C–F Bond activation at Ni(0) and simple reactions of square planar Ni(II) fluoride complexes

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Received 14th July 2005, Accepted 19th August 2005

First published as an Advance Article on the web 7th September 2005

The reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with triethylphosphine and pentafluoropyridine in hexane has been shown previously to yield trans- $[NiF(2-C_5NF_4)(PEt_3)_2]$ (1a) with a preference for reaction at the 2-position of the heteroaromatic. The corresponding reaction with 2,3,5,6-tetrafluoropyridine was shown to yield *trans*-[NiF(2-C₅NF₃H)(PEt₃)₂] (**1b**). In this paper, we show that reaction of Ni(COD)₂ with triethylphosphine and pentafluoropyridine in THF yields a mixture of 1a and 1b. Competition reactions of Ni(COD)₂ with triethylphosphine in the presence of mixtures of heteroaromatics in hexane reveal a kinetic preference of k(pentafluoropyridine) : k(2,3,5,6-tetrafluoropyridine) = 5.4 : 1. Treatment of **1a** and **1b** with Me₃SiN₃ affords $trans-[Ni(N_3)(2-C_5NF_4)(PEt_3)_2]$ (2a) and $trans-[Ni(N_3)(2-C_5NHF_3)(PEt_3)_2]$ (2b), respectively. The complex trans-[Ni(NCO)(2-C₅NHF₃)(PEt₃)₂] (**3b**) is obtained on reaction of **1b** with Me₃SiNCO and by photolysis of **2b** under CO, while *trans*-[Ni(η^1 -C=CPh)(2-C₅NF₄)(PEt₃)₂] (4a) is obtained by reaction of phenylacetylene with 1a. Addition of KCN, KI and NaOAc to complex 1a affords *trans*-[Ni(X)(2-C₃NF₄)(PEt₃)₂] (5a X = CN, 6a X = I, 7a X = OAc), respectively. The PEt₃ groups of complex 1a are readily replaced by addition of 1,2-bis(dicyclohexylphosphino)ethane (dcpe) to produce $[NiF(2-C_5F_4N)(dcpe)]$ (8a). Addition of dcpe to trans- $[Ni(OTf)(2-C_5F_4N)(PEt_3)_2]$ (10a), however, yields the salt $[Ni(2-C_5F_4N)(dcpe)(PEt_3)](OTf)$ (9a) by substitution of only one PEt₃ and displacement of the triflate ligand. The structures of 2b, 4a, 7a and 8a were determined by X-ray crystallography. The influence of different ancillary ligands on the bond lengths and angles of square-planar nickel structures with polyfluoropyridyl ligands is analysed.

Introduction

Activation of the carbon-fluorine bond of fluoroaromatics by transition metal reagents is now a well-recognised process¹⁻³ that has been exploited in catalysis and forms a systematic route for the synthesis of fluorinated organics.^{4,5} It also forms an important route to metal fluoride complexes. There have been striking recent advances in C-F activation of fluorinated alkenes by nickel, rhodium, ruthenium and zirconium complexes;6 the reactivity of the zirconium complexes extends to fluorinated alkanes and arenes.3,7 Our understanding of the reactivity of fluoroalkyl derivatives has also expanded greatly through the work of Caulton⁸ and Hughes.⁹ The C-F activation of pentafluoropyridine10 and other nitrogencontaining fluoroaromatics11 by nickel is a rapid process studied by Perutz and co-workers, with metallation occurring predominantly at the 2-position. The mechanism of C-F activation is thought to involve pre-coordination of the aromatic ring to the Ni(0) centre prior to intramolecular oxidative addition.¹² The fluoride ligand can be replaced by various nucleophiles including triflate, phenyl, phenoxide and methyl to produce new (2-tetrafluoropyridyl)nickel derivatives.13 The subsequent reductive elimination of such complexes leads to otherwise inaccessible 2-substituted tetrafluoropyridines by C-C coupling reactions, as was observed for generation of 2-C5NF4Me and $2-C_5NF_4(COMe)$ from trans-[Ni(Me)($2-C_5F_4N$)(PEt₃)₂].¹³ However, reductive elimination succeeds only in a limited number of cases. In a recent theoretical paper, we showed that C-F oxidative addition at nickel bis(phosphine) was favoured relative to platinum bis(phosphine) as a result of the greater strength of the Ni-F bond.¹⁴ We have also reported substantial differences in products of reaction of $M(PR_3)_2$ (M = Ni, Pd, Pt) with fluoropyridines down the group. Reactions of pentafluoropyridine with $Pd(PR_3)_2$ and $Pt(PR_3)_2$ (R = Cy, *i*Pr) result in attack at

the 4-position of the ring only, yielding for palladium *trans*- $Pd(F)(4-C_5NF_4)(PR_3)_2$, while the platinum reaction results in a rearrangement yielding *trans*- $Pt(R)(4-C_5NF_4)(PR_3)(PR_2F)$.¹⁵

We address here the relative rates of reaction of Ni(COD)₂ and PEt₃ with different fluorinated heteroaromatics *via* competition reactions and the effect of solvent on the C–F activation reaction. The synthesis of further nickel(2-fluoropyridyl) derivatives is presented both as a prelude to further reductive elimination and to provide structural comparisons among complexes in this class. Among these, we selected the azide derivative for investigation because of the reported photolability of the azide ligand from cobalt and platinum complexes. For instance, $[Co(NH_3)_5N_3]Cl_2$ forms azide radicals upon photolysis¹⁶ while $[Pt^{II}(N_3)_2(PPh_3)_2]$ is reduced photochemically in 2-MeTHF to the azide-free product $[Pt^0(PPh_3)_2(2-MeTHF)_n]$.¹⁷ We also investigate the alternative possibility of replacing the PEt₃ groups with a chelating phosphine, thus constraining the groups to be eliminated in a *cis* geometry.

Results

1. Mechanistic studies of C-F oxidative addition

Effect of solvent on C–F oxidative addition. The syntheses of *trans*-[NiF(2- C_5NF_4)(PEt_3)₂] (1a) and *trans*-[NiF(2- C_5NF_3H)(PEt_3)₂] (1b) by reaction of Ni(COD)₂ with PEt₃ and pentafluoropyridine or 2,3,5,6-tetrafluoropyridine, respectively, in hexane have been reported previously.¹⁰ It should be noted that the reaction with pentafluoropyridine also gives up to 15% of the 4- C_5NF_4 isomer and traces of the 3- C_5NF_4 isomers of 1a; these may be removed on recrystallisation. The reaction with 2,3,5,6-tetrafluoropyridine gives *ca.* 1% of the 3- C_5NF_3H isomer. We now report that the reaction of Ni(COD)₂ with PEt₃ and pentafluoropyridine in THF (in place of hexane) leads to

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Entry	Ni(COD) ₂	C_5NF_5	$C_5 NHF_4$	1a : 1b
1 2 3 4 5 6 7	1 1 1 1 1 1	1.33 1.22 1.00 0.67 0.50 1.3 2.1	0.67 0.78 1.00 1.33 1.50 1.4	9.7 7.2 4.4 1.5 0.87 ^a 5.5
8	1	0.56	3.33	0.51^{a}

^{*a*} The proportion of **1a** is limited by availability of pentafluoropyridine for these entries.

a mixture of **1a** and **1b**, in a ratio of 1 : 0.57 in favour of **1a**, as indicated by integration of the ¹⁹F NMR spectrum. The unexpected formation of **1b** was also shown by the resonance at δ 6.24 in the ¹H NMR spectrum, assigned to the aromatic ring proton of **1b**. The ³¹P{¹H} NMR spectrum contains the doublet resonances consistent with PEt₃ coupled to fluorine for **1a** and **1b**. As a consequence of this unusual reactivity, it is essential to avoid the use of THF for the synthesis of **1a** (even when used directly without isolation), otherwise trifluoropyridyl derivatives are formed.[†]

