), 2.20 (m, 1H, H$_\beta$ or H$_\gamma$), 3.28 (ps-septet, $J_{HH} = 11$, 1H, H$_\alpha$)	15.29 (d, $J_{PP} = 37$), 19.65 (dd, $J_{PP} = 37$, $J_{PF} \approx 5$)	-173.2 (tm, $J = 21$, 2F, F$_{ortho}$), -169.83 (tm, $J = 22$, 2F, F$_{meta}$), -149.02 (m, CF, 1F, F$_{para}$)	8.64 (d, $J = 1$, CH$_3$), 8.85 (s, CH$_3$), 18.8 (dd, $J = 18$, 3, CH$_2$), 19.6 (dd, $J = 18$, 3, CH$_2$), 34.6 (dm, $J = 21$, CH=CH$_2$), 37.4 (d, $J = 18$, CH=CH$_2$), 126.2 (m, C$_{ipso}$), 135.5 (dm, $J = 244$, CF), 138.7 (dm, $J = 245$, CF), 144.1 (dm, $J = 241$, CF)
7a (THF-d_8)		13.6 (d, $J_{PF} = 46$)	-385.38 (tt, $J_{FP} = 46$, $J_{FF} = 9$, NiF)	
7b (THF-d_8)		13.1 (d, $J_{PF} = 46$)	-385.65 (tt, $J_{FP} = 46$, $J_{FF} = 9$, NiF)	
7c (THF-d_8)		c	-389.43 (tt, $J_{FP} = 46$, $J_{FF} = 9$, NiF)	
8a (C_6D_6)		13.32 (d, $J_{PF} = 46$)	-389.03 (t, $J_{FP} = 45$, NiF)	
8b (C_6D_6)		13.01 (d, $J_{PF} = 46$)	-389.49 (t, $J_{FP} = 45$, NiF)	
9 (C_6D_6)		6.28 (d, $J_{PF} = 45$)	-388.03 (s, br, NiF), -164.08 (tm, $J = 20$, 2F, F$_{meta}$), -161.77 (t, $J = 19$, 1F, F$_{para}$), -115.30 (d, $J = 27$, 2F, F$_{ortho}$)	

[a] Reported in ppm (δ) and J values in Hertz. [b] One CF resonance is masked by solvent. [c] Obscured. [d] ^{1}H{^{31}P} spectrum of **6**: 1.02 (t, $J = 7.4$), 1.19 (dt, $J = 7.5$, 2.6), 1.39 (ps-sextet, $J = 7.2$), 1.54 (ps-sextet, $J = 7.2$), 1.74 (q, $J = 7.4$), 2.20 (d, $J = 12$), 3.28 (t, $J = 11$). [e] Virtual coupling.

Results

Reaction with Hexafluorobenzene. Nickel tetrakis(triethylphosphine) was isolated from the reaction of Ni(1,5-cyclooctadiene)$_2$ with PEt$_3$.[24] Reaction of Ni(PEt$_3$)$_4$ with C$_6$F$_6$ (20% excess) in hexane solution at room temperature for 4 weeks yielded *trans*-Ni(PEt$_3$)$_2$-(C$_6$F$_5$)F (**1**) (Scheme 1), which was crystallized at -20 °C. The isolated yield of 48% (c.f. 7% previously)[19] was limited principally by the extreme solubility of the product. The structure of the product was determined definitively by multinuclear NMR spectroscopy (Table 1). The ^{31}P{^{1}H} NMR spectrum shows a doublet at δ 12.24 ($J_{PF} = 46$ Hz), indicative of coupling to a single

fluorine nucleus. The ^{19}F NMR spectrum shows a triplet of triplets at δ -390.33 characteristic of the metal fluoride, with coupling to both phosphorus nuclei ($J_{PF} = 48$ Hz) and the two ortho fluorine nuclei of the Ni-(C$_6$F$_5$) group ($^4J_{FF} = 9$ Hz). Three further resonances at δ -163.75, -161.05, and -115.39 reveal the presence of the C$_6$F$_5$ group. The *trans* geometry is indicated by the equivalence of the ^{31}P nuclei and the characteristic virtual coupling pattern in the ^{13}C resonance for the CH$_2$ groups. The structure of **1** was also determined crystallographically (see below). The complex can be handled without decomposition in a glovebox but decomposes over a few hours under vacuum.

The same product was obtained by addition of PEt$_3$ (5 equiv) and C$_6$F$_6$ (1.3 equiv) to Ni(COD)$_2$ in hexane

(24) Ittel, S. D. *Inorg. Synth.* **1974**, *17*, 117.
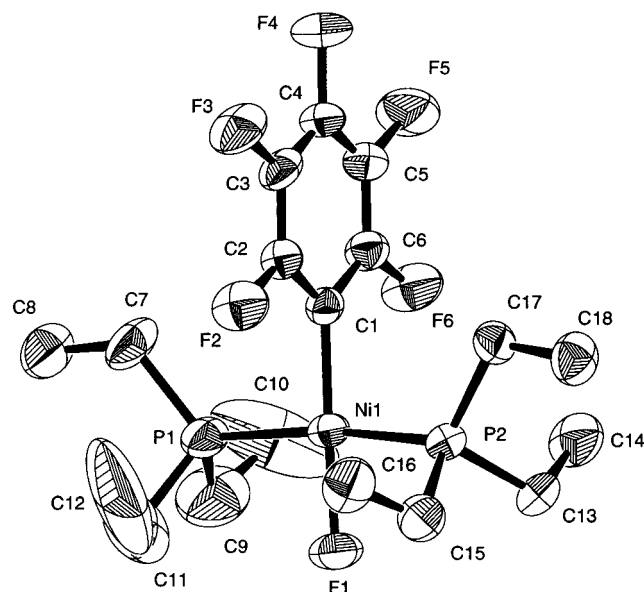
Figure 1. Molecular structure of **1**, *trans*-Ni(PEt₃)₂-(C₆F₅)F: ORTEP[26] plot with 30% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 2. Principal Bond Lengths (Å) and Angles (deg) of *trans*-Ni(PEt₃)₂(C₆F₅)F, 1

