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Chemistry of nickel tetrafluoropyridyl derivatives: their versatile behaviour with Brønsted acids and the Lewis acid BF_3 †

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Received 24th March 2000, Accepted 9th May 2000
Published on the Web 9th June 2000

Treatment of *trans*-[NiF(2-C_5NF_4)$(PEt_3)_2$] (C_5NF_4 = tetrafluoropyridyl) (**1**) with HCl effects the formation of the air stable chloride complex *trans*-[NiCl(2-C_5NF_4)$(PEt_3)_2$] (**2**). The reaction of **2** with excess HCl slowly yields 2,3,4,5-tetrafluoropyridine (**4**). On reaction of **4** with [Ni(COD)$(PEt_3)_2$], the C–F activation product *trans*-[NiF(2-C_5NF_3H)$(PEt_3)_2$] (**5**) is formed instantly. The bifluoride compound *trans*-[Ni(FHF)(2-C_5NF_4)$(PEt_3)_2$] (**6**) is obtained on treatment of **1** with $Et_3N{\cdot}3HF$. Reaction of **2** with HBF_4 yields the binuclear complex [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (**7**). The X-ray crystal structure of **7** reveals a "butterfly"-shaped dimeric complex with square-planar coordination at both nickel atoms, with Ni–N distances of 1.965(4) and 1.955(4) Å and Ni–C distances of 1.884(5) and 1.875(5) Å. Treatment of **1** with $BF_3{\cdot}OEt_2$ in the presence of acetonitrile yields the cationic compound *trans*-[Ni(2-C_5NF_4)(NCMe)$(PEt_3)_2$]BF_4 (**8**), while reaction of *trans*-[Ni(OTf)(2-C_5NF_4)$(PEt_3)_2$] (**3**) with $NaBAr'_4$ and acetonitrile gives *trans*-[Ni(2-C_5NF_4)(NCMe)$(PEt_3)_2$]BAr'_4 (**9**) [Ar′ = 3,5-$C_6H_3(CF_3)_2$]. The studies reported in this paper provide methods for the synthesis of tetrafluoropyridines substituted in the 2-position and demonstrate the behaviour of nickel derivatives with Brønsted acids and the Lewis acid BF_3.

Introduction

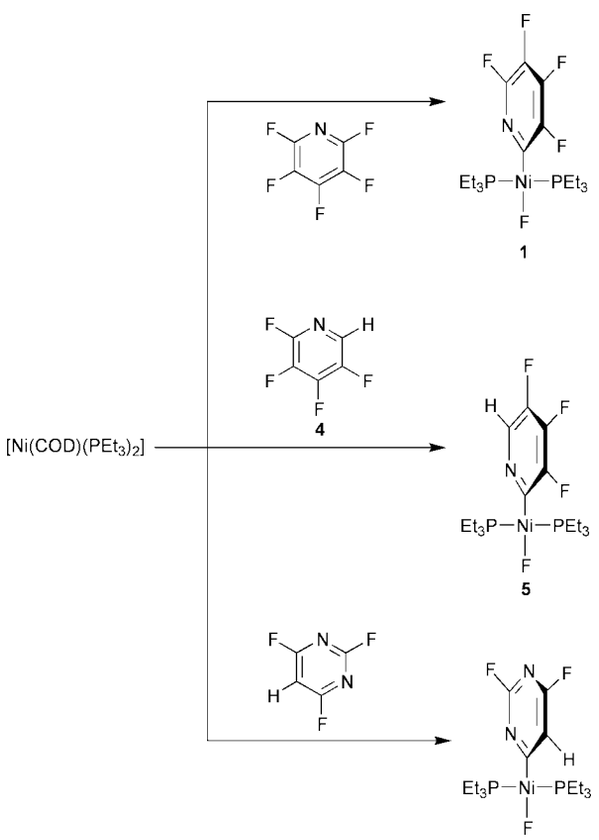
Several methods have been reported for activating carbon–fluorine bonds of fluoroaromatic compounds by reaction at appropriate transition metal centres.[1–7] One approach we have studied is the fast oxidative addition of fluorinated heteroaromatics, such as pentafluoropyridine or 2,4,6-trifluoropyrimidine, at a nickel centre yielding *trans*-[NiF(2-C_5NF_4)$(PEt_3)_2$] (**1**) and *trans*-[NiF(2-$C_4N_2F_2H$)$(PEt_3)_2$], respectively (Scheme 1).[6,7] These nickel heteroaryl units possess remarkable stability, as a result of strong π-backbonding from the metal centre to the fluorinated aromatic ring.[8–12] In order to investigate the properties of compound **1**, we tested its reactivity towards Brønsted acids and the Lewis acid BF_3. In both cases, we may anticipate the formation of cationic compounds by removing the fluoride ligand or by protonating **1** either at the nitrogen atom or the metal centre. This should lead to complexes with increased reactivity and a more accessible nickel–carbon bond.

In this paper we report the synthesis of new neutral and cationic (2-tetrafluoropyridyl)nickel derivatives as well as the preparation of a dimeric complex with a "butterfly" structure and bridging tetrafluoropyridyl ligands. The nickel-mediated formation of 2,3,4,5-tetrafluoropyridine and its C–F activation by nickel is also described.