Control reactions were performed in which PEt₃ was reacted with pentafluoropyridine alone in THF and hexane. The ¹H and ¹⁹F NMR spectra showed that 2,3,5,6-tetrafluoropyridine was formed in both solvent systems. We have observed this reaction previously, but only in THF.¹⁸ It contrasts with the reaction with primary and secondary phosphines which yields phosphorussubstituted heterocycles.¹⁹

Competition reactions between heteroaromatics. The effect of the degree of fluorination of the pyridyl ring on the rate of C-F activation was studied by competition reactions between pairs of heteroaromatics. In the first series (Table 1, entries 1-5), Ni(COD)₂ (1 equiv.) was treated with PEt₃ (2.2 equiv.) to which was added a solution in hexane containing pentafluoropyridine and 2,3,5,6-tetrafluoropyridine totalling 2 equiv. The proportions of trans-[NiF(2-C5NF4)(PEt3)2] (1a) and trans- $[NiF(2-C_5NF_3H)(PEt_3)_2]$ (1b) were determined by ¹⁹F NMR spectroscopy. A plot of [1a]/[1b] versus [C5NF5]/[C5NHF4] yielded a gradient of 5.4 \pm 0.4 (95% confidence limit) corresponding to the kinetic preference ratio (Scheme 1). In a second series of experiments (entries 6-8), the proportion of PEt₃ was held at 4 equiv and the excess of heteroaromatic was increased. The results were consistent with the first series. The results of competition reactions of this type with different reagent ratios are listed in Table 1. A control with 1a + tetrafluoropyridine in hexane showed no reaction.





Reactions of 1a and 1b

2 Synthesis of azido derivatives 2a and 2b. A solution of 1a in hexane was reacted with Me₃SiN₃ producing trans- $[Ni(N_3)(2-C_5NF_4)(PEt_3)_2]$ (2a) in 62% yield after 2 h. Similarly, Me_3SiN_3 reacted with a solution of **1b** to form *trans*-[Ni(N₃)(2-C₅NHF₃)(PEt₃)₂] (2b) in 71% yield. Both compounds were characterised by ¹H, ³¹P and ¹⁹F NMR spectroscopy (Table 2). The ³¹P NMR spectrum of complex 2a contains one resonance only, a singlet at δ 16.1, indicating that the two phosphorus nuclei are equivalent and the complex adopts the trans geometry (see Scheme 2). For the azidotrifluoropyridylnickel complex 2b, the phosphorus peak appears at a lower chemical shift of δ 15.7. The ¹⁹F NMR spectrum of **2a** contains four fluorine resonances: an apparent triplet of doublets at δ -85.3, an apparent triplet at δ -132.9, a multiplet at δ -150.3 and a multiplet at δ -172.6. The ¹⁹F NMR spectrum of 2b contains three peaks: a triplet of doublets at δ -90.9, a doublet at δ -111.5 and a multiplet at δ -150.6. The infrared bands observed at 2055 cm⁻¹ and 2054 cm⁻¹ for complexes 2a and 2b respectively are consistent with azide stretching modes. The structure of 2b was also determined by X-ray crystallography.

Crystals of 2b were obtained from hexane at -20 °C. An ORTEP diagram of the crystal structure (Fig. 1a) confirms the trans-square-planar geometry. Selected bond lengths and angles are summarised in Table 3. Coordination of the trifluoropyridyl ring to the nickel centre occurs at position 2, adjacent to the ring nitrogen atom and the hydrogen is at the 4-position. The angles between the adjacent ligands at nickel vary from 89.78(8)° to 90.55(7)°. In previous studies, tetrafluoropyridyl complexes have been disordered whereas complexes with a trifluoropyridyl ligand have been ordered.³ In keeping with this observation, disorder about the Ni(1)-C(1) bond is not observed. The Ni(1)-N(1) bond length is 1.923(2) Å while the N(1)-N(2)and N(2)-N(3) bond distances are 1.185(3) Å and 1.160(3) Å respectively. The azido ligand is close to linear with a N(1)-N(2)-N(3) bond angle of 175.3(3)°. The Ni(1)-N(1)-N(2) bond angle of 132.3(2)° compares favourably with other metal azido complexes; the complex $[Co(N_3)_2(L)_4](L = 2-(p-pyridyl)-4,4,5,5$ tetramethylimidazoline-1-oxyl-3-oxide) contains two azido ligands with a Co(1)-N(1)-N(2) bond angle of 128.91°,20 while the $[Ru(tpy)(PPh_3)_2(N_3)]^+$ cation²¹ has a Ru(1)-N(1)-N(2) bond angle of 139.6(4)°. A recent structure of an octahedral nickel(II) azido complex with terminal and bridging azides has a Ni-N(terminal) bond length of 2.057(3) Å.²²

Photochemical reactivity of azide 2b under CO and formation of isocyanato derivatives. A sample of 2b in hexane, under an atmosphere of CO, was irradiated for 30 h (Hg arc, $\lambda > 290$ nm). A second sample of 2b in hexane, under a CO atmosphere, was stirred without photolysis at room temperature. Both reactions were monitored by IR spectroscopy and the same products formed in each, although the photolytic reaction was more rapid than the thermal one.

The IR spectra of the reaction showed that the azide stretching mode of the starting material **2b** at 2054 cm⁻¹ decreases in intensity and three new bands are formed at 2225, 2066 and 1992 cm⁻¹. The ¹H, ³¹P and ¹⁹F NMR spectra confirm the presence of two products. The major product appears at

[†] In addition to the resonances of **1a** and **1b**, the ¹⁹F spectrum contains two minor resonances that appear as doublets at δ – 38.3 and – 39.4 with couplings of $J_{\rm FP} = 643$ and 631 Hz, respectively. These large coupling constants are characteristic of PF bonds in fluorophosphoranes of type PR₃F₂. The presence of two such compounds may be explained by partial fluorination of the ethyl groups. We reported previously that similar fluorophosphoranes are also formed in reactions of Ni(COD)2 with PEt3 and C₆F₆ in hexane. They can be observed in the pentafluoropyridine reactions both when conducted in THF and in hexane, and increase in significance with excess pentafluoropyridines. Similar fluorinated phosphorane by-products were produced upon reaction of PEt₃ with pentafluoropyridine. The most prominent of these exhibited the following NMR data (reaction and NMR spectroscopy in a THF/C₆D₆, 90 : 10, mixture):¹⁹F δ -38.3 d, J_{PF} = 648 Hz; ³¹P δ -17.3 t, J_{PF} = 648 Hz. Notably, this species was also observed in the reaction of pentafluoropyridine with triethylphosphine in hexane. It matches the spectroscopic data for one of the fluorophosphoranes observed in the reaction of Ni(COD)₂ with $PEt_3 + C_5NF_5$ in THF.

Table 2	NMR Data for 2a–9a in C ₆ D ₆ at 298 K (δ (ppm) (J/Hz)) ^a
	C_6D_6 at 298 K (0 (ppin) (57 Hz))	J

