Synthesis, Structure, and Characterization of a Bridging Ethylidene (Perfluoroalkyl)phosphine Platinum Complex

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Thermolysis of (dfepe)Pt(Et)(O_2CCF_3) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) in benzene at 80 °C results in the formation of (dfepe)Pt(η^2-C_2H_4). However, at 120 °C in CF_3CO_2H a bridging ethylidene platinum dimer, [(dfepe)$_2$Pt$_2$(μ-CHMe)(μ-H)][O_2CCF_3], is produced instead. Product isolation by precipitation with diethyl ether afforded the neutral dimer (dfepe)$_2$Pt$_2$(μ-CHMe$_3$). Alternatively, (dfepe)$_2$Pt$_2$(μ-CHMe) may be prepared at 20 °C by treatment of [(dfepe)Pt(μ-H)]$_2$(H)$^+$ with 1 atm of ethylene. Complete characterization of this species was accomplished by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, as well as X-ray diffraction. Investigations probing the mechanism of formation for this μ-alkylidene product are presented. The synthesis of the benzyl complex (dfepe)Pt(CH_2Ph)(O_2CCF_3) and its reversible rearrangement to the η^3-benzyl complex [(dfepe)Pt(η^3-CH_2Ph)]$^+$ upon labilization of trifluoroacetate anion is also reported.

Introduction

We have recently reported the catalytic dimerization of ethylene by (perfluoroalkyl)phosphine complexes of platinum and palladium in trifluoroacetic acid.[1] A key feature of the proposed catalytic cycle is the stability of alkyl intermediates (dfepe)M(R)X (R = Et, Bu) toward further protonolysis under catalytic reaction conditions (CF_3CO_2H, 80 °C) (Scheme 1).

Since related work with (dfepe)Pt(Me)(O_2CCF_3) showed that protonolysis to form (dfepe)Pt(O_2CCF_3)$_2$ only occurs at significant rates above 150 °C,[2] we also wished to examine the thermal stability of the dimerization catalytic resting state, (dfepe)Pt(Et)(O_2CCF_3), to establish an effective upper thermal limit for Pt−alkyl insertion chemistry in trifluoroacetic acid. Surprisingly, we find that thermolysis of (dfepe)Pt(Et)(O_2CCF_3) at 120 °C does not result in ethane evolution and production of (dfepe)Pt(O_2CCF_3)$_2$ as expected but, rather, leads to the quantitative formation of an ethylidene-bridged dimeric product, [(dfepe)$_2$Pt$_2$(μ-CHMe)(μ-H)][O_2CCF_3], which is readily deprotonated to form (dfepe)$_2$Pt$_2$(μ-CHMe). In this paper we present the synthesis, structure, and characterization of these μ-alkylidene products and some observations regarding the mechanism of dimer formation. We also report the synthesis of the benzyl complex (dfepe)Pt(CH_2Ph)(O_2CCF_3) and its reversible rearrangement to the η^3-benzyl complex [(dfepe)Pt(η^3-CH_2Ph)]$^+$ upon abstraction of trifluoroacetate anion.

Results and Discussion

Warming (dfepe)Pt(Et)(O_2CCF_3) (**1**) in benzene to 80 °C results in reversible CF_3CO_2H elimination and the formation of previously reported (dfepe)Pt(η^2-C_2H_4).[3] However, thermolysis in trifluoroacetic acid at 120 °C for 2 h resulted in the complete disappearance of starting material resonances and the appearance of new proton signals at δ 8.97 and 2.78, a Pt$_2$(μ-H) hydride resonance at δ 0.26 (tt, $^1J_{PtH}$ = 635 Hz, $^1J_{PH}$ = 163 Hz), and a distinctive carbon resonance at 152.4 ppm coupled to two platinum centers and two phosphorus atoms (t, $^2J_{PC}$ = 130 Hz, $^1J_{PtC}$ = 491 Hz; Pt(μ-*C*HMe)). Two ^{31}P NMR resonances for this new product **2** appeared at δ 73.5 (m, $^1J_{PtP}$ = 4894 Hz) and 67.8 (m, $^1J_{PtP}$ = 2045 Hz), consistent with a dfepe chelate coordinated trans to weak and strong sigma-donors, respectively. Attempted isolation of **2** by either precipitation with diethyl ether or removal of trifluoroacetic acid under vacuum yielded the yellow solid product **3**, which, apart from the lack of a hydride resonance, exhibited very similar spectroscopic properties. Dissolution of **3** in trifluoroacetic acid resulted in a quantitative reversion to **2**. Both ^{1}H and ^{13}C data are consistent with the presence of a bridging ethylidene moiety (μ-CHMe) for both complexes **2** and **3** (Scheme 2). In addition to the formation of ethylidene dimer products, ca. 0.5 equiv of 2-(trifluoroacetato)-butane was also observed by NMR in the thermolysis mixture. This butyl ester product comes from the platinum-catalyzed dimerization of released ethylene, followed by 1,2-acid addition,[1] and satisfactorily accounts for the mass balance required in Scheme 2.

A number of hydrocarbyl ligand-bridged dimeric platinum complexes are known;[4−7] the most closely

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(5) (a) Bandini, A. L.; Banditelli, G.; Minghetti, G. *J. Organomet. Chem.* **2000**, *595*, 224. (b) Minghetti, G.; Albinati, A.; Bandini, A. L.; Banditelli, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 120.

