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# PROTONATION STUDIES OF ELECTROPHILIC PLATINUM(II) ALKYL COMPLEXES: SYNTHESIS AND CHARACTERIZATION OF (dfepe)Pt(Me)X ($X = O_2CCF_3$, $OSO_2CF_3$, $OSO_3H$)*

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**Abstract**—The platinum methyl complexes (dfepe)Pt(Me)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, $X = O_2CCF_3$, $OSO_2CF_3$, $OSO_3H$) have been prepared by the reaction of $(dfepe)Pt(Me)_2$ with an excess of the corresponding acid, HX. These compounds have been characterized by $^1H$, $^{19}F$ and $^{31}P$ NMR data. $(dfepe)Pt(Me)_2$ and $(dfepe)Pt(Me)(OSO_2CF_3)$ have also been characterized in the solid state by X-ray diffraction. Both of these compounds exhibit short Pt—Me bonds, consistent with the highly electrophilic nature of the (dfepe)Pt moiety. In contrast to analogous donor phosphine systems $(R_3P)_2Pt(Me)_2$, which undergo complete protonolysis and methane loss by HX at −78°C to give $(R_3P)_2Pt(X)_2$, (dfepe)Pt(Me)X complexes are remarkably stable to further protonolysis even in neat strong acid media. In dichloromethane, treatment of $(dfepe)Pt(Me)(OSO_2CF_3)$ with excess $CF_3SO_3H$ results in the association of one equivalent of acid with the bound triflate ligand to form $(dfepe)Pt(Me)((OTf)_2H)$.

The activation of simple alkane C—H bonds by aqueous $Pt^{2+}/Pt^{4+}$ mixtures was reported by Shilov and coworkers a number of years ago.[1] More recently, these systems have been examined in some detail by Bercaw and coworkers[2] and others,[3] with the eventual goal of devising electrophilic C—H activation systems compatible with oxidizing media. The selective oxidation of methane in neat sulfuric acid by $Hg^{2+}$ has recently been reported and has also stimulated considerable practical interest in the alkane chemistry of late metal electrophiles.[4] A key proposed step in electrophilic alkane activation is the heterolysis of a C—H bond to generate a metal–alkyl complex [eq. (1)]:

$$L_nM^+ + R\text{—}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_nM\text{—}R + H^+ \qquad (1)$$

The reverse of this process, protonolysis of a metal alkyl bond, is a common reaction mode for organometallic systems. The equilibrium described above should be sensitive to the electrophilicity of the metal center: given a sufficiently electrophilic and coordinatively unsaturated metal center, $k_1$ should be favored over $k_{-1}$ and the equilibrium should be shifted to the right. However, this fundamentally important transformation has not been observed directly.

As part of our continuing studies examining the coordination properties of electron-withdrawing (fluoroalkyl)phosphine chelates, we recently reported the synthesis and reactivity properties of the platinum dialkyl and diaryl complexes $(P_2)PtR_2$ ($P_2 = (C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ ("dfepe"), $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$; R = Ph, Me).[5] This work suggested that the $(dfepe)Pt^{2+}$ moiety is exceptionally electrophilic and stable to ancillary phosphine degradation. Accordingly, we have begun to examine the reactivity properties of $(dfepe)Pt^{2+}$ systems relating to eq. (1). Here we report that protonolysis of $(dfepe)Pt(Me)_2$ by the

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* Dedicated to Professor John E. Bercaw, on the occasion of his 50th birthday.

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strong acids $CF_3CO_2H$, $CF_3SO_3H$, or $H_2SO_4$ cleanly yield (dfepe)Pt(Me)X complexes incorporating the corresponding conjugate base. The remarkable stability of these (dfepe)Pt(Me)X complexes toward further protonation in neat strong acid media is of particular significance and may have some bearing on the heterolysis equilibrium shown in eq. (1).

## 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. $CF_3SO_3H$ (Aldrich, Milwaukee, Wisconsin) was vacuum distilled prior to use and stored under nitrogen. $CF_3SO_3D$ was prepared by treatment of triflic anhydride (Aldrich) with $D_2O$ followed by removal of excess anhydride under vacuum. $CF_3CO_2D$ and $D_2SO_4$ were obtained from Cambridge Isotope Laboratories (Massachusetts), and were used as received. Elemental analyses were performed by Desert Analytics. IR spectra were recorded on a Perkin–Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL GSX-400 instrument. $^{31}P$ spectra were referenced to a 85% $H_3PO_4$ external standard. $SO_2$ $^1H$ NMR spectra were locked and referenced externally to $CDCl_3$ or $C_6D_6$ capillaries. (dfepe)Pt(Me)$_2$ was prepared as described previously.[5,6]

### *Syntheses*

(dfepe)$PtCl_2$. A more direct synthesis for (dfepe)$PtCl_2$ than that described previously[5] has been developed: a 250 cm$^3$ flask fitted with a reflux condenser was charged with $K_2PtCl_4$ (2.67 g, 6.46 mmol), dfepe (5.48 g, 9.69 mmol) and 150 cm$^3$ of ethanol and heated to reflux for 5 days. During this time a gradual color change from an orange to an opaque-white suspension was observed. Upon cooling, the solvent was removed under vacuum and the solid residue was repeatedly extracted with acetone. Removal of acetone and addition of $Et_2O$ yielded a slurry, which after filtration and drying afforded 3.54 g (66%) of (dfepe)$PtCl_2$.