Complex	'H	${}^{31}P{}^{1}H{}$	¹⁹ F
2a	1.05 (m, 12H, CH ₂), 0.90 (t, 18H, CH)	16.1 (s)	-85.3 (td, $J = 28.6$, 15.2, 1F, F ⁶), -132.9 (t, $J = 28.6$, 1F, F^{3}), -150.3 (m, 1F, F^{4}), -172.6 (m, 1F, F^{5})
2b	6.25 (m, 1H, CH), 1.10 (m, 12H, CH ₂) 0.93 (m, 18H, CH ₂)	15.7 (s)	-90.9 (td, $J = 30.5$, 5.7, 1F, F ⁶), -111.5 (d, $J = 32.4$, 1F F ³) -150.6 (m 1F F ⁵)
3b	6.25 (m, 1H, CH), 1.05 (m, 12H, CH2), 0.85 (m, 18H, CH2)	15.8 (s)	-91.0 (m, 1F, F ⁶), -111.5 (d, $J = 30.5$, 1F, F ³), -150.7 (m, 1F, F ⁵)
4a	7.44 (d, $J = 7, 2H, CH$), 7.11 (m, 2H, CH) ^b , 6.98 (t, $J = 7, 1H, CH$), 1.37 (m, 12H, CH) 0.96 (m, 18H, CH)	20.7 (s)	-85.7 (m, 1F, F ⁶), -133.8 (m, 1F, F ³), -151.9 (m, 1F, F ⁴), -173.6 (m, 1F, F ⁵)
5a	$(m, 12H, CH_2), 0.90 (m, 10H, CH_3)$ 1.36 (m, 12H, CH ₂), 0.95(m, 18H, CH ₃)	21.6 (s)	-84.2 (td, $J = 28.6$, 15.3, 1F, F ⁶), -132.9 (t, $J = 28.6$, 1F, F ³), -149.9 (m, 1F, F ⁴), -171.3 (m, 1F, F ⁵)
6a	1.36 (m, 12H, CH ₂), 0.90 (m, 18H, CH ₃)	15.6 (s)	-84.5 (td, $J = 28.6$, 15.2, 1F, F ⁶), -131.9 (t, $J = 28.6$, 1F, F ³), -149.4 (m, 1F, F ⁴), -172.0 (m, 1F, F ⁵)
7a	1.99 (s, 3H, CH ₃), 1.07 (m, 12H, CH ₂), 1.00 (m, 18H, CH ₃)	13.0 (s)	-84.5 (td, $J = 28.6$, 15.3, 1F, F ⁶), -131.0 (t, $J = 26.7$, 1F, F ³), -149.9 (m, 1F, F ⁴), -171.9 (m, 1F, F ⁵)
8a ^c	$\begin{array}{l} 2.56\ (m,2H,CH_2),2.45\ (m,2H,CH_2),\\ 1.940.76\ (m,44H,C_6H_{11}) \end{array}$	71.6 (dd, $J_{PF} = 99$, $J_{PP} = 31$, P^2), 66.2 (m, P^1)	-87.4 (td, $J = 28.6$, 13.4, 1F, F ⁶), -132.3 (t, $J = 28.6$, 1F, F ³), -150.1 (m, 1F, F ⁴), -171.0 (m, 1F, F ⁵),
9a ^c	2.38–0.72 (m, 63H, dcpe and PEt_3)	72.4 (dd, $J = 39, 27, P^1$), 67.5 (dd, $J = 198, 27, P^2$), 7.6 (dd, $J = 198, 39, PEt_3$)	-539.6 (br m, 1F, NIF) -76.7 (s, 3F, CF ₃), -83.0 (td, $J = 28$, 16, 1F, F ⁶), -128.8 (t, $J = 28$, 1F, F ³), -147.2 (m, 1F, F ⁴), -168.4 (m, 1F, F ⁵)

^a F numbering as shown in Scheme 2. ^b Peak partly obscured by solvent. ^c P numbering as shown in Scheme 3.





Fig. 1 ORTEP diagrams of molecular structure with 50% ellipsoids of (a) 2b, (b) 4a, (c) 7a. Hydrogen atoms are omitted except for the hydrogen on the trifluoropyridyl ring of 2b. Note that the structures of 4a and 7a exhibit disorder about the Ni–C bond (not illustrated) such that N(1) exchanges places with one of the CF groups.

chemical shifts almost identical to the starting material **2b**. The ³¹P NMR spectrum contains two singlets, the major resonance at δ 15.76 and a minor singlet at δ 21.1. The ¹⁹F NMR spectrum contains three major signals at δ -89.6, -111.5 and -150.5 consistent with a coordinated trifluoropyridyl ring, and three minor resonances at δ -88.5, -121.9 and -132.1. The IR spectrum also confirms that one of the products was very similar to the azido complex **2b**. The IR product peak at 2225 cm⁻¹ falls in the range where isocyanates absorb suggesting that the isocyanate derivative *trans*-[Ni(NCO)(2-C₅NHF₃)(PEt₃)₂] (**3b**) has been formed. The minor product was not identified.^{+,23}

Table 3 Principal bond lengths (Å) and angles (°) of *trans*- $[Ni(N_3)(2-C_5F_3HN)(PEt_3)_2]$ (2b)

Ni(1)–C(1) Ni(1)–P(1) Ni(1)–P(2)	1.881(2) 2.2053(9) 2.2003(9)	Ni(1)–N(1) N(1)–N(2) N(2)–N(3)	1.923(2) 1.185(3) 1.160(3)
N(1)-Ni(1)-C(1) P(1)-Ni(1)-P(2) C(1)-Ni(1)-P(1) C(1)-Ni(1)-P(2) N(1)-Ni(1)-P(1)	170.40(10) 174.35(3) 90.54(8) 90.55(7) 89.78(8)	N(1)-Ni(1)-P(2) Ni(1)-N(1)-N(2) N(1)-N(2)-N(3) N(4)-C(1)-Ni(1)	90.08(8) 132.3(2) 175.3(3) 117.17(18)

The isocyanato derivative **3b** was synthesised independently to confirm its identity following a similar route to that for complex **2b**. Treatment of **1b** with trimethylsilyl isocyanate, afforded *trans*-[Ni(NCO)(2-C₅NHF₃)(PEt₃)₂] (**3b**) in 79% yield. The product contains one strong band in the IR spectrum at 2225 cm⁻¹. The NMR data confirm that the isocyanato derivative is very similar to the azido analogue, with resonances occurring at almost identical chemical shifts to those of **2b** qand the photoproduct of **2b** with CO (see Table 2). Thus the major reaction product of **2b** with CO is confirmed as **3b**.

Reaction of 1a with phenylacetylene. The complex *trans*- $[Ni(\eta^1-C\equiv CPh)(2-C_5NF_4)(PEt_3)_2]$ (**4a**) was prepared in 26% yield by treating a solution of **1a** in hexane with phenylacetylene in the presence of $[Me_4N]F$ (Table 2). The IR spectrum of the product exhibited the characteristic stretching mode of the $C\equiv C$ bond of the phenylacetylenyl at 2090 cm⁻¹, close to the value of 2111 cm⁻¹ for free PhC \equiv CH.¹² The driving force behind the synthesis of **4a** was the formation of HF, which was then trapped by $[Me_4N]F$. It was anticipated that F⁻ would help deprotonate the alkyne and $[Me_4N]F$ would trap HF as $[Me_4N]F$ failed to produce the phenylacetylenyl complex.

The structure of 4a was determined by X-ray crystallography following crystallisation from hexane at 4 °C. Selected bond lengths and angles are summarised in Table 4. Compound 4a exhibits a square-planar geometry with the tetrafluoropyridyl ring, metalated at the 2-position, positioned trans to the phenylacetylenyl ligand (Fig. 1b). The Ni-tetrafluoropyridyl (Ni–C(21)) distance is 1.919(10) Å, but there is disorder about the Ni-C(21) bond as has been observed in other complexes of this type.^{3,6} There is also disorder in the methyl group of C(12) which appears to occupy two sites. The angles between the adjacent ligands at nickel vary from $87.1(3)^{\circ}$ to $93.3(3)^{\circ}$ and the rms deviation from square planar geometry is 0.021 Å. The tetrafluoropyridyl ring is almost orthogonal both to the coordination plane and to the phenyl ring of the ligand trans to it with dihedral angles of 90.6° and 81.6° respectively. The Ni-C(8) distance to the phenylacetylenyl ligand is 1.866(12) Å. The $C \equiv C \text{ bond } C(7) - C(8) \text{ is significantly shorter at } 1.208(13) \text{ Å than}$ all other CC bonds in the molecule. The Ni–C(8)–C(7)–C(6) four atom fragment is almost linear with angles C(7)-C(8)-Ni and C(6)-C(7)-C(8) of 177.2(10)° and 175.8(11)°, respectively.

Salt metathesis reactions: KCN, KI, NaOAc. Reaction of a suspension of KCN in THF with a hexane solution of 1a formed *in-situ* resulted in the formation of *trans*-[Ni(CN)(2- C_5NF_4)(PEt₃)₂] (5a) as yellow crystals in 43% yield (Table 2).