Results

1 Reaction of *trans*-[NiF(2-C_5NF_4)$(PEt_3)_2$] (1) with HCl

The complex **1** reacts immediately with a solution of HCl in diethyl ether to give the air-stable chloride complex *trans*-[NiCl(2-C_5NF_4)$(PEt_3)_2$] (**2**) (Scheme 2). Complex **2** may be obtained by an alternative pathway, *via* treatment of a hexane solution of **1** with Me_3SiCl. The stepwise treatment in one pot of [Ni$(PEt_3)_2$(COD)] with C_5F_5N and Me_3SiCl also generates **2**

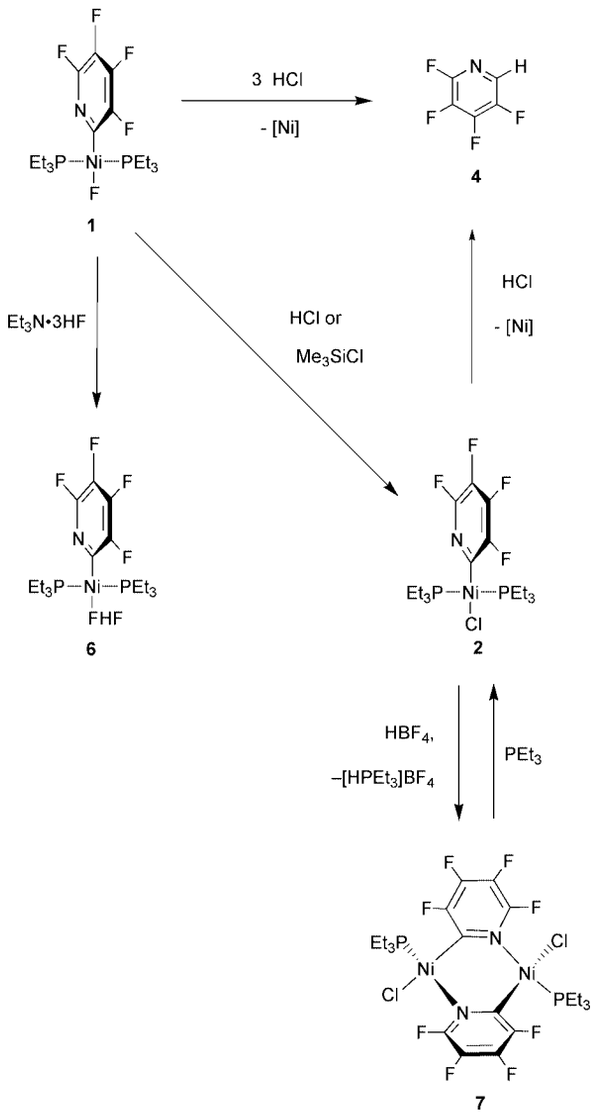


Scheme 1 C–F activation by [Ni(COD)$(PEt_3)_2$].

in a synthesis analogous to that of the triflate complex *trans*-[Ni(OTf)(2-C_5NF_4)$(PEt_3)_2$] (**3**).[8] The structure proposed for **2** is supported by the ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR data. The assignment as a 2-pyridyl nickel derivative is based on the presence of four fluorine signals in the ^{19}F NMR spectrum at δ −170.08, −147.59, −129.46 and −82.08, which appear at almost the same chemical shifts as those found for **1**.[6]

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b002333g/

DOI: 10.1039/b002333g



Scheme 2 Reactions with Brønsted acids.

Treatment of **2** with excess HCl in C_6D_6–diethyl ether for five days (Scheme 2) affords 2,3,4,5-tetrafluoropyridine (**4**), a compound which has been described previously.[13,14] The reaction is quantitative according to the NMR spectra and GC. It is worth mentioning that the reaction does not take place in a more polar solvent, such as THF. The ^{19}F NMR data for **4** in the literature are not consistent.[13,14] However, we found four signals at δ −158.63, −149.92, −141.69 and −84.96. The resonance for the aromatic hydrogen atom in the ^{1}H NMR spectrum appears at δ 7.36. The proton–fluorine coupling constants were obtained by ^{1}H{^{19}F} selective decoupling experiments (see Table 1).

2 Formation of *trans*-[NiF(2-C_5NF_3H)(PEt_3)$_2$] (5)

In a reaction analogous to that of pentafluoropyridine, the reaction of **4** with [Ni(COD)(PEt_3)$_2$] instantly affords the C–F activation product *trans*-[NiF(2-C_5NF_3H)(PEt_3)$_2$] (**5**) (Scheme 1).[6] The compounds [Ni(PEt_3)$_4$] and *trans*-[NiCl(2-C_5NF_3H)(PEt_3)$_2$] are present as minor products. The ^{19}F NMR spectrum of **5** shows a broad singlet at δ −366.5, characteristic of the metal fluoride, and three further resonances at δ −163.60, −159.98 and −130.47, revealing the presence of a trifluoropyridyl group. There is no indication of a fluorine atom in an *ortho* position to the nitrogen atom,[6] demonstrating that the activation of **4** takes place to yield the 2-metallated derivative. The ^{31}P NMR spectrum displays a doublet resonance at δ 14.5 (J_{PF} = 43.3 Hz) for the two equivalent phosphorus nuclei coupled to the metal-bound fluorine. The ^{1}H NMR spectrum reveals a doublet at δ 8.36 for the aromatic hydrogen atom.