(dfepe)Pt(Me)($O_2CCF_3$) (**2**). Excess $CF_3CO_2H$ (*ca* 1.0 cm$^3$) was vacuum transferred into a 50 cm$^3$ flask charged with 0.500 g of (dfepe)Pt(Me)$_2$ at $-78$°C. Rapid release of methane was observed upon warming to ambient temperature. After 15 min, the volatiles were removed and the residue was slurried in 10 cm$^3$ of diethyl ether. Filtration and washing of the white solid with diethyl ether yielded 0.434 g (76%) of **2**. Anal. found for $C_{13}H_7F_{23}O_2P_2Pt$: C, 17.54; H, 0.59. Anal. calc: C, 17.56; H, 0.79. IR (cm$^{-1}$): 1704(s), 1407(m), 1306(s), 1232(s), 1189(m), 1138(s), 966(s). $^1H$ NMR (acetone-$d_6$, 399.65 MHz, 20°C): $\delta$ 3.32 (m, 2H; $PCH_2$), 2.98 (m, 2H; $PCH_2$), 1.25 (d, $^2J_{PtH} = 51$ Hz, $^3J_{PH} = 8$ Hz, 3H; $PtCH_3$). $^{19}F$ NMR ($SO_2$, 376.05 MHz, 20°C): $\delta$ $-76.2$ (s, 3F; $O_2CCF_3$), $-81.5$ (s, 6F; $PCF_2CF_3$), $-82.3$ (s, 6F; $PCF_2CF_3$), $-110$ to $-115$ (overlapping ABX multiplets).

(dfepe)Pt(Me)($OSO_2CF_3$) (**3**). To a solution of (dfepe)Pt(Me)$_2$ (1.01 g, 1.27 mmol) in 20 cm$^3$ of $CH_2Cl_2$ was added 0.121 cm$^3$ (1.36 mmol) of $CF_3SO_3H$. After stirring for 3 h at 20°C, the volume was reduced to *ca* 2 cm$^3$. 20 cm$^3$ of ether were added, and the solution was cooled to $-78$°C. The resulting white precipitate was cold filtered and dried under vacuum. The isolated yield of **3** was 1.03 g (87%). Anal. found for $C_{12}H_7F_{23}O_3P_2PtS$: C, 15.11; H, 0.86. Anal. calc: C, 15.58; H, 0.76. IR (KBr pellet, cm$^{-1}$): 1299(vs), 1234(vs), 1152(vs), 1040(m), 971(s), 871(w), 809(w), 752(m), 699(w), 655(m). $^1H$ NMR (acetone-$d_6$, 399.65 MHz, 20°C): $\delta$ 3.50 (m, 2H; $PCH_2$), 3.14 (m, 2H; $PCH_2$), 1.40 (d, $^2J_{PtH} = 44$ Hz, $^3J_{PH} = 8$ Hz, 3H; $PtCH_3$). $^{19}F$ NMR ($SO_2$, 376.05 MHz, 20°C): $\delta$ $-76.3$ (s, 3F; $O_3SCF_3$), $-77.3$ (s, 6F; $PCF_2CF_3$), $-78.3$ (s, 6F; $PCF_2CF_3$), $-106$ to $-110$ (overlapping ABX multiplets).

(dfepe)Pt($CH_3$)($OSO_3H$) (**4**) To a flask charged with 0.250 g (0.316 mmol) of (dfepe)Pt($CH_3$)$_2$ and 15 cm$^3$ of $CH_2Cl_2$ was added 0.20 cm$^3$ of 18 M $H_2SO_4$ dropwise via syringe at 20°C. After 1 h the volatiles were removed and 20 cm$^3$ of ether were added. The resulting white precipitate was collected by filtration and washed repeatedly with ether to remove all traces of residual acid. Yield of **4**: 0.200 g (72%). Anal. found for $C_{11}H_8F_{20}O_4P_2PtS$: C, 15.11; H, 0.77. Anal. calc: C, 15.13; H, 0.92. IR (cm$^{-1}$): 1411(w), 1302(s), 1220(vs), 1152(vs), 1036(s), 968(s), 870(m), 814(w), 752(w). $^1H$ NMR ($SO_2$, 399.65 MHz, 20°C): $\delta$ 9.33 (br, s, 1H; $SO_4H$) 3.55 (m, 2H; $PCH_2$), 3.22 (m, 2H; $PCH_2$), 2.09 (d, $^2J_{PtH} = 40$ Hz, $^3J_{PH} = 7$ Hz, 3H; $PtCH_3$). $^{19}F$ NMR ($SO_2$, 376.05 MHz, 20°C): $\delta$ $-77.7$ (s, 6F; $PCF_2CF_3$), $-78.4$ (s, 6F; $PCF_2CF_3$), $-106$ to $-111$ (overlapping ABX multiplets).

### *Crystal structure of* (dfepe)Pt(Me)$_2$ (**1**)

X-ray data were collected at $-110$°C on a Siemens R3m/V automated diffractometer system using Mo-$K_\alpha$ radiation. Crystal data collection and refinement parameters are summarized in Table 1. All computations used the SHELXTL/IRIS (version 4.2) program library (Siemens Corp., Madison, Wisconsin).[7] A suitable crystal of **1** was grown from methanol at $-50$°C. Monoclinic unit cell dimensions were derived from a least-squares fit of 46 random reflections (18° $< 2\theta <$ 28°). Data were collected using the Wyckoff scan technique with a variable scan rate of 4.0 to 30.0 deg min$^{-1}$. Three standard reflections monitored after every 100 data collected showed no systematic variation; the residual for averaging 121 redundant data was 4.31%. Data were corrected for absorption using an empirical ellipsoidal model based on 360° $\psi$-scans for six reflections with 10° $< 2\theta <$ 35°. *Cc* space group symmetry was initially deduced from a statistical analysis of all collected data; however, an analysis of correlations in least-squares refinements indicated that the centric alternative *C*2/*c* was clearly the correct space group, with the molecule residing on a crystallographic two-fold axis.