Table 4 Principal bond lengths (Å) and angles (°) of trans-[Ni($\eta^{1}-C\equiv CPh$)(2- $C_{5}NF_{4}$)(PEt₃)₂] (4a)

Ni(1)-C(8)	1.866(12)	Ni(1)–P(2)	2.190(3)
Ni(1)-C(21)	1.919(10)	C(8)–C(7)	1.208(13)
Ni(1)-P(1)	2.186(3)	C(6)–C(7)	1.437(14)
P(1)-Ni(1)-P(2)	174.52(14)	C(21)-Ni(1)-P(1)	93.3(3)
C(21)-Ni(1)-C(8)	177.6(5)	C(21)-Ni(1)-P(2)	92.2(3)
C(8)-Ni(1)-P(1)	87.5(3)	C(7)-C(8)-Ni(1)	177.2(10)
C(8)-Ni(1)-P(2)	87.1(3)	C(8)-C(7)-C(6)	175.8(11)

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[‡] The minor product may be the O-bonded isomer with a cyanato ligand *trans*-[Ni(OCN)(2-C₅NHF₃)(PEt₃)₂]. There is very little information about NCO/OCN linkage isomerism although they have been investigated theoretically, and there is one claim on the basis of vibrational spectra.²³

The complex displayed the characteristic C=N stretching mode of the cyanide ligand in the infrared spectrum at 2107 cm⁻¹. The C=N stretching frequency of **5a** was considerably higher than that of free CN⁻ at 2080 cm⁻¹ (in aqueous solution), in keeping with the shift to higher frequency often observed for CN⁻ ligands.²⁴ The synthesis of 2-cyanotetrafluoropyridine was attempted by exposure to air but the complex was air stable and failed to react.

In a method similar to that employed for the cyano derivative, the iodo complex was prepared by addition of a hexane solution of **1a** (containing a trace of the 4-pyridyl isomer) to a suspension of KI in THF resulting in the formation of *trans*-[NiI(2- C_5NF_4)(PEt₃)₂] (**6a**) in 53% yield as red crystals (Table 2). The ³¹P and ¹⁹F NMR spectra confirmed the formation of **6a** as the 2-pyridyl isomer by the four ¹⁹F resonances of equal intensity. The 4-pyridyl isomer was formed in less than 5% yield.

The acetato derivative was prepared similarly: NaOAc was added to a THF solution of **1a** to yield *trans*-[Ni(OAc)(2- C_5NF_4)(PEt_3)₂] (**7a**) after stirring overnight. The air-stable complex **7a** was obtained in 74% yield and exhibits a C=O stretching mode of the acetate ligand at 1622 cm⁻¹ in the infrared spectrum (ATR). This compares with 1560 cm⁻¹ for NaOAc (ATR).

Complex **7a** was crystallised by slow evaporation of hexane at room temperature to afford orange blocks suitable for X-ray diffraction. Selected bond lengths and angles are summarised in Table 5. The crystal structure revealed that the acetato group acts as a unidentate ligand. As expected the pentafluoropyridyl ligand coordinates at the 2-position with disorder about the Ni(1)–C(1) bond (Fig. 1c). The square-planar geometry of the complex is confirmed with adjacent ligands having bond angles which vary from $85.77(3)^{\circ}$ to $93.80(3)^{\circ}$. The acetate ligand is separated from the metal centre by a Ni(1)–O(1) bond length of 1.9154(10) Å. The O(1)–C(6) bond length of the acetate at 1.2908(19) Å is significantly longer than the formal double bond C(6)–O(2) of 1.2275(19) Å. The acetate ligand and the pentafluoropyridyl ring are almost coplanar, and lie approximately perpendicular to the P–Ni–P vector.

Replacement of triethylphosphine by a bidentate ligand, synthesis of $[NiF(2-C_5NF_4)(dcpe)]$ (8a). The triethylphosphine ligands of 1a were displaced by direct addition of dcpe [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] to a benzene solution of 1a, producing air-sensitive [NiF(2-C₅NF₄)(dcpe)] (8a) as a yellow solid in 52% yield (Scheme 3). The isolated yield was limited by the extreme solubility of 8a. The ³¹P NMR spectrum clearly indicated the loss of triethylphosphine, with only two signals evident, representing the coordinated diphosphine. The phosphorus trans to fluoride appeared as a doublet of doublets at δ 71.6, with $J(PF_{trans}) = 99$ Hz and J(PP) = 31 Hz. The phosphorus *cis* to fluoride appeared as a multiplet at δ 66.2. The ¹⁹F NMR spectrum contains the characteristic tetrafluoropyridyl ligand signals at $\delta - 87.4$, -132.3, -150.1 and -171.0. The fluoride ligand appears at δ –339.8 as a broad multiplet, shifted significantly downfield compared to the trans analogue 1a which appears at δ -371.4. Complex 8a may be compared to Pörschke's [NiF(C₆F₅)(tBu₂PCH₂CH₂PtBu₂)] which was made by thermolysis of $[Ni(\eta^2-C_6F_6)(tBu_2PCH_2CH_2PtBu_2)]^{25}$

Table 5 Principal bond lengths (Å) and angles (°) of trans-[Ni(OAc)(2-C_5NF_4)(PEt_3)_2] (7a)

Ni(1)-C(1) Ni(1)-O(1) Ni(1)-P(1) Ni(1)-P(2)	1.8753(14) 1.9154(10) 2.2106(4) 2.1983(4)	C(6)-O(1) C(6)-O(2) C(6)-C(7)	1.2908(19) 1.2275(19) 1.517(2)
P(1)-Ni(1)-P(2) C(1)-Ni(1)-O(1) C(1)-Ni(1)-P(1) C(1)-Ni(1)-P(2) O(1)-Ni(1)-P(1)	175.540(15) 177.53(5) 88.55(4) 91.83(4) 93.80(3)	O(1)-Ni(1)-P(2) C(6)-O(1)-Ni(1) O(1)-C(6)-C(7) O(2)-C(6)-O(1)	85.77(3) 116.27(9) 114.33(13) 124.97(14)



Complex 8a was crystallised from benzene at room temperature as small yellow crystals. Selected bond lengths and angles are summarised in Table 6. The dcpe complex crystallises with two molecules in the asymmetric unit as $8a \cdot 2\frac{1}{4}C_6H_6$. Equivalent bond distances and bond angles around the metal centre in the two complexes are essentially the same (Table 6). As expected, the complex is square-planar with adjacent ligand bond angles between $88.86(4)^{\circ}$ to $93.20(6)^{\circ}$ (values for molecule 1, Fig. 2). The Ni-F and Ni-C bond lengths are 1.8473(12) Å and 1.917(2) Å, respectively. The bite angle of the chelating phosphine at $89.09(2)^{\circ}$ is similar to the $88.82(5)^{\circ}$ bite angle in [NiCl₂(dcpe)].²⁶ The main differences between the two molecules in the asymmetric unit, apart from inversion, lie in the out-ofplane distances and the torsional angles. The nickel atom lies 0.021(1) Å out of the plane of the coordinating atoms P(1), P(2), C(1) and F(1) for molecule 1 and 0.041(1) Å for molecule 2. It lies out of the plane of the pyridyl ring atoms by 0.276(1) Å (molecule 1) and 0.174(1) Å (molecule 2). The torsional angles between the pyridyl ring and the Ni-F bond are 105.38(17)° and $-96.15(17)^{\circ}$ for molecules 1 and 2, respectively.



Fig. 2 ORTEP diagram of molecular structure of 8a with 50% ellipsoids. Molecule 1 is illustrated. Hydrogen atoms are omitted.

