Activation of Aromatic Carbon–Fluorine Bonds by Organoplatinum Complexes

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The ligand $Me_2NCH_2CH_2N{=}CHC_6F_5$ (**1a**) reacts with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**2**) in acetone solution to give sequentially $[PtMe_2(Me_2NCH_2CH_2N{=}CHC_6F_5)]$ (**3a**), $[PtFMe_2(Me_2NCH_2CH_2N{=}CHC_6F_5)]$ (**4**), and $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$ (**5**). Complex **5**, which is formed by reaction of **4** with acetone, was characterized by an X-ray structure determination and shown to contain hydrogen-bonded NH···FPt dimers in the solid state. The ligand $PhN{=}CHC_6F_5$ (**6**) reacts with **2** to give $[PtFMe_2(PhN{=}CHC_6F_4)(SMe_2)]$ which may exist in two isomeric forms **7a** and **7b**. The reactions to form **4** and **7** give the first examples of oxidative addition of C—F bonds to platinum(II). The ligand $Me_2NCH_2CH_2N{=}CH(2,6\text{-}C_6H_3F_2)$ reacts with **2** to give $[PtMe_2\{Me_2NCH_2CH_2N{=}CH(2,6\text{-}C_6H_3F_2)\}]$ (**3b**), but this failed to give oxidative addition of a C—F bond. The ligands $Me_2NCH_2CH_2N{=}CHAr$, Ar = 2,6-, 2,5-, or 2,3-$C_6H_3F_2$, react with **2** to give $[PtMe_2(Me_2NCH_2CH_2N{=}CHAr)]$, and then CH_4 and $[PtMe(Me_2NCH_2CH_2N{=}CHC_6H_2F_2)]$. These reactions involve activation of a C—H bond rather than a C—F bond of the aryl group. The results show that activation of a C—F bond of a pentafluorophenyl group is facilitated by incorporation into a monodentate or bidentate nitrogen-donor ligand so that intramolecular oxidative addition can occur, but that C—H bond activation is always easier than C—F bond activation in $C_6H_xF_{5-x}$ groups and that more than two fluorine substituents on the phenyl group are necessary for C—F bond activation to occur.

Introduction

Organofluorine compounds have many applications as specialty chemicals, and there is considerable interest in the possibility of developing useful transition-metal catalysts for the synthesis or functionalization of such compounds. The latter is difficult because the C—F bond is strong and generally unreactive.[2] Nevertheless there have been several reports of the activation of CF bonds by transition metal, lanthanide, and actinide derivatives, as well as the synthesis of unusual fluorocarbon derivatives of such elements.[3-12] In particular, Richmond and coworkers have discovered intramolecular activation of aromatic C—F bonds by oxidative addition to tungsten(0).[3,5,8] For example, the ligand $2\text{-}NH_2C_6H_4N{=}CHC_6F_5$ reacted with $[W(CO)_3(EtCN)_3]$ to give $[W(CO)_3F(NH_2\text{-}C_6H_4N{=}CHC_6F_4)]$.[3] At the time of Richmond's first report, we had begun research using the similar ligand

Table I. ^{1}H NMR Data[a] for the Ligands $Me_2{}^aNCH_2{}^bCH_2{}^cN{=}CH^dR$

R	δ (H[a])	δ (H[b])[b]	δ (H[c])[b]	δ (H[d])
C_6F_5 (**1a**)	2.25	2.61	3.79	8.46
2,6-$C_6H_3F_2$ (**1b**)	2.21	2.55	3.23	8.48
2,5-$C_6H_3F_2$ (**1c**)	2.21	2.55	3.24	8.53
2,3-$C_6H_3F_2$ (**1d**)	2.20	2.55	3.74	8.58
2-C_6H_4F (**1e**)	2.30	2.64	3.70	8.60
2-C_6H_4F[c]	2.12	2.59	3.42	

[a] Solvent: acetone-d_6. [b] In all cases $^3J(H^bH^c)$ was in the range 6.5–7.0 Hz. [c] Ligand $Me_2NCH_2CH_2N{=}C(C_6H_5)(2\text{-}C_6H_4F)$.