Ni(1)−F(1)	1.836(5)	F(5)−C(5)	1.355(10)
Ni(1)−C(1)	1.878(7)	F(6)−C(6)	1.339(9)
Ni(1)−P(1)	2.199(3)	C(1)−C(2)	1.375(10)
Ni(1)−P(2)	2.201(3)	C(1)−C(6)	1.409(10)
F(2)−C(2)	1.358(8)	C(2)−C(3)	1.370(11)
F(3)−C(3)	1.347(9)	C(3)−C(4)	1.381(12)
F(4)−C(4)	1.358(9)	C(4)−C(5)	1.339(13)
		C(5)−C(6)	1.354(11)
F(1)−Ni(1)−C(1)	177.4(3)	F(2)−C(2)−C(3)	117.4(8)
F(1)−Ni(1)−P(1)	87.7(2)	F(2)−C(2)−C(1)	117.4(7)
C(1)−Ni(1)−P(1)	92.8(2)	C(3)−C(2)−C(1)	125.1(8)
F(1)−Ni(1)−P(2)	85.6(2)	F(3)−C(3)−C(2)	121.1(9)
C(1)−Ni(1)−P(2)	94.2(2)	F(3)−C(3)−C(4)	120.0(8)
P(1)−Ni(1)−P(2)	171.52(11)	C(2)−C(3)−C(4)	118.8(8)
C(9)−P(1)−Ni(1)	115.1(6)	C(5)−C(4)−F(4)	122.5(9)
C(7)−P(1)−Ni(1)	121.0(4)	C(5)−C(4)−C(3)	118.8(8)
C(11)−P(1)−Ni(1)	109.1(8)	F(4)−C(4)−C(3)	118.7(9)
C(13)−P(2)−Ni(1)	111.7(4)	C(4)−C(5)−C(6)	121.2(8)
C(17)−P(2)−Ni(1)	120.2(3)	C(4)−C(5)−F(5)	117.9(8)
C(15)−P(2)−Ni(1)	109.5(3)	C(6)−C(5)−F(5)	120.9(9)
C(2)−C(1)−C(6)	112.4(7)	F(6)−C(6)−C(5)	117.2(7)
C(2)−C(1)−Ni(1)	124.8(6)	F(6)−C(6)−C(1)	119.1(7)
C(6)−C(1)−Ni(1)	122.8(6)	C(5)−C(6)−C(1)	123.6(8)

without isolating Ni(PEt₃)₄. The reaction may be monitored by following the decrease in the ³¹P resonance of Ni(PEt₃)₂(COD) at δ 18 relative to that of residual Et₃-PO at δ 46. The resonances of Ni(PEt₃)₄/Ni(PEt₃)₃ (δ ca. 3 to 4) and of PEt₃ (δ −19) are broadened by exchange[23,25] and are unsuitable for monitoring the reaction, although the former sharpens on cooling. After 4 weeks, NMR spectra showed that all precursor complexes were consumed and converted to **1**, leaving only excess PEt₃ and a trace amount of Et₃PO. Attempts to use higher temperatures or different solvents (35 and 45 °C in C₆D₆ or 35 °C in THF-d₈) failed to speed up the reaction. Addition of an excess of hexafluorobenzene (2−10-fold) was also attempted without success. Under these conditions the reaction yielded, in addition to **1**, three difluorophosphoranes, PR₃F₂ (R = Et, CH₂-FCH₂, etc.), characterized by triplets in the ³¹P NMR spectrum at ca. δ −12 to −20 with J_{PF} = 550−650 Hz and corresponding doublet resonances around δ −40 in the ¹⁹F NMR spectrum. These species were also formed in other reactions with excess fluoroarenes discussed in this paper (see Experimental Section), but their full identification will not be pursued here.

Crystal Structure of *trans*-Ni(PEt₃)₂(C₆F₅)F (1). Complex **1** was crystallized from hexane at −20 °C. The crystal structure (ORTEP diagram[26] in Figure 1, Table 2) shows the expected *trans* disposition of the phosphine ligands with approximately square-planar coordination at nickel (F(1), C(1), P(1), and P(2) form a plane with rms deviation of 0.069 Å and Ni(1) lies out of the plane by 0.027 Å). Angles between adjacent ligands at nickel vary from 85.6(2)° to 94.2(2)°. The most important parameter is the nickel−fluorine distance of 1.836(5) Å, since there are no measurements of other Ni−F distances at four-coordinate Ni(II) according to CSD.[27] The nickel−carbon distance of 1.878(7) Å lies within the

lower quartile of Ni−(η¹-aryl) distances, as would be anticipated with a C₆F₅ group,[28] but is almost identical to that for Ni(PPh₂Me)₂(C₆F₅)Br (1.880(4) Å). The dihedral angle between the plane of the aryl ring and the nickel coordination plane is 89.2(2)°. For comparison, a search of CSD for related Ni(phosphine)₂(aryl)X (X = halide) complexes revealed a range of dihedral angles from 84° to 101°.[27] Two of the ethyl groups on P(1) show very large thermal ellipsoids, but alternative solutions in which the occupancy was split over several positions proved unsatisfactory. There are no close intermolecular contacts.

Reaction with Pentafluoropyridine. Addition of PEt₃ to Ni(COD)₂ suspended in hexane generated the characteristic cloudy purple-red color of Ni(PEt₃)₃. Subsequent addition of pentafluoropyridine (30% excess) resulted in a change in color to yellow-orange after 3 min. The three products, isolated after 2 h reaction at room temperature, were readily assigned as fluoride complexes on the basis of characteristic ¹⁹F resonances at ca. δ −370 and were present in a ratio of 85:12:3 (Table 1). The dominant product (**2a**) is assigned as the 2-pyridyl isomer of *trans*-Ni(PEt₃)₂(C₅F₄N)F on the basis of the four multiplets of equal integration in the ¹⁹F NMR spectrum for the fluoroaromatic region and a doublet coupling of 6 Hz between the fluoride at δ −371 and the multiplet at δ −131 (Scheme 1, Table 1). The assignments of the remaining ¹⁹F resonances were completed on the basis of selective ¹⁹F−¹⁹F decoupling experiments and chemical shift data for free pentafluorobenzene. Activation of the C−F bond adjacent to the metal is consistent with the crystallographic data on the product of the reaction with tetrafluoropyridine (see below). The minor resonances are tentatively assigned as the 3-pyridyl and 4-pyridyl isomers (**2b,c**). The ³¹P resonances of **2** show some exchange broadening in the presence of excess PEt₃.

Reaction with 2,3,5,6-Tetrafluoropyridine. The reaction with 2,3,5,6-tetrafluoropyridine was designed

(25) Cundy, C. S. *J. Organomet. Chem.* **1974**, *69*, 305.

(26) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge, National Laboratory: Oak Ridge, TN, 1976.

(27) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

(28) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. Churchill, M. R.; Kaira, K. L.; Veidis, V. *Inorg. Chem.* **1973**, *12*, 1656.
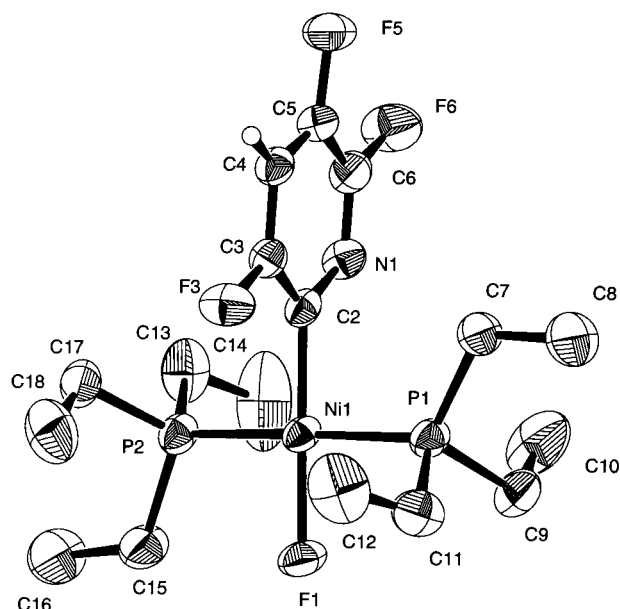
Figure 2. Molecular structure of **3a**, *trans*-Ni(PEt$_3$)$_2$(C$_5$-HF$_3$N)F (C$_5$HF$_3$N = 2,5,6-trifluoropyrid-2-yl): ORTEP[26] plot with 30% probability thermal ellipsoids. The hydrogen atoms, with the exception of H(4), have been omitted for clarity.