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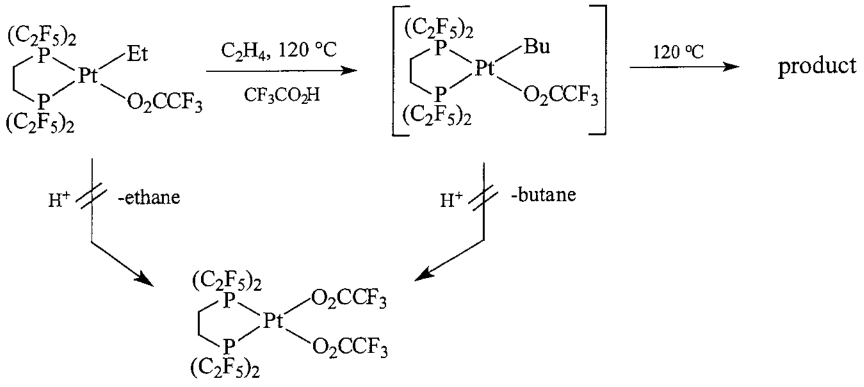
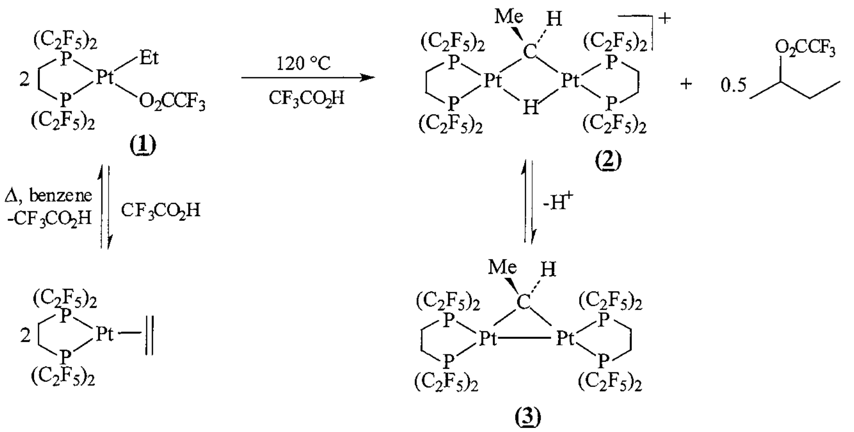
Scheme 1



Scheme 2



comparable μ-alkylidene systems are $[Pt_2(dppe)_2(\mu\text{-}CHCH_2R)(\mu\text{-}H)]^+$ (R = H, Ph)[5] and $[Pt_2(dppf)_2(\mu\text{-}CHCH_2Ar)(\mu\text{-}H)]^+$ (dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$, Ar = *p*-MeO-C_6H_4).[6] ^{13}C and ^1H NMR alkylidene resonances reported for these compounds are shifted uniformly upfield relative to data for **2**, reflecting the significantly lower platinum electron density induced by the dfepe ligands.

The presence of a bridging ethylidene group in compound **3** was confirmed by an X-ray crystallographic study (Figure 1). A summary of data collection parameters and a listing of selected metrical parameters are presented in Tables 1 and 2, respectively. Disorder of the bridging ethylidene group between the sides of the plane defined by Pt(1), Pt(2), and the bridging carbon reduced the precision of this structure. However, a general comparison between the diplatinum core of this molecule with related structures can be made. The observed Pt−Pt distance, 2.6540(8) Å, for **3** is substantially shorter than metal−metal distances reported for μ-methylene complexes without a supporting Pt−Pt bond (>3 Å)[7] and for the cationic hydride-bridged dimers $[Pt_2(dppe)_2(\mu\text{-}CHCH_2Ph)(\mu\text{-}H)]^+$ (2.735(1) Å)[5] and $[Pt_2(dppf)_2(\mu\text{-}CHCH_2Ar)(\mu\text{-}H)]^+$ (2.7314(4) Å)[6] but similar to Pt−Pt distances reported for the neutral trimeric complexes $Pt_3[\mu\text{-}C(OMe)Ar]_3(CO)_3$ (2.621(1) Å) and $(^tBu_2MeP)_2Pt_2[\mu\text{-}C(OMe)Ph]W(CO)_6$ (2.628(1) Å).[8,9] The geometry about each platinum center is distorted square planar, with each (dfepe)Pt chelate moiety twisted ~20° from the plane defined by $Pt_2(\mu\text{-}C(21b))$. The Pt−P bonds opposite to the ethylidene bridge (2.253(5) and 2.245(3) Å) are somewhat longer than the Pt−P bonds opposite to the Pt−Pt bond (2.211(4), 2.206(4) Å) and are indicative of a stronger trans influence for the alkylidene bridge relative to the neighboring platinum center.

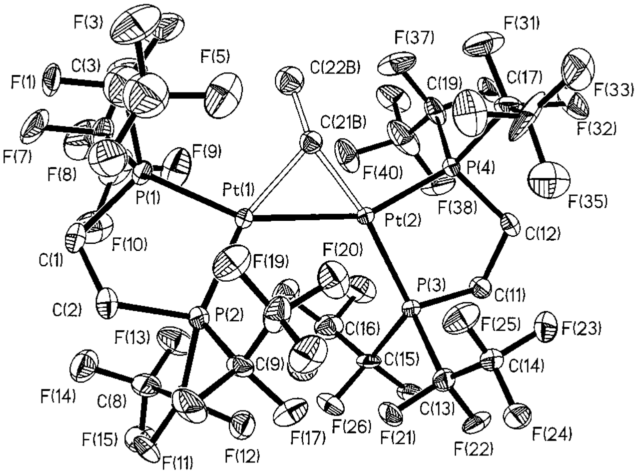


Figure 1. Molecular structure of $(dfepe)_2Pt_2(\mu\text{-}CHMe)$ (**3**) with the atom-labeling scheme (30% probability ellipsoids). Only one of the disordered ethylidene groups is shown.