Scheme I

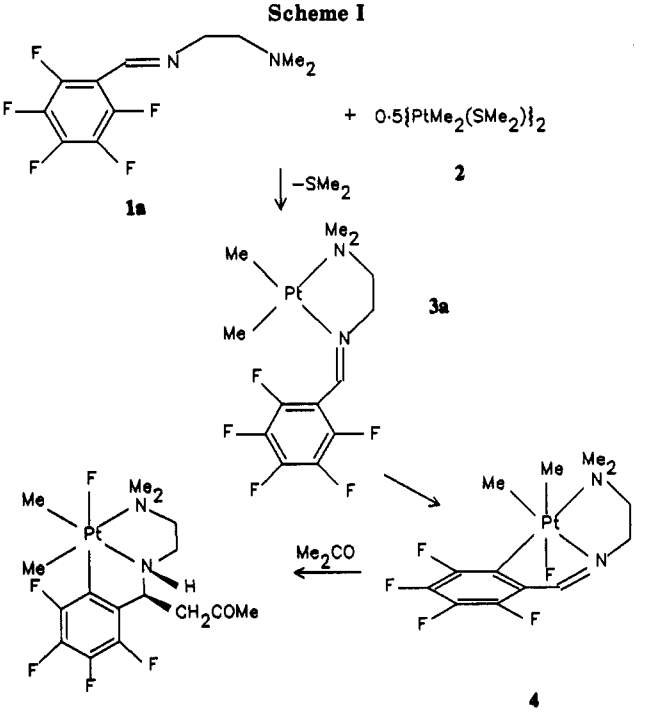

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Table II. ^{1}H NMR Data for the Complexes [PtMe^{a}Me^b(Me$_2$N^{c}CH$_2$^{d}CH$_2$^{e}N=CH^{f}R)]^g

R	δ (Me^a)^b	δ (Me^b)^c	δ (H^c)^d	δ (H^d)^e	δ (H^e)^e	δ (H^f)	^3J(PtH^f), Hz
C_6F_5	0.44	−0.29	2.76	2.96	4.20	8.90	52
2,6-$C_6H_3F_2$	0.36	−0.21	2.70	2.71	4.10	9.20	52
2,5-$C_6H_3F_2$	0.47	0.04	2.76	2.73	4.10	9.30	48
2,3-$C_6H_3F_2$	0.45	−0.03	2.75	2.7[f]	4.1[f]	9.37	48
2-C_6H_4F	0.43	−0.01	2.72	2.66	4.14	9.18	46
2-C_6H_4F[g]	0.40	−0.29	2.76	2.7[f]	3.86		

[a] Solvent acetone-d_6. Me^a trans to imine, Me^b trans to NMe$_2$. [b] ^2J(PtMe^a) = 84–85 Hz. [c] ^2J(PtMe^b) = 90–92 Hz. [d] ^3J(PtH^c) = 20–22 Hz. [e] ^3J(H^{c}H^d) = 6–8 Hz. [f] Partly obscured. [g] Ligand is Me$_2$NCH$_2$CH$_2$N=CPhR.

$Me_2NCH_2CH_2N{=}CHC_6F_5$, with the aim of activating a CF bond by intramolecular oxidative addition to platinum(II).[13] Richmond has since independently used this and related ligands for C—F bond oxidative addition to tungsten.[5,9] This paper gives details of the scope and limitations of the intramolecular oxidative addition of C—F bonds to platinum(II) and some competing orthometalation reactions. A preliminary account of parts of this work has been published,[13] and an account of the related activation of aryl—chloride and aryl—bromide bonds has also been given.[14]

Results

Reactions of the Ligand $Me_2NCH_2CH_2N{=}CHC_6F_5$ (1a). Initial work was carried out by reacting the pentafluorophenyl derivative **1a** (Table I) with [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**2**), and the results are shown in Scheme I. The dimethyl sulfide ligands of **2** are easily displaced,[15] and complex **3a** was formed. Complex **3a** could not be isolated in pure form, since it reacted further to give **4** in dichloromethane solution or **5** in acetone solution, but it was readily characterized by its NMR spectra. The ligand resonances of **3a** (Table II) were easily assigned by comparison with those of the free ligand (Table I). Coupling of both the Me_2N protons and the imine proton to ^{195}Pt (Table II) clearly indicated that both nitrogen atoms of the ligand were coordinated in complex **3a**, while a resonance due to free SMe_2 showed that this ligand had been displaced from platinum. Two methylplatinum resonances were observed with ^2J(PtH) values of 84 and 92 Hz, and these were assigned to the methylplatinum groups trans to the imine and NMe_2 nitrogen atoms, respectively, since imine nitrogens have the stronger trans influence.[14]

Complex **4** was formed over a period of about 1 h in CH_2Cl_2 solution. It was characterized by methylplatinum resonances at δ = 0.48 [d, J(HF) = 1, ^2J(PtH) = 75] and 1.17 [dd, J(HF) = 3, 8, ^2J(PtH) = 68], which are assigned to the methyl groups trans to F and imine, respectively. The reduced coupling constants ^2J(PtH) for **4** compared to **3a** are typical of platinum(IV) compared to platinum(II).[13-15] In acetone solution complex **4** could be identified spectroscopically but it reacted with the solvent to give **5**, which was highly insoluble and which crystallized from solution in almost quantitative yield. The main difference in the spectrum of **4** in acetone was that the MePt resonances each lacked one J(HF) coupling when compared to the spectrum in CH_2Cl_2. We tentatively suggest that in the more polar solvent acetone the PtF bond is reversibly solvolyzed and hence coupling to this fluorine atom is lost. The imine group was shown to be intact in **4** since the characteristic N=CH resonance was observed at δ = 8.82 [s, J(PtH) = 44 Hz] in CH_2Cl_2 and δ = 9.04 [s, J(PtH) = 45 Hz] in acetone solution.

