Reactivity of a Nickel Fluoride Complex: Preparation of New Tetrafluoropyridyl Derivatives[†]

Thomas Braun,[‡] Simon Parsons,[§] Robin N. Perutz,*[,‡] and Matthias Voith[‡]

Departments of Chemistry, University of York, Heslington, York YO10 5DD, U.K., and University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

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Treatment of *trans*-[NiF(2-C_5F_4N)(PEt_3)$_2$] (**1**), obtained by reaction of Ni(COD)$_2$ with PEt_3 and pentafluoropyridine, with Me_3SiOTf effects the formation of the air-stable triflate complex *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (**2**). The X-ray crystal structure reveals a molecular complex with approximately square-planar coordination at nickel, a Ni−O distance of 1.957(2) Å, and a Ni−C distance of 1.851(3) Å. The reaction of **2** with NaOPh yields the phenoxy complex *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (**3**). The crystal structure of **3** was determined. The Ni−O and Ni−C distances are 1.894(4) and 1.861(6) Å, respectively. The complexes *trans*-[NiPh(2-C_5F_4N)(PEt_3)$_2$] (**5**) and *trans*-[NiMe(2-C_5F_4N)(PEt_3)$_2$] (**6**) were obtained on treatment of **1** with PhLi and Me_2Zn, respectively. Treatment of **6** with CO yielded 2-acetyltetrafluoropyridine, while reaction with air yielded 2-methyltetrafluoropyridine. The studies reported in this paper demonstrate the synthesis of nickel derivatives of tetrafluoropyridine with the metal in a 2-position as well as the preparation of new 2-substituted tetrafluoropyridines by C−C coupling reactions.

Introduction

Several methods have recently been reported for activating carbon−fluorine bonds of fluoroaromatic and fluoroaliphatic compounds by reaction at appropriate transition-metal centers.[1−5] One of the most striking reactions we have encountered is the fast oxidative addition of pentafluoropyridine at a nickel center, yielding *trans*-[NiF(2-C_5F_4N)(PEt_3)$_2$] (**1**).[5] The special properties of the transition-metal−fluorine bonds are increasingly being recognized,[3,6] as is the role of carbon−metal−fluorine fragments in synthesis and catalysis.[1−3,7] The ease of synthesis of **1** offered new opportunities for investigating the reactivity of the Ni−F bond in a molecular system. The replacement of the metal-bound fluorine in **1** by a new anionic ligand would provide an entry to compounds of the general structure *trans*-[NiR(2-C_5F_4N)(PEt_3)$_2$]. Although several nickel pentafluorophenyl derivatives of the type *trans*-[NiX(C_6F_5)L_2][8,9] and *trans*-[Ni(C_6F_5)$_2$$L_2$][8] have been reported, to the best of our knowledge no other transition-metal compound with a 2-tetrafluoropyridyl ligand is known. In this paper we describe the synthesis and molecular structures of (2-tetrafluoropyridyl)nickel derivatives with triflate, phenoxide, phenyl, and methyl ligands as well as the preparation of new 2-substituted tetrafluoropyridines by C−C coupling reactions.

Results

Synthesis of *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (2). The complex *trans*-[NiF(2-C_5F_4N)(PEt_3)$_2$] (**1**) reacts immediately with Me_3SiOTf to give the air-stable triflate complex *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (**2**) in 83% yield. An additional pathway to **2** is the stepwise treatment of a hexane solution of [Ni(PEt_3)$_2$(COD)] with C_5F_5N and Me_3SiOTf without isolation of **1**. The structure proposed for **2** (Scheme 1) is supported by the ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR data (Table 1). The presence of the triflate ligand is indicated by a quartet at δ 121.2 in the ^{13}C NMR spectrum at 233 K and a broad singlet

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[†] Dedicated to Prof. Helmut Werner on the occasion of his 65th birthday.

[‡] University of York.

[§] University of Edinburgh.

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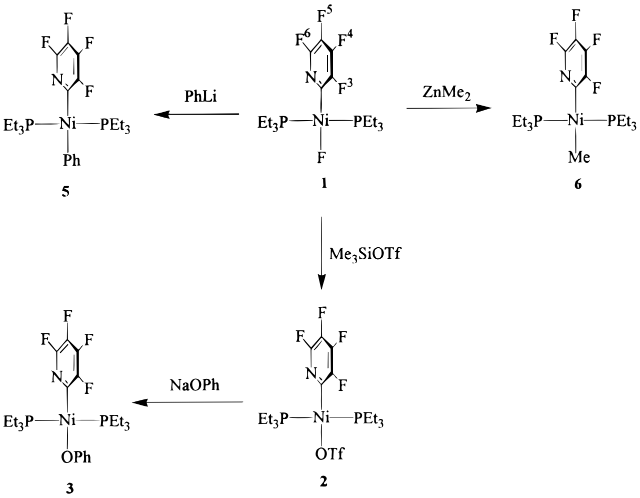
Table 1. NMR Data at 298 K (δ (*J*/Hz))