3 Reaction of *trans*-[NiF(2-C_5NF_4)(PEt_3)$_2$] (1) with Et_3N·3HF

The reaction of **1** with Et_3N·3HF, as a source of HF, yields the bifluoride complex *trans*-[Ni(FHF)(2-C_5NF_4)(PEt_3)$_2$] (**6**) (Scheme 2). The presence of the bifluoride unit is revealed by two signals in the ^{19}F NMR spectrum at 190 K at δ −179.37 (dd, J_{FH} = 422, J_{FF} = 85 Hz, 1 F, NiFH*F*) and −339.06 (s, br, 1 F, NiF), and a broad doublet of doublets at δ 11.58 (dd, br, J_{FH} = 424, J_{FH} = 41 Hz) in the ^{1}H NMR spectrum.[7,15–19] The doublet in the ^{31}P NMR spectrum at δ 14.4 (J_{PF} = 37.9 Hz) demonstrates the presence of the nickel-bound fluorine.

4 Reaction of *trans*-[NiCl(2-C_5NF_4)(PEt_3)$_2$] (2) with HBF_4

In contrast to the reaction of **2** with HCl described above, treatment of **2** with a solution of HBF_4 in diethyl ether affords the dimeric compound [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (**7**) and [$HPEt_3$]BF_4. There is no indication of protonation of the nitrogen in the aromatic ring or release of 2,3,4,5-tetrafluoropyridine **4**. The reaction of **2** with $B(C_6F_5)_3$ also gives **7**. However, there is no reaction between **2** and BPh_3, a reagent known to remove phosphine.[20] The coordinated nitrogen atoms of **7** can be displaced from nickel using an excess of phosphine, regenerating **2**.

The most characteristic features in the ^{1}H NMR spectrum of **7** are the resonances of the methylene protons of the coordinated phosphines. Their inequivalence indicates a non-planar-structure in which these protons are prochiral.[21] The ^{31}P NMR spectrum reveals only a singlet. The four signals for the tetrafluoropyridyl groups, at δ −166.81, −144.82, −130.68 and −82.74, are present in the ^{19}F NMR spectrum, but there is no indication of the coordination of a fluorine to the nickel centres. A dimeric structure for **7** with the pyridyl ligands coordinated *via* the nitrogen to a second nickel atom, as found for [NiCl(PEt_3){μ-κ^2(*C*,*N*)-(2-C_5ClH_3N)}]$_2$ and [NiCl(PPh_3)-{μ-κ^2(*C*,*N*)-(2-C_5H_4N)}]$_2$, seems to be conceivable.[22,23] The NMR data indicate that the dimeric structure must have equivalent phosphorus nuclei and equivalent tetrafluoropyridyl groups. However, bridging by the chlorine ligands cannot be excluded.[21,22] The signal of the *ipso* carbon in the ^{13}C NMR spectrum appears as a doublet of doublets (J = 56, 46 Hz) because of coupling to ^{31}P and ^{19}F. The value of J_{PC} leads to the presumption that the phosphines are *cis* to the pyridyl ligands.[8]

5 Crystal structure of [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (7)

The orange binuclear complex **7** was crystallised from toluene–diethyl ether at −20 °C. Its structure was determined by X-ray diffraction at low temperature (Fig. 1). Selected bond lengths and angles are summarised in Table 2. The space group $P2_1/a$ indicates that both enantiomers are present in the unit cell. The structure consists of two square-planar nickel units bridged by two tetrafluoropyridyl groups, each coordinated to one nickel atom through carbon and through the nitrogen. This "double flyover" arangement results in approximate C_2 symmetry, in keeping with the prochiral CH_2 groups described above and the equivalence of the phosphines. The dihedral angle between the two nickel coordination planes is 61.31(7)°, while the two planes defined by the pyridyl groups are almost perpendicular to one another [88.78(12)°]. The chlorine atoms are *trans* to the carbon atoms of the pyridyl group and the phosphine ligands are *cis* to the carbon atoms and *trans* to the nitrogen atoms.

The Ni–Ni separation of 2.889(2) Å is shorter than the comparable distance found in [NiCl(PEt_3){μ-κ^2(*C*,*N*)-(2-C_5ClH_3N)}]$_2$ [3.076(2) Å], but implies no bonding interaction between the two metal atoms.[23] The nickel–carbon [1.884(5), 1.875(5) Å] and nickel–nitrogen [1.965(4), 1.955(4) Å] distances are in the same range as those found in [NiCl(PEt_3){μ-κ^2(*C*,*N*)-

Table 1 NMR data at 298 K; δ (J/Hz)

