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Metal−Alkyl Bond Protonolysis Studies of (dfepe)Pt(Me)X Complexes in Acidic Media

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Protonolyses of (dfepe)Pt(Me)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; X = O_2CCF_3, OSO_2H, OSO_2CF_3, OSO_2F) complexes in their respective neat acid solutions cleanly yield (dfepe)-$Pt(X)_2$ products with rates dependent on relative acid strengths. No $(dfepe)Pt(Me)(X)_2(H)^+$ intermediates were observed by variable-temperature NMR in dichloromethane. The (perfluoroaryl)phosphine analogue $(dfppe)Pt(Me)_2$ (dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$) is much less resistant to protonolysis and rapidly converts to $(dfppe)Pt(OTf)_2$ in HOTf at 20 °C. Kinetic studies for protonolysis in $CF_3CO_2H(D)$ and $CF_3SO_3H(D)$ solvents were carried out. Examination of ionic strength and chloride anion effects in trifluoroacetic acid indicate that prior association of anion to (dfepe)Pt(Me)X systems is not kinetically important. k_H/k_D values were obtained from competitive protonolysis studies (CF_3CO_2H, 9 ± 2 (20 °C); H_2SO_4, 7 ± 2 (100 °C); CF_3SO_3H, 2.7 ± 0.7 (100 °C)). In the case of CF_3CO_2H, separate kinetic runs in protio and deuterio acids gave a lower k_H/k_D value of 3.6(4). The data obtained in these studies do not differentiate between limiting S_E2 and S_E(oxidative) protonolysis mechanisms.

Introduction

The reactivity of metal−carbon bonds forms the basis of organometallic chemistry and is fundamental to our understanding of many important metal-mediated organic transformations.[1] For the most part, classic mechanistic studies of key organometallic transformations such as oxidative addition/reductive elimination of C−X bonds and insertion/deinsertion and nucleophilic or electrophilic cleavage of M−alkyl bonds have focused on electron-rich metal complexes where a $L_nM(\delta^+)-C(\delta^-)$ bond polarity may be reasonably assumed. Less is known, however, about analogous transformations in complexes where M−C bonds are either nonpolar or may even have reversed $L_nM(\delta^-)-C(\delta^+)$ polarity. A classic case in point is the protonolysis of metal−alkyl complexes. Because electron-rich metal centers and metal−alkyl bonds are readily susceptible to electrophilic attack, most organometallic systems are intrinsically incompatible with acidic media:

$$L_nM-R + HX \rightarrow L_nM-X + R-H$$

We have reported that the reactions of $(dfepe)Pt(Me)_2$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) with the strong acids CF_3CO_2H, CF_3SO_3H, and H_2SO_4 cleanly yield the corresponding methyl complexes (dfepe)Pt(Me)X (X = O_2CCF_3 (**2**), OSO_3H (**3**), OSO_2CF_3 (**4**)).[2] In comparison to conventional organometallics, however, these systems are unusually resistant toward further protonolysis. For example, protonolysis of the Pt−Me bond of **2** in neat trifluoroacetic acid does not occur at significant rates below 100 °C, and complexes **3** and **4** are also moderately stable toward further protonolysis in neat sulfuric acid and triflic acid media at 20 °C. More remarkably, we have recently found that the cationic methyl carbonyl complex $(dfepe)Pt(Me)(CO)^+$ persists for several days at 20 °C in the neat superacid FSO_3H.[3] The resistance of (dfepe)Pt alkyl complexes to protonolysis is attributed to the extremely electron-poor nature of the (dfepe)Pt center relative to $(L)_2Pt$ systems incorporating donor ligands.

Protonolysis reactions for main-group organometallics such as alkylmercury compounds are believed to take place via concerted electrophilic attack at the M−C bond.[4] The situation is more complex, however, for transition-metal systems, which may also react via a stepwise mechanism involving initial protonation at the metal center followed by alkane reductive elimination.[5] This complicating feature is particularly well manifested in Pt(II) protonolysis chemistry, where both concerted and stepwise mechanisms have been proposed for a number of closely related systems.[6−8] Except for a few recent cases where discrete Pt(IV) hydride intermedi-

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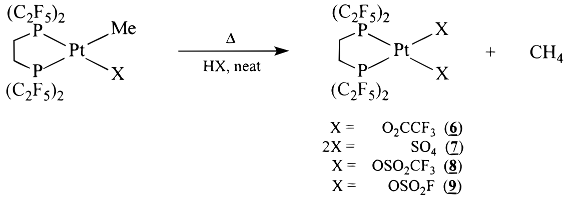
ates have been observed,[9,10] differentiation between concerted and stepwise protonolysis mechanisms has generally relied on indirect k_H/k_D evidence.

We report here that (dfepe)Pt(Me)X complexes undergo protonolysis at moderate temperatures to give the corresponding (dfepe)Pt$(X)_2$ systems as the only detectable products. Since the rates of these conversions may be conveniently followed by ^1H and ^{31}P NMR, we have carried out a series of kinetic studies on (dfepe)Pt complexes in order to gain some insight into the mechanism of protonolysis for these electron-poor fluoroalkylphosphine systems. Although definitive evidence differentiating between $S_E(ox)$ (stepwise) or S_E2 (concerted) was not obtained, this study provides some useful insights regarding the use of neat acids as both the reaction media and the protic reagent in these reactions.

