

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

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Thermolysis of (dfepe)Pt(Et)(O₂CCF₃) (dfepe = (C₂F₅)₂PCH₂CH₂P(C₂F₅)₂) in benzene at 80 °C results in the formation of (dfepe)Pt(η²-C₂H₄). However, at 120 °C in CF₃CO₂H a bridging ethylidene platinum dimer, [(dfepe)₂Pt₂(μ-CHMe)(μ-H)][O₂CCF₃], is produced instead. Product isolation by precipitation with diethyl ether afforded the neutral dimer (dfepe)₂Pt₂(μ-CHMe₃). Alternatively, (dfepe)₂Pt₂(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 ¹H, ¹³C, and ³¹P 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(CH₂Ph)(O₂CCF₃) and its reversible rearrangement to the η³-benzyl complex [(dfepe)Pt(η³-CH₂Ph)]⁺ 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 (CF₃CO₂H, 80 °C) (Scheme 1).

Since related work with (dfepe)Pt(Me)(O₂CCF₃) showed that protonolysis to form (dfepe)Pt(O₂CCF₃)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)(O₂CCF₃), to establish an effective upper thermal limit for Pt–alkyl insertion chemistry in trifluoroacetic acid. Surprisingly, we find that thermolysis of (dfepe)Pt(Et)(O₂CCF₃) at 120 °C does not result in ethane evolution and production of (dfepe)Pt(O₂CCF₃)₂ as expected but, rather, leads to the quantitative formation of an ethylidene-bridged dimeric product, [(dfepe)₂Pt₂(μ-CHMe)(μ-H)][O₂CCF₃], which is readily deprotonated to form (dfepe)₂Pt₂(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(CH₂Ph)(O₂CCF₃) and its reversible rearrangement to the η³-benzyl complex [(dfepe)Pt(η³-CH₂Ph)]⁺ upon abstraction of trifluoroacetate anion.

Results and Discussion

Warming (dfepe)Pt(Et)(O₂CCF₃) (**1**) in benzene to 80 °C results in reversible CF₃CO₂H elimination and the

formation of previously reported (dfepe)Pt(η²-C₂H₄).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(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-CHMe)). Two ³¹P 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 ¹H and ¹³C 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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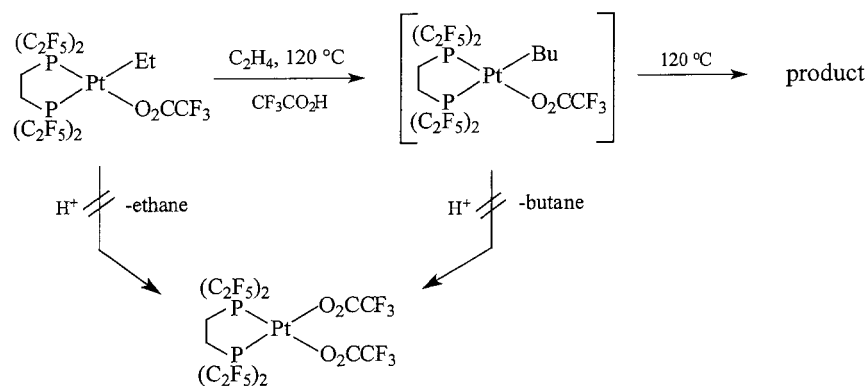
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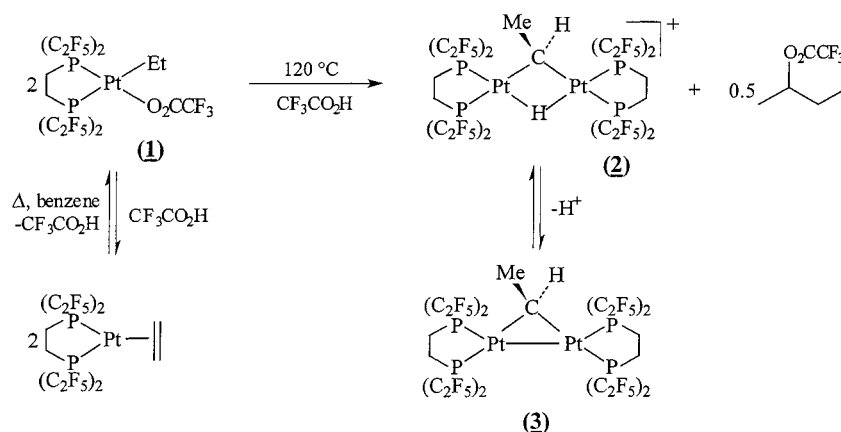
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Scheme 1