Table 3. Principal Bond Lengths (Å) and Angles (deg) of *trans*-Ni(PEt$_3$)$_2$(C$_5$HF$_3$N)F, 3a

Ni(1)−F(1)	1.856(2)	F(3)−C(3)	1.361(4)
Ni(1)−C(2)	1.869(4)	N(1)−C(6)	1.301(5)
Ni(1)−P(2)	2.191(3)	N(1)−C(2)	1.360(5)
Ni(1)−P(1)	2.198(3)	C(2)−C(3)	1.391(5)
F(6)−C(6)	1.356(5)	C(6)−C(5)	1.368(5)
F(5)−C(5)	1.365(4)	C(5)−C(4)	1.353(5)
F(3)−C(3)	1.361(4)	C(4)−C(3)	1.376(5)
F(1)−Ni(1)−C(2)	176.58(12)	N(1)−C(2)−C(3)	115.9(3)
F(1)−Ni(1)−P(2)	92.10(9)	N(1)−C(2)−Ni(1)	122.0(3)
C(2)−Ni(1)−P(2)	90.45(12)	C(3)−C(2)−Ni(1)	121.9(3)
F(1)−Ni(1)−P(1)	86.46(9)	N(1)−C(6)−F(6)	116.8(4)
C(2)−Ni(1)−P(1)	91.10(12)	N(1)−C(6)−C(5)	124.9(4)
P(2)−Ni(1)−P(1)	176.70(4)	F(6)−C(6)−C(5)	118.4(4)
C(9)−P(1)−Ni(1)	110.9(2)	C(4)−C(5)−F(5)	120.9(3)
C(7)−P(1)−Ni(1)	119.9(2)	C(4)−C(5)−C(6)	119.1(4)
C(11)−P(1)−Ni(1)	110.1(2)	F(5)−C(5)−C(6)	120.0(4)
C(15)−P(2)−Ni(1)	111.9(2)	C(5)−C(4)−C(3)	115.6(3)
C(13)−P(2)−Ni(1)	115.1(2)	F(3)−C(3)−C(4)	117.7(3)
C(17)−P(2)−Ni(1)	114.9(2)	F(3)−C(3)−C(2)	117.4(3)
C(6)−N(1)−C(2)	119.7(3)	C(4)−C(3)−C(2)	124.8(3)

to test the preference for C−H compared to C−F activation. It was conducted as for the reaction with pentafluoropyridine and generated two fluoride complexes, with one formed in a far higher yield than the other (100:1). These products were identified as isomers of *trans*-Ni(PEt$_3$)$_2$(C$_5$HF$_3$N)F (**3**). The doublet of doublets pattern for the ^{13}C resonance of the pyridyl-CH group provides evidence that the major isomer is metalated at the 2-position of the ring (**3a**). The minor isomer is metalated at the 3-position (**3b**) (Scheme 1, Table 1). This conclusion is confirmed crystallographically (see below).

Crystal Structure of *trans*-Ni(PEt$_3$)$_2$(3,5,6-trifluoropyrid-2-yl)F (3a). Complex **3a** was crystallized from hexane at −20 °C. The crystal structure of **3a** (Figure 2, Table 3) closely resembles that of **1**, but is free of any signs of incipient disorder. The trifluoropyridyl ligand is metalated at the 2-position with the hydrogen at the 4-position. The angles between adja-

cent ligands at nickel vary from 86.5(1)° to 91.1(1)°. The Ni−C distance at 1.869(4) Å and Ni−F distances at 1.856(2) Å differ little from those in **1**. The coordination plane is better defined than in **1**, with a rms deviation of 0.047 Å and the Ni atom 0.009 Å from the plane. The aryl ring and nickel coordination planes are again almost orthogonal (dihedral angle 86.8(1)°). There is a significant intermolecular contact between the fluoride F(1) on one molecule and the C(4)−H(4) group of the pyridine ring on the adjacent molecule (r(F···C) = 3.007-(4) Å). The riding model gives an estimate of the H···F distance of 2.08(4) Å and the F···H−C angle of 174(1)°.

Reaction with 3,5-Dichloro-2,4,6-trifluoropyridine. The reaction with 3,5-dichloro-2,4,6-trifluoropyridine was designed to test the selectivity for C−Cl compared to C−F bond activation. It was conducted as for the reaction with pentafluoropyridine. A single product was formed in 85% yield, characterized as the product of C−Cl activation, *trans*-Ni(PEt$_3$)$_2$(5-chloro-2,4,6-trifluoropyrid-3-yl)Cl (**4**) (Scheme 1, Table 1).

Reaction with Chloropentafluorobenzene. The reaction with chloropentafluorobenzene had already been demonstrated by Fahey and Mahan to yield the product of C−Cl and not C−F bond activation.[19] We repeated it in order to obtain high-quality NMR and IR data of the product, *trans*-Ni(PEt$_3$)$_2$(C$_6$F$_5$)Cl (**5**, Table 1).

Reaction with Pentafluorostyrene. The reaction with pentafluorostyrene was carried out in order to test whether C−F bond activation might be assisted by precoordination of the alkene moiety in the same way as we surmised that the nitrogen atom assists with the reaction of pentafluoropyridine. The reaction yielded completely different spectra from those described above. The ^{1}H spectrum showed resonances for two of the alkene protons at δ 2.20 and 3.28, providing immediate evidence for alkene coordination (Table 1, the third alkene proton was obscured by a CH$_2$ resonance of the PEt$_3$ ligand). Two sets of resonances were found for the CH$_3$ and two for the CH$_2$ groups of the phosphine in the ^{1}H and ^{13}C{^{1}H} spectra (coupling constants were identified with the aid of a ^{1}H{^{31}P} spectrum). They showed coupling to a single ^{31}P nucleus, unlike the virtual coupling pattern observed in the ^{13}C{^{1}H} spectra of complexes **1**−**5**. The ^{31}P{^{1}H} spectrum exhibited two mutually coupled doublets (J_{PP} = 37 Hz), one of which showed a small coupling to a single ^{19}F nucleus (ca. 5 Hz). The ^{19}F spectrum revealed three resonances in the aromatic region and none elsewhere. The product could be identified readily as the Ni(0) complex Ni(PEt$_3$)$_2$(η^2-CH$_2$=CHC$_6$F$_5$) (**6**) (Scheme 1) and was also characterized crystallographically. In the presence of excess PEt$_3$, the two ^{31}P resonances coalesced to a single broad peak at ca. δ 18 and the peak due to free PEt$_3$ was also broadened, providing direct evidence for intermolecular exchange of the PEt$_3$ ligands with free phosphine.

Crystal Structure of Ni(PEt$_3$)$_2$(η^2-CH$_2$=CHC$_6$F$_5$) (6). Complex **6** was crystallized from hexane at −20 °C. The structure (Figure 3, Table 4) shows a characteristic trigonal-planar Ni(0) geometry. The dihedral angle between the planes NiC(1)C(2) and NiP(1)P(2) is only 2.1(3)°, smaller than in many comparable complexes.[29−33] The Ni−C distances average 1.960(6) Å.

