Contrasting Reactivity of Fluoropyridines at Palladium and Platinum: C−F Oxidative Addition at Palladium, P−C and C−F Activation at Platinum†

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The divergent behavior of palladium(0) and platinum(0) is revealed in the reactivity of $[M(PR_3)_2]$ (M = Pd or Pt; R = Cy or ^{i}Pr) toward pentafluoropyridine and 2,3,5,6-tetrafluoropyridine. The palladium complexes react with pentafluoropyridine at 100 °C to yield the fluoride complexes *trans*-$[Pd(F)(4\text{-}C_5NF_4)(PR_3)_2]$. They do not react with 2,3,5,6-tetrafluoropyridine. The reaction of platinum(0) complexes $[Pt(PR_3)_2]$ with pentafluoropyridine in THF at ambient temperature yields *trans*-$[Pt(R)(4\text{-}C_5NF_4)(PR_3)(PFR_2)]$ complexes, whereas the reaction of $[Pt(PCy_3)_2]$ with 2,3,5,6-tetrafluoropyridine results in C−H activation to form *cis*-$[Pt(H)(4\text{-}C_5NF_4)(PCy_3)_2]$; this complex may be converted to the *trans* isomer by photolysis. The *cis*-hydride also forms during the reaction of $[Pt(PCy_3)_2]$ with C_5NF_5 in hexane. These reactions also contrast with earlier studies of the reactivity of the same substrates toward $\{Ni(PEt_3)_2\}$, which yield $[Ni(F)(2\text{-}C_5NF_5)(PEt_3)_2]$ with pentafluoropyridine and $[Ni(F)(2\text{-}C_5NF_4H)(PEt_3)_2]$ with tetrafluoropyridine. Thus palladium has different regioselectivity from nickel and is the least reactive. Platinum is capable of both C−F and C−H activation and is alone in the triad in undergoing rearrangement to the alkyl complex with the fluorophosphine ligand. Mechanisms for the rearrangement are proposed. The platinum dihydride complex *trans*-$[Pt(H)_2(PR_3)_2]$ reacts with pentafluoropyridine at room temperature, yielding a 1:1:1 mixture of *trans*-$[PtH(FHF)(PR_3)_2]$, *trans*-$[Pt(H)(4\text{-}C_5NF_4)(PR_3)_2]$, and *trans*-$[Pt(R)(4\text{-}C_5NF_4)(PR_3)(PFR_2)]$. Crystal structures are reported for *trans*-$[Pd(F)(4\text{-}C_5NF_4)(PCy_3)_2]\cdot H_2O\cdot C_6H_6$, *trans*-$[Pd(F)(4\text{-}C_5NF_4)(P^iPr_3)_2]$, *trans*-$[Pt(C_6H_{11})(4\text{-}C_5NF_4)(PCy_3)(PFCy_2)]\cdot CH_2Cl_2$, and *cis*-$[Pt(H)(4\text{-}C_5NF_4)(PCy_3)_2]$.

Introduction

In the past decade, the selective activation of aromatic C−F bonds has developed from a curiosity to a well-recognized process.[1] Recently, the focus has been on stoichiometric[2−7] and catalytic[2,8−10] derivatization reactions of fluoroaromatics via C−F activation at a transition metal center. We achieved the functionalization of heteroaromatic molecules within the coordination sphere of nickel[2−5,7,8] and showed that these routes yield fluorinated heterocycles that are otherwise not accessible. A key feature is the unusual regio- and chemoselectivity of the attack by nickel at the heterocycle.[2,3,7,8] Thus, $[Ni(COD)_2]$ (COD = 1,5-cyclo-octadiene) reacts

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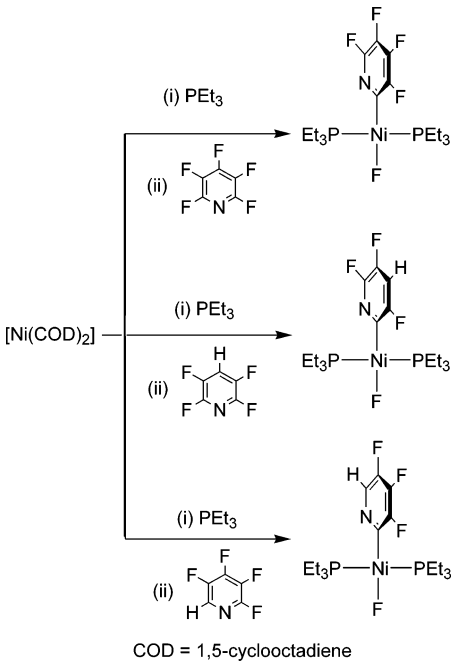
Table 1. NMR Data for Palladium Complexes 1a and 1b at 300 K in C_6D_6; δ (*J*/Hz)

complex	^{1}H	^{31}P{^{1}H}	^{19}F	^{13}C{^{1}H}
1a	0.74−2.10 (m)	30.3 (d, J_{PF} = 14.1)	−322 (s, br, 1 F) PdF −115.7 (m, 2 F) −99.4 (m, 2 F)	
1b	1.08 (dd, J_{HH} = 7, J_{PH} = 14, 18 H), 1.97 (m, 6 H)	39.1 (d, J_{PF} = 16.0)	−323 (s, br, 1 F) PdF −115.0 (m, 2 F) −97.7 (m, 2 F)	19.7 (m, CH_3), 23.7 (vtt, apparent J_{CP} = 24.8, J_{CF} = 9.7, CH), 143.1 (ddd, J_{CF} = 256.8, 24.8, 12.4, CF), 144.3 (m, *ipso*-C), 144.7 (dm, J_{CF} = 230.7, CF).

Scheme 1. Reactivity of [Ni(COD)$_2$] toward Pentafluoropyridine and 2,3,5,6-Tetrafluoropyridine in the Presence of Triethylphosphine



with pentafluoropyridine in the presence of triethylphosphine to form *trans*-[Ni(F)(2-C_5NF_4)(PEt_3)$_2$]. This selective insertion of the {Ni(PEt_3)$_2$} moiety into a C−F bond at the 2-position forms the basis of the metal-mediated synthesis of new pyridines.[2,3,8] Another important feature of the reactions at nickel is the selectivity for C−F over C−H bonds within the fluoropyridine substrates. For instance, 2,3,5,6-tetrafluoropyridine and 2,3,4,5-tetrafluoropyridine both undergo C−F activation exclusively (Scheme 1).[2,3c] Carbon−fluorine bond activation also acts as a source of transition metal fluoride complexes that can otherwise be demanding to synthesize[2,11] and are applied increasingly in catalysis and as starting materials for synthesis.[1,8,12]

Previous work on C−F activation at phosphine complexes of platinum is limited. Hofmann et al.[11] have shown that the {Pt(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)} moiety can activate the C−F bond of C_6F_6 to form [Pt(F)(C_6F_5)(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)]. Hintermann et al. showed that *trans*-[Pt(H)$_2$(PCy_3)$_2$] reacts with 4-RC_6F_4CN (R = H, F, CN, and OCH_3) to give the C−F activated product *trans*-[Pt(H){C_6F_3R(CN)}(PCy_3)$_2$].[13] An electron transfer reaction involving the formation of a caged radical pair was postulated. Reaction of *trans*-[Pt(H)$_2$(PCy_3)$_2$] with pentafluorobenzene yields *trans*-[Pt(H)(C_6F_5)(PCy_3)$_2$],[14] while reaction with hexafluorobenzene in the presence of [NMe_4]F yields a mixture of the latter and *trans*-[Pt(H)(FHF)(PCy_3)$_2$].[15] There is no direct information about formation of palladium phosphine fluorides by C−F activation,[16] but there are some examples of catalytic cross-coupling reactions of fluoroaromatics with palladium catalysts.[9] For instance, [Pd(PPh_3)$_4$] catalyzes the coupling of arylboronic acids to 2-fluoronitrobenzene to form the corresponding biphenyl; the authors postulated formation of a palladium aryl fluoride via a S_NAr mechanism.[9f]

In this paper, we report the C−F activation of fluorinated pyridines at Pd(0) and Pt(0). We show that the selectivity of the reactions is distinct from the corresponding reactions at nickel with respect to both the position of activation and the comparative reactivity of C−H and C−F bonds within the same molecule. The reactions at palladium lead to direct C−F oxidative addition and allow us to determine the molecular structure of two palladium fluoride complexes. However, the reactions at platinum afford unexpected complexes bearing a fluorophosphine ligand and a platinum alkyl bond.