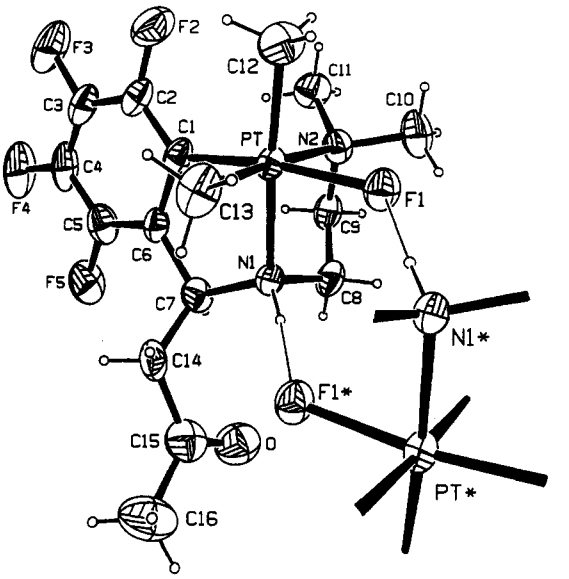

Figure 1. View of the structure of [PtFMe$_2$-{$Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4$}] (**5**) showing how dimerization occurs through hydrogen bonding of the NH···Pt groups of neighboring molecules. The distance N(1)···F(1*) is 2.805 (10) Å. A region of electron density maximum was found corresponding to the expected position of the H-atom, but it was not refined and was placed in the idealized position on nitrogen with N(1)–H = 0.95 Å, and the dimensions H···F(1*) = 1.86 Å and N(1)–H–F(1*) = 172° were then calculated.

Formation of **5** involves the cis addition of a C—H bond of acetone across the C=N bond of **4**. Complex **5** was insoluble in common organic solvents, and so it could not be characterized by NMR methods. The ketone group gives a strong IR band at 1718 cm^{-1} due to ν(C=O) while the NH group gives a band at 3100 cm^{-1} due to ν(NH). This unusually low frequency for ν(NH) is due to strong hydrogen bonding to the Pt—F fluoride ligand of a neighbouring molecule, as shown by an X-ray structure determination (see below). The addition of a C—H bond of acetone to an imine group is unusual and is probably made possible in this case by the activation by the strongly electronegative fluoroaryl group and also by coordination to platinum (IV).

Structure of Complex 5. Since complex **5** was too insoluble to recrystallize, crystals were grown by diffusion of acetone solutions of the ligand **1a** and complex **2**, whereupon **5** crystallized as it was formed. The crystals were suitable for an X-ray structure determination, and the structure is shown in Figure 1. Molecular dimensions are in Table III. The platinum atoms are octahedrally coordinated by three carbon donors in a facial arrangement, two nitrogen donors, and a fluoride ligand. The two nitrogen donors and the metalated aryl group are constituents of a tridendate ligand which occupies facial positions of the octahedron. In complex **4** the imine group

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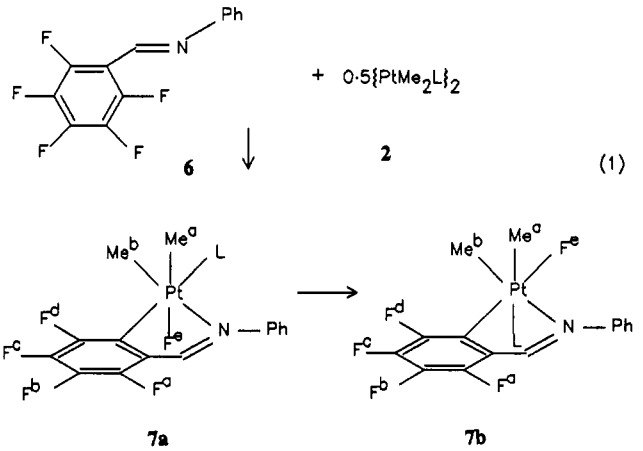
lends rigidity to the tridendate ligand and both the NMR properties and molecular mechanics calculations indicate that meridional stereochemistry is preferred for the N_2C donors. The acetone addition to the imine group to give **5** leads to a more flexible ligand, and the *fac* stereochemistry is then adopted as shown in Figure 1. Within each molecule, the Pt–N(2) and Pt–F bond are long and presumably weak and the stereochemical change probably occurs by reversible dissociation of either the Pt–NMe_2 or Pt–F group, followed by rearrangement within a 5-coordinate intermediate and recoordination. Few Pt–F bond distances have been determined, but the Pt–F(1) distance of 2.070 (5) Å appears to be the longest known.[16] It is expected to be weakened by the trans aryl group which has a high trans influence. For comparison, other values of Pt–F distances are 2.043 (7) Å in $[PtF(PEt_3)_3]^+$, 2.03 (1) Å in *cis*-$[PtF\{CH(CF_3)_2\}(PPh_3)_2]$, and 1.89–1.91 Å in $[PtF_6]^{2-}$.[16]