Results

Synthesis of (dfepe)Pt$(X)_2$ (X = O_2CCF_3, O_3SCF_3, OSO_2F) and (dfepe)Pt(SO_4). As discussed above, the reactions of (dfepe)Pt$(Me)_2$ (**1**) with neat CF_3CO_2H, CF_3SO_3H, and H_2SO_4 afford (dfepe)Pt(Me)(X) complexes at ambient temperature. Treatment of **1** with excess fluorosulfonic acid similarly gave (dfepe)Pt(Me)(OSO_2F) (**5**). In trifluoroacetic acid, complete conversion of **2** to (dfepe)Pt$(O_2CCF_3)_2$ (**6**) required warming to 120 °C for 5 days. For the stronger acids H_2SO_4 ($H_0 = -12$) and CF_3SO_3H ($H_0 = -14.1$),[11] complete conversion of the monomethyl derivatives (dfepe)Pt(Me)(OSO_3H) and (dfepe)Pt(Me)(OTf) to (dfepe)Pt$(\eta^2\text{-}SO_4)$ (**7**) and (dfepe)Pt$(OTf)_2$ (**8**) required warming in the appropriate neat acid to 100 °C for 1.5 h and 15 min, respectively (eq 1).



(1)

In fluorosulfonic acid, the strongest acid system examined ($H_0 = -15.1$), protonolysis to give (dfepe)Pt$(OSO_2F)_2$ (**9**) was complete within 4 h at 20 °C.

Complexes **6**−**9** in their respective neat acid solutions exhibit single ^{31}P resonances with $^2J_{PF}$ coupling fine structure. As reported previously for (dfepe)Pt(Me)X derivatives, the observed $^1J_{PtP}$ values (**6**, 3750 Hz; **8**, 4250 Hz; **9**, 4180 Hz) inversely correlate with the expected trans influence (or donor ability) of the anionic ligand: O_2CCF_3 > $OSO_2CF_3^-$ ≈ OSO_2F^-.[12] For **7**, characteristic infrared bands in the region between 1050 and 1250 cm^{-1} which would help distinguish between alternative sulfate coordination modes are obscured by strong dfepe ν(C−F) bands. Nevertheless, the formulation of **7** as an η^2-SO_4 complex rather than (dfepe)Pt$(OSO_3H)_2$ is consistent with analytical data and the absence of any low-field proton NMR resonances due to a bisulfate ligand.[13]

Table 1. Kinetics Data for the Protonolysis of (dfepe)Pt(Me)X (X = O_2CCF_3 (2), OSO_2CF_3 (3))

complex	solvent	temp (°C)	10^5k_{obs} (s^{-1})
(dfepe)Pt(Me)(O_2CCF_3)	CF_3CO_2D	150	2.07(9)
(dfepe)Pt(Me)(O_2CCF_3)	CF_3CO_2H	150	7.39(14)
(dfepe)Pt(Me)(OSO_2CF_3)	CF_3SO_3D	65	3.25(4)
(dfepe)Pt(Me)(OSO_2CF_3)	CF_3SO_3D	80	10.3(1)
(dfepe)Pt(Me)(OSO_2CF_3)	CF_3SO_3D	95	24.3(6)
(dfepe)Pt(Me)(OSO_2CF_3)	CF_3SO_3D	100	45.0(13)

Protonolysis reactions of the perfluoroaryl analogue (dfppe)Pt$(Me)_2$ (**10**; dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$) were also briefly examined. In contrast to (dfepe)Pt(Me)(OTf), which persists in neat triflic acid for several days, addition of **10** to triflic acid at 20 °C resulted in rapid evolution of methane and the clean generation of (dfppe)Pt$(OTf)_2$ (**11**).

Pt(IV) hydride protonation intermediates have recently been characterized by NMR in dichloromethane at low temperatures.[9,10] For (dfepe)Pt(Me)(OTf), however, protonation of the ligated triflate group by triflic acid rather than the metal center takes place.[2] Monitoring (dfepe)Pt(Me)X thermolyses in neat acid by ^1H and ^{31}P NMR likewise did not reveal any detectable Pt(IV) hydride protonation intermediates. Since the protonolysis of (dfepe)Pt$(Me)_2$ with HX is rapid at 20 °C and requires only stoichiometric quantities of acid, the reactions of (dfepe)Pt$(Me)_2$ with both CF_3CO_2H and HCl were followed by variable-temperature NMR in CD_2Cl_2. At −80 °C, only resonances attributable to the unreacted dimethyl complex and the free acids were observed. No changes were noted until −30 °C, whereupon slow conversions to (dfepe)Pt(Me)(O_2CCF_3) and (dfepe)Pt(Me)(Cl) (**12**) took place without any detectable intermediates.

The electrochemistry of (dfepe)Pt(Me)(O_2CCF_3) was briefly examined in order to assess the potential stability of Pt(IV) intermediates. Cyclic voltammetric experiments of (dfepe)Pt$(OTf)_2$ showed no oxidation wave in acetonitrile up to +2.0 V.