(29) Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113.
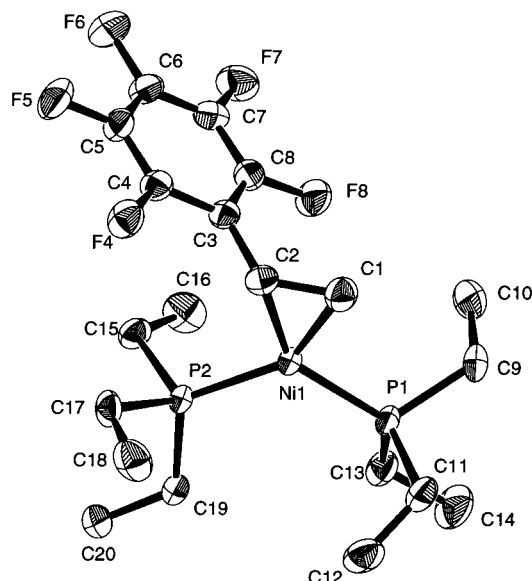
Figure 3. Molecular structure of **6**, Ni(PEt₃)₂(η²-CH₂=CHC₆F₅): ORTEP[26] plot with 30% probability thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 4. Principal Bond Lengths (Å) and Angles (deg) of Ni(PEt₃)₂(η²-CH₂=CHC₆F₅), 6

Ni(1)−C(1)	1.934(7)	F(8)−C(8)	1.360(6)
Ni(1)−C(2)	1.985(6)	C(3)−C(8)	1.397(7)
Ni(1)−P(1)	2.161(3)	C(3)−C(4)	1.403(7)
Ni(1)−P(2)	2.171(2)	C(3)−C(2)	1.468(7)
F(4)−C(4)	1.363(6)	C(4)−C(5)	1.362(8)
F(5)−C(5)	1.347(6)	C(5)−C(6)	1.370(8)
F(6)−C(6)	1.354(6)	C(6)−C(7)	1.367(8)
F(7)−C(7)	1.347(6)	C(7)−C(8)	1.365(7)
		C(2)−C(1)	1.420(8)
C(1)−Ni(1)−C(2)	42.5(2)	F(4)−C(4)−C(3)	118.6(5)
C(1)−Ni(1)−P(1)	99.0(2)	F(5)−C(5)−C(4)	120.9(5)
C(2)−Ni(1)−P(1)	141.4(2)	F(5)−C(5)−C(6)	119.4(5)
C(1)−Ni(1)−P(2)	146.0(2)	C(4)−C(5)−C(6)	119.7(5)
C(2)−Ni(1)−P(2)	103.6(2)	F(6)−C(6)−C(7)	120.6(5)
P(1)−Ni(1)−P(2)	114.97(11)	F(6)−C(6)−C(5)	120.5(5)
C(11)−P(1)−Ni(1)	112.8(2)	C(7)−C(6)−C(5)	118.9(5)
C(13)−P(1)−Ni(1)	120.0(2)	F(7)−C(7)−C(8)	119.9(5)
C(9)−P(1)−Ni(1)	115.3(2)	F(7)−C(7)−C(6)	119.9(5)
C(17)−P(2)−Ni(1)	112.6(2)	C(8)−C(7)−C(6)	120.2(5)
C(15)−P(2)−Ni(1)	115.1(2)	F(8)−C(8)−C(7)	116.7(5)
C(19)−P(2)−Ni(1)	119.3(2)	F(8)−C(8)−C(3)	119.1(5)
C(8)−C(3)−C(4)	112.5(5)	C(7)−C(8)−C(3)	124.1(5)
C(8)−C(3)−C(2)	126.0(5)	C(1)−C(2)−C(3)	124.9(5)
C(4)−C(3)−C(2)	121.5(5)	C(1)−C(2)−Ni(1)	66.8(3)
C(5)−C(4)−F(4)	116.8(5)	C(3)−C(2)−Ni(1)	115.1(4)
C(5)−C(4)−C(3)	124.6(5)	C(2)−C(1)−Ni(1)	70.7(3)

The P(1)−Ni−P(2) angle is 115.0(1)°, again closer to the ideal angle of 120° than in many analogues because of the lack of steric constraints. The plane of the C₆F₅ group is almost orthogonal to the Ni−C(1)−C(2) plane (dihedral angle = 86.9(2)°).

Reaction with Pentafluorobenzene and Pentafluoromethoxybenzene. The reaction with pentafluorobenzene was investigated in order to establish whether the nickel system is selective for C−F or C−H bond activation. The reaction was conducted only on

(30) Jarvis, A. P.; Haddleton, D. M.; Segal, J. A.; McCamley, A. *J. Chem. Soc., Dalton Trans.* **1995**, 2033.

(31) Dreissig, W.; Dietrich, H. *Acta Crystallogr., Sect. B* **1981**, *37*, 931.

(32) Stanger, A.; Boese, R. *J. Organomet. Chem.* **1992**, *430*, 235.

(33) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884; *J. Organomet. Chem.* **1974**, *77*, 423.

an NMR scale with Ni(COD)₂, 5 equiv of PEt₃, and 5 equiv of C₆F₅H in THF-*d₈*. The reaction proceeded very slowly, as for hexafluorobenzene, reaching ca. 85% conversion after 20 days at 35 °C. Three nickel fluoride complexes (**7a**−**c**) were formed with ¹⁹F resonances at ca. δ −385 in a ratio of 7:2:1 (see Table 1). These species are tentatively identified as the *ortho*, *meta*, and *para* isomers of *trans*-Ni(PEt₃)₂(C₆F₄H)F, though we cannot distinguish the individual isomers. In addition to the nickel complexes and phosphoranes (see above), a considerable amount of *p*-C₆F₄H₂ is formed (identified by NMR and gc/ms). A similar NMR experiment with pentafluoromethoxybenzene yielded two nickel fluoride complexes in approximately equal proportions, with traces of a third species. These species are provisionally assigned as isomers of *trans*-Ni(PEt₃)₂(C₆F₄OMe)F (**8a,b**).

Reaction with Hexafluorobenzene in the Presence of other Phosphines. The effect of changing the phosphine on the reaction of Ni(PR₃)₂(COD) and Ni(PR₃)₄/Ni(PR₃)₃ with hexafluorobenzene was examined. Of the phosphines, PMe₃, Me₂PCH₂CH₂PMe₂, PMePh₂, and P^nBu₃, only the last proved to give a reaction. When monitored by NMR, the reaction with P^nBu₃ gave strong evidence for the formation of *trans*-Ni(P^nBu₃)₂-(C₆F₅)F (**9**) with complete conversion after ca. 12 days (Table 1); pentafluorobenzene was also formed. However, **9** was not isolated. A control experiment with Ni-(COD)₂ and C₆F₆, but without phosphine, led to decomposition.

