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Isolation and reactivity of palladium hydrido complexes: intermediates in the hydrodefluorination of pentafluoropyridine†‡

David Breyer, Thomas Braun* and Anna Penner

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The hydrido complexes *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**3**) and *trans*-[Pd(H)(4-C_5NF_4)(PCy_3)$_2$] (**5**) can be prepared by reaction of *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**2**) or *trans*-[Pd(F)(4-C_5NF_4)(PCy_3)$_2$] (**4**) with HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane). The iodo and triflato complexes *trans*-[Pd(I)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**7**) and *trans*-[Pd(OTf)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**9**) are generated on treatment of complex **3** with MeI or ethyltrifluoromethanesulfonate (EtOTf), respectively. Treatment of **3** with Ph_3CPF_6 in MeCN results in the formation of *trans*-[Pd(4-C_5NF_4)(NCMe)(P*i*Pr_3)$_2$]PF_6 (**6a**). Heating **3** to 60 °C gives the products of reductive elimination 2,3,5,6-tetrafluoropyridine as well as [Pd(P*i*Pr_3)$_2$] (**1**). In the presence of pentafluoropyridine [Pd(P*i*Pr_3)$_2$] (**1**) affords the oxidative addition product **2**. In a catalytic experiment, pentafluoropyridine can be converted into 2,3,5,6-tetrafluoropyridine in the presence of HBpin with 44% yield when 10% of **3** is employed as catalyst.

Introduction

There is an ongoing interest to develop new routes to access fluoroorganic compounds, because of their versatile applications.[1] An organometallic strategy involves the selective defluorination of easily available highly fluorinated precursors.[2,3] For instance, the selective activation of carbon–fluorine bonds in the coordination sphere of palladium or nickel followed by functionalisation of the fluorinated ligands can lead to fluorinated compounds, which are often not accessible otherwise.[2,4-6] However, so far, most of the routes to access fluoroorganic compounds *via* transition metal mediated C–F activation comprise hydrodefluorination reactions, *e.g.* the replacement of a C–F by a C–H moiety.[2,7] Convenient hydrogen sources can be silanes, alanes, boranes or even dihydrogen itself.[2,5,8] Because of the strength of the E–F bonds (E = H, Si, Al, B) which are formed the conversions are thermodynamically favourable.[9] Metal fluoro or hydrido complexes often play a crucial role in hydrodefluorination reactions, either as catalysts or as intermediates.[2,5,8,10]

The transition metal mediated activation and hydrodefluorination of pentafluoropyridine has been investigated thoroughly. In a very recent example, Whittlesey *et al.* described the use of a ruthenium hydrido catalyst in the presence of alkylsilanes for the hydrodefluorination of hexafluorobenzene, and pentafluoropyridine.[11] Holland *et al.* reported the catalytic conversion of pentafluoropyridine into 2,3,5,6-tetrafluoropyridine in the presence of Et_3SiH on using an iron(II) fluoro complex as a catalyst.[12] Rosenthal and Krossing achieved a significantly better performance in the hydrodefluorination of pentafluoropyridine on using zirconocene hydrides and zirconocene fluorides in the presence of iBu_2AlH.[13] We developed a selective and catalytic hydrodefluorination of pentafluoropyridine to give 2,3,5,6-tetrafluoropyridine in the coordination sphere of rhodium using dihydrogen as hydrogen source and [Rh(4-C_5NF_4)(PEt_3)$_3$] as catalyst.[14] [Rh(H)(PEt_3)$_3$] serves presumably as an intermediate.

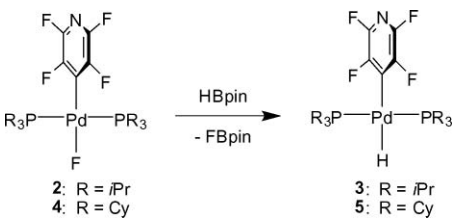
The hydrodefluorination of pentafluoropyridine at [Pd(P*i*Pr_3)$_2$] (**1**) is based on the selective oxidative addition of a C–F bond to give *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**2**), which can be isolated.[4] On reaction of the latter with Ph_3SiH 2,3,5,6-tetrafluoropyridine was generated. The existence of a Pd(II)-hydrido intermediate has been postulated, but such a compound was not detected.[5]

In this work we succeeded in the isolation and characterisation of *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**3**) and *trans*-[Pd(H)(4-C_5NF_4)(PCy_3)$_2$] (**5**). Both complexes are unusually stable.[15-18] Compound **3** gives at 60 °C the reductive elimination product 2,3,5,6-tetrafluoropyridine. Further studies on the reactivity of **3** and **5** are also reported.

Results

Synthesis of *trans*-[Pd(H)(4-C_5NF_4)(PR_3)$_2$] (3: R = *i*Pr; 5: R = Cy)

Complex *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**2**) reacted at room temperature with HBpin to give the hydrido compound *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr_3)$_2$] (**3**) and FBpin (Scheme 1).



Scheme 1 Synthesis of the hydrido complexes **3** and **5**.

Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489, Berlin, Germany. E-mail: thomas.braun@chemie.hu-berlin.de

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Table 1 Selected bond lengths (Å) and angles (°) in *trans*-[Pd(H)(4-C_5NF_4)(PCy_3)$_2$] (**5**) with estimated standard deviations in parentheses[a]

Pd(1)–P(1)	2.2956(6)	C(1)–C(5)	1.390(6)
Pd(1)–P(1#)	2.2955(6)	C(2)–F(1)	1.367(4)
Pd(1)–H(1)	1.48(5)	C(3)–F(2)	1.339(6)
Pd(1)–C(1)	2.102(4)	C(4)–F(3)	1.366(5)
C(1)–C(2)	1.373(6)	C(5)–F(4)	1.356(6)
C(2)–C(3)	1.374(6)	C(3)–N(1)	1.337(6)
C(4)–C(5)	1.372(6)	C(4)–N(1)	1.302(6)
P(1#)–Pd(1)–P(1)	165.09(3)	C(5)–C(1)–Pd(1)	125.6(3)
P(1)–Pd(1)–H(1)	83.29 (12)	C(2)–C(1)–C(5)	112.2(4)
C(2)–C(1)–Pd(1)	122.3(3)	C(1)–C(2)–C(3)	123.1(4)
C(1)–Pd(1)–H(1)	178.6(19)	C(4)–C(5)–C(1)	121.5(5)
N(1)–C(3)–C(2)	123.5(4)	N(1)–C(4)–C(5)	125.7(4)
C(1)–Pd(1)–P(1)	96.63(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x, y, z$.

The structure which is proposed for **3** is supported by the ^{1}H, ^{19}F, ^{31}P NMR data. In the ^{1}H NMR spectrum a signal at δ –9.30, which can be assigned to the hydride, appears as a multiplet. Fluorine decoupling experiments reveal a hydrogen–phosphorus coupling of $J_{PH} = 0.7$ Hz. The assignment of **3** as a 4-tetrafluoropyridyl palladium derivative is based on the presence of two signals at δ –110.5 and δ –115.3 in the ^{19}F NMR spectrum. The *trans* geometry is indicated by one signal in the ^{31}P{^{1}H} NMR spectrum at δ 57.4 (t, $J_{PF} = 1.5$ Hz). We were also able to synthesise *trans*-[Pd(H)(4-C_5NF_4)(PCy_3)$_2$] (**5**) on treatment of *trans*-[Pd(F)(4-C_5NF_4)(PCy_3)$_2$] (**4**) with HBpin. The NMR data of **5** are comparable to these of **3**. The molecular structure of **5** was confirmed by X-ray crystallography (Fig. 1). Complex **5** was crystallised from toluene at room temperature. Selected bond lengths and angles are summarised in Table 1.

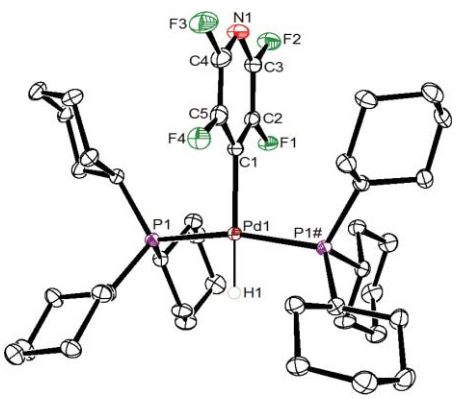
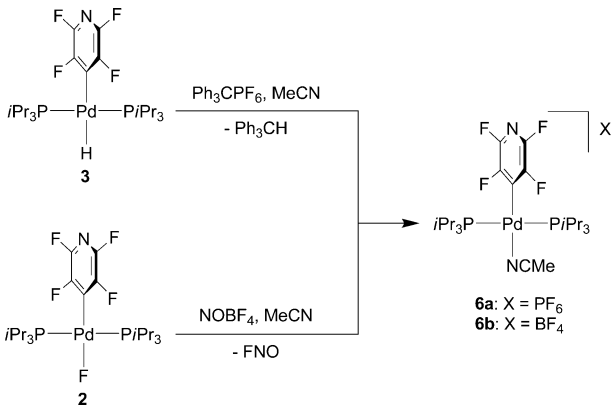


Fig. 1 An ORTEP diagram of **5**; ellipsoids are drawn at the 50% probability level; a toluene molecule and hydrogen atoms are omitted for clarity, except for H(1).

The structure shows the expected *trans* disposition of the phosphine ligands with an approximately square-planar coordination geometry at the metal centre. The palladium–carbon distance in **5** is 2.102(4) Å. For comparison, in **2** the Pd–C separation of 1.988(3) Å is shorter.[4] The hydride at the palladium centre has been located. The palladium–hydrogen distance is 1.48(5) Å. The Pd–H length in *trans*-[Pd(H)(OC_6F_5·C_6F_5OH)(PCy_3)$_2$] is 1.46(2) Å and in *trans*-[Pd(H)(OC_6H_5·C_6H_5OH)(PCy_3)$_2$] it is 1.57(2) Å.[15]