The structure of **1** was solved using the SHELXTL Patterson interpretation program; all non-hydrogen atoms were located on a series of difference Fourier maps. Hydrogen atom positions were added in ideal calculated positions with $d$(C—H) = 0.96 Å and with fixed isotropic thermal parameters set at 1.2 to 1.3 times the isotropic equivalent of the attached carbon atom, with a maximum value of $U = 0.10$. All non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement gave an $R$ value of 4.26% ($R_w$ = 5.32%) for 2701 data with $I > 2\sigma(I)$. The final difference Fourier map showed residual peaks of 2.61 and $-1.18$ e Å$^{-3}$ associated with the platinum atom with no other residual electron density greater than 1.0 e Å$^{-3}$.

### *Crystal structure of* (dfepe)Pt(Me)(OSO$_2$CF$_3$) (**3**)

X-ray data were collected at $-110$°C as described above. A suitable crystal of **3** was grown from a saturated 1,2-difluorobenzene solution. Monoclinic unit cell dimensions were derived from a least-squares fit of 42 random reflections (18 $< 2\theta <$ 28°). Data were collected using the Wyckoff scan technique with a variable scan rate of 4.0 to 30.0 deg min$^{-1}$. Three standard reflections monitored after every 100 data collected showed no systematic variation; the residual for averaging 301 redundant data was 2.59%. Data were corrected for absorption using an empirical ellipsoidal model based on 360° $\psi$-scans for six reflections with 10 $< 2\theta <$ 40°. $P2_1/c$ space group symmetry was deduced from a statistical analysis of all collected data.

The structure of **3** was solved using the SHELXTL Patterson interpretation program and refined anisotropically as described above. Full-matrix least-squares refinement gave an $R$ value of 3.90% ($R_w$ = 4.65%) for 4031 data with $I > 2\sigma(I)$. The final difference Fourier map showed a residual peak of 1.46 e Å$^{-3}$ associated with the platinum

Table 1. Crystallographic data for (dfepe)Pt(Me)$_2$ (**1**) and (dfepe) Pt(Me)(OSO$_2$CF$_3$) (**3**)

| | **1** | **3** |
|---|---|---|
| Chemical formula | $C_{12}H_{10}F_{20}P_2Pt$ | $C_{12}H_7F_{23}O_3P_2PtS$ |
| Formula weight | 791.2 | 925.3 |
| Space group | *C*2/*c*(No. 15) | $P2_1/c$(No. 14) |
| $a$ (Å) | 17.885(4) | 10.033(2) |
| $b$ (Å) | 8.611(2) | 16.168(3) |
| $c$ (Å) | 13.981(3) | 15.328(3) |
| $\beta$ (°) | 93.88(3) | 101.25(3) |
| $V$ (Å$^3$) | 2148.4(8) | 2438.6(8) |
| $Z$ | 4 | 4 |
| $T$ (°C) | $-110$ | $-110$ |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $D_{calc}$ (g cm$^{-3}$) | 2.446 | 2.520 |
| $\mu$ (cm$^{-1}$) | 68.51 | 61.64 |
| $R$ ($F_o$)$^a$ (%) | 4.26 | 3.90 |
| $R_w$ (F$_o$)$^b$(%) | 5.32 | 4.65 |

[a] $R(F_o) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $R_w(F_o) = \Sigma(w^{1/2}(|F_o| - |F_c|))/\Sigma(w^{1/2}|F_o|)$; $w^{-1} = \sigma^2(F_o) + 0.0008(F_o)^2$.

atom with no other residual electron density greater than 1.0 e Å$^{-3}$.

## RESULTS AND DISCUSSION

### *Synthesis and characterization of* (dfepe)Pt(Me)X *complexes*

Treatment of the dimethyl complex (dfepe)Pt(Me)$_2$ (**1**) with neat $CF_3CO_2H$ at ambient temperature resulted in the rapid evolution of methane and quantitative formation of the corresponding monomethyl complex, (dfepe) Pt(Me)($O_2CCF_3$) (**2**) [eq. (2)]. Similarly, addition of excess $CF_3SO_3H$ or $H_2SO_4$ to dichloromethane solutions of **1** followed by precipitation and repeated washing with diethyl ether to remove traces of acid gave (dfepe)Pt(Me)($OSO_2CF_3$) (**3**) and (dfepe)Pt(Me)($OSO_3H$) (**4**), respectively, in good yield [eq. (3)].

$$\text{(dfepe)Pt(Me)}_2 \xrightarrow[\text{CF}_3\text{CO}_2\text{H}]{20^\circ\text{C}} \underset{\mathbf{2}}{\text{(dfepe)Pt(Me)O}_2\text{CCF}_3} + \text{CH}_4 \quad (2)$$

$$\text{(dfepe)Pt(Me)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{xs. HX, }20^\circ\text{C}} \text{(dfepe)Pt(Me)X} + \text{CH}_4 \quad (3)$$

$$[\text{X} = \text{OSO}_2\text{CF}_3\ (\mathbf{3}),\ \text{OSO}_3\text{H}\ (\mathbf{4})]$$