Molecule 1		Molecule 2	
Ni(1)–F(1) Ni(1)–C(1) Ni(1)–P(1)	1.8473(12) 1.917(2) 2.1970(6)	Ni(2)–F(6) Ni(2)–C(32) Ni(2)–P(3)	1.8498(12) 1.916(2) 2.1993(6)
Ni(1) - P(2)	2.1361(6)	Ni(2) - P(4)	2.1355(6)
$\begin{array}{l} C(1)-Ni(1)-P(1) \\ F(1)-Ni(1)-P(2) \\ F(1)-Ni(1)-C(1) \\ C(1)-Ni(1)-P(2) \\ F(1)-Ni(1)-P(1) \\ P(1)-Ni(1)-P(2) \\ F(1)-Ni(1)-C(1)-N(1) \\ P(2)-Ni(1)-C(1)-N(1) \end{array}$	175.08(7) 176.98(5) 89.01(7) 93.20(6) 88.86(4) 89.09(2) -96.15(17) 81.80(16)	$\begin{array}{l} C(32)-Ni(2)-P(3)\\ F(6)-Ni(2)-P(4)\\ F(6)-Ni(2)-C(32)\\ C(32)-Ni(2)-P(4)\\ F(6)-Ni(2)-P(3)\\ P(3)-Ni(2)-P(4)\\ F(6)-Ni(2)-C(32)-N(2)\\ P(4)-Ni(2)-C(32)-N(2)\\ \end{array}$	174.52(7) 178.04(4) 89.76(7) 92.04(6) 89.37(4) 88.91(2) 105.38(17) -73.86(16)

Table 6Principal bond lengths (Å) and angles (°) of $[NiF(2-C_5NF_4)(dcpe)]$ (8a)

The phosphine ligand substitution was also attempted on the air-stable triflate complex *trans*-[Ni(OTf)(2-C₅NF₄)(PEt₃)₂] (10a) in order to provide a simpler route to depe derivatives. Substitution was successful but in this case only one triethylphosphine ligand was displaced, together with the triflate ligand, affording [Ni(2-C₅F₄N)(dcpe)(PEt₃)][OTf] (9a) with the triflate acting as the counterion (Scheme 3). The ³¹P NMR spectrum contains three resonances of equal intensity (Table 1). A doublet of doublets at δ 7.6 is consistent with a coordinated triethylphosphine ligand, with a *trans* coupling to a doublet of doublets at δ 67.5 of J(PP) = 198 Hz and a *cis* coupling to a doublet of doublets at δ 72.4 of J(PP) = 39 Hz. The two resonances at low field are therefore attributed to the coordinated dcpe ligand with a cis coupling to each other of J(PP) = 27 Hz. The ¹⁹F NMR spectrum was also used to characterise the product showing a singlet at δ -76.7, assigned as the CF₃ of the triflate group, that was considerably sharper and shifted slightly from its position in the starting complex 10a. Complex 9a could be converted to 8a by reaction with an excess of [Me₄N]F.

Discussion

The exact conditions under which the C-F activation of fluorinated heteroaromatics is performed influences the nature of the products formed. The reaction of Ni(COD)₂ with PEt₃ and pentafluoropyridine in THF afforded a mixture of 1a and 1b whereas 1a was the nickel-containing product when the reaction was performed in hexane. (Note that small amounts of the 3- C_5NF_4 and 4- C_5NF_4 isomers of 1a are always detected prior to recrystallisation, see above.) It was found that PEt₃ reacts with pentafluoropyridine in the absence of nickel complexes either in THF or in hexane, to produce 2,3,5,6-tetrafluoropyridine. This observation indicates that the reaction of PEt₃ and pentafluoropyridine to form 2,3,5,6-tetrafluoropyridine occurs prior to C-F activation in THF. The failure to produce an appreciable amount of 1b when the synthesis is performed in hexane suggests that the reaction of pentafluoropyridine with the nickel complex is very rapid and occurs in preference to the reaction with PEt₃.

The competition reactions explore the effect on the rate of C–F activation of the degree of fluorination of the pyridyl ring. They indicate that the relative rates of reaction at room temperature of pentafluoropyridine and 2,3,5,6-tetrafluoropyridine are 5.4 : 1. This gives immediate mechanistic insight into the C–F activation process. The rates of nucleophilic attack should follow the order pentafluoropyridine $\gg 2,3,5,6$ -tetrafluoropyridine and should be separated by several orders of magnitude.§,²⁷ A nucleophilic mechanism would also result in almost 100% attack at the 4-position of pentafluoropyridine. The only example of

nucleophilic attack of pentafluoropyridine at the 2-position is with PH'Bu2.19 Our relative rate data and the observed regioselectivity are inconsistent with nucleophilic attack. It might be thought that the preference we observe for the 2position of the ring is associated with the steric demands of the Ni(PEt₃)₂. However, this argument is wholly inconsistent with the preference for the 4-position shown by the far bulkier $Pd(PCy_3)_2$ and $Pt(PCy_3)_2$ (see below). Our observations also contrast with the reaction of pentafluoropyridine at the 4position with sterically demanding anionic complexes such as [Rh(CO)₂(PPh₃)₂]^{-.28} We, therefore, rule out nucleophilic attack by nickel(0) and propose an alternative mechanism (Scheme 4). This mechanism involves pre-coordination with the fluorinated substrate, following the dissociation of COD from Ni(COD)(PEt₃)₂ to produce [Ni(PEt₃)₂(C₅NF₅)] (A) as an intermediate, followed by oxidative addition of the pyridine to produce the new nickel-fluorine bond; the oxidative addition must take place with a kinetic preference for attack at the 2position over the 4-position.



The regioselectivity of oxidative addition for nickel contrasts with that we reported recently for reaction of $Pd(PR_3)_2$ and $Pt(PR_3)_2$ (R = cyclohexyl or isopropyl).¹⁵ In the palladium case oxidative addition results exclusively in the 4-pyridyl isomer. For platinum, activation also occurs at the 4-position but a major rearrangement generates a P–F and Pt–C bond resulting in [Pt(R)(4-C₅NF₄)(PR₃)(PFR₂)]. It is plausible that the reactions with Pd(PR₃)₂ and Pt(PR₃)₂ take place by direct nucleophilic attack at the 4-position without pre-coordination.

Two X-ray structures of complexes of pentafluoropyridine are known, one *N*-coordinated [PtMe(Me₂NCH₂CH₂NMe₂)(η^{1} -*N*-C₅NF₅)][BAr']₄ [Ar' = 3,5-C₆H₃(CF₃)₂] and one *C*=*C* coordinated, [Rh(η^{5} -C₅H₅)(PMe₃)(η^{2} -3,4-*CC*-C₅NF₅)].^{29,30} Molecular orbital calculations show that the HOMO of pentafluoropyridine is the 1a₂ π -orbital which has a nodal plane through N and C4 while the LUMO is the 3b₁ π^{*} orbital which has significant

[§] The rate constant for attack by methoxide at -7.6 °C on C₃NF₅ is *ca.* 5 × 10⁴ higher than for attack on 2,3,5,6-C₅NF₄H. Relative rates for the reaction of methoxide at the same temperature with 2,3,4,6-C₅NF₄H and 2,3,4,5-C₅NF₄H are *ca.* 80 and 30 respectively.²⁷

electron density on all ring atoms. The *N*-based 'lone pair' is found to lie 0.7 eV below the HOMO.³¹ If the interaction of the NiP₂ fragment with pentafluoropyridine is principally covalent and dominated by HOMO–LUMO interactions, the transitionmetal complex is expected to be C=C coordinated as indeed found. The balance may evidently be tipped in favour of an *N*coordinated complex by a positive charge if electrostatic forces become more important, *i.e.* the fragment becomes a harder Lewis acid.

The syntheses of complexes 2a, 2b and 3b were achieved by reacting the corresponding trimethylsilyl derivative with trans- $[NiF(2-C_5F_3NR)(PEt_3)_2]$ [(1a) R = F, (1b) R = H], prepared in situ due to the air-sensitive nature of the Ni-F complexes. Trimethylsilyl reagents were chosen for the strength of the bond formed between the trimethylsilyl group and the fluorine atom displaced from the precursor complex. The photolysis of trans- $[Ni(N_3)(2-C_5NHF_3)(PEt_3)_2]$ (2b) in hexane, under an atmosphere of CO, afforded the isocyanate complex trans-[Ni(NCO)(2- C_5NHF_3 (PEt₃)₂ (**3b**), implying loss of N₂ rather than N₃. The thermal reaction under the same conditions also gave 3b, which was prepared independently with Me₃SiNCO. The similarity of the spectroscopic data of complexes 2b and 3b is consistent with isoelectronic complexes. While trimethylsilyl derivatives were employed in the initial stages of this study, we later showed that simple salt displacement was sufficient to form iodide, acetato and cyano complexes. The preference of the nickel bis(phosphine) pyridyl system for these ligands is consistent with simple hard/soft expectations.