Scheme 2



comparable μ -alkylidene systems are $[\text{Pt}_2(\text{dppe})_2(\mu\text{-CHCH}_2\text{R})(\mu\text{-H})]^+$ ($\text{R} = \text{H}, \text{Ph}$)⁵ and $[\text{Pt}_2(\text{dppf})_2(\mu\text{-CHCH}_2\text{-Ar})(\mu\text{-H})]^+$ ($\text{dppf} = \text{Ph}_2\text{PC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{PPh}_2$, $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$).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 $\text{Pt}(1)$, $\text{Pt}(2)$, 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 $\text{Pt}\text{--}\text{Pt}$ distance, $2.6540(8) \text{ \AA}$, for **3** is substantially shorter than metal–metal distances reported for μ -methylene complexes without a supporting $\text{Pt}\text{--}\text{Pt}$ bond ($>3 \text{ \AA}$)⁷ and for the cationic hydride-bridged dimers $[\text{Pt}_2(\text{dppe})_2(\mu\text{-CHCH}_2\text{Ph})(\mu\text{-H})]^+$ ($2.735(1) \text{ \AA}$)⁵ and $[\text{Pt}_2(\text{dppf})_2(\mu\text{-CHCH}_2\text{Ar})(\mu\text{-H})]^+$ ($2.7314(4) \text{ \AA}$)⁶ but similar to $\text{Pt}\text{--}\text{Pt}$ distances reported for the neutral trimeric complexes $\text{Pt}_3[\mu\text{-C}(\text{OMe})\text{Ar}]_3(\text{CO})_3$ ($2.621(1) \text{ \AA}$) and $(t\text{-Bu-MeP})_2\text{Pt}_2[\mu\text{-C}(\text{OMe})\text{Ph}]\text{W}(\text{CO})_6$ ($2.628(1) \text{ \AA}$).^{8,9} The geometry about each platinum center is distorted square planar, with each (dfepe) Pt chelate moiety twisted $\sim 20^\circ$

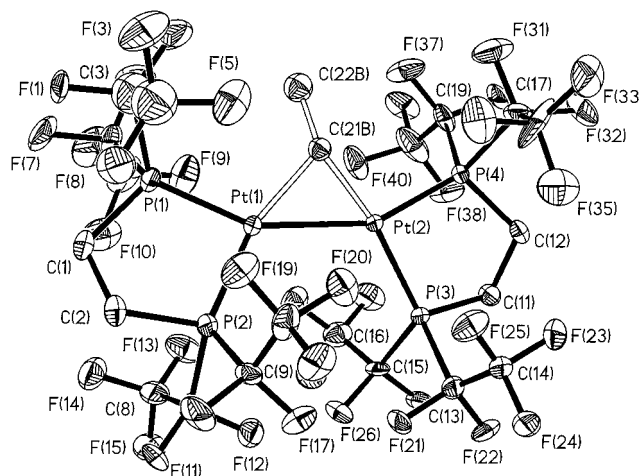


Figure 1. Molecular structure of $(\text{dfepe})_2\text{Pt}_2(\mu\text{-CHMe})$ (**3**) with the atom-labeling scheme (30% probability ellipsoids). Only one of the disordered ethylidene groups is shown.

from the plane defined by $\text{Pt}_2(\mu\text{-C}(21\text{b}))$. The $\text{Pt}\text{--}\text{P}$ bonds opposite to the ethylidene bridge ($2.253(5)$ and $2.245(3) \text{ \AA}$) are somewhat longer than the $\text{Pt}\text{--}\text{P}$ bonds opposite to the $\text{Pt}\text{--}\text{Pt}$ bond ($2.211(4)$, $2.206(4) \text{ \AA}$) and are indicative of a stronger trans influence for the alkylidene bridge relative to the neighboring platinum center.

