J. Am. Chem. Soc. **2000,** *122,* 8685−8693 8685

Hydrogen Bonding in Transition Metal Complexes: Synthesis, Dynamics, and Reactivity of Platinum Hydride Bifluoride Complexes

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Received March 28, 2000

Abstract: Platinum hydride bifluoride (FHF) complexes *trans*-[Pt(PR_3)$_2$H(FHF)] (R = Cy, ^{i}Pr) were prepared from the reaction of the corresponding *trans*-dihydride complexes with NEt_3·3(HF) in THF. They were also formed in C−F activation reactions of the same precursors with C_6F_6 in the presence of [Me_4N]F. The low-temperature NMR spectra exhibit a complete network of coupling between the spin $^1/_2$ nuclei, ^{1}H, ^{31}P, ^{19}F, and ^{195}Pt. At higher temperatures, fluxional behavior is observed which is principally associated with intermolecular exchange of HF between platinum centers. However, satisfactory simulation of the spectra also requires inclusion of intermolecular exchange of the distal fluoride. Addition of [Bu_4N]FHF results in coalescence of the bifluoride proton resonance of the complex and the added bifluoride, demonstrating that the bifluoride ligand can exchange with free bifluoride, FHF^-. The IR spectrum of *trans*-[Pt(PCy_3)$_2$H(FHF)] shows two broad bands at 2604 and 1832 cm^{-1} assigned to the H−F stretching modes and a sharp band at 2272 cm^{-1} for the Pt−H stretching mode. Bifluoride is a weakly coordinated ligand which can be replaced to give *trans*-[Pt(PCy_3)$_2$(H)X] complexes where X = N_3, OTf. Hydrogen fluoride may be removed from *trans*-[Pt(PCy_3)$_2$H(FHF)] by treatment with CsOH in the presence of [NMe_4]F, yielding *trans*-[Pt(PCy_3)$_2$(H)F]. In addition, these bifluoride complexes fluorinate organic compounds, such as CH_3I, CH_3COCl, and C_6H_5COCl, to give CH_3F, CH_3COF, and C_6H_5COF together with *trans*-[Pt(PCy_3)$_2$(H)X] (X = Cl, I). Reactions with PPh_3 and pyridine yield *trans*-[Pt(PCy_3)$_2$(PPh_3)H]FHF and *trans*-[Pt(PCy_3)$_2$(C_5H_5N)H]FHF.

Introduction

The role of hydrogen bonding in the chemistry of transition metal complexes is now recognized both in solution and the solid state, and new types of hydrogen bonds have been discovered. Crabtree and Morris have shown that metal hydride complexes can hydrogen bond to conventional H-bond donors forming M−H···HX interactions where H−X is an H-bond donor.[1] Richmond has reviewed the role of hydrogen bonding in transition metal fluoride complexes.[2] For instance, the crystal structure of a tungsten−fluoride complex reveals head-to-tail dimerization via N−H···F−W hydrogen bonds.[2] Brammer et al. have shown that hydrogen bonding at metal fluoride complexes is stronger than that for other halides, and that H···F−M angles are more obtuse than angles to other H···X−M bonds.[3] Crabtree et al. reported a complex exhibiting intramolecular hydrogen bonding between Ir−F and a pendant NH_2 group attached to another ligand.[1] This interaction is revealed in solution by the coupling *J*(HF) of 52 Hz in one of the amino proton resonances. Upon protonation at low temperature, a complex is formed with coordinated F−H as Ir−F−H···NH_2^+, with a much larger value of *J*(HF) (440 Hz).[1]

The strongest known hydrogen bond is found in bifluoride, FHF^-.[4] This ion has only recently been recognized as a ligand in transition metal complexes. There is extensive documentation of the hydrogen bonding of HF to nonmetal bases, for instance via matrix isolation,[5] but the bonding of HF to a metal fluoride has the scope for altering the strength of the M−F interaction substantially. Parkin et al. reported the bifluoride complexes, [Mo(PMe_3)$_4$$H_2$F(FHF)] and [W($PMe_3$)$_4$$H_2$F(FHF)], synthesized with aqueous HF.[6] The best evidence of structure in the solid state comes from X-ray and neutron diffraction of [W(PMe_3)$_4$$H_2$F(FHF)].[6] The structure is based on a trigonal dodecahedron, with a distorted tetrahedral array of PMe_3 ligands. The hydrogen bonding is far from symmetric, with the hydrogen atom located much closer to the distal fluorine (0.961 Å) than to the proximal fluorine (1.43 Å) (the distal fluorine is furthest from the metal, while the proximal fluorine is directly bound to the metal). The FHF unit approaches linearity with a bond angle of 170.6°. The observation that *J*(HF) exceeds 400 Hz suggests that the HF in these complexes is nearly dissociated in solution.

Perutz et al. were the first to characterize an η^1-FHF complex in solution and solid state. They prepared *trans*-[Ru(dmpe)$_2$H(FHF)] by the reaction of *cis*-[Ru(dmpe)$_2$$H_2$] either with fluoroarenes (C_6F_6, C_5F_5H, or others) or with NEt_3·3(HF).[7] The NMR and IR parameters suggest the presence of an asymmetric bifluoride ligand with predominant M−F···H−F character (note

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10.1021/ja0010913 CCC: $19.00

$J(HF_{distal}) = 274$ Hz and $J(HF_{proximal}) < 30$ Hz). It was proposed that the reaction of the transition metal dihydride with C_6F_6 yields *trans*-[Ru(dmpe)$_2$(C_6F_5)H] with release of HF which reacts with *cis*-[Ru(dmpe)$_2$H$_2$] to form the bifluoride complex.[7]

Perutz and Parkin[6,7] both found that the bifluoride ligand is not coordinated linearly to the metal center but exhibits an M−F⋯F angle of ~130°. The F⋯F separation in each of these complexes is considerably less than twice the van der Waals radius of fluorine (1.4 Å).[8] The metal−fluorine bond lengths are extremely long, probably as a result of weakening through the hydrogen bond to the distal fluorine.

Recently, we have described the crystal structure and solution NMR spectra of a nickel bifluoride complex, *trans*-[Ni(PEt$_3$)$_2$-(difluoropyrimidinyl)(FHF)].[9] Of the remaining reports of bifluoride complexes, the one for [Rh═CCHPh(P^{i}Pr$_3$)$_2$(FHF)] is the most complete.[10] The NMR spectrum shows low-temperature fluorine resonances at δ −228 and δ −179 (J(HF) = 418 Hz and J(FF) = 101 Hz). The coupling constants indicate that the M−F⋯H−F interaction is weaker than the *trans*-[Ru-(dmpe)$_2$H(FHF)] system and similar to [MoH$_2$F(FHF)(PMe$_3$)$_4$]. There are a few other incomplete reports of bifluoride complexes. Coulson reported the elemental analysis of *trans*-[Pt-(PEt$_3$)$_2$(C$_6$H$_5$)(FHF)] without further evidence.[11] Hintermann et al. detected *trans*-[Pt(PCy$_3$)$_2$H(FHF)] in solution by NMR spectroscopy following the electron-transfer reaction of *trans*-[Pt(PCy$_3$)$_2$H$_2$] with fluorinated benzonitrile, but the complex was not isolated.[12] Grushin et al. identified *trans*-[Pd(PPh$_3$)$_2$-(FHF)R] (R = Me, Ph) from the reaction of [Pd$_2$(PPh$_3$)$_2$R$_2$(μ-OH)$_2$] with NEt$_3$·3(HF) on the basis of microanalysis and a broad proton NMR resonance.[13] One report describes FHF as a bridging ligand in the structure of a niobium dimer, but no evidence is given for this species in solution.[14]

We have now isolated the complex originally detected by Hintermann et al.,[12] *trans*-[Pt(PCy$_3$)$_2$H(FHF)], by using NEt$_3$·3(HF) as a mild source of HF. We report its characterization, solution dynamics, and reactivity and also investigate its triisopropylphosphine analogue. We show that the connectivity of these complexes can be established completely by low-temperature NMR spectroscopy. We find that they are also generated in C−F bond activation reactions.