The new nickel fluoropyridyl derivatives described here proved stable to reductive elimination of 2-substituted fluoropyridines at room temperature, as did others such as the phenyl derivative. An alternative approach was taken to encourage elimination, namely forcing the adoption of a cis geometry by introduction of a bidentate phosphine. Several bidentate phosphines were investigated including bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,1'bis(diphenylphosphino)ferrocene (dppf) but substitution was only achieved using 1,2-bis(dicyclohexylphosphino)ethane (dcpe). Bennett and Wenger³² reported the displacement of triphenylphosphine from an analogous four-coordinate nickel(0) complex $[NiBr(2-Br-4,5-F_2C_6H_2)(PPh_3)_2]$ by heating with dcpe to produce [NiBr(2-Br-4,5- $F_2C_6H_2$)(dcpe)]. This method was adopted for the preparation of both complexes 8a and 9a although heating was not required. While the displacement of PEt₃ from complex 1a produced the dcpe analogue 8a as expected, the addition of dcpe to trans-[Ni(OTf)(2- $C_5NF_4)(PEt_3)_2$] (10a) resulted in the displacement of only one PEt₃ and the triflate group to produce the cationic complex $[Ni(2-C_5F_4N)(dcpe)(PEt_3)](OTf)$ (9a).

The crystal structures reported here provide the first data for *trans*-[NiX(Ar^F)P₂] complexes with N or C ligands *trans* to fluoroaryl and the first example of a *cis*-[NiF(Ar^F)P₂] complex. Table 7 shows the variation of four crystallographic parameters for the tetrafluoropyridyl and trifluoropyridyl complexes studied here together with those studied earlier. We believe that the comments below are justified, although some caution is needed in interpreting the data because several structures suffer from disorder problems and the structure of **1b** was determined at ambient temperature. All the complexes have bond angles very close to the ideal square-planar geometry. In the *trans* complexes, the Ni– C_{aryl} bond length varies from 1.851(3) Å for the triflate to 1.881(2) Å for the azido complex, leaving aside the phenylacetylide complex that is less well determined. The fluoride complexes exhibit Ni– C_{aryl} bond lengths close to the upper end of the range for oxygen ligands, suggesting that the *trans* influence of fluoride is comparable to that of oxygen ligands. The azido complex provides the only example with a nitrogen ligand and its Ni– C_{aryl} bond length exceeds that for any of the complexes with oxygen or fluorine ligands.

The shortest Ni–X distances are found for the fluoride complexes with the minimum value at 1.8473(12) Å for **8a**. The value for the phenylacetylide is slightly longer, but values above 1.9 Å are found for $X = N_3$ and X = OAc reaching a maximum for X = OTf at 1.957(2) Å. Variation in Ni–O bond lengths between the different complexes with oxygen ligands is certainly significant and follows the order OTf > OAc > OPh. If the fluorinated pyridyl or fluorinated aryl ligands exert a much higher *trans* influence than phosphine like their hydrocarbyl analogues, the Ni–F bond should be shorter in a complex with *cis* phosphines than one with *trans* phosphines. However, the difference in Ni–F bond length of **8a** and **1b** at 0.009(2) Å is barely significant and smaller than predicted by the DFT calculations for the *cis/trans* pair *trans*-NiF(C₆F₅)(PH₃)₂ (1.79 Å) and [NiF(C₆F₅)(H₂PCH₂CH₂PH₂)] (1.76 Å).¹⁴

Conclusions

In this paper we have reported two advances in the understanding of the mechanism of oxidative addition of polyfluorinated pyridines to Ni(0). Firstly, we have revealed the existence of the competing reaction between free triethylphosphine and pentafluoropyridine yielding 2,3,5,6-tetrafluoropyridine. This process is significant in THF as solvent but does not compete effectively with oxidative addition in hexane at room temperature. Secondly, we have shown that there is a modest kinetic selectivity for pentafluoropyridine over 2,3,5,6-tetrafluoropyridine of 5.4 : 1. When taken together with the regioselectivity of reaction, these observations argue in favour of a mechanism involving pre-coordination followed by oxidative addition.

We also report the synthesis of the nickel fluoropyridyl complexes, *trans*-[NiX(C_5F_3NR)(PEt₃)₂] (where R = F, H and $X = N_3$, NCO, C=CPh, CN, I, OAc), all exhibiting the rare coordination of the pyridyl ring at the 2-position. Two methodologies have been adopted, reaction of 1a or 1b with trimethylsilyl derivatives and salt displacement reactions. In the special case of the phenylacetylene reaction, [Me₄N]F was added to abstract fluoride from 1a. The X-ray structures of *trans*-[Ni(N₃)(2-C₅NHF₃)(PEt₃)₂] (**2b**), *trans*-[Ni(η^1 -C=CPh)(2- $C_5NF_4)(PEt_3)_2$] (4a) and trans-[Ni(OAc)(2-C_5NF_4)(PEt_3)_2] (7a) have been determined. The azido derivative 2b may be converted to the isocyanato complex 3b by photolysis under CO. Substitution of the monophosphine ligands of complex 1a with a chelating phosphine yielded the analogous nickel-fluoride complex $[NiF(2-C_5NF_4)(dcpe)]$ (8a), with the geometry now fixed in the *cis* position, as confirmed by the X-ray crystal structure. Surprisingly, a similar substitution reaction of the

Table 7 Comparative crystallographic parameters for tetrafluoropyridyl and trifluoropyridyl nickel complexes, *trans*-[NiX(Ar^F)P₂]

Complex	Х	T/K	r(Ni–C _{Ar})/Å	r(Ni–X)/Å	P-Ni-P/°	C–Ni–X/°
1b ¹⁰	F	296	1.869(4)	1.856(2)	176.70(4)	176.58(12)
2b	N_3	150	1.881(2)	1.923(2)	174.35(3)	170.40(10)
4a	CCPh	150	1.919(10)	1.866(12)	174.52(14)	177.6(5)
7a	OAc	115	1.8753(14)	1.9154(10)	175.540(15)	177.53(5)
8a	F	120	1.917(2)	1.8473(12)	89.09(2)	89.01(7)
10a ¹³	OTf	220	1.851(3)	1.957(2)	171.14 (4)	170.7 (1)
trans-[Ni(OPh)(2- C_5NF_4)(PEt ₃) ₂] ¹³	OPh	220	1.861(6)	1.894(4)	172.44(8)	175.7(2)

trans-nickel triflate complex afforded the cationic complex [Ni(2- C_5F_4N)(dcpe)(PEt₃)](OTf) (**9a**). We will now undertake synthesis of derivatives of the new chelated complexes with appropriate nucleophiles, which should eliminate the desired substituted fluoropyridine products more readily than the corresponding *trans*-complexes.

Experimental

General methods

Synthetic work was carried out on a Schlenk line or in an argonfilled 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 transferring under vacuum into NMR tubes fitted with Young's taps. Pentafluoropyridine and 2,3,5,6-tetrafluoropyridine were obtained from Fluorochem Ltd and dried over molecular sieves (4 Å). 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) was obtained from Strem Chemicals Inc. All other chemicals were obtained from Aldrich Chemical Company Ltd. Complexes 1a, 1b,10 and 10a,13 were prepared as described in the literature though the amount of PEt₃ was reduced to 2.2 equiv. [NMe₄]F was synthesised as described previously.33 Ni(COD)2 was either purchased from Aldrich or prepared according to a literature procedure by sodium reduction of NiCl₂(py)₄.³⁴

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 ¹³C{¹H} spectra were referenced to C_6D_6 at δ 128.0 and THF at δ 26.7. The ¹⁹F and the ³¹P{¹H}NMR spectra were referenced to external CFCl₃ and external H₃PO₄, respectively. Infrared spectra were recorded on a Unicam Research Series FTIR spectrometer while mass spectra were recorded on a VG Autospec mass spectrometer. Elemental Microanalysis Ltd., Devon, carried out elemental analysis. NMR data are listed in Table 2.