Complex	^{1}H	^{31}P{^{1}H}	^{19}F	^{13}C{^{1}H}
2 (C_6D_6)	0.95 (t, 18 H, CH_3), 1.20 (m, 12 H, CH_2)	14.8 (s)	−170.08 (m, 1 F), −147.59 (m, 1 F), −129.46 (m, 1 F), −82.08 (m, 1 F, F[6])	7.9 (s, CH_3), 14.0 (vt, J_{PC} = 12.7, CH_2), 131 (m, CF), 143.80 (dm, J_{CF} = 254, CF), 147.07 (dm, J_{CF} = 229, CF), 147.86 (dm, J_{CF} = 233, CF), 165.79 (m, C_{ipso})
4 (C_6D_6)	7.36 (dt, J_{HF} = 7.8, J_{HF} = 2.1)		−158.63 (dddd, J_{FF} = 25.6, 18.8, 3.0, J_{FH} = 2.3, 1 F), −149.92 (dddd, J_{FF} = 26.3, 19.2, 3.1, J_{FH} = 0.4, 1 F), −141.69 (dddd, J_{FF} = 19.2, 18.8, 16.3, J_{FH} = 7.8, 1 F), −84.96 (m, J_{FF} = 25, 1 F)	
5 (THF-d_8)	8.36 (d, J_{HF} = 8.0)[a]	14.5 (d, J_{PF} = 43.3)[b]	−366.51 (s, br, NiF), −163.60 (d, br, J_{FF} = 16.9, 1 F), −159.98 (m, 1 F), −130.47 (d, J_{FF} = 27.3, 1 F)	
6 (d_8-toluene, 190 K)	0.94 (m, br 30 H, CH_2CH_3), 11.58 (dd, br, J_{FH} = 424, J_{FH} = 41, FHF)	14.4 (d, J_{PF} = 37.9)	−339.06 (s, br, 1 F, Ni*F*HF), −179.37 (dd, J_{FH} = 422, J_{FF} = 85, 1 F, NiFH*F*), −170.34 (m, 1 F), −147.92 (m, 1 F), −131.84 (m, 1 F), −83.22 (m, 1 F, F[6])	9.3 (s, CH_3), 14.9 (vt, J_{PC} = 12.0, CH_2), 131 (m), 131.7 (dm, J_{CF} = 256.8, CF), 145.2 (dm, J_{CF} = 267.6, CF), 150.9–147.4 (m, 2 CF), 161.1 (m, C_{ipso})[c]
7 (C_6D_6)	0.99 (m, 18 H, CH_3), 1.53 (m, 6 H, CHH′), 1.98 (m, 6 H, CHH′)	25.5 (s)	−166.81 (m, 1 F), −144.82 (m, 1 F), −130.68 (t, J_{FF} = 25.4, 1 F), −82.74 (m, 1 F, F[6])	8.8 (d, J_{PC} = 3.4, CH_3), 17.7 (d, J_{PC} = 29, CH_2), 133.6 (dm, J_{CF} = 259, CF), 144.5 (dm, J_{CF} = 264, CF), 149.4–151.4 (m, 2 CF), 164.2 (dd, J = 56, 46, C_{ipso})
8 (THF-d_8)	1.29 (m, 18 H, CH_2CH_3), 1.60 (m, 12 H, CH_2), 2.59 (s, br, 3 H, $NCCH_3$)	17.2 (s)	−172.27 (m, 1 F), −154.47 (s, br, 4 F, BF_4), −139.31 (m, 1 F), −130.41 (t, J_{FF} = 26.6, 1 F), −84.22 (dt, J_{FF} = 26.9, 15.8, 1 F, F[6])	
9 (THF-d_8)	1.30 (m, 18 H, CH_2CH_3), 1.58 (m, 12 H, CH_2), 2.70 (s, br, 3 H, $NCCH_3$), 7.65 (s, br, 4 H, CH), 7.86 (s, br, 8 H, CH)	16.7 (s)	−167.9 (m, 1 F), −144.72 (m, 1 F), −131.22 (t, J_{FF} = 25.9, 1 F), −82.66 (dt, J_{FF} = 26.9, 15.8, 1 F, F[6]), −61.00 (s, 24 F, CF_3)	4.0 (s, br, $NCCH_3$), 8.8 (s, CH_2CH_3), 15.3 (t, J_{PC} = 13, CH_2), 119.2 (s, C_{para} of Ar′), 126.5 (q, J_{CF} = 272, CF_3), 131.1 (q, J_{CF} = 32, C_{meta} of Ar′), 133.9 (s, br, $NCCH_3$), 134.0 (dm, J_{CF} = 262, CF), 136.7 (s, C_{ortho} of Ar′), 146.4 (dm, J_{CF} = 273, CF), 149.2 (dm, J_{CF} = 235, CF), 149.6 (dm, J_{CF} = 227, CF), 155.1 (m, C_{ipso} of C_5F_4N), 163.9 (q, J_{BC} = 50, sept J_{BC} = 17, C_{ipso} of Ar′)

[a] The resonances for the CH_2CH_3 group are partly masked by the signals for *trans*-[NiCl(2-C_5NF_3H)(PEt_3)$_2$] and [Ni(PEt_3)$_4$]. [b] At 223 K. [c] In THF-d_8.