Synthesis of a cationic palladium complex

The reaction of *trans*-[Pd(H)(4-C_5NF_4)($PiPr_3$)$_2$] (**3**) with Ph_3CPF_6 in the presence of acetonitrile led to the formation of the cationic complex *trans*-[Pd(4-C_5NF_4)(NCMe)($PiPr_3$)$_2$]PF_6 (**6a**) by abstraction of the hydrido ligand and formation of Ph_3CH.[19] Compound **6a** was characterised by its NMR spectroscopic data. The ^{31}P NMR spectrum displays a signal at δ 43.7 (t, $J_{PF} = 3.7$ Hz) for the phosphines in a mutually *trans*-position and a septet at δ –143.2 ($J_{PF} = 706.2$ Hz) for the PF_6^- anion. The ^{19}F NMR spectrum reveals two signals at δ –97.1 and δ –114.4 for the tetrafluoropyridyl ligand and a doublet at δ –73.3 ($J_{PF} = 706$ Hz) which can be assigned to the anion. The cation in **6a** was also generated *via* an independent pathway starting from the fluoride *trans*-[Pd(F)(4-C_5NF_4)($PiPr_3$)$_2$] (**2**). Thus, a solution of **2** in acetonitrile reacts with $NOBF_4$ to give complex *trans*-[Pd(4-C_5NF_4)(NCMe)($PiPr_3$)$_2$]BF_4 (**6b**) (Scheme 2). The formation of FNO was monitored *via* IR spectroscopy in MeCN. An absorption band at 1871 cm^{-1} is compatible with the presence of FNO.[20]



Scheme 2 Synthesis of **6a** and **6b**.

The structure of **6b** was confirmed by X-ray diffraction analysis at 100 K (Fig. 2, Table 2). The cation reveals a square planar configuration at palladium with a *trans* disposition of the phosphine ligands. The palladium–carbon distance to the pyridyl ring is 2.005(3) Å and is similar to the Pd–C separation in **2**,

Table 2 Selected bond lengths (Å) and angles (°) in *trans*-[Pd(4-C_5NF_4)(NCMe)($PiPr_3$)$_2$]BF_4 (**6b**) with estimated standard deviations in parentheses

Pd(1)–P(1)	2.3715(8)	C(4)–C(5)	1.386(5)
Pd(1)–P(2)	2.3661(8)	C(1)–C(5)	1.377(4)
Pd(1)–N(2)	2.062(2)	C(2)–F(1)	1.347(4)
Pd(1)–C(1)	2.005(3)	C(3)–F(2)	1.345(4)
C(24)–N(2)	1.132(4)	C(4)–F(3)	1.348(4)
C(24)–C(25)	1.444(5)	C(5)–F(4)	1.351(4)
C(1)–C(2)	1.381(4)	C(3)–N(1)	1.314(5)
C(2)–C(3)	1.371(4)	C(4)–N(1)	1.309(5)
P(1)–Pd(1)–P(2)	173.68(3)	C(5)–C(1)–Pd(1)	127.7(2)
P(1)–Pd(1)–N(2)	89.86 (8)	C(5)–C(1)–C(2)	113.8(3)
P(2)–Pd(1)–N(2)	88.27(8)	C(3)–C(2)–C(1)	121.4(3)
C(1)–Pd(1)–N(2)	173.11(13)	N(1)–C(3)–C(2)	124.5(3)
C(1)–Pd(1)–P(1)	92.03(9)	C(1)–C(5)–C(4)	120.6(3)
C(1)–Pd(1)–P(2)	90.50(9)	N(1)–C(4)–C(5)	124.8(3)
C(2)–C(1)–Pd(1)	118.5(2)	C(4)–N(1)–C(3)	114.8(3)
C(24)–N(2)–Pd(1)	171.2(3)	N(2)–C(24)–C(25)	178.5(4)

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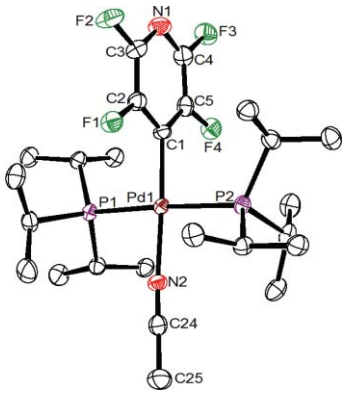


Fig. 2 An ORTEP diagram of the cation in **6b**; ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity.

1.988(3) Å.[4] The metal–nitrogen bond length to the acetonitrile ligand is 2.062(2) Å.

Synthesis of *trans*-[Pd(X)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (7: X = I; 8: X = Cl; 9: X = OTf; 10: X = O_2CCF_3)

To estimate the reactivity of the hydride *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**), it has been treated with several electrophiles. A reaction with MeI in C_6D_6 afforded after 26 days at room temperature the iodo complex *trans*-[Pd(I)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**7**). An NMR experiment revealed the evolution of methane. Complex **7** was also prepared *via* an alternative synthesis. NaI was added to a THF solution of *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) to yield **7** after stirring overnight. **7** was characterized by its ^{1}H, ^{19}F and ^{31}P NMR spectra. The ^{19}F NMR spectrum shows two multiplets at δ –97.9 and δ –113.6, which indicate the presence of the tetrafluoropyridyl ligand with the palladium at the 4-position. The ^{31}P NMR spectrum exhibits a triplet at δ 38.6 (J_{PF} = 3.5 Hz). Complex **7** was crystallised from a hexane solution by slow evaporation of the solvent at room temperature. The colourless crystals were suitable for X-ray diffraction analysis (Fig. 3). Selected bond lengths and angles are summarised in Table 3. Compound **7** exhibits a square-planar geometry with the pyridyl group coordinated in the *trans* position to the iodo ligand. The angles about the palladium atom are distorted from an ideal square-planar geometry and vary from 88.08(4) to 92.56(19)°. The palladium–carbon bond in **7** of 2.019(6) Å is similar to the corresponding distance in *trans*-[Pd(Cl)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**8**) (2.012(2) Å).[5]