The coordination environment of these (dfepe)Pt(Me)X complexes is well defined by $^1H$ and $^{31}P$ NMR. The $^1H$ methyl proton resonances of **2**, **3**, and **4** appear as doublets due to coupling with the *trans* phosphorous ($^3J_{PH} \approx 8$ Hz), with characteristic platinum satellites ($^2J_{PtH} = 40$–51 Hz). The bisulfate ligand proton in **4** undergoes rapid H/D exchange in acetone-$d_6$, but appears as a broad singlet at $\delta$ 9.33 in sulfur dioxide. The sensitivity of $^{31}P$ NMR $^1J_{PtP}$ couplings to the relative donor ability of the *trans* ligand in *cis*-$(R_3P)_2Pt(X)(Y)$ complexes is particularly diagnostic.[8] For (dfepe)Pt(Me)$_2$, a single phosphorus resonance is observed at $\delta$ 74.2 with a small $^1J_{PtP}$ of 1403 Hz.[5,9] When one methyl group is replaced by successively weaker donor ligands $O_2CCF_3$, $OSO_3H$, and $OSO_2CF_3$, new high-field phosphorus resonances are observed which exhibit extremely large $^1J_{PtP}$(*trans* to X) values of 4652, 5197, and 5356 Hz, respectively, in $SO_2$ as a solvent (Table 2). Over this same series, the $^1J_{PtP}$ for the low-field phosphorus resonance is relatively constant, consistent with its assignment to the phosphorus *trans* to the remaining methyl group. A representative $^{31}P$ NMR spectrum of **3** is shown in Fig. 1. The fine coupling structure observed in Fig. 1 is due to $^3J_{PP}$ (32 Hz) and the fortuitous equivalence of $^2J_{PF}$ coupling constants (61 Hz) for the diastereotopic (dfepe)$CF_2$ groups, resulting in a pseudopentet of doublets multiplet pattern. In general diastereotopic $^2J_{PF}$ values for dfepe complexes are not equivalent and $^{19}F$ and $^{31}P$ NMR spectra are not as readily analyzed. Although facile solvation of Pt—OTf bonds for donor systems such as (dppe)Pt (OTf)$_2$ has been noted,[10] discreet solvated adducts of **2**–**4** have not been isolated. The $^{31}P$ values observed for **3** and **4** in $CD_3CN$ are essentially identical, however, indicating that anion displacement to form a common (dfepe)Pt(Me)(L)$^+$ species likely occurs in this more strongly-coordinating solvent. No reaction was found between **3** and excess $H_2O$ in acetone.

Except for complex **2**, which exhibits a 1704 cm$^{-1}$ $\nu(CO_2)$ IR band characteristic of unidentate trifluoromethylacetate coordination, IR data for **3** and **4** are not diagnostic for $CF_3SO_3$ and $SO_4H$ coordination modes due to masking of the $\nu_{as}(SO_3)$ bands by the dfepe $\nu(CF_3)$ modes. The expected unidentate coordination of triflate in **3**, however, has been confirmed by its crystal structure (see next section); an analogous disposition of the $SO_4H$ ligand in **4** is inferred. No $\nu$(OH) band was observed for **4**.

### *Crystal structures of* (dfepe)Pt(Me)$_2$ (**1**) *and* (dfepe)Pt(Me)($OSO_2CF_3$) (**3**)

In prior studies we have observed significant structural changes in the (dfepe)$ML_n$ coordination sphere relative to donor phosphine systems which reflect the electron-withdrawing nature of the dfepe ligand.[11] Accordingly, the crystal structures of **1** (Fig. 2) and **3** (Fig. 3) have been determined for structural comparison with donor phosphine platinum systems. Selected bond distances and angles are presented in Table 3. Compound **1** crystallizes in *C*2/*c*, with the molecule residing on a crystallographic two-fold axis resulting in equivalent Pt—P and equivalent Pt—C distances. Both **1** and **3** are essentially square planar, with maximum deviations from planarity of 0.020 and 0.024 Å, respectively. The 2.233(2) Å Pt—P bond length observed for **1** is 0.05 Å shorter than values reported for *cis*-$(MePh_2P)_2Pt(Me)_2$ [2.284(2), 2.285(2) Å][12] and $(Ph_2PCH(Ph)CH_2PPh_2)Pt(CH_2CMe_3)_2$ [2.291(4), 2.283(4) Å],[13] a feature that is comparable to the 0.07 Å internal bond length difference seen in the mixed donor/acceptor complex $[(Ph_2PCH_2CH_2P(CF_3)_2]PtCl_2$.[14] The Pt—C distance of 2.074(5) Å for **1** is also significantly shorter than Pt—Me(*trans* to $R_3P$) values reported for cor-