Table 2 Selected bond lengths (Å) and angles (°) for [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (**7**) with the estimated standard deviations in parentheses

Ni(1)–C(6)	1.884(5)	C(1)–C(2)	1.400(6)
Ni(1)–N(1)	1.965(4)	C(2)–C(3)	1.374(7)
Ni(1)–P(1)	2.1704(14)	C(3)–C(4)	1.381(7)
Ni(1)–Cl(1)	2.2100(13)	C(4)–C(5)	1.365(6)
Ni(2)–C(1)	1.875(5)	N(2)–C(6)	1.369(5)
Ni(2)–N(2)	1.955(4)	N(2)–C(10)	1.329(6)
Ni(2)–P(2)	2.1697(16)	C(6)–C(7)	1.375(7)
Ni(2)–Cl(2)	2.1991(14)	C(7)–C(8)	1.372(7)
N(1)–C(1)	1.364(6)	C(8)–C(9)	1.376(8)
Ni(1)–C(5)	1.317(6)	C(9)–C(10)	1.368(8)
C(6)–Ni(1)–N(1)	86.17(17)	N(2)–Ni(2)–P(2)	176.16(12)
C(6)–Ni(1)–P(1)	92.35(14)	C(1)–Ni(2)–Cl(2)	176.15(15)
N(1)–Ni(1)–P(1)	177.58(12)	N(2)–Ni(2)–Cl(2)	91.54(12)
C(6)–Ni(1)–Cl(1)	176.27(16)	P(2)–Ni(2)–Cl(2)	89.14(6)
N(1)–Ni(1)–Cl(1)	91.88(12)	C(1)–N(1)–Ni(1)	113.2(3)
P(1)–Ni(1)–Cl(1)	89.49(5)	C(6)–N(2)–Ni(2)	114.5(3)
C(1)–Ni(2)–N(2)	85.88(18)	N(1)–C(1)–Ni(2)	113.5(3)
C(1)–Ni(2)–P(2)	93.25(15)	N(2)–C(6)–Ni(1)	112.1(3)

(2-C_5ClH_3N)}]$_2$ [Ni–C: 1.866(10), 1.867(9); Ni–N: 1.931(7), 1.919(7) Å].[23]

6 Reaction of *trans*-[NiF(2-C_5NF_4)(PEt_3)$_2$] (1) with BF_3·OEt_2

The reaction of **1** with BF_3·OEt_2 in the presence of acetonitrile leads to the cationic complex *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BF_4 (**8**) (Scheme 3). Compound **8**, which is only slightly soluble in THF and CH_2Cl_2, was characterised by its ^{1}H, ^{31}P, ^{19}F NMR and IR data.[25] The presence of the bound acetonitrile is indicated by a signal in the ^{1}H NMR spectrum at δ 2.59, as well as a weak absorption band at 2284 cm^{-1} in the IR spectrum. The ^{19}F NMR spectrum reveals four signals in the aromatic region at δ −172.27, −139.31, −130.41 and −84.22, and a broad singlet at δ −154.47 due to the BF_4^- anion. The reaction of **8** with NaCl in d_8-THF was monitored by NMR spectroscopy. After 3 days, **8** is completely converted to *trans*-[NiCl(2-C_5NF_4)(PEt_3)$_2$] (**2**), free acetonitrile and $NaBF_4$.

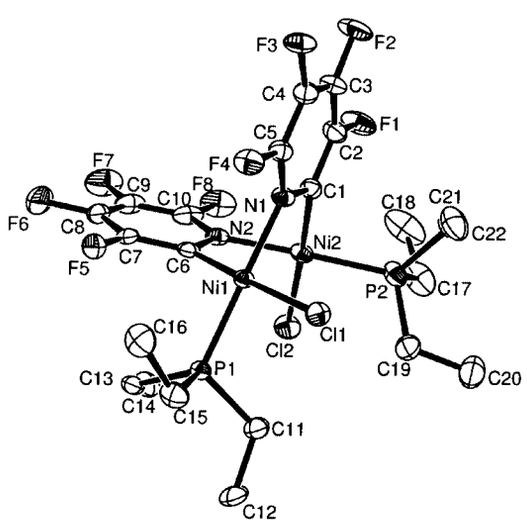
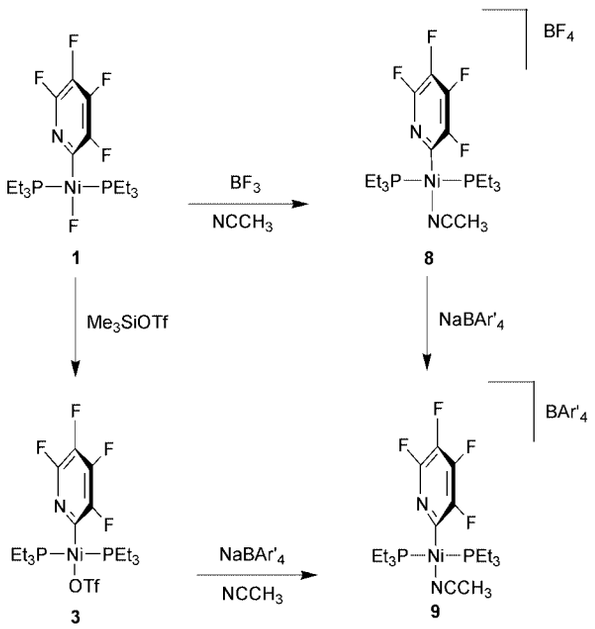


Fig. 1 An ORTEP[24] diagram of **7**. Ellipsoids are drawn at the 50% probability level.



Scheme 3 Synthesis of cationic acetonitrile complexes.