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

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Table 1. Crystallographic Data for (dfepe)₂Pt₂(μ-CHMe) (3)

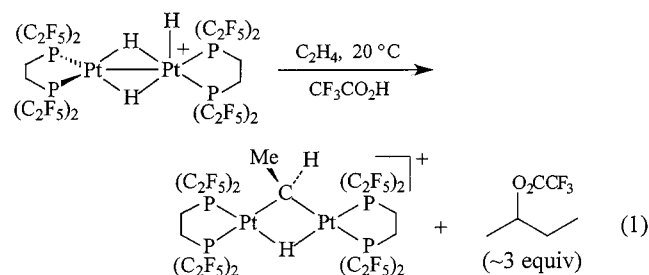
chem formula	C ₂₂ H ₁₂ F ₄₀ P ₄ Pt ₂
fw	1550.38
space group	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	16.880(2)
<i>b</i> (Å)	16.1793(13)
<i>c</i> (Å)	29.049(5)
<i>V</i> (Å ³)	7933(2)
<i>Z</i>	8
<i>λ</i> (Å)	0.710 73
<i>T</i> (°C)	−102
<i>ρ</i> _{calcd} (g cm ^{−3})	2.596
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0767
<i>R</i> 1 (all data)	0.1412

$$^a R1 = \sum(|F_o| - |F_c|)/\sum|F_o|.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (dfepe)₂Pt₂(μ-CHMe) (3)

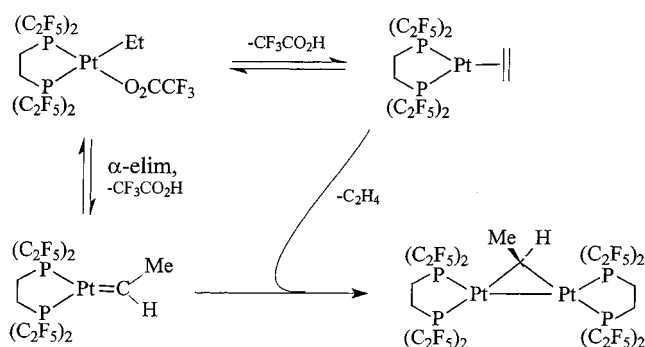
Pt(1)–Pt(2)	2.6540(8)	Pt(1)–C(21a)	2.11(3)
Pt(1)–C(21b)	2.03(4)	Pt(2)–C(21a)	2.02(2)
Pt(2)–C(21b)	2.01(4)	Pt(1)–P(1)	2.211(4)
Pt(1)–P(2)	2.253(5)	Pt(2)–P(3)	2.245(4)
Pt(2)–P(4)	2.206(4)	C(21a)–C(22a)	1.48(5)
C(21b)–C(22b)	1.55(7)		
P(1)–Pt(1)–P(2)	86.3(2)	P(3)–Pt(2)–P(4)	86.3(2)
C(21a)–Pt(1)–Pt(2)	48.5(6)	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)
P(1)–C(21a)–Pt(2)	80.0(8)	P(1)–C(21b)–Pt(2)	82(2)

alternative route to **2** and **3**.⁵ As described previously,³ treatment of [(dfepe)Pt(μ-H)]₂ in aprotic media with 1 atm of ethylene results in H₂ loss and formation of (dfepe)Pt(η²-C₂H₄). In CF₃CO₂H, however, the trihydride cation [(dfepe)Pt(μ-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)₂Pt₂(μ-CHMe)(μ-H)]⁺ after 24 h (eq 1). It is significant that some catalytic dimerization



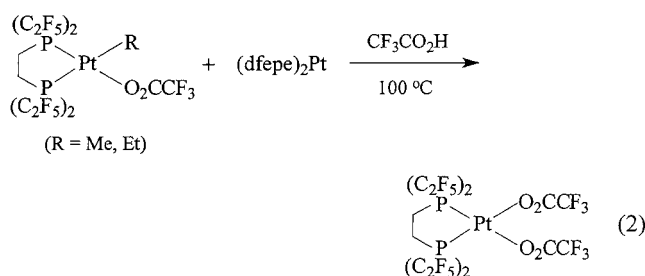
of ethylene to form 2-(trifluoroacetato)butane (ca. 3 equiv) was also observed under these mild reaction conditions.

