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Protolytic Stability of (dfepe)Pt(Ph)O_2CCF_3: Supporting Evidence for a Concerted S_E2 Protonolysis Mechanism

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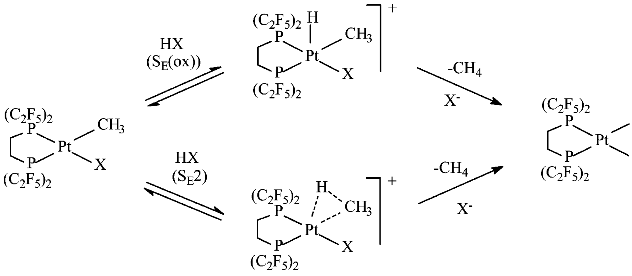
An extension of prior protonolysis studies of platinum−carbon bonds to Pt−aryl bonds is reported. The protolytic stability of (dfepe)Pt(Ph)(O_2CCF_3) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) in trifluoroacetic acid is found to be much less than (dfepe)Pt(Me)(O_2CCF_3), indicating that a concerted S_E2 protonolysis mechanism is most likely operative in these electron-poor platinum systems. VT NMR experiments show that benzene coordination to the (dfepe)Pt^{2+} center in neat fluorosulfonic acid to form (dfepe)Pt(η^6-C_6H_6)$^{2+}$ at −80 °C is competitive with benzene dissociation in this weakly coordinating medium.

Introduction

Metal−carbon bond protonolysis processes have received increasing recent attention as a model of the microscopic reverse of heterolytic C−H bond activation.[1] However, uncertainty still remains regarding the detailed mechanism of metal−carbon bond cleavage by H^+ and the factors that control the kinetics and thermodynamics of this process.[2−4] Several years ago we examined the protolytic behavior of perfluoroalkylphosphine platinum methyl complexes, (dfepe)Pt(Me)(X) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; X = O_2CCF_3, OTf, OSO_2F). These compounds are remarkable for the unusually high protolytic resistance observed for Pt−Me bonds relative to donor phosphine analogues. Despite extensive kinetic studies (and the failure to observe any detectable Pt(IV) hydride intermediates), we were unable to determine whether these protonolyses proceed via a stepwise S_E(ox) or a concerted S_E2 mechanism.[5]



Prior Pt(II)−alkyl and Pt(II)−aryl protonolysis studies are similarly ambiguous and have invoked both S_E(ox) and S_E2 limiting mechanisms in very closely related $(L)_2Pt(R)(X)$ systems.[2−4] Noting the contrasting selectivity of mixed Au(III)(aryl)(alkyl) and Pt(II)(aryl)(alkyl) complexes toward protonolysis (k_{prot}(Au−Ar) ≫ k_{prot}(Au−Me); k_{prot}(Pt−Ar) ≪ k_{prot}(Pt−Me)), Puddephatt proposed that relative M−Me and M−Ph protonolysis rates in an isostructural series may serve to distinguish between S_E(ox) and S_E2 mechanisms: for cases in which $k(Me)/k(Ph) \gg 1$, a stepwise S_E(ox) mechanism can be inferred, whereas metal complexes where $k(Ph)/k(Me) \gg 1$ can alternatively imply a concerted S_E2 mechanism.[4b] The underlying factors for this kinetic discrimination are as follows: (1) S_E2 proton addition to a metal−aryl bond is promoted via a “Wheland-type” charge-delocalized intermediate,[6] and (2) metal protonation and alkane reductive elimination steps in a stepwise S_E(ox) process are generally favored for L_nM−Me systems relative to L_nM−Ph. The preference for Au(III)−aryl bond cleavage follows from the inaccessibility of a Au(V) hydride S_E(ox) intermediate. To our knowledge, this simple mechanistic test has not been extended beyond the initial reported work, which focused on platinum and gold donor phosphine systems.

In this article we report the synthesis of (dfepe)Pt(Ph)O_2CCF_3 and its protolytic stability relative to the methyl analogue (dfepe)Pt(Me)O_2CCF_3. The formation of a dicationic arene complex after Pt−aryl bond protonolysis under highly acidic conditions is also presented.

Results and Discussion

Synthesis and Protonolysis of (dfepe)Pt(Ph)O_2CCF_3 (1). The inherent instability of (dfepe)Pt$(Ph)_2$ toward reductive elimination of biphenyl at ambient temperatures has been demonstrated in previous work.[7] Accordingly, (cod)Pt(Ph)O_2CCF_3 was either isolated or

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[1] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961.

[2] (a) Romeo, R., Plutino, M. R.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 5909. (b) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107. (c) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565. (d) de Luca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359.