The reported synthesis of $[Pt_2(dppe)_2(\mu\text{-}CHCH_2R)(\mu\text{-}H)]^+$ from $(dppe)Pt_2(H)_3{}^+$ and alkene suggested an

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Table 1. Crystallographic Data for $(dfepe)_2Pt_2(\mu\text{-}CHMe)$ (3)

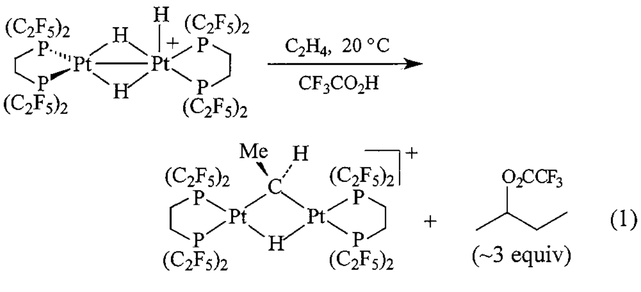
chem formula	$C_{22}H_{12}F_{40}P_4Pt_2$
fw	1550.38
space group	*Pbca* (No. 61)
a (Å)	16.880(2)
b (Å)	16.1793(13)
c (Å)	29.049(5)
V (Å^3)	7933(2)
Z	8
λ (Å)	0.710 73
T (°C)	−102
ρ_{calcd} (g cm^{-3})	2.596
R1 ($I > 2\sigma(I)$)[a]	0.0767
R1 (all data)	0.1412

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(dfepe)_2Pt_2(\mu\text{-}CHMe)$ (3)

Pt(1)−Pt(2)	2.6540(8)	Pt(1)−C(21a)	2.11(3)
Pt(1)−C(21b)	2.03(4)	Pt(2)−C(21a)	2.02(2)
Pt(2)−C(21b)	2.01(4)	Pt(1)−P(1)	2.211(4)
Pt(1)−P(2)	2.253(5)	Pt(2)−P(3)	2.245(4)
Pt(2)−P(4)	2.206(4)	C(21a)−C(22a)	1.48(5)
C(21b)−C(22b)	1.55(7)		
P(1)−Pt(1)−P(2)	86.3(2)	P(3)−Pt(2)−P(4)	86.3(2)
C(21a)−Pt(1)−Pt(2)	48.5(6)	C(21b)−Pt(1)−Pt(2)	48.5(10)
C(21a)−Pt(2)−Pt(1)	51.5(7)	C(21b)−Pt(2)−Pt(1)	49.2(12)
P(1)−Pt(1)−C(21a)	104.9(12)	P(1)−Pt(1)−C(21b)	107.7(10)
P(2)−Pt(1)−C(21a)	168.8(6)	P(2)−Pt(1)−C(21b)	158.0(13)
P(3)−Pt(2)−C(21a)	163.9(8)	P(3)−Pt(2)−C(21b)	168.3(13)
P(4)−Pt(2)−C(21a)	102.7(7)	P(4)−Pt(2)−C(21b)	104.9(12)
Pt(1)−C(21a)−Pt(2)	80.0(8)	Pt(1)−C(21b)−Pt(2)	82(2)

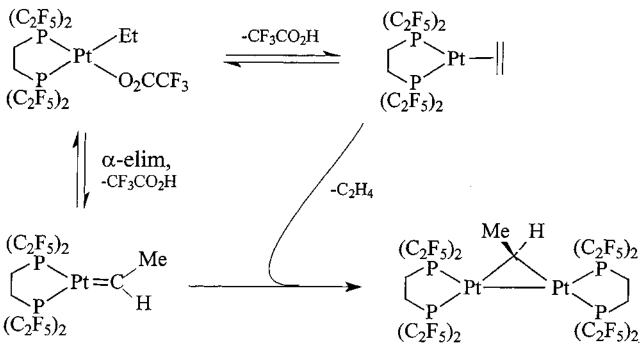
alternative route to **2** and **3**.[5] As described previously,[3] treatment of $[(dfepe)Pt(\mu\text{-}H)]_2$ in aprotic media with 1 atm of ethylene results in H_2 loss and formation of $(dfepe)Pt(\eta^2\text{-}C_2H_4)$. In CF_3CO_2H, however, the trihydride cation $[(dfepe)Pt(\mu\text{-}H)]_2(H)^+$ (**4**) is present as the major species in solution (see Experimental Section). In the presence of 1 atm of ethylene at 20 °C, **4** quantitatively converts to $[(dfepe)_2Pt_2(\mu\text{-}CHMe)(\mu\text{-}H)]^+$ after 24 h (eq 1). It is significant that some catalytic dimerization of ethylene to form 2-(trifluoroacetato)butane (ca. 3 equiv) was also observed under these mild reaction conditions.



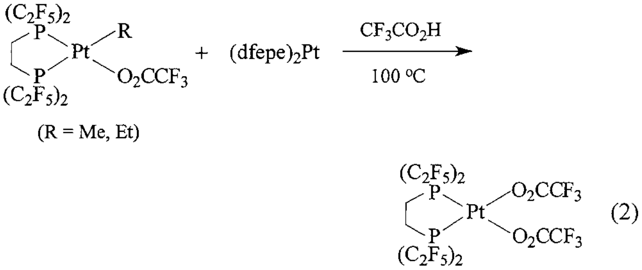
(1)

Mechanism of Ethylidene Dimer Formation. A common mechanism to explain the formation of **2** from the thermolysis of $(dfepe)Pt(Et)O_2CCF_3$ as well as from the trihydride cation **4** is not readily apparent. Accordingly, we shall consider each of these transformations separately. One possible mechanism to explain the formation of products **2** and **3** from $(dfepe)Pt(Et)(O_2CCF_3)$ is outlined in Scheme 3. Here, α-H elimination by $(dfepe)Pt(Et)(O_2CCF_3)$ followed by acid loss affords the platinum carbene complex $(dfepe)Pt{=}C(H)Me$, which is trapped by $(dfepe)Pt(C_2H_4)$. Previous studies indicate that a rapid equilibrium between $(dfepe)Pt(Et)(O_2CCF_3)$ and $(dfepe)Pt(C_2H_4)$ must exist at superambient temperatures.[1] Although α-H elimination is not generally favored for late-transition-metal systems,[10] a considerable body of work by Stone et al. provides ample precedent for the bimolecular trapping step.[11]