Reaction of the Ligand PhN=CHC$_6$F$_5$ (6). Ligand **6** reacted with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give oxidative addition of a C—F bond and formation of two isomers of $[PtFMe_2(C_6F_4CH{=}NPh)(SMe_2)]$ (**7a** and **7b**) (eq 1, L = SMe_2). Over a period of 1 day, **7a** was converted completely to **7b**. Complex **7a** was characterized by MePt resonances in the ^{1}H NMR spectrum at δ = 0.77 [^2J(Pt(H) = 70 Hz, Me^a] and 1.37 [^2J(PtH) = 68 Hz, Me^b], while **7b** had MePt resonances at 1.16 [^2J(PtH) = 68 Hz, Me^a] and 1.76 [^2J(PtH) = 66 Hz, Me^b]. Both isomers gave a through-space coupling J(Me^{b}F^d) of 3 Hz, confirmed by ^{19}F NMR spectroscopy, and **7b** also gave couplings ^3J(Me^{a}F^e) = ^3J(Me^{b}F^e) = 7 Hz. Complex **7b** was isolated in pure form and was fully characterized by its ^{1}H, ^{13}C, ^{19}F, and ^{195}Pt NMR spectra. The presence of a Pt—F bond was proved by the observation of a resonance in the ^{19}F NMR spectrum at δ(^{19}F) = −241 [^1J(PtF) = 145 Hz].



This experiment clearly shows that a chelate diamine ligand is not necessary for C—F bond activation but that a single nitrogen donor atom is sufficient.

Reactions of the Ligands Me$_2$NCH$_2$CH$_2$N=CHR, R = C$_6$H$_n$F$_{5-n}$. Several derivatives were studied (Table I) to determine whether the pentafluorophenyl group was a necessary prerequisite for C—F bond activation in this system. When R = 2,6-$C_6H_3F_2$, reaction of **1b** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gave the substitution complex **3b** (Table II, Scheme II) only. No subsequent oxidative addition occurred, and so it is clear that the presence of only *o*-fluorine substituents is not a sufficient condition for C—F bond activation. When both an *o*-hydrogen and an *o*-fluorine substituent were present, as in **3c–3e**, activation of the C—H bond, with subsequent loss of methane, always occurred in preference to C—F bond activation. Thus **3c**, **3d**, and **3e**[14] gave **8a**, **8b**, and **8c**, respectively (Scheme II), which were readily characterized by their NMR spectra.[14]

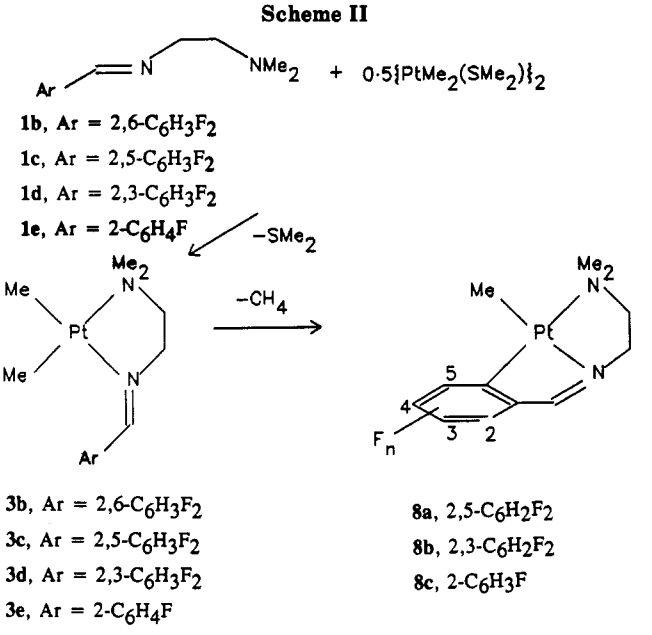
The ligand $Me_2NCH_2CH_2N{=}C(C_6H_5)(2\text{-}C_6H_4F)$ reacted with **2** to give $[PtMe\{Me_2NCH_2CH_2N{=}C(C_6H_4)(2\text{-}C_6H_4F)\}]$ by orthometalation of the phenyl group in preference to the 2-fluorophenyl group. Again, no C—F oxidative addition occurred.

Approximate rate constants for the orthometalation of **3** to give **8** (Scheme II) were measured in acetone solution at 25 °C, by monitoring the reactions by UV–visible

Table III. Molecular Dimensions in $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$