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[4] (a) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (b) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332. (c) Lucey, D. W.; Helfer, D. S.; Atwood, J. D. *Organometallics* **2003**, *22*, 826.

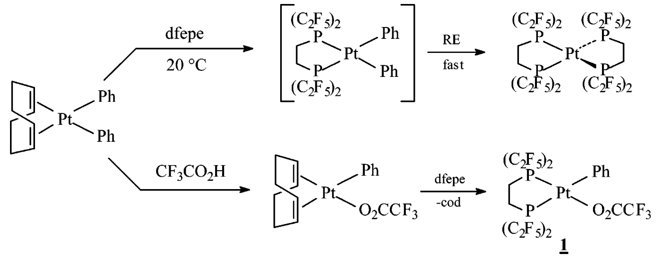
[5] Bennett, B. L.; Hoerter, J. M.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2000**, *19*, 615.

[6] A reviewer has also suggested that less orbital reorganization for M−C(sp^2) versus M−C(sp^3) protonolysis may favor the S_E2 pathway for M−aryl systems.

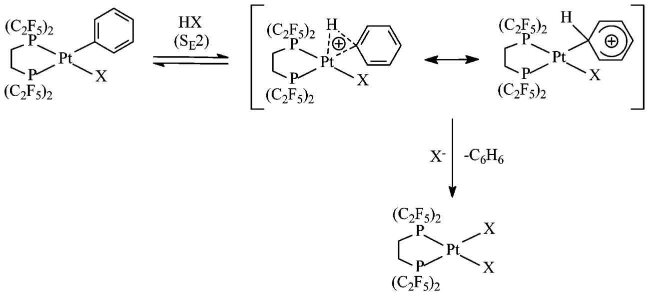
[7] Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972.

10.1021/om049682f CCC: $27.50

Scheme 1

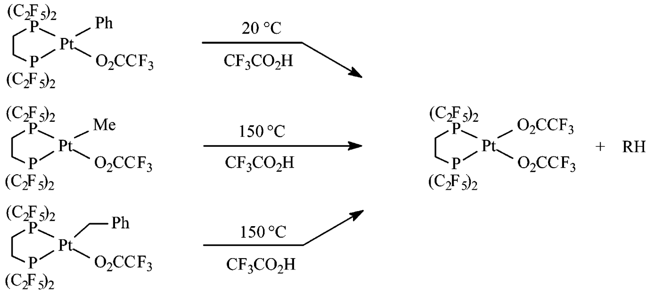


Scheme 2



prepared in situ by the addition of 1 equiv of CF_3CO_2H to (cod)Pt(Ph)$_2$ in dichloromethane followed by the addition of dfepe to cleanly form (dfepe)Pt(Ph)O_2CCF_3 (**1**) (Scheme 1). Complex **1** exhibits two ^{195}Pt-coupled phosphorus resonances at δ 68.2 ($^1J_{PtP} = 1270$ Hz) and 49.0 ($^1J_{PtP} = 4735$ Hz) assigned as the phosphorus groups trans to the phenyl and O_2CCF_3 groups, respectively.

The protolytic stability of **1** was monitored by ^{1}H and ^{31}P NMR in neat trifluoroacetic acid. After several hours at 20 °C, resonances for **1** were completely replaced by a single resonance at 59.4 ppm due to (dfepe)Pt(O_2CCF_3)$_2$.[5] Thus, the acid stability of **1** is considerably less than that of (dfepe)Pt(Me)(O_2CCF_3), which loses methane only at very high temperatures ($t_{1/2}$(150 °C) ≈ 9 h). It is significant that (dfepe)Pt(benzyl)(O_2CCF_3) has a high protolytic stability similar to (dfepe)Pt(Me)(O_2CCF_3), demonstrating that the aromatic ring must be alpha to the metal center in order to facilitate protonolysis.[8]



Recent work has shown that Ar−H and Me−H reductive elimination rates are comparable in Pt(IV) systems,[9] and it is very unlikely that the greatly increased resistance to protonolysis of (dfepe)Pt(Me)(X) relative to (dfepe)Pt(Ph)(X) could be attributed to an anomalously large difference in metal basicities. Therefore, we conclude that a concerted S_E2 protonolysis mechanism is operative specifically for **1** (Scheme 2) and for (dfepe)Pt(R)X compounds in general.

