3-Fluoropyridyl nickel complexes as useful tools for the selective synthesis of new 2,4,5,6-tetrafluoropyridines: a route complementing the established methods to access fluorinated pyridines

Marianna I. Sladek, Thomas Braun,* Beate Neumann and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Postfach 100131, 33501 Bielefeld, Germany. E-mail: thomas.braun@uni-bielefeld.de

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Treatment of $[Ni(COD)_2]$ with 3-chlorotetrafluoropyridine in the presence of PEt_3 or PCy_3 effects the formation of the complexes *trans*-$[NiCl(3\text{-}C_5NF_4)(PEt_3)_2]$ (**1**) and *trans*-$[NiCl(3\text{-}C_5NF_4)(PCy_3)_2]$ (**2**), respectively. Reaction of **1** with MeLi gives *trans*-$[NiMe(3\text{-}C_5NF_4)(PEt_3)_2]$ (**3**). Treatment of **3** with air yields 3-methyltetrafluoropyridine. The reaction of **1** with CO affords 1-(2,4,5,6-tetrafluoropyridin-3-yl)ethanone (**6**), which slowly converts into 1-(2,5,6-trifluoropyridin-3-yl)ethanone (**7**) in the presence of PEt_3. The structure of the complexes **1** and **3** have been determined by X-ray crystallography. The Ni–C distances to the pyridyl ligand are 1.894(1) and 1.936(2) Å, respectively. The Ni–C bond length to the methyl group in **3** is 1.991(3) Å. The studies reported in this paper demonstrate the synthesis of nickel derivatives of tetrafluoropyridine with the metal in the 3-position as well as the preparation of otherwise not accessible 3-substituted tetrafluoropyridines by C–C coupling reactions.

Introduction

Selective routes to synthesise higher fluorinated pyridines bearing additional functional groups are often limited to fluorination reactions or to nucleophilic attack at already fluorinated precursors.[1,2] However, in the last few years the use of metal derivatives has also led to a variety of substituted fluoropyridines.[2,3] It has been demonstrated that fluorinated heteroaryl groups in the coordination sphere of nickel can be applied as building blocks to afford fluoro compounds, which are otherwise not accessible.[4–8] Thus, we have been successful in developing a nickel mediated way to prepare chlorodifluoropyrimidines.[6] Previously unknown tetrafluoropyridines, which are functionalised in the 2-position, have also been synthesised.[4,7,8] The methods usually involve C–F activation by oxidative addition of the heterocycle as a crucial step.[5–8]

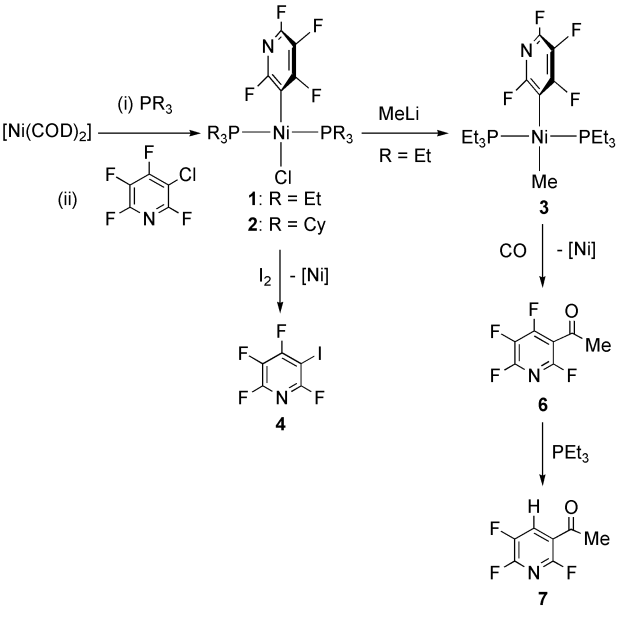
A route to 2,4,5,6-tetrafluoropyridines, such as 2,4,5,6-tetrafluoronicotinic acid and 3-formyltetrafluoropyridine, has been established starting from the 3-lithio derivative.[3,9] However, the limitation of this method is revealed by the attempted syntheses of ketones by reaction of lithiated fluoropyridines with acid chlorides.[2,3] This has not been achieved, because the carbonyl group of the ketone is very activated towards a second nucleophilic attack due to the presence of the highly electron withdrawing tetrafluoropyridine ring.

In this paper we present studies on the synthesis, reactivity and structure of nickel compounds with a fluorinated pyridyl ligand bound at the metal in the 3-position. The nickel derivatives of 2,5,5,6-tetrafluoropyridine can be obtained by oxidative addition of a C–Cl bond. We show, that a pyridyl complex also bearing a methyl ligand is accessible. The isolation of that compound allows the preparation of new 3-substituted tetrafluoropyridines by C–C coupling reactions in the coordination sphere of the metal.