complex	^1H	$^{31}P\{^1H\}$	^{19}F[a]	$^{13}C\{^1H\}$
2 (THF-d_8)	1.11 (m, 12H, CH_2), 0.90 (m,[b] 18H, CH_3)	11.9 (s)	−77.82 (s, 3F, CF_3), −84.90 (dt, $J(FF) = 15.3$, $J(FF) = 26.7$, 1F, F^6), −131.79 (t, $J(FF) = 26.7$, 1F, F^3), −148.60 (m, 1F, F^4), −171.45 (m, 1F, F^5)[c]	151.1 (m, C_{ipso} of C_5F_4N), 148.3 (dm, $J(CF) = 237.1$, CF), 148.1 (dm, $J(CF) = 230.9$, CF), 145.4 (dm, $J(CF) = 269.1$, CF), 132.1 (dm, $J(CF) = 259.9$, CF), 121.2 (s, br,[d] CF_3), 14.6 (t, $J(PC) = 12.5$, CH_2), 8.7 (s, CH_3)
3 (C_6D_6)	7.52 (d, $J(HH) = 7.7$, 2H, H_{ortho}), 7.31 (t, $J(HH) = 7.7$, 2H, H_{meta}), 6.73 (t, $J(HH) = 7.2$, 1H, H_{para}), 1.01 (m, 12H, CH_2), 0.90 (m, 18H, CH_3)	11.8 (s)	−85.19 (m, 1F, F^6), −132.52 (t, $J(FF) = 26.6$, 1F, F^3), −150.66 (m, 1F, F^4), −172.62 (m, 1F, F^5)	170.1 (s, C_{ipso} of C_6H_5), 165.6 (m, C_{ipso} of C_5F_4N), 149.5 (tm, $J(CF) = 237.1$, CF), 145.2 (dm, $J(CF) = 289.2$, CF), 130.4, 121.7, 114.8 (all s, CH), 14.9 (t, $J(PC) = 11.8$, CH_2), 8.9 (s, CH_3)[e,f]
4 (C_6D_6)	8 (s, OH), 7.64−6.69 (m, 10H, Ph), 1.00 (m, 12H, CH_2), 0.90 (m, 18H, CH_3)[g]	11.2 (s)[f]	−85.07 (m, 1F, F^6), −132.22 (t, $J(FF) = 27.7$, 1F, F^3), −150.24 (m, 1F, F^4), −172.22 (m, 1F, F^5)[g]	169.9 (s, C_{ipso} of C_6H_5), 165.5 (m, C_{ipso} of C_5F_4N), 159.9 (s, C_{ipso} of C_6H_5), 149.5 (tm, $J(CF) = 227.9$, CF), 145.2 (dm, $J(CF) = 268.1$, CF), 131.1, 130.4, 121.7, 120.8, 117.3, 114.9 (all s, CH), 14.8 (t, $J(PC) = 12.0$, CH_2), 8.9 (s, CH_3)[e−g]
5 (C_6D_6)	7.70 (m, 1H, H_{ortho}), 7.52 (m, 1H, H_{ortho}), 7.12 (t, $J(HH) = 7.5$, 2H, H_{meta}), 6.73 (m, 1H, H_{para}), 0.88 (m, 30H, CH_2CH_3)	14.0 (s)[f]	−85.47 (m, 1F, F^6), −132.89 (t, $J(FF) = 29.9$, 1F, F^3), −152.33 (m, 1F, F^4), −173.62 (m, 1F, F^5)	184.3 (m, C_{ipso} of C_5F_4N), 165.9 (t, $J(CP) = 30.2$, C_{ipso} of C_6H_5), 150.4−147.0 (m, CF), 143.8 (t, $J(CF) = 267.2$, CF), 137.9 (t, $J(CF) = 3.0$, CH), 137.2 (t, $J(CF) = 3.0$, CH), 126.7 (t, $J(CF) = 2.4$, CH), 126.4 (t, $J(CF) = 2.3$, CH), 121.9 (t, $J(CF) = 2.1$, CH), 14.2 (t, $J(PC) = 12.5$, CH_2), 7.9 (s, CH_3)[h]
6 (THF-d_8)	1.38 (m, 12H, CH_2), 1.09 (m, 18H, CH_2CH_3), −0.89 (t, $J(PH) = 9.0$, 3H, $NiCH_3$)	20.1 (s)	−91.59 (m, 1F, F^6), −138.25 (t, $J(FF) = 30.5$, 1F, F^3), −159.00 (m, 1F, F^4), −180.81 (m, 1F, F^5)	198.0 (m, C_{ipso} of C_5F_4N), 150.6 (dm, $J(CF) = 223.0$, CF), 149.0 (dm, $J(CF) = 270.9$, CF), 132.0−129.6 (m, CF), 16.1 (t, $J(PC) = 12.3$, CH_2), 9.5 (s, CH_2CH_3), −8.5 (t, $J(PC) = 25.4$, $NiCH_3$)
7 (C_6D_6)	1.84 (dm, $J(HF) = 2.2$, CH_3)		−85.29 (m, 1F), −141.53 (m, 1F), −146.63 (m, 1F), −161.71 (m, 1F)	
8 (C_6D_6)	2.16 (s, CH_3)		−83.00 (m, 1F), −137.13 (m, 1F), −141.16 (m, 1F), −149.92 (m, 1F)	

[a] Numbering of fluorine atoms as in Scheme 1. [b] t in $^1H\{^{31}P\}$, $J(HH) = 7.5$ Hz. [c] In C_6D_6. [d] At 233 K: q, $J(CF) = 338.6$. [e] In THF-d_8. [f] One CF resonance is masked by the signal at δ 130.4. [g] The δ values can be slightly shifted, depending on the phenol concentration. [h] One CF resonance is masked by the solvent.

Scheme 1. Reactions of Nickel Tetrafluoropyridyl Complexes



at δ −77.82 in the ^{19}F NMR spectrum. The observation of the asymmetric sulfonyl stretching frequency at 1314 cm^{-1} is consistent with a metal-bonded triflate group with the assumed η^1-coordination mode.[10] The assignment of **2** as the 2-pyridyl isomer is based on the chemical shifts of four further fluorine resonances at δ −84.90, −131.79, −148.60, and −171.45 for the aromatic fluorine atoms. The assignments were made by comparison with the data found for *trans*-[NiF(2-C_5F_4N)(PEt_3)$_2$] (**1**), which are based on $^{19}F-^{19}F$ decoupling experiments.[5] The *trans* geometry is indicated by the equivalence of the ^{31}P nuclei in the ^{31}P NMR spectrum. The structure of **2** was also determined by X-ray crystallography.