Discussion

Reactivity. The reactions of the Ni(0) complexes with hexafluorobenzene, pentafluoropyridine and related compounds, and pentafluorostyrene are summarized in Scheme 1. These reactions confirm the conclusions of Fahey and Mahan[19] concerning the product of the reaction with C₆F₆. The reactions of Ni(0) complexes with fluoropyridines demonstrate that intermolecular C−F activation of a fluoroaromatic can take place rapidly, and in good yield, at a first row transition metal through suitable choice of the substrate. Of particular note is the contrast between the very slow reaction with hexafluorobenzene and the rapid reactions with the other substrates. The nitrogen atom of the pentafluoropyridine accelerates the reaction and makes it regioselective. Even though pentafluoropyridine is not a Lewis base,[34] it is probable that it can act as a weak π-acceptor ligand when bound through nitrogen and that the nickel center attacks at nitrogen initially. The reactions of fluoropyridines at Ni(0) are selective for C−F over C−H activation, and for C−Cl over C−F activation. The alkene group of pentafluorostyrene, however, binds strongly to Ni(0) in the η²-mode and prevents C−F insertion. A methoxy substituent, as in pentafluoranisole, appears to have little influence on C−F activation, neither accelerating the reaction nor directing its selectivity. The effects of substituents are substantially different from other C−F activation reactions which we have studied (see Introduction). Thus, a methoxy group enhances photochemical C−F activation at Rh(η⁵-C₅H₅)(PMe₃)[7] but a pyridyl nitrogen does not.[35] However, a ring carbon−hydrogen bond is pho-

(34) Burdon, J.; Gilman, D. J.; Patrick, C. R.; Stacey, M.; Tatlow, J. C. *Nature* **1960**, *186*, 231. Banks, R. E.; Burgess, J. E.; Cheng, W. M.; Haszeldine, R. N. *J. Chem. Soc.* **1965**, 575.

(35) Perutz, R. N.; Whitlesey, M. K. Unpublished observations.

toactivated in preference to a C−F bond at Rh(η^5-C$_5$H$_5$)-(PMe$_3$).[18] The thermal reactions of Ru(dmpe)$_2$H$_2$ are closer to the nickel reactions in selectivity for C−F over C−H bonds, but in that case the regioselective influence of a ring hydrogen or methoxy group is very strong.[13] Selectivity for C−F over C−H activation is also observed in the chelate-assisted reactions of Ni(COD)$_2$ with partially fluorinated Schiff bases.[36] At platinum, the selectivity in intramolecular C−F activation can go a stage further and overcome competition from C−Cl bonds.[37,38]

The reaction of Ni(PEt$_3$)$_2$(COD) with C$_6$F$_6$ is clearly related to the conversion of Ni(dtbpe)(η^2-C$_6$F$_6$) to Ni-(dtbpe)(C$_6$F$_5$)F.[23a] However, we have neither observed Ni(PEt$_3$)$_2$(η^2-C$_6$F$_6$) nor *cis*-Ni(PEt$_3$)$_2$(C$_6$F$_5$)F in our NMR investigations of the reaction of Ni(PEt$_3$)$_2$(COD) with C$_6$F$_6$. We are now carrying out mechanistic studies of this reaction and the reaction with pentafluoropyridine.

Spectra and Structure of Nickel Fluoride Complexes. Since there is little information on nickel fluoride complexes and considerable interest in the combination of fluoride with phosphine and carbon ligands,[39] we use this section to point out the key structural and spectroscopic features of the *trans*-Ni(PR$_3$)$_2$(R^F)F complexes. The structure of **3a** provides a more reliable determination of the Ni−F bond length (1.856(2) Å) than that obtained from **1**. For comparison, the mean value of the Ni−O distance in four-coordinate Ni(II) aryloxy complexes is 1.865 Å.[28] A palladium analogue of **1** containing a phenyl group has been described very recently, Pd(PPh$_3$)$_2$(Ph)F, with a Pd−F bond length 2.085(3) Å.[40] The ^{19}F NMR resonances for the nickel-bound fluorine in **1**−**4** and **7**, **8** lie in the range from δ −390 to −367 with J_{PF} between 45 and 50 Hz.

The IR spectra provide sufficient information to identify the Ni−F stretching modes. Nakamoto[41] lists the ν(MF) region as 750−500 cm^{-1} and ν(MCl) region as 400−200 cm^{-1}. The values of ν(NiCl) decrease in the order NiCl$_2$ triatomic > *trans*-Ni(PR$_3$)$_2$Cl$_2$ > *cis*-Ni(PR$_3$)$_2$-Cl$_2$ > tetrahedral Ni(PR$_3$)$_2$Cl$_2$ > octahedral *trans*-Ni(py)$_4$Cl$_2$.[41] Further assistance in identification of the bands is provided by values of ν_{as}(NiX$_2$) for NiF$_2$ and NiF$_2$(CO) in matrices (779 and 713 cm^{-1}, respectively, for ^{58}Ni) and NiCl$_2$ and NiCl$_2$CO (520 and 469 cm^{-1}).[42] The value of ν_{as}(NiCl$_2$) in *trans*-NiCl$_2$(PEt$_3$)$_2$ is quoted[43] as 403 cm^{-1}, while Fahey and Mahan list ν(NiCl) in **5** as 373 cm^{-1}.[19] We have recorded IR spectra for complexes **1**−**6** (see Experimental Section) and compared them with the spectra of C$_6$F$_5$Cl and C$_6$F$_5$I. The value of ν(NiCl) in **5** has been confirmed. The chloride complexes **4** and **5** show no bands between 430 and 600 cm^{-1}. In contrast, the fluoride complexes, **1** and **2**, each exhibit two bands between 480 and 540 cm^{-1}. The

fundamental Ni−F stretching mode is assigned to the stronger of the bands: 535 cm^{-1} for **1** and 530 cm^{-1} for **2**. The weaker bands at 486 cm^{-1} for **1** and 501 cm^{-1} for **2** may arise from a combination mode which is in Fermi resonance with the fundamental. The assignment for **3** is complicated by ligand modes in the same region.

Conclusions

This paper reports the reactions of Ni(COD)$_2$ in the presence of PEt$_3$ with hexafluorobenzene and with analogues containing other functional groups. The prototypical reaction with C$_6$F$_6$ yields *trans*-Ni(PEt$_3$)$_2$-(C$_6$F$_5$)F (**1**), but is very slow. The analogous reaction of pentafluoropyridine proceeds far more rapidly and yields one regioisomer of *trans*-Ni(PEt$_3$)$_2$(C$_5$F$_4$N)F (**2a**) selectively. A similar reaction occurs with 2,3,5,6-tetrafluoropyridine, generating *trans*-Ni(PEt$_3$)$_2$(C$_5$HF$_3$N)F (**3**). The structures of **1** and **3a** provide the first values for Ni−F distances at square-planar Ni (II) of 1.836(5) and 1.856(2) Å, respectively. The reaction with penta-fluorostyrene yields Ni(PEt$_3$)$_2$(η^2-CH$_2$=CHC$_6$F$_5$) (**6**), a complex with trigonal-planar geometry at nickel.