Results

Synthesis of Bifluoride Complexes. The dihydride complexes *trans*-[Pt(PR$_3$)$_2$H$_2$] (R = Cy, ^{i}Pr) react immediately with NEt$_3$·3(HF) in THF solution to give hydrogen and *trans*-[Pt(PR$_3$)$_2$H(FHF)], respectively. Hydrogen bubbled off for the first few minutes of the reaction. All products were characterized by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy (Table 1), IR (Table 2), mass spectrometry, and elemental analysis (C, H). Twinning of crystals prevented us from obtaining useful crystallographic data.

The complexes *trans*-[Pt(PR$_3$)$_2$H$_2$] (R = Cy, ^{i}Pr) react with C_6F_6 in the presence of [NMe$_4$]F in THF at 50 °C for 48 h to yield *trans*-[Pt(PCy$_3$)$_2$H(FHF)] and *trans*-[Pt(PCy$_3$)$_2$H(C$_6$F$_5$)].

Table 1. NMR Data for Complexes *trans*-[Pt(PR$_3$)$_2$H(FHF)] (R = Cy, P^{i}Pr$_3$) in [^{2}H$_8$]-THF at 193 K[a]

complex	temp (K)	δ(^{1}H) acidic	δ(^{1}H) hydride	δ(^{19}F)	δ(^{31}P)
Pt(PCy$_3$)$_2$H(FHF)	290	11.3	−27.2	−283.3 −185	42.5
Pt(PCy$_3$)$_2$H(FHF)	190	11.9	−27.2	−283.6 −182.5	42.4
Pt(P^{i}Pr$_3$)$_2$H(FHF)	290	11.3	−26.8	−281.5 −179.5	55.9
Pt(P^{i}Pr$_3$)$_2$H(FHF)	190	11.6	−27.0	−280 −179	54.6

[a] Coupling constants are shown in Figure 5.

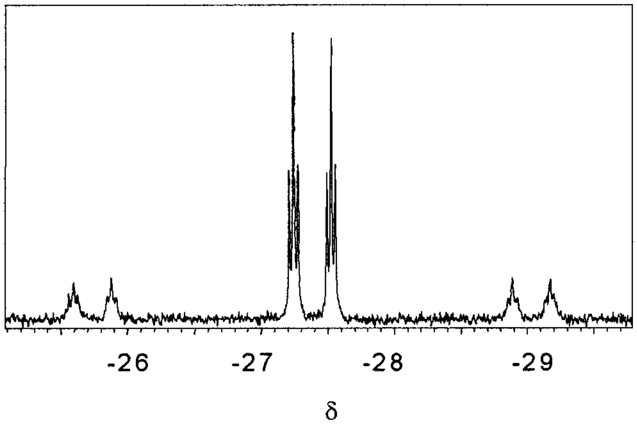

Figure 1. ^{1}H NMR spectra (300 MHz) of hydride region of *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] in [^{2}H$_8$]-THF at 273 K.

Table 2. IR Data (ν/cm^{-1}) for *trans*-[Pt(PR$_3$)$_2$H(X)] (X = H, FHF, or F; R = Cy or P^{i}Pr$_3$)

X	Pt(PCy$_3$)$_2$H(X)	Pt(P^{i}Pr$_3$)$_2$H(X)	assignment
H	1707	1736	ν_{asym}(Pt−H)
F	2206, 2235		ν(Pt−H)
FHF	2272	2273	ν(Pt−H)
	1832	1903	ν(H−F)
	2604, 2630	2528	ν(H−F)
	426, 442	424−432	ν(Pt−F)

The complexes, *trans*-[Pt(PR$_3$)$_2$H(FHF)], were also identified among the products of reaction of *trans*-[Pt(PR$_3$)$_2$H$_2$] with pentafluoropyridine.

Identification of Bifluoride Complexes by NMR Spectroscopy. The ^{19}F NMR spectra for each of the platinum bifluoride complexes show two resonances, a doublet at ~δ −280 and a broad resonance at δ −180, which appears as a doublet of doublets at low temperature (more details are given below). The ^{1}H NMR spectrum for each of the platinum bifluoride complexes exhibits a hydride resonance at ~δ −27 which appears as a doublet with platinum satellites. Upon cooling, this resonance resolves into a doublet of triplets with platinum satellites (Figure 1), consistent with coupling to one fluorine nucleus and two equivalent phosphine nuclei. The values of J(PtH) of ~1340 Hz are close to those assigned by Hintermann for *trans*-[Pt(PCy$_3$)$_2$H(FHF)].[12] With selective ^{19}F decoupling at ~δ −283, the hydride doublet of *trans*-[Pt(PCy$_3$)$_2$H(FHF)] collapses to a singlet with platinum satellites.

The acidic proton of each complex appears as a broad resonance at room temperature at ~δ 11.5. At low temperature (193 K), this resonance resolves into a doublet of doublets at δ 11.9 for *trans*-[Pt(PCy$_3$)$_2$H(FHF)] with coupling constants of 412 and 48 Hz. For *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)], the resonance is observed at δ 11.3 and has couplings of 393 and 43 Hz. In

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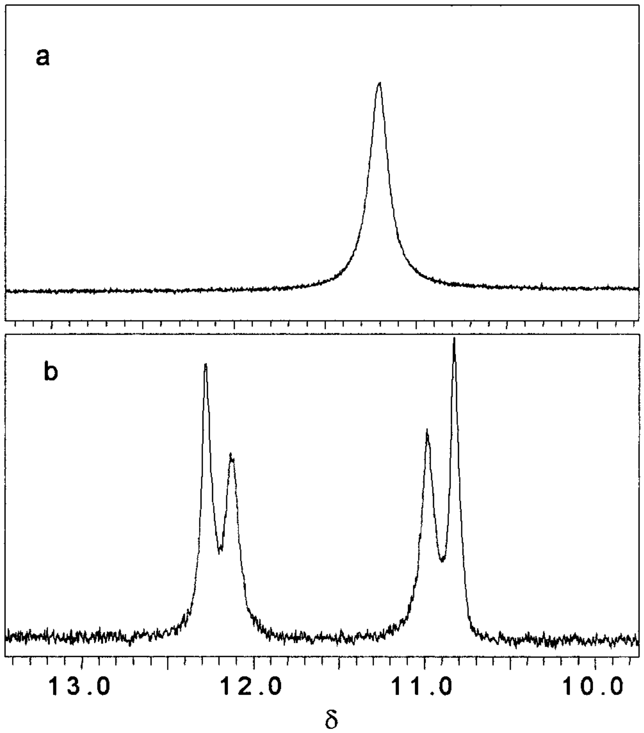

Figure 2. ^{1}H NMR spectrum (300 MHz) of acidic proton region of *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] in [^{2}H$_8$]-THF (a) at room temperature, (b) at 193 K.

both cases, the small coupling arises from interaction with the proximal fluorine and the large coupling from the distal fluorine of the bifluoride ligand (Figure 2). The ^{1}H NMR spectrum of *trans*-[Pt(PCy$_3$)$_2$H(FHF)] recorded with selective ^{19}F decoupling at ∼δ −283 at low temperature collapses to a doublet which retains the large coupling. The corresponding spectrum with ^{19}F decoupling at ∼δ −182 at low temperature shows an unresolved singlet, providing evidence that the distal fluorine is most strongly coupled to the acidic proton.

The ^{31}P{^{1}H} NMR spectrum of *trans*-[Pt(PCy$_3$)$_2$H(FHF)] shows a singlet with platinum satellites at δ 42.5 at room temperature. At low temperature, the resonance resolves into a doublet with satellites (J(PtP) = 2860 Hz and J(PF) = 8 Hz). NMR data for the P^{i}Pr$_3$ analogue are given in Table 1. The solution geometry of Pt(PR$_3$)$_2$X$_2$ complexes can be deduced from the magnitude of J(PtP): for cis complexes, typically greater than 3000 Hz, for trans complexes J(PtP), usually less than 3000 Hz.[15]

In the ^{19}F NMR spectra, two resonances are observed at room temperature for the *trans*-[Pt(PR$_3$)$_2$H(FHF)] complexes. One resonance is a doublet with platinum satellites at δ −283 (J(HF) = 112 Hz and J(PtF) = 572 Hz) for *trans*-[Pt(PCy$_3$)$_2$H(FHF)] and δ −281 (J(HF) = 116 Hz and J(PtF) = 588 Hz) for *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] (Figure 3a). This resonance is assigned to the proximal fluorine, which is coupled to the Pt and hydride nuclei. When the hydride resonance at δ −27 is decoupled, the fluorine spectrum collapses to a singlet with platinum satellites (Figure 3b). At room temperature, coupling is not observed from the proximal fluorine to either the acidic hydrogen or the distal fluorine. The fully coupled ^{19}F resonance turns into a broad triplet upon cooling to 193 K for *trans*-[Pt(PCy$_3$)$_2$H(FHF)] and a triplet of doublets for *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] (Figure 3c).