[(dfepe)Pt(η^6-C_6H_6)]$^{2+}$ Formation. The stability of **1** in fluorosulfonic acid was also examined. Dissolving **1** in FSO_3H at 20 °C immediately produced (dfepe)Pt(OSO_2F)$_2$ as the only product. At −80 °C, however, dissolution of **1** generated a 1:2 mixture of (dfepe)Pt(OSO_2F)$_2$ as well as a new symmetrically substituted product at 76.1 ppm. The large $^1J_{PtP}$ observed for (dfepe)Pt(OSO_2F)$_2$ under these conditions, 4140 Hz, is diagnostic for weak coordination by the fluorosulfonate anion in a square-planar coordination geometry. Interestingly, the observed $^1J_{PtP}$ for the new product at 76.1 ppm is significantly higher (4455 Hz). ^{1}H NMR revealed the presence of free benzene at δ 6.38 as well as a new singlet at δ 7.04 in a 1:2 ratio, corresponding to the product ratio observed by ^{31}P NMR that we assign to the arene complex dication, [(dfepe)Pt(η^6-C_6H_6)]$^{2+}$ (**2**). A similar mixture of (dfepe)Pt(OSO_2F)$_2$ and **2** was obtained by the addition of 1 equiv of benzene to (dfepe)Pt(OSO_2F)$_2$ in FSO_3H at −20 °C, and addition of excess (>3 equiv) benzene gave >90% conversion to **2**. Addition of excess benzene to triflic acid solutions of (dfepe)Pt(OTf)$_2$ similarly afforded the arene dication. However, attempts to isolate **2** from triflic acid solution by precipitation with ether yielded only (dfepe)Pt(OTf)$_2$. Addition of excess (10 equiv) C_6D_6 to a solution of (dfepe)Pt(η^6-C_6H_6)$^{2+}$ in HOTf at 20 °C resulted in complete C_6D_6/C_6H_6 ligand exchange within 5 min.

Arene coordination is dependent on both the donating ability of the arene substrate and the labilizing acid media: under identical conditions in triflic acid, no [(dfepe)Pt(η^6-C_6H_5F)]$^{2+}$ was formed in the presence of 20 equiv of fluorobenzene or 1,2-difluorobenzene. In trifluoroacetic acid, addition of greater than 10 equiv of benzene to a solution of (dfepe)Pt(O_2CCF_3)$_2$ did not produce detectable amounts of **2**.

We could not readily differentiate between inter- and intramolecular arene complex formation after the initial proton transfer step because the same mixture of (dfepe)Pt(OSO_2F)$_2$ and **2** was produced by either protonation of **1** or addition of free benzene to (dfepe)Pt(OSO_2F)$_2$. To address this issue, we examined the protonolysis of (dfepe)Pt(C_6H_5)(O_2CCF_3) in the presence of 3 equiv of added C_6D_6 in FSO_3H at −70 °C. Upon dissolution, the initial ^{1}H NMR spectrum showed a 2.8:1 ratio of [(dfepe)Pt(η^6-C_6H_6)]$^{2+}$ to free C_6H_6, not the 1:3 ratio expected from statistical scrambling of released C_6H_6 with the added C_6D_6.[10] The quantity of unbound C_6H_6 did not change significantly with time, suggesting that it was formed during the initial mixing period and did not arise from ligand exchange at this temperature. Thus, we may conclude that benzene protonolysis product is preferentially retained in the inner coordination sphere and incorporated into the observed η^6-arene product. Formation of a (dfepe)Pt(η^2-C_6H_6)(OSO_2F)$^+$ intermediate prior to the ultimate formation of **2** is reasonable, since η^2-arene coordination has been observed in (diimine)Pt(II) chemistry.[11] However, addition

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(8) White, S.; Kalberer, E. W.; Bennett, B. L.; Roddick, D. M. *Organometallics* **2001**, *20*, 5731.

(9) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846.

(10) No H/D exchange of free C_6D_6 with FSO_3H was observed under these conditions.

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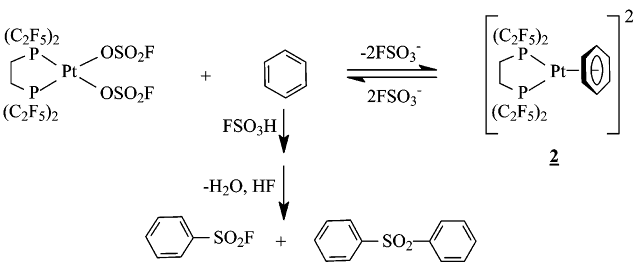
Scheme 3



of excess benzene to (dfepe)Pt(Me)(OSO_2F) in FSO_3H does not result in any spectroscopic changes due to the formation of (dfepe)Pt(Me)(η^2-benzene)$^+$.