Scheme 3



Since any potential α-H elimination equilibrium occurring in $(dfepe)Pt(Et)O_2CCF_3$ would be effectively masked by competing reversible β-H processes, we have considered the thermal chemistry of related (dfepe)Pt(R)X systems, where β-H elimination is not possible. In previous work we have noted that $(dfepe)Pt(Me)O_2CCF_3$ is thermally stable in CF_3CO_2H at temperatures below 150 °C for extended periods and converts solely to $(dfepe)Pt(O_2CCF_3)_2$ at higher temperatures.[2] The absence of any significant deuterium scrambling into the methyl group of $(dfepe)Pt(Me)O_2CCF_3$ in CF_3CO_2D prior to protonolysis argues against an energetically accessible α-H elimination mechanism. Since the mechanism outlined in Scheme 3 requires a $(dfepe)Pt^0$ trap, we have also reexamined the thermal stability of $(dfepe)Pt(Me)O_2CCF_3$ in CF_3CO_2H in the presence of $(dfepe)_2Pt$. Only $(dfepe)Pt(O_2CCF_3)_2$ was observed in solution after 4 days at 100 °C (eq 2). The effect of an added [(dfepe)Pt(0)] source on the thermolysis of $(dfepe)Pt(Et)(O_2CCF_3)$ was also investigated. Warming $(dfepe)Pt(Et)(O_2CCF_3)$ in the presence of 1 equiv of $(dfepe)_2Pt$ to 100 °C for 10 days in CF_3CO_2H produced no detectable μ-ethylidene product; rather, $(dfepe)Pt(O_2CCF_3)_2$ (**3**) was again observed as the sole product. A control experiment was carried out to test the effect of added dfepe to (dfepe)Pt(R)X systems: addition of dfepe to a solution of $(dfepe)Pt(Et)(O_2CCF_3)$ in CF_3CO_2H resulted in the rapid



(2)

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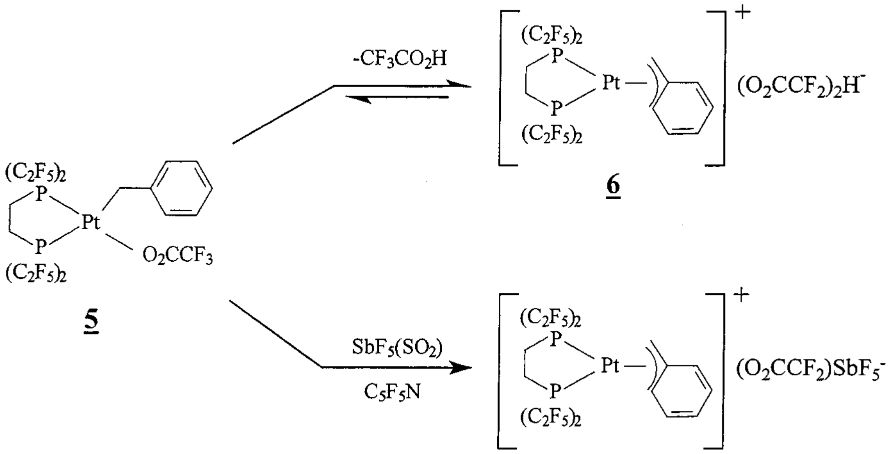
Scheme 4



evolution of ethylene and the formation of (dfepe)$_2$Pt at room temperature. Heating this resulting solution to 100 °C resulted in a quantitative conversion to (dfepe)Pt(O_2CCF_3)$_2$ after several days. From these observations, we conclude that the role of added (dfepe)$_2$Pt in the thermolysis of (dfepe)Pt(R)X systems is most likely as a source of free dfepe. Interestingly, the thermal conversion of (dfepe)Pt(Me)(O_2CCF_3) to (dfepe)Pt(O_2CCF_3)$_2$ in trifluoroacetic acid is somewhat accelerated in the presence of (dfepe)$_2$Pt.

We have also examined [(dfepe)Pt(μ-H)]$_2$(H)$^+$ as an alternative source of (dfepe)Pt^0. A 1:1 mixture of (dfepe)Pt(Et)(O_2CCF_3) and [(dfepe)Pt(μ-H)]$_2$ in trifluoroacetic acid did not react at ambient temperature. However, warming to 90 °C for 30 min did result in a complete conversion to [(dfepe)$_2$Pt$_2$(μ-CHMe)(μ-H)][O_2CCF_3].

As a further test for the viability of any α-H-mediated processes, we have prepared (dfepe)Pt(CH_2Ph)O_2CCF_3 (**5**) and examined its thermal and protolytic stability. Spectroscopic data for **5** are fully consistent with an (dfepe)Pt(R)X formulation in benzene. In neat trifluoroacetic acid, however, a dramatic change in ^{31}P NMR chemical shifts and $^1J_{\mathrm{PtP}}$ values occurs, which indicates that simple σ-benzyl coordination is not present under these conditions (see Experimental Section). Removal of CF_3CO_2H under vacuum and dissolution in benzene results in the regeneration of **5**. On the basis of our previous work in strongly acidic solvents,[2b] we conclude that acid-induced labilization of trifluoroacetate anion and an accompanying allylic rearrangement to form [(dfepe)Pt(η^3-CH_2Ph)]$^+$ (**6**) is taking place in CF_3CO_2H (Scheme 4). The equivalence of ortho and meta aryl protons in ambient-temperature ^{1}H NMR spectra indicate that rotation about the CH_2-Ph bond must be rapid, in accord with a fluxional benzylic unit (see below). All attempts to isolate **6** from solution resulted in the regeneration of **5**.

In an effort to favor the η^3-benzyl complex under aprotic conditions, we have examined the effect of added $SbF_5(SO_2)$, a potent anion abstraction agent.[12] Pentafluoropyridine proved to be a suitable weakly coordinating solvent for this reaction. Upon addition of $SbF_5(SO_2)$ to (dfepe)Pt(CH_2Ph)O_2CCF_3, an immediate change was noted in the ^{31}P NMR and ^{1}H NMR corresponding to the generation of **6**. The lack of any ^{1}H or ^{31}P NMR spectroscopic changes down to −75 °C confirm that the benzylic unit in **6** is highly fluxional.