Table 3 Selected bond lengths (Å) and angles (°) in *trans*-[Pd(I)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**7**) with estimated standard deviations in parentheses

Pd(1)–P(1)	2.3642(16)	C(1)–C(5)	1.364(9)
Pd(1)–P(2)	2.3670(16)	C(2)–F(1)	1.354(7)
Pd(1)–I(1)	2.6945(7)	C(3)–F(2)	1.354(7)
Pd(1)–C(1)	2.019(6)	C(4)–F(3)	1.360(8)
C(1)–C(2)	1.406(9)	C(5)–F(4)	1.366(7)
C(2)–C(3)	1.354(9)	C(3)–N(1)	1.297(9)
C(4)–C(5)	1.362(10)	C(4)–N(1)	1.302(9)
P(1)–Pd(1)–P(2)	176.20(6)	C(5)–C(1)–Pd(1)	124.5(5)
P(1)–Pd(1)–I(1)	88.08 (4)	C(5)–C(1)–C(2)	113.2(6)
P(2)–Pd(1)–I(1)	88.26(4)	C(3)–C(2)–C(1)	120.3(6)
C(1)–Pd(1)–I(1)	176.09(18)	N(1)–C(3)–C(2)	125.3(6)
C(1)–Pd(1)–P(1)	92.56(19)	C(4)–C(5)–C(1)	121.5(6)
C(1)–Pd(1)–P(2)	91.16(19)	N(1)–C(4)–C(5)	124.6(6)
C(2)–C(1)–Pd(1)	122.3(5)		

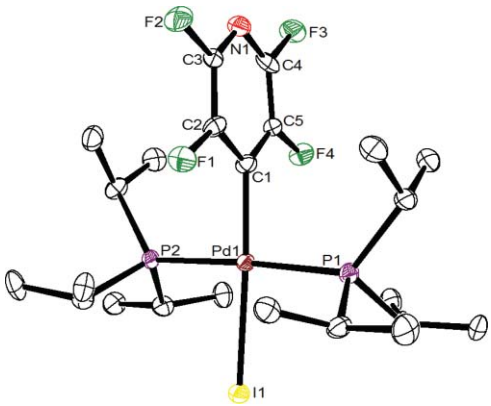
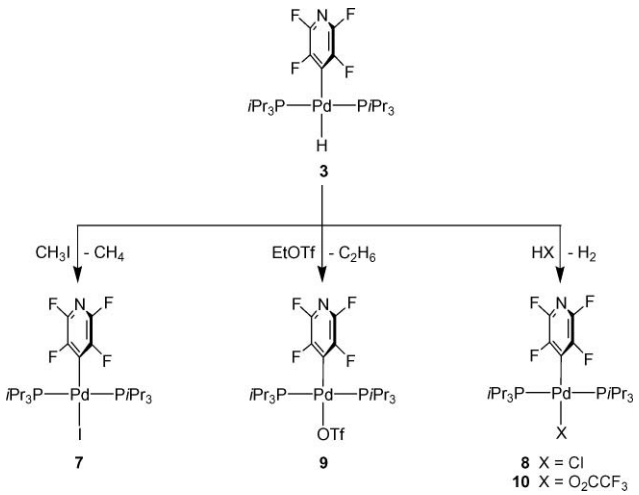


Fig. 3 An ORTEP diagram of **7**; ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity.

A solution of **3** was reacted with EtOTf to produce the triflate complex *trans*-[Pd(OTf)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**9**) and ethane. The ^{31}P NMR spectrum of **9** exhibits a triplet at δ 42.5 (J_{PF} = 4.6 Hz) which can be assigned to the phosphines. The presence of three signals in the ^{19}F NMR spectrum results from the tetrafluoropyridyl ligand (δ –96.4, δ –113.9) and the triflate ligand (δ –77.2).

Whereas **3** did not react with acetic acid, treatment of **3** with HCl or trifluoroacetic acid in C_6H_6 affords the known compound *trans*-[Pd(Cl)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**8**)[5] and complex *trans*-[Pd(O_2CCF_3)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**10**), respectively.



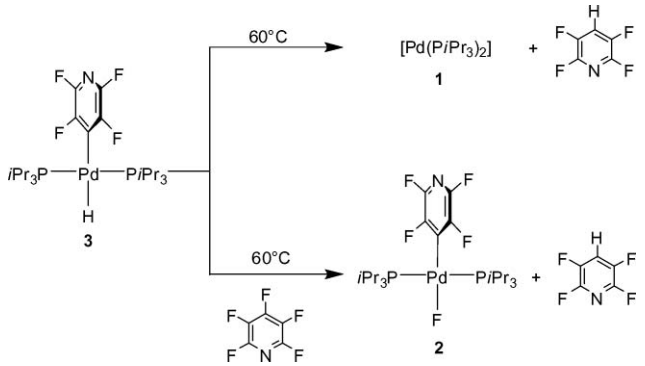
Scheme 3 Reactivity of **3** towards electrophilic compounds.

