Synthesis and Protonation Chemistry of (dfepe)Pt(η^2-alkyne) Complexes

Eric W. Kalberer and Dean M. Roddick*

Department of Chemistry, Box 3838, University of Wyoming, Laramie, Wyoming 82071

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An extension of prior protonolysis studies of platinum−carbon bonds to *in situ* generated Pt−C(sp^2) bonds is reported. A series of (dfepe)Pt(η^2-RC≡CR′) complexes (R = Me, R′ = H; R = *tert*-butyl, R′ = H; R = Me_3Si, R′ = Me; R = Ph, R′ = Me; R = R′ = Me; R = R′ = Ph) have been prepared by treatment of [(dfepe)Pt(μ-H)]$_2$ with the corresponding alkyne in order to examine the addition of Brønsted acids to form the alkenyl complexes (dfepe)Pt(C(R′)=C(H)R)(X). In the case where RC≡CR′ = propyne, a small (5%) amount of the propyne-bridged dimer [(dfepe)Pt]$_2$(μ-η^2:η^2-MeC≡CH) was also formed which could be prepared in pure form by the thermolysis of (dfepe)Pt(η^2-HC≡CMe) (**1**) at 90 °C. Dissolution of **1** in FSO_3H at −80 °C produced the double-proton-transfer propene adduct [(dfepe)Pt(η^2-H_2C=C(H)Me)(X)]$^+$, without evidence for a propenyl Pt(II) intermediate. In contrast, dissolution of **1** in FSO_3D at −80 °C cleanly produced the fully deuterated propenyl complex (dfepe)Pt(C(D)=C(D)CD_3)(OSO_2F), which was characterized by ^{31}P and ^{13}C NMR. The direct observation of this initial proton-transfer intermediate in deuterated acid is ascribed to an unusually large kinetic isotope effect for the second proton-transfer step.

Introduction

Reactivity patterns of organometallic compounds with electrophiles such as halogens and protons play an important role in a variety of metal-mediated processes.[1] While protonolysis reactions often are the termination or product-releasing step in organometallic transformations, this termination step is at times undesirable and may be induced by adventitious water or protic impurities. The protolytic cleavage of M−C bonds specifically in Pt(II) systems has been the subject of numerous studies[2−4] and more recently has been considered as a model of the microscopic reverse of heterolytic alkane C−H bond activation in "Shilov-type" chemistry.[5] Despite the obvious importance of protolytic reactions, uncertainty still remains regarding the detailed mechanism of metal−carbon bond cleavage by H^+ and the factors which control the kinetics and thermodynamics of this fundamental reaction mode.

We have reported the synthesis of square-planar acceptor phosphine platinum(II) complexes of the general form (dfepe)Pt(R)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; R = Me, Et; X = Cl, O_2CCF_3, OSO_3H, OTf, OSO_2F).[6,7] Unlike most transition-metal alkyl complexes, these compounds are remarkably resistant to metal−carbon bond protonolysis: (dfepe)Pt(R)(O_2CCF_3) compounds, for example, function as ethylene dimerization catalysts with long-term stability and activity in neat trifluoroacetic acid at 120 °C.[7] The related cationic methyl carbonyl complex (dfepe)Pt(Me)(CO)$^+$ is stable in neat fluorosulfonic acid for days at ambient temperatures and even has significant stability in $FSO_3H/SbF_5/SO_2$ solvent mixtures.[8] While we were unable to determine whether these protonolyses proceed via a stepwise S_E(ox) or concerted S_E2 mechanism on the basis of kinetic data,[9] the substantially lower protolytic resistance (dfepe)Pt(Ph)(O_2CCF_3) indicates that an S_E2 mechanism is most likely.[10]

We are interested in extending the generality of Pt(II)−R protolytic resistance in perfluoroalkylphosphine systems as a function of both ancillary phosphine variation and the nature of R. Recently we have reported *trans*-[$(C_2F_5)_2PMe]_2$Pt(Me)(X) compounds which display significant differences in Pt−C protolytic resistance due to trans-X ligand effects.[11] For sp^2-hybridized R groups, direct Pt−C bond protonolysis as well as the additional possibility of β-proton attack on the hydrocarbon π-system must be considered. Proton addition in the latter case would result in cationic carbene complex formation, which may be either directly ob-

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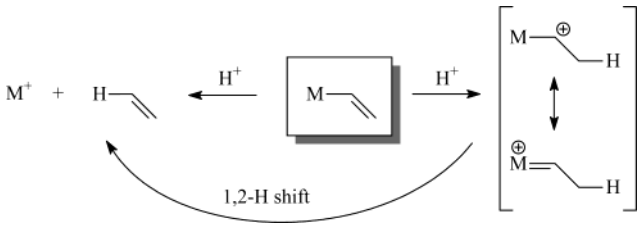
Scheme 1