Crystal Structure of *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (2). The triflate complex **2** was crystallized from hexane at −20 °C. An ORTEP diagram of the crystal structure is shown in Figure 1. The principal bond lengths and angles are summarized in Table 2. Despite a rotational disorder about the Ni−C(2)−C(50) axis the structure provides useful data. The angles between the adjacent ligands at nickel vary from 86.8(1) to 92.90(8)°. The dihedral angle between the nickel coordination plane and the plane of the aryl ring is 87.8°. The Ni−C distance of 1.851(3) Å differs little from the values found for *trans*-[NiF(2-C_5F_3HN)(PEt_3)$_2$] (1.869(4) Å)[5] or for the dimeric pyridyl complex [NiCl(PEt_3){μ-κ^2(*C*,*N*)-(2-C_5ClH_3N)}]$_2$ (1.866(10), 1.867(9) Å).[11] The triflate anion is monodentate oxygen-bonded with a Ni−O bond length of 1.957(2) Å, which is longer than the mean value of Ni−O distances of four-coordinate Ni(II) aryloxy complexes of 1.865 Å.[12] It is, however, significantly shorter than the Ni−O bond lengths in the octahedral complex [Ni(bipy)$_2$(OTf)$_2$] (2.148(4), 2.135(5) Å).[13]

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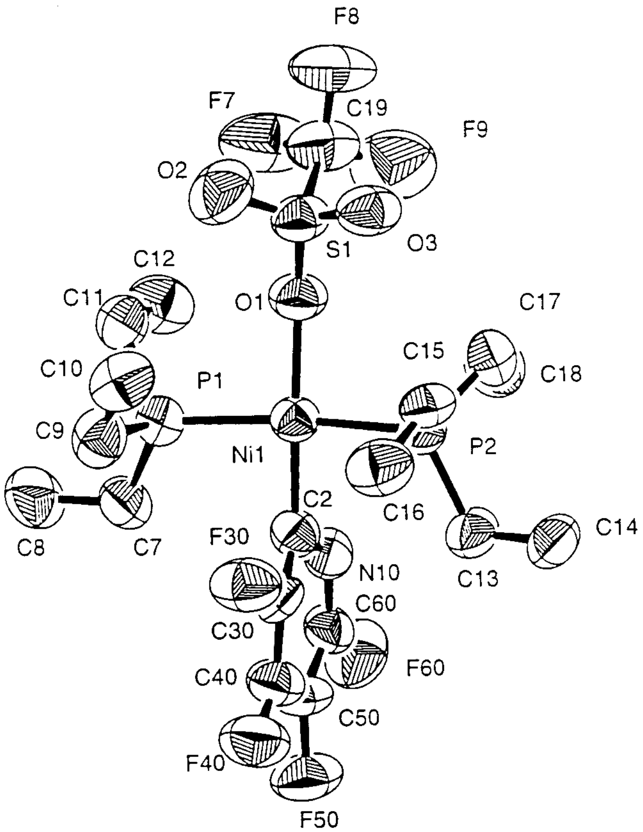

Figure 1. ORTEP[36] diagram of the structure of *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (**2**) with ellipsoids shown at the 30% level. Note that the rotational disorder about Ni−C2−C50 leads to averaging of the locations across the pyridyl ring.

Table 2. Principal Bond Lengths (Å) and Angles (deg) of One Rotamer of *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (2)[a]

Ni(1)−O(1)	1.957(2)	C(50)−F(50)	1.343(8)
Ni(1)−C(2)	1.851(3)	C(60)−F(60)	1.339(8)
Ni(1)−P(1)	2.224(1)	N(10)−C(2)	1.38(1)
Ni(1)−P(2)	2.229(1)	N(10)−C(60)	1.29(3)
O(1)−S(1)	1.455(2)	C(2)−C(30)	1.37(1)
S(1)−C(19)	1.803(5)	C(30)−C(40)	1.42(2)
C(30)−F(30)	1.340(9)	C(40)−C(50)	1.36(2)
C(40)−F(40)	1.339(8)	C(50)−C(60)	1.37(2)
P(1)−Ni(1)−P(2)	171.14(4)	O(1)−Ni(1)−C(2)	170.7(1)
P(1)−Ni(1)−O(1)	92.43(8)	Ni(1)−C(2)−C(30)	130.6(7)
P(2)−Ni(1)−O(1)	92.90(8)	Ni(1)−C(2)−N(10)	113.9(7)
P(1)−Ni(1)−C(2)	86.8(1)	Ni(1)−O(1)−S(1)	151.1(2)
P(2)−Ni(1)−C(2)	89.0(1)		

[a] The two rotamers have nearly identical bond distances. Any differences are less than 2σ, except for N(10)−C(60) (4σ).

Synthesis of *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (3) and *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$]·HOPh (4). The preparation of *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (**3**) proceeds by a metathesis reaction involving **2** and NaOPh. The resulting yellow crystals are moderately air-stable. The reaction of **1** with NaOPh, which was monitored by NMR, also yields the phenoxy complex **3**. No reaction is observed between **1** and phenol. The ^{1}H NMR spectrum of **3** shows three well-resolved resonances of the *ortho*, *meta*, and *para* protons of the phenoxy ligand at δ 7.52, 7.31, and 6.77. This is consistent with a rapid rotation around the C−O bond, which causes the equivalence of the two *ortho* and two *meta* protons on the NMR time scale. The most characteristic feature in the ^{13}C NMR spectrum is the low-field position of the *ipso* carbon signal of the phenyl group at δ 170.1.[14,15] The ^{19}F NMR spectrum reveals only the four signals in the aromatic region at δ −85.19, −132.52, −150.66, and −172.62, which appear at almost the same chemical shifts as those found for **2**.