The structure of complex **10** is supported by the ^{1}H, ^{19}F, ^{31}P NMR data. The assignment as a 4-tetrafluoropyridyl palladium derivative is based on the presence of two signals in the ^{19}F NMR spectrum at δ –97.1 and δ –114.9 . The signal for the trifluoroacetato ligand appears at δ –74.4. The *trans* geometry is indicated by a triplet in the ^{31}P NMR spectrum at δ 38.3 (J_{PF} = 3.7 Hz).

Catalytic hydrodefluorination of pentafluoropyridine

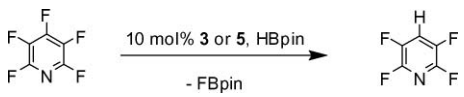
Heating a solution of *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) in THF at 60 °C led to the reductive elimination of 2,3,5,6-tetrafluoropyridine and the formation of [Pd(P*i*Pr$_3$)$_2$] (**1**).[21] In the presence of 10 equiv. P*i*Pr$_3$ the reductive elimination is inhibited.

This suggests that prior to the reductive elimination step a dissociation of a phosphine ligand occurs. Heating a solution of **3** with pentafluoropyridine affords the C–F activation product *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) and 2,3,5,6-tetrafluoropyridine (Scheme 4).[4]



Scheme 4 Formation of 2,3,5,6-tetrafluoropyridine from **3**.

Therefore, we turned our attention to catalytic experiments for the catalytic hydrodefluorination of pentafluoropyridine to give 2,3,5,6-tetrafluoropyridine with HBpin on using **3** or **5** as catalysts. At 60 °C in THF as a solvent 2,3,5,6-tetrafluoropyridine has been obtained in 44% and 30% yield, respectively, on employing 10 mol% catalyst (Scheme 5).



Scheme 5 Catalytic hydrodefluorination of pentafluoropyridine.

Discussion

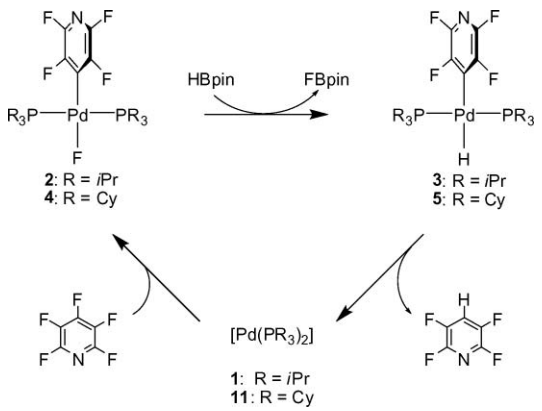
The synthesis of the palladium hydrido complexes *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) and *trans*-[Pd(H)(4-C_5NF_4)(PCy$_3$)$_2$] (**5**) are shown in Scheme 1. Both compounds are stable in solution at room temperature and can be prepared on treatment of the fluoro precursors *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) or *trans*-[Pd(F)(4-C_5NF_4)(PCy$_3$)$_2$] (**4**) with HBpin. A comparable reaction with the corresponding chloro compounds is not possible. It has been shown before that fluoro complexes often exhibit a higher reactivity than their chloro or bromo counterparts.[5,6,10] There are only a few mononuclear palladium hydrido complexes known that exhibit an additional palladium carbon bond. All of them are pincer complexes.[16,18] Note, that complexes that bear a tetrafluoropyridyl ligand often exhibit an unusual stability.[22] The formation of **3** could only be achieved on using HBpin as a "hydride source". Complex **3** does not react with NaH, LiEt$_3$BH or LiAlH$_4$. We have no evidence for a reaction of **3** with HBpin to produce H_2 and a boryl complex. Generation of H_2 and pinBBpin from two equivalents of HBpin by a dehydrodimerization pathway would also be conceivable in the presence of **3**, but such a transformation, which is endothermic, was not observed.[23]

Stoichiometric reactions of **3** are summarised in Schemes 2–4. The abstraction of the hydrido ligand on using Ph_3CPF_6 in MeCN gave the cationic complex *trans*-[Pd(4-C_5NF_4)(NCMe)(P*i*Pr$_3$)$_2$]PF$_6$ (**6a**). Comparable reactions to abstract a hydrido ligand at a palladium centre have been reported before.[19,24] The Reaction of **2** with $NOBF_4$ leads to the generation of *trans*-[Pd(4-C_5NF_4)(NCMe)(P*i*Pr$_3$)$_2$]BF$_4$ (**6b**) and FNO. This reactivity pattern is unprecedented. FNO can be applied as a fluorinating reagent.[25] $NOBF_4$ has been used for the synthesis of nitrosyl compounds.[26]

Treatment of **3** with electrophiles such as MeI or EtOTf yielded the compounds *trans*-[Pd(I)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**7**) or *trans*-[Pd(OTf)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**9**), respectively. An S_N2 type oxidative addition followed by a C–H reductive elimination may be more likely for MeI than a radical mechanism, which is although conceivable.[27] A comparable reaction for the generation of a triflate complex was reported by Ozerov *et al.*[18,28] We did not observe any C–C coupling reactions, as has been found on treatment of [Rh(4-C_5NF_4)(PEt$_3$)$_2$] with MeI.[29]