Protonolysis Kinetics. From the results described above, it is clear that the rates of protonolysis for (dfepe)Pt(Me)X complexes depend qualitatively on acid strength. Given the clean well-defined nature of these systems and the exceptionally slow rates of protonolysis, the conversions of (dfepe)Pt(Me)X to (dfepe)Pt$(X)_2$ were studied in some detail. Kinetic data are given in Table 1. The rates for protonolysis of (dfepe)Pt(Me)(O_2CCF_3) and (dfepe)Pt(Me)(OTf) in their parent acids were monitored by ^1H NMR. Rate constants were initially evaluated by following the disappearance of the methyl

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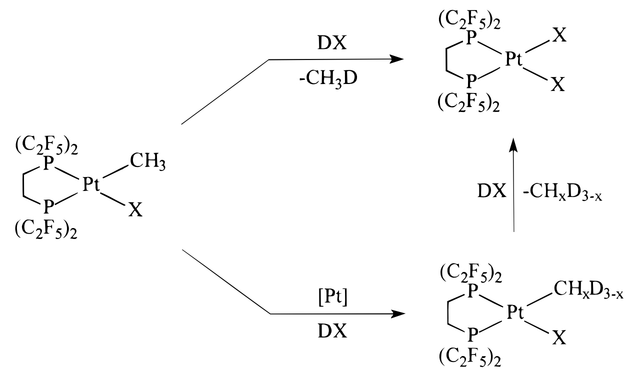
Scheme 1



resonance (integrated versus the dfepe backbone resonance as an internal standard). Preliminary kinetic studies for the formation of **6** in trifluoroacetic acid-*d* gave inconsistent results and showed an apparent rate of disappearance of the Pt−CH_3 resonance that accelerated with time. During the course of these reactions, the methyl resonance of unreacted (dfepe)Pt(Me)(O_2CCF_3) gradually broadened and lost its J_{PH} coupling fine structure, and CH_2D_2 and CHD_3 as well as CH_3D were observed. Small traces of insoluble black material also appeared at latter stages of these kinetic runs. On the basis of these observations we concluded that H/D exchange of the platinum-bound methyl group was being catalyzed by heterogeneous platinum decomposition products *prior* to protonolysis (Scheme 1). Further investigations revealed that the appearance of the black solid and the polydeuterated isotopomers of methane roughly correlated with the presence of small amounts of water in the CF_3CO_2D.[14] Since significant deuteration of the (dfepe)Pt(Me)(O_2CCF_3) methyl group was observed even in the presence of ~5% trifluoroacetic anhydride, kinetic runs were typically monitored for 2−3 half-lives using the integrated intensities of the dfepe backbone resonances, and the observed rates were not corrected for secondary kinetic isotope effects.

In contrast to the complications encountered in the trifluoroacetic acid, kinetic studies for (dfepe)Pt(Me)(OTf) (**4**) in triflic acid-*d* were linear over 3 half-lives (Figure 1) and CH_3D was the only methane product observed. The absence of any detectable heterogeneous decomposition products and H/D scrambling may be due to the lower nucleophilicity of this solvent system. Variable-temperature kinetic data yielded activation parameters of $\Delta H^\ddagger = 17.3 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = -28 \pm 6$ eu for the formation of **8** in DOTf.

Kinetic Isotope Effects. Apparent kinetic isotope effects were measured for the sequential protonolysis of both methyl groups of (dfepe)Pt($Me)_2$ in CF_3CO_2H, CF_3SO_3H, and H_2SO_4 solvents at several temperatures. Evolution of the labeled methane product ratio CH_3D/CH_4 was not followed in situ due to the poor solubility of methane in neat acid solvents. Instead, competitive protonolysis reactions were run in 5:1 DA/HA mixtures, and the volatile products were transferred via syringe to benzene-d_6 for analysis by ^1H NMR. Integrations of CH_4 and CH_3D resonances yielded CH_3D:CH_4 ratios, from which k_H/k_D values were calculated. The results of these studies are presented in Table 2. The protonolysis rates for (dfepe)Pt(Me)(O_2CCF_3) in CF_3CO_2H and CF_3CO_2D were also measured separately (Table 1) at 150 °C and the k_H/k_D was calculated to be 3.6(4).

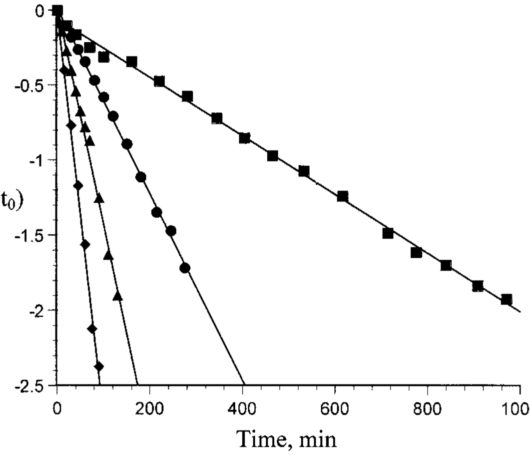


Figure 1. Variable-temperature first-order plots for the protonolysis of (dfepe)Pt(Me)(OSO_2CF_3) (**4**) in triflic acid-*d*: (■) 65 °C; (●) 80 °C; (▲) 95 °C; (◆) 100 °C.

Table 2. Competitive Protonolysis Data for (dfepe)Pt($Me)_2$ in HX/DX Acid Mixtures

	CH4:CH3D ratio		
acid system[a]	(dfepe)Pt(Me)X formation	(dfepe)Pt($X)_2$ formation	temp (°C)
$CF_3CO_2H(D)$	18 ± 2		0
$CF_3CO_2H(D)$	9 ± 1		20
$CF_3CO_2H(D)$		9 ± 2	100
$(D_2)H_2SO_4$	17 ± 1		0
$(D_2)H_2SO_4$	8 ± 1		20
$(D_2)H_2SO_4$		7 ± 2	100
$CF_3SO_3H(D)$	3.4 ± 0.5		0
$CF_3SO_3H(D)$	3.6 ± 0.2		20
$CF_3SO_3H(D)$		2.7 ± 0.7	100

[a] DX:HX ratios were set to 5:1 for all competitive protonolysis experiments. The listed CH_4:CH_3D ratios are corrected for this DX:HX value.