The ^{19}F and ^{31}P NMR signals of **3** are slightly shifted in the presence of phenol by an amount which depends on the phenol concentration. The signals in the ^{1}H NMR spectrum for the aromatic hydrogen atoms together with the eight resonances in the ^{13}C NMR spectrum for the carbon atoms are consistent with the presence of two chemically inequivalent aromatic rings. The ^{13}C NMR spectrum now reveals two resonances for quaternary *ipso* carbon atoms at δ 170 and 160. We therefore assume that the phenol adduct *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$]·HOPh (**4**) is formed, in which a phenol molecule is bound to the phenoxide ligand via an O−H···O bond in a way similar to that for the complex *trans*-[NiMe(OPh)(PMe_3)$_2$]·HOPh.[15] The presence of the hydrogen bonding is also indicated in the ^{1}H NMR spectra. The resonance at about δ 8 is due to the OH hydrogen, which is at considerably lower field than the OH resonance at ca. δ 5.5 of free phenol.[14c,15] Crystallization of **4** from a hexane solution regenerates compound **3**.

Crystal Structure of *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (3). The phenoxy complex **3** was crystallized from hexane at −20 °C. An ORTEP diagram of the crystal structure is shown in Figure 2. Selected bond lengths and angles are summarized in Table 3. Compound **3** exhibits a square-planar geometry with the pyridyl group coordinated *trans* to the phenoxy ligand. The angles about the nickel atom are distorted from an ideal square-planar geometry and vary from 85.3(2) to 93.6(1)°. Both the phenyl plane of the phenoxy ligand and the plane defined by the pyridyl ring are nearly perpendicular to the coordination plane. The dihedral angle between the nickel coordination plane and the plane of the fluorinated aryl ring is 94.4°, while the angle between the nickel coordination plane and the phenyl plane is 102.9°. The angle between the nickel coordination plane and the plane defined by Ni(1)−O(19)−C(19) is 97.2°. The Ni−O−C angle (123.1(4)°) is somewhat smaller than the one found in *trans*-[NiMe(OPh)(PMe_3)$_2$]·HOPh (127.1°)[15] but almost the same as the equivalent angle in *trans*-[NiH(OPh)(PBz_3)$_2$]·HOPh (123.4(4)°),[16] where a phenol moiety is also associated with the phenoxy ligand through O−H···O hydrogen bonding. As a consequence of the lack of hydrogen bonding the Ni−O bond in **3** of 1.894(4) Å is shorter than the distances in *trans*-[NiMe(OPh)(PMe_3)$_2$]·HOPh (1.932(5) Å)[15] and *trans*-[NiH(OPh)(PBz_3)$_2$]·HOPh (1.949(7) Å)[16] but longer than the one found in *trans*-[Ni{O-(*o,o*-C_6*t*BuMeH_3)}$_2$(PMe_3)$_2$] (1.861(3) Å).[14a] It is also significantly shorter than the equivalent bond

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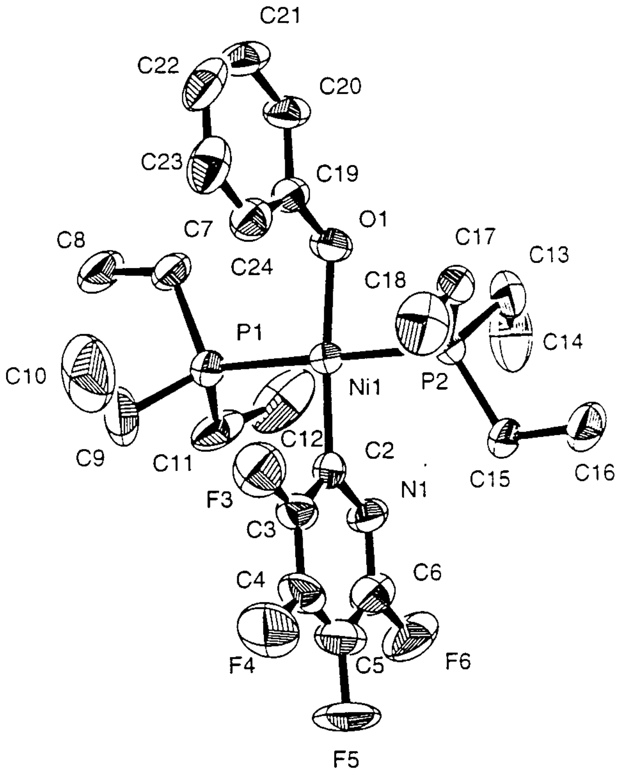


Figure 2. ORTEP[36] diagram of the structure of *trans*-[Ni(OPh)(2-C_5F_4N)$(PEt_3)_2$] (**3**) with ellipsoids shown at the 30% level.

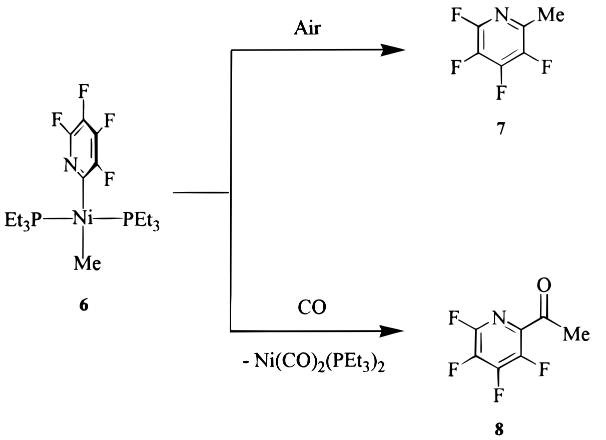
Table 3. Principal Bond Lengths (Å) and Angles (deg) of *trans*-[Ni(OPh)(2-C_5F_4N)$(PEt_3)_2$] (3)