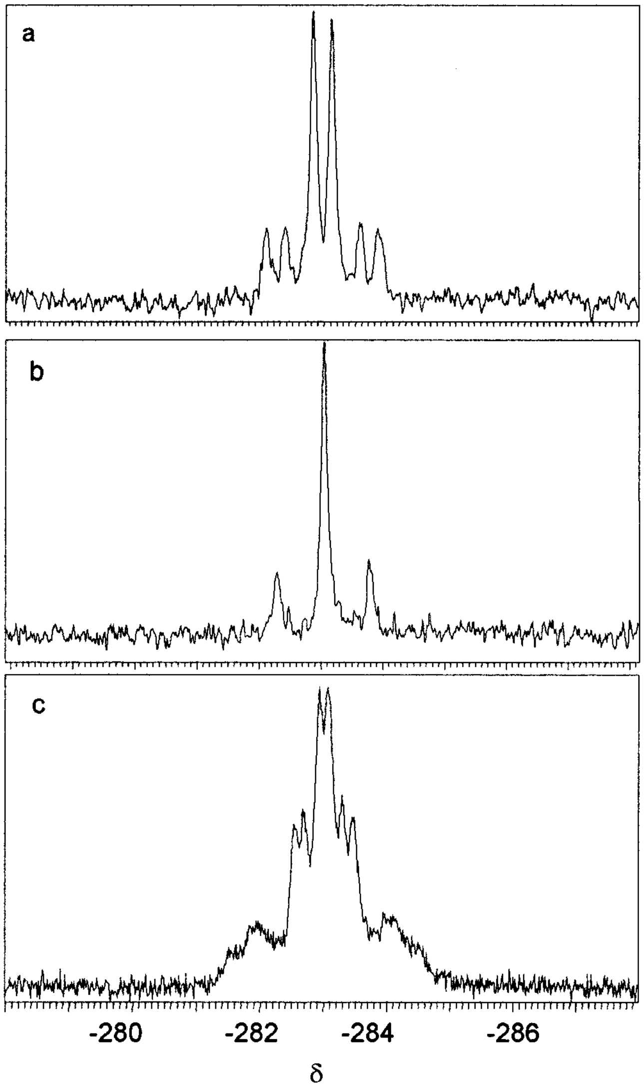

Figure 3. ^{19}F NMR spectra (376 MHz) of *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] in [^{2}H$_8$]-THF in the region of the proximal fluorine (a) at room temperature, (b) with ^{1}H decoupling at ∼δ −27 at room temperature, (c) without decoupling at 193 K.

The second ^{19}F resonance observed is at ∼δ −180 and appears as a doublet of doublets at low temperature with coupling constants J(HF) ≈ 400 and J(FF) = 103 Hz (Figure 4a). This resonance is assigned to the distal fluorine of the bifluoride ligand. The ^{19}F NMR spectrum, recorded with proton decoupling at δ 12−13, shows a doublet with the small coupling retained (Figure 4b). With the full set of couplings, it becomes apparent why the ^{19}F resonance of the proximal fluorine is poorly resolved, even at low temperature: the coupling to the distal fluorine is close to twice the coupling to the acidic hydrogen. Additional small couplings to ^{31}P will reduce the apparent resolution.

The NMR coupling patterns at low temperature provide a complete and unambiguous demonstration of the presence of the complexes *trans*-[Pt(PR$_3$)$_2$H(FHF)] (Figure 5). However, the room-temperature data make it evident that dynamic processes are occurring (see below).

IR Spectroscopy of the Bifluoride Complexes. The IR spectra of the dihydride and the bifluoride complexes were recorded from 4000 to 200 cm^{-1} in Nujol mulls. The ν(M−H) bands for the dihydride starting materials at 1700−1750 cm^{-1} were replaced by new bands on formation of the bifluoride complex (Table 2 and Figure 6). Each product complex shows

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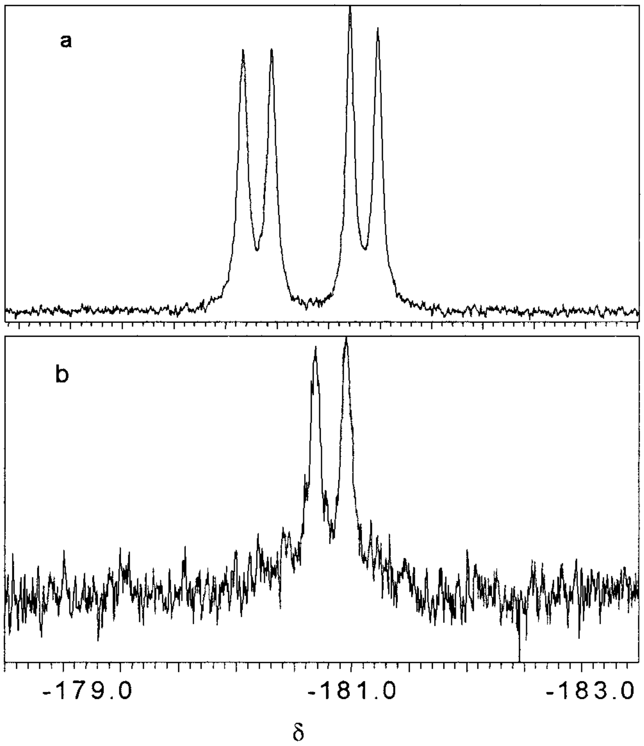

Figure 4. ^{19}F NMR spectra (376 MHz) of *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] in [^{2}H$_8$]-THF at 193 K in the region of distal fluorine (a) fully coupled, (b) with ^{1}H decoupling at ~δ 11.

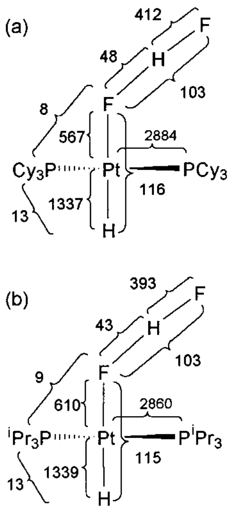

Figure 5. Coupling constants (Hz) in the low-temperature NMR spectra of (a) *trans*-[Pt(PCy$_3$)$_2$H(FHF)], (b) *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)].

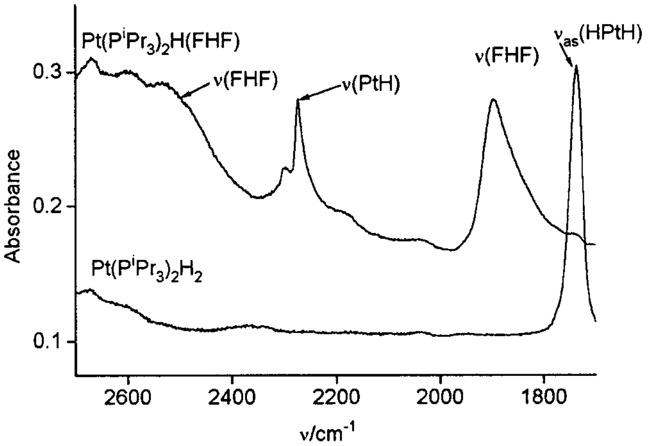

Figure 6. IR spectra (Nujol mull) of *trans*-[Pt(P^{i}Pr$_3$)$_2$H(FHF)] and *trans*-[Pt(P^{i}Pr$_3$)$_2$H$_2$].