Conjugate Base Effects. A number of earlier studies have reported kinetically significant associative[7] as well as dissociative conjugate anion effects.[8] For comparison, we have investigated the rate dependence of protonolysis of **2** on both overall ionic strength and chloride anion concentration. In the presence of added NH_4Cl an initial metathesis of **2** occurs in CF_3CO_2H to afford (dfepe)Pt(Me)Cl (**12**). No changes in the ^{31}P NMR spectrum of (dfepe)Pt(Me)Cl in the presence of excess chloride anion were noted. Since the protonolysis of both **2** and **12** in CF_3CO_2D at 150 °C in the presence of 0.200 M NaOTf produced nearly identical rates (Figure 2), all kinetic runs with excess Cl^- were carried out using **12**. The kinetic effects of increased total ion concentration (using NaOTf) and [Cl^-] are summarized in Table 3.

Discussion

Protonolysis mechanisms reflect the relative accessibility of metal-based (nonbonding) and M−C σ-bonding orbital electron density.[15] For systems having a σ-bond-localized HOMO, direct M−C bond electrophilic displacement (S_E2) can occur. For systems with metal-

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[14] No additional solution species were noted. The decomposition of (dfepe)Pt compounds in the presence of water may be due to hydrolysis of the perfluorinated ligand.

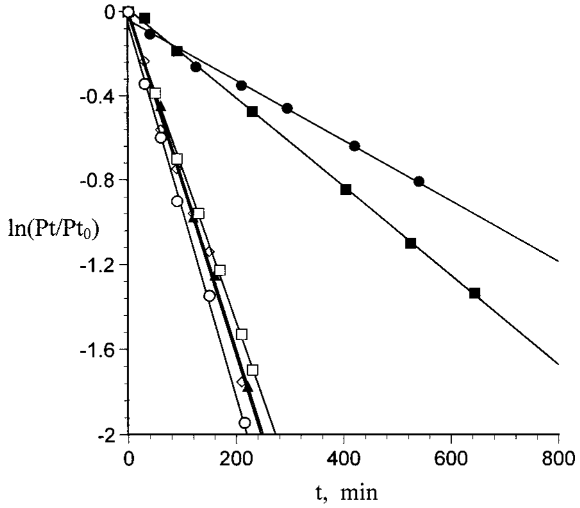

Figure 2. First-order protonolysis plots (CF_3CO_2D, 150 °C) showing the effect of added chloride and ionic strength: (●) (dfepe)Pt(Me)(O_2CCF_3) (0.10 M); (■) (dfepe)-Pt(Me)Cl, (0.10 M); (□) (dfepe)Pt(Me)Cl (0.10 M; 0.20 M NaOTf); (▲) (dfepe)Pt(Me)(O_2CCF_3) (0.10 M; 0.20 M NaOTf); (◇) (dfepe)Pt(Me)Cl (0.10 M; 0.27 M NaOTf); (○) (dfepe)-Pt(Me)Cl (0.10 M; 0.12 M NaOTf, 0.15 M NaCl).

Table 3. Effect of Ionic Strength and [Cl$^-$] on the Protonolysis of (dfepe)Pt(Me)X (X = O_2CCF_3 (2), Cl (12)) Complexes in CF_3CO_2D Solutions at 150 °C

complex	[Pt]$_0$, M	[NaOTf], M	[Cl$^-$], M	10^5k_{obs} (s^{-1})
(dfepe)Pt(Me)(O_2CCF_3)	0.10	0	0	2.07(9)
(dfepe)Pt(Me)(O_2CCF_3)	0.10	0.20	0	13.4(3)
(dfepe)Pt(Me)(Cl)	0.10	0	0	3.51(3)
(dfepe)Pt(Me)(Cl)	0.10	0.20	0	13.5(5)
(dfepe)Pt(Me)(Cl)	0.10	0.27	0	12.1(2)
(dfepe)Pt(Me)(Cl)	0.10	0.12	0.15	14.7(4)

based HOMO's, a stepwise oxidative addition (S_E(oxidative)) mechanism is anticipated. In the case of (dfepe)-Pt(Me)X complexes, slow protonolysis rates together with the previously reported[2] preferential association of excess triflic acid with the triflate ligand rather than the platinum center in (dfepe)Pt(Me)OTf indicate that protonation either at the Pt−Me bond or at the platinum center is not favorable. Our failure to observe any platinum(IV) alkyl hydride intermediates prior to methane loss, therefore, does not help discriminate between S_E2 and S_E(oxidative) mechanisms.

A qualitative measure of the electron-withdrawing ability of the (dfepe)Pt moiety relative to other metal systems is given by platinum−methyl $^1J_{CH}$ data. As shown in Table 4, $^1J_{CH}$ values for X−Me compounds vary in a consistent fashion with the nature of the X group. The variation of $^1J_{CH}$ has been related to changes in the hybridization about the methyl carbon[16] and has been linearly correlated with the product of the electronegativity of the X group and the X−C bond distance.[17] For s- and p-block X groups, an increase of $^1J_{CH}$ with increasing electronegativity is generally observed.