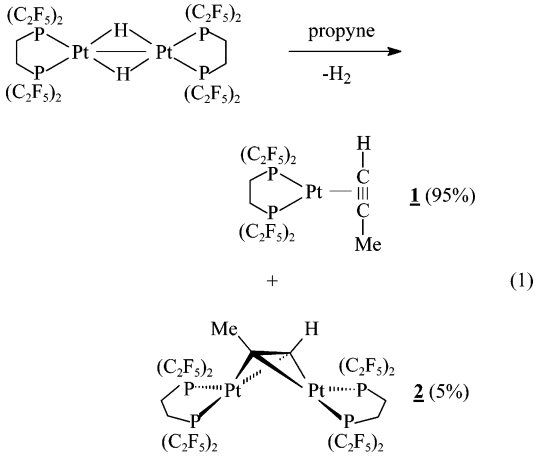


served or subsequently undergo a rapid 1,2-hydride shift to ultimately form Pt−C cleavage products (Scheme 1)

In this paper we report our efforts to access (dfepe)-Pt(vinyl)X complexes for study via the protonation of (dfepe)Pt(η^2-alkyne) systems. Rapid double protonation of (dfepe)Pt(η^2-propyne) by fluorosulfonic acid is observed at low temperatures in FSO_3H by NMR to produce (dfepe)Pt(η^2-propene)$(OSO_2F)^+$. Surprisingly, an unexpectedly large kinetic isotope effect for the second proton-transfer step is found for this process, which results in the stabilization and direct observation of the initial proton-transfer product in deuteriofluorosulfonic acid.

Results and Discussion

Synthesis of (dfepe)Pt(η^2-alkyne) Complexes. Our efforts to extend previous platinum perfluoroalkylphosphine H^+ addition studies to Pt−C(sp^2) systems initially focused on the synthesis of alkenyl complexes, (dfepe)Pt(η^1-vinyl)(X). Direct alkylations of (dfepe)$PtCl_2$ with vinyl Grignard, lithium, or tin reagents have not been successful. Accordingly, we have examined (dfepe)-Pt(η^2-alkyne) complexes as potential precursors to this class of compounds, since HX addition to form the corresponding (dfepe)Pt(η^1-vinyl)(X) complex has been demonstrated.[12,13] Following our previously reported synthesis of (dfepe)Pt(η^2-alkene) complexes,[14] treatment of the hydride dimer [(dfepe)Pt(μ-H)]$_2$ with excess propyne in acetone gave (dfepe)Pt(η^2-MeC≡CH) (**1**) as the major product (95%), as well as ∼5% of the propyne-bridged dimer [(dfepe)Pt]$_2$(μ-η^2:η^2-MeC≡CH) (**2**) (eq 1).

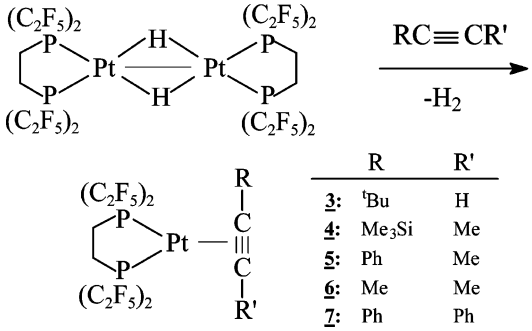


(1)

The ν(C≡C) band in the infrared spectrum for **1** appears at 1758 cm^{-1}, which is somewhat higher in energy than the 1712 cm^{-1} value reported for $(Ph_3P)_2Pt(\eta^2$-MeC≡CH) and is in accord with the reduced back-bonding ability of the (dfepe)Pt moiety.[12a]

Previously reported square-planar unsymmetrical alkyne complexes *cis*-$(R_3P)_2Pt(\eta^2$-RC≡CR′) display inequivalent ^{31}P NMR resonances.[13] For **1**, a single broad $^{31}P\{^1H\}$ resonance is observed centered at 77.2 ppm with unresolved $^2J_{PF}$ coupling. However, the ^{195}Pt satellites ($J \approx 3350$ Hz) are unsymmetrical in shape and low-intensity shoulders on the central resonance indicated a non-first-order XY + QXY composite spin system which was modeled satisfactorily by simulation (δ_X 76.8, δ_Y 77.5, $^2J_{PP} = 197$ Hz, $^1J_{PtP} = 3430$, 3315 Hz). The ^1H NMR resonances for the acetylenic and methyl protons appear as complex multiplets at δ 7.95 and 2.96, respectively, and exhibit ^{195}Pt coupling and ^{31}P coupling to both phosphorus centers. Interestingly, both the acetylenic and methyl resonances display distinctly asymmetrical sets of satellites due to the non-first-order ^{31}P component of the AM_3QXY spin system. VT NMR experiments indicate that no equilibration of phosphorus environments by alkyne rotation or reversible alkyne dissociation occurs on the NMR time scale up to 100 °C in toluene-d_8.