Complex *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) reacts with Brønsted acids HX (X = O_2CCF_3, Cl) to give *trans*-[Pd(O_2CCF_3)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**10**) and *trans*-[Pd(Cl)-(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**8**).[5] We did not observe any generation of 2,3,5,6-tetrafluoropyridine. Note that the fluoro complex *trans*-[Ni(F)(2-C_5NF_4)(PEt$_3$)$_2$] reacts with HCl to give 3,4,5,6-tetrafluoropyridine.[30]

However, heating of a solution of **3** at 60 °C gave the products of reductive elimination 2,3,5,6-tetrafluoropyridine and [Pd(P*i*Pr$_3$)$_2$] (**1**). Treatment of **1** with pentafluoropyridine affords the regeneration of the C–F activation product *trans*-[Pd(F)-(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**), which completes a cyclic process for a selective hydrodefluorination of pentafluoropyridine at the 4-position (Scheme 6). Our studies show that 2,3,5,6-tetrafluoropyridine can also be generated catalytically starting from pentafluoropyridine and HBpin with the hydrido complexes **3** (TON = 4) or **5** (TON = 3) as catalysts.[31] However, the yields are very low; possibly in part because of the formation of HF and F_2Bpin^- salts. The F_2Bpin^- anion could be identified by ^{19}F NMR spectroscopy.[32] We did not observe the formation of fluorinated phosphoranes.[4,33]



Scheme 6 Cyclic process for the hydrodefluorination of pentafluoropyridine.

Conclusions

In conclusion, we presented studies on the synthesis and reactivity of palladium hydrido complexes *trans*-Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) and *trans*-[Pd(H)(4-C_5NF_4)(PCy$_3$)$_2$] (**5**) Both compounds exhibit an unexpected stability. These hydrido complexes as well

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as the fluorides *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) and *trans*-[Pd(F)(4-C_5NF_4)(PCy$_3$)$_2$] (**4**) might serve as intermediates in the hydrodefluorination of pentafluoropyridine.

Experimental

The synthetic work was carried out on a Schlenk line. All solvents were purified and dried by conventional methods and distilled under argon before use. [D_6]Benzene and [D_8]THF were dried by stirring over Na/K and then distilled. Complexes *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) and *trans*-[Pd(F)(4-C_5NF_4)(PCy$_3$)$_2$] (**4**) were prepared according to the literature procedures.[4]

The NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer at 300 K. The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ = 7.15 or [D_8]THF at δ = 1.8. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ = –162.9. The ^{31}P{^{1}H} NMR spectra were referenced externally to H_3PO_4 at δ 0.0. Infrared spectra were recorded on a Bruker Vector 22 spectrometer that was equipped with an ATR unit (diamond).

Synthesis of *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (3)

A solution of *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**2**) (43 mg, 0.07 mmol) in C_6H_6 (4 mL) was treated with HBpin (13 μL, 0.087 mmol). The reaction mixture was stirred for 2 h at room temperature. The volatiles were then removed *in vacuo* to give a white solid. Yield 41 mg (98%). (Found: C, 47.86; H, 7.45; N, 1.94%. $C_{23}H_{43}F_4NP_2Pd$ requires C, 47.82; H, 7.51; N 2.43%); $\tilde{\nu}$ (ATR, diamond)/cm^{-1} 1911 (PdH); ^{1}H NMR (300.1 MHz, C_6D_6): δ 1.72 (m, br, 6 H, CH), 0.96 (dd, J_{HH} = 7.1, J_{PH} = 14.3 Hz, 36 H, CH_3), –9.06 (m, J_{PH} = 0.74 Hz, 1 H, PdH); ^{19}F NMR (282.4 MHz, C_6D_6): δ –100.5 (m, 2 F), –115.3 (m, 2 F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 57.4 (t, J_{PF} = 1.5 Hz).

Synthesis of *trans*-[Pd(H)(4-C_5NF_4)(PCy$_3$)$_2$] (5)

A solution of *trans*-[Pd(F)(4-C_5NF_4)(PCy$_3$)$_2$] (**4**) (38 mg, 0.045 mmol) in toluene (5 mL) was treated with HBpin (8 μL, 0.054 mmol). The reaction mixture was stirred for 2 h at room temperature. The volatiles were removed under vacuum to give a white solid. Yield 36 mg (98%). (Found: C, 63.37; H, 8.20; N, 1.33%. $C_{41}H_{66}F_4NP_2PdC_7H_8$ requires C, 63.34; H, 8.31; N 1.54%); $\tilde{\nu}$ (ATR, diamond)/cm^{-1} 1886 (PdH); ^{1}H NMR (300 MHz, C_6D_6): δ 1.01–1.93 (m, 66 H, Cy), –9.06 (s, br, 1 H, PdH); ^{19}F NMR (282.4 MHz, C_6D_6): δ –100.6 (m, 2 F), –115.5 (m, 2 F); ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 45.5 (s).