Table 4. Selected $^1J_{CH}$ Data for X−CH_3 Compounds

compound	$^1J_{CH}$, Hz	ref
Main-Group-Metal Systems		
Li−CH_3	98	21
(Me)Be−CH_3	106	22
$(Me)_3Si-CH_3$	118	21
(Me)Zn−CH_3	122	21
H−CH_3	125	16b
(Me)Hg−CH_3	130	22
CF_3-CH_3	130	16a
HO−CH_3	141	16b
X-CH_3	149 (F), 150 (Cl), 152 (Br), 152 (I)	17
"CH_3^{+}"	166	23
Transition-Metal Systems		
Cp_2(Me)Zr−CH_3	115	
Cp^*_2(Me)W−CH_3	123	18
(nbd)(Me)Pt−CH_3	125(2)	19a
trans-$(Me_3As)_2$(CO)Pt−CH_3^+	128(2)	19b
(dmpe)(O_2CCF_3)Pt−CH_3	126	20
Cp^*_2(O)W−CH_3^+	134	18
(dfepe)(O_2CCF_3)Pt−CH_3	139	2
(dfepe)(Cl)Pt−CH_3	137	this work
(dfepe)(CO)Pt−CH_3^+	137	3
(dfepe)(OSO_2F)Pt−CH_3	138	this work

Note that for X = halogen, $^1J_{CH}$ values are essentially invariant; this has been attributed to the counteracting effect of X−CH_3 bond overlap, which depends on both the X−C bond distance and the overlap characteristics of the X bonding orbital.[16] Although this spectroscopic marker has not been generally exploited in organometallic chemistry, methyl $^1J_{CH}$ values appear to correlate well with the effective electronegativity of L_nM and may be particularly useful in comparisons involving closely related metal systems. For example, while a "normal" methyl coupling constant of 123 Hz is reported for $Cp^*_2W(Me)_2$, oxidation to $Cp^*_2W(O)(Me)^+$ results in an increase to 134 Hz.[18] In an extensive series of *cis*- and *trans*-$(L)_2$Pt(X)(Me) complexes where L is a donor ancillary ligand, $^1J_{CH}$ is observed to be relatively insensitive (~125 ± 2 Hz) to substituent effects.[19] A similar value is found for the donor phosphine system (dmpe)Pt(O_2CCF_3)Me (126 Hz),[20] but a significantly higher value of 139 Hz is found for (dfepe)Pt(O_2CCF_3)-Me. Qualitatively we take this to indicate that, while the Pt−Me bond in the former complex is essentially nonpolar, the rehybridization of the methyl carbon induced by the (dfepe)Pt moiety approaches that observed for electronegative elements and the Pt−C bond in (dfepe)Pt(Me)X complexes may therefore be more appropriately described as bearing a partial positive charge on carbon.

Enhanced protonolysis rates in the presence of chloride have been demonstrated in earlier Pt(II) alkyl reactions with HCl.[8] Since these studies indicated that decreased electron density at platinum in some cases favored anion preassociation, conjugate anion and ionic strength effects were also examined for (dfepe)Pt(Me)X. The data in Table 3 reveal that protonolysis rates are sensitive to increasing ionic strength, but there is no kinetic dependence on chloride concentration. Thorn has recently reported a significant trans kinetic effect on

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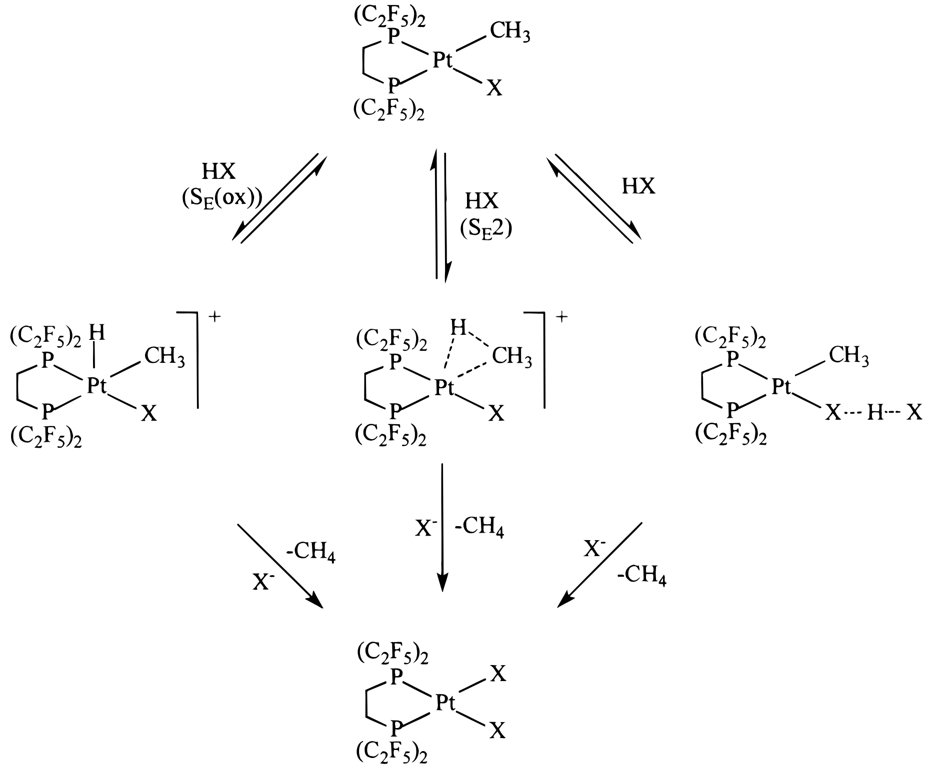
Scheme 2



Pt−Me protonolyses in *trans*-(^{i}Pr$_3$P)$_2$Pt(X)Me systems, with a substantially greater rate of protonolysis observed for X = Cl relative to X = OTf.[24] In contrast, (dfepe)Pt(Me)X compounds are relatively insensitive to the nature of the X group (X = Cl, CF_3CO_2), in keeping with the lesser importance of cis ligand effects in square-planar d^8 chemistry.