The reaction of [(dfepe)Pt(μ-H)]$_2$ with other alkynes RC≡CR′ (R = *tert*-butyl, R′ = H; R = Me_3Si, R′ = Me; R = Ph, R′ = Me; R = R′ = Me; R = R′ = Ph) produces the corresponding alkyne complexes **3**−**7** (eq 2). In the cases



(2)

of the more distinctly unsymmetrical alkyne complexes **3** and **5**, two discrete mutually coupled ^{31}P resonances are observed. The $^2J_{PP}$ couplings (160, 167 Hz) are substantially larger than couplings reported for other *cis*-$(R_3P)_2Pt(\eta^2$-RC≡CR′) systems ($^2J_{PP}$(av) ≈ 33 Hz)[13a] and are comparable to the large $^2J_{PP}$ value derived from a spectral simulation for **1**.

We anticipated that the formation of **2** from [(dfepe)-Pt(μ-H)]$_2$ could be favored by suitable variations in propyne stoichiometry, order of addition, and/or the temperature of reaction; however, only minor changes in the relative yield of **1** and **2** were observed. Pure **2** was instead obtained as a pure yellow crystalline solid by vacuum sublimation of **1** at 90 °C. ^1H and ^{31}P NMR spectroscopy and elemental analysis are in accord with a μ-η^2:η^2-propyne-bridged structure. Two phosphorus resonances were observed, which reflect the lateral asymmetry of the dimeric structure, and proton resonances for the bridging propyne acetylenic proton and methyl group appear as triplets due to coupling with the trans-disposed phosphorus centers with associated ^{195}Pt satellites consistent with coupling to two ^{195}Pt

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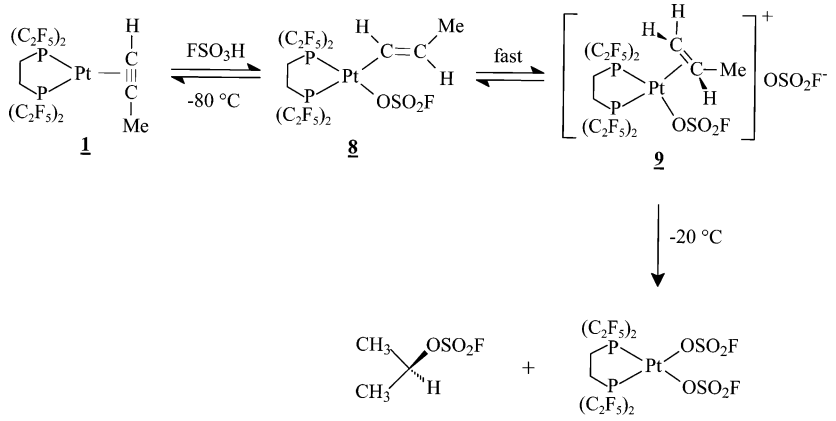
Scheme 2



centers. The bent dimetallic structure depicted in eq 1 is in accord with previously reported structurally characterized analogous $[(L)_2Pt]_2(\mu$-alkyne) complexes.[15]

(dfepe)Pt(η^2-MeC≡CH) Protonation Studies. The reactivity of propyne complex **1** with trifluoroacetic acid was monitored by NMR. In methylene chloride, no reaction between **1** and excess CF_3CO_2H (1−5 equiv) was observed at ambient temperatures. In neat trifluoroacetic acid, however, 75% conversion to (dfepe)Pt$(O_2CCF_3)_2$ took place after 2 days without any evidence for intermediates. Since the initial protonation step with trifluoroacetic acid is unfavorable, we examined acid addition with the much stronger acid FSO_3H. Addition of 1−5 equiv of fluorosulfonic acid to solutions of **1** in methylene chloride resulted in a complex mixture of products. Dissolving **1** in neat FSO_3H immediately produced the exhaustive protonolysis product (dfepe)-Pt$(OSO_2F)_2$ at ambient temperatures.