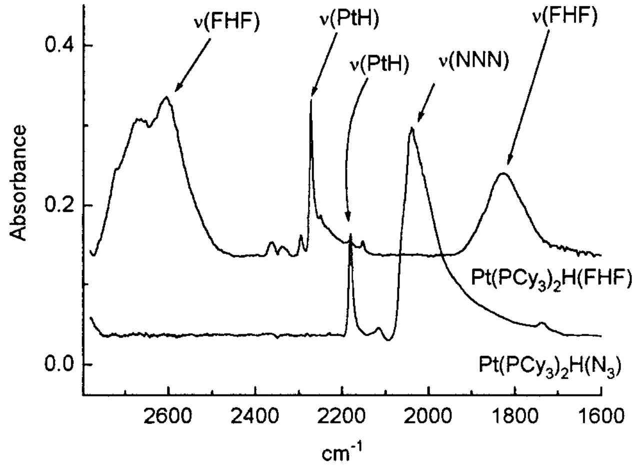

Figure 7. IR spectra (Nujol mull) of *trans*-[Pt(PCy$_3$)$_2$H(FHF)] and Pt(PCy$_3$)$_2$(H)N$_3$.

a broad peak around 2500−2650 cm^{-1}, a sharp peak at ~2270 cm^{-1}, and a broad peak at 1800−1900 cm^{-1}. In this region, three modes are expected: two H−F modes and one M−H stretching mode. The two broad bands are assigned to the H−F stretching modes. The higher frequency band is very close to that of the molybdenum bifluoride complex at 2682 cm^{-1}.[6] The value of ν(H−F) is higher than that of the bifluoride anion in its salts (1225−1740 cm^{-1}),[16] demonstrating that the hydrogen bonding interaction in the bifluoride ligand is asymmetric. The sharp band at ~2270 cm^{-1} is assigned to the ν(M−H) stretching mode, since it lies close to those found for *trans*-[Pt(PR$_3$)$_2$HCl][17] and *trans*-[Pt(PPh$_3$)$_2$HF] (2240 cm^{-1}).[18] In a complex with a ligand trans to H with low trans influence, such as *trans*-[Pt(PR$_3$)$_2$HCl], the value of (PtH) is very high (~2270 cm^{-1}), whereas, in the parent *trans*-[Pt(PR$_3$)$_2$H$_2$], the IR active modes ν_{asym}(PtH$_2$) have very low frequencies (~1700 cm^{-1}) because of the strong trans influence of hydride.

Two broad bands found at 420−445 cm^{-1} for *trans*-[Pt(PR$_3$)$_2$H(FHF)] are assigned to the metal−fluoride stretching mode. Our assignments are supported by the observation that the bifluoride and the metal fluoride stretching bands disappeared when the bifluoride ligand was exchanged with any other ligands (H$^-$, OTf$^-$, N$_3^-$, PPh$_3$, and pyridine, Figure 7).

Andrews and associates have studied complexes formed between HF and a variety of organic bases by IR spectroscopy in matrixes. For the majority of bases the H−F stretching mode lies above 3000 cm^{-1};[19] even with strong bases such as NMe$_2$H, it lies no lower than 2670 cm^{-1}. In contrast, ν_{asym} of FHF$^-$ has been found at 1377 cm^{-1} in an argon matrix.[20] Our observations of H−F stretching modes of coordinated bifluoride complexes lie in an intermediate region.

Dynamic NMR. To explain the temperature dependence of the NMR spectra, we considered five intermolecular dynamic processes (loss of HF, loss of FHF$^-$, exchange with free FHF$^-$,

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exchange of HF between platinum complexes, and exchange of F^- between platinum complexes (eqs 1−5)) and intramolecular exchange of the fluorine within the bifluoride ligand (eq 6). Asterisks distinguish equivalent atoms.

$$\mathrm{M{-}F{-}H{-}F} \rightleftharpoons \mathrm{MF} + \mathrm{H{-}F} \tag{1}$$

$$\mathrm{M{-}F{-}H{-}F} \rightleftharpoons \mathrm{M}^+ + \mathrm{F{-}H{-}F}^- \tag{2}$$

$$\mathrm{M{-}F{-}H{-}F} + \mathrm{F^*{-}H^*{-}F^{*-}} \rightleftharpoons \mathrm{M{-}F^*{-}H^*{-}F^*} + \mathrm{F{-}H{-}F}^- \tag{3}$$

$$\mathrm{M{-}F{-}H{-}F} + \mathrm{M^*{-}F^*{-}H^*{-}F^*} \rightleftharpoons \mathrm{M{-}F{-}H^*{-}F^*} + \mathrm{M^*{-}F^*{-}H{-}F} \tag{4}$$

$$\mathrm{M{-}F{-}H{-}F} + \mathrm{M^*{-}F^*{-}H^*{-}F^*} \rightleftharpoons \mathrm{M{-}F{-}H{-}F^*} + \mathrm{M^*{-}F^*{-}H^*{-}F} \tag{5}$$

$$\mathrm{M{-}F{-}H{-}F^*} \rightleftharpoons \mathrm{M{-}F^*{-}H{-}F} \tag{6}$$

Free bifluoride anion is expected to exchange with coordinated bifluoride if eq 3 applies. In addition to measurements on the complexes on their own, we therefore carried out experiments in which a solution of bifluoride as dry $[\mathrm{Bu_4N}]$-FHF was mixed with the complex *trans*-$[\mathrm{Pt(PCy_3)_2H(FHF)}]$ in $[^2\mathrm{H}_8]$-THF. Variable-temperature NMR spectra were recorded at 300 MHz for the following solutions: (a) a solution of each bifluoride complex alone both in $[^2\mathrm{H}_8]$-THF and in $[^2\mathrm{H}_8]$-THF/$[^2\mathrm{H}_8]$-toluene mixtures; (b) a solution of $[\mathrm{Bu_4N}]$FHF in $[^2\mathrm{H}_8]$-THF; (c) a solution of a 1:1 mixture of $[\mathrm{Bu_4N}]$FHF and bifluoride complex; (d) a solution of a 2:1 mixture of $[\mathrm{Bu_4N}]$-FHF and bifluoride complex.

It is instructive to consider first the high-temperature spectra of the pure complexes together with the chemical evidence. The solutions of these complexes in THF are stable for months, and there is no sign of etching of the glass. Moreover, we have been unable to abstract HF by adding bases such as triethylamine or pyridine. We therefore exclude loss of HF (eq 1). The room-temperature ^{1}H NMR spectrum shows the hydride resonance as a doublet with platinum satellites; the splitting arises from coupling to the proximal fluoride and is essentially temperature independent. This evidence demonstrates that the Pt−F bond remains intact and that loss of FHF^- (eq 2) is insignificant under these conditions, as is exchange of proximal with distal fluorine (eq 6). These conclusions are confirmed by the room-temperature ^{19}F NMR spectra showing the proximal fluorine as a doublet with platinum satellites (Figure 3).

We now turn to the effect of cooling on the NMR spectra of solutions of the pure complexes. The acidic proton resonance appears as a broad singlet at δ 11.6 at room temperature. Upon cooling, this resonance separates and sharpens into a doublet ($T_c \sim 265$ K) and at lower temperatures into a distorted doublet of doublets ($T_c \sim 220$ K). The spectrum is sharpest at 210 K; even then, this spectrum shows sharp outer peaks with broader inner peaks (Figure 2b). Upon cooling further (with THF/toluene mixtures, we have measured down to 165 K), the inner resonances broaden again. Over the complete temperature range, the chemical shift of the acidic proton changes by only ∼0.3 ppm, suggesting that exchange with species of different chemical shift is insignificant. The resonance of the hydride proton shows little temperature dependence. In the ^{19}F NMR spectrum, the resonance of the proximal fluorine is a doublet with platinum satellites at room temperature but resolves into a complex multiplet upon cooling. The resonance of the distal fluorine is broad at room temperature and resolves into a doublet of doublets upon cooling. By 213 K, the dd pattern is clear and well resolved.