At ambient temperatures the resonances due to arene complex **2** in FSO_3H diminish over the course of several hours concomitant with the growth of resonances due to (dfepe)Pt(OSO_2F)$_2$ and a ~2:1 mixture of benzenesulfonyl fluoride and diphenyl sulfone.[12] Subsequent addition of additional excess benzene to solutions of **1** in FSO_3H cleanly regenerated **2**. These observations are consistent with the reversible coordination of benzene to (dfepe)Pt^{2+} coupled with the electrophilic aromatic substitution reaction of free benzene with FSO_3H (Scheme 3).[13]

Summary

In all electron-rich mixed aryl/alkyl platinum(II) systems examined to date, preferential protonolysis of Pt(II)−alkyl bonds is observed, which is consistent with an S_E(ox) mechanism involving the intermediacy of Pt(IV) hydrides. These systems all possess donor phosphine or diimmine supporting ligands. The (dfepe)-Pt(II) system has a substantially lower electron density and is the only class of Pt(II) compounds that we are aware of which displays a distinct kinetic protonolysis preference for Pt(II)−aryl bonds. We have previously noted the inaccessibility of the formal Pt(IV) oxidation state in (dfepe)Pt systems.[5] We believe that this pronounced lowering of electron density is accompanied by a discrete change to a concerted S_E2 protonolysis mechanism, a mechanism that is generally operative in main-group organometallic systems.[14] We expect that competitive S_E2 and S_E(ox) M−C cleavage mechanisms will be encountered in platinum(II) systems with ancillary ligands of intermediate donating ability.

(dfepe)Pt^{2+} is shown to bind readily to benzene under conditions where the counterions are weakly binding. Although the single ^1H and ^{13}C NMR aromatic resonances observed for (dfepe)Pt(C_6H_6)$^{2+}$ at low temperature could be accommodated by a highly fluxional (dfepe)Pt(η^2-C_6H_6)(OSO_2F)$^+$ coordination geometry, the inability of (dfepe)Pt(Me)$^+$ to form a (dfepe)Pt(Me)(η^2-arene)$^+$ complex leads us to favor a (dfepe)Pt(η^6-C_6H_6)$^{2+}$ bonding description. The lowered coordination ability of arene to the (dfepe)Pt(II) center extends the lability trend established for other d^8 (dfepe)M systems: while (dfepe)Ru(η^6-C_6H_6) undergoes arene exchange very slowly at 180 °C,[15] and (dfepe)Ir(η^6-C_6H_6)$^+$ exchanges at 80 °C,[16] we observe rapid arene exchange for (dfepe)Pt(η^6-C_6H_6)$^{2+}$ at 20 °C and favorable arene complex formation only in the presence of very weakly coordinating anions. This lability trend correlates with the relative back-bonding capabilities of these isoelectronic moieties.

Experimental Section

General Procedures. All manipulations were conducted under N_2 using high-vacuum, Schlenk, and glovebox techniques. All reactions were carried out under an ambient pressure of approximately 590 Torr (elevation ~2195 m). All organic solvents were dried over sodium benzophenone ketyl and stored under vacuum. Deuterated solvents were dried over activated 3 or 4 Å molecular sieves. Fluorosulfonic acid was distilled under nitrogen and stored at −30 °C in an inert atmosphere glovebox prior to use. Elemental analyses were performed by Desert Analytics. NMR spectra were recorded with a Bruker Avance DRX-400 instrument. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. (dfepe)-Pt(OTf)$_2$ and (dfepe)Pt(OSO_2F)$_2$ were prepared as described previously.[5] (cod)Pt(Ph)$_2$ was prepared according to a modification of Manzer's procedure:[17] after arylation, quenching of the excess Grignard was carried out with NH_4Cl in methanol; removal of volatiles and extraction with ether afforded high (>80%) yields of pure diphenyl after crystallization.

(cod)Pt(Ph)O_2CCF_3. (cod)Pt(Ph)$_2$ (105 mg, 23 mmol) was dissolved in 10 mL of CH_2Cl_2, and 1 equiv of CF_3CO_2H (17μL) was added via syringe. The reaction mixture was stirred for 5 h, and all volatiles were removed. Ether was added, and the solution was filtered, concentrated, and cold filtered at −78 °C, yielding 80 mg of off-white product (71% yield). Anal. Calcd for $C_{18}H_9O_2F_{23}P_2Pt$: C, 38.96; H, 3.40. Found: C, 38.61; H, 3.58. ^1H NMR (400 MHz, C_6D_6, 27 °C): δ 1.20 (m, 4H); δ 1.55 (m, 4H), 3.94 (s, 2H; $^2J_{PtH} = 40$ Hz) 5.31 (s, 2H), 6.95 (t, $^3J_{HH} = 7$ Hz, 1H; p-C_6H_5), 7.07 (t, $^3J_{HH} = 7$ Hz, 2H; m-C_6H_5), 7.32 (d, $^3J_{HH} = 7$ Hz, $^3J_{PtH} = 36$ Hz, 2H; o-C_6H_5).