Ni(1)−O(1)	1.894(4)	C(6)−F(6)	1.348(8)
Ni(1)−C(2)	1.861(6)	N(1)−C(2)	1.367(8)
Ni(1)−P(1)	2.215(2)	N(1)−C(6)	1.319(9)
Ni(1)−P(2)	2.202(2)	C(2)−C(3)	1.381(8)
O(1)−C(19)	1.322(7)	C(3)−C(4)	1.356(9)
C(3)−F(3)	1.358(7)	C(4)−C(5)	1.36(1)
C(4)−F(4)	1.351(8)	C(5)−C(6)	1.36(1)
C(5)−F(5)	1.325(8)		
P(1)−Ni(1)−P(2)	172.44(8)	Ni(1)−O(1)−C(19)	123.1(4)
P(1)−Ni(1)−O(1)	93.6(1)	O(1)−C(19)−C(24)	123.1(6)
P(2)−Ni(1)−O(1)	85.2(1)	O(1)−C(19)−C(20)	119.2(6)
P(1)−Ni(1)−C(2)	89.3(2)	Ni(1)−C(2)−N(1)	120.2(5)
P(2)−Ni(1)−C(2)	91.4(2)	Ni(1)−C(2)−C(3)	123.1(5)
O(1)−Ni(1)−C(2)	175.7(2)		

length found in *trans*-[Ni(OTf)(2-C_5F_4N)$(PEt_3)_2$] (**2**). The Ni−C distance of 1.861(6) Å is almost the same as the value found for **2**.

Synthesis of *trans*-[NiPh(2-C_5F_4N)$(PEt_3)_2$] (5). After we had shown that we can replace the triflate ligand in **1** or **2** by using a phenoxide anion as nucleophile, we became interested in extending these studies to reactions with carbon nucleophiles. On treatment of a hexane solution of **1** with excess PhLi at −78 °C and subsequent addition of methanol the phenyl complex **5** is obtained, which was crystallized at −20 °C. The very low yield of 14% is probably due to the extreme solubility of the product. However, it is necessary to recrystallize **5** in order to get a pure complex. Attempts to displace the triflate ligand of **2** using PhLi or PhMgCl were less successful. In the latter case, the chloro derivative *trans*-[NiCl(2-C_5F_4N)$(PEt_3)_2$][17] is formed instead. The proposed structure of **5** is based mainly on NMR spectroscopic data. The ^{13}C NMR spectrum displays a triplet at δ 165.9 with a coupling of $J(PC) = 30$ Hz for the *ipso* carbon atom of the phenyl group, which is consistent with a metal-bonded phenyl group. The restricted rotation of the phenyl group around the Ni−C bond causes inequivalence of the carbon atoms on the NMR time scale. All five resonances appear as triplets (Table 1). This is in sharp contrast to the ^{13}C NMR data found for the compound *trans*-[NiBr(Ph)$(PMe_3)_2$], which is fluxional at room temperature and where only the signal for the *ipso* carbon atom appears as a triplet.[18] The resonance for the *ipso* carbon atom of the tetrafluoropyridyl group is found at rather low field, δ 184.3. The ^1H NMR spectrum reveals four different signals for the five inequivalent aromatic protons (Table 1).

Scheme 2. Reactivity of 6



Synthesis of *trans*-[NiMe(2-C_5F_4N)$(PEt_3)_2$] (6). The reaction of **2** with MeLi proceeds in a way similar to that with PhLi, and the methyl complex *trans*-[NiMe(2-C_5F_4N)$(PEt_3)_2$] (**6**) is obtained in moderate yield as a yellow solid. However, **6** is more conveniently prepared from *trans*-[NiF(2-C_5F_4N)$(PEt_3)_2$] (**1**) and Me_2Zn in 87% yield. The ^1H NMR spectrum of **6** displays a triplet at δ −0.89 ($J(PH) = 9.0$ Hz), indicating that the methyl group is bound to the metal. This structure is also supported by the ^{13}C NMR spectrum, which shows a triplet at δ −8.5 ($J(PC) = 25.4$ Hz). The resonance for the *ipso* carbon atom of the pyridyl ligand appears at δ 198.0, a rather higher chemical shift than for **2** and **3**.

Reactivity of *trans*-[NiMe(2-C_5F_4N)$(PEt_3)_2$] (6). Preliminary investigations on the reactivity of **6** reveal C−C coupling reactions of the organic ligands (Scheme 2). On admission of air to a solution of **6** the reductive-elimination product 2-C_5MeF_4N (**7**) is formed. Treatment of **6** with CO affords the corresponding ketone 2-$C_5(COMe)F_4N$ (**8**) and [$Ni(CO)_2(PEt_3)_2$]. The proposed structures for both tetrafluoropyridines are supported by the ^1H and ^{19}F NMR and mass spectrometric data. The IR spectrum of **8** displays an absorption at 1713 cm^{-1}, which is assigned to the vibration of the C=O bond.

Discussion

The syntheses of compounds of the general type *trans*-[NiR(2-C_5F_4N)$(PEt_3)_2$] (R = F, OTf, OPh, Ph, Me) are

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[17] Braun, T.; Perutz, R. N., unpublished results.