Results

1. C−F Activation of Pentafluoropyridine at Palladium. Treatment of the palladium(0) complex [Pd(PCy_3)$_2$] with excess pentafluoropyridine in toluene at 100 °C yields a single product **1a**, which was characterized by its ^{19}F and ^{31}P NMR spectra (Table 1). The ^{19}F NMR spectrum shows two multiplets at δ −99.4 and −115.7, which indicate the presence of the tetrafluoropyridyl ligand with the palladium in the 4-position. A broad signal at δ −322 is characteristic of a fluoride ligand coordinated at the metal center.[17−21] The ^{31}P NMR spectrum exhibits a doublet at δ 30.3 with a coupling constant J_{PF} of 14.1 Hz to the metal-bound fluorine. Product **1a** is therefore readily assigned as the product of C−F oxidative addition at the 4-position of

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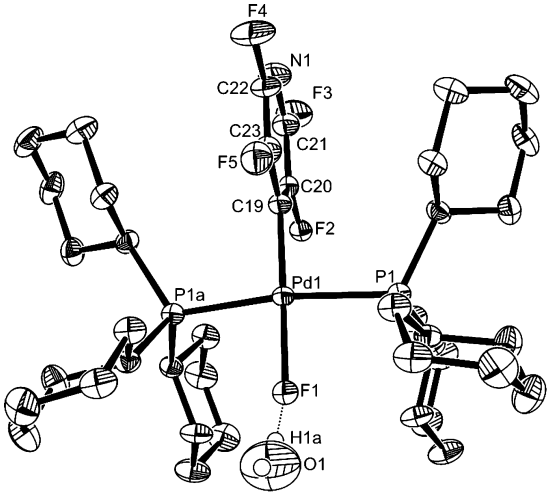
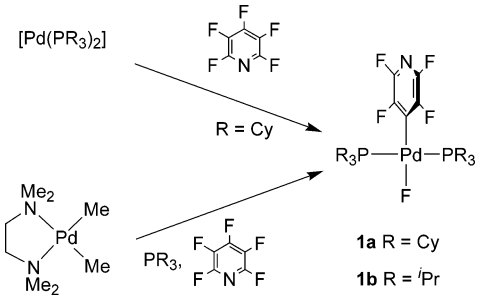


Figure 1. ORTEP diagram of **1a**·H_2O·C_6H_6 (**1a′**) (ellipsoids at 50% probability level, hydrogens and solvent omitted).

Scheme 2. C-F Oxidative Addition of Pentafluoropyridine at Palladium



pentafluoropyridine, *trans*-[Pd(F)(4-C_5NF_4)(PCy_3)$_2$] (Scheme 2). This product may also be formed by refluxing in THF. The regioselectivity of reaction may be contrasted with the corresponding reaction of {Ni(PEt_3)$_2$} (Scheme 1). We note that [Pd(PCy_3)$_2$] does not react with excess 2,3,5,6-tetrafluoropyridine in toluene at 100 °C.

The C−F activation product **1a** can be obtained in better yield starting from [$PdMe_2$(tmeda)] (tmeda = tetramethylethylenediamine), pentafluoropyridine, and PCy_3 (Scheme 2). The complex [$PdMe_2$(tmeda)] also proved to be a useful starting material for the synthesis of the P^iPr_3 analogue, *trans*-[Pd(F)(4-C_5NF_4)(P^iPr_3)$_2$] (**1b**). The ^{19}F and ^{31}P NMR data for **1b** resemble those found for **1a**.

2. Molecular Structures of *trans*-[Pd(F)(4-C_5NF_4)(PCy_3)$_2$]·H_2O·C_6H_6 (1a′) and *trans*-[Pd(F)(4-C_5NF_4)(P^iPr_3)$_2$] (1b). The colorless complex **1a′** was crystallized from a solution of **1a** in wet benzene at 20 °C, while colorless crystals of **1b** were obtained from a hexane solution at −80 °C. The structures were determined by X-ray diffraction at low temperature (Figures 1, 2). Selected bond lengths and angles are summarized in Tables 2 and 3. The molecular structures show the expected *trans* disposition of the phosphine ligands with approximately square-planar coordination at palladium. The torsion angle between the plane defined by the tetrafluoropyridyl ring in **1b** and the coordination plane of palladium is 96.5°. The palladium−fluorine distances in **1a′** and **1b** are 2.041(3) and 2.0158(16) Å, respectively. The latter represents the shortest Pd−F separation found in palladium fluoride complexes according to CSD.[17,19−22] A recent example of particular relevance is [Pd(F)$_2$(dippp)] (dippp = bis(diisopropylphosphino)-propane) with Pd−F bond lengths of 2.065(3) Å.[23]

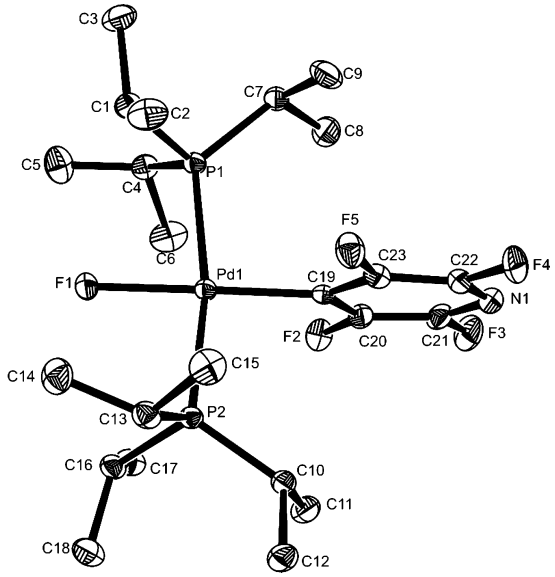


Figure 2. ORTEP diagram of **1b** (ellipsoids at 50% probability level, hydrogens omitted).

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1a·H_2O·C_6H_6 (1a′) with the Estimated Standard Deviations in Parentheses

bond	length	bond	length
Pd−C(19)	1.986(4)	C(20)−C(21)	1.379(7)
Pd−F(1)	2.041(3)	C(22)−C(23)	1.393(8)
Pd−P(1)	2.3369(7)	F(2)−C(20)	1.422(5)
N(1)−C(21)	1.295(7)	F(3)−C(21)	1.342(7)
N(1)−C(22)	1.291(8)	F(4)−C(22)	1.349(6)
C(19)−C(20)	1.376(7)	F(5)−C(23)	1.357(6)
C(19)−C(23)	1.378(8)	F(1)···O(1)	2.601(6)
bonds	**angle**	**bonds**	**angle**
C(19)−Pd−P(1)	93.04(3)	C(20)−C(19)−C(23)	112.4(5)
F(1)−Pd−P(1)	87.21(3)	C(19)−C(20)−C(21)	122.0(5)
C(19)−Pd−F(1)	176.38(16)	N(1)−C(21)−C(20)	124.7(5)
P(1)−Pd−P(1a)	170.30(3)	C(22)−N(1)−C(21)	115.0(5)
C(20)−C(19)−Pd	125.6(3)	N(1)−C(22)−C(23)	124.7(5)
C(23)−C(19)−Pd	122.0(4)	C(19)−C(23)−C(22)	121.3(6)

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 1b with the Estimated Standard Deviations in Parentheses

bond	length	bond	length
Pd−C(19)	1.988(3)	C(19)−C(23)	1.385(4)
Pd−F(1)	2.0158(16)	C(20)−C(21)	1.376(4)
Pd−P(1)	2.3479(6)	C(22)−C(23)	1.378(4)
Pd−P(2)	2.3310(6)	F(2)−C(20)	1.360(3)
N(1)−C(21)	1.314(4)	F(3)−C(21)	1.350(3)
N(1)−C(22)	1.322(4)	F(4)−C(22)	1.346(3)
C(19)−C(20)	1.392(4)	F(5)−C(23)	1.354(3)
bonds	**angle**	**bonds**	**angle**
C(19)−Pd−P(1)	97.08(7)	C(20)−C(19)−C(23)	112.8(2)
F(1)−Pd−P(1)	82.52(5)	C(19)−C(20)−C(21)	121.8(3)
C(19)−Pd−F(1)	177.02(9)	N(1)−C(21)−C(20)	124.3(3)
P(1)−Pd−P(2)	168.94(2)	C(22)−N(1)−C(21)	114.9(2)
C(20)−C(19)−Pd	120.7(2)	N(1)−C(22)−C(23)	124.5(3)
C(23)−C(19)−Pd	126.6(2)	C(19)−C(23)−C(22)	121.6(3)