Bond Lengths/Å			
Pt–F(1)	2.070 (5)	N(2)–C(10)	1.478 (14)
Pt–N(1)	2.173 (9)	N(2)–C(11)	1.492 (15)
Pt–N(2)	2.242 (10)	C(1)–C(2)	1.386 (15)
Pt–C(1)	1.978 (9)	C(1)–C(6)	1.432 (16)
Pt–C(12)	2.060 (14)	C(2)–C(3)	1.372 (15)
Pt–C(13)	2.038 (14)	C(3)–C(4)	1.348 (19)
F(2)–C(2)	1.345 (15)	C(4)–C(5)	1.387 (18)
F(3)–C(3)	1.366 (14)	C(5)–C(6)	1.369 (14)
F(4)–C(4)	1.329 (13)	C(6)–C(7)	1.510 (15)
F(5)–C(5)	1.369 (16)	C(7)–C(14)	1.502 (18)
O–C(15)	1.209 (18)	C(8)–C(9)	1.510 (17)
N(1)–C(7)	1.493 (12)	C(14)–C(15)	1.508 (18)
N(1)–C(8)	1.459 (15)	C(15)–C(16)	1.476 (23)
N(2)–C(9)	1.476 (15)	N(1)–F(1)*	2.805 (10)
Selected Bond Angles/deg			
F(1)–Pt–N(1)	89.8 (3)	Pt–N(1)–C(7)	111.0 (6)
F(1)–Pt–N(2)	89.6 (3)	Pt–N(1)–C(8)	106.4 (7)
F(1)–Pt–C(1)	172.0 (4)	Pt–N(2)–C(9)	104.7 (7)
F(1)–Pt–C(12)	87.1 (4)	Pt–N(2)–C(10)	111.5 (7)
F(1)–Pt–C(13)	88.8 (4)	Pt–N(2)–C(11)	114.7 (8)
N(1)–Pt–N(2)	81.5 (4)	Pt–C(1)–C(2)	130.4 (9)
N(1)–Pt–C(1)	82.7 (4)	Pt–C(1)–C(6)	114.0 (7)
N(1)–Pt–C(12)	176.1 (5)	C(7)–C(14)–C(15)	115 (1)
N(1)–Pt–C(13)	95.3 (5)	O–C(15)–C(14)	121 (1)
N(2)–Pt–C(1)	92.0 (4)	O–C(15)–C(16)	123 (1)
N(2)–Pt–C(12)	96.1 (5)	C(14)–C(15)–C(16)	116 (1)
N(2)–Pt–C(13)	176.4 (4)		
C(1)–Pt–C(12)	100.4 (5)		
C(1)–Pt–C(13)	89.1 (5)		
C(12)–Pt–C(13)	87.0 (6)		

Scheme II



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spectrophotometry. The first-order rate constants were R = C_6H_5, 6×10^{-6} s^{-1}; R = 2,5-$C_6H_3F_2$, 2×10^{-6} s^{-1}; R = 2,3-$C_6H_3F_2$, 5×10^{-6} s^{-1}. The fluoro substituents have only a small retarding effect on the rate of orthometalation.

Discussion

There have been several recent reports of the activation of C–F bonds at transition-metal centers, and the results described above can therefore be placed in a more general context.[3-14] The closest analogy is with the activation of the ligands **1a**, **1b**, and **1e** by $[W(CO)_3(MeCN)_3]$.[3,8] The tungsten complex activates a C–F bond in each case,[3,8] whereas the dimethylplatinum(II) system only activates the C–F bond of **1a**. It fails to activate the C–F bond of **1b** and activates the C–H bond of **1e**.[14] The marked difference in selectivity may be due to the "harder" nature of tungsten compared to platinum,[17] so that the ratio of the M–F to M–H bond energy is greater for M = tungsten than for M = platinum and this is reflected in the relative activation energies for C–F versus C–H oxidative addition. Alternatively, the trapping of the product of C–H activation in the platinum case by the irreversible reductive elimination of methane could be responsible for the difference in behavior.

In terms of mechanism, it has been shown that photochemical activation of a C–F bond in the arene complex $[Rh(\eta\text{-}C_5Me_5)(PMe_3)(\eta^2\text{-}C_6F_6)]$ occurs to give $[Rh(\eta\text{-}C_5Me_5)(PMe_3)F(C_6F_5)]$, although the mechanism of the photochemical step is not known.[9b] Similar arene coordination to platinum(II) may well precede C–F bond activation in the chemistry of Scheme I. We have proposed elsewhere that the aromatic C–H, C–Cl, and C–Br oxidative additions to platinum(II) occur by a concerted mechanism, and this was supported by the observation that other electron-attracting or electron-withdrawing substituents on the aryl group had little effect on the rates of reaction.[14] The C–F oxidative addition is different in that the pentafluorophenyl group was the only reactive fluorophenyl group of those tested, and the less activated ligand **1b** failed to give C–F oxidative addition. The complex intramolecular oxidative addition of C_6F_6 to $[IrMe(PEt_3)_3]$ has been suggested to involve initial electron transfer from iridium to C_6F_6,[11a] and an analogous mechanism is also possible with the dimethylplatinum(II) complexes studied here. Alternatively, an S_NAr mechanism, with the platinum(II) center as nucleophile is consistent with the data.[11b] In either case, the pentafluorophenyl group in **1a** would then be expected to be much more reactive than the 2,6-difluorophenyl group in **1b**, whereas in a concerted mechanism **1a** and **1b** would be expected to display similar reactivity. We have not been successful in monitoring the kinetics of the C–F oxidative additions, and so activation energies for these reactions could not be obtained. The mechanistic conclusion is therefore tentative.

Experimental Section

^1H and ^{19}F NMR spectra were recorded by using a Varian XL200 and ^{13}C and ^{195}Pt NMR spectra by using a Varian XL300 spectrometer. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared as described previously.[15] Coupling constants are reported in hertz.