7 Synthesis of *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BAr′$_4$ (9) [Ar′ = 3,5-$C_6H_3(CF_3)_2$]

An NMR experiment shows that the solubility of **8** can be considerably increased by reaction with NaBAr′$_4$ in order to exchange the BF_4^- anion with BAr′$_4^-$. Compound **9**, *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BAr′$_4$, can also be prepared more conveniently by treatment of the triflate complex **3** with NaBAr′$_4$ in acetonitrile solution. The signals for the metal-bound acetonitrile appear in the ^{13}C NMR spectrum at δ 133.9 for the quaternary carbon atom and δ 4.0 for the methyl group.

Discussion

The syntheses of the complexes *trans*-[NiX(2-C_5F_4N)(PEt_3)$_2$] (**2**: X = Cl; **6**: X = FHF) by protonation of *trans*-[NiF(2-C_5NF_4)(PEt_3)$_2$] (**1**) with HCl or $Et_3N{\cdot}3HF$ are shown in Scheme 2. An alternative approach to the synthesis of **2** is fluoride abstraction with Me_3SiCl. A similar reaction was described by Bergman *et al.*, who generated the complex [(C_5Me_5)IrCl(Ph)(PMe_3)] from the corresponding fluoride.[26] $Et_3N{\cdot}3HF$ was recently employed as a mild source of HF for the synthesis of the nickel bifluoride complex *trans*-[Ni(FHF)(2-$C_4N_2F_2H$)(PEt_3)$_2$], which bears a pyrimidyl instead of a pyridyl ligand as in **6**.[7] Few other stable adducts of metal fluorides and HF have so far been reported.[15–19,27] The fluorine–proton coupling constant of 422 Hz for the distal fluorine at δ −179.37 in the bifluoride unit is close to that for free HF, indicating that the interaction in **6** may be best described as a hydrogen bond between Ni–F and HF.[7,15,18] This conclusion is supported by comparison of the ^{1}H and ^{19}F NMR spectroscopic data for **6** and *trans*-[Ni(FHF)(2-$C_4N_2F_2H$)(PEt_3)$_2$], for which X-ray crystallography reveals a similar bonding situation.[7]

The complex *trans*-[NiCl(2-C_5NF_4)(PEt_3)$_2$] (**2**) reacts with the Brønsted acids HCl and HBF_4 leading to 2,3,4,5-tetrafluoropyridine (**4**) and the dimeric complex [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (**7**), respectively. The two reaction pathways—removing the fluoride ligand or the phosphine—are remarkably different. In neither case is there any indication of protonation of the nitrogen atom. A different approach may be used to remove the fluoride ligand: reaction of **1** with the Lewis acid BF_3 in the presence of acetonitrile, yields the cationic complex *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BF_4 (**8**). A similar compound, *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BAr′$_4$ (**9**), with the anion BAr′$_4^-$ and with a higher solubility in THF or CH_2Cl_2, can be prepared using *trans*-[Ni(OTf)(2-C_5NF_4)(PEt_3)$_2$] (**3**) as a starting compound.

Only two binuclear nickel compounds with bridging pyridyl ligands have been reported.[22,23] The coordination of a highly fluorinated pyridyl unit *via* the nitrogen atom is unusual, but was recently observed by Bercaw *et al.* in the cationic complex [(tmeda)Pt(CH_3)(NC_5F_5)]BAr′$_4$.[28] Although pentafluoropyridine does not act as a Brønsted base, we anticipate that it should be able to act as a good σ-donor and π-acceptor ligand.[29,30] The precoordination of pentafluoropyridine is likely to be a crucial step in the activation of the carbon–fluorine bond by nickel, controlling the regioselectivity for attack at the 2-position.[6] Here, coordination on a neutral nickel complex is assisted by chelation.

The reaction of **4** with [Ni(COD)(PEt_3)$_2$] results in C–F activation at the 2-position yielding *trans*-[NiF(2-C_5NF_3H)(PEt_3)$_2$] (**5**). There is no indication of insertion of nickel into the carbon–hydrogen bond. This observation shows clearly that C–F activation is preferred over C–H activation. Note that this is the reverse of the chemoselectivity recently observed at rhodium and osmium towards partially fluorinated benzenes.[31]

Conclusions

This paper reports the behaviour of nickel tetrafluoropyridyl complexes, with the metal in the 2-position, towards Brønsted acids and the Lewis acid BF_3. The reaction pathways vary remarkably with the nature of the protic acid and the anionic ligand X in the compounds *trans*-[NiX(2-C_5NF_4)(PEt_3)$_2$] (**1**: X = F, **2**: X = Cl). By using the Lewis acid BF_3 in the presence of acetonitrile, it is possible to remove the fluoro ligand in **1** and form the cationic compound *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BF_4 (**8**).

The new nickel complexes retain the tetrafluoropyridyl group coordinated to the metal in the 2-position.[6,8] This is of special interest since it is very difficult to prepare tetrafluoropyridines substituted in the 2-position.[8,13,14,32–37] 2-Chloro-3,4,5,6-tetrafluoropyridine is only formed in traces on conproportionation of 3,5-dichloro-2,4,6-trifluoropyridine and pentafluoropyridine.[37] 2-Bromo-3,4,5,6-tetrafluoropyridine is accessible by Diels–Alder and retro-Diels–Alder reactions using perfluorocyclohexa-1,3-diene and cyanogen bromide as starting compounds.[36] Two different approaches have been described for the synthesis of 2,3,4,5-tetrafluoropyridine (**4**).[13,14] However, it was only obtained in low yield (5%) or *via* a multi-step reaction. Our synthesis of 2,3,4,5-tetrafluoropyridine (**4**) provides an excellent opportunity to obtain this simple compound starting from pentafluoropyridine in a two step reaction in high yield (Schemes 1 and 2).