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Table 4. NMR Data for Platinum Complexes 2 and 3 at 300 K, δ, *J*/Hz

complex	^{1}H	^{31}P{H}	^{19}F	^{195}Pt
2a CD_2Cl_2	1.2−2.0 (m)	18.5 (dd, J_{PtP} = 2716, J_{PP} = 428, J_{PF} = 37) PCy_3 181.0 (dd, J_{PtP} = 3710, J_{PF} = 910, J_{PP} = 428) PCy_2F	−176.2 (ddt, J_{PF} = 910, J_{PtF} = 372, J_{PP} = 36, J_{PF} = 17) PF −117.8 (m, J_{PtF} = 181) F_{ortho} −93.3 (m) F_{meta}	−4405
2b CD_2Cl_2	0.95 (m) $P(CH\mathit{Me}_2)_3$ 0.98 (m) $PF(CH\mathit{Me}_2)_2$ 1.75 (d J = 7.6, J_{PtH} = 43) $PtCH\mathit{Me}_2$ 1.80 (m) $PF(C\mathit{H}Me_2)_2$ 2.0 (m) $P(C\mathit{H}Me_2)_3$ 2.25 (m) $PtC\mathit{H}Me_2$	29.8 (dd, J_{PtP} = 2745, J_{PP} = 430, J_{PF} = 36) P^iPr_3 188 (dd J_{PtP} = 3808, J_{PF} = 914, J_{PP} = 430) P^iPr_2F	−179 (ddt, J_{PF} = 914, J_{PtF} = 365, J_{PF} = 37, J_{FF} = 17) PF −116.8 (m, J_{PtF} = 180) F_{ortho} −98.7 (m) F_{meta}	−4550
3-*trans* C_6D_6	−8.35 (tm, J_{HF} = 11, J_{PtH} = 703)	36.7 (s, J_{PtP} = 2732)	−118.3 (dm, J_{PtF} = 259, J_{HF} = 11) F_{ortho} −100.4 (m) F_{meta}	
3-*cis* C_6D_6	−7.05 (ddt $J_{HPtrans}$ = 167.5, J_{HPcis} = 26.0, J_{HF} = 4.4, J_{PtH} = 885)	26.4 (dd, J_{PtP} = 2073, J_{PP} = 13, J_{PF} = 10) $P_{trans\ to\ H}$ 30.6 (m, J_{PtP} = 2574) $P_{trans\ to\ C}$	−120.5 (m, J_{PtF} = 366) F_{ortho} −100.3 (td, J_{PF} = 26, J_{FF} = 6, J_{PtF} = 48) F_{meta}	

Notably, *trans*-[Pt(F)(Ph)(PPh_3)$_2$], the nearest crystallographically characterized platinum fluoride analogue of **1b**, exhibits a substantially longer metal−fluorine bond (2.117(3) Å).[24] The short distances in **1a′** and **1b** may indicate a less pronounced Pd−F d_π−p_π filled/filled repulsion,[25−27] perhaps due to delocalization of electron density from filled metal d-orbitals into a π*-orbital of the aromatic system. The Pd−C(19) bond length of 1.986(4) Å in **1a′** and 1.988(3) Å in **1b** are comparable to other Pd−C distances with a fluoro ligand in the position *trans* to an aryl ligand.[17,18,20] The Pd−C separation in *trans*-[PdBr(4-C_5NH_4)(PEt_3)$_2$] of 2.030(17) Å is in a similar range.[28]

The structure of compound **1a′** reveals short intermolecular F···O contacts from a water of crystallization to the fluoride ligand [F(1)···O(1): 2.602 Å]. The hydrogen atoms at the oxygen were located in the difference Fourier map, but were not refined. They were fixed with an O−H bond length of 0.84 Å and a displacement parameter of 1.2 times that of O(1). This results in an estimate of the H(1a)···F(1) distance of 1.76 Å, a value well below the sum of the van der Waals radii of 2.67 Å.[20] For comparison, we identified intramolecular F···C contacts of 2.87 Å in [(η^5-C_5H_5)Ir(C_2H_4)(η^2-C_6F_6)].[29] The general principles of hydrogen bonding to halide ligands are summarized in Brammer's review.[30]

3. Reactions of Pt(0) Complexes with Pentafluoropyridine. Reaction of [Pt(P^iPr_3)$_2$] with pentafluoropyridine in THF at room temperature produced a white precipitate that was recrystallized from THF−hexane to yield complex **2b**. An analogous complex (**2a**) was prepared from [Pt(PCy_3)$_2$]. Complexes **2a** and **2b** were identified initially by NMR spectroscopy (Table 4); their characterization is best illustrated by the ^{i}Pr complex because of its higher solubility and its distinct isopropyl resonances.

The ^{31}P NMR spectrum of **2b** shows two resonances, a doublet of doublets at δ 29.8 (J_{PtP} = 2745, J_{PP} = 430, and J_{PF} = 36 Hz) and a second resonance at δ 188 (dd, J_{PtP} = 3808, J_{PP} = 430, and J_{PF} = 914 Hz). The coupling of 914 Hz is close to that found in the literature for a fluorine directly bonded to phosphorus.[31] The large value of J_{PP} demonstrates the presence of inequivalent mutually *trans* phosphorus nuclei. Thus the complex contains one P^iPr_3 group and one PF^iPr_2 group.

The ^{19}F NMR spectrum of **2b** shows three resonances. A second-order multiplet with platinum satellites at δ −116.8 (J_{PtF} = 180 Hz) is assigned to the fluorine *ortho* to the platinum nucleus of a tetrafluoropyridyl ligand, and a multiplet at δ −98.7, which was not coupled to platinum, is assigned to the fluorine *meta* to the platinum center. These two resonances are consistent with a tetrafluoropyridyl group bound to the metal at the 4-position, as in **1a** and **1b**. The third resonance is a doublet of doublets of triplets with platinum satellites at δ −179.3 (J_{PtF} = 365, J_{PF} = 914, $J_{PF(far)}$ = 36, and J_{FF} = 17 Hz) corresponding to the fluorine of the PF^iPr_2 group. No resonance was observed in the ^{19}F NMR spectra for fluorine directly bonded to platinum.

The ^{1}H NMR spectrum of **2b** shows a multiplet at δ 0.95, a doublet with conspicuous platinum satellites at δ 1.75, a broad multiplet at δ 2.0, and a multiplet at δ 2.25. The resonance at δ 2.25 collapses to a doublet with platinum satellites when the resonance at δ 1.75 is selectively decoupled. Phosphorus correlation experiments show no coupling with these two proton resonances when the delay is appropriate to a two-bond P−H coupling. These spectra provide direct evidence for a platinum-bound isopropyl group with resonances at δ 2.25 Pt($C\mathit{H}Me_2$) and 1.75 Pt($CH\mathit{Me}_2$) for the isopropyl directly attached to platinum. The resonance at δ 2.0 is coupled to the resonance at δ 0.95, with both resonances showing a correlation with a ^{31}P resonance at δ 29.8 consistent with isopropyl groups bound to

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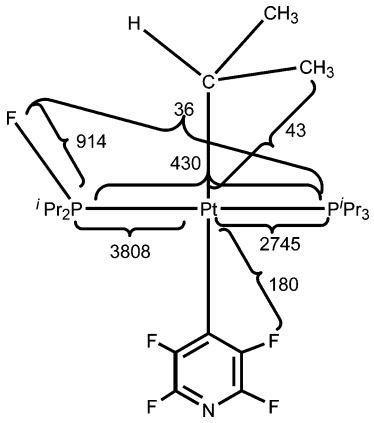
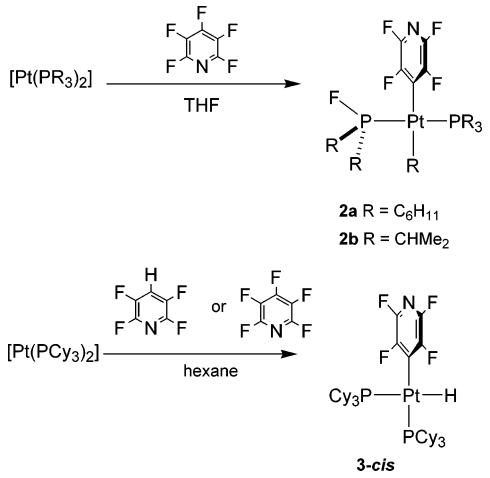


Figure 3. Chemical shifts and coupling constants (Hz) of *trans*-[Pt(4-C_5NF_4)($CHMe_2$)(P^iPr_3)(PF^iPr_2)], **2b**.