Variable-temperature NMR studies with **1** were performed in fluorosulfonic acid in an effort to track the HX reaction pathway. At −80 °C, dissolution of **1** in FSO_3H cleanly produced a new species with inequivalent ^{31}P NMR resonances at δ 75.8 ($^1J_{PtP}$ = 3200 Hz) and δ 54.1 ($^1J_{PtP}$ = 4040); the larger coupling observed for the latter resonance is consistent with phosphorus trans to a coordinated fluorosulfonate anion. ^{1}H NMR data indicated the presence of a η^2-propene ligand, with three separate broadened vinylic resonances at δ 7.24, 5.21, and 4.96 which are integrated as 1:1:1 with respect to the methyl resonance at δ 1.46. COSY experiments confirmed the assignment of the mutually coupled δ 7.24 and 4.96 resonances as the internal vinylic proton and the cis (with respect to the methyl group) terminal vinyl proton, respectively. ^{13}C NMR spectra exhibit a vinylic doublet at δ 163.7 ($^1J_{CH}$ = 162 Hz) and a triplet at δ 92.9 with coupling to the trans phosphorus (td, $^2J_{CP}$ = 65 Hz, $^1J_{CH}$ = 166 Hz). This low-temperature protonation product is thus identified as the Pt(II) propene complex $\{$(dfepe)Pt[η^2-H_2C=C(H)Me](OSO$_2$F)$\}^+SO_3F^-$ (**9**). Warming FSO_3H solutions of **9** to −20 °C for 20 min resulted in a 55% conversion to (dfepe)Pt$(OSO_2F)_2$ and free isopropylfluorosulfonate (δ 4.55 heptet, δ 0.69 doublet, $^3J_{HH}$ = 6 Hz; 1H:6H) (Scheme 2). $(CH_3)_2$CH-(OSO$_2$F) decomposed within minutes at ambient temperature, as noted previously.[16]

VT NMR studies in protiofluorosulfonic acid gave no evidence for the intermediate formation of (dfepe)Pt-(C(H)=C(H)Me)(OSO$_2$F) at −80 °C. However, monitoring the reaction of **1** in FSO_3D at −75 °C revealed the clean formation of an intermediate which we assign as the fully deuterated propenyl complex (dfepe)Pt(C(D)=C(D)CD_3)(OSO$_2$F) (**8**). This observation is fully reproducible. ^{1}H NMR spectra showed only a broad resonance due to the dfepe chelate backbone. ^{31}P NMR, however, revealed signals at δ 74.5 ($^1J_{PtP}$ = 1470 Hz) and δ 42.2 ($^1J_{PtP}$ = 5465 Hz), whose distinctive coupling magnitudes indicate the presence of a strongly donating trans σ-vinyl group and a weakly donating OSO$_2$F group, respectively. Warming to −70 °C for 15 min resulted in conversion to a 1:1 mixture of **8** and **9**, and ^{31}P spectra at −50 °C showed essentially complete conversion to the propene complex **9**.

The observation of the initial proton-transfer product **8** in FSO_3D with complete H/D scrambling is quite surprising. Our previous study of k_H/k_D trends in Pt−methyl protonolyses revealed a substantial increase in the apparent kinetic isotope ratio on going from 20 °C (8 ± 1) to 0 °C (17 ± 1) in sulfuric acid that was ascribed to a composite of protic solvent partitioning and temperature effects.[9] In the successive conversion of the propyne complex **1** to **8** and then ultimately **9**, the direct observation of the intermediate propenyl complex in FSO_3D suggests a kinetic isotope effect for the second proton transfer that is sufficiently high at this temperature to become rate determining (Scheme 3). Additional evidence for the high effective KIE is afforded by examining the reaction of **1** in a 1:1 mixture of FSO_3H and FSO_3D at −75 °C. The product observed under these conditions is exclusively **9**, consistent with an effective $k_H/k_D \geq 10$. Since the isotopic purity of FSO_3D used in our experiments is ∼95% (i.e., a 20:1 mixture of FSO_3D and FSO_3H), and we see only **8** in the presence of 95% FSO_3D, we can infer that the composite kinetic isotope effect favoring **9** over **8** falls between 10 and 20.[17]

Dramatic increases in observed KIE's with lowering temperature for proton-transfer reactions are often