Despite the additional complication introduced by the benzallylic equilibrium, the potential for reversible α-H elimination for this system was examined. Warming a solution of **6** in CF_3CO_2D to 80 °C for 24 h resulted in a 50% decrease in the integrated intensity of the aromatic resonance at δ 6.76, with no significant changes in the other aromatic signals or the methylene resonance at δ 3.71. After 2 days at 120 °C the signal at δ 6.76 was ~10% of its initial intensity and the remainder of the spectrum was unchanged. No (dfepe)Pt(O_2CCF_3)$_2$ was observed. From these data, we conclude that α-H elimination is not significant in this system but that deuterium exchange with the ortho protons of the benzyl group is occurring instead via an intramolecular metalation process (Scheme 5).

Two plausible alternative pathways for the formation of [(dfepe)$_2$Pt$_2$(μ-CHMe)(μ-H)]$^+$ from (dfepe)Pt(Et)(O_2CCF_3) are given in Schemes 6 and 7. In the first scheme, intramolecular vinyl C−H activation from (dfepe)Pt(η^2-C_2H_4) to give (dfepe)Pt(CH=CH$_2$)(H) and subsequent bimolecular trapping by “(dfepe)Pt” and hydride migration leads to the observed product. C−H bond activation is known for (R_3P)$_2$Pt^0 systems,[13] and vinylic activation is precedented for other late transition metals.[14]

The key step in Scheme 7 is intermolecular attack on coordinated ethylene by an unsaturated (dfepe)Pt^0 center to generate [(dfepe)$_2$Pt$_2$(μ-η^1:η^1-C_2H_4)(H)]$^+$, followed by β-H elimination to form a μ,η^1:η^2-vinyl complex which serves as a common intermediate in both Schemes 6 and 7. A number of examples of metal-centered nucleophilic attack on $L_nM(\eta^2$-$C_2H_4)$ lend precedent to this key bimolecular step.[15] With few exceptions,[16] however, most of these reports have involved addition of anionic metal centers to cationic ethylene complexes. In principle, nucleophilic attack on coordinated ethylene

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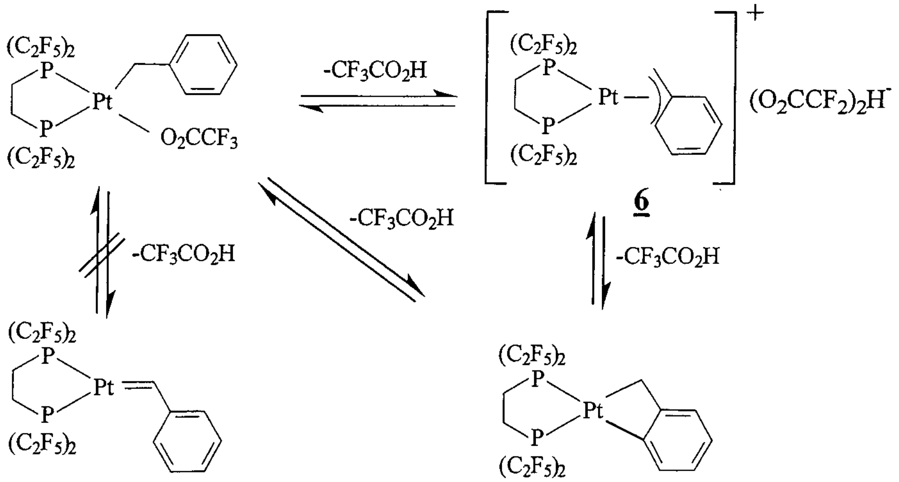
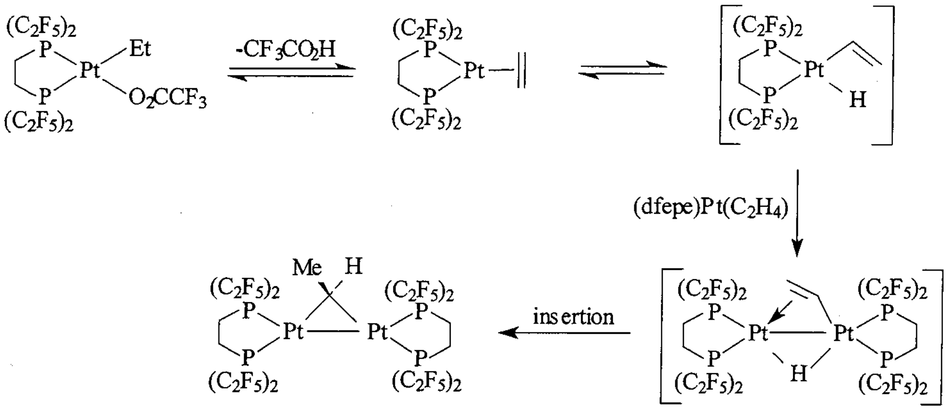
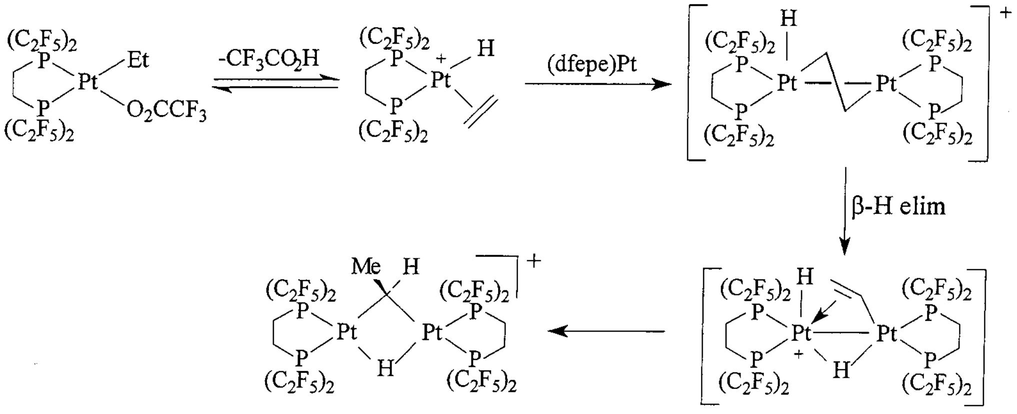
Scheme 5