Scheme 3. Reactions of Pentafluoropyridine and 2,3,5,6-Tetrafluoropyridine at Pt(0)



phosphorus. Further evidence for a metal alkyl group comes from the $^{13}C\{^1H\}$ spectrum which exhibits a resonance at δ 19.2 (s) with prominent platinum satellites (J_{PtC} = 18 Hz).

The $\{^1H-^{195}Pt\}$ HMQC correlation (Supporting Information) reveals a ^{195}Pt resonance at δ −4550 with passive couplings to two ^{31}P nuclei as well as two *ortho* ^{19}F nuclei. This resonance is strongly correlated to the proton resonances of the isopropyl group bound directly to platinum, and there is also correlation to other isopropyl protons. The multinuclear NMR spectra, therefore, establish the identity of **2b** as *trans*-[Pt(4-C_5NF_4)($CHMe_2$)(P^iPr_3)(PF^iPr_2)] (Figure 3, Scheme 3).

The ^{19}F and ^{31}P NMR spectra of the product of reaction of [Pt(PCy_3)$_2$] with pentafluoropyridine are very similar to those of **2b** and consistent with an assignment as *trans*-[Pt(C_6H_{11})(4-C_5NF_4)(PCy_3)($PFCy_2$)], **2a**. NMR data for this complex are listed in Table 4. We also investigated the same reaction at 235 K in THF-d_8 in order to detect possible intermediates, but the only product observed was **2a**. The reaction of [Pt(PCy_3)$_2$] with pentafluoropyridine in hexane, however, takes a different course as described below.

4. Reaction of [Pt(PCy_3)$_2$] with 2,3,5,6-Tetrafluoropyridine. A solution of [Pt(PCy_3)$_2$] in hexane was reacted overnight with 2,3,5,6-tetrafluoropyridine (2 equiv) at room temperature, yielding colorless crystals of ***3-cis***. The ^1H NMR spectrum of ***3-cis*** shows a hydride resonance with a doublet of doublets of triplets splitting at δ −7.05 (J_{PtH} = 885, $J_{PHtrans}$ = 167.5, J_{PHcis} = 26.0, and J_{HF} = 4.4 Hz, Table 4). This resonance collapses to a triplet with ^{31}P decoupling, leaving the ^{19}F coupling unaffected. The ^{31}P NMR spectrum shows two resonances, a doublet of doublets at δ 26.4 (J_{PtP} = 2073, J_{PP} = 13, J_{PF} =10 Hz) and a multiplet at δ 30.6 (J_{PtP} = 2574 Hz). The $^1H-^{31}P$ correlation shows that the ^{31}P resonances are coupled to the hydride resonance. The ^{19}F NMR spectrum shows two resonances each with platinum satellites at δ −100.3 (td, J_{PtF} = 48, J_{PF} = 26, J_{FF} = 6 Hz, F *meta* to Pt) and at δ −120.5 (m, J_{PtF} = 366 Hz, F *ortho* to Pt). This complex exhibits a characteristic ν(Pt−H) vibration at 2054 cm^{-1} in the IR spectrum. The spectroscopic data indicate that the C−H bond of tetrafluoropyridine has been activated so that ***3-cis*** may be identified as *cis*-[Pt(H)(4-C_5F_4N)(PCy_3)$_2$] (Scheme 3).

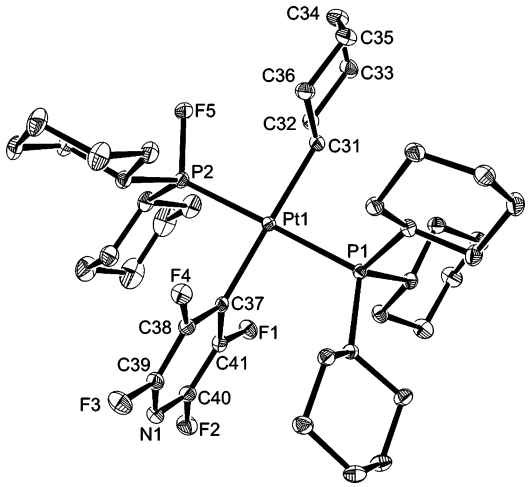


Figure 4. ORTEP diagram of **2a**·CH_2Cl_2 (ellipsoids at 50% probability level, hydrogens and solvent omitted).

The same hydride complex, ***3-cis***, was obtained from the reaction of [Pt(PCy_3)$_2$] with pentafluoropyridine using hexane as the solvent. It can be isolated from this reaction but in lower yield than from the reaction of [Pt(PCy_3)$_2$] with tetrafluoropyridine. This reaction proceeds more slowly than the conversion to **2b** in THF. To find the source of the hydride in the complex, the reaction was repeated in dry [$^2H_{12}$]-cyclohexane and in C_6F_6 as solvents, but the hydride complex still formed. We deduce that one of the C−H bonds of a PCy_3 ligand acts as the source of the hydride ligand, but the byproducts have not been identified.

Photolysis of a solution of ***3-cis*** in C_6D_6 (broad band λ > 290 nm, 2 h) caused complete conversion of ***3-cis*** to the corresponding *trans* isomer ***3-trans*** (see below for characterization). The isomerization also takes place thermally at 80 °C. Attempts to replace the hydride ligand by halides via reaction with Et_3N·3HF, HCl, or HBr resulted instead in displacement of the tetrafluoropyridyl group, yielding *trans*-Pt(H)(X)(PCy_3)$_2$ (X = F, Cl, Br)[15] whether starting with ***3-cis*** or ***3-trans***.

5. Molecular Structures of *trans*-[Pt(C_6H_{11})(4-C_5NF_4)(PCy_3)($PFCy_2$)]·CH_2Cl_2 (2a·CH_2Cl_2) and *cis*-[Pt(H)(4-C_5NF_4)(PCy_3)$_2$] (*3-cis*). Complex **2a**·CH_2Cl_2 was crystallized by slow evaporation from a dichloromethane solution to form colorless crystals and characterized by X-ray crystallography (Figure 4, Table 5). The bond angles at platinum are close to the ideal of

Table 5. Selected Bond Lengths (Å) and Angles (deg) of *trans*-Pt(Cy)(C_5NF_4)(PCy_3)($PFCy_2$), 2a·CH_2Cl_2, with the Estimated Standard Deviations in Parentheses

bond	length	bond	length
Pt−P(1)	2.3527(8)	C(37)−(38)	1.392(4)
Pt−P(2)	2.2567(8)	C(38)−(39)	1.379(4)
Pt−C(31)	2.139(3)	C(37)−(41)	1.393(5)
Pt−C(37)	2.100(3)	C(40)−C(41)	1.373(4)
P(2)−F(5)	1.597(2)	C(31)−C(32)	1.536(4)
N−C(39)	1.310(5)	C(31)−C(36)	1.541(5)
N−C(40)	1.317(5)	C(32)−C(33)	1.538(4)
F(1)−C(41)	1.361(3)	C(33)−C(34)	1.519(5)
F(3)−C(39)	1.348(4)	C(34)−C(35)	1.529(5)
F(4)−C(38)	1.358(4)	C(35)−C(36)	1.533(5)
F(2)−C(40)	1.344(4)		

bonds	angle	bonds	angle
C(31)−Pt−P(1)	88.57(8)	F(5)−P(2)−C(19)	98.32(13)
C(31)−Pt−P(2)	92.64(8)	F(5)−P(2)−C(25)	97.75(14)
C(37)−Pt−P(1)	91.88(8)	F(5)−P(2)−Pt	116.34(8)
C(37)−Pt−P(2)	87.48(8)	C(38)−C(37)−Pt	126.0(2)
P(1)−Pt−P(2)	177.31(10)	C(41)−C(37)−Pt	122.8(2)

square planar coordination. The tetrafluoropyridyl ring is approximately perpendicular to the platinum coordination plane with a torsion angle of 82.7(1)°. The plane formed by the central four carbon atoms of the cyclohexyl group, C(32), C(33), C(35), and C(36), lies perpendicular to the platinum coordination plane with a torsion angle of 86.4(2)°. The P−F bond lies in the plane of the platinum center; its length (1.597(2) Å) lies within 3σ of that found in [Ir(C_6F_5)(PEt_3)$_2$(PEt_2F)] (IrP−F = 1.630(12) Å).[31] The Pt−C(31) (cyclohexyl) bond length is 2.139(3) Å, while the Pt−C(37) (tetrafluoropyridyl) is shorter, 2.100(3) Å. The Pt−PCy_2F distance (2.2567(8) Å) is shorter than the Pt−PCy_3 distance (2.3527(8) Å) as in [Ir(C_6F_5)(PEt_3)$_2$(PEt_2F)].[31]