Table 3. Apparent Rate Constants and Second Order Rate Constants Simulated for Intermolecular Exchange for *trans*-$[\mathrm{Pt(PCy_3)_2H(FHF)}]$ in THF Solution

temp (K)	k_4^{app} ($\times 10^2$ s^{-1})	k_4 (dm^3 mol^{-1} s^{-1})	k_5^{app} (s^{-1})	k_5 (dm^3 mol^{-1} s^{-1})
290	8.0	2.00×10^4	4.69×10^3	1.17×10^5
285	8.0	2.00×10^4	3.79×10^3	9.48×10^4
275	8.0	2.00×10^4	2.85×10^3	7.13×10^4
270	8.0	2.00×10^4	2.04×10^3	5.10×10^4
265	8.0	2.00×10^4	1.62×10^3	4.05×10^4
260	8.0	2.00×10^4	1.1×10^3	2.75×10^4
255	8.0	2.00×10^4	9.8×10^2	2.45×10^4
250	8.0	2.00×10^4	7.28×10^2	1.82×10^4
245	8.0	2.00×10^4	6.3×10^2	1.58×10^4
240	8.0	2.00×10^4	4.38×10^2	1.10×10^4
235	5.0	1.25×10^4	3.33×10^2	8.33×10^3
230	2.5	6.25×10^3	2.47×10^2	6.18×10^3
225	1.5	3.75×10^3	1.81×10^2	4.53×10^3
215	1.5	3.75×10^3	1.9×10^2	4.75×10^3

At this stage, only eqs 4 and 5 remain in play for the solutions of the pure complexes. These equations describe intermolecular exchange processes, implying that the rates of exchange should be dependent on the concentration of complex. To test this hypothesis, we recorded 400 MHz ^{1}H NMR spectra at low temperatures for a concentrated sample and then diluted the sample by a factor of ∼10 and recorded the spectrum again at the same temperature. The concentrated sample showed two peaks in the region of the acidic proton, with full width at half maximum (fwhm) of 185 Hz separated by 210 Hz. They were not resolved to the baseline. The peaks in the dilute sample were narrower (fwhm 92 Hz), much better resolved, and further apart (390 Hz separation). These experiments give strong support for intermolecular exchange processes.

Simulation of the NMR spectra of the acidic resonance for *trans*-$[\mathrm{Pt(PCy_3)_2H(FHF)}]$ in THF for these processes was carried out by using the program *g-NMR*.[21] Fitting of the spectra gives the average rate of exchange (Table 3, Figure 8) for a particular exchange process. The exchange is simulated under the assumption of a pseudo-first-order process, yet eqs 4 and 5 require second-order kinetics. We refer to the first-order rate constant from the simulation as k^{app}, and the resulting first-order lifetime $\tau^{\mathrm{app}} = (k^{\mathrm{app}})^{-1}$. By noting the expressions for the half-life of a first-order reaction as $(\ln 2)/k$, and that for a second-order reaction (of type $\mathrm{A} + \mathrm{A} \rightarrow$ products) as $1/k[\mathrm{A}]_0$, we derive an approximate expression for the second-order rate constant as $k^{\mathrm{app}}/([\mathrm{Pt}] \times \ln 2)$, where [Pt] is the concentration of the complex (∼0.06 mol dm^{-3}).[22]

The first process which we simulate is exchange of distal fluoride between Pt centers (eq 5). Such an exchange removes the large coupling on the acidic proton and the distal fluorine, while maintaining the smaller coupling (Figure 8, column 2). This process also maintains the distinction between the two types of fluorine nuclei and maintains the coupling of the hydride to proximal fluorine. Coalescence of the large doublet on the acidic proton occurs when $k_5^{\mathrm{app}} = 2 \times 10^3$ s^{-1}.

Equation 5 does not account for the loss of the smaller coupling between the acidic proton and the proximal fluorine and the corresponding sharpening of the resonances (cf. columns 2 and 3 in Figure 8). We therefore postulate that a second

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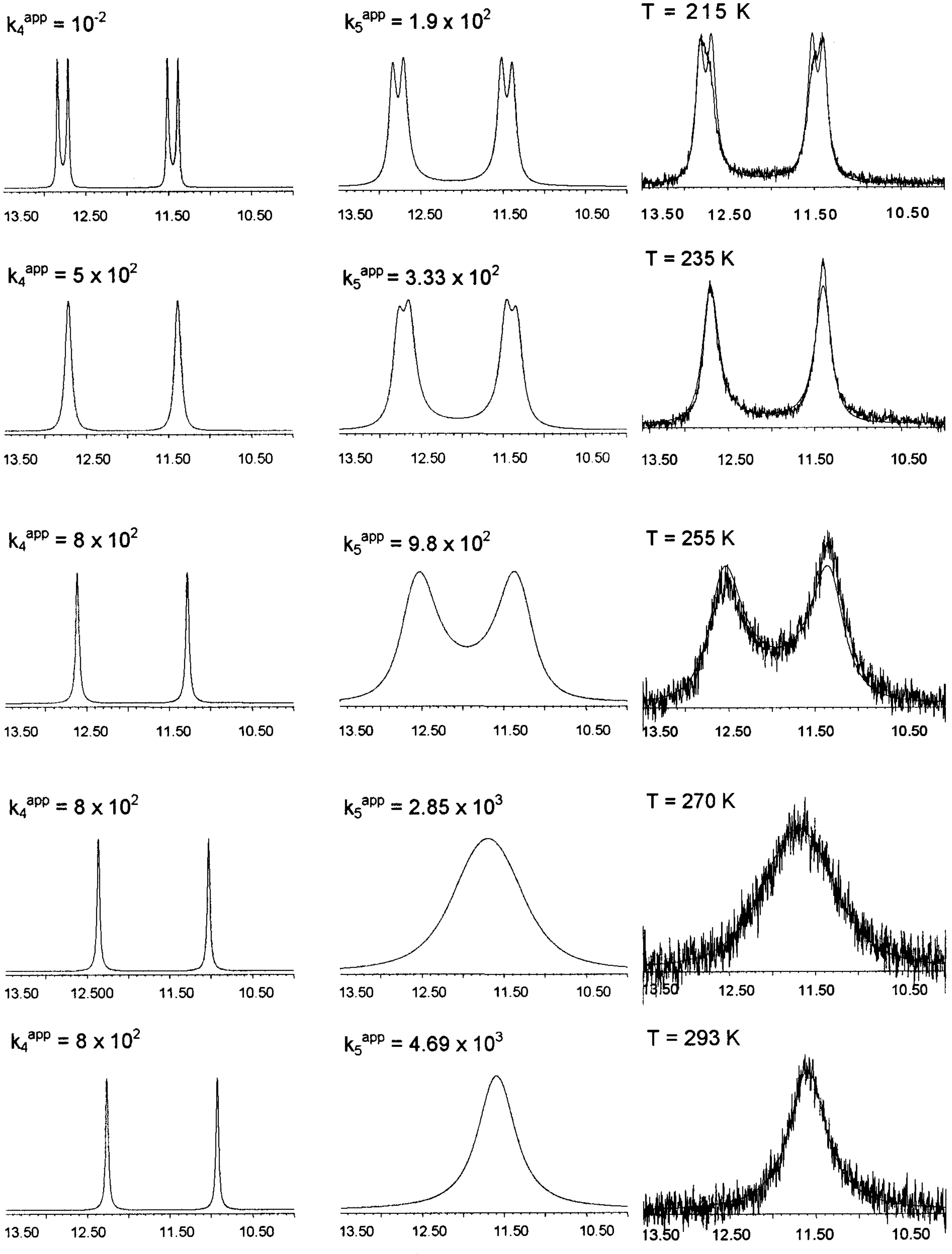


Figure 8. Variable-temperature NMR spectra (300 MHz) in [$^2H_8$]-THF for the acidic proton of *trans*-[Pt(PCy_3)$_2$H(FHF)]. Left-hand column: simulated spectra for exchange as in eq 4. Central column: simulated spectra for exchange as in eq 5. Right column: experimental spectra overlaid with simulated spectra for exchange as in eqs 4 and 5 combined.

process contributes to the exchange, namely the intermolecular exchange of H−F between platinum complexes (eq 4). If this process operated alone, the integrity of the H−F unit and the larger couplings would be maintained, but the couplings of these nuclei to the proximal fluorine would be lost (Figure 8, column 1). Coalescence of the smaller coupling of the acidic proton is predicted when $k_4^{app} = 1.9 \times 10^2$ s^{-1} and is observed around 215−220 K. However, when eqs 4 and 5 operate together, collapse of the smaller doublet of the acidic proton is predicted, followed by collapse of the large doublet splitting, as observed. The simulated spectra for both processes operating together are overlaid with the observed spectra in the third column of Figure 8. The resulting kinetic data are listed in Table 3, and the Eyring plot for k_5 is shown in Figure 9, yielding $\Delta H_5^{\ddagger} = 25.2 \pm 1.0$

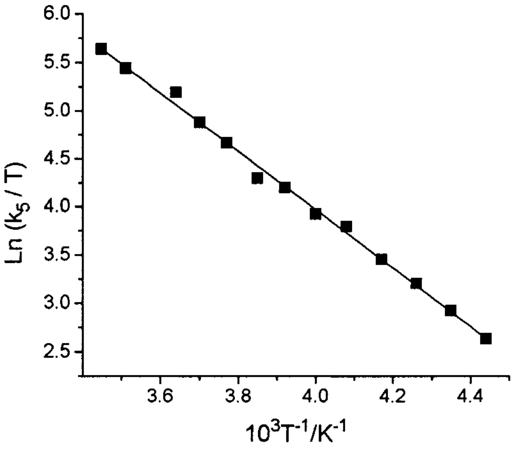


Figure 9. Eyring plot for the simulated rate constant, k_5.

kJ mol^{-1} and $\Delta S_5^{\ddagger} = -61 \pm 4$ J K^{-1} mol^{-1}. Values of k_4 were not sufficiently well determined to deduce reliable enthalpies and entropies of activation, since the simulation is only sensitive to k_4 over a narrow temperature range. The value of $\Delta G_4^{\ddagger}$ is 39 kJ mol^{-1} at 235 K; for comparison, $\Delta G_5^{\ddagger}$ is 39.5 kJ mol^{-1} at 235 K. The changes in the spectra with the concentration described above support the postulated bimolecular exchange. Additionally, the low value of $\Delta H_5^{\ddagger}$ and the very negative value of $\Delta S_5^{\ddagger}$ are fully consistent with a bimolecular process.