Scheme 6



Scheme 7



may occur at either [(dfepe)Pt(η^2-C_2H_4)(H)]$^+$, as shown, or on the neutral Pt(0) ethylene complex (dfepe)Pt(η^2-C_2H_4). We believe that the former is most likely, since a Pt(II) cationic alkene complex is expected to be more reactive and ethylidene formation is only observed under acidic conditions.[17]

A vinyl-bridged intermediate similar to that proposed in Schemes 6 and 7 has been prepared by the reaction of $(PR_3)_2$Ir(CO)(OTf) with $(PPh_3)_2$Pt(η^2-C_2H_4) (eq 3).[18] Although this report claimed the first example of intermolecular, homogeneous transition-metal vinylic C−H activation of a π-complexed alkene, no evidence was presented to support this assertion.

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(17) We have recently characterized a related Pt(II) alkene complex, (dfepe)Pt($H_2C{=}C(H)Me$)(OSO_2F)$^+$: Kalberer, E.; Roddick, D. M. Unpublished observations.

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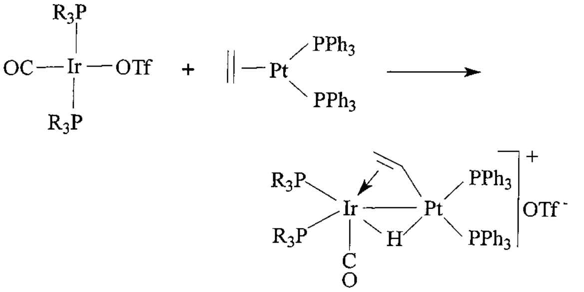

(3)

All mechanisms proposed thus far for the synthesis of μ-ethylidene products require a bimolecular trapping by "(dfepe)Pt". As discussed earlier, (dfepe)$_2$Pt is not an effective trap, due to the noninnocence of dfepe released under the reaction conditions. The use of [(dfepe)Pt(μ-H)(H)]$_2$$^+$ as a (dfepe)Pt^0 source in the thermolysis of (dfepe)Pt(Et)(O_2CCF_3) did afford **2** in CF_3CO_2H under milder conditions, but it is possible that ethylidene product formation in this case derives from the reaction of released ethylene with [(dfepe)Pt(μ-H)]$_2$(H)$^+$.

Any mechanism to account for the formation of μ-ethylidene product from (dfepe)$_2$Pt$_2$(μ-H)$_2$H$^+$ must explain the much milder reaction conditions required in this synthetic route. A proposed mechanism is shown in Scheme 8. While fragmentation of the dimeric $Pt_2H_3^+$ induced by ethylene addition is possible, this would simply lead to (dfepe)Pt(Et)O_2CCF_3 formation. A likely alternative lower energy pathway involves a dimeric ethylene intermediate, [(dfepe)$_2$Pt$_2$(H)(η^2-C_2H_4)]$^+$. Analogous carbonyl complexes have been produced in the reaction of $L_4Pt_2H_3^+$ with CO.[19] Conversion of (dfepe)$_2$Pt$_2$(H)(η^2-C_2H_4)$^+$ to a bridged ethylene complex leads to an ethylidene mechanism analogous to Schemes 6 and 7.

An unexplained observation in the reaction of (dfepe)$_2$Pt$_2$(H)$_3$$^+$ with ethylene is the formation of the butyl ester under these mild conditions. It is possible that ethylene dimerization for this system involves a bimetallic reaction pathway similar to that proposed for (dfepe)$_2$Ir$_2$H$_4$.[20]

Summary

The underlying mechanism of Pt$_2$(μ-CHR) complex formation remains open to question. A pathway involving α-H elimination and carbene trapping does not appear reasonable in light of other (dfepe)Pt(R)X reactivity data. We cannot rule out C−H vinylic activation (Scheme 6) but currently favor the convergent processes outlined in Schemes 7 and 8, which can more readily explain the formation of alkylidene products from both (dfepe)Pt(Et)(O_2CCF_3) and [(dfepe)Pt(μ-H)]$_2$(H)$^+$ precursors. The chemistry of coordinatively unsaturated bridged-alkene complexes M$_2$(μ-η^1:η^1-C_2H_4) such as those proposed in Schemes 7 and 8 is currently undeveloped and merits future study.

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of purified nitrogen using 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_3CO_2D was obtained from Cambridge Isotope Laboratories (Cambridge, MA), and used as received. Elemental analysis was performed by Desert Analytics. NMR spectra were obtained with a Bruker DRX-400 instrument. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. (dfepe)Pt(Et)(O_2CCF_3),[1] (dfepe)Pt(Me)(O_2CCF_3),[19] (cod)Pt(benzyl)$_2$ (cod = 1,5-cyclooctadiene),[22] and dfepe[23] were prepared using literature methods.