Table 2. Solvent-dependent $^{31}$P NMR data for (dfepe)Pt(Me)(X) complexes

| Complex | Solvent | Pt—P(*trans* to Me) | Pt—P(*trans* to X) |
|---|---|---|---|
| (dfepe)Pt(Me)($O_2CCF_3$) | $CF_3CO_2D$ | $\delta$ 79.1 (m, $^1J_{PtP}$ = 1412 Hz) | $\delta$ 58.6 (m, $^1J_{PtP}$ = 4814 Hz) |
| | $SO_2$ | $\delta$ 79.6 (m, $^1J_{PtP}$ = 1453 Hz) | $\delta$ 60.5 (m, $^1J_{PtP}$ = 4652 Hz) |
| | acetone-$d_6$ | $\delta$ 81.5 (m, $^1J_{PtP}$ = 1403 Hz) | $\delta$ 62.1 (m, $^1J_{PtP}$ = 4500 Hz) |
| | $CD_3CN$ | $\delta$ 80.5 (m, $^1J_{PtP}$ = 1400 Hz) | $\delta$ 61.0 (m, $^1J_{PtP}$ = 4584 Hz) |
| (dfepe)Pt(Me)($OSO_3H$) | $D_2SO_4$ | $\delta$ 82.7 (m, $^1J_{PtP}$ = 1480 Hz) | $\delta$ 54.7 (m, $^1J_{PtP}$ = 5438 Hz) |
| | $SO_2$ | $\delta$ 81.9 (m, $^1J_{PtP}$ = 1382 Hz) | $\delta$ 57.3 (m, $^1J_{PtP}$ = 5197 Hz) |
| | acetone-$d_6$ | $\delta$ 81.3 (m, $^1J_{PtP}$ = 1443 Hz) | $\delta$ 59.4 (m, $^1J_{PtP}$ = 4867 Hz) |
| | $CD_3CN$ | $\delta$ 80.7 (m, $^1J_{PtP}$ = 1396 Hz) | $\delta$ 64.0 (m, $^1J_{PtP}$ = 4689 Hz) |
| (dfepe)Pt(Me)($OSO_2CF_3$) | $CF_3SO_3D$ | $\delta$ 84.6 (m, $^1J_{PtP}$ = 1538 Hz) | $\delta$ 54.2 (m, $^1J_{PtP}$ = 5664 Hz) |
| | $SO_2$ | $\delta$ 82.9 (m, $^1J_{PtP}$ = 1462 Hz) | $\delta$ 56.7 (m, $^1J_{PtP}$ = 5356 Hz) |
| | acetone-$d_6$ | $\delta$ 83.4 (m, $^1J_{PtP}$ = 1453 Hz) | $\delta$ 59.2 (m, $^1J_{PtP}$ = 5034 Hz) |
| | $CD_3CN$ | $\delta$ 80.7 (m, $^1J_{PtP}$ = 1396 Hz) | $\delta$ 64.2 (m, $^1J_{PtP}$ = 4694 Hz) |

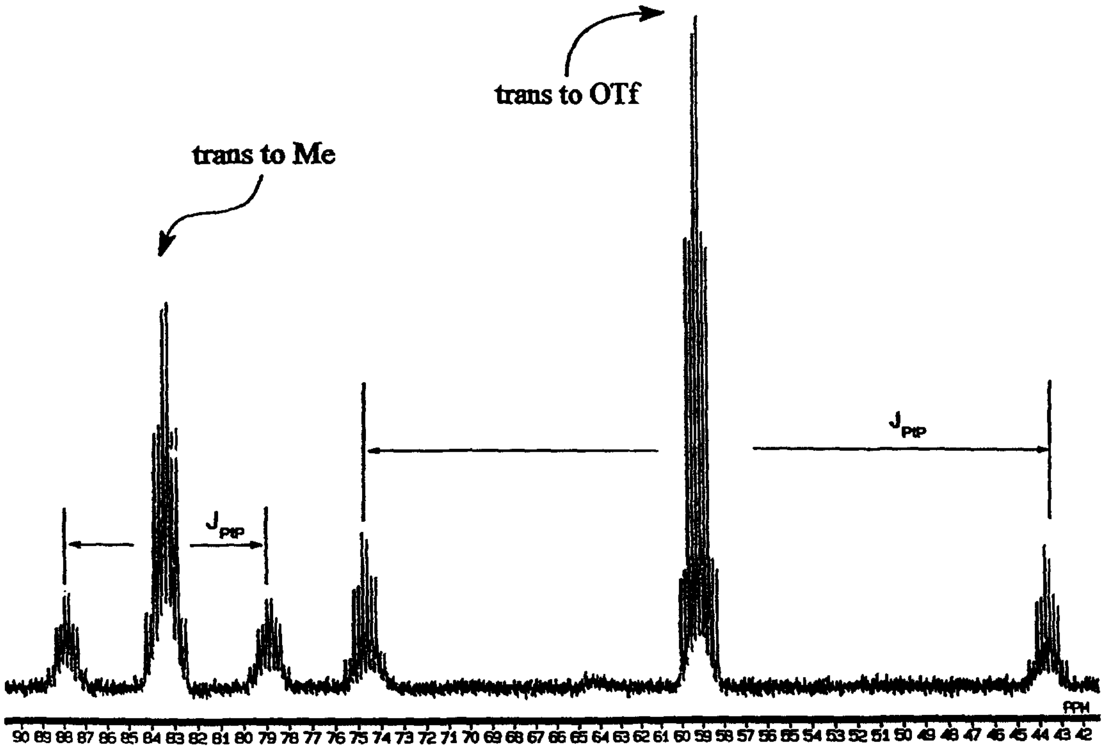


Fig. 1. $^{31}$P NMR spectrum of (dfepe)Pt(Me)($OSO_2CF_3$) (**3**) in acetone-$d_6$.

responding donor phosphine complexes, which average 2.13 Å.[12,15]