The binuclear complex **7** is of special interest because of the coordination of a highly fluorinated pyridyl unit to the metal centre *via* a nitrogen atom, which does not normally act as a Brønsted base.[29,30] Moreover, **7** may be an excellent starting compound for the synthesis of highly reactive monomeric tetrafluoropyridyl nickel derivatives bearing only one phosphine. Further investigations into the reactivity of this compound are in progress.

Experimental

Most of the synthetic work was carried out on a Schlenk line or in an argon-filled glove box 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's stopcocks. $Et_3N{\cdot}3HF$, HBF_4 and a 1.0 M solution of HCl in diethyl ether were obtained from Aldrich.

$NaBAr'_4$ was prepared according to the literature.[38] Pentafluoropyridine was obtained from Apollo Scientific Ltd. and was dried over molecular sieves (4 Å). $[Ni(COD)_2]$ (Strem Chemicals) was used as received. Complexes **1** and **3** were prepared as described in the literature.[6,8]

The NMR spectra were recorded with a Bruker AMX 500 spectrometer, except for the $^1H\{^{19}F\}$ decoupling experiments, which were carried out on a Bruker DRX 400 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. The $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ 0. Mass spectra were recorded on a VG Autospec (EI) or a Finnigan LCQ (electrospray) instrument. Infrared spectra were recorded on a Mattson-Unicam RS spectrometer fitted with a CsI beamsplitter. NMR data are listed in Table 1.

Syntheses

Synthesis of *trans*-[NiCl(2-C_5NF_4)(PEt_3)$_2$] (2). (a) A solution of **1** (473 mg, 1.02 mmol) in hexane (5 mL) was treated with a solution of HCl in diethyl ether (1.02 mL, 1.02 mmol). After stirring for 1 h, the solvent was removed under vacuum and 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*. Orange crystals of **2** precipitated at −20 °C. Yield 147 mg (30%). (b) A solution of **1** (223 mg, 0.48 mmol) in 5 mL of hexane was treated with Me_3SiCl (60 μL, 0.48 mmol). After stirring for 1 h, the solvent was removed under vacuum, and 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*. Orange crystals of **2** precipitated at −20 °C. Yield 180 mg (78%). (c) $[Ni(COD)_2]$ (568 mg, 2.07 mmol) was suspended in 5 mL hexane, and PEt_3 (671 μL, 4.54 mmol) was added, giving a yellow solution. After addition of C_5F_5N (249 μL, 2.27 mmol), the reaction mixture was cooled to 0 °C and Me_3SiCl (288 μL, 2.27 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 hexane (5 mL) and the solution was filtered through a cannula. Orange crystals of **2** precipitated at −20 °C. Yield 794 mg (80%). IR (Nujol) ν/cm^{-1}: 1720vw, 1592vw, 1483s, 1465vs, 1408s, 1250vw, 1164w, 1090w, 1034m, 995m, 808w, 765s and 724vw (Found: C, 42.72; H, 6.77; N, 2.92. $C_{17}H_{30}ClF_4NNiP_2$ requires C, 42.49; H, 6.29; N, 2.92%).

Synthesis of C_5NF_4H (4). A solution of **2** (56 mg, 0.17 mmol) in 1.5 mL of C_6D_6 was treated with a solution of HCl in diethyl ether (351 μL, 0.35 mmol). After 5 d the volatiles were transferred under vacuum to an ampoule fitted with a Young's tap. The resulting colourless distillate was shown, using NMR spectroscopy and GC, to contain C_6D_6 and **4** only. MS (EI): *m*/*z* 151 (M^+, 100), 132 ([M − F]$^+$, 19%).

Formation of *trans*-[NiF(2-C_5NF_3H)(PEt_3)$_2$] (5). The distillate containing **4** in C_6D_6 was treated with $[Ni(COD)_2]$ (30 mg, 0.11 mmol) and PEt_3 (34 μL, 0.23 mmol). The resulting solution contained mainly *trans*-[NiF(2-C_5NF_3H)(PEt_3)$_2$] (**5**), with the compounds $[Ni(PEt_3)_4]$ and *trans*-[NiCl(2-C_5NF_3H)(PEt_3)$_2$] present as minor products. Complex **5** was converted into *trans*-[NiCl(2-C_5NF_3H)(PEt_3)$_2$] by treatment with HCl. Selected NMR data for *trans*-[NiCl(2-C_5NF_3H)(PEt_3)$_2$]: ^1H NMR (THF-d_8): δ 8.44 (d, J_{HF} = 7.5 Hz, CH). ^{31}P NMR (THF-d_8): δ 14.2 (s). ^{19}F NMR (THF-d_8): −162.55 (d, br, J_{FF} = 16.0, 1 F), −158.56 (m, 1 F), −129.58 (d J_{FF} = 27.8 Hz, 1 F).