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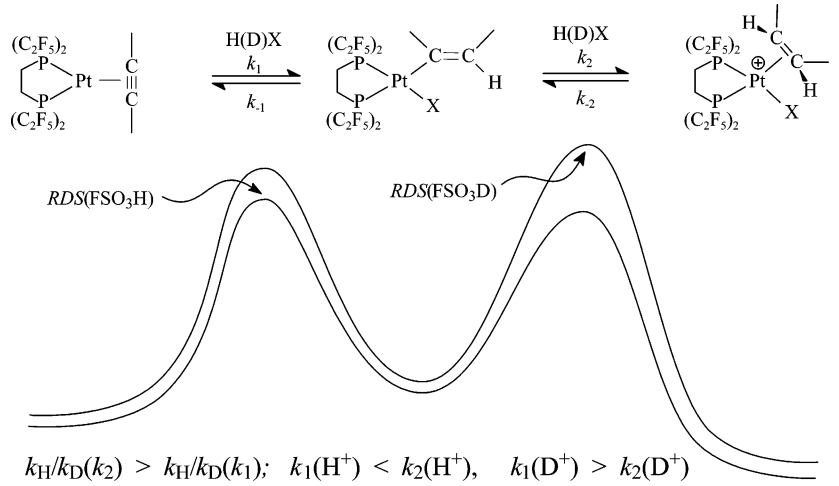
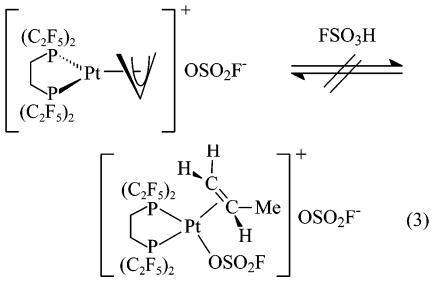
(17) Under the conditions of the experiment (20 mg of [(dfepe)Pt-(μ-H)]$_2$ converted to **1**, 0.6 mL 95 atom % FSO_3D), there is at least a 20-fold stoichiometric excess of FSO_3H available for reaction and therefore the production of **9** is not acid limited.

Scheme 3



attributed to tunneling effects.[18] Furthermore, the second proton-transfer step, which involves addition to a Pt(II) center, should be significantly less exothermic than the initial addition to a Pt(0)−alkyne complex. Earlier studies have shown maximal KIE's for proton transfers where $\Delta pK \approx 0$ (the "Bell Criterion"),[19] and therefore, we can further rationalize a relatively large KIE for the second step. A possible changeover in proton-transfer mechanism from $S_E(ox)$ to S_E2 may also contribute to a substantial KIE difference between the first and second steps in Scheme 3.

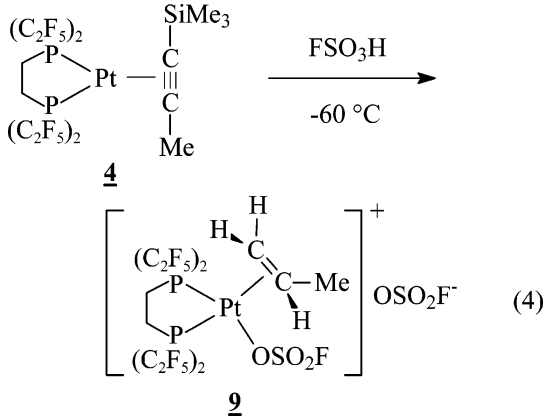
Synthesis and Protolytic Stability of (dfepe)Pt(η^3-C_3H_5)$^+$. The absence of proton resonances in low-temperature FSO_3D studies assignable to either the propene or propenyl ligand methyl groups indicated that rapid H/D scrambling had occurred under these conditions in both the vinylic and methyl positions. Since this observation could be reasonably accommodated via a H/D exchange mechanism involving the allylic intermediate (dfepe)Pt[η^3-$H_2CC(H)CH_2$]$^+$, we tested this possibility directly. Treatment of [(allyl)Pt(Cl)]$_4$ with $AgBF_4$ in acetone followed by the addition of dfepe afforded [(dfepe)Pt(η^3-C_3H_5)]$^+BF_4^-$ (**10**). No reaction of **10** in neat FSO_3H was observed up to 110 °C; moreover, no H/D scrambling of the terminal or central allylic protons was found in FSO_3D at 25 °C (eq 3). This lack



(3)

of reactivity is in marked contrast to facile allylic proton transfer observed in similar Pt(II) alkene systems[20] and clearly indicates that H/D scrambling via an allylic intermediate is not a viable reaction pathway.