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summarized in Scheme 1. The reactions reported represent two ways of substituting a fluorine ligand by a new anionic group. One approach is fluoride abstraction using Me_3SiOTf, which leads to the air-stable complex *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (**2**) and Me_3SiF (identified by ^1H and ^{19}F NMR spectroscopy). Similar reactions were recently described by Caulton et al., who generated the complexes [RuPh(OTf)(CO)(P*t*Bu_2Me)$_2$] and [Ir(H)$_2$(OTf)(P*t*Bu_2Ph)$_2$] from the corresponding fluorides.[6f,19] So far there has been only one square-planar nickel triflate compound in the literature.[20] Compound **2** is an excellent starting material for the synthesis of *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (**3**) by a salt metathesis reaction. Complex **3** is air-stable over weeks, in contrast to *trans*-[NiMe(OPh)(PEt_3)$_2$],[21] which is very unstable, or *trans*-[NiMe(OPh)(PMe_3)$_2$],[15] which could only be isolated as a phenol adduct. However, a phenol adduct of **3**, *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$]·HOPh (**4**), was observed in solution.

Compounds bearing the tetrafluoropyridyl *and* a second carbon ligand may be synthesized by nucleophilic substitution reactions of the fluoride in **1** or the triflate in **2** by a phenyl or methyl group. Although pentafluoropyridine itself undergoes nucleophilic substitution at the *para* position, there is no sign of substitution on the perfluorinated ring in these reactions.[22] The air-sensitive methyl compound **6** is more easily prepared from **1** and an excess of $ZnMe_2$. In contrast to the nickel complexes *trans*-[NiR(4-C_5H_4F)(PEt_3)$_2$] (R = Ph, Me)[23] and *trans*-[$NiPh_2$(PEt_3)$_2$],[24] **5** and **6** are stable in solution over a few days. However, the complexes *trans*-[NiMe(C_6F_5)(PPh_2Me)$_2$][25] and *trans*-[NiPh(2-C_6H_4Cl)(PEt_3)$_2$][26] are also of remarkable stability. This stability could be due to a strong π-back-bonding from the nickel center to the perfluorinated aromatic ring.[25,27,28] The high chemical shift of the signal for the *ipso* carbon at δ 198.0 of the pyridyl ligand in **6** may also be an indicator of back-bonding.

According to CSD only a few Ni−O bond lengths are known in square-planar nickel phosphine complexes.[29] The X-ray structures of **2** and **3** are therefore of particular interest. Probably because of the more weakly bonded triflate ligand the Ni−O distance of 1.957(2) Å in **2** is clearly larger than the value found for **3** (1.894(4) Å). There is not much difference in the Ni−C bond lengths between **2**, **3**, and *trans*-[NiF(2-C_5F_3HN)(PEt_3)$_2$].[5]

The C−C coupling products 2-C_5MeF_4N (**7**) and 2-C_5(COMe)F_4N (**8**) are observed on treatment of **6** with air or CO, respectively. It is known that O_2 can act as a phosphine scavenger by either complexation or oxidation, which can lead to the observed pyridine.[26] Since **1** does not react with CO, we assume that the incorporation of CO occurs via an insertion−migration process of CO into the M-CH_3 bond. The C−C coupling reaction is then induced by a second CO molecule, and the final products are formed.

Conclusions

Nickel−pyridyl complexes are uncommon and, when they do occur, are often dimeric species.[11,30] Compounds with a perfluorinated pyridyl ligand in the 2-position were unknown until we reported the C−F activation of pentafluoropyridine on a nickel center.[5] This paper details the preparation of the monomeric pentafluoropyridyl complexes *trans*-[NiR(2-C_5F_4N)(PEt_3)$_2$] (R = OTf, OPh, Ph, Me) by using *trans*-[NiF(2-C_5F_4N)(PEt_3)$_2$] (**1**) or *trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (**2**) as precursor. The X-ray structures of **2** and *trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (**3**) have been determined.

Since it is very difficult to prepare tetrafluoropyridines substituted in the 2-position (2-XC_5F_4N) by either electrophilic or nucleophilic substitution, very few are known.[22,31] There are no magnesium, lithium, copper, or other derivatives of tetrafluoropyridine with a metal in the 2-position.[22] Not only do the nickel compounds **1**−**6** represent some rare examples of metal tetrafluoropyridyl complexes[28,32] but also they are the first derivatives where the tetrafluoropyridine is coordinated to the metal in the 2-position. This is of special interest as the compounds **3**, *trans*-[NiPh(2-C_5F_4N)(PEt_3)$_2$] (**5**), and *trans*-[NiMe(2-C_5F_4N)(PEt_3)$_2$] (**6**) provide an opportunity to synthesize new 3,4,5,6-tetrafluoropyridines. Preliminary investigations show that on treatment of **6** with air or CO the pyridines 2-C_5MeF_4N (**7**) and 2-C_5(COMe)F_4N (**8**) are formed, respectively. We have found no previous descriptions of these compounds.

Experimental Section

General Methods. Most of the synthetic work was carried out on a Schlenk line or in an argon-filled glovebox with oxygen levels below 10 ppm. All solvents (AR grade) were dried over sodium benzophenone ketyl and distilled under argon before use. Benzene-d_6 and THF-d_8 (Apollo Scientific Ltd) were dried by stirring over potassium and then transferred under vacuum into NMR tubes fitted with Young stopcocks. The lithium and zinc reagents were obtained from Aldrich. Sodium phenoxide was prepared by adding sodium hydride to a solution of phenol in toluene. Pentafluoropyridine was obtained from Fluorochem Ltd and was dried over molecular sieves (4 Å). Ni(COD)$_2$ (Strem Chemicals) was used as received. Complex **1** was prepared as described in the literature.[5]

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Table 4. Crystal Structure Data for Complexes 2 and 3