The ^{1}H NMR spectra measured at very low temperature show broadening of the inner resonances of the doublet of doublets. This broadening increases upon lowering the temperature, the opposite of expectations for a dynamic exchange process close to the low-temperature limit. Although there could be dynamic processes with very low activation energies which we do not freeze out, this broadening could arise from differences in the relaxation rates of the different spin combinations.[23]

Further dynamic behavior was observed upon addition of [Bu$_4$N]FHF (see the Experimental Section for synthesis of anhydrous [Bu$_4$N]FHF). We first describe the behavior of solutions of [Bu$_4$N]FHF alone. At room temperature in [^{2}H$_8$]-THF, the bifluoride proton is observed as the expected triplet at δ 16.57 (J(HF) = 120 Hz), but on cooling, the outer resonances of the triplet broaden and weaken without change in frequency. This effect probably originates in ion-pair formation. A spectrum of a mixture of [Bu$_4$N]FHF and *trans*-[Pt(PCy$_3$)$_2$H(FHF)] at 193 K corresponds fairly closely to the spectra for the components alone. Upon warming, the resonances of the bifluoride complex and the free bifluoride coalesce into one resonance at δ 13.1 (Figure 10). This can be understood in terms of associative exchange of bifluoride (eq 3).

Ligand Replacement and Reactivity. The bifluoride complexes, *trans*-[Pt(PR$_3$)$_2$H(FHF)], might be expected to lose HF on reaction with base. We did not succeed in removing HF with pyridine, Et$_3$N, NaH, or [NMe$_4$]F. Nevertheless, other products were identified in the reactions with pyridine and sodium hydride (see below). However, reaction with anhydrous CsOH in THF yielded evidence for *trans*-[Pt(PCy$_3$)$_2$(H)F] together with traces of PF$_6^-$. Reasoning that the latter arose from HF, we repeated the reaction with CsOH in the presence of [NMe$_4$]F. Under these conditions, we obtained clean conversion to *trans*-[Pt(PCy$_3$)$_2$(H)F] (see Table 4).

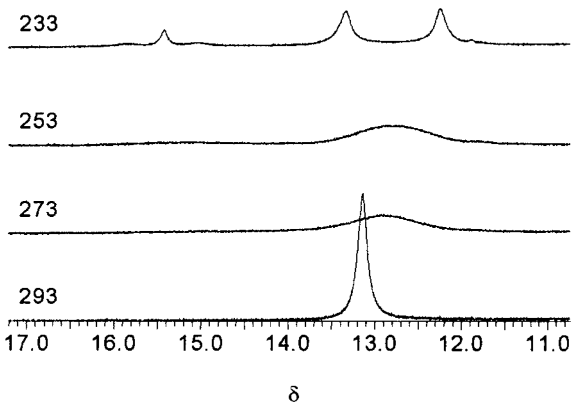
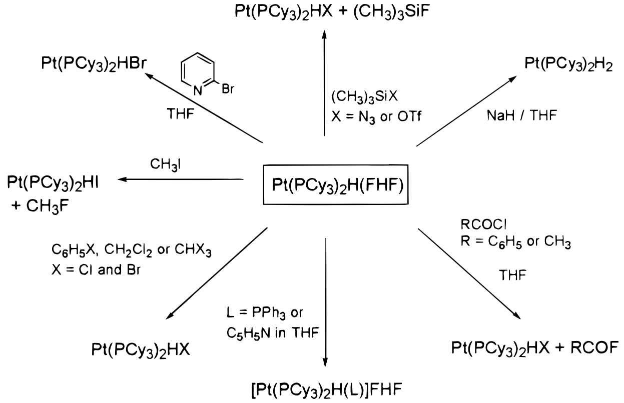


Figure 10. Variable-temperature ^{1}H NMR spectra (300 MHz) of Pt(PCy$_3$)$_2$H(FHF) + [Bu$_4$N]FHF in [^{2}H$_8$]-THF.

Scheme 1. Ligand Replacement Reactions of *trans*-[Pt(PCy$_3$)$_2$H(FHF)]



Reaction of *trans*-[Pt(PCy$_3$)$_2$H(FHF)] with NaH in dry THF regenerates *trans*-[Pt(PCy$_3$)$_2$H$_2$]. The same complex reacts with Me$_3$SiX (X = N$_3$ or OTf) in THF to give the products *trans*-[Pt(PR$_3$)$_2$HX], which have been fully characterized (Scheme 1). The ^{1}H NMR spectrum of the triflate complex shows a triplet resonance with platinum satellites at δ −27.1 (J(PH) = 14 Hz and J(PtH) = 1548 Hz), which is assigned to the hydride ligand. The corresponding resonance of the azide complex is found at δ −18.9 (J(PH) = 13 Hz and J(PtH) = 1132 Hz). Further NMR data are listed in Table 4.

The IR spectrum of the platinum hydride triflate complex showed a band at 2359 cm^{-1} for the Pt−H stretching mode and two bands at 1311 and 1204 cm^{-1} which were assigned to ν(SO$_3$) and ν(CF$_3$) of the OTf ligand. A further band at 623 cm^{-1} was assigned to the δ_a(SO$_3$) vibrational mode. These values agree well with reported values.[24] The IR spectrum of the platinum hydride azide complex shows a sharp band at 2185 cm^{-1} and a strong band at 2030 cm^{-1}, which were assigned to ν(Pt−H) and the azide stretching mode, respectively (Figure 7).[25]

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(23) The effect of relaxation on the low-temperature ^{1}H NMR spectrum of the acidic proton may be considered as follows. With the usual conventions for labeling the spins and the same signs for the coupling constants, the outer transitions are labeled $\alpha\alpha\alpha \rightarrow \beta\alpha\alpha$ and $\alpha\beta\beta \rightarrow \beta\beta\beta$ (written in the order proton, fluorine, fluorine). The inner lines arise from the transitions $\alpha\alpha\beta \rightarrow \beta\alpha\beta$ and $\alpha\beta\alpha \rightarrow \beta\beta\alpha$. The spin states of the inner lines are subject to zero quantum relaxation processes of the fluorine nuclei, usually labeled W$_0$ (e.g., $\alpha\beta\alpha \rightarrow \alpha\alpha\beta$), in addition to single-quantum processes (W$_1$). When the temperature is very low, the W$_0$ processes may contribute significantly to the spectral density function, resulting in broad inner lines and sharp outer lines, especially when the spectral density profile varies rapidly with ω. Harris, R. K. In *Nuclear Magnetic Resonance Spectroscopy;* Pitman: London, 1983.