Other (dfepe)Pt(η^2-RC≡CR′) Protonation Studies. Rapid deuterium scrambling with **1** under acidic conditions masks any stereochemical information which would address the nature of the proton addition steps to coordinated alkyne. For example, protonation of $Cp_2V(\eta^2$-PhC≡CPh) was reported to yield predominately (85%) *cis*-stilbene, consistent with initial protonation at the metal center followed by rate-determining migration of hydride to from a *cis*-alkenyl intermediate prior to loss of alkene product.[21] Accordingly, we examined the reactions of the internal alkyne adducts **4**−**7** with fluorosulfonic acid by VT NMR. Dissolution of the trimethylsilyl-substituted alkyne complex **4** in FSO_3H at −60 °C produced spectra identical with those for propene adduct **9**, indicating that silyl cleavage occurs under these conditions (eq 4).



(4)

Complexes **5** and **7** did not readily dissolve in FSO_3H at low temperatures to give well-defined solutions for study. The 2-butyne adduct **6** does dissolve in FSO_3H at −70 °C to cleanly afford {(dfepe)Pt[η^2-Me(H)C═C(H)-Me](OSO$_2$F)}$^+SO_3F^-$ (**11**), with ^{31}P resonances at δ 74.8 ($^1J_{PtP}$ = 3220 Hz) and 52.1 ($^1J_{PtP}$ = 4290 Hz) that are similar to those observed for **9**. ^{1}H NMR spectra reveal a single methyl resonance at 1.33 ppm, a major singlet resonance in the vinylic region at δ 6.49, and a minor (<5%) singlet at δ 6.31. The integration ratios 4:6:2 are in accord with a 2-butene complex formulation. The

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thermal instability of **11** above −20 °C does not allow us to assign the stereochemistry of the 2-butene ligand. Nevertheless, the formation of **11** is stereoselective.

Summary

Our failure to prepare (dfepe)Pt(vinyl)(X) complexes using standard alkylation procedures is unfortunate, since monitoring the direct reaction of such systems with protic reagents was a primary goal of this work. The observed low conjugate basicity of (dfepe)Pt(alkyne) complexes suggests that the target (dfepe)Pt(vinyl)(X) systems possess a substantial intrinsic Brønsted acidity and may be incompatible with this synthetic strategy.

We have been able to prepare a series of platinum alkyne complexes and examine their proton addition chemistry. Determining the regio- and stereoselectivity of proton addition to M−alkyne and M−alkenyl systems is a very complicated and challenging problem, owing to the surprising variety observed in kinetic and thermodynamic control in other transition-metal systems.[22] The markedly low basicity of (dfepe)Pt^{II} systems has necessitated the use of neat strong acids as both the solvent and protic reagent, and therefore, the addition of discrete stoichiometric reagents is not possible. However, it is apparent that the first and second steps of proton transfer have comparable kinetics, since a shifting of the rate-determining proton-transfer step has been shown to be induced by shifting to FSO_3D as a reaction media. We are not aware of any precedence for this type of isotopic discrimination in an organometallic system.

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 Å molecular sieves. Propyne (Aldrich) was degassed and used as received. Fluorosulfonic acid was distilled under nitrogen and stored at −30 °C in an inert-atmosphere glovebox prior to use. Deuteriofluorosulfonic acid was prepared according to literature methods and was determined to be of 95% isotopic purity by integration against an external acetone standard.[23] Elemental analyses were performed by Desert Analytics. Infrared spectra were obtained on a Bomem MB100 FTIR instrument. 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. [(allyl)Pt(Cl)]$_4$ was prepared by following a published procedure.[24]

(dfepe)Pt(η²-MeC≡CH) (1). A mixture of 250 mg of [(dfepe)Pt(μ-H)]$_2$ in 20 mL of acetone under nitrogen was cooled to −78 °C and treated with 20 mL of propyne gas. An immediate fading from dark to light orange was noted. The reaction mixture was warmed to ambient temperature and stirred for 15 min. The volatiles were removed, and the residue was taken up in 20 mL of petroleum ether and filtered. Concentration and cooling of the filtrate to −78 °C yielded a white precipitate, which upon filtration and warming melted to form a colorless oil. NMR revealed that small amounts of **2** form in the neat oil upon standing for several days. IR (neat oil, cm^{-1}): 1758 (m), 1440 (vw), 1415 (w), 1305 (vs), 1218 (vs), 1126 (vs), 1049 (w), 964 (s), 872 (w), 841 (w), 805 (m), 751 (s). ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 7.95 (*A*M$_3$QXY, $^3J_{HP}$ = 28, 9 Hz, $^2J_{HPt}$ = 91 Hz; 4H; *H*C≡CCH$_3$), 2.96 (AM$_3$QXY, $^4J_{HP}$ = 11, 1 Hz, $^3J_{HPt}$ = 52 Hz; 3H; HC≡CC*H*$_3$), 2.62 (m, 4H; PCH$_2$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 77.5, 76.8 (XY + QXY pattern, unresolved ^{19}F coupling, $^2J_{PP}$ = 197 Hz, $^1J_{PtP}$ = 3430, 3315 Hz). ^{13}C NMR (100.6 MHz, acetone-d_6, 27 °C): δ 123−112 (overlapping CF_2CF_3 resonances), 103.3 (dd, $^1J_{CH}$ = 230 Hz, $^2J_{CP}$ = 46 Hz, $^1J_{CPt}$ = 142 Hz; H*C*≡CCH$_3$), 22.1 (tm, $^1J_{CH}$ = 139 Hz, PCH$_2$), 15.4 (tm, $^1J_{CH}$ = 131 Hz, HC≡C*C*H$_3$).