Experimental Section

General Methods. Most of the synthetic work was carried out in an argon-filled glovebox with oxygen levels below 10 ppm. Some of the preparations were, however, carried out on a Schlenk line. All solvents (AR grade) were dried over sodium benzophenone ketyl and distilled under argon before use. Benzene-d_6 and THF-d_8 (Goss Scientific Instruments) were dried by stirring over potassium and then transferring under vacuum into NMR tubes fitted with Young's stopcocks. Fluoroarenes and fluoropyridines were obtained from Aldrich, except for pentafluoropyridine, pentafluorostyrene, and pen-tafluoroanisole which were obtained from Fluorochem Ltd. The fluoroaromatics were dried over molecular sieves (4 Å). Ni-(COD)$_2$ (Strem Chemicals) was used as received. The NMR spectra were recorded with Bruker MSL 300 or AMX 500 spectrometers. Selective ^{19}F−^{19}F decoupling experiments were carried out on a Bruker DRX 400 spectrometer. The ^{1}H NMR chemical shifts were referenced to residual C$_6$D$_5$H at δ 7.15 or THF-d_7 at δ 1.8. The ^{13}C{^{1}H} spectra were referenced to C$_6$D$_6$ at δ 128.0 and THF at δ at 26.7. The ^{19}F NMR spectra were referenced either to internal C$_6$F$_6$ at δ −162.9 or to external CFCl$_3$ at δ 0, and the ^{31}P{^{1}H} NMR spectra were referenced externally to H$_3$PO$_4$ at δ 0. Infrared spectra were recorded on a Mattson-Unicam RS spectrometer fitted with a CsI beamsplitter. NMR data are listed in Table 1.

trans-Ni(PEt$_3$)$_2$(C$_6$F$_5$)(F) (1). Ni(COD)$_2$ (160 mg, 0.58 mmol) was suspended in hexane (1.5 cm^3), and PEt$_3$ (309 mg, 2.62 mmol) was added. After the mixture had been stirred at 25 °C for 1 h, the solution was cooled to −78 °C. A white solid precipitated. The supernatant was removed with a cannula. The white solid Ni(PEt$_3$)$_4$ was dissolved in hexane (4 cm^3), and C$_6$F$_6$ (130 mg, 0.70 mmol) was added. The solution was stirred for 4 weeks at 25 °C. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. After filtration through a cannula, the yellow solution was concentrated under vacuum to 1 cm^3 and a yellow solid crystallized at −20 °C overnight. The super-natant was removed with a pipette, and the remaining yellow solid was dried rapidly under vacuum. The complex is very soluble in THF, benzene, and hexane. It decomposes when left under vacuum for several hours. Yield: 0.13 g (0.28 mmol, 48%). Anal. Calcd for C$_{18}$H$_{30}$F$_6$NiP$_2$: C, 44.94; H, 6.29. Found: C, 44.89; H, 6.36.

IR (C$_6$D$_6$, cm^{-1}): 1496 (s), 1448 (s), 1434 (m), 1416 (w). IR (Nujol, cm^{-1}): 1495 (vs), 1446 (m), 1434 (s), 1416 (m), 1276 (w), 1251 (w), 1053 (s), 1034 (s), 1003 (w), 947 (vs), 789 (m), 764 (s), 733 (m), 535 (m), 486 (w), 351 (vw). MS (EI, *m/z*,

(36) Osterberg, C. E. Ph.D. Thesis, University of Utah, 1990 (cited in ref 1).

(37) Crespo, M.; Martinez, M.; Sales, J. *J. Chem. Soc., Chem Commun.* **1992**, 823.

(38) Crespo, M.; Martinez, M.; de Pablo, E. *J. Chem. Soc., Dalton Trans.* **1997**, 1231.

(39) Doherty, N. M.; Hoffmann, N. W. *Chem. Rev.* **1991**, *91*, 553. Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478.

(40) Fraser, S. L.; Antipin, M. Y.; Hhroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769.

(41) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(42) Van Leirsburg, D. A.; De Kock, C. W. *J. Phys. Chem.* **1974**, *78*, 134.

(43) Shobatke, K.; Nakamoto, K. *J. Am. Chem. Soc.* **1970**, *9*, 3332.

relative intensity): 628 (5, $[(C_6F_5)_2Ni(PEt_3)_2]^+$), 480 (1.5, $[M]^+$), 294 (44, $[Ni(PEt_3)_2]^+$), 285 (100, $[Et_3P(C_6F_5)]^+$), 118 (58, $[PEt_3]^+$).

***trans*-Ni(PEt$_3$)$_2$(C$_5$F$_4$N)(F) (2).** Ni(COD)$_2$ (117 mg, 0.42 mmol) was suspended in hexane (1 cm^3), and PEt$_3$ (226 mg, 1.91 mmol) was added. The cloudy red-purple solution was stirred for 15 min at 25 °C, and C$_5$F$_5$N (92 mg, 0.55 mmol) was added. Within 3 min the color of the solution changed to yellow-orange. After 2 h of stirring at 25 °C, the volatiles were removed under vacuum. The orange oily residue was dissolved in hexane (10 cm^3) and filtered through a cannula, and the resulting yellow solution was concentrated to ca. 1 cm^3. A yellow solid was crystallized at −78 °C overnight. Yield: 96 mg (0.21 mmol, 49%). Anal. Calcd for C$_{17}$H$_{30}$F$_5$NNiP$_2$: C, 44.00; H, 6.52; N, 3.02. Found: C, 43.84; H, 6.44; N, 2.93.

IR (THF-d_8, cm^{-1}): 1617 (vw), 1597 (vw), 1481 (s), 1474 (m), 1462 (w), 1405 (vs), 1386 (m), 1289 (vw), 1248 (vw), 994 (s). IR (nujol, cm^{-1}): 1619 (vw), 1583 (w), 1482 (s), 1418 (m), 1406 (vs), 1386 (m), 1288 (vw), 1247 (vw), 1208 (vw), 1088 (m), 1035 (s), 994 (s), 811 (m), 764 (m), 734 (m), 711 (vw), 679 (vw), 633 (vw), 530 (w), 501 (vw), 433 (w), 414 (vw), 375 (vw), 348 (m), 330 (m). MS (EI, m/z, relative intensity): 463 (0.5, $[M]^+$), 444 (1.5, $[M − F]^+$), 431 (3), 413 (1), 268 (80, $[Et_3P(C_5F_4N)]^+$), 118 (100, $[PEt_3]^+$).

***trans*-Ni(PEt$_3$)$_2$(C$_5$F$_3$HN)(F) (3) (C$_5$F$_3$HN = 3,5,6-Trifluoropyrid-2-yl).** Ni(COD)$_2$ (189 mg, 0.69 mmol) was suspended in hexane (5 cm^3). After addition of PEt$_3$ (366 mg, 3.10 mmol), the resulting cloudy, purple-red solution was stirred for another 15 min before adding 2,3,5,6-tetrafluoropyridine (136 mg, 0.90 mmol). Within 10 min the color of the solution changed to orange-yellow. After 3 h of stirring at 25 °C, the volatiles were removed under vacuum and the remaining yellow, oily residue was dissolved in hexane (8 cm^3) and filtered through a cannula. The solution was concentrated to ca. 2 cm^3, and a yellow powder precipitated at 0 °C. The yellow solid was recrystallized twice from hexane (2 cm^3) at −20 °C and dried under vacuum. The complex is very soluble in THF and benzene and soluble in hexane. Yield: 0.19 g (0.43 mmol, 63%). Anal. Calcd for C$_{17}$H$_{31}$F$_4$NNiP$_2$: C, 45.77; H, 7.00; N, 3.14. Found: C, 45.77; H, 6.99; N, 3.13.