Ligand Synthesis. To a solution of $Me_2NCH_2CH_2NH_2$ (14 mmol) in benzene (20 mL) was added C_6F_5CHO (14 mmol). The solution was stirred for 90 min, and then water was removed by addition of $MgSO_4$, the solution was filtered, and the solvent was evaporated under vacuum to give $Me_2NCH_2CH_2N{=}CHC_6F_5$ (85% yield). NMR (acetone-d_6): ^1H δ = 2.25 [s, 6 H, MeN], 2.61 [*t*, 2 H, *J*(HH) = 7, CH_2], 2.79 [*t*, 2 H, *J*(HH) = 7, CH_2], 8.46 [s, 1 H, N=CH]. MS: *m/e* calc for $C_{11}H_{11}F_5N_2$ 266.0842; found 266.0843.

The ligands **1b–1e** were prepared similarly and were characterized by their NMR spectra (Table I). ^{19}F NMR spectra: **1b**, δ = −113.8 [dd, *J*(HF) = 7.3]; **1c**, δ = −118.5 [m, *o*-F], −128.0 [m, *m*-F]; **1d**, δ = −139.7 [m], −148.3 [m]; $Me_2NCH_2CH_2NPh(2\text{-}FC_6H_4)$, δ = −112.5 [m, *o*-F].

The ligand $C_6H_5N{=}CHC_6F_5$ was prepared similarly from $C_6H_5NH_2$ and C_6F_5CHO. NMR (acetone-d_6): ^1H δ = 7.2–7.5 [m, 5 H, C_6H_5], 8.67 [s, 1 H, N=CH]; ^{19}F δ = −142.6 [m, 2 F, *m*-F], −152.2 [m, 1 F, *J*(FF) = 21, *p*-F], −163.5 [m, 2 F, *o*-F]. MS: *m/e*, calc for $C_{13}H_6F_5N$ 271.0424; found 271.0415.

$Me_2NCH_2CH_2N{=}C(C_6H_5)(2\text{-}C_6H_4F)$. A solution of $Me_2NCH_2CH_2NH_2$ (1.23 g) and $Ph(2\text{-}C_6H_4F)C{=}O$ (2.80 g) in benzene (200 mL) was heated under reflux for 4 days using a Dean-Stark separator to remove the water formed. The solvent was evaporated under vacuum to give the product (Table I).

$[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$ (5). To a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.121 g) in acetone (20 mL) was added $Me_2NCH_2CH_2N{=}CHC_6F_5$ (0.15 g). The solution became yellow in color and a colorless precipitate of **5** formed slowly. After 2 h, the product was isolated by filtration, washed with acetone and then ether, and dried under vacuum. Yield: 0.17 g. Mp: 360 °C dec. Anal. Calc for $C_{16}H_{23}F_5N_2OPt$: C, 35.0; H, 4.1; N, 5.2. Found: C, 35.3; H, 4.3; N, 5.2. IR (Nujol): 1718 [ν(CO)], 3100 cm^{-1} [ν(NH)].

$[PtFMe_2(Me_2NCH_2CH_2N{=}CHC_6F_4)]$ (4). This complex was characterized in acetone-d_6 solution but could not be isolated in pure form. To a solution of **2** (33 mg) in acetone-d_6 (0.5 mL) was added ligand **1a** (31 mg). Complex **3a** was identified after 5 min (Table II), and after 30 min this had rearranged to **4**, as major product. NMR: ^1H δ = 0.74 [s, 3 H, ^2J(PtH) = 74, MePt trans to NMe_2], 1.34 [s, 3 H, ^2J(PtH) = 60, *J*(HF) = 4.6, MePt trans to imine], 3.74 and 3.75 [6 H, Me_2N], 4.70–5.44 [*m*, = 4 H, CH_2CH_2], 9.14 [s, 1 H, ^3J(PtH) = 45, CH=N]; ^{19}F δ = −129 [m, F^d], −141 [m, F^a], −145 [m, F^c], −159 [m, F^b], −247 [s, PtF]. Evaporation of the solution at this stage gave impure **4**. IR: 1653 cm^{-1} [ν(C=N)].

Table IV. Crystallographic Data for $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$

formula, fw	$C_{16}H_{23}F_5N_2OPt$, 549.46
F(000)	528
cryst dimens, mm	0.18 × 0.30 × 0.60
peak width at half-ht, deg	0.30
radiation; λ, Å	Mo Kα; 0.710 73
temp, °C	21
space group	triclinic, $P\bar{1}$
cell dimens	
a, *b*, *c*, Å	9.463 (2), 12.153 (2), 8.066 (2)
α, β, γ, deg	93.49 (2), 98.48 (2), 104.99 (1)
V, Å^3	881.5 (6)
Z; D_c, g cm^{-3}; μ, cm^{-1}	2; 2.07; 81.0
instrument	Enraf-Nonius CAD4 diffractometer
monochromator	graphite cryst, incident beam
attenuator	Zr foil, factor 17.0
takeoff angle, deg	2.8
detector aperture, mm	2.0–2.5 horiz, 4.0 vert
crystal–detector dist, cm	21
scan type; scan rate, deg min^{-1}	ω–2θ; 1–4
scan width, max 2θ, deg	0.6 + 0.350 tan θ, 50.0
no. refl measd	3382 tot., 3116 unique
corrections	Lorentz–polarization, numerical absorption, extinction
struct soln	Patterson method
min function	$\sum w(\|F_o\| - \|F_c\|)^2$
no. of reflections incl	2811 with $I > 3\sigma(I)$
no. of params refined	227
R, R_w	0.062, 0.075
convergence, largest shift	0.06
high peak in diff map, e Å^{-2}	5.78 (37) adj to Pt
computer hardware	PDP-11
computer software	SDP-PLUS

(17) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson and Ross: Stroudsberg, PA, 1973.