Results

1 Synthesis of *trans*-$[NiCl(3\text{-}C_5NF_4)(PEt_3)_2]$ (1) and *trans*-$[NiCl(3\text{-}C_5NF_4)(PCy_3)_2]$ (2)

Reaction of $[Ni(COD)_2]$ with 3-chlorotetrafluoropyridine in the presence of PEt_3 or PCy_3 yields *trans*-$[NiCl(3\text{-}C_5NF_4)(PEt_3)_2]$ (**1**) and *trans*-$[NiCl(3\text{-}C_5NF_4)(PCy_3)_2]$ (**2**), respectively (Scheme 1). The ^{31}P NMR spectra of **1** displays a singlet at δ 15.4 for the two equivalent phosphorus nuclei (Table 1). The ^{19}F NMR spectrum shows four signals at δ −171.20, −98.40,



Scheme 1 Synthesis and reactivity of fluoropyridyl complexes.

Table 1 NMR data at 300 K in C_6D_6; δ (J/Hz)

Complex	^1H	$^{31}P\{^1H\}$	^{19}F	$^{13}C\{^1H\}$
1	0.90 (m, 18 H, CH_3), 1.16 (m, 12 H, CH_2)	15.4 (s)	−171.20 (ddm, J_{FF} 47.0, 24.1, 1 F), −98.40 (m, 1 F), −95.89 (m, 1 F), −50.22 (m, 1 F)	6.8 (s, CH_3), 13.5 (vt, apparent J_{PC} 12.0, CH_2), 112.2 (m, C_{ipso}), 131.6 (dm, J_{CF} 236.7, CF), 147.6 (dm, J_{CF} 231.9, CF), 155.5 (ddd, J_{CF} 227.1, 30.0, 14.4, CF), 160.0 (ddm, J_{CF} 241.5, 21.6, CF)
2	0.88–2.13 (m, br, CH_2CH_3)	17.6 (s)	−173.46 (m, 1 F), −101.20 (m, 1 F), −90.30 (m, 1 F), −45.06 (m, 1 F)	
3	−0.54 (t, J_{PH} 8.8, 3H, $NiCH_3$), 0.95 (m, 18 H, CH_2CH_3), 1.23 (m, 12 H, CH_2)	20.4 (s)	−173.59 (ddm, J_{FF} 51.6, 22.9, 1 F), −100.72 (ddm, J_{FF} 36.7, 17.2, 1 F), −97.0 (m, 1 F), −50.81 (m, 1 F)	−10.3 (t, J_{CP} 27.8, $NiCH_3$), 6.9 (s, CH_2CH_3), 13.6 (vt, apparent J_{PC} 13.2, CH_2), 127.1 (m, C_{ipso}), 131.6 (dm, J_{CF} 261.9), 147.3 (dm, J_{CF} 235.4, CF), 157.1 (ddd, J_{CF} 239.9, 36.2, 14.2, CF), 161.4, (ddm, J_{CF} 231.5, 26.5, CF)
4			−169.97 (m, 1 F), −115.78 (m, 1 F), −86.59 (m, 1 F), −69.52 (m, 1 F)	
5	1.67 (vt, apparent J_{FH} 1.3, CH_3)		−167.62 (m, 1 F), −118.65 (m, 1 F), −89.50 (m, 1 F), −73.67 (m, 1 F)	
6	2.02 (s, CH_3)		−165.12 (dd, J_{FF} 43.6, 21.8, 1 F), −114.62 (m, 1 F), −79.82 (m, 1 F), −66.12 (m, 1 F)	
7	2.01 (s, 3 H, CH_3), 7.52 (vt, apparent J_{FH} 7.0, 8.8, 1 H, CH)		−143.86 (m, 1 F), −80.24 (m, 1 F), −66.08 (m, 1 F)	

−95.89 and −50.22, which appear at similar chemical shifts as those found for 3-$Bu_3Sn(C_5NF_4)$.[3] The ^{13}C NMR spectrum reveals a resonance for the quaternary *ipso* carbon atom at δ 112.2 at rather high field.[7,10] The NMR spectroscopic data for **2** resemble those found for **1** and therefore need no further discussion (Table 1).

2 Crystal structure of *trans*-[NiCl(3-C_5NF_4)(PEt_3)$_2$] (1)

The yellow complex **1** was crystallised from toluene at −30 °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 geometry around the nickel is almost square-planar. The angles between the adjacent ligands at nickel vary from 91.31(4) to 89.32(2)°. The dihedral angle between the nickel coordination plane and the plane defined by the heteroaryl ligand is 88.1°. The nickel–carbon distance of 1.894(1) Å is longer than the Ni–C bond length in *trans*-[NiF(2-C_5HF_3N)(PEt_3)$_2$] [1.869(4) Å], but is comparable to the Ni–C separation in *trans*-[NiCl(5-$C_4F_3N_2$)(PEt_3)$_2$]-[1.885(1) Å].[6,10]