Synthesis of *trans*-[Ni(FHF)(2-C_5NF_4)(PEt_3)$_2$] (6). A solution of **1** (115 mg, 0.25 mmol) in hexane (5 mL) was treated with a solution of $Et_3N{\cdot}3HF$ in THF (0.60 mL, 0.60 mmol). After stirring for 5 min at room temperature, the solvents were removed under vacuum. The resulting yellow oil was washed with hexane (3 mL). The resulting solid was then recrystallised twice from hexane (3 mL) at −20 °C, providing yellow crystals of **6**. Yield 61 mg (50%). IR (Nujol) ν/cm^{-1}: 1617vw, 1584w, 1483vs, 1405vs, 1387w, 1250vw, 1230vw, 1090m, 1034m, 995s, 809m, 765w and 735vw (Found: C, 42.70; H, 6.48; N, 2.89. $C_{17}H_{31}F_6NNiP_2$ requires C, 42.18; H, 6.46; N, 2.89%).

Synthesis of [NiCl{μ-κ^2(*C*,*N*)-(2-C_5NF_4)}(PEt_3)]$_2$ (7). A solution of **2** (98 mg, 0.20 mmol) in diethyl ether (10 mL) was treated with a solution of HBF_4 in diethyl ether (39 μL, 0.24 mmol). After stirring for 1.5 h, the solvent was removed under vacuum and the yellow residue was extracted with toluene (5 mL). The extract was then filtered through a cannula and the solvent pumped off. The resulting orange solid was washed with hexane and dried *in vacuo*. Yield 51 mg (70%). IR (Nujol) ν/cm^{-1}: 1627s, 1593w, 1500vs, 1426s, 1300vw, 1271vw, 1262vw, 1164w, 1118s, 1110s, 1037s, 1015vs, 828s, 771m, 754m, 740s and 732m (Found: C, 36.95; H, 4.30; N, 3.16. $C_{22}H_{30}Cl_2F_8N_2Ni_2P_2$ requires C, 36.46; H, 4.17; N, 3.87%).

Synthesis of *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BF_4 (8). A solution of **1** (146 mg, 0.30 mmol) in acetonitrile (10 mL) was treated with $BF_3{\cdot}OEt_2$ (38 μL, 0.30 mmol). After stirring for 1 h, the solvent was removed under vacuum. The pale yellow solid was washed with hexane and dried *in vacuo*. Yield 147 mg (86%). IR (KBr) ν/cm^{-1}: 2284vw, 1619w, 1484m, 1462w, 1404vs, 1384w, 1110vs, 1087vs, 1036vs, 991m, 917w, 806s, 761s and 726s. MS (ES): *m*/*z* 485 (M^+, 100), 444 ([M − MeCN]$^+$, 52), 367 ([M − PEt_3]$^+$, 7%) (Found: C, 39.85; H, 5.85; N, 4.68. $C_{19}H_{33}BF_8N_2NiP_2$ requires C, 39.83; H, 5.81; N, 4.89%).

Synthesis of *trans*-[Ni(2-C_5NF_4)(NCMe)(PEt_3)$_2$]BAr'_4 (9). A solution of **3** (300 mg, 0.50 mmol) in acetonitrile (20 mL) was treated with $NaBAr'_4$ (448 mg, 0.50 mmol). After stirring for 1 h, the solvent was removed under vacuum and the yellow residue was extracted with CH_2Cl_2 (5 mL). The extract was then filtered through a cannula, the solvent was pumped off and the yellow solid washed with hexane (10 mL). The residue was dissolved in CH_2Cl_2 (2 mL) and the solution was chromatographed on silica (grade 12, 28–200 mesh, length of column 6 cm). A yellow fraction was eluted, from which the solvent was removed *in vacuo*. The residue was washed with hexane (5 mL) to give a yellow solid. Yield 675 mg (76%). IR (KBr) ν/cm^{-1}: 1619w, 1586w, 1489m, 1415m, 1354s, 1275vs, 1180m, 1160s, 1118vs, 1034m, 999m, 887m, 839s, 810w, 762m and 714s (Found: C, 45.76; H, 3.28; N, 2.00. $C_{51}H_{45}BF_{28}N_2NiP_2$ requires C, 45.40; H, 3.36; N, 2.08%).

Structure determination for complex 7

Orange crystals were obtained from a solution of **7** in toluene–diethyl ether at −20 °C. Diffraction data were collected for a block with dimensions 0.25 × 0.20 × 0.60 mm on a Rigaku AFC6S diffractometer.

Crystal data. $C_{22}H_{30}Cl_2F_8N_2Ni_2P_2$, M = 724.74, monoclinic, space group $P2_1/a$, a = 13.519(3), b = 14.205(7), c = 15.858(3) Å, β = 101.188(2)°, U = 2987.4 Å^3, T = 150 K, Z = 4, μ(Mo-Kα) = 1.612 mm^{-1}, 5492/5251 measured/unique data, R_{int} = 0.042. The structure was solved by direct methods (SIR-92)[39] and refined against F^2 (SHELXL 93).[40] H-atoms were placed in idealised positions. Final R_1, wR_2 on all data 0.093, 0.1145. R_1, wR_2 on [$I_o > 2\sigma(I_o)$] data 0.0379, 0.0915.

CCDC reference number 186/1977.

See http://www.rsc.org/suppdata/dt/b0/b002333g/ for crystallographic files in .cif format.

Acknowledgements

We would like to acknowledge the EPSRC and the Nuffield Foundation for financial support.

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