Metrical comparisons between **1** and the unsymmetrical methyl triflate complex **3** readily reflect the low *trans* influence of the triflate ligand. For **3**, the Pt—P bonds *trans* to methyl [2.301(2) Å] and *trans* to triflate [2.149(2) Å] are shifted +0.07 and −0.08 Å, respectively, relative to **1**. A similar shift in Pt—P bond distances due to the replacement of a strong *trans* influence ligand by triflate have been seen for $[(^t\text{Bu})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(^t\text{Bu})_2]\text{Pt(Et)}_2$ [Pt—P: 2.320(2), 2.329(2) Å] and $[(^t\text{Bu})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(^t\text{Bu})_2]\text{Pt(H)(OTf)}$ [Pt—P(*trans* to H): 2.374(3) Å; Pt—P(*trans* to OTf): 2.201(3) Å].[16] The observed Pt—OTf bond distance [2.090(6) Å] is significantly shorter than the value reported for $[(^t\text{Bu})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(^t\text{Bu})_2]\text{Pt(H)(OTf)}$ [2.181(9) Å] and more comparable to the values reported for $[1,2\text{-}(\text{PMePh})_2\text{C}_6\text{H}_4]\text{Pt}(\text{OSO}_2\text{CF}_3)_2$ [2.117 Å (ave)].[17] The short Pt—O bond in **3** is suggestive of an unusually strong bonding interaction between the triflate ligand and the electrophilic metal center,

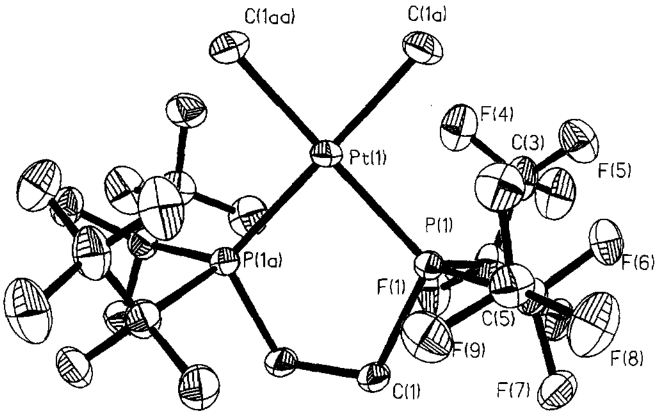


Fig. 2. ORTEP view of (dfepe)Pt(Me)$_2$ (**1**) with labeling scheme (30% probability ellipsoids).

following similar trends observed in other (dfepe)M systems.[11]

### (dfepe)Pt(Me)X *protonation studies*

The selective protonolysis of (dfepe)Pt(Me)$_2$ in the presence of excess strong acid is in marked contrast to the reactivity reported for the donor phosphine complex [1,2-$C_6H_4$(PMePh)$_2$]Pt(Me)$_2$, which rapidly reacts with two equivalents of triflic acid at −78°C to give [1,2-$C_6H_4$(PMePh)$_2$] Pt($OSO_2CF_3$)$_2$.[17] Although treatment of **3** with triflic acid in dichloromethane at 20°C does not result in methane elimination,[18] monitoring the addition of triflic acid to **3** by $^1$H and $^{31}$P NMR in $CD_2Cl_2$ indicates that association of **3** with an additional equivalent of $CF_3SO_3H$ does occur (Fig. 4). Upon addition of 0.3 equivalents HOTf to **3**, a single low-field protic resonance was observed at 11.48 ppm. In the presence of 1.0 equivalent HOTf, a slight upfield shift of the original acid resonance to 11.38 ppm was noted and a new low-field resonance appeared at 12.00 ppm. After the addition of a total of 3.0 equivalents HOTf, the major HOTf proton

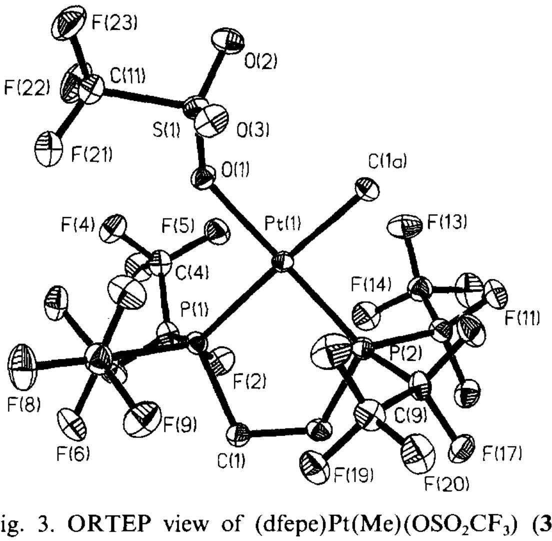


Fig. 3. ORTEP view of (dfepe)Pt(Me)($OSO_2CF_3$) (**3**) with labeling scheme (30% probability ellipsoids).

Table 3. Selected bond lengths (Å) and angles (°) for (dfepe)Pt(Me)$_2$ (**1**) and (dfepe)Pt(Me)($OSO_2CF_3$) (**3**)