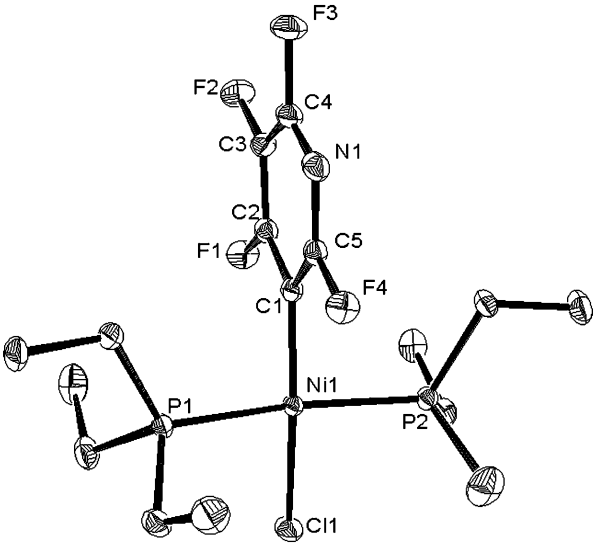


Fig. 1 An ORTEP diagram of **1**. Ellipsoids are drawn at the 50% probability level.

3 Synthesis of *trans*-[NiMe(3-C_5NF_4)(PEt_3)$_2$] (3)

On treatment of a solution of **1** with MeLi the complex *trans*-[NiMe(3-C_5NF_4)(PEt_3)$_2$] (**3**) was obtained. Compound **3** was characterised by its NMR and analytical data. The presence of the nickel bound methyl ligand is indicated by a triplet in the ^1H NMR spectrum at δ −0.54 with a coupling to the phosphorus nuclei of 8.8 Hz.[7,11–13] The ^{19}F NMR spectrum reveals four signals at δ −173.59, −100.72, −97.03 and −50.81 for the fluorine atoms at the heteroaryl ligand. They appear in the same region as the resonances found for **1**, which confirms the existence of a tetrafluoropyridyl complex with the nickel in the 3-position. The ^{13}C NMR spectrum displays a triplet

Table 2 Selected bond lengths (Å) and angles (°) of *trans*-[NiCl(3-C_5NF_4)(PEt_3)$_2$] (**1**) with the estimated standard deviations in parentheses

Ni(1)–Cl(1)	2.1921(4)	C(1)–C(5)	1.390(2)
Ni(1)–C(1)	1.894(1)	N(1)–C(4)	1.311(2)
Ni(1)–P(1)	2.2155(4)	N(1)–C(5)	1.323(2)
Ni(1)–P(2)	2.2212(4)	C(2)–F(1)	1.344(2)
C(1)–C(2)	1.387(2)	C(3)–F(2)	1.335(2)
C(2)–C(3)	1.391(2)	C(4)–F(3)	1.352(2)
C(3)–C(4)	1.375(2)	C(5)–F(4)	1.351(2)
C(1)–Ni(1)–P(1)	91.31(4)	C(2)–C(1)–Ni(1)	121.82(11)
Cl(1)–Ni(1)–P(1)	89.32(2)	C(5)–C(1)–Ni(1)	126.77(10)
C(1)–Ni(1)–P(2)	91.20(4)	C(2)–C(1)–C(5)	111.39(13)
Cl(1)–Ni(1)–P(2)	89.55(1)	C(1)–C(2)–C(3)	123.08(13)
P(1)–Ni(1)–P(2)	168.95(1)	C(4)–C(3)–C(2)	116.70(13)
C(1)–Ni(1)–Cl(1)	172.80(4)	N(1)–C(4)–C(3)	124.20(14)
C(4)–N(1)–C(5)	115.59(13)	N(1)–C(5)–C(1)	129.02(13)

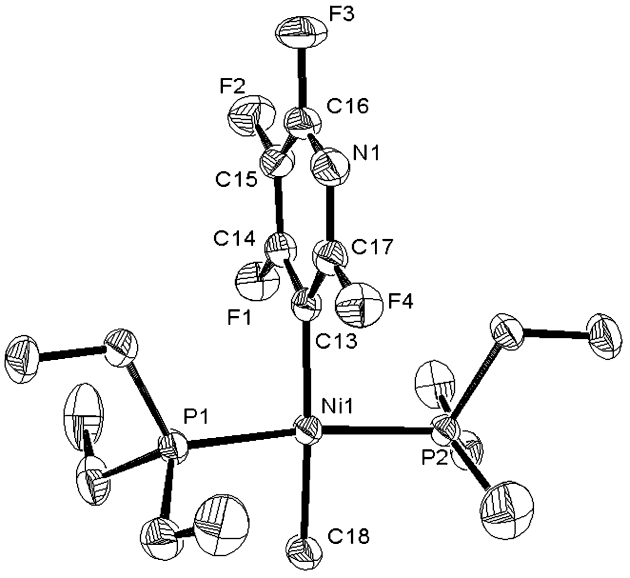


Fig. 2 An ORTEP diagram of **3**. Ellipsoids are drawn at the 50% probability level.

at δ −10.3 with a phosphorus carbon coupling constant of 27.8 Hz. The resonance for the *ipso* carbon atom of the pyridyl ligand appears at δ 121.7, at significantly higher field than the signal at δ 198.0 for the *ipso* carbon in the isomeric compound *trans*-[NiMe(2-C_5NF_4)(PEt_3)$_2$].[7]