Photolysis ($\lambda > 290$ nm) of samples was carried out in Pyrex NMR tubes using a Philips HPK 125 W medium pressure mercury lamp at room temperature equipped with a water filter.

Synthesis of 1a and 1b in THF

The reaction of $Ni(COD)_2$ with PEt_3 and pentafluoropyridine was carried out as in the literature but the reaction medium was THF.¹⁰ The residue after pumping down was extracted with hexane as previously.

Competition reaction—pentafluoropyridine *versus* 2,3,5,6-tetrafluoropyridine

Entries 1–5 of Table 1. Ni(COD)₂ (50 mg, 0.18 mmol) suspended in hexane (2 mL) was treated with PEt₃ (60 μ L, 0.4 mmol) and was stirred to give a red solution. To this was added a hexane solution (2 mL) containing 2 equiv. of fluoropyridine mixture (Table 1). The mixture turned yellow and was stirred for 2 h. The volatiles were removed under vacuum and the residue dissolved in hexane (4 mL) and filtered through a cannula. The solvent was removed from a portion of the filtrate and the residue redissolved in C₆D₆ and transferred to an NMR tube sealed with a Young's tap. The product ratio was determined by ¹⁹F NMR spectroscopy.

Entries 6–8 of Table 1. Ni(COD)₂ (25 mg, 0.09 mmol), suspended in hexane (2 mL), was treated with PEt₃ (53 μ l, 0.36 mmol). To this was added a solution containing penta-fluoropyridine and 2,3,5,6-tetrafluoropyridine in hexane (2 mL) at the concentrations specified in Table 1. The solution was stirred for 1 h and the volatiles were removed under vacuum. The residue was dissolved in C₆D₆ and analysed as above.

trans-[Ni(N₃)(2-C₅NF₄)(PEt₃)₂] (2a)

Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 mL) was treated with PEt₃ (140 µl, 0.81 mmol) and pentafluoropyridine (50 µl, 0.45 mmol). The solution was stirred for 2 h and the volatiles were removed under vacuum. The residue was redissolved in hexane and treated with trimethylsilyl azide (50 µl, 0.38 mmol). The solution was stirred overnight and the volatiles were removed under vacuum. The residue was redissolved in hexane (5 mL). Crystals formed overnight at -20 °C and were filtered off and dried under vacuum. Yield: 110 mg (0.23 mmol, 62%). Anal. Calcd for C₁₇H₃₀N₄F₄P₂Ni: C, 41.92; H, 6.21; N, 11.50. Found: C, 42.16; H, 6.32; N, 10.84%. IR (Nujol, cm⁻¹): 2055 (ν_{N3}). MS (EI, m/z, relative intensity): 444 (13, [Ni(C₅F₄N)(PEt₃)₂]), 294 (8, [Ni(PEt₃)₂]⁺), 118 (51, [PEt₃]⁺).

trans-[Ni(N₃)(2-C₅NHF₃)(PEt₃)₂] (2b)

Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 mL) was treated with PEt₃ (140 μ l, 0.81 mmol) and 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50 mmol). The solution was stirred for 2 h and the volatiles were removed under vacuum. The residue was redissolved in hexane and treated with trimethylsilyl azide (50 μ l, 0.38 mmol). The solution was stirred overnight and the volatiles were removed under vacuum. The residue was redissolved in hexane (5 mL). Crystals formed overnight at -20 °C and were filtered off and dried under vacuum. Yield: 120 mg (0.26 mmol, 71%). Anal. Calcd for C₁₇H₃₁N₄F₃P₂Ni: C, 43.53; H, 6.66; N, 11.94. Found: C, 43.13; H, 6.93; N, 11.63%. IR (Nujol, cm⁻¹): 2054 (ν_{N3}). MS (EI, *m/z*, relative intensity): 426 (5, [Ni(C₅F₃HN)(PEt₃)_2]), 294 (6, [Ni(PEt₃)_2]⁺), 118 (46, [PEt₃]⁺).

trans-[Ni(NCO)(2-C₅NHF₃)(PEt₃)₂] (3b)

Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 mL) was treated with PEt₃ (140 μ l, 0.81 mmol) and 2,3,5,6-tetrafluoropyridine (50 μ l, 0.50 mmol). The solution was stirred for 2 h and the volatiles were removed under vacuum. The residue was redissolved in hexane and treated with trimethylsilyl isocyanate (50 μ l, 0.37 mmol). The solution was stirred overnight and the volatiles were removed under vacuum. The residue was redissolved in hexane (5 mL). Crystals formed overnight at -20 °C and were filtered off and dried under vacuum. Yield: 130 mg (0.28 mmol, 79%). Anal. Calcd for C₁₈H₃₁N₂F₃P₂NiO: C, 46.09; H, 6.66; N, 5.97. Found: C, 46.43; H, 6.72; N, 6.00%. IR (Nujol, cm⁻¹): 2225 (ν_{NCO}).

trans-[Ni(η^1 -C=CPh)(2-C₅NF₄)(PEt₃)₂] (4a)

Ni(COD)₂ (100 mg, 0.36 mmol) suspended in hexane (5 mL) was treated with PEt₃ (140 µl, 0.95 mmol) and pentafluoropyridine (50 µl, 0.45 mmol). The solution was stirred for 2 h and the volatiles were removed under vacuum. The oily residue was extracted with hexane (5 mL) and filtered through a cannula. The solution was treated with phenylacetylene (40 µl, 0.36 mmol) and tetramethylammonium fluoride (33 mg, 0.36 mmol) and stirred for 48 h. The solution was then cooled to -78 °C to precipitate the ammonium salts and the mixture was filtered through a cannula. The solution was concentrated to 2 mL and yellow crystalline needles formed at 4 °C, which were filtered off and dried under vacuum. Yield: 50 mg (0.09 mmol, 26%). Anal. Calcd for C₂₅H₃₅NF₄P₂Ni: C, 54.97; H, 6.46; N, 2.56. Found: C, 55.18; H, 6.66; N, 3.21%. IR (Nujol, cm⁻¹): 2090 $(v_{C=C})$. MS (EI, m/z, relative intensity): 545 (4, [M]⁺), 427 (2, $[Ni(PEt_3)(C_5F_4N)(C \equiv CPh)]^+)$, 307 (3), 294 (10, $[Ni(PEt_3)_2]^+)$, 268 (6, $[Et_3P-C_5F_4N]^+$), 251 (34, $[PhC \equiv C-C_5F_4N]^+$), 219 (100, [Et₃P–C≡CPh]⁺), 118 (23, [PEt₃]⁺).

$trans-[Ni(C \equiv N)(2-C_5NF_4)(PEt_3)_2]$ (5a)

 $Ni(COD)_2$ (100 mg, 0.36 mmol) suspended in hexane (5 mL) was treated with PEt₃ (140 µl, 0.95 mmol) and pentafluoropyridine (50 µl, 0.45 mmol). The solution was stirred for 2 h. The solution

was then added to a suspension of KCN (28 mg, 0.43 mmol) in THF (15 mL) and the mixture stirred overnight. The volatiles were removed under vacuum, the residue redissolved in hexane (5 mL) and the solution filtered through a cannula. Large yellow crystals formed at -20 °C, which were filtered off and dried under vacuum. Yield: 73 mg (0.16 mmol, 43%). Anal. Calcd for C₁₈H₃₀N₂F₄P₂Ni: C, 45.89; H, 6.42; N, 5.95. Found: C, 45.89; H, 6.62; N, 5.90%. IR (Nujol, cm⁻¹): 2107 ($\nu_{C=N}$).

trans-[NiI(2-C5NF4)(PEt3)2] (6a)