[(dfepe)$_2$Pt$_2$(μ-CHMe)](μ-H)]$^+$ (2) and (dfepe)$_2$Pt$_2$(μ-CHMe) (3). A solution of (dfepe)Pt(Et)(O_2CCF_3) (0.122 g, 0.135 mmol) in 5 mL of trifluoroacetic acid was warmed to 120 °C. After 2 h, ^{31}P NMR data indicated that conversion to [(dfepe)$_2$Pt$_2$(μ-CHMe)(μ-H)][O_2CCF_3] was complete. Spectroscopic data for **2**: ^{1}H NMR (CF_3CO_2H, 400 MHz, 23 °C) δ 8.93 (br s, 1H; Pt(μ-C*H*Me), 3.13 (m, 4H, PCH$_2$), 2.90 (m, 4H; PCH$_2$), 2.72 (br s, 3H, Pt(μ-C(H)C*H*$_3$), 0.26 (tt, 1H, $^1J_{PtH}$ = 635 Hz, $^1J_{PH}$ = 163 Hz, Pt(μ-H)); ^{13}C NMR (CF_3CO_2D, 100.6 MHz, 23 °C) δ 151.8 (t, $^2J_{PC}$ = 130 Hz, $^1J_{PtC}$ = 491 Hz; Pt(μ-*C*HMe)), 114.7−124.4 (overlapping mm, 8C, CF$_2$CF$_3$), 30.2 (s, C(H)*C*H$_3$), 25.6 (s, 4C, PCH$_2$), 21.8 (s, 4C, PCH$_2$); ^{31}P NMR (CF_3CO_2H, 161.9 MHz, 23 °C) δ 73.2 (m, $^1J_{PtP}$ = 4866 Hz), 68.0 (m, $^1J_{PtP}$ = 1845 Hz). Attempts to isolate this protonated dimer from CF_3CO_2H were unsuccessful, due to facile loss of CF_3CO_2H under vacuum. After the mixture was cooled to ambient temperature, all volatiles were removed and Et$_2$O (5 mL) was added to dissolve the yellow solid. Filtration was performed to isolate the product from any unreacted starting material **1**, followed by a cold filtration (−78 °C) to yield a pure yellow solid, which was dried under vacuum (0.06 g, 57%). Anal. Calcd for $C_{22}H_{12}F_{40}P_4Pt_2$: C, 17.04; H, 0.78. Found: C, 17.08; H, 0.85. ^{1}H NMR (acetone-d_6, 400 MHz, 23 °C): δ 9.07 (br s, 1H; Pt-(μ-C(*H*)CH$_3$)), 2.99 (m, 2H; PCH$_2$), 2.80 (m, 3H; Pt(μ-C(H)C*H*$_3$)), 2.44 (m, 2H; PCH$_2$). ^{13}C NMR (acetone-d_6, 100.6 MHz, 23 °C): δ 157.6 (t, $^2J_{PC}$ = 139 Hz, $^1J_{PtC}$ = 814 Hz; Pt(μ-*C*(H)CH$_3$)), 123.7−112.2 (overlapping mm, 8C, CF$_2$CF$_3$), 30.3 (s, C(H)*C*H$_3$), 25.3 (s, 4C, PCH$_2$), 21.5 (s, 4C, PCH$_2$). ^{31}P NMR (acetone-d_6, 161.9 MHz, 23 °C): δ 85.2 (m, $^1J_{PtP}$ = 1153 Hz), 74.5 (m, $^1J_{PtP}$ = 2199 Hz).

[(dfepe)Pt(μ-H)]$_2$(H)$^+$ (4). A 10 mg portion of [(dfepe)Pt(μ-H)]$_2$ was dissolved in 0.5 mL of CD_2Cl_2, and 30 μL of CF_3CO_2H was added via microliter syringe. An immediate color change from orange-brown to light yellow was observed. ^{1}H and ^{31}P NMR indicate complete conversion to a new species assigned as [(dfepe)$_2$Pt$_2$(μ-H)$_2$(H)]$^+$. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 27 °C): δ 3.02 (m, 8H; PCH$_2$), −2.60 (m, $^1J_{PtH}$ = 517 Hz, $^2J_{PH}$ = 50 Hz; 3H; Pt(μ-H)). ^{31}P NMR (CD_2Cl_2, 161.97 MHz, 25 °C): δ 85.3 (m, $^1J_{PtP}$ = 3010 Hz).

(dfepe)Pt(CH$_2$Ph)(O_2CCF_3) (5). Trifluoroacetic acid (30 μL, 0.044 g, 0.45 mmol) was added to a solution of (cod)Pt(benzyl)$_2$ (0.010 g, 0.025 mmol) in 15 mL of methylene chloride at −78 °C via syringe under N$_2$ and stirred at −78 °C for 1 h. When the mixture was warmed to ambient temperature, dfepe (0.1 mL, 0.22 g, 0.39 mmol) was added via syringe under N$_2$ and the resulting mixture stirred for 4 h. A cold filtration (−78 °C) was done to isolate a white solid, which was dried under vacuum (0.18 g, 54%). Anal. Calcd for $C_{19}H_{11}F_{23}P_2Pt$: C, 23.64; H, 1.15. Found: C, 23.25; H, 1.03. ^{1}H NMR (C_6D_6, 400 MHz, 23 °C): δ 7.37 (m, 2H, *o*-C$_6$H$_5$), 7.18 (m, 1H, *p*-C$_6$H$_5$), 7.00 (m, 2H, *m*-C$_6$H$_5$), 3.78 (s, $^2J_{PtH}$ = 28 Hz; Pt−CH$_2$Ph), 1.62 (m, 2H, PCH$_2$), 1.41 (m, 2H, PCH$_2$). ^{31}P NMR (C_6D_6, 161 MHz, 23 °C): δ 76.8 (m, $^2J_{PtP}$ = 1200 Hz), 56.4 (m, $^2J_{PtP}$ = 4830 Hz). NMR data for (dfepe)Pt(benzyl)(O_2CCF_3) in CF_3CO_2D: ^{1}H NMR δ 7.97 (t, $^3J_{CH}$ = 7.7 Hz, 2H; *m*-C$_6$H$_5$), 7.49 (m, 1H; *p*-C$_6$H$_5$), 6.71