[(dfepe)Pt]$_2$(μ-η²:η²-MeC≡CH) (2). Warming 50 mg of propyne complex **1** to 90 °C in a small sublimation apparatus at 10^{-3} Torr resulted in slow conversion to the dimeric complex **3**, which was collected by sublimation to afford 30 mg (62%) of yellow crystalline product. Anal. Calcd for $C_{23}H_{11}F_{40}P_4Pt_2$: C, 17.70; H, 0.76. Found: 17.81; H, 0.75. ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 6.98 (t, $^3J_{HP}$ = 18 Hz, $^2J_{HPt}$ = 38 Hz; 1H; *H*C≡CCH$_3$), 3.32 (t, $^4J_{HP}$ = 9 Hz, $^3J_{HPt}$ = 52 Hz; 3H; HC≡CC*H*$_3$), 2.70 (m, 4H; PCH$_2$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 73.2 (m, $^1J_{PtP}$ = 3740 Hz), 71.5 (m, $^1J_{PtP}$ = 3370 Hz).

(dfepe)Pt(η²-RC≡CR′) Preparation. Alkyne complexes **3**−**6** were prepared in situ from the reaction of ca. 5 equiv of alkyne with [(dfepe)Pt(μ-H)]$_2$ in acetone-d_6 and were characterized by NMR spectroscopy.

(dfepe)Pt(η²-^{t}BuC≡CH) (3). ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 7.94 (dd, $^3J_{HP}$ = 29.2, 9.4 Hz, $^2J_{HPt}$ = 87.5 Hz; 1H; *H*C≡C(CH$_3$)$_3$), 2.71 (m, 4H; PCH$_2$), 1.32 (s, 9H; HC≡CC-(C*H*$_3$)$_3$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 83.8 (m, $^2J_{PP}$ = 167 Hz, $^1J_{PtP}$ = 3160 Hz), 72.7 (m, $^2J_{PP}$ = 167 Hz,$^1J_{PtP}$ = 3495 Hz).

(dfepe)Pt(η²-(Me$_3$Si)C≡CMe) (4). ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 3.04 (m, $^4J_{HP}$ = 8 Hz, $^3J_{HPt}$ = 46 Hz, 3H; C*H*$_3$C≡CSi(CH$_3$)$_3$), 2.65 (m, 4H; PCH$_2$), 0.24 (s, 9H; CH$_3$C≡CSi(C*H*$_3$)$_3$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 77.8 (m, J_{PtP} = 3500 Hz).

(dfepe)Pt(η²-PhC≡CMe) (5). ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 7.69 (d, $^3J_{HH}$ = 7.4, 2H; *o*-C$_6$H$_5$), 7.44 (t, $^3J_{HH}$ = 7.8 Hz, 2H; *m*-C$_6$H$_5$), 3.15 (d, $^4J_{HP}$ = 9 Hz, $^3J_{HPt}$ = 51 Hz, 3H; PhC≡CC*H*$_3$), 2.78 (m, 4H; PCH$_2$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 78.1 (m, $^2J_{PP}$ = 160 Hz, $^1J_{PtP}$ = 3230 Hz), 74.8 (m, $^2J_{PP}$ = 160 Hz,$^1J_{PtP}$ = 3180 Hz).

(dfepe)Pt(η²-MeC≡CMe) (6). ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 2.81 (m, $^3J_{HPt}$ = 56 Hz; 6H; (C*H*$_3$)C≡C(C*H*$_3$)), 2.66 (m, 4H; PCH$_2$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 76.6 (m, $^1J_{PtP}$ = 3220 Hz).