Synthesis of *trans*-[Pd(4-C_5NF_4)(NCMe)(P*i*Pr$_3$)$_2$]PF$_6$ (6a)

Ph_3CPF_6 (23 mg, 0.058 mmol) was added to a solution of *trans*-Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) (42 mg, 0.073 mmol) in CH_3CN (4 mL). The reaction mixture was stirred for 24 h at room temperature and the volatiles were removed under vacuum. The remaining yellow solid was washed with hexane to give a white powder. Yield 31 mg (85%). (Found: C, 39.85; H, 5.68; N, 3.40%. $C_{25}H_{45}F_{10}NP_3Pd$ requires C, 39.36; H, 5.95; N 3.67%); ^{1}H NMR (300.1 MHz, [D_8]THF): δ 2.38 (s, 3 H, NCMe), 1.94 (m, br, 6 H, CH), 0.98 (dd, J_{HH} = 7.3, J_{PH} = 14.9 Hz, 36 H, $CHCH_3$); ^{19}F NMR (282.4 MHz, [D_8]THF): δ –73.3 (d, J_{PF} = 706 Hz, 6 F, PF_6^-), –97.1 (m, 2 F, CF), –114.4 (m, 2 F, CF); ^{31}P{^{1}H} NMR (121.5 MHz, [D_8]THF): δ 43.7 (t, J_{PF} = 3.7 Hz, PdP), –143.4 (sep, J_{PF} = 706.2 Hz, PF_6^-).

Synthesis of *trans*-[Pd(4-C_5NF_4)(NCMe)(P*i*Pr$_3$)$_2$]BF$_4$ (6b)

$NOBF_4$ (12 mg, 0.103 mmol) was added to a solution of **2** (77 mg, 0.129 mmol) in MeCN (4 mL). The reaction mixture was stirred for 5 h at room temperature and the volatiles were removed under vacuum. The remaining yellow solid was washed with hexane to give a white powder. Yield 48 mg (66%). (Found: C, 42.19; H, 5.98; N, 3.77%. $C_{25}H_{45}BF_8NP_2Pd$ requires C, 42.60; H, 6.44; N 3.97%); ^{1}H NMR (300.1 MHz, [D_8]THF): δ 2.38 (s, 3 H, NCMe), 1.98 (m, br, 6 H, CH), 0.98 (dd, J_{HH} = 7.2, J_{PH} = 14.9 Hz, 36 H, $CHCH_3$); ^{19}F NMR (282.4 MHz, [D_8]THF): δ –92.2 (m, 2 F, CF), –114.4 (m, 2 F, CF), –152.7 (s, 4 F, BF_4); ^{31}P{^{1}H} NMR (121.5 MHz, [D_8]THF): δ 43.9 (t, J_{PF} = 3.7 Hz).

Synthesis of *trans*-[Pd(I)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (7)

(a) A solution of **2** (55 mg, 0.092 mmol) in THF (5 mL) was treated with NaI (80 mg, 0.534 mmol). After stirring for 24 h the volatiles were removed under vacuum. The yellow solid was washed with hexane (5 mL) and dried under vacuum to afford a yellow solid. Yield 56 mg (87%). (Found: C, 38.87; H, 6.00; N, 1.60%. $C_{23}H_{42}F_4INP_2Pd$ requires C, 39.26; H, 6.02; N 1.99%); ^{1}H NMR (300.1 MHz, C_6D_6): δ 2.39 (m, br, 6 H, CH), 1.02 (dd, J_{HH} = 7.1, J_{PH} = 14.3 Hz, 36 H, $CHCH_3$); ^{19}F NMR (282.4 MHz, C_6D_6): δ –97.9 (m, 2 F), –113.6 (m, 2 F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 38.6 (t, J_{PF} = 3.5 Hz).

(b) In an NMR tube CH_3I (0.04 ml, 0.66 mmol) was added to a solution of **3** (74 mg, 0.128 mmol) in C_6D_6 (0.6 mL). The reaction mixture was stirred for 26 days at room temperature. The yield of **7** was determined by measuring NMR spectra of the reaction solution on using an internal standard. Yield 77%. The formation of methane was observed by ^{1}H NMR spectroscopy.

Synthesis of *trans*-[Pd(OTf)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (9)

A solution of **3** (31 mg, 0.054 mmol) in C_6H_6 (4 mL) was treated with EtOTf (38 μL, 0.54 mmol). After stirring for 24 h the reaction mixture was filtered and the volatiles were removed under vacuum. A brown solid was obtained. Yield 32 mg (81%). (Found: C, 39.97; H, 6.09; N, 1.58%. $C_{24}H_{42}F_7NO_3P_2PdS$ requires C, 39.72; H, 5.84; N 1.93%); ^{1}H NMR (300.1 MHz, C_6D_6): δ 2.22 (m, br, 6 H, CH), 0.96 (dd, J_{HH} = 7.2, J_{PH} = 14.6 Hz, 36 H, $CHCH_3$; ^{19}F NMR (282.4 MHz, C_6D_6): δ –77.2 (s, 3 F, CF_3), –96.4 (m, 2 F, CF), –113.9 (m, 2 F, CF); ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 42.5 (t, J_{PF} = 4.6 Hz).

Formation of *trans*-[Pd(Cl)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (8)

A solution of **3** (44 mg, 0.076 mmol) in 3 mL THF was treated with HCl (0.02 ml, 0.152 mmol). After stirring for 24 h the reaction mixture was filtered, the volatiles were removed under vacuum. A white solid was obtained which consisted of **8** according to the NMR spectra.[4] Yield 38 mg (82%).