IR (Nujol, cm^{-1}): 1602 (m), 1586 (w), 1559 (m), 1425 (s), 1410 (m), 1256 (w), 1239 (w), 1220 (m), 1174 (m), 1147 (m), 1035 (m), 1002 (m), 962 (w), 808 (s), 764 (m), 730 (m), 705 (m), 625 (m), 567 (m), 503 (m), 473 (m), 415 (w), 374 (w), 364 (m), 331 (w), 314 (w), 291 (w), 282 (w). MS (EI, m/z, relative intensity): 445 (0.5, $[M]^+$), 426 (1, $[M − F]^+$), 377 (2), 294 (2), 264 (7, $[(C_5F_3HN)_2]^+$), 250 (65, $[Et_3P(C_5F_3HN)]^+$), 118 (100, $[PEt_3]^+$).

***trans*-Ni(PEt$_3$)$_2$(C$_5$F$_3$ClN)(Cl) (4) (C$_5$F$_3$ClN = 2,4,6-trifluoro-5-chloropyrid-3-yl).** Ni(COD)$_2$ (234 mg, 0.85 mmol) was suspended in hexane (6 cm^3). After addition of PEt$_3$ (452 mg, 3.82 mmol), the resulting cloudy, purple-red solution was stirred for 15 min at 25 °C before 2,4,6-trifluoro-3,5-dichloropyridine (223 mg, 1.10 mmol) was added. The resulting red-brown solution was stirred for another hour at 25 °C. The volatiles were removed under vacuum. The remaining red-brown, oily solid was dissolved in toluene (8 cm^3), and the solution was filtered through a cannula. The solvent was removed under vacuum, and the remaining solid was dissolved in hexane (5 cm^3). An orange solid was crystallized at −20 °C overnight. Further precipitation of product was achieved by stirring the solution at −78 °C. After removing the supernatant with a pipette, the resulting orange solid was dried under vacuum. A yellow-orange powder was obtained, which is soluble in hexane and very soluble in benzene and THF. Yield: 0.36 g (0.73 mmol, 85%). Anal. Calcd for C$_{17}$H$_{30}$Cl$_2$F$_3$NNiP$_2$: C, 41.08; H, 6.08; N, 2.82. Found: C, 41.10; H, 6.13; N, 2.75.

IR (C$_6$D$_6$, cm^{-1}): 1570 (w), 1554 (m), 1459 (w), 1420 (w), 1406 (s), 1385 (m), 1371 (w), 1336 (w), 1330 (m). IR (Nujol, cm^{-1}): 1590 (w), 1571 (m), 1555 (m), 1418 (m), 1402 (s), 1385 (m), 1370 (m), 1326 (m), 1252 (w), 1098 (w), 1034 (s), 1017 (vs),

764 (s), 722 (s), 635 (w), 425 (vw), 351 (m), 233 (m). MS (EI, m/z, relative intensity): 497 (0.1, $[M]^+$), 332 (0.6), 284 (100), 153 (40, $[ClPEt_3]^+$), 118 (37, $[PEt_3]^+$).

***trans*-Ni(PEt$_3$)$_2$(C$_6$F$_5$)(Cl) (5).** Ni(COD)$_2$ (110 mg, 0.4 mmol) was suspended in hexane (1.5 cm^3), and PEt$_3$ (240 mg, 2 mmol) was added, yielding a red solution. A white solid, Ni(PEt$_3$)$_4$, was precipitated by cooling the tube to −78 °C. The red supernatant was removed with a cannula filter. The white solid was dissolved in hexane (4 cm^3) to form a wine-colored solution, and C$_6$F$_5$Cl (120 mg, 0.60 mmol) was added. The solution turned yellow immediately and was left to stir for 2 h. The solvent and excess PEt$_3$ were removed under vacuum. Hexane (10 cm^3) was added to the residue, and any undissolved material was removed by filtration. The solvent was removed from the filtrate under vacuum and hexane (1 cm^3) was added. The sample was left to crystallize overnight at −20 °C, yielding yellow **5**.

IR (Nujol, cm^{-1}): 1623 (w), 1596 (w), 1547 (w), 1497 (vs), 1449 (vs), 1436 (s), 1415 (m), 1362 (w), 1350 (w), 1275 (w), 1254 (w), 1102 (w), 1054 (m), 1044 (sh), 1035 (s), 1003 (w), 951 (vs), 786 (m), 757 (m), 725 (m), 713 (w), 627 (w), 421 (w), 374 (w), 338 (w), 232 (w).

Ni(PEt$_3$)$_2$(η^2-CH$_2$=CHC$_6$F$_5$) (6). Ni(COD)$_2$ (131 mg, 0.48 mmol) was suspended in hexane (6 cm^3). After addition of PEt$_3$ (255 mg, 2.16 mmol), the cloudy red-purple solution was stirred for 15 min at 25 °C. On addition of CH$_2$=CHC$_6$F$_5$ (121 mg, 0.62 mmol), the color of the solution immediately changed to orange. The solution was stirred for another 2 h, and the volatiles were removed under vacuum. The orange oily residue was dissolved in hexane (6 cm^3), filtered through a cannula, and concentrated to ca. 1 cm^3. By storing the solution at −78 °C overnight, orange-red crystals were obtained. The supernatant was removed with a pipette, and the resulting solid was dried under vacuum. The complex was very soluble in hexane, benzene, and THF. Yield: 0.13 g (0.27 mmol, 57%). Anal. Calcd for C$_{20}$H$_{33}$F$_5$NiP$_2$: C, 49.11; H, 6.80. Found: C, 48.23; H, 7.06.

IR (THF-d_8, cm^{-1}): 1508 (vs), 1492 (s), 1455 (w), 1424 (vw), 1376 (vw). IR (Nujol, cm^{-1}): 1505 (vs), 1493 (vs), 1417 (w), 1203 (w), 1063 (m), 1035 (w), 966 (s), 917 (m), 762 (m), 707 (w), 621 (w), 559 (vw), 474 (vw), 415 (vw). MS (EI, m/z, relative intensity): 412 (0.5), 294 (0.8, $[Ni(PEt_3)_2]^+$), 194 (24, $[(C_6F_5)-CH=CH_2]^+$), 118 (100, $[PEt_3]^+$). The parent ion was not observed.

Reactions of Ni(PEt$_3$)$_4$ or Ni(PEt$_3$)$_2$(COD) with C$_6$F$_5$H. Ni(COD)$_2$ (21 mg, 0.08 mmol) was suspended in THF-d_8 (2 cm^3), and PEt$_3$ (45 mg, 0.38 mmol) was added, giving a red-purple solution. Pentafluorobenzene (67 mg, 0.40 mmol) was added, and the subsequent reaction was monitored by ^{31}P{^{1}H} and ^{19}F NMR spectroscopy. The ^{31}P NMR spectrum shows the formation of the three nickel fluoride isomers (**7a**−**c**) and three phosphoranes. According to the ^{19}F NMR spectrum, the main product of the reaction is p-C$_6$F$_4$H$_2$. Further NMR resonances could not be assigned. After 18 days (ca. 80% conversion) the reaction was interrupted and the volatiles were collected and investigated in a GC/MS experiment. The GC/MS showed a strong signal for p-C$_6$F$_4$H$_2$ and two weak signals for o- and m-C$_6$F$_4$H$_2$. A very weak signal for one isomer of C$_6$F$_3$H$_3$ was also detected.