Colorless crystals of **3-*cis*** were grown from hexane. Its crystal structure reveals a distorted square planar coordination geometry at platinum (Figure 5, Table 6). The P(1)−Pt−P(2) angle was 106.96(3)°, while the C(3)−Pt−P(1) angle was 96.39(9)°. The tetrafluoropyridyl carbon C(3) lies approximately *trans* to P(2), but the angle C(3)−Pt−P(2) is 155.35(9)°. The Pt−P(1) bond (2.3686(8) Å) is longer than the Pt−P(2) bond (2.2904(9) Å), indicating that the hydride has a stronger *trans* influence than the tetrafluoropyridyl ligand. The Pt−C bond length is 2.058(3) Å, appreciably shorter than the corresponding bond of complex **2a** (2.100(3) Å), presumably as a result of the different *trans* ligand. The hydride was located leading to a Pt−H bond length of 1.68(5) Å. The platinum lies out of the plane of P(1), P(2), and C(3) by 0.124(1) Å. The pyridyl ring lies exactly perpendicular to the best Pt coordination plane defined by Pt, P(1), P(2), and C(3).

6. Reaction of *trans*-[Pt(H)$_2$(PCy_3)$_2$] with Pentafluoropyridine. Since platinum C−F activation chemistry is not limited to Pt(0) complexes,[13,32] we decided to compare the reactivity of *trans*-[Pt(H)$_2$(PCy_3)$_2$] toward pentafluoropyridine with the Pt(0) reaction. The platinum dihydride complex reacts with pentafluoropyridine in THF at room temperature to give a 1:1:1 mixture of *trans*-[Pt(H)(FHF)(PCy_3)$_2$], **3-*trans***, and **2a** (Scheme 4). The presence of *trans*-[Pt(H)(FHF)(PCy_3)$_2$] is revealed by the ^{1}H NMR spectrum, which shows a broad resonance at δ 11.2 for the acidic proton and a hydride as a doublet of triplets with platinum satellites at δ −27. The NMR and IR spectra of this product are identical to the published spectra.[15]

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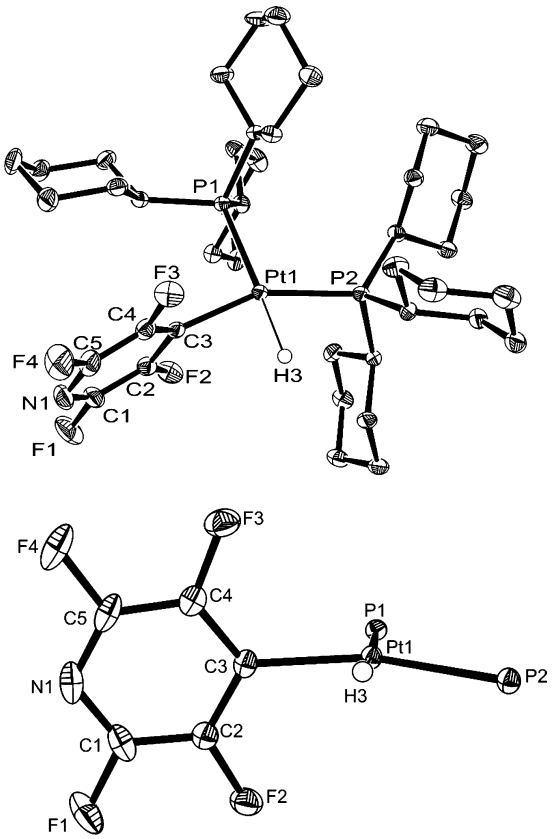


Figure 5. ORTEP diagram of **3-*cis*** (ellipsoids at 50% probability level, hydrogens omitted except for hydride). Top: General view. Bottom: View showing distortion of platinum coordination plane with cyclohexyl groups removed.

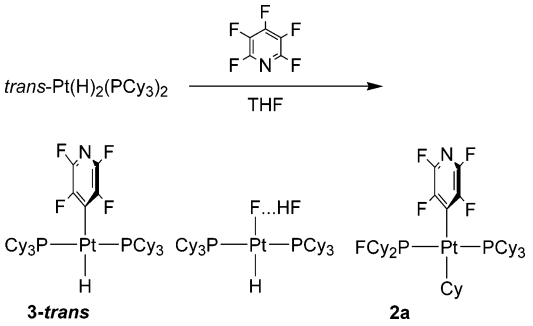
Table 6. Selected Bond Lengths (Å) and Angles (deg) of *cis*-[PtH(C_5NF_4)(PCy_3)$_2$], 3-*cis*, with the Estimated Standard Deviations in Parentheses

bond	length	bond	length
Pt−P(2)	2.2904(9)	F(2)−C(2)	1.357(4)
Pt−P(1)	2.3686(8)	F(3)−C(4)	1.354(4)
Pt−C(3)	2.058(3)	F(4)−C(5)	1.351(4)
Pt−H(3)	1.68(5)	C(1)−C(2)	1.375(5)
N−C(5)	1.303(5)	C(4)−C(5)	1.378(5)
N−C(1)	1.317(5)	C(3)−C(4)	1.378(4)
F(1)−C(1)	1.345(4)	C(3)−C(2)	1.383(5)

bonds	angle	bonds	angle
C(3)−Pt−P(1)	96.39(9)	C(3)−Pt−H(3)	81.5(17)
C(3)−Pt−P(2)	155.35(9)	P(1)−Pt−H(3)	75.8(17)
P(1)−Pt−P(2)	106.96(3)	P(2)−Pt−H(3)	175.4(15)

The second product, **3-*trans***, was characterized by NMR spectroscopy. The ^{1}H NMR spectrum shows a hydride resonance at δ −8.35 as a multiplet with platinum satellites. The ^{1}H{^{31}P} NMR spectrum appears as a triplet with platinum satellites due to a hydride coupled to two *ortho* fluorines (J_{PtH} = 703, J_{HF} = 11 Hz). The ^{31}P NMR spectrum shows a singlet with platinum satellites at δ 36.7 (J_{PtP} = 2732 Hz), indicating that the complex adopts a *trans* geometry. The ^{19}F NMR spectrum shows two resonances for **3-*trans***: the signal at δ −118.3 with a clear hydride coupling and platinum

Scheme 4. Reaction of Pentafluoropyridine with *trans*-[Pt(H)$_2$(PCy$_3$)$_2$]



satellites is assigned to the fluorines *ortho* to platinum (dm $J_{PtF} = 259$, $J_{HF} = 11$ Hz). The resonance at δ −100.4 (m) is assigned to the fluorines *meta* to platinum. The reaction of *trans*-[Pt(H)$_2$(P^{i}Pr$_3$)$_2$] with pentafluoropyridine gave products analogous to the tricyclohexylphosphine complex with a very similar distribution.

Discussion

The C−F activation of pentafluoropyridine at [Pd(PCy$_3$)$_2$] yielding *trans*-[Pd(F)(4-C$_5$NF$_4$)(PCy$_3$)$_2$] (**2**) is shown in Scheme 2. Complex **1a** and its P^{i}Pr$_3$ analogue **1b** can also be prepared by treatment of [PdMe$_2$(tmeda)] with pentafluoropyridine in the presence of the appropriate phosphine. It is reasonable that the formation of the 14-electron compounds [Pd(PCy$_3$)$_2$] and [Pd(P^{i}Pr$_3$)$_2$] precedes the activation step in this case.[33,34] This assumption was confirmed by monitoring the reactions by ^{31}P NMR spectroscopy.

The insertion of the metal into the C−F bond proceeds selectively at the 4-position of the heterocycle. This selectivity contrasts with the comparable reaction at {Ni(PEt$_3$)$_2$}, which yields a metal tetrafluoropyridyl derivative with the metal in the 2-position.[2,35] Furthermore, C−F activation at Ni occurs very rapidly at room temperature, whereas the reaction at Pd is slower and needs more drastic reaction conditions. Our experiments do not distinguish concerted from ionic mechanisms of oxidative addition. Although C−F oxidative addition at palladium has been assumed in order to explain cross-coupling reactions,[9] this is the first direct observation of such a reaction.