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Table 4. NMR Data (δ/ppm, *J*/Hz C_6D_6) for Complexes of the Type *trans*-$[Pt(PCy_3)_2HX]$ and *trans*-$[Pt(PCy_3)_2H(L)](FHF)$

complex	$\delta(^1H)$ hydride	$\delta(^{19}F)$	$\delta(^{31}P)$	*J*(PtP)	*J*(PtH)	*J*(PH)
$Pt(PCy_3)_2(H)F$	−24.4 dt	−293.0, *J*(HF) = 88, *J*(PF) = 11, *J*(PtF) = 402	42.1	2938	1115	13
$Pt(PCy_3)_2(H)Cl$	−17.9 t		39.1	2813	1250	13
$Pt(PCy_3)_2(H)Br$	−16.7 t		38.6	2792	1302	12
$Pt(PCy_3)_2(H)I$	−14.05 t		37.6	2747	1330	12
$Pt(PCy_3)_2(H)N_3$	−18.9 t		40.9	2776	1132	13
$Pt(PCy_3)_2(H)(OTf)$	−27.1 t	−75.5 (CF_3)	45.8	2838	1548	14
$[Pt(PCy_3)_2(H)(PPh_3)]FHF$	−6.1 dt	−171	34.5 d	2530	778	15
	14.1 (acidic)		20.5 t, *J*(PP) = 19	2280		160
$[Pt(PCy_3)_2(H)\ (C_5H_5N)]FHF$	−19.3 t 12.8	−175	36.5	2706	1050	13

Reaction of *trans*-$[Pt(PCy_3)_2H(FHF)]$ with triphenylphosphine or pyridine resulted in displacement of the bifluoride ligand to form the complexes *trans*-$[Pt(PCy_3)_2(H)L](FHF)$ (L = PPh_3, pyridine) which were identified by NMR spectroscopy (Table 4, Scheme 1). The triphenylphosphine complex exhibits a hydride resonance at δ −6.1 (dt, $J = 160$, 15 Hz) with a large coupling to the trans phosphine ligand and smaller couplings to the *cis*-PCy_3 ligands. The bifluoride is characterized by a broad resonance in the ^1H NMR at δ 14.1 and in the ^{19}F NMR spectrum at δ −171. The absence of a high-field resonance in the ^{19}F NMR spectrum supports our assignment of the bifluoride as a counterion and not a ligand. However, it is likely that there is association between the platinum cation and the bifluoride anion. The identification of the pyridine analogue was made similarly.

The complex, *trans*-$[Pt(PCy_3)_2H(FHF)]$, undergoes exchange of halide in the reaction with various halo-organic compounds in THF. In the cases of CH_3I, CH_3COCl, and C_6H_5COCl, we have established the formation of CH_3F, CH_3COF, and C_6H_5COF (Scheme 1, NMR data in Table 4), together with the corresponding halo complex $[Pt(PCy_3)_2(H)X]$ (X = Cl, I). Reactions with CH_2Cl_2, $CHBr_3$, $CHCl_3$, C_6H_5X (X = Cl, Br, I), and 2-bromopyridine also result in the formation of platinum halo complexes $[Pt(PCy_3)_2(H)X]$ (X = Cl, Br, I) (Scheme 1). The organic products of this group of reactions have not been investigated.

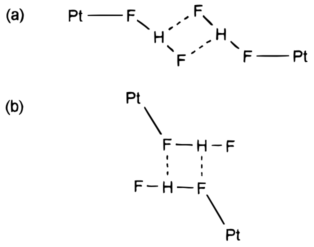
C−F Activation. The bifluoride complexes can also be synthesized by a C−F activation route. Reaction of *trans*-$[Pt(PCy_3)_2H_2]$ with hexafluorobenzene in the presence of $[NMe_4]F$ yields the bifluoride complex *trans*-$[Pt(PCy_3)_2H(FHF)]$ and *trans*-$[Pt(PCy_3)_2H(C_6F_5)]$ in a ratio of 1:13 (eq 7). The latter was characterized by Stone et al. following C−H activation of C_6F_5H with $Pt(PCy_3)_2$.[26] A control experiment showed no reaction between *trans*-$[Pt(PCy_3)_2H_2]$ and $[NMe_4]F$.

$$\textit{trans}\text{-}Pt(PCy_3)_2H_2 \xrightarrow[\text{THF/50 °C}]{C_6F_6,\ NMe_4F} \textit{trans}\text{-}Pt(PCy_3)_2H(C_6F_5) + \textit{trans}\text{-}Pt(PCy_3)_2H(FHF) \quad (7)$$

Discussion

Detailed spectroscopic analysis has enabled us to characterize two platinum bifluoride complexes. Their IR and NMR spectra make it evident that the hydrogen bond is far from symmetric and that they should be described as containing the Pt−F⋯H−F moiety. Nevertheless, the vibrational frequency of the HF unit is lower than that for typical HF adducts with organic bases. It is also a surprise that simple removal of HF is so difficult, occurring only with CsOH. Instead of removal of HF, we find that the entire FHF unit may be replaced by a variety of reagents.

Chart 1. Transition States for Bimolecular Exchange of (a) Distal Fluoride as in Eq 5 and (b) HF as in Eq 4



The analysis of the dynamic NMR spectra shows exchange of hydrogen fluoride or of the distal fluoride between platinum centers (eqs 4 and 5). The intermediates and transition states for these exchange processes must contain at least two platinum centers linked by hydrogen bonds. Such networks would facilitate the exchange process (Chart 1).

This investigation demonstrates the importance of hydrogen bonding to metal fluoride complexes. Such possibilities need to be considered[3] as awareness grows that the metal−fluorine bond coexists with traditional soft ligands[9,27] and that transition metal−fluoride complexes have significant applications in catalysis.[28,29] There has also been considerable recent interest in the determination of coupling constants between nuclei linked by a hydrogen bond.[30,31] The bifluoride unit offers opportunities for such couplings, but *J*(FF) is only accessible by calculation in free FHF^-. Our work provides experimental values of 103 Hz for this coupling in both platinum bifluoride complexes, compared to a calculated value of 225 Hz in the free bifluoride ion.

Conclusions

Two platinum bifluoride complexes, *trans*-$[Pt(PCy_3)_2H(FHF)]$ and *trans*-$[Pt(P^iPr_3)_2H(FHF)]$, have been synthesized by reaction of the corresponding dihydride complexes with $NEt_3{\cdot}3(HF)$ or via C−F activation of C_6F_6. The NMR and IR spectra show that the bifluoride ligand involves a hydrogen bond Pt−F⋯H−F. The distal fluoride of the bifluoride ligand undergoes exchange between two platinum centers, and exchange of HF between platinum centers occurs similarly. The bifluoride ligand can be replaced easily by anionic ligands (e.g. OTf^-) or neutral ligands, such as PPh_3 or pyridine. The bifluoride complex, *trans*-

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$[Pt(PCy_3)_2H(FHF)]$, may be converted to *trans*-$[Pt(PCy_3)_2(H)F]$ by reaction with CsOH in the presence of $[NMe_4]F$.

Experimental Section

All syntheses and manipulations were carried out under argon using standard Schlenk (10^{-2} mbar) and high-vacuum techniques (10^{-4} mbar) or in a glovebox. Ether, toluene, benzene, hexane, and tetrahydrofuran (Fison AR or HPLC grade) were dried over sodium/benzophenone and distilled under argon. Ethanol (Fison AR grade) was dried over magnesium turnings and iodine and distilled under argon. The dried solvents were stored under argon in ampules fitted with a Young's ptfe cap. All deuterated solvents, $[^2H_6]$-benzene, $[^2H_8]$-toluene, and $[^2H_8]$-tetrahydrofuran (Goss Scientific) were dried over potassium and vacuum distilled prior to use. All NMR tubes (Wilmad 528-PP) either were fitted with a Young's tap to allow sealing under argon atmosphere or were flame sealed under vacuum.

Most NMR spectra were recorded on a Bruker MSL300 (^1H recorded at 300.13 MHz, ^{19}F at 282.35 MHz, ^{31}P at 121.49 MHz) or Bruker AMX500 spectrometer (^1H recorded at 500.13 MHz, ^{19}F at 470.4 MHz, ^{31}P at 202.46 MHz). The temperature of the spectrometer was calibrated with an internal capillary containing 4% MeOD in MeOH.[32] ^{19}F NMR spectra with ^1H decoupling were recorded on a Bruker DRX400 spectrometer, as were ^1H spectra with ^{19}F decoupling. Simulations were carried out with *g-NMR*.[21] Mass spectra were recorded on a VG Autospec instrument and are quoted for ^{195}Pt.

Chemicals were obtained from the following sources: potassium tetrachloroplatinate was supplied by Aldrich (or recovered from platinum residues by a standard procedure); PCy_3, P^iPr_3, $[NMe_4]F$, $[NBu_4]F\cdot 3H_2O$, and $NEt_3\cdot 3HF$ were supplied by Aldrich, Me_3SiOTf was obtained from Gelest, and Me_3SiN_3 was synthesized by standard methods.