Complex **1a** (80 mg, 0.17 mmol) was dissolved in hexane (10 mL). This solution was then added to a suspension of KI (34 mg, 0.21 mmol) in THF (5 mL) and the mixture darkened after stirring for 2 h. The volatiles were removed under vacuum, the residue extracted with hexane (5 mL) and the solution filtered through a cannula. The volume of the solution was reduced and the solution placed in the freezer. Red crystals formed which were filtered off and dried. Yield 52 mg (0.09 mmol, 53%). Anal. Calcd for $C_{17}H_{30}NF_4P_2NiI$: C, 35.7, H, 5.29, N, 2.45. Found: C, 36.16, H, 5.29, N, 2.47%.

trans-[Ni(OAc)(2-C₅NF₄)(PEt₃)₂] (7a)

Complex **1a** (300 mg, 0.65 mmol) was dissolved in THF (20 mL) and NaOAc (64 mg, 0.78 mmol) was added. The suspension was stirred overnight and the volatiles were removed under vacuum to yield a yellow solid. The product was extracted with hexane (20 mL) and dried under vacuum to afford orange crystals of **7a** which may be recrystallised from hexane at -20 °C. Yield: 242 mg (0.48 mmol, 74%). Anal. Calcd for C₁₉H₃₃NF₄P₂O₂Ni: C, 45.27; H, 6.60; N, 2.78. Found: C, 45.57; H, 6.65; N, 2.83%. IR (ATR, cm⁻¹): 1622 ($\nu_{c=0}$). MS (FAB, *m/z*, relative intensity): 444 (31, [Ni(PEt₃)₂(C₃F₄N)]⁺), 268 (100, [Et₃P–C₃F₄N)]⁺), 221 (15, [AcO–C₃F₄N]).

$[NiF(2-C_5NF_4)(dcpe)]$ (8a)

A solution of dcpe (91 mg, 0.22 mmol) in benzene (2 mL) was added to a solution of complex **1a** (100 mg, 0.22 mmol) in benzene (5 mL). The solution was stirred for 2 h and the volatiles were removed under vacuum. The residue was washed vigorously with hexane (2×5 mL) and filtered. The residue was dried under vacuum affording a waxy yellow solid. The complex was recrystallised from benzene at room temperature yielding small yellow crystals. Yield: 75 mg (0.12 mmol, 52%). Anal. Calcd for C₃₁H₄₈NF₅P₂Ni: C, 57.25; H, 7.44; N, 2.15. Found: C, 58.01; H, 7.52; N, 2.02%.

Table 8 Crystallographic data for 2b, 4a, 7a and $8a \cdot 2\frac{1}{4}C_6H_6$

A solution of dcpe (71 mg, 0.17 mmol) in benzene (2 mL) was added to a solution of *trans*-[Ni(OTf)(2-C₅NF₄)(PEt₃)₂] (**10a**) (100 mg, 0.17 mmol) in benzene (5 mL). The solution was stirred for 2 h and the volatiles were removed under vacuum. The residue was washed with diethyl ether (5 mL), filtered off and dried under vacuum affording a microcrystalline yellow solid. Yield: 62 mg (0.07 mmol, 41%). Anal. Calcd for $C_{38}H_{63}NF_7P_3O_3SNi$: C, 50.79; H, 7.07; N, 1.56. Found: C, 50.18; H, 6.92; N, 1.30%.

X-Ray crystallography

Crystallographic data for **2b**, **4a**, **7a** and **8a** $\cdot 2\frac{1}{4}C_6H_6$ is shown in Table 8.

Crystal structure of 2b. A crystal was mounted on a glass fibre using perfluoropolyether oil and transferred to a Stöe IPDS II imaging plate diffractometer equipped with an Oxford Cryosystems 700 series cooling system. No absorption correction was applied. The structure was solved by direct methods (SHELXS 97)³⁵ and refined by full-matrix least-squares on F^2 using SHELXL 97.³⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions. Structures were displayed with the aid of ORTEP for Windows.³⁷

Crystal structure of 4a. The crystal structure of **4a** was determined with a Rigaku AFC-6S 4-circle diffractometer with cooling provided by an Oxford Cryosystems Cryostream. The structure was solved, refined and displayed as for **2b**. In complex **4a**, the fluoropyridyl ligand exhibits disorder in the form of two rotameric superpositions (differing by 180° rotation about the C(21)–Ni bond). The relative importance of each rotamer was refined yielding occupancies for C(22), F(1) and N(1) of 0.73 and for C(22B), F(1B) and N(1B) of 0.27. These atoms were refined isotropically. The methyl group also occupied two positions, C(12) and C(12B); their occupancies were refined to yield values of 0.71 and 0.29. Hydrogen atoms were placed with a riding model.

Crystal structure of 7a and 8a· $2\frac{1}{4}C_6H_6$. Crystal structures of **7a** and **8a** were determined using a Bruker SMART Apex X-ray diffractometer. The crystals were cooled, using an Oxford Cryosystems Cryostream. Diffractometer control, data collection and initial unit cell determination was performed using SMART.³⁸ Frame integration and unit-cell refinement software was carried out with SAINT+.³⁸ Absorption corrections were applied by SADABS.³⁸ Structures were solved,

	2b	4a	7a	$\pmb{8a}{\cdot}2\tfrac{1}{4}C_6H_6$
Formula	$C_{17}H_{31}F_3N_4NiP_2$	$C_{25}H_{35}F_4NNiP_2$	$C_{19}H_{33}F_4NNiO_2P_2$	$2(C_{31}H_{48}F_5NNiP_2)\cdot 4\frac{1}{2}(C_6H_6)$
M	469.11	546.19	504.11	1652.19
a/Å	9.1396(12)	30.943(4)	10.7713(7)	14.2302(6)
b/Å	12.7408(12)	30.943(4)	13.1418(9)	14.8904(6)
c/Å	19.819(3)	11.522(2)	16.9266(12)	21.0407(9)
$a /^{\circ}$				87.9680(10)
β/°	97.383(11)		92.929(2)	77.0250(10)
y/°				76.7500(10)
$V/Å^3$	2288.7(5)	11032(3)	2392.9(3)	4228.3(3)
T/K	150(2)	150(2)	115(2)	120(2)
Space group	$P2_1/c$	$I4_1/a$	$P2_1/n$	PĪ
Z	4	16	4	2
μ (Mo-K _a)/mm ⁻¹	1.020	0.859	0.990	0.588
Reflxn measd	29439	4856	16257	29431
Reflxn indep.	9834	4856	5489	19340
$R_{\rm int}$	0.1246	0.000	0.0235	0.0278
Final $R[I > 2\sigma(I)]$	R1 = 0.0450	R1 = 0.0617	R1 = 0.0275	R1 = 0.0426
	wR2 = 0.0858	wR2 = 0.1354	wR2 = 0.0694	wR2 = 0.1025
Final <i>R</i> (all data)	R1 = 0.1477	R1 = 0.3019	R1 = 0.0327	R1 = 0.0656
	wR2 = 0.1082	wR2 = 0.2219	wR2 = 0.0721	wR2 = 0.1151

refined and displayed as for **2b**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a riding model and included in the refinement at calculated positions.

In complex **7a**, the fluoropyridyl ligand exhibits disorder in the form of two rotameric superpositions (differing by 180° rotation about the C(1)–Ni bond). The relative importance of each rotamer has been refined using a second FVAR parameter which determined the occupancy of F(1) and F(1A) and is approximately 3 : 1. Each pair of C(2), N(1A) and C(2A), N(1) is constrained to be coincident with identical anisotropic displacement parameters. The sites of C(3)–C(5) and F(2)–F(5) are assumed to be identical to those of the corresponding atoms of the major rotamer and the occupancy is not refined for these atoms (assumed to be unity). This disorder also manifests itself in somewhat larger U values for these atoms.

CCDC reference numbers 278468, 280119, 278469 and 280118.

See http://dx.doi.org/10.1039/b510052f for crystallographic data in CIF or other electronic format.

Acknowledgements

We acknowledge the support of EPSRC and the European Commission (Marie Curie programme). We also thank Dr P. Timmins and Prof. P. H. Walton for assistance with a crystal structure and thank Professor Todd Marder (Durham) and Dr John McGrady for advice.

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