(dfepe)Pt(Ph)O_2CCF_3 (1). A solution of 0.465 g (1.02 mmol) of (cod)Pt(Ph)$_2$ in 15 mL of CH_2Cl_2 was cooled to −78 °C, 80 μL CF_3CO_2H (1.03 equiv) was added via syringe, and the solution was allowed to warm to ambient temperature over the course of 15 min with stirring. After 4 h, 0.35 mL of dfepe (1.24 mmol) was added. Volatiles were removed after 16 h at ambient temperature, and the residue was redissolved in 10 mL of CH_2Cl_2 and filtered to remove a small amount of insoluble white solid. Cooling to −78 °C and filtering afforded 0.74 g of crude product, which NMR indicated was contaminated with a small amount of (dfepe)$_2$Pt. Washing this crude product thoroughly with petroleum ether to remove residual (dfepe)$_2$Pt gave 0.640 g (66.2%) of (dfepe)Pt(Ph)O_2CCF_3 as an analytically pure white solid. Anal. Calcd for $C_{18}H_9F_{23}P_2O_2$-Pt: C, 22.85; H, 0.95. Found: C, 22.84; H, 0.91. ^1H NMR (400 MHz, acetone-d_6, 27 °C): δ 7.33 (m, 2H; Pt(C_6H_5)), 7.16 (m, 2H; Pt(C_6H_5)), 7.06 (m, 1H, Pt(C_6H_5)), 3.38 (m, 2H; PCH_2), 3.12 (m, 2H; PCH_2). ^{31}P NMR (161.7 MHz, C_6D_6, 27 °C): δ 68.2 (m, $^1J_{PtP} = 1270$ Hz; trans to Ph), 49.0 (m, $^1J_{PtP} = 4735$ Hz; trans to O_2CCF_3).

[(dfepe)Pt(η^6-C_6H_6)]$^{2+}$ (2). To a solution of 25 mg of (dfepe)-Pt(OSO_2F)$_2$ or (dfepe)Pt(OTf)$_2$ in 0.5 mL of FSO_3H or HOTf, respectively, was added 5 μL (~3 equiv) of benzene. After 30 min, ^1H and ^{31}P NMR indicated the clean generation of **2** as the major solution species, with <10% unreacted starting material. Spectroscopic data in FSO_3H: ^1H NMR (400 MHz,

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[12] NMR spectroscopic data for $PhSO_2F$ in FSO_3H: ^1H: δ 7.15 (d, $J = 8$ Hz, 2H; o-C_6H_5), 7.01 (t, $J = 8$ Hz, 1H; p-C_6H_5), 6.82 (t, $J = 8$ Hz, 2H; m-C_6H_5). ^{19}F: δ 64.52. NMR spectroscopic data for Ph_2SO_2 in FSO_3H: ^1H: δ 7.12 (d, $J = 8$ Hz, 2H; o-C_6H_5), 6.90 (t, $J = 8$ Hz, 1H; p-C_6H_5), 6.79 (t, $J = 8$ Hz, 2H; m-C_6H_5).

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[15] Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450.

[16] (a) Hoerter, J. M.; Roddick. D. M., unpublished results. (b) Schnabel, R. C.; Roddick, D. M. *Organometallics* **1996**, *15*, 3550.

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−20 °C): δ 7.22 (s, 6H; Pt(C_6H_6)), 2.45 (m, 4H; PCH_2). ^{31}P NMR (161.7 MHz, −20 °C): δ 70.5 (ps. p, $^2J_{PF} = 87$ Hz, $^1J_{PtP} = 4470$ Hz). Spectroscopic data in HOTf: ^{1}H NMR (400 MHz, 27 °C): δ 6.84 (s, 6H; Pt(C_6H_6)), 2.11 (m, 4H; PCH_2). ^{31}P NMR (161.7 MHz, 27 °C): δ 77.2 (ps. p, $^2J_{PF} = 89$ Hz, $^1J_{PtP} = 4480$ Hz). ^{13}C{^{1}H} NMR (100.6 MHz, 27 °C): δ 117.4 (s, $^1J_{PtC} = 91$ Hz).

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