Mechanism of Ethylidene Dimer Formation. A common mechanism to explain the formation of **2** from the thermolysis of (dfepe)Pt(Et)(O₂CCF₃) 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)(O₂CCF₃) is outlined in Scheme 3. Here, α-H elimination by (dfepe)Pt(Et)(O₂CCF₃) followed by acid loss affords the platinum carbene complex (dfepe)Pt=C(H)Me, which is trapped by (dfepe)Pt(C₂H₄). Previous studies indicate that a rapid equilibrium between (dfepe)Pt(Et)(O₂CCF₃) and (dfepe)Pt(C₂H₄) must exist at superambient tem-

Scheme 3

peratures.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

Since any potential α-H elimination equilibrium occurring in (dfepe)Pt(Et)O₂CCF₃ 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)O₂CCF₃ is thermally stable in CF₃CO₂H at temperatures below 150 °C for extended periods and converts solely to (dfepe)Pt(O₂CCF₃)₂ at higher temperatures.² The absence of any significant deuterium scrambling into the methyl group of (dfepe)Pt(Me)O₂CCF₃ in CF₃CO₂D prior to protonolysis argues against an energetically accessible α-H elimination mechanism. Since the mechanism outlined in Scheme 3 requires a (dfepe)Pt⁰ trap, we have also reexamined the thermal stability of (dfepe)Pt(Me)-O₂CCF₃ in CF₃CO₂H in the presence of (dfepe)₂Pt. Only (dfepe)Pt(O₂CCF₃)₂ was observed in solution after 4 days at 100 °C (eq 2). The effect of an added [(dfepe)Pt(0)]

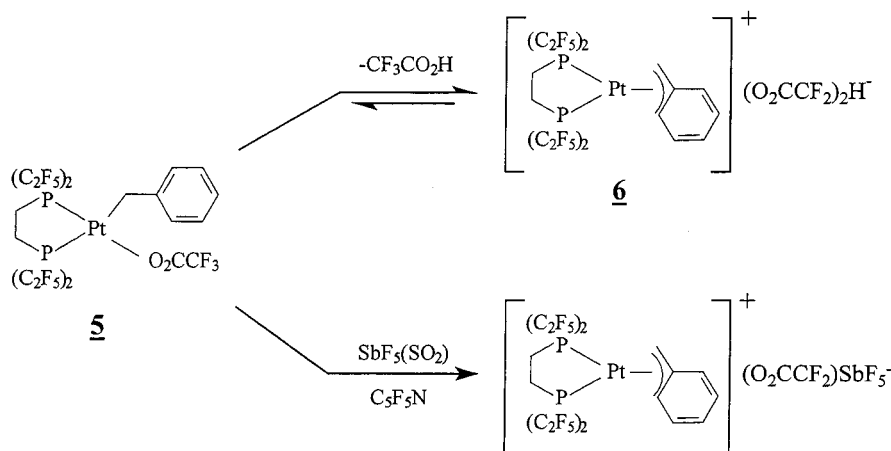


source on the thermolysis of (dfepe)Pt(Et)(O₂CCF₃) was also investigated. Warming (dfepe)Pt(Et)(O₂CCF₃) in the presence of 1 equiv of (dfepe)₂Pt to 100 °C for 10 days in CF₃CO₂H produced no detectable μ-ethylidene product; rather, (dfepe)Pt(O₂CCF₃)₂ (**3**) was again observed as the sole product. A control 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)(O₂CCF₃) in CF₃CO₂H resulted in the rapid

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Scheme 4



evolution of ethylene and the formation of $(\text{dfepe})_2\text{Pt}$ at room temperature. Heating this resulting solution to 100 °C resulted in a quantitative conversion to $(\text{dfepe})\text{-Pt}(\text{O}_2\text{CCF}_3)_2$ after several days. From these observations, we conclude that the role of added $(\text{dfepe})_2\text{Pt}$ in the thermolysis of $(\text{dfepe})\text{Pt}(\text{R})\text{X}$ systems is most likely as a source of free dfepe . Interestingly, the thermal conversion of $(\text{dfepe})\text{Pt}(\text{Me})(\text{O}_2\text{CCF}_3)$ to $(\text{dfepe})\text{Pt}(\text{O}_2\text{-CCF}_3)_2$ in trifluoroacetic acid is somewhat accelerated in the presence of $(\text{dfepe})_2\text{Pt}$.

We have also examined $[(\text{dfepe})\text{Pt}(\mu\text{-H})_2(\text{H})]^+$ as an alternative source of $(\text{dfepe})\text{Pt}^0$. A 1:1 mixture of $(\text{dfepe})\text{-Pt}(\text{Et})(\text{O}_2\text{CCF}_3)$ and $[(\text{dfepe})\text{Pt}(\mu\text{-H})_2]$ in trifluoroacetic acid did not react at ambient temperature. However, warming to 90 °C for 30 min did result in a complete conversion to $[(\text{dfepe})_2\text{Pt}_2(\mu\text{-CHMe})(\mu\text{-H})][\text{O}_2\text{CCF}_3]$.