4 Crystal structure of *trans*-[NiMe(3-C_5NF_4)(PEt_3)$_2$] (3)

The methyl complex **3** was crystallised from toluene at −30 °C. An ORTEP diagram is shown in Fig. 2. The principal bond lengths and angles are summarised in Table 3. Compound **3** exhibits an approximately square-planar geometry with the pyridyl group coordinated *trans* to the methyl ligand. The angles about the nickel atom are distorted from ideal square-planar geometry and vary from 87.95(8) to 92.99(7)°. The plane defined by the pyridyl ring is nearly perpendicular to the cooordination plane with a dihedral angle of 87.5°. The Ni–C distance to the methyl ligand of 1.991(3) Å is almost the same as the comparable Ni–C bond lengths in [{*trans*-$NiMe_2(PMe_3)$}$_2${μ-κ^2(*C*,*C*)-(*t*$BuN_2C_3H_2$)$_2$$CH_2$}] [1.983(4), 2.001(4) Å] and lies in the expected range for a methyl ligand *trans* to another anionic ligand.[13,14] The Ni–C distance to the tetrafluoropyridyl ligand [1.936(2) Å] is longer than the comparable seperation found for **1**. This observation can be attributed to the larger *trans*-influence of a methyl ligand compared to the chloro ligand.

Table 3 Selected bond lengths (Å) and angles (°) of *trans*-[NiMe(3-C_5NF_4)(PEt_3)$_2$] (**3**) with the estimated standard deviations in parentheses

Ni(1)–C(13)	1.936(2)	C(15)–C(16)	1.364(4)
Ni(1)–C(18)	1.991(3)	N(1)–C(16)	1.309(4)
Ni(1)–P(1)	2.190(1)	N(1)–C(17)	1.328(3)
Ni(1)–P(2)	2.185(1)	C(14)–F(1)	1.346(3)
C(13)–C(14)	1.375(4)	C(15)–F(2)	1.327(3)
C(13)–C(17)	1.383(4)	C(16)–F(3)	1.351(3)
C(14)–C(15)	1.380(4)	C(17)–F(4)	1.351(3)
C(13)–Ni(1)–P(1)	92.37(7)	C(14)–C(13)–Ni(1)	122.7(2)
C(18)–Ni(1)–P(1)	88.05(8)	C(17)–C(13)–Ni(1)	126.6(2)
C(13)–Ni(1)–P(2)	92.99(7)	C(14)–C(13)–C(17)	110.7(2)
C(18)–Ni(1)–P(2)	87.95(8)	C(13)–C(14)–C(15)	124.3(3)
P(1)–Ni(1)–P(2)	167.87(3)	C(16)–C(15)–C(14)	116.3(3)
C(13)–Ni(1)–C(18)	173.02(13)	N(1)–C(16)–C(15)	124.4(2)
C(16)–N(1)–C(17)	115.1(3)	N(1)–C(17)–C(13)	129.2(3)

5 Formation of 3-iodotetrafluoropyridine (4)

Treatment of **1** or **2** with an excess of iodine in C_6D_6 affords, after distillation under vacuum, a solution of 3-iodotetrafluoropyridine (**4**) (Scheme 1). The yield was determined by using an external standard of 4-fluorotoluene and is about 25% after distillation. Compound **4** has been described before and has been identified by a GC/MS spectrum as well as by comparison of the ^{19}F NMR spectroscopic data.[3]

6 Formation of 3-methyltetrafluoropyridine (5)

On admission of air to a solution of complex **3** the 3-methyltetrafluoropyridine (**5**) is formed. After distillation under vacuum a solution has been obtained containing **5** and considerable amounts (18%) of a second compound, which we assign as 2,4,5,6-tetrafluoropyridine by comparison of the ^{19}F NMR data.[3,15] Compound **5** was characterised by a GC/MS spectrum and the NMR spectroscopic data. The ^{19}F NMR spectrum shows the expected four signals at δ −167.62, −118.65, −89.50 and −73.67 indicating the presence of four fluorine atoms in the 2-, 4-, 5- and 6-position.[16] The resonances for the four fluorine atoms in the ^{19}F NMR spectrum of the known 2-methyltetrafluoropyridine appear at higher field.[7] The methyl group in **5** is revealed by a signal at δ 1.67 in the ^{1}H NMR spectrum.[7]

7 Formation of 1-(2,4,5,6-tetrafluoropyridin-3-yl)ethanone (6)

Treatment of a solution of the methyl complex **3** with CO leads to a C–C coupling reaction and the generation of the ketone **6**. In the presence of free PEt_3, compound **6** slowly converts into a second compound, which was assigned as 1-(2,5,6-trifluoropyridin-3-yl)ethanone (**7**). The carbonyl compound [Ni(CO)$_2$(PEt_3)$_2$] and minor amounts of [Ni(CO)$_3$(PEt_3)], which have also been formed, could be identified by their IR and ^{31}P NMR spectroscopic data.[17,18] An independent experiment shows that **6** can be converted into **7** on treatment with PEt_3.