The invariance of ^{31}P NMR data for (dfepe)Pt(Me)Cl in the presence of excess chloride indicates that any equilibrium for the formation of an "ate" complex (i.e., [(dfepe)Pt(Me)Cl$_2$]$^-$) must be unfavorable. Thus, despite the electron-poor nature of the (dfepe)Pt moiety a protonolysis pathway involving anion preassociation is not kinetically important. The dependence of the rate of Pt−Me bond cleavage on ionic strength is consistent with a mechanism involving either charge separation or the formation of an explicit cationic intermediate such as [(dfepe)Pt(Me)(X)H]$^+$. The negative entropy of activation found for (dfepe)Pt(Me)(OTf) protonolysis is also consistent with S$_E$2, S$_E$(oxidative), or H−X preassociation with coordinated X,[25] since each of these pathways are associative in nature (Scheme 2). Previous kinetic studies have reported similar negative $\Delta S^‡$ values for protonolysis.[6,8]

The extreme difference in rates of protonolysis for the dimethyl complex **1** and (dfepe)Pt(Me)X complexes suggested that the mode of protonolysis for the first methyl group and the second may be different. Namely, the increased electron density on platinum in (dfepe)Pt(Me)$_2$ may facilitate direct protonation of the metal, whereas direct Pt−C bond protonolysis may be the favored reaction pathway for (dfepe)Pt(Me)X. To probe this, kinetic isotope effects for protonolysis of both the first and second methyl groups in (dfepe)Pt(Me)$_2$ were determined. As seen in Table 2, apparent k_H/k_D(first) and k_H/k_D(second) values in trifluoroacetic, sulfuric, and triflic acids are quite similar.[26] High k_H/k_D values such as those found in trifluoroacetic and sulfuric acid solvents have previously been cited as strong evidence for a concerted S$_E$2 protonolysis mechanism for platinum involving substantial proton transfer in the transition state.[7] However, some of these studies derived k_H/k_D values from internal competition experiments in protic solvents, which are subject to solvent D$^+$/H$^+$ site partitioning effects.[27] In a recent study the protonolysis of (tmeda)Pt(Me)Cl by H(D)OTf in CD_3OD/CH_3OH mixtures yielded an apparent kinetic isotope effect of 9.1(5), whereas separate rate measurements in protio- and deuteriomethanol gave a more "normal" k_H/k_D = 2.3(5).[9b] Separate rate experiments for the protonolysis of (dfepe)Pt(Me)(O_2CCF_3) in CF_3CO_2H and CF_3CO_2D similarly gave a lower k_H/k_D value of 3.6(4). The substantial increase found for CH_4/CH_3D ratios for the first protonolysis step going from T = 20 °C to 0 °C in trifluoroacetic and sulfuric acids is unusual and may reflect a composite of partitioning and temperature effects. The smaller apparent k_H/k_D values observed for triflic acid may reflect a lower importance of H$^+$/D$^+$ partitioning effects in this solvent.

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Summary

The enhanced stability of (dfepe)Pt(Me)(X) complexes toward protonolysis of the remaining methyl group is in keeping with the strongly electron-withdrawing nature of the (dfepe)Pt(X) moiety, which differs from (dfepe)Pt$(Me)_2$ by substitution of an electron-donating group with a poorly donating anion, X^-. The stabilizing effect of dfepe with perfluoroethyl substituents is also found to be significantly greater than the perfluorophenyl analogue dfppe, in keeping with the greater donor ability of perfluoroarylphosphines.[28] Moreover, the quantitative formation of (dfepe)Pt$(X)_2$ products from (dfepe)Pt(Me)X also indicates that phosphine metalation reactions are not significant in these fluorocarbon-modified systems.[24] The failure to observe protonolysis intermediates or significant kinetic differences between the various acid media does not allow us to differentiate between S_E2 and S_E(oxidative) mechanisms. Indeed, since prior association of acid with coordinated conjugate base has been observed for (dfepe)-Pt(Me)(OTf), an additional possibility exists that proton transfer to the Pt−Me group may be mediated by the adjacent X group.

A cautionary note is warranted in light of our observation of heterogeneously catalyzed H/D exchange of DX into coordinated methyl ligands: considerable care must be taken to ensure that traces of heterogeneous decomposition products are not responsible for H/D scrambling prior to alkane loss, especially in systems where this observation is attributed to reversible alkane adduct formation. Finally, the lack of an accessible Pt(II)/Pt(IV) redox couple for (dfepe)Pt$(OTf)_2$ does not preclude redox chemistry for more electron-rich (dfepe)Pt$(Me)_2$ and (dfepe)Pt(Me)(X) derivatives and does not directly probe the ease of oxidative addition but, nevertheless, does suggest that S_E(oxidative) is less likely for (dfepe)Pt systems.