As a further test for the viability of any $\alpha\text{-H}$ -mediated processes, we have prepared $(\text{dfepe})\text{Pt}(\text{CH}_2\text{Ph})\text{O}_2\text{CCF}_3$ (**5**) and examined its thermal and protolytic stability. Spectroscopic data for **5** are fully consistent with an $(\text{dfepe})\text{Pt}(\text{R})\text{X}$ formulation in benzene. In neat trifluoroacetic acid, however, a dramatic change in ^{31}P NMR chemical shifts and $^1J_{\text{PtP}}$ values occurs, which indicates that simple σ -benzyl coordination is not present under these conditions (see Experimental Section). Removal of $\text{CF}_3\text{CO}_2\text{H}$ 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 $[(\text{dfepe})\text{Pt}(\eta^3\text{-CH}_2\text{Ph})]^+$ (**6**) is taking place in $\text{CF}_3\text{CO}_2\text{H}$ (Scheme 4). The equivalence of ortho and meta aryl protons in ambient-temperature ^1H NMR spectra indicate that rotation about the $\text{CH}_2\text{-Ph}$ 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 $\text{SbF}_5(\text{SO}_2)$, a potent anion abstraction agent.¹² Pentafluoropyridine proved to be a suitable weakly coordinating solvent for this reaction. Upon addition of $\text{SbF}_5(\text{SO}_2)$ to $(\text{dfepe})\text{Pt}(\text{CH}_2\text{Ph})\text{O}_2\text{CCF}_3$, an immediate

change was noted in the ^{31}P NMR and ^1H NMR corresponding to the generation of **6**. The lack of any ^1H 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 benzylic equilibrium, the potential for reversible $\alpha\text{-H}$ elimination for this system was examined. Warming a solution of **6** in $\text{CF}_3\text{CO}_2\text{D}$ 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 $(\text{dfepe})\text{-Pt}(\text{O}_2\text{CCF}_3)_2$ was observed. From these data, we conclude that $\alpha\text{-H}$ 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 $[(\text{dfepe})_2\text{Pt}_2(\mu\text{-CHMe})(\mu\text{-H})]^+$ from $(\text{dfepe})\text{Pt}(\text{Et})(\text{O}_2\text{-CCF}_3)$ are given in Schemes 6 and 7. In the first scheme, intramolecular vinyl C-H activation from $(\text{dfepe})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ to give $(\text{dfepe})\text{Pt}(\text{CH}=\text{CH}_2)(\text{H})$ and subsequent bimolecular trapping by “ $(\text{dfepe})\text{Pt}$ ” and hydride migration leads to the observed product. C-H bond activation is known for $(\text{R}_3\text{P})_2\text{Pt}^0$ systems,¹³ and vinylic activation is preceded for other late transition metals.¹⁴

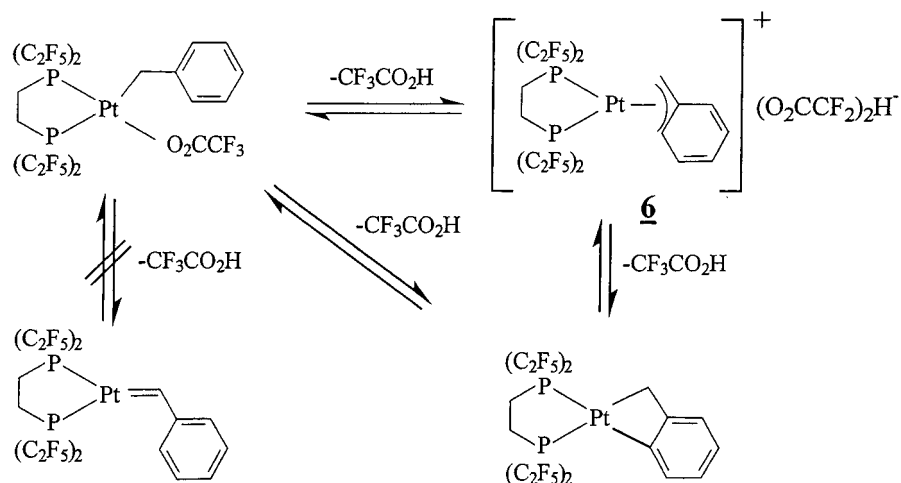
The key step in Scheme 7 is intermolecular attack on coordinated ethylene by an unsaturated