The molecular structures of **1b** and an H$_2$O adduct of **1a** (**1a′**) have been determined by X-ray diffraction. Complex **1b** exhibits the shortest known Pd−F distance for a molecular complex, and according to CSD, **1a′** is the first example of a structure of a water adduct of a transition metal fluoro complex.[22,36] It is conceivable that the short Pd−F distances in **1a′** and **1b** might result from a push/pull interaction induced by the π-acceptor properties of the fluoroaryl ligand.[3,28,37] Transfer of electron density from metal d-orbitals into a π^*-orbital of the aromatic system can diminish the pπ−dπ filled/filled repulsion shortening the Pd−F bond.[19,25−27] Consequently, removal of electron density by hydrogen bonds can result in a reduction in the donating properties of the fluorine ligand and a slight elongation of the Pd−F bond in **1a′** compared to **1b**. An alternative view is that the hydrogen bond diminishes the polar character of the metal−fluorine bond, resulting in an elongation of the bond according to the principles of Pauling electronegativity.[27,38] Coordination of HF to a fluoro ligand also leads to an elongation of the metal−fluorine bond.[4,21] It has been observed previously that coordination of water to a fluoride ligand facilitates dissociation of fluoride.[39]

The multinuclear NMR spectra provide conclusive evidence that Pt^0 complexes also activate the C−F bond of pentafluoropyridine at the 4-position at room temperature. In a remarkable rearrangement, the fluoride attacks one of the phosphorus atoms and an alkyl group migrates from phosphorus to platinum to give the complexes *trans*-[Pt(R)(4-C$_5$NF$_4$)(PR$_3$)(PFR$_2$)] **2a** (R = Cy) and **2b** (R = ^{i}Pr) (Scheme 3). Since the product is formed immediately, even at low temperature, it is hard to establish the mechanism. There are three relevant examples of P−C cleavage in the literature. In the first example, [Pt(dppe)(*trans*-stilbene)] reacts with PHMes$_2$ to give [Pt(Mes)(dppe)(PHMes)] as the thermodynamic product.[40] In the second, [Ir(PEt$_3$)$_3$Me] reacts with hexafluorobenzene to give [Ir(C$_6$F$_5$)(PEt$_3$)$_2$(PEt$_2$F)]; the authors postulated a radical-ion-pair mechanism for this reaction.[31] Third, Grushin and Marshall showed very recently that [Rh(F)(PPh$_3$)$_3$] disproportionates at 80 °C to form *trans*-[Rh(F)(PPh$_2$F)(PPh$_3$)$_2$] and *trans*-[Rh(PPh$_2$C$_6$H$_4$)(PPh$_3$)$_2$]; the authors postulate that [Rh(F)(PPh$_3$)$_3$] rearranges initially to *trans*-[Rh(Ph)(PPh$_2$F)(PPh$_3$)$_2$].[41] The reaction that we have observed at platinum is consistent with formation of a platinum fluoride analogous to palladium complex **1a**, followed by rearrangement as postulated by Grushin and Marshall for their rhodium fluoride complex. Grushin also considered related reactions when studying the thermal decomposition of *trans*-[Pd(F)(Ar)(PPh$_3$)$_2$].[16]

We were unable to detect any intermediates in the reaction of [Pt(PCy$_3$)$_2$] with pentafluoropyridine in THF, even at low temperatures. Grushin's rearrangement at rhodium fluoride strongly suggests, however, that platinum analogues of **1a/b** act as intermediates. Three possible mechanisms are shown in Scheme 5, the first involving a phosphorus(V) cation and a platinum(0) anion (mechanism a, see ref 16). The second combines the cation and anion into a metallophosphorane as either an intermediate or transition state (mechanism b).[41,42] The third involves formation of a platinum(IV)

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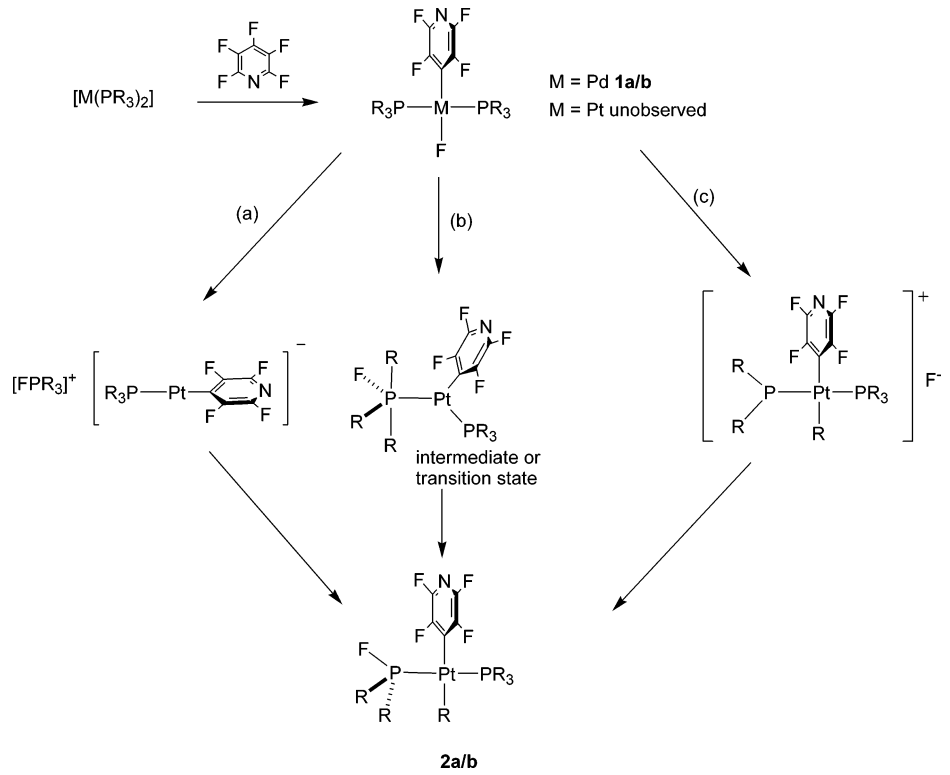
Scheme 5. Proposed Mechanisms of Formation of 2a and 2b



phosphide complex that is attacked by fluoride (mechanism c). At this stage we cannot distinguish these mechanisms. The first and third pathways of Scheme 5 postulate ionic intermediates that should be favored by the polarity of THF compared to hexane. Attempts to test the mechanism by converting **3-*cis*** or **3-*trans*** to fluoride complexes displaced the tetrafluoropyridyl ligand instead of the hydride.

Comparison with Milstein's reaction of $[IrMe(PEt_3)_3]$ to form $[Ir(C_6F_5)(PEt_3)_2(PEt_2F)]$ leads to a radical mechanism[31] for formation of **2a/b** in which the $[Pt(PR_3)_2]^+$ cation is attacked by free fluoride released from pentafluoropyridine anion. We note that several steps would be required before the complex recovered a closed-shell configuration.

The reaction of $[Pt(PCy_3)_2]$ with 2,3,5,6-tetrafluoropyridine is likely to be a conventional C−H activation. The platinum reaction gives a *cis*-product as expected for concerted oxidative addition. The reaction of $[Pt(PCy_3)_2]$ with pentafluoropyridine in hexane results in slow conversion to the same hydride as formed with tetrafluoropyridine, but in lower yield. Since a control reaction of PCy_3 and C_5NF_5 in THF at room temperature yielded 2,3,5,6-tetrafluoropyridine,[43] the unexpected reaction of $[Pt(PCy_3)_2]$ in hexane may go via intermediate formation of tetrafluoropyridine.

Comparison of the platinum(0) and platinum(II) systems shows that C−F activation of Pt(0) with pentafluoropyridine was faster and more selective than with Pt(II). The *cis*-hydride complex was detected in the Pt(0) reactions, but only *trans* products were detected with Pt(II).