$[NMe_4]F$ was dried by heating at 50−55 °C under high vacuum ($1-2 \times 10^{-4}$ mbar) for several days.[33] It was dissolved in dry 2-propanol and the volume of the solvent reduced to precipitate most of the material as $[NMe_4]F\cdot(^iPrOH)_x$. The mother liquor was decanted off. The 2-propanol was removed from the crystallized material under dynamic vacuum and then under high vacuum for a few days. The NMR spectrum of the product showed no signs of bifluoride or water. $[NBu_4]$-FHF was synthesized by heating $[NBu_4]F\cdot 3H_2O$ at 90 °C under high vacuum for 48 h.[34] Under these conditions the only involatile product should be anhydrous $[NBu_4]FHF$. A room-temperature ^1H NMR spectrum of our product in dry $[^2H_8]$-THF showed a 1:2:1 triplet at δ 16.57 ($J(HF) = 120$ Hz) and fwhm 24 Hz. The ^{19}F NMR spectrum showed a doublet at δ −150.2 ($J(HF) = 118$ Hz, fwhm = 25 Hz); both are consistent with $[NBu_4]FHF$.

Synthesis of Platinum Dihydride Complexes. The complexes *trans*-$[Pt(PR_3)_2H_2]$ (R = Cy, ^iPr) were prepared according to the literature procedures.[26,35]

Synthesis of *trans*-$[Pt(PCy_3)_2H(FHF)]$. *trans*-$[Pt(PCy_3)_2H_2]$ (0.5 g, 0.66 mmol) was dissolved in THF (50 cm^3) in a Schlenk tube, and a 3-fold excess of $NEt_3\cdot 3(HF)$ (0.32 g, 1.98 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the product was dissolved in benzene and filtered through a cannula and dried under vacuum. The product was recrystallized from THF/hexane at −30 °C to give white crystals (yield 76%). Anal. Found: C, 53.87; H, 8.73. Calcd for $C_{36}F_2H_{68}P_2Pt$: C, 54.38; H, 8.60. Mass spectra (FAB-MS): $m/z = 795$ (M^+), 755 for ($M^+ - 2HF$).

The ^1H NMR spectrum shows a complicated multiplet at δ 1.2−2.4 which is assigned to the cyclohexyl protons. Other NMR data are listed in Table 1. IR (Nujol ν/cm^{-1}): 2630 (m, br), 2604 (m, br), 1832 (s), 1342 (w), 1302 (w), 1262 (w), 1110 (w), 1003 (m), 970 (w), 848 (m), 745 (w), 717 (w), 514 (w), 490 (w), 442 (w), 426 (w).

Synthesis of *trans*-$[Pt(P^iPr_3)_2H(FHF)]$. This complex was prepared in identical fashion to *trans*-$[Pt(PCy_3)_2H(FHF)]$. The product was recrystallized from hexane at −30 °C to give white crystals (yield 65%). Anal. Found: C, 38.9; H, 8.19. Calcd for $C_{18}F_2H_{44}P_2Pt$: C, 38.8; H, 7.96. MS (FAB): $m/z = 555$ (M^+), 515 ($M^+ - 2HF$).

The ^1H NMR spectrum shows a multiplet at δ 1.4 which is assigned to the CH_3 protons of the isopropyl groups and a complicated multiplet at δ 2.52 assigned to the C−H protons of the isopropyl group. Other NMR data are listed in Table 1. IR (Nujol ν/cm^{-1}): 2532 (b), 2273 (m), 1903 (s), 1242 (sh), 1230 (m), 1159 (w), 1094 (w), 1061 (w), 1032 (m), 928 (w), 885 (w), 849 (w), 670 (m), 581 (w), 528 (w), 424 (m, br).

Synthesis of *trans*-$[Pt(PCy_3)_2(H)N_3]$. *trans*-$[Pt(PCy_3)_2H(FHF)]$ (0.1 g, 0.125 mmol) was dissolved in THF (20 cm^3) in a Schlenk tube, and $(CH_3)_3SiN_3$ (0.0144 g, 0.125 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h, and the solvent was then removed under vacuum. The product was extracted with benzene and then dried under vacuum. The product was recrystallized from THF/hexane at −30 °C to give white crystals (yield 80%). Anal. Found: C, 54.15; H, 8.51; N, 5.05. Calcd for $C_{36}H_{67}N_3P_2Pt$: C, 54.12; H, 8.45; N, 5.26. MS (FAB): m/z 798 (M^+), 755 ($M^+ - HN_3$).

The ^1H NMR spectrum shows a complicated multiplet at δ 1.0−2.4 for the cyclohexyl groups. Other data are listed in Table 4. IR (Nujol ν/cm^{-1}): 2180 (s), 2036 (vs), 1340 (vw), 1392 (vw), 1294 (m), 1264 (w), 1171 (m), 1128 (w), 1108 (w), 915 (vw), 896 (w), 888 (w), 865 (s), 816 (vw), 741 (s), 542 (w), 512 (m), 490 (m), 453 (vw), 427 (vw), 409 (vw), 402 (vw), 396 (vw), 336 (vw).

Synthesis of *trans*-$[Pt(PCy_3)_2H(OTf)]$. *trans*-$[Pt(PCy_3)_2H(FHF)]$ (0.1 g, 0.125 mmol) was dissolved in THF (20 cm^3) in a Schlenk tube, and $(CH_3)_3SiOTf$ (0.027 g, 0.125 mmol) was added to the solution. The mixture was stirred at room temperature for 2 h, and the solvent was then removed under vacuum. The product was extracted with hexane (50 cm^3). The solution volume was then reduced to ~10 cm^3, and white crystals formed at −30 °C (yield 80%). Anal. Found: C, 49.57; H, 7.26. Calcd for $C_{37}F_3H_{67}O_3P_2PtS$: C, 49.05; H, 7.45. MS (FAB): m/z 905 (M^+), 755 ($M^+ - OTf$).

The ^1H NMR spectrum shows a complicated multiplet at δ (1.2−2.4) for the cyclohexyl protons. Other data are listed in Table 4. IR (Nujol ν/cm^{-1}): 1311 (m), 1232 (w), 1204 (m), 1159 (w), 1114 (vw), 1073 (vw), 1014 (s), 888 (w), 851 (w, sh), 842 (w), 818 (vw), 806 (vw), 721 (m), 632 (m), 523 (m), 471 (vw), 404 (vw), 380 (vw).

Platinum Dihydride $[Pt(PCy_3)_2H_2]$ with Hexafluorobenzene. [*trans*-$Pt(PCy_3)_2H_2$] (0.5 g, 0.66 mmol) was dissolved in THF (60 cm^3) in a Schlenk tube, and a 2-fold excess of dried C_6F_6 (0.24 g, 1.3 mmol) and an excess of dried tetramethylammonium fluoride were added. The Schlenk tube was heated at 50 °C for 48 h, yielding a mixture of 5% *trans*-$[Pt(PCy_3)_2H(FHF)]$ and 65% of *trans*-$[Pt(PCy_3)_2H(C_6F_5)]$, according to NMR spectroscopy. The bifluoride complex *trans*-$[Pt(PCy_3)_2H(FHF)]$ was extracted with hexane. The reaction products were characterized by ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy.

Reaction of *trans*-$[Pt(PCy_3)_2H(FHF)]$ with CsOH. *trans*-$[Pt(PCy_3)_2H(FHF)]$ (0.1 g, 0.125 mmol) was dissolved in THF (20 cm^3) in a Schlenk tube. The solution was added to a mixture of excess solid $[NMe_4]F$ (~20 mg) and CsOH (~20 mg) under argon. The resulting suspension was stirred at room temperature for 1 h, and the solvent was then removed under vacuum. The product was extracted with hexane (30 cm^3) and then dried under vacuum to yield a white product. IR (Nujol ν/cm^{-1}): 2235 (w), 2236 (m), 1296 (vw), 1294 (m), 1267 (w), 1173 (m), 1128 (w), 1109 (w), 1070 (m), 1003 (m), 916 (vw), 898 (w), 887 (w), 865 (s), 848 (s), 819 (vw), 739 (s), 721 (s).

Acknowledgment. We acknowledge financial support from the EPSRC and the University of York for a studentship. We wish to thank Professor B. Mann, Dr. S. B. Duckett, and C. Aspley for help and advice.

JA0010913

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