(dfepe)Pt(η²-PhC≡CPh) (7). A mixture of [(dfepe)Pt(μ-H)]$_2$ (115 mg, 0.0754 mmol) and 13 mg (0.073 mmol) of diphenylacetylene was dissolved in acetone at −78 °C and warmed to ambient temperature with stirring, during which time the initially orange solution became colorless. After 15 min the solution was filtered, the volatiles were removed, and the residue was redissolved in 20 mL of petroleum ether. Concentration and cooling to −78 °C and filtration yielded 70 mg (49%) of off-white crystalline **7**. Anal. Calcd for $C_{24}H_{14}F_{20}P_2Pt$: C, 27.21; H, 1.13. Found: C, 27.30; H, 0.98. ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 7.78 (d, $^3J_{HH}$ = 7.5 Hz, 4H; *o*-C$_6$H$_5$), 7.50 (t, $^3J_{HH}$ = 7.5 Hz, 4H; *m*-C$_6$H$_5$), 7.38 (t,$^3J_{HH}$ = 7.5 Hz, 2H; *p*-C$_6$H$_5$), 2.85 (m, 4H; PCH$_2$). ^{31}P NMR (161.7 MHz, acetone-d_6, 27 °C): δ 69.5 (m, $^1J_{PtP}$ = 3220 Hz).

{(dfepe)Pt[η²-H$_2$C=C(H)Me](OSO$_2$F)}$^+$SO$_3$F$^-$ (9). Dissolution of ca. 20 mg of **1** in 0.5 mL of FSO_3H at −80 °C cleanly produced a solution of **9**, which was characterized by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H chemical shifts were referenced to an external acetone-d_6 capillary standard. ^{1}H NMR (400 MHz, FSO_3H, −20 °C): δ 7.31 (m, 1H; (CH$_3$)*H*C=C(H$_{trans}$)(H$_{cis}$)), 5.25 (m, 1H; (CH$_3$)HC=C(*H*$_{trans}$)(H$_{cis}$)), 5.11 (dd, $^3J_{HH}$ = 18 Hz, $^2J_{HH}$ = 5 Hz, 1H; (CH$_3$)HC=C(H$_{trans}$)(*H*$_{cis}$)), 2.32 (m, 4H; PCH$_2$), 1.55 (s, 3H; (C*H*$_3$)HC=C(H$_{trans}$)(H$_{cis}$)). ^{31}P NMR (161.7 MHz, FSO_3H, −80 °C): δ 75.8 (m, $^1J_{PtP}$ = 3200 Hz), 54.1 (ps. P, $^2J_{PF}$ = 76 Hz, $^1J_{PtP}$ = 4040 Hz). ^{13}C NMR (100.6 MHz, FSO_3H, −50 °C):

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δ 163.7 (d, $^1J_{CH}$ = 162 Hz; $(CH_3)HC{=}CH_2$), 120−108 (overlapping complex multiplets; CF_2CF_3), 92.9 (td, $^2J_{CP}$ = 65 Hz, $^1J_{CH}$ = 166 Hz; $(CH_3)HC{=}CH_2$), 23.9 (q, $^1J_{CH}$ = 128 Hz; $(CH_3)HC{=}CH_2$), 17.7 (t, $^1J_{CH}$ = 138 Hz; PCH_2).

[(dfepe)Pt(η^3-C_3H_5)]$^+BF_4^-$ (10). A mixture of 285 mg (0.262 mmol) of [(allyl)Pt(Cl)]$_4$ and 205 mg (1.04 mmol) of $AgBF_4$ was dissolved in 30 mL of acetone at −78 °C. After the mixture was stirred and warmed to 25 °C, 0.30 mL of dfepe (1.3 mmol) was added via syringe, and this yellow solution was stirred in the absence of light for 16 h, during which time it became colorless and AgCl precipitated. After filtration, the volatiles were removed and the residue was slurried in ether. Subsequent filtration yielded 230 mg (25%) of off-white crude product, which was recrystallized from acetone/ether to afford the analytically pure white compound. Anal. Calcd for $C_{13}H_9BP_2F_{24}Pt$: C, 17.41; H, 1.16. Found: C, 17.56; H, 1.01. ^{1}H NMR (400 MHz, acetone-d_6, 27 °C): δ 6.28 (tt, $^3J_{HH}$ = 7.1, 13.8 Hz, $^2J_{PtH}$ = 34 Hz, 1H; CH_2CHCH_2), δ 5.95 (dd; $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 9 Hz, 2H, *syn*-CH_2CHCH_2), δ 4.07 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{HH}$ = 9 Hz, 2H, *anti*-CH_2CHCH_2), δ 3.60 (m, 4H; PCH_2). ^{31}P NMR (400 MHz, acetone-d_6, 27 °C): δ 77.4, ($^1J_{PtP}$ = 3910 Hz).

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