Synthesis of *trans*-[Pd(O_2CCF_3)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (10)

A solution of **3** (31 mg, 0.054 mmol) in C_6H_6 (4 mL) was treated with CF_3COOH (42 μL, 0.54 mmol). After stirring for 24 h the

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Table 4 Crystallographic data

Compound	**5**·C_7H_8	**6b**	**7**
Crystal dimensions/mm^3	0.36 × 0.10 × 0.08	0.40 × 0.26 × 0.11	0.24 × 0.16 × 0.16
Empirical formula	$C_{48}H_{75}F_4NP_2Pd$	$C_{25}H_{45}BF_8N_2P_2Pd$	$C_{23}H_{42}F_4INP_2Pd$
Formula weight	910.43	704.78	703.82
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pmn2_1$	$P2_1/n$	$P\bar{1}$
a/Å	13.9664(9)	10.3812(4)	10.1655(8)
b/Å	16.9951(9)	8.1047(2)	10.3275(9)
c/Å	9.6839(6)	37.4697(16)	14.6934(14)
α/°	—	—	103.329(7)
β/°	—	97.560(3)	100.118(7)
γ/°	—	—	108.091(7)
V/Å^3	2298.6(2)	3125.2(2)	1374.9(2)
Z	2	4	2
Density (calcd.)/Mg m^{-3}	1.315	1.498	1.700
μ(Mo-Kα)/mm^{-1}	0.522	0.762	1.953
θ range/°	2.40 to 29.02	3.29 to 29.50	3.17 to 25.50
Reflections collected	22 622	15 491	9749
Independent reflections	6337	8573	5100
R_{int}	0.0676	0.0458	0.0596
Goodness-of-fit on F^2	1.031	0.971	1.003
R_1, wR_2 on all data	0.0459, 0.0827	0.0683, 0.1186	0.0716, 0.1084
R_1, wR_2 [$I_o > 2\sigma(I_o)$]	0.0392, 0.0807	0.0482, 0.1116	0.0483, 0.1013
Reflect. with $I_o > 2\sigma(I_o)$]	5765	6522	3925
Max diff peak, hole e Å^{-3}	1.502 and –0.915	0.801 and –1.551	1.415 and –1.030

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reaction mixture was filtered, the volatiles were removed under vacuum. A white solid was obtained. Yield 29 mg (77%). (Found: C, 43.72; H, 6.12; N, 1.81%. $C_{25}H_{42}F_7NO_2P_2Pd$ requires C, 43.53; H, 6.14; N 2.03%); ^{1}H NMR (300.1 MHz, C_6D_6): δ 1.79 (m, br, 6 H, CH), 0.97 (dd, J_{HH} = 7.2, J_{PH} = 14.5 Hz, 36 H, CHCH_3), –9.06 (s, br, 1 H, PdH); ^{19}F NMR (282.4 MHz, C_6D_6): δ –74.4 (s, 3 F, CF_3), –97.1 (m, 2 F, CF), –114.9 (m, 2 F, CF); ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 38.3 (t, J_{PF} = 3.7 Hz).

Formation of 2,3,5,6-tetrafluoropyridine

A solution of **3** (13 mg, 0.023 mmol) in THF (0.5 mL) was heated for 5 h to 60 °C. The formation of [Pd(P*i*Pr$_3$)$_2$] (**1**)[21] and 2,3,5,6-tetrafluoropyridine was observed. The yield of 2,3,5,6-tetrafluoropyridine was determined by using a capillary which contained fluorobenzene as an external standard. Yield 84%.

Formation of *trans*-[Pd(F)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (2)

Pentafluoropyridine (0.01 ml, 0.097 mmol) was added to a solution of **3** (56 mg, 0.097 mmol) in THF (3 mL). The reaction mixture was heated for 4 h at 60 °C and was allowed to cool to room temperature. The black mixture was filtered and the volatiles were removed under vacuum from the filtrate to give a brown solid. Yield 49 mg (85%).

Catalytic formation of 2,3,5,6-tetrafluoropyridine

(a) In an NMR tube HBpin (97 µL, 0.64 mmol) was added to a mixture of *trans*-[Pd(H)(4-C_5NF_4)(P*i*Pr$_3$)$_2$] (**3**) (37 mg, 0.064 mmol) and pentafluoropyridine (70 µL, 0.64 mmol) in [D_8]THF (0.4 mL). The reaction mixture was heated for 3 days at 60 °C. The yield of 2,3,5,6-tetrafluoropyridine was determined on using an external standard of fluorobenzene and is 44% (TON = 4).

(b) In an NMR tube HBpin (44 µL, 0.29 mmol) was added to a mixture of *trans*-[Pd(H)(4-C_5NF_4)(PCy$_3$)$_2$] (**5**) (24 mg, 0.029 mmol) and pentafluoropyridine (32 µL, 0.29 mmol) in THF (0.4 mL). The reaction mixture was heated for 3 days at 60 °C. The yield of 2,3,5,6-tetrafluoropyridine was determined by NMR spectroscopy on using an external standard of fluorobenzene and is 30% (TON = 3).

Structure determinations for the complexes 5, 7 and 8

White crystals of **5**·C_7H_8 and **7** and yellow crystals of **6b** were obtained by slow evaporation of the solvent (**5**, toluene; **6b**, MeCN, **7**, hexane) at 293 K. The diffraction data were collected on a STOE IPDS 2T diffractometer at 100 K. Crystallographic data are depicted in Table 4. The structures were solved by direct methods and refined with the full matrix least squares method on F^2 (SHELX-97).[34] For complex **5** the metal bound hydrogen was located in the difference fourier map and refined isotropically. All other hydrogen atoms were placed at calculated positions and refined using a riding model.

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