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of purified nitrogen using Schlenk, high vacuum, and/or glovebox techniques. Dry oxygen-free solvents were prepared using standard procedures. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. CF_3SO_3H, CF_3CO_2H, and CF_3CO_2D were distilled prior to use and stored under nitrogen. CF_3SO_3D was prepared by treatment of triflic anhydride (Aldrich) with D_2O followed by the removal of excess anhydride under vacuum. D_2SO_4 was obtained from Cambridge Isotope Laboratories and used as received. Fluorosulfonic acid (Aldrich) was distilled prior to use. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on either a Perkin-Elmer 1600 or a Bomem MB100 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL GSX-400 instrument. ^{31}P NMR spectra were referenced to a 85% H_3PO_4 external standard. (dfepe)Pt$(Me)_2$ and (dfppe)PtMe_2 were prepared as described previously.[2,29]

(dfepe)Pt(Me)(FSO_3) (5). To a flask containing 250 mg (dfepe)Pt$(Me)_2$ (0.315 mmol) was added 20 μL of FSO_3H (0.347 mmol). After the reaction mixture was agitated for 5 min, 5 mL of ether was added and the resulting white precipitate was filtered off, washed repeatedly with ether, and dried under vacuum. The yield of **5** was 0.236 g (86%). Anal. Calcd for $C_{11}H_7F_{21}O_3P_2PtS$: C, 15.09; H, 0.80. Found: C, 14.91; H, 0.92. ^1H NMR ($HFSO_3$, 20 °C): δ 2.96 (m, 2H; PCH_2), 2.63 (m, 2H; PCH_2), 1.44 (br s, 3H; $PtCH_3$). ^{31}P NMR (FSO_3H, 20 °C): δ 84.5 (p, $^2J_{PF} = 62$ Hz, $^1J_{PtP} = 1475$ Hz; P trans to Me), 54.4 (p, $^2J_{PF} = 68$ Hz, $^1J_{PtP} = 5675$ Hz; P trans to OSO_2F). ^{13}C NMR ($HFSO_3$, 20 °C): δ 24.2 (tm, $^1J_{CH} = 141$ Hz; PCH_2), 17.1 (td, $^1J_{CH} = 140$ Hz, $^2J_{PC} = 22$ Hz; PCH_2), 2.9 (qd, $^1J_{CH} = 139$ Hz, $^2J_{PC} = 73$ Hz; $Pt(CH_3)$). ^{19}F NMR ($HFSO_3$, 20 °C): δ −78.00 (s, 6F; PCF_2CF_3), −78.51 (s, 1F; SO_3F), −79.20 (s, 6F; PCF_2CF_3), −107.09 to −110.07 (overlapping ABX multiplets, 8F; PCF_2-CF_3).

(dfepe)Pt(CF_3CO_2)$_2$ (6). A Carius tube fitted with a 4 mm Teflon valve was charged with 0.250 g (0.316 mmol) of (dfepe)-Pt$(CH_3)_2$, and excess CF_3CO_2H (ca. 3 mL) was added via vacuum transfer. After melting, methane was evolved and the tube was cooled to −78 °C and evacuated. The reaction mixture was then heated to 120 °C for 5 days. After cooling, the solution was transferred to a filtration assembly and all volatiles were removed. Ether (10 mL) was added, and the resulting slurry was cold-filtered at −78 °C. Complex **6** was obtained as a light yellow solid (0.140 g, 45%). Anal. Calcd for $C_{14}H_4F_{26}O_4P_2Pt$: C, 17.02; H, 0.40. Found: C, 17.04; H, 0.34. ^1H NMR (CF_3-CO_2D, 20 °C): δ 3.05 (m; PCH_2). ^{31}P NMR (CF_3CO_2D, 20 °C): δ 59.80 ($^1J_{PtP} = 3753$ Hz). IR (cm^{-1}): 1726 (s), 1397 (m), 1302 (m), 1229 (s), 1184 (s), 1145 (s), 1116 (m), 974 (m).

(dfepe)Pt(η^2-SO_4) (7). To a 50 mL flask charged with 0.270 g (0.340 mmol) of (dfepe)Pt$(Me)_2$ was added 1 mL of H_2SO_4 via syringe. After dissolution of the solid and evolution of methane, the flask was attached to a small filtration assembly and the reaction mixture was heated to 100 °C with stirring for 1.5 h. After cooling, the colorless product was precipitated with 30 mL of ether, filtered, washed repeatedly with ether, and dried under vacuum. The yield of **7** was 0.180 g (55%). Anal. Calcd for $C_{10}H_4F_{20}O_4P_2PtS$: H, 0.47; C, 14.01. Found: H, 0.34; C, 13.81. ^1H NMR (D_2SO_4, 27.0 °C): δ 3.03 (m; PCH_2). ^{31}P NMR (D_2SO_4, 27.0 °C): δ 60.2 ($^1J_{PtP} = 4087$ Hz). IR (cm^{-1}): 1317 (s), 1294 (s), 1212 (s), 1179 (m), 1149 (s), 1128 (sh), 1128 (sh), 990 (sh), 973 (m), 862 (m), 842 (w), 812 (w), 754 (m), 672 (m).

(dfepe)Pt$(OTf)_2$ (8). To a 50 mL flask charged with 0.375 g (0.473 mmol) of (dfepe)Pt$(Me)_2$ was added 1 mL of HOTf via syringe. After initial dissolution of the solid and evolution of methane the flask was transferred to a small filtration assembly and the reaction mixture was heated to 100 °C with stirring for 45 min. Upon cooling, the product was precipitated with 30 mL of Et_2O, isolated by filtration, and washed repeatedly with ether. The yield of **8** was 0.452 g (90%). Anal. Calcd for $C_{12}H_4F_{26}O_6P_2PtS_2$: H, 0.38; C, 13.61. Found: H, 0.39; C, 13.36. ^1H NMR (DOTf, 27.0 °C): δ 2.89 (m; PCH_2). ^{31}P (DOTf, 27.0 °C): δ 61.2 ($^1J_{PtP} = 4254$ Hz). IR (cm^{-1}): 1297 (s), 1236 (s), 1196 (s), 1170 (sh), 1159 (s), 1118 (sh), 998 (m), 961 (s), 865 (w), 808 (w), 755 (w).