Table V. Positional and Thermal Parameters and Their Esd's

atom	x	y	z	B,[a] Å²
Pt	0.07440 (4)	0.22350 (3)	0.04465 (4)	2.181 (8)
F(1)	−0.1132 (7)	0.0909 (5)	−0.0454 (8)	3.0 (1)
F(2)	0.2460 (10)	0.4991 (6)	0.0114 (11)	5.0 (2)
F(3)	0.5052 (11)	0.6244 (7)	0.1702 (12)	6.1 (2)
F(4)	0.6774 (9)	0.5344 (7)	0.3914 (12)	6.1 (2)
F(5)	0.5766 (8)	0.3155 (7)	0.4613 (11)	4.9 (2)
O	0.3001 (12)	−0.0414 (8)	0.4332 (13)	5.0 (2)
N(1)	0.1453 (9)	0.1189 (7)	0.2314 (11)	2.4 (2)
N(2)	−0.0371 (10)	0.2741 (9)	0.2517 (11)	2.9 (2)
C(1)	0.2657 (12)	0.3338 (9)	0.1443 (13)	2.9 (2)
C(2)	0.3234 (13)	0.4472 (10)	0.1188 (14)	3.3 (2)
C(3)	0.4590 (14)	0.5128 (10)	0.2011 (16)	3.7 (3)
C94)	0.5473 (13)	0.4698 (11)	0.3102 (17)	4.2 (3)
C95)	0.4911 (13)	0.3577 (11)	0.3434 (16)	3.7 (3)
C(6)	0.3571 (11)	0.2886 (9)	0.2639 (14)	2.6 (2)
C(7)	0.3056 (12)	0.1665 (9)	0.3039 (14)	2.8 (2)
C(8)	0.0452 (12)	0.1103 (9)	0.3539 (14)	3.0 (2)
C(9)	0.0252 (12)	0.2267 (10)	0.4006 (14)	3.2 (2)
C(10)	−0.1994 (13)	0.2241 (12)	0.2132 (18)	4.3 (3)
C(11)	−0.0090 (15)	0.4000 (10)	0.2920 (17)	4.0 (3)
C(12)	−0.0072 (15)	0.3178 (11)	−0.1301 (17)	4.1 (3)
C(13)	0.1751 (15)	0.1680 (10)	−0.1374 (14)	3.8 (3)
C(14)	0.3913 (11)	0.0887 (10)	0.2432 (16)	3.2 (2)
C915)	0.3704 (14)	−0.0231 (11)	0.3199 (16)	3.9 (3)
C(16)	0.4365 (17)	−0.1076 (12)	0.2457 (21)	5.5 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac(\cos\beta B_{13} + bc(\cos\alpha)B_{23}]$.

Complex **4** was formed and characterized similarly in CD_2Cl_2 solution, but it could not be isolated in pure form.

[PtFMe$_2$(SMe$_2$)(PhN=CHC$_6$F$_4$)] (7b). To a solution of complex **2** (0.2 mmol) in acetone (20 mL) was added PhN=CHC$_6$F$_5$ (0.4 mmol). The solution was stirred for 16 h at ambient temperature, the volume of solvent was reduced, and the product was precipitated as a white solid by addition of ether. Yield: 71%. Mp: 106 °C. Anal. Calc for $C_{17}H_{18}F_5NPtS$: C, 36.6; H, 3.25; N, 2.5. Found: C, 36.9; H, 3.5; N, 2.5. NMR (acetone-d_6): ^{1}H δ = 1.16 [d, 3 H, ^2J(PtH) = 68, J(HF) = 7, MePt], 1.76 [dd, 3 H, ^2J(PtH) = 66, J(HF) = 7 and 3, MePt], 2.09 [s, 6 H, ^3J(PtH) = 12, MeS], 7.4–7.9 [m, 5 H, C$_6$H$_5$], 9.36 [s, 1 H, ^3J(PtH) = 42, CH=N]; ^{13}C δ = 20.1 [dd, ^1J(PtC) = 620, J(CF) = MePt], 26.5 [d, ^1J(PtC) = 595, J(CF) = 6.6, MePt], 42.0 [^2J(PtC) = 6, MeS], 188.1 [^2J(PtC) = 54, CH=N], 124, 129, 130, 161 [^1J(CF) = 248], 169 [^1J(CF) = 252], 172, 173 [^1J(CF) = 248], 177 [^1J(CF) = 241], 178, 180 [aryl carbons]; ^{19}F δ = −127 [m, $J(F^dF^a)$ = 16, $J(F^dF^c)$ = 20, $J(PtF^d)$ = 80, $J(F^dMe^b)$ = 3, F^d], −139 [m, $J(F^aF^b)$ = 20, $J(F^aF^d)$ = 16, $J(PtF^a)$ = 25, F^a], −148 [m, $J(F^cF^b)$ = 20, $J(F^cF^d)$ = 20, $J(PtF^c)$ = 80, F^c], −163 [m, $J(F^bF^a)$ = 20, $J(F^bF^c)$ = 20, $J(PtF^b)$ = 9, F^b], −241 [s, ^1J(PtF) = 145, PtF^e].