The proposed structures of **6** and **7** are supported by their ^{1}H and ^{19}F NMR (Table 1) spectra and the mass spectrometric data.[3] Four resonances in the ^{19}F NMR spectrum of **6** at δ −165.12, −114.62, −79.82 and −66.12 indicate the presence of four fluorine atoms in the 2-, 4-, 5- and 6-position. The three signals which are assigned to **7** at δ −143.86, −80.24 and −66.08 appear at almost the same chemical shift as those found for 3-chloro-2,5,6-trifluoropyridine and are distinctively different to the signals of 3-chloro-2,4,6-trifluoropyridine.[19] The presence of two fluorine atoms in *ortho* position to the nitrogen is indicated by the considerable broadness of the two adsorptions at low field, which is attributed to the quadrupolar effect of the adjacent ^{14}N nucleus. The IR spectrum of **6** displays an absorption at 1698 cm^{-1}, which was assigned to the vibration of the C=O bond.

Discussion

The syntheses of the complexes *trans*-[NiCl(3-C_5NF_4)(PEt_3)$_2$] (**1**) and *trans*-[NiCl(3-C_5NF_4)(PCy_3)$_2$] (**2**) by oxidative addition of 3-chlorotetrafluoropyridine at Ni(0) are shown in Scheme 1. The comparable chlorotrifluoropyridyl complex *trans*-[NiCl(3-C_5NClF_3)(PEt_3)$_2$] has been prepared in a similar manner.[10] There are only a few metal derivatives of tetrafluoropyridine with the metal in the 3-position described in the literature.[3,9,20] [Hg(3-C_5NF_4)$_2$] is the only transition metal compound which has been known so far, but no analytical or spectroscopic data are given.[20] Despite the directing influence of the nitrogen atom in the heteroaromatic ring for an oxidative addition at

nickel in the 2-position, the experiments show a clear preference for C–Cl activation in the 3-position over C–F activation.[5,6,10,21] There is no influence of the phosphine on the chemo- or regioselectivity. This is in contrast to the selectivity obtained for the activation of 5-chlorotrifluoropyridine at nickel, which is controlled by the size of the phosphine. Thus, a reaction of 5-chlorotrifluoropyridine with $[Ni(COD)_2]$–PCy_3 gives the C–F activation product *trans*-$[NiF(4\text{-}C_4N_2ClF_2)(PCy_3)_2]$, while upon use of PEt_3 instead of PCy_3 insertion into the C–Cl bond is observed.[6] The regioselectivity for the generation of **1** and **2** indicates that the oxidative addition is likely to proceed *via* a concerted reaction pathway or *via* a tight ion-pair $\{Ni(PR_3)_3^+ \cdot C_5NClF_4^-\}$.[22,23] A nucleophilic mechanism is not very plausible, as it would lead to an attack in the 2- or 4-position.[1]

Complex **1** can be converted into *trans*-$[NiMe(3\text{-}C_5NF_4)(PEt_3)_2]$ (**3**) by reaction with MeLi. It is worth mentioning that we did not observe any nucleophilic attack at the pyridyl ligand.[24] We note that *trans*-$[NiMe(2\text{-}C_5NF_4)(PEt_3)_2]$, which is isomeric to complex **3**, was synthesised by R. N. Perutz *et al.* using a comparable method (Scheme 2).[7] Compound **3** is stable in solution and in the solid state over weeks. This remarkable stability might be attributed to some π-back-bonding from the metal centre to the perfluorinated aromatic ring.[7,25]

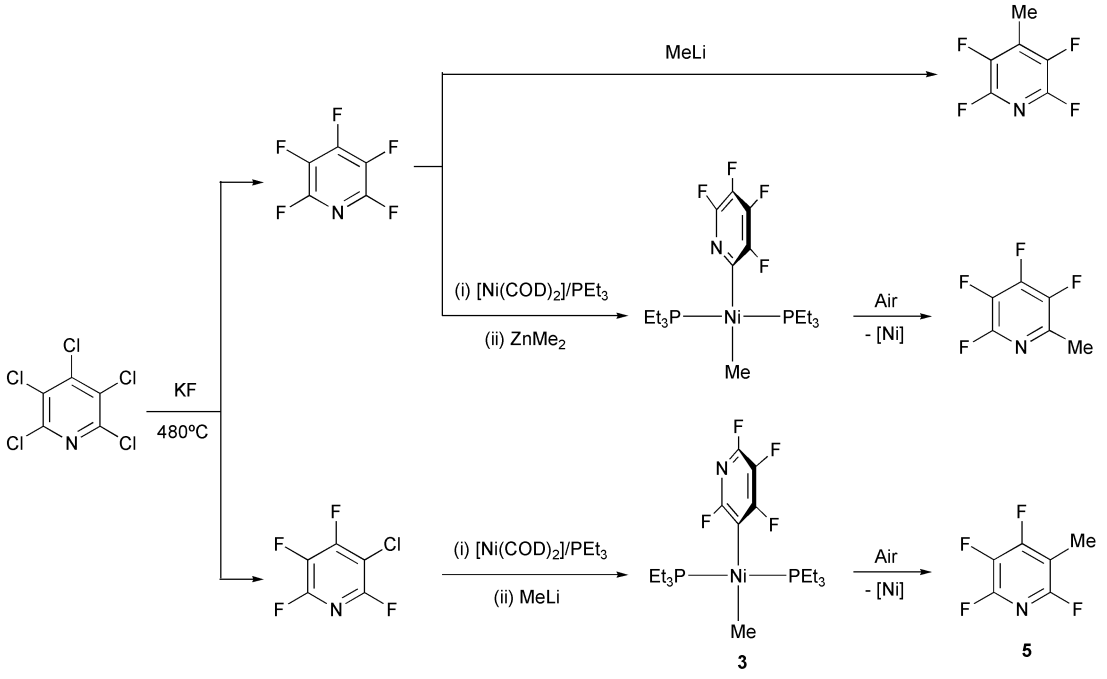
The X-ray structures of **1** and **3** reveal complexes with approximately square-planar coordination at nickel. It is worth mentioning that with $[\{trans\text{-}NiMe_2(PMe_3)\}_2\{\mu\text{-}\kappa^2(C,C)\text{-}(t\text{Bu}N_2C_3H_2)_2CH_2\}]$ only one other square-planar nickel complex which exhibits two anionic carbon ligands in *trans*-position has been characterised by X-ray crystallography.[13]