	2	**3**
empirical formula	$C_{18}H_{30}F_7NNiO_3P_2S$	$C_{23}H_{35}F_4NNiOP_2$
M_r	594.14	538.19
radiation	Cu Kα	Mo Kα
wavelength/Å	1.541 80	0.710 73
temp/K	220	220
cryst size/mm^3	0.54 × 0.47 × 0.35	0.50 × 0.25 × 0.08
color, habit	orange block	yellow lath developed in (001)
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
lattice params		
a/Å	16.068(3)	16.551(5)
b/Å	15.342(3)	9.1992(18)
c/Å	21.406(3)	18.253(5)
β/deg	90	104.55(2)
V/Å^3	5276.92	2689.95
Z	8	4
D_{calcd}/g cm^{-3}	1.50	1.33
abs coeff/mm^{-1}	3.60	0.88
$F(000)$	2438.85	1130.16
scan type	$\omega-\theta$	$\omega-\theta$
θ range/deg	2.75−70.26	2.51−24.99
index ranges	$0 \le h \le 19, 0 \le k \le 18, -26 \le l \le 0$	$-19 \le h \le 19, -1 \le k \le 10, 0 \le l \le 21$
no of rflns measd	5247	6909
no of indep rflns	4723	4740
R_{int}	0.00	0.20
abs cor	ψ-scans ($T_{min} = 0.061$, $T_{max} = 0.176$)	numerical ($T_{min} = 0.632$, $T_{max} = 0.799$)
no. of data/params	3292/380	2369/290
goodness of fit on F^2	1.1273	1.1780
residuals R	0.0446	0.0576
R_w	0.0484	0.0521
observn criterion	$>2\sigma(I)$	$>2\sigma(I)$
final max δ/σ	0.19	0.0019
weighting scheme	Chebychev polynomial	Chebychev polynomial
max peak in final diff map/e Å^{-3}	0.36	0.61
min peak in final diff map/e Å^{-3}	−0.20	−0.49

The NMR spectra were recorded with a Bruker AMX 500 spectrometer. The ^1H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15 or THF-d_7 at δ 1.8. The $^{13}C\{^1H\}$ spectra were referenced to C_6D_6 at δ 128.0 and THF at δ 26.7. The ^{19}F NMR spectra were referenced either to internal C_6F_6 at δ 162.9 or to external $CFCl_3$ at δ 0, and the $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ 0. Mass spectra were recorded on a VG Autospec. Infrared spectra were recorded on a Mattson-Unicam RS spectrometer fitted with a CsI beam splitter. NMR data are listed in Table 1.

***trans*-[Ni(OTf)(2-C_5F_4N)(PEt_3)$_2$] (2).** (a) A solution of **1** (64 mg, 0.14 mmol) in 5 mL of toluene was treated with Me_3SiOTf (25 μL, 0.14 mmol) at −78 °C. After the reaction mixture had been warmed to room temperature, the solvent was removed under vacuum. The residue was washed with hexane (10 mL) and extracted with ether (20 mL). The extract was filtered through a cannula, and the resulting solution was concentrated to 10 mL. A yellow powder precipitated at −20 °C, which was separated from the mother liquor and dried in vacuo. Yield: 68 mg (83%).

(b) $Ni(COD)_2$ (651 mg, 2.4 mmol) was suspended in 5 mL of hexane, and PEt_3 (744 μL, 5.0 mmol) was added, giving a yellow solution. After addition of C_5F_5N (307 μL, 2.8 mmol) the reaction mixture was cooled to 0 °C and Me_3SiOTf (516 μL, 2.8 mmol) was added. The solution was stirred for 30 min at room temperature, and the volatiles were removed under vacuum. The remaining yellow solid was dissolved in ether (5 mL), and the solution was filtered through a cannula. Addition of hexane (5 mL) afforded a yellow precipitate, which was filtered off and dried in vacuo. Yield: 114 mg (80%). Anal. Calcd for $C_{18}H_{30}F_7NNiO_3P_2S$: C, 36.39; H, 5.09; N, 2.36. Found: C, 36.39; H, 5.24; N, 2.32. IR (Nujol, cm^{-1}): 1620 (vw), 1590 (w), 1489 (s), 1413 (vs), 1386 (w), 1314 (s), 1300 (w), 1234 (s), 1215 (s), 1175 (s), 1095 (m), 1034 (vs), 997 (s), 812 (m).

***trans*-[Ni(OPh)(2-C_5F_4N)(PEt_3)$_2$] (3).** A solution of **2** (94 mg, 0.16 mmol) in 5 mL of THF was treated with NaOPh (745 mg, 0.64 mmol) and stirred for 30 min at room temperature. After the solvent was removed under vacuum, the yellow residue was extracted with hexane (5 mL). The extract was then filtered through a cannula, and the filtrate was concentrated to about 2 mL in vacuo. Yellow crystals precipitated at −20 °C, which were separated from the mother liquor and dried in vacuo. Yield 58 mg (68%). Anal. Calcd for $C_{23}H_{35}F_4NNiOP_2$: C, 51.33; H, 6.56; N, 2.60. Found: C, 51.43; H, 6.36; N, 2.44. IR (Nujol, cm^{-1}): 1620 (w), 1586 (s), 1482 (vs, br), 1450 (s), 1405 (vs), 1385 (m), 1315 (m), 1300 (vs), 1273 (m, br), 1250 (m, br), 1159 (m, br), 1087 (s), 1037 (s), 994 (s), 806 (s), 763 (s), 726 (m), 692 (m).

***trans*-[NiPh(2-C_5F_4N)(PEt_3)$_2$] (5).** A solution of **1** (190 mg, 0.40 mmol) in hexane (5 mL) was treated at −78 °C with a solution of PhLi in cyclohexane/ether (70:30, 1.13 mL, 1.82 mmol). After the reaction mixture had been warmed to room temperature, methanol (1 mL) was added and the volatiles were removed under vacuum. The residue was then extracted with hexane (10 mL), the extract was filtered, and the filtrate was reduced to 1 mL in vacuo. A yellow powder was obtained at −20 °C, which was separated from the mother liquor and dried in vacuo. Yield: 30 mg (14%). Anal. Calcd for $C_{23}H_{35}F_4NNiP_2$: C, 52.91; H, 6.76; N, 2.68. Found: C, 53.04; H, 7.14; N, 2.47. IR (Nujol, cm^{-1}): 1617 (vw), 1597 (vw), 1583 (w), 1482 (s), 1436 (m), 1406 (s), 1387 (m), 1366 (m), 1291 (w), 1259 (w), 1248 (w), 1089 (br, m), 1034 (br, m), 994 (m), 809 (br, m), 763 (m), 735 (vw), 530 (w), 501 (w).