(dfepe)Pt$(OSO_2F)_2$ (9). To a 10 mL flask containing 250 mg of (dfepe)Pt$(Me)_2$ (0.315 mmol) was added excess $HFSO_3$ (∼1 mL). Methane was evolved, and the solution was stirred at ambient temperature for 24 h. The reaction mixture was rapidly quenched with 10 mL of ether, and the resulting white precipitate was filtered off, washed repeatedly with ether, and dried under vacuum. The yield of (dfepe)Pt$(OSO_2F)_2$ was 0.230 g (76%). Anal. Calcd for $C_{10}H_4F_{22}O_6P_2PtS_2$: C, 12.52: H, 0.42. Found: C, 12.96; H, 0.68. ^1H NMR (FSO_3H, 20 °C): δ 2.24 (m; PCH_2). ^{31}P NMR (FSO_3H, 20 °C): δ 61.4 (m, $^1J_{PtP} = 4187$ Hz). ^{19}F NMR (acetone-d_6, 20 °C): δ −76.18 (s, 6F; PCF_2CF_3), −76.79 (s, 2F; SO_3F), −77.26 (s, 6F; PCF_2CF_3), −105.48 to −109.19 (overlapping ABX multiplets, 12F; PCF_2CF_3).

(dfppe)Pt$(OTf)_2$ (11). The synthesis of **11** follows that described above for **8** and **9**. Samples of **11** which were spectroscopically pure by ^1H and ^{31}P NMR were consistently low in carbon analysis. Anal. Calcd for $C_{28}H_4F_{26}O_6P_2PtS_2$: C, 26.87; H, 0.32. Found: C, 25.73; H, 0.29. ^1H NMR (HOTf, 20

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°C): δ 2.31 (m; PCH_2), ^{31}P NMR (HOTf, 20 °C): δ 4.16 (s, $^1J_{PtP}$ = 4523 Hz). ^{19}F NMR (HOTf, 20 °C): δ −124.7 (s, 8F; PC_6F_5), −136.6 (s, 4F; PC_6F_5), −154.9 (s, 8F, PC_6F_5).

(dfepe)Pt(Me)Cl (12). A 25 mL flask was charged with 0.195 g (0.219 mmol) of **2**, 11.6 mg of H_4NCl (0.219 mmol), and 10 mL of CF_3CO_2H. After the mixture was stirred for 6 h at ambient temperature, all volatiles were removed and 5 mL of ether was added. The resulting slurry was filtered, and the white powder was washed several times with ether and dried under vacuum. The yield of **12** was 0.160 g (90%). Anal. Calcd for $C_{11}H_7ClF_{20}P_2Pt$: C, 16.26; H, 0.86. Found: C, 16.40; H, 0.60. ^1H NMR (acetone-d_6, 20 °C): δ 3.22 (m, 2H; PCH_2), 2.95 (m, 2H; PCH_2), 1.22 (d, $^2J_{PtH} = 58$ Hz, $^3J_{PH} = 7$ Hz, 3H; $PtCH_3$). ^{31}P NMR (acetone-d_6, 20 °C): δ 64.15 ($^1J_{Pt-P} = 4123$ Hz; P-trans Cl), δ 74.11 ($^1J_{Pt-P} = 1332$ Hz; P-trans Me). ^{13}C NMR (CF_3CO_2H, 20 °C): δ 23.1 (tm, $^1J_{CH} = 135$ Hz; PCH_2), 17.1 (td, $^1J_{CH} = 135$ Hz, $^2J_{PC} = 24$ Hz; PCH_2), 4.5 (qd, $^1J_{CH} = 137$ Hz, $^2J_{PC} = 93$ Hz; $Pt(CH_3)$). IR (cm^{-1}): 1299 (m), 1230 (s), 1138 (s), 1103 (sh), 969 (m), 752 (w).

Kinetic Studies. (dfepe)Pt(Me)X protonolyses were monitored by ^1H NMR spectroscopy. In a typical experiment, 41.7 mg (0.0514 mmol) of **12** and 23.5 mg (0.1366 mmol) of NaOTf were placed in a dry 5 mm NMR tube (Wilmad) and dissolved in 0.5 mL of CF_3CO_2D under an N_2 atmosphere. The sample was then sealed under vacuum. Reaction progress was determined by integration of either the $Pt-CH_3$ resonance (in the case of (dfepe)Pt(Me)OTf kinetic runs) versus the total dfepe backbone region or the relative intensities of the partially overlapping dfepe backbone resonances for **2** and **6**. Sufficient digital resolution to allow accurate integrations was employed in all cases.

Kinetic isotope effects for the protonation of **1** were determined by competition experiments in DX/HX mixtures. In a typical run, 50 mg (0.063 mmol) of **1** was weighed into a 5 mm NMR tube (septa seal) and 0.5 mL of acid (thermostated to the appropriate temperature) was added via syringe. Product gases were captured via syringe and transferred to another 5 mm NMR tube containing 0.4 mL of benzene-d_6. Integrations of CH_3D vs CH_4 were carried out using cut and weigh methods (weights ±0.1 mg). Protonations of **2**−**4** at 100 °C were carried out in a similar fashion. After thermolysis the NMR tubes were cooled to −195 °C, opened, and resealed with septa. After slow warming to ambient temperature the gases were captured, transferred, and analyzed as described above.

Electrochemistry. Electrochemical measurements were made under a nitrogen purge using a Paar Model 270 with a platinum electrode and a silver-wire pseudoreference in 0.2 M TBAP. Potentials were corrected using a ferrocene internal reference, taken as +0.40 V versus SCE.

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