Reaction of Ni(PEt$_3$)$_4$ or Ni(Et$_3$)$_2$(COD) with C$_6$F$_5$-(OCH$_3$). Ni(COD)$_2$ (24 mg, 0.09 mmol) was suspended in C$_6$D$_6$ (ca. 1.5 cm^3), and PEt$_3$ (52 mg, 0.44 mmol) was added. To the red-purple solution, C$_6$F$_5$OMe (23 mg, 0.12 mmol) was added. The reaction was monitored by ^{31}P{^{1}H} and ^{19}F NMR spectroscopy. After 2 weeks the reaction was nearly complete and was stopped. The NMR spectra showed the continuous formation of the nickel fluoride species **8a** and **8b**.

Reactions of Ni(P^{n}Bu$_3$)$_4$ or Ni(P^{n}Bu$_3$)$_2$(COD) with C$_6$F$_6$. Ni(COD)$_2$ (28 mg, 0.10 mmol) was suspended in C$_6$D$_6$ (1.5 cm^3). On addition of P^{n}Bu$_3$ (67 mg, 0.33 mmol), a red-purple solution was formed, to which 2 equiv of C$_6$F$_6$ was added. The reaction was monitored by ^{31}P{^{1}H} and ^{19}F NMR spectroscopy. The

Table 5. Crystal Structure Data for Complexes 1, 3a, and 6

	1	3a	6
empirical formula	$C_{18}H_{30}F_6NiP_2$	$C_{17}H_{31}F_4NNiP_2$	$C_{20}H_{33}F_5NiP_2$
M_r	481.09	446.10	489.14
dimens mm^3	$0.6 \times 0.5 \times 0.4$	$0.6 \times 0.3 \times 0.2$	$0.6 \times 0.3 \times 0.3$
color, habit	yellow block	yellow needle	yellow block
cryst syst	orthorhombic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
lattice params			
a, Å	9.406(6)	11.91(2)	10.260(9)
b, Å	9.447(5)	12.571(8)	14.994(12)
c, Å	26.62(2)	15.582(3)	8.151(14)
α, deg	90	90	97.59(10)
β, deg	90	99.29(4)	106.86(12)
γ, deg	90	90	90.44(7)
V, Å^3	2365(3)	2303(4)	1188(3)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.351	1.287	1.367
μ (Mo Kα),^{a} cm^{-1}	10.00	10.13	9.93
$F(000)$	1000	936	512
transmission coeff	0.93−1.00	0.91−1.00	0.84−1.00
temp, K	296(3)	296(3)	296(3)
scan type	ω	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	$1.05 + 0.3 \tan\theta$	$1.05 + 0.3 \tan\theta$	$1.31 + 0.3 \tan\theta$
2θ range, deg	5.28−50.00 (+h, +k, +l)	5.16−50.08 (+h, +k, l)	5.08−49.98 (+h, k, l)
no. of reflns measd	2484	4575	3438
no. of indep reflns	2400	4049	3140
R_{int}		0.0224	0.0351
no. of obs reflns ($I > 2\sigma(I)$)	1763	2865	2442
data/param	2398/249	4047/232	3140/268
refln/param ratio	9.63	17.44	11.72
residuals			
$R(F_o)^b$	0.0534	0.0436	0.0459
w$R(F_o^2)^c$	0.1543	0.1241	0.1337
goodness of fit	1.03	1.01	1.06
max diff peak, e Å^{-3}	0.42	0.39	0.57
min diff peak,^{d} e Å^{-3}	− 0.33	− 0.30	− 0.56

$^a \lambda = 0.710\ 73$ Å. $^b R = \sum|F_o| - |F_c|/\sum|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. ^{c} w$R = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. ^{d} There was no shift/esd in the last cycle of refinement.

^{31}P$\{^1$H$\}$ NMR resonance of the starting material at δ 11.65 had disappeared after 10−12 days. Product resonances were observed for the nickel fluoride complex (**9**), pentafluorobenzene, and two phosphoranes.

Difluorophosphoranes. Difluorophosphoranes were observed by NMR spectroscopy in reactions of fluoroarenes and fluoropyridines with Ni(0) complexes in the presence of excess phosphine. The formation of the difluorophosphoranes appeared to be catalyzed by the nickel complexes, but this aspect was not pursued. The reaction with C_6F_6 yielded difluorophosphoranes **A**, **B**, **C**, and **D**. The reaction with pentafluoropyridine yielded **A** and **C**, together with two further difluorophosphoranes **E** and **F**. The reaction with C_6F_5H yielded **A**, **B**, and **C**. NMR data for **A**−**F**: ^{31}P$\{^1$H$\}$ NMR: −16.64 (t, **A**, $J = 642$ Hz), −12.35 (t, **B**, $J = 589$ Hz), −19.97 (t, **C**, $J = 575$ Hz), **D** obscured, −27.15 (t, **E**, $J = 598$ Hz), **F** obscured. ^{19}F NMR: −37.7 (d, **A**, $J = 642$ Hz), −37.0 (d sept, **B**, $J = 589$, 11 Hz), −40.1 (d, **C**, $J = 571$ Hz), −39.45 (d, **D**, $J = 642$ Hz), −42.95 (d quin, **E**, $J = 597$, 12 Hz), −42.01 (d, **F**, $J = 578$ Hz).

X-ray Crystallographic Studies of Compounds 1, 3a, and 6. Crystals of compounds **1**, **3a**, and **6** were grown at −20 °C from hexane (see above). The resulting crystals were mounted in Lindemann tubes in a glovebox and sealed with epoxy cement. X-ray data were collected on a Rigaku AFC6S diffractometer. Cell constants and an orientation matrix for the data collection were obtained from a least-squares refinement of the positions of 20 automatically centered reflections. Equivalent reflections were merged, and data were corrected for Lorentz and polarization factors. The structures of compounds **1**, **3a**, and **6** were solved using direct methods with SHELXS86 and expanded using Fourier techniques with DIRDIF.[44] Full-matrix least-squares refinement on F^2 was carried out with SHELXL 93.[45] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined on

all structures using a riding model with isotropic temperature factors 1.2 times that of their carrier atoms (1.5 times for methyl groups). Bond lengths and angles are given in Tables 2−4, crystallographic details are summarized in Table 5, and ORTEP[26] representations are shown in Figures 1−3. Full details of atomic coordinates, anisotropic temperature factors, and other details of the refinement are given in the Supporting Information.

Supporting Information Available: Tables of X-ray crystallographic data, data collection, structure solution, and refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and least-squares planes and packing and ORTEP diagrams of **1**, **3a**, and **6** (29 pages). Ordering information is given on any current masthead page.

(44) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, G.; Garcia-Granda, W. P.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System. Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(45) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M. Krüger, C. Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189. Sheldrick, G. M. *SHELXL 93, Program for Crystal Structure Refinement;* University of Göttingen: Göttingen, Germany, 1993.