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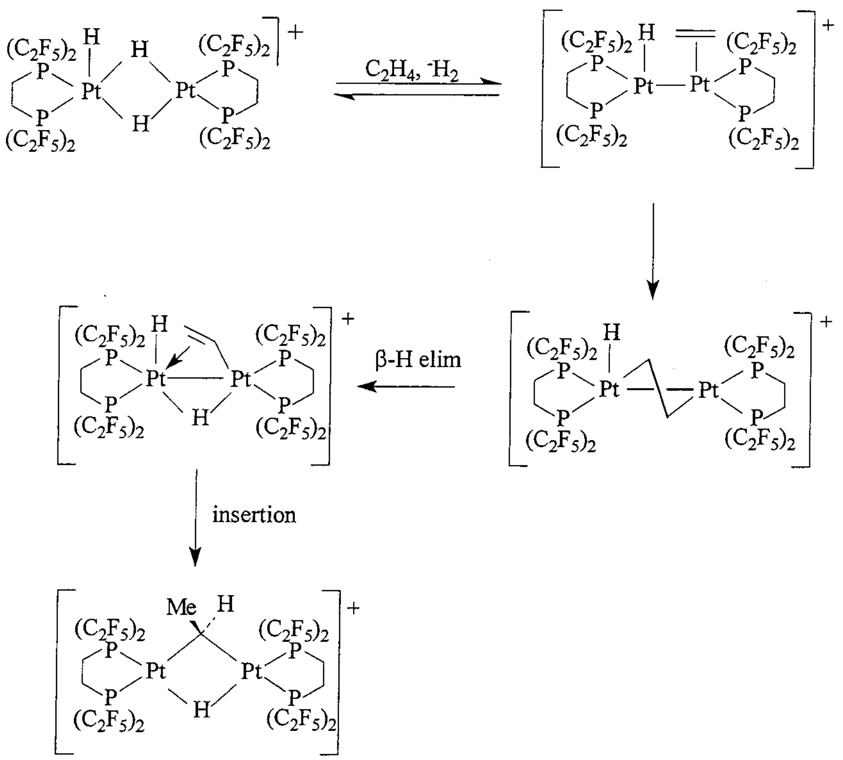
Scheme 8



(m, 2H; *o*-C_6H_5), 3.66 (AB pattern, ${}^2J_{PH} = 9.7$ Hz, 2H; PtCH_2-Ph), 2.94 (m, PCH_2), 2.72 (m, PCH_2); ^{31}P NMR: δ 74.3 (pseudo p, ${}^2J_{PtP} = 3240$ Hz, ${}^2J_{PF} = 63$ Hz), 71.3 (pseudo p, ${}^2J_{PtP} = 5190$ Hz, ${}^2J_{PF} = 66$ Hz).

[(dfepe)Pt(η^3-CH_2Ph)][(CF_3CO_2)SbF_5] (6). $SbF_5(SO_2)$ (5 mg, 0.012 mmol) was added to a solution of (dfepe)Pt(CH_2Ph)-(O_2CCF_3) (15 mg, 0.012 mmol) in 1 mL of pentafluoropyridine. Immediate conversion to **6** was observed by ^{31}P NMR spectroscopy. Isolation of this compound was not accomplished. ^{1}H NMR (pentafluoropyridine, 400 MHz, 23 °C): δ 7.99 (t, ${}^3J_{CH} = 6.0$ Hz, 2H; *m*-C_6H_5), 7.51 (m, 1H; *p*-C_6H_5), 6.75 (m, 2H; *o*-C_6H_5), 3.70 (AB pattern, ${}^2J_{PH} = 9.1$ Hz, 2H; PtCH_2Ph), 2.91 (m, PCH_2), 2.67 (m, PCH_2). ^{31}P NMR (pentafluoropyridine, 161 MHz, 23 °C): δ 74.6 (pseudo p, ${}^2J_{PtP} = 3234$ Hz, ${}^2J_{PF} = 62$ Hz), 71.4 (pseudo p, ${}^2J_{PtP} = 5188$ Hz, ${}^2J_{PF} = 66$ Hz).

Crystal Structure of (dfepe)$_2$Pt$_2$(μ-CHMe) (3). Slow evaporation from benzene afforded yellow plates of **3**. A crystal of suitable size was mounted on a glass fiber using grease. Data were collected using a Siemens SMART CCD diffractometer using monochromatic molybdenum radiation and an LT-2 low-temperature apparatus operating at 171 K. A summary of crystal data is presented in Table 1. Cell parameters were obtained from a least-squares fit to the angular coordinates of 51 reflections of a series of oscillation frames. Data were measured using ω scans of 0.3° per frame for 30 s. The first 50 frames were recollected at the end of data collection to monitor for decay. The data were corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS.

The structure was solved by direct methods and standard difference Fourier techniques and refined by full-matrix least-squares techniques on F^2 using structure solution programs from the SHELXTL system (version 5.04).[24] The compound crystallized in the centrosymmetric orthorhombic space group *Pbca* ($Z = 8$). All non-hydrogen atoms except for those noted below were refined anisotropically. The C(3) and C(4) perfluoroethyl carbons were restrained (DFIX) during refinement with fixed C−F bond distances, due to some positional disorder in this perfluoroethyl group. In addition, the bridging ethylidene group was disordered with respect to the disposition of the methyl group above and below the plane defined by the bridging carbon and the two platinum centers. A large anisotropic displacement of the bridging C(21) carbon also suggested disorder in this position, so the two independent bridging CHMe sets C(21a), C(22a) and C(21b), C(22b) were modeled isotropically; a population refinement gave sof's of 0.56 and 0.44, respectively, for the A and B ethylidene sets. Hydrogen atom positions were added in ideal calculated positions and with fixed isotropic thermal parameters set at 1.5 times the isotropic equivalent of the attached carbon atom for the disordered methyl groups and 1.2 times that for the remaining hydrogen atoms. The final *R* factor values were R1 = 0.0767 and wR2 = 0.1374 for 7682 data with $F > 4\sigma(F)$, with a goodness of fit on F^2 of 1.038. The maximum and minimum residual electron densities were 1.70 and −2.69 e Å^3. Selected metrical parameters for **3** are presented in Table 2.

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Supporting Information Available: Tables of crystal data, atomic coordinates and temperature factors, and intramolecular bond distances and angles of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0107237

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[24] Sheldrick, G. M. SHELXTL Crystallographic System, version 5.04/Iris; Siemens Analytical X-ray Instruments, Inc., Madison, WI.