Insight into the origin of the very different behavior of zerovalent Ni and Pt toward pentafluoropyridine and tetrafluoropyridine can be obtained by reference to recent calculations on reactions of $[M(H_2PCH_2CH_2PH_2)]$ (M = Ni, Pt) with benzene and hexafluorobenzene.[44] These calculations showed that C−F activation is exothermic for both metals, while C−H activation is energetically favorable only for platinum. The metal−fluorine bond is found to be substantially weaker for Pt because of increased $p_\pi-d_\pi$ repulsions, and the barrier to C−F activation is higher for Pt. The barrier to C−H activation at Pt is far lower than for C−F activation. The present work suggests that the same principles apply to the reactions of heteroaromatics at $[M(PR_3)_2]$ under investigation in the present study. The recent structure of *trans*-$[Pt(F)(Ph)(PPh_3)_2]$ is consistent with these calculations.[24]

Conclusions

C−F activation is possible in both palladium and platinum systems, but the behavior of the two metals is very different. Neither metal behaves similarly to $\{Ni(PEt_3)_2\}$.

1. $[Pt(PR_3)_2]$ (R = ^{i}Pr, Cy) can activate the C−F bond of C_5NF_5 in THF to yield *trans*-$[Pt(4\text{-}C_5NF_4)(R)(PR_3)(PFR_2)]$ as a single product at room temperature. This reaction can be considered as a combination of C−F and P−C activation.The reaction takes a different course in hexane, giving *cis*-$[Pt(4\text{-}C_5NF_4)(H)(PCy_3)_2]$. In contrast, $[Pd(PR_3)_2]$ reacts at 100 °C in toluene to form *trans*-$[Pd(F)(4\text{-}C_5NF_4)(PCy_3)_2]$, providing a new route to palladium fluoride complexes and an example of C−F oxidative addition. These reactions are all regioselective

(43) The control reaction of PCy_3 with pentafluoropyridine also yielded three ^{31}P NMR product resonances at δ −33.7, 30.0, and −26.3 and a ^{19}F NMR resonance at δ −58.5, d, J = 736 Hz. The same resonances were detected in the spectra after reaction of $[Pt(PCy_3)_2]$ with C_5NF_5.

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Table 7. Crystallographic Data for 1a′, 1b, 2a·CH_2Cl_2, and 3-*cis*

	1a′	1b	2a·CH_2Cl_2	3-*cis*
color, habit	colorless plate	colorless plate	colorless plate	colorless plate
cryst dimens/mm^3	0.20 × 0.12 × 0.04	0.15 × 0.14 × 0.05	0.30 × 0.10 × 0.05	0.23 × 0.13 × 0.03
empirical formula	$C_{47}H_{74}F_5NOP_2Pd$	$C_{23}H_{42}F_5NP_2Pd$	$C_{42}H_{68}Cl_2F_5NP_2Pt$	$C_{41}H_{67}F_4NP_2Pt$
diffractometer	Bruker Smart CCD	Nonius Kappa CCD	Bruker Smart CCD	Bruker Smart CCD
monochromator	graphite	graphite	graphite	graphite
fw	718.77	595.92	1009.90	906.99
temp/K	193(2)	100(2)	115(2)	115(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pmn2_1$	$P2_1$	$P2_1/c$	$P2_1/c$
unit cell dimens a/Å	14.0615(8)	8.7100(2)	19.5509(10)	9.5184(5)
b/Å	17.1605(9)	13.0340(4)	9.6008(5)	19.6473(9)
c/Å	9.5865(5)	12.0380(2)	23.0223(11)	21.8841(11)
β/deg		95.9540(15)	94.2310(10)	100.9810(10)
volume/Å^3	2313.2(2)	1359.26(6)	4309.6(4)	4017.6(3)
Z	2	2	4	4
density(calcd)/Mg m^{-3}	1.339	1.456	1.557	1.499
μ/mm^{-1}	0.525	0.846	3.506	3.620
F(000)	984	616	2056	1856
θ range/deg	1.87 to 26.99	3.04 to 27.50	1.04 to 30.01	2.16 to 27.54
index ranges	$-17 \le h \le 11$, $-20 \le k \le 21$, $-12 \le l \le 12$	$-11 \le h \le 11$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-20 \le h \le 27$, $-13 \le k \le 13$, $-32 \le l \le 32$	$-12 \le h \le 10$, $-25 \le k \le 25$, $-28 \le l \le 28$
no. of reflns collected	13 420	24 473	33 814	27 404
no. of indep reflns	5158	5957	12 354	9246
R(int)	0.0304	0.058	0.0269	0.0392
completeness to θ	99.6% to 26.99°	99.6% to 27.50°	98.2% to 30.01°	99.6% to 30.01°
absorption correction	multiscan	multiscan	multiscan	multiscan
max./min. transmn	0.835 and 1.000	0.884 and 0.960	0.839 and 0.663	
no. of data/restraints/params	5158/5/324	5957/1/301	12 354/0/478	9246/0/446
structure soln	direct methods	direct methods	direct methods	direct methods
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
programs	SHELXTL PLUS, SHELX-97[49,50]	SHELXTL PLUS, SHELX-97	SHELXS-97, SHELXL-97	SHELXS-97, SHELXL-97
H atoms	riding + diff	riding	riding	riding + diff
goodness-of-fit on F^2	1.009	1.039	1.038	1.007
final R indices [$I>2\sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0778$ on 4479 reflections	$R_1 = 0.0259$, $wR_2 = 0.0551$ on 5617 reflections	$R_1 = 0.0311$, $wR_2 = 0.0789$ on 10590 reflections	$R_1 = 0.0298$, $wR_2 = 0.0672$ on 7622 reflections
R indices (all data)	$R_1 = 0.0460$, $wR_2 = 0.0821$	$R_1 = 0.0294$, $wR_2 = 0.0568$	$R_1 = 0.0390$, $wR_2 = 0.0827$	$R_1 = 0.0418$, $wR_2 = 0.0714$
max. diff peak & hole/e Å^{-3}	0.828 & −0.330	0.432 & −0.424	3.428 & −2.233	2.875 & −0.992
CCDC ref number	245385	245386	245387	245388

for attack at the 4-position of pentafluoropyridine (typical of nucleophilic attack), unlike {Ni(PEt_3)$_2$}, which is selective for attack at the 2-position.

2. [Pt(PR_3)$_2$] reacts via C−H activation with 2,3,5,6-C_5NHF_4 at room temperature to form *cis*-[Pt(4-C_5F_4N)(H)(PCy_3)$_2$]. The latter is converted to the *trans* isomer on UV irradiation. In contrast, [Pd(PR_3)$_2$] does not react with 2,3,5,6-C_5NHF_4 at 100 °C.

3. *trans*-[Pt(H)$_2$(PCy_3)$_2$] can activate the C−F bonds of C_5NF_5 at room temperature to yield three compounds: *trans*-[Pt(H)(FHF)(PCy_3)$_2$], *trans*-[Pt(4-C_5NF_4)(H)(PCy_3)$_2$], and *trans*-[Pt(4-C_5NF_4)(Cy)(PCy_3)($PFCy_2$)].

4. Once again, C−F activation has proved to be a useful source of metal fluoride complexes. Our mechanistic interpretation carries the implication that platinum fluoride complexes behave very differently from palladium fluoride complexes because the Pt−F bond is weaker and longer than the Pd−F bond.[44] Moreover, the platinum complexes are susceptible to a rearrangement similar to that observed by Grushin and Marshall at rhodium.[41]

Experimental Section

1. General Procedures. Most of the synthetic work was carried out on a Schlenk line or in a glovebox (under N_2 or Ar) 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. The complexes [Pd(PCy_3)]$_2$[45] and [$PdMe_2$(tmeda)][34] and [Pt(PR_3)$_2$][46] (R = Cy, ^{i}Pr) were synthesized by published methods. The phosphines, PCy_3 and P^iPr_3, were either purchased from Strem or synthesized according to the literature.[47,48]

The NMR spectra were recorded on Bruker DRX 500 or AMX500 spectrometers (^{1}H 500.13, ^{31}P 202.46. ^{19}F 407.4, ^{13}C 125.78, ^{195}Pt 107.52 MHz). The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15. The ^{13}C{^{1}H} spectra were referenced to C_6D_6 at δ 128.0. The ^{31}P{^{1}H} NMR spectra are reported downfield of an external solution of H_3PO_4 (85%). The ^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The ^{195}Pt spectra were referenced relative to the absolute frequency of 86.024 MHz as δ 0.The infrared spectra were recorded on Bruker Vector 22 or Mattson Research Series spectrometers. Mass spectra were recorded on a VG Autospec instrument and are listed for ^{196}Pt. Elemental analyses were

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performed by Elemental Microanalysis Ltd, Devon, UK, or in house (Bielefeld).