The cleavage of the Ni–C bond in **3** affords the iodopyridine **4**, which has been prepared recently by reaction of 3-lithiotetrafluoropyridine with iodine.[3] It has been shown before that a Ni–C bond can be cleaved on reaction with halogens, possibly by oxidative induction.[4,26]

The generation of the C–C coupling product **5** by treatment of complex **3** with air could be explained by the effect of oxygen. It is known that O_2 can act as a phosphine scavenger and therefore supports dissociative loss of a phosphine ligand, which in turn favours reductive elimination.[17,27] However, oxidation of the metal complex with oxygen can be an alternative explanation.[27] The resulting cationic radical should have an enhanced lability towards reductive elimination.[27] The observed generation of 2,4,5,6-tetrafluoropyridine indicates a competitive reaction pathway, possibly *via* the arylphosphonium cation $[3\text{-}C_5F_4(PEt_3)N]^+$. It has been shown that such cations can arise from reductive elimination of a metastable arylnickel(III)phosphine species.[28] Presumably, $[3\text{-}C_5F_4(PEt_3)N]^+$ is not stable and gives 2,4,5,6-tetrafluoropyridine.[8] Note that reductive elimination of *ortho*-xylene from *trans*-$[NiMe(o\text{-}C_5H_4CH_3)(PEt_3)_2]$ is also accompanied by the formation of toluene (*ca.* 10%).[27]

Overall, all three isomers of methyltetrafluoropyridine are now accessible starting from either pentafluoropyridine or 3-chlorotetrafluoropyridine, which can both be obtained by fluorination of pentachloropyridine with KF (Scheme 2).[3,19] Thus, C–F activation of pentafluoropyridine at $\{Ni(PEt_3)_2\}$ and subsequent reaction of *trans*-$[NiF(2\text{-}C_5NF_4)(PEt_3)_2]$ with $ZnMe_2$ gives *trans*-$[NiMe(2\text{-}C_5NF_4)(PEt_3)_2]$, which on treatment with air yields a solution of 2-methyltetrafluoropyridine.[7] The isomeric 4-methyltetrafluoropyridine can also be synthesised from pentafluoropyridine by nucleophilic substitution (Scheme 2).[29] We note that the 3-methyltetrafluoropyridine **5** has been described before by fluorination of 3-methylpyridine with caesium tetrafluorocobaltate.[16] However, it was only obtained as by-product in very low yield ($< 0.1\%$).

The carbonylation product **6** is observed on treatment of complex *trans*-$[NiMe(3\text{-}C_5NF_4)(PEt_3)_2]$ (**3**) with CO. Since complex **1** does not react with CO and metal carbon bonds to fluorinated anionic ligands are very strong, we assume that the incorporation of CO occurs *via* an insertion–migration process into the Ni–CH_3 bond.[30] Reductive elimination is then induced by a second molecule of CO. It should be stressed that the reaction of 3-lithiotetrafluoropyridine with acetyl chloride does not lead to **6**.[3] In this case **6** is assumed to be an intermediate, but the carbonyl group is very activated towards nucleophilic attack and a second reaction of 3-lithiotetrafluoropyridine occurs to give a bispyridylacetate.[2,3] The generation of the ketone **7** bearing a trifluoropyridyl group is due to a defluorination reaction of **6**, which is probably induced by the phosphine.[8,31] This has been confirmed by carrying



Scheme 2 Synthesis of methyltetrafluoropyridines.[3,7,29]

out an independent experiment. A comparable reaction of pentafluoropyridine with PEt_3, which leads to 2,3,5,6-tetrafluoropyridine, has been mentioned before.[8]

Conclusions

This paper reports the syntheses of nickel complexes *trans*-[NiR(3-C_5NF_4)L_2] (**1**: R = Cl, L = PEt_3; **2**: R = Cl, L = PCy_3; **3**: R = Me, L = PEt_3) bearing a tetrafluoropyridyl ligand with the nickel in the 3-position. The X-ray structures of **1** and **3** have been determined. Except for [Hg(3-C_5NF_4)$_2$] no tetrafluoropyridyl complexes with the metal in the 3-position had been described previously.[20]