| | **1** | **3** |
|---|---|---|
| Bond lengths | | |
| Pt(1)—P(1) | 2.233(2) | 2.301(2) |
| Pt(1)—P(2) | – | 2.149(2) |
| Pt(1)—C(1A) | 2.074(5) | 2.070(7) |
| Pt(1)—O(1) | – | 2.090(6) |
| O(1)—S(1) | – | 1.487(6) |
| S(1)—O(2) | – | 1.420(6) |
| S(1)—O(3) | – | 1.421(6) |
| S(1)—C(11) | – | 1.834(9) |
| Bond angles | | |
| P(1)—Pt(1)—P(1A) | 85.0(1) | – |
| P(1)—Pt(1)—P(2) | – | 86.6(1) |
| P(1)—Pt(1)—C(1A) | 95.8(1) | 177.5(2) |
| P(1A)—Pt(1)—C(1A) | 178.5(2) | – |
| P(2)—Pt(1)—C(1A) | – | 91.2(2) |
| C(1A)—Pt(1)—C(1AA) | 83.5(3) | – |
| P(1)—Pt(1)—O(1) | – | 92.4(2) |
| P(2)—Pt(1)—O(1) | – | 177.7(2) |
| C(1A)—Pt(1)—O(1) | – | 89.9(3) |
| Pt(1)—O(1)—S(1) | – | 130.2(3) |
| O(1)—S(1)—O(2) | – | 112.8(3) |
| O(1)—S(1)—O(3) | – | 113.5(4) |
| O(1)—S(1)—C(11) | – | 100.2(4) |
| O(2)—S(1)—O(3) | – | 118.5(4) |
| O(2)—S(1)—C(11) | – | 102.9(4) |
| O(3)—S(1)—C(11) | – | 106.3(4) |

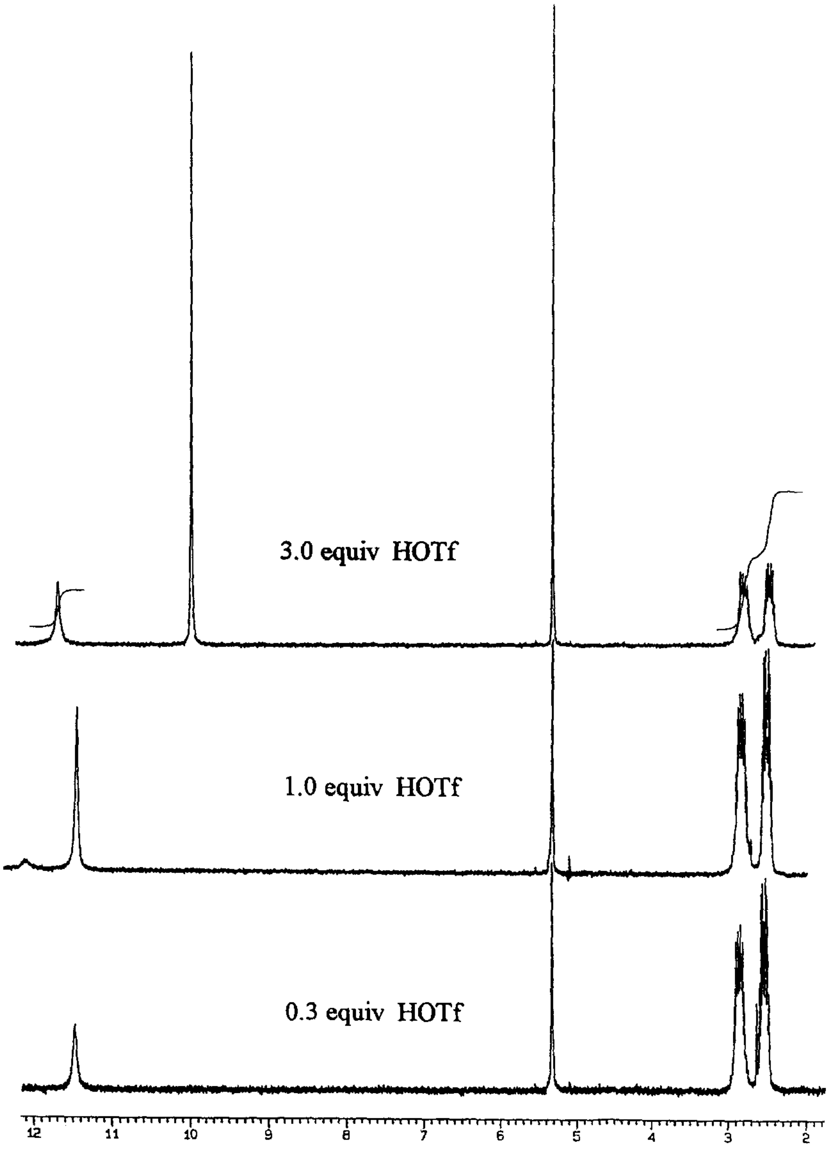
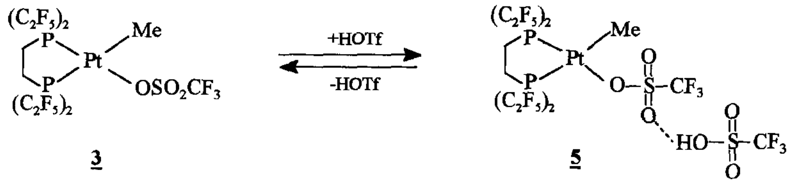


Fig. 4. Addition of triflic acid to (dfepe)Pt(Me)($OSO_2CF_3$) (3) in $CD_2Cl_2$. The resonance at 5.32 ppm is due to the residual solvent protons.

resonance was shifted further upfield to 9.70 ppm and the downfield protic resonance was shifted to 11.65 ppm and integrated as one proton versus **3**. Throughout the addition of acid, the dfepe backbone (2.86 and 2.52 ppm) and platinum–methyl (1.50 ppm) resonances for **3** were essentially unchanged.