2. Syntheses. ***trans*-[PdF(4-C_5NF_4)(PCy_3)$_2$] (1a).** (a) [$Pd(PCy_3)_2$] (48 mg, 0.07 mmol) was dissolved in toluene (10 mL), giving a yellow solution. After addition of pentafluoropyridine (9 μL, 0.8 mmol) the reaction mixture was stirred for 6 h at 100 °C, and the volatiles were removed under vacuum. The remaining colorless solid was washed with hexane (5 mL), giving a colorless powder (yield 18 mg, 30%). (b) [$PdMe_2$(tmeda)] (221 mg, 0.88 mmol) and PCy_3 (509 mg, 1.94 mmol) were dissolved in toluene (20 mL). After stirring the reaction mixture for 1 h at room temperature, pentafluoropyridine (193 μL, 1.76 mmol) was added. The reaction mixture was stirred for another 15 min, after which the resulting light yellow solution was heated to 90 °C. The reaction temperature was maintained for 4 h, during which the solution turned to dark orange. The solution was then cooled and filtered from a gray residue through a cannula, and the volatiles were removed from the toluene filtrate in the vacuum, giving a dark red residue. This residue was washed with hexane (10 mL), resulting in a colorless powder. The gray residue was suspended in toluene (10 mL) and the suspension filtered. Evaporation of the solvent under vacuum yields a colorless substance. Both colorless powders consisted of compound **1a** and were combined (yield 368 mg, 50%). Anal. Calcd for $C_{41}H_{66}F_5NP_2Pd$: C, 58.89; H, 7.95; N 1.67. Found: C, 59.07; H, 7.78; N, 1.51. IR (KBr, cm^{-1}): 1615 (s), 1586 (w), 1497 (w), 1443 (s), 1424 (s), 1409 (s), 1352 (w), 1325 (vw), 1298 (w), 1268 (m), 1199 (s), 1174 (m), 1128 (m), 1112 (m), 1048 (w), 1005 (m), 922 (s), 888 (m), 849 (m), 823 (s), 733 (s), 695 (m), 533 (w), 524 (m), 512 (m), 493 (w), 468 (m), 401 (w), 393 (w).

***trans*-[PdF(4-C_5NF_4)(P^iPr_3)$_2$] (1b).** [$PdMe_2$(tmeda)] (163 mg, 0.65 mmol) was dissolved in toluene (10 mL). The solution was cooled to −20 °C, and P^iPr_3 was added (280 μL, 1.47 mmol). After stirring the reaction mixture for 1 h at −20 °C, pentafluoropyridine (160 μL, 1.56 mmol) was added at −10 °C. The reaction mixture was stirred for another 15 min at −10 °C, after which the resulting light yellow solution was heated to 90 °C. The reaction temperature was maintained for 4 h, during which the solution turned to dark orange. The solution was then cooled and filtered through a cannula, and the volatiles were removed from the filtrate in the vacuum. The resulting light orange residue was washed with hexane (10 mL) at −60 °C, giving a colorless powder (yield 310 mg, 80%). Anal. Calcd for $C_{23}H_{42}F_5NP_2Pd$: C, 46.36; H, 6.94; N 2.24. Found: C, 46.31; H, 7.10; N, 2.24. IR (KBr, cm^{-1}): 1617 (s), 1591 (m), 1554 (m), 1451 (s), 1425 (s), 1389 (s), 1369 (m), 1245 (m), 1200 (s), 1091 (m), 1962 (m), 1036 (m), 921 (s), 883 (m), 824 (m), 731 (w), 693 (w), 660 (s), 619 (w), 527 (s), 458 (s).

***trans*-[Pt(4-C_5NF_4)(C_6H_{11})(PCy_3)(PFCy_2)] (2a).** The method was identical to that for **2b** (see below) and gave a 70% yield of **2a.** The $^{13}C\{^1H\}$ spectrum exhibited a resonance at δ 32.0 with prominent platinum satellites (J_{PtC} = 59 Hz). Anal. Calcd for $C_{41}H_{66}F_5NP_2Pt$: C, 53.24; H, 7.19; N, 1.51. Found: C, 52.31; H, 7.19; N, 1.51. MS (EI) (*m*/*z*): 924.4 (M^+, 8%), 905.4 ($M^+ - F$, 22%), 841 ($M^+ - C_6H_{11}$, 100%).

***trans*-[Pt(4-C_5NF_4)($CHMe_2$)(P^iPr_3)(PF^{i}Pr$_2$)] (2b).** Pentafluoropyridine (0.131 g, 0.78 mmol) was added to a solution of [$Pt(P^iPr_3)_2$] (0.2 g, 0.39 mmol) in THF. The mixture was stirred for 1 h at room temperature to yield a white precipitate. The precipitate was recrystallized from a layered solution of THF−hexane at −20 °C overnight to give **2b** (yield 0.21 g, 80%). The complex was not obtained analytically pure, since it was not stable under vacuum.

Reaction of [$Pt(PCy_3)_2$] with Pentafluoropyridine in Hexane. A 2-fold excess of pentafluoropyridine (0.17 g, 1.01 mmol) was added to a hexane solution of [$Pt(PCy_3)_2$] (0.4 g, 0.53 mmol). The solvent was decanted and the mixture was left to stand overnight at room temperature to give a colorless crystal precipitate of ***cis*-3**. The precipitate was recrystallized from a layered solution of THF−hexane at −20 °C overnight to give 25% (0.12 g, 0.132 mmol) yield.

***cis*-[Pt(H)(4-C_5NF_4)(PCy_3)$_2$] (*cis*-3).** A solution of [$Pt(PCy_3)_2$] (0.2 g, 0.26 mmol) in hexane was reacted with 2,3,5,6-tetrafluoropyridine (0.08 g, 0.53 mmol) under argon; colorless crystals were formed overnight at room temperature (yield 0.18 g, 77%). Anal. Calcd for $C_{41}H_{66}F_5NP_2Pt$: C, 54.29; H, 7.45; N, 1.54. Found: C, 54.30; H, 7.70; N, 1.58. MS (EI) (*m*/*z*): 905.4 ($M^+ - H$, 2%), 755.4 (29%, $Pt(PCy_3)_2^+$).

Isomerization of *cis*-3 to *trans*-3. Two identical NMR samples of ***cis*-3** were prepared in NMR tubes containing ***cis*-3** (ca. 5 mg) in C_6D_6, and the reactions were followed by NMR spectroscopy. The first one was irradiated for 2 h (broad band irradiation with Philips HPK 125 W mercury arc, $\lambda > 290$ nm), causing complete conversion of ***cis*-3** to the corresponding *trans* isomer ***trans*-3**. The second sample was heated at ∼80 °C, giving the following conversions of ***cis*-3** to ***trans*-3** determined by the integration ratio of the hydride resonances: after 2 h integration H_{cis}/H_{trans} = 1:0.2, after 6 h 1:0.4, after heating overnight 1:0.9.

Reaction of *cis*-[$Pt(H)_2(PCy_3)_2$] with Pentafluoropyridine. [$Pt(H)_2(PCy_3)_2$] (0.5 g, 0.66 mmol) was dissolved in THF (15 mL), and C_5NF_5 (0.2 g, 1.18 mmol) was added to the solution. The reaction mixture was stirred for 1 h. The solvent was removed under vacuum. The residue was extracted with benzene and recrystallized from THF−hexane at −30 °C to yield a mixture of (1:1:1) three products (0.34 g).

Crystal Structures. Crystallographic data for **1a′**, **1b**, **2a**, and ***cis*-3** are listed in Table 7.

Methods for 1a′. Hydrogen atoms at O(1) were located in the difference Fourier map, but could not be refined isotropically. They were fixed with a bond length of 0.84 Å and a displacement parameter of 1.2 times that of O(1). The Flack parameter of 0.13(3) indicates racemic twinning.

Methods for *cis*-3. The hydride was located on a difference map after all non-hydrogen atoms had been located and riding hydrogen atoms included.

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Supporting Information Available: Figure S1 (2D {$^{195}Pt-^1H$} correlation spectrum), Figure S2-S9 (ORTEP diagrams and packing diagrams of **1a′**, **1b**, **2a** and ***cis*-3**), and tables of atomic coordinates, anisotropic displacement parameters, and bond distances and angles for **1a′**, **1b**, **2a**, and ***cis*-3**. Crystallographic data are also available in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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