3-Lithiotetrafluoropyridine provides access to 2,4,5,6-tetrafluoropyridines by nucleophilic attack of the metal compound at a fluorinated substrate, but this methology is limited by the nucleophilicity of the metal derivative.[3,9] Nucleophilic attack at 3-chlorotetrafluoropyridine usually takes place in the 2- or 4-position, while pentafluoropyridine is attacked in the 4-position.[1] Our strategy is initiated by the derivatisation of tetrafluoropyridyl ligands bound at the 3-position at a transition metal. Consequently, the reactions have the attraction of producing a different regiochemistry from the typical organic route. In addition, C–C coupling reactions can be performed under non-nucleophilic conditions. Therefore the reactions of 3-chlorotetrafluoropyridine at nickel provide access to fluorinated heterocycles, which are otherwise not accessible or only in very low yield. This is demonstrated by the preparation of the methylpyridine **5** and the ketone **6**.

We note that highly fluorinated pyridines serve as precursors for lower fluorinated heterocycles, which are of interest as building blocks in pharmaceuticals, dyes and agrochemicals.[4,32,33]

Experimental

Most of the synthetic work was carried out on a Schlenk line or in a nitrogen-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under argon before use. Benzene-d_6 was dried by stirring over potassium and then distilled under vacuum. A solution of MeLi in ether was obtained from Aldrich. [Ni(COD)$_2$] was prepared according to the literature.[34] 3-Chlorotetrafluoropyridine was obtained from Fluorochem Ltd. and distilled before use.

The NMR spectra were recorded on a Bruker DRX 500 (^{1}H and ^{19}F NMR) or a Bruker Avance 600 (^{13}C NMR) spectrometer. The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15. The $^{13}C\{^1H\}$ spectra were referenced to C_6D_6 at δ 128.0. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The $^{31}P\{^1H\}$ NMR spectra are reported downfield of an external solution of H_3PO_4 (85%). Infrared spectra were recorded on a Bruker IFS-66 spectrometer. NMR data are listed in Table 1. Mass spectra were recorded on a MS QP5050A fitted with a Shimadzu GC 17a.

Syntheses

Synthesis of *trans*-[NiCl(3-C_5NF_4)(PEt_3)$_2$] (1). [Ni(COD)$_2$] (654 mg, 2.40 mmol) was suspended in hexane (8 mL). After addition of PEt_3 (724 mg, 6.13 mmol), the resulting orange solution was stirred for 15 min at room temperature before 3-chloro-2,4,5,6-tetrafluoropyridine (574 mg, 3.00 mmol) was added. The resulting yellow–brown solution was stirred for another hour at room temperature. The volatiles were then removed under vacuum. The remaining yellow oil was dissolved in toluene (8 mL) and the solution was filtered through a cannula. The solution was concentrated under vacuum to *ca.* 4 mL, and yellow crystals formed at −30 °C. The supernatant was removed and the resulting yellow crystals were dried under vacuum. Yield 982 mg (70%). (Found: C, 42.27; H, 6.16; N, 2.88. $C_{17}H_{30}ClF_4NiP_2$requires C, 42.46; H, 6.30; N, 2.92%).

Synthesis of *trans*-[NiCl(3-C_5NF_4)(PCy_3)$_2$] (2). [Ni(COD)$_2$] (165 mg, 0.60 mmol) was suspended in tetrahydrofuran (10 mL). After addition of PCy_3(370 mg, 1.32 mmol), the resulting green–brown solution was stirred for 15 min at room temperature before 3-chloro-2,4,5,6-tetrafluoropyridine (133 mg, 0.72 mmol) was added. The resulting yellow–brown solution was stirred for another hour at room temperature. The volatiles were then removed under vacuum. The remaining yellow–brown oil was dissolved in hexane (8 mL) and the solution was filtered through a cannula. The solution was concentrated under vacuum to *ca.* 4 mL, and yellow crystals formed at −30 °C. The supernatant was removed and the resulting yellow crystals were dried under vacuum. Yield 94 mg (17%). (Found: C, 60.53; H, 8.15; N,1.51. $C_{41}H_{66}ClF_4NiP_2$ requires: C, 61.17; H, 8.26; N, 1.74%).

Synthesis of *trans*-[NiMe(3-C_5NF_4)(PEt_3)$_2$] (3). A solution of *trans*-[NiCl(3-C_5NF_4)(PEt_3)$_2$] (**1**) (769 mg, 1.60 mmol) in tetrahydrofuran (10 mL) was treated at −60 °C with a solution of MeLi in ether (1.20 mL, 1.68 mmol). After the resulting red suspension had been warmed to room temperature, methanol (0.5 mL) was added to the now orange suspension. The volatiles were then removed under vacuum. The residue was extracted with toluene (5 mL), the extract was filtered, and the filtrate was reduced to 1 mL *in vacuo*. Yellow crystals were obtained at −30 °C, which were separated from the mother liquor and dried *in vacuo*. Yield 486 mg (66%). (Found: C, 46.92; H, 7.11; N, 2.76. $C_{18}H_{33}F_4NiP_2$ requires C, 46.90; H, 7.22; N, 3.04%).