[PtMe$_2$(Me$_2$NCH$_2$CH$_2$N=CHR)], R = 2,6-C$_6$H$_3$F$_2$ (3b). To a solution of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.020 g, 0.035 mmol) in acetone (10 mL) was added Me$_2$NCH$_2$CH$_2$N=CHR (0.08 mmol). The solution was stirred for 30 min, the volume was reduced under vacuum, and pentane was added to precipitate the product, which was then isolated as an orange-yellow solid and dried under vacuum. Yield: 75%. Anal. Calc for $C_{13}H_{20}F_2N_2Pt$: C, 35.7; H, 4.6; N, 6.4. Found: C, 35.6; H, 4.9; N, 6.3.

[PtMe{Me$_2$NCH$_2$CH$_2$N=CH(2,5-C$_6$H$_2$F$_2$)}] (8a). To a solution of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.020 g, 0.035 mmol) in acetone (10 mL) was added Me$_2$NCH$_2$CH$_2$N=CH(2,5-C$_6$H$_3$F$_2$) (0.08 mmol) in acetone (3 mL). The solution was allowed to stir for 5 days and slowly became red in color during this time. The product was isolated by reducing the volume of solvent and adding pentane to precipitate a red solid, which was dried under vacuum. Yield: 62%. Anal. Calc for $C_{12}H_{17}F_2N_2Pt$: C, 34.1; H, 4.1; N, 6.6. Found: C, 34.1; H, 4.5; N, 6.3. NMR (acetone-d_6): ^{1}H δ = 1.09 [d, 3 H, J(HF) = 4, ^2J(PtH) = 79, MePt], 2.76 [s, 6 H, ^3J(PtH) = 24, Me$_2$N], 3.23 [t, 2 H, ^3J(HH) = 6, ^3J(PtH) = 20, CH$_2$N], 4.14 [t, 2 H, ^3J(HH) = 6, CH$_2$N], 9.02 [s, ^3J(PtH) = 60, CH=N]; ^{19}F δ = −103.7 [m, ^3J(PtF) = 149, 5-F], −122.7 [m, ^4J(PtF) = 61, 2-F].

Similarly were prepared [PtMe{Me$_2$NCH$_2$CH$_2$N=CH(2,3-C$_6$H$_2$F$_2$)}]. Anal. Calc for $C_{12}H_{17}F_2N_2Pt$: C, 34.1; H, 4.1; N, 6.6. Found: C, 34.1; H, 4.6; N, 6.2. NMR (acetone-d_6): ^{1}H δ = 0.83 [s, 3 H, ^2J(PtH) = 80, MePt], 2.78 [s, 6 H, ^3J(PtH) = 22, Me$_2$N], 3.22 and 4.22 [t, 2 H, ^3J(HH) = 6, CH$_2$], 9.06 [s, ^3J(PtH) = 62, CH=N]; ^{19}F δ = −143.0 [m, ^4J(PtF) = 56, ^3J(FF) = 20, ^3J(HF) = 7, 2-F], −150.5 [m, 3-F]. [PtMe{Me$_2$NCH$_2$CH$_2$N=C(C$_6$H$_4$(2-C$_6$H$_4$F))}]; Anal. Calc for $C_{18}H_{21}FN_2Pt$: C, 45.1; H, 4.4; N, 5.8. Found: C, 44.9; H, 4.4; N, 5.4. NMR (acetone-d_6): ^{1}H δ = 0.90 [s, 3 H, ^2J(PtH) = 80, MePt], 2.78 [s, 6 H, ^3J(PtH) = 20, Me$_2$N], 3.16 and 3.86 [t, 2 H, ^3J(HH) = 6, CH$_2$]; ^{19}F δ = −122.7 [dd, J = 16, 6, no ^{195}Pt^{19}F coupling].

X-ray Structure Determination. Crystals of [PtFMe$_2$-{Me$_2$NCH$_2$CH$_2$NHCH(CH$_2$COMe)C$_6$F$_4$}] were grown from a reaction mixture in acetone solution. Details of the structure determination are given in Table IV, and positional and thermal parameters are in Table V. Further data are in supplementary Tables S1 (molecular dimensions), S2 (calculated hydrogen coordinates), S3 (general temperature factor expressions), S4 (torsional angles), S5 (least-squares planes), and S6 (structure factors).

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Supplementary Material Available: Tables of crystallographic data for complex **5** including Table S1, molecular dimensions, Table S2, calculated hydrogen atom coordinates, Table S3, general temperature factor expressions, Table S4, torsion angles, and Table S5, least-squares planes (8 pages); Table S6, listing structure factors (29 pages). Ordering information is given on any current masthead page.