Although these observations are consistent with the association of one equivalent of triflic acid with **3**, the nature of this acid adduct is not certain. We anticipated that protonation at the triflate ligand of **3** should be readily reflected in $^1J_{PtP}$ changes for the *trans* phosphorus. However, while a steady increase in $^1J_{PtP}$ (*trans* to OTf) from 5389 Hz (0.3 equivalents HOTf added) to 5542 Hz (3.0 equivalents HOTf added) was found, a commensurate relative (*ca* 3%) increase in $^1J_{PtP}$ (*trans* to Me) from 1440 to 1483 Hz was also observed. Nevertheless, the new low-field proton resonance at 11.65 ppm is closely comparable to the chemical shift of the $[(OTf)_2H]^-$ ion in dichloromethane (11.79 ppm),[19] indicating that formulation of the equilibrium protonation product of **3** as the hydrogen-bonded acid adduct (dfepe)Pt(Me)($(OTf)_2H$) (**5**) is reasonable [eq. (4)]. Additional support for **5** is the recently reported structural characterization of *cis*-($(Me_3P)_2$Pt(Me)($OCH(CF_3)_2$)($HOCH(CF_3)_2$), which exhibits hydrogen-bonding between the fluoroalkoxide ligand and the acidic OH proton of hexafluoroisopropanol.[20] Analogous Lewis acid interactions have also been suggested by Trogler for $(CO)_5Mn(OTf)$ in superacid media.[21]

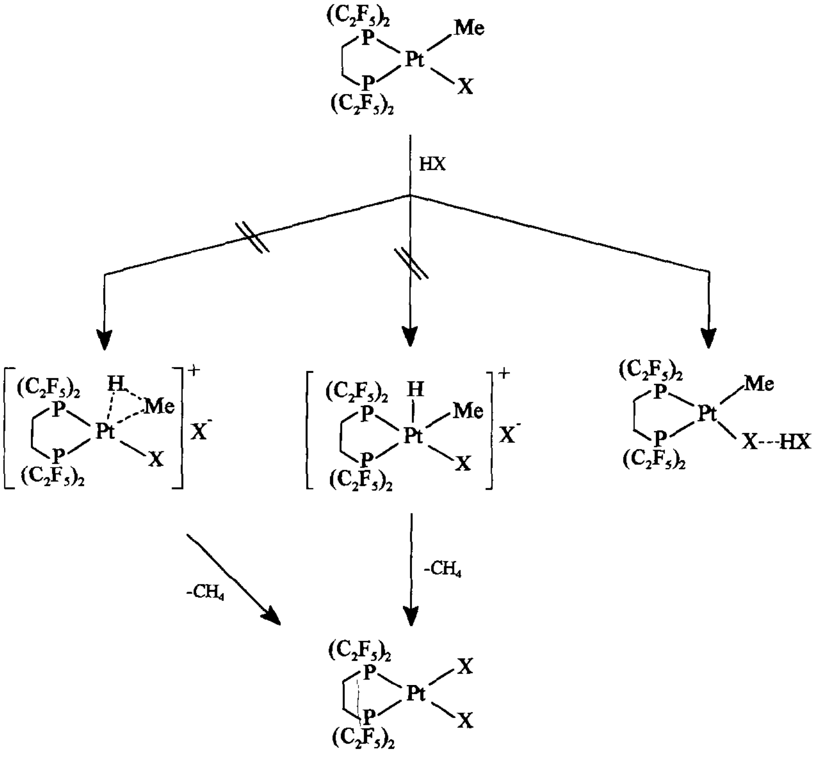


**3** **5** (4)

As noted in the synthesis of **2**, further protonation in neat trifluoroacetic acid does not occur at 20°C. More remarkably, (dfepe)Pt(Me)X systems **3** and **4** are also stable toward further protonolysis in neat triflic and sulfuric acid media at 20°C. In neat acid solvents, $^{31}P$ NMR spectra of **2**–**4** again exhibit two separate resonances with characteristic $^{195}Pt$ couplings. The larger $^1J_{PtP}$(*trans* to X) values relative to more donating solvents (Table 2) follow the trend observed for protonation of **3** in $CD_2Cl_2$ by increasing amounts of HOTf, suggesting substantial hydrogen-bonding for **2**–**4** under these conditions. The 5664 Hz coupling observed for **3** in triflic acid appears to be one of the largest values yet reported for square-planar platinum complexes, indicative of a very small *trans* influence for triflate in this medium.[8]

## CONCLUSIONS

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. It was anticipated that a reduction in electron density and/or the shift in the polarity of the (dfepe)(X)Pt—Me bond should disfavor a concerted proton attack at the methyl group. Alternatively, reduced metal lone-pair basicity should also disfavor protonation at the platinum center followed by reductive elimination of methane



Scheme 1.

(Scheme 1). The observation of preferential hydrogen-bonding of strong acids to the conjugate acid ligand in **2**–**4** supports our expectation that protonolysis pathways in these electrophilic systems are relatively unfavorable. In light of these results, it is significant that the Hg—Me bond in $MeHg(SO_4H)$, a product of methane activation by $Hg^{2+}$, also has unusual enhanced stability under the stringent reaction conditions employed ($H_2SO_4$, 180°C).[4]

The compatibility of metal–alkyl bonds with strongly acidic media is counter to "normal" expectations, and opens up the novel possibility of exploring organometallic transformations in superacidic media. Also, since uncoordinated dfepe does not protonate in neat triflic acid to any significant extent,[22] the development of metal complexes with elaborated metal coordination environments containing labile phosphine ligands is an additional intriguing option. We are currently examining the thermolysis and reaction chemistry of (dfepe)Pt(Me)(X) systems in acidic media and exploring the applicability of $(dfepe)Pt(X)_2$ derivatives to alkane heterolysis chemistry.

*Supplementary materials*—Atomic Coordinates have been deposited with the Cambridge Crystallographic Data centre.

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