Synthesis of 3-C_5NF_4I (4). A solution of **1** (80 mg, 0.17 mmol) in C_6D_6 (0.4 mL) was treated with iodine (30 mg, 0.24 mmol). The volatiles were then transferred under vacuum into an NMR tube. The ^{19}F NMR spectrum demonstrated that the distillate consisted of a solution of **4** in C_6D_6.[3] The yield of **4** was determined by NMR with 4-fluorotoluene as external standard, based on **1**. Yield (25%, not optimized) Mass spectrum (EI, m/z, relative intensity): 277 (31%) $[M]^+$.

Synthesis of CH_3(3-C_5NF_4) (5). A solution of **3** (67 mg, 0.15 mmol) in C_6D_6 (0.4 mL) was saturated with air. The volatiles were transferred under vacuum into an NMR tube. Comparison of the ^{19}F NMR spectra with the literature demonstrated that the distillate consisted of a solution of **5** and 2,4,5,6-tetrafluoropyridine in C_6D_6 (*ca.* 18%).[15,31] The yield of **5** after distillation was determined by NMR with 4-fluorotoluene as external standard, based on **3**. Yield (16%, not optimized). Mass spectrum (**5**) (EI, m/z, relative intensity): 165 (89%) $[M]^+$, 164 (100%) $[M–H]^+$, 146 (29%) $[M–F]^+$.

Synthesis of 3-$C_5NF_4(CO)CH_3$ (6) and 3-$C_5NF_3H(CO)CH_3$ (7). A solution of **3** (93 mg, 0.20 mmol) in C_6D_6 (0.4 mL) was saturated with CO. The volatiles were transferred under vacuum into an NMR tube. The ^{19}F and ^{1}H NMR spectra demonstrated that the distillate consisted of a solution of **6** in C_6D_6. In the presence of residual PEt_3 compound **6** slowly converts into **7** within days. The yield of **6** after distillation was determined by NMR with 4-fluorotoluene as external standard, based on **3**. Yield (56%, not optimized). Mass spectrum (**6**) (EI, m/z, relative intensity): 193 (19%) $[M]^+$, 178 (100%) $[M–CH_3]^+$, 150 (31%)$[M–COCH_3]^+$, 43 (80%) $[COCH_3]^+$. IR (**6**) [C_6D_6, ν/cm^{-1}]: 1698 (C=O). Mass spectrum (**7**) (EI, m/z, relative intensity): 175 (24%) $[M]^+$, 160 (100%) $[M–CH_3]^+$, 132 (30%) $[M–COCH_3]^+$, 43 (59%) $[COCH_3]^+$. IR (**7**) [C_6D_6, ν/cm^{-1}]: 1713 (C=O).

Structure determination for complex 1

Yellow crystals of **1** were obtained from a solution in toluene at −30 °C. Diffraction data were collected for a plate with the dimensions 0.30 × 0.15 × 0.15 mm on a Nonius Kappa CCD diffractometer.

Crystal data. $C_{17}H_{30}ClF_4NNiP_2$, $M = 480.52$, orthorhombic, space group $Pna2_1$, $a = 23.3630(1)$, $b = 8.5540(1)$, $c = 10.9840(2)$ Å, $U = 2195.12(5)$ Å^3, $T = 100(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.19 mm^{-1}, 43 259 reflections measured, 6102 unique ($R_{int} = 0.038$). The structure was solved by direct methods (SHELXTL PLUS) and refined with the full matrix least square methods on F^2 (SHELX-97).[35,36] Final R_1, wR_2 values on all data: 0.0216, 0.0513. R_1, wR_2 values for 5943 reflexions with $I_o > 2\sigma(I_o)$: 0.0205, 0.0508.

CCDC reference number 190943

Structure determination for complex 3

Yellow crystals of **3** were obtained from a solution in toluene at −30 °C. Diffraction data were collected for a block with the dimensions 0.14 × 0.18 × 0.18 mm on a Nonius Kappa CCD diffractometer.

Crystal data. $C_{18}H_{33}F_4NNiP_2$, $M = 460.10$, orthorhombic, space group $Pna2_1$, $a = 23.4610(3)$, $b = 8.7220(4)$, $c = 10.8680(9)$ Å, $U = 2223.9(2)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.051 mm^{-1}, 18 038 reflections measured, 6029 unique ($R_{int} = 0.0290$). The structure was solved by direct methods (SHELXTL PLUS) and refined with the full matrix least square methods on F^2 (SHELX-97).[35,36] Final R_1, wR_2 values on all data: 0.0521, 0.0846. R_1, wR_2 values for 5201 reflexions with $I_o > 2\sigma(I_o)$: 0.0337, 0.0762.

CCDC reference number 190944

See http://www.rsc.org/suppdata/nj/b2/b207943g/ for crystallographic data in CIF or other electronic format.

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