***trans*-[NiMe(2-C_5F_4N)(PEt_3)$_2$] (6).** (a) A solution of **2** (134 mg, 0.22 mmol) in 5 mL of toluene was treated at −78 °C with a solution of MeLi in cumene/THF (90:10, 247 μL, 0.25 mmol). After the reaction mixture had been warmed to room temperature, the solvents were removed under vacuum. The resulting residue was extracted with hexane (5 mL), the extract was filtered through Celite, and the filtrate was concentrated to about 2 mL in vacuo. A yellow powder precipitated at −20 °C, which was separated from the mother liquor and dried in vacuo. Yield: 24 mg (24%).

(b) A solution of **1** (80 mg, 0.17 mmol) in hexane (5 mL) was treated at −78 °C with a solution of Me_2Zn in toluene (431 μL, 0.85 mmol). After the reaction mixture had been stirred for 4 h at room temperature, methanol (1 mL) was added. The solution was stirred for 1 h, and the volatiles were removed under vacuum. The resulting residue was then extracted with hexane (10 mL), the extract was filtered through Celite, and the solvent was removed under vacuum. A yellow powder was obtained, which was dried in vacuo. Yield: 68 mg (87%). Anal. Calcd for $C_{18}H_{33}F_4NNiP_2$: C, 46.99; H, 7.23; N, 3.04. Found: C, 46.30; H, 7.22; N, 2.82. IR (Nujol, cm^{-1}): 1617 (vw), 1588 (vw), 1579 (w), 1477 (vs), 1396 (s), 1381 (m), 1279 (w), 1259 (br, w), 1243 (w), 1224 (vw), 1176 (vw), 1161 (br, w), 1081 (m), 1063 (vw) 1033 (s), 989 (s).

Treatment of 6 with Air. A solution of **6** in C_6D_6 was saturated with air. The volatiles were transferred under vacuum into an NMR tube. ^{19}F and ^{1}H NMR spectra demonstrated that this distillate consisted of a solution of **7** in C_6D_6. High-resolution mass spectrum (EI, *m*/*z*): calcd for $C_6H_3F_4N$, 165.020 16; found, 165.020 26.

Reaction of 6 with CO. A solution of **6** in C_6D_6 was saturated with CO. The volatiles were transferred under vacuum into an NMR tube. ^{19}F and ^{1}H NMR spectra demonstrated that this distillate consisted of a solution of **8** in C_6D_6. Mass spectrum (EI, *m*/*z*, relative intensity): 193 (22%) $[C_5(COMe)F_4N]^+$, 178 (12%) $[C_5(CO)F_4N]^+$, 150 (29%) $[C_5F_4N]^+$, 43 (100%) $[COMe]^+$.

X-ray Crystallographic Studies of 2 and 3. Crystals of **2** and **3** were grown at −20 °C from hexane solutions. Data were collected on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device.[33] Intensities were measured in the $\omega-\theta$ mode with Cu Kα radiation for **2** and Mo Kα radiation for **3**. Following data reduction both structures were solved by Patterson methods (DIRDIF)[34] and refined by full-matrix least squares against *F* (Crystals).[35] H atoms were placed in calculated positions. Other relevant crystal data are given in Table 4.

In **2** the C_5NF_4 ring is disordered via a 180° rotation about the Ni(1)−C(2) axis. An approximate model for this disorder was refined in which all the ring sites were assigned full-weight atoms, those *ortho* to the metal atom being modeled with composite scattering factors (0.5N + 0.5C) with half-weight F atoms attached. All other F atoms were full-weight. This refinement converges to $R = 4.47\%$ for 309 parameters. All bonds and angles adopted normal values except the bond lengths to the partial-weight F atoms, which were 1.202(5) and 1.278(5) Å—i.e., rather too short. The anisotropic displacement parameters (adp's) suggested that a more chemically reasonable model would be to allow small displacement between the two alternative ring orientations in addition to the 180° rotation, with all atoms except the pivot atom, C(2), split over two sites with equal weight. Refinement of this model naturally suffered from correlation effects, and it was at first necessary to refine two intersecting rigid bodies with common U_{iso}'s for nearby atomic sites. Later it was possible to relax these constraints and refine the positions of all atoms freely, the least-squares parameters being constructed of linear combinations of parameters anticipated to be closely correlated (e.g. $N1(x) \pm C30(x)$, where N(1) is the equivalent of N(10) in Figure 1 after rotation about Ni(1)−C(2)). The adp's of the F atoms were refined freely, while common adp's were refined for C and N sites within 1 Å of each other. The bond lengths to C(2) and C−F bond lengths were respectively made subject to similarity restraints. All other non-H atoms were refined freely with apd's. *R* for this model was 4.46% for 380 parameters, and though this does not statistically improve the data fitting over the first model described, it is chemically more realistic, and for this reason it is presented here.

Refinement of the crystal structure of **3** proceeded normally; R_{int} is rather high because the majority of the contributing data are quite weak and lie between 45 and 50° in 2θ.

Full details of atomic coordinates, anisotropic displacement parameters, and other details of the refinements are given in the Supporting Information.

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Supporting Information Available: X-ray crystallographic data for **2** and **3**, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and U_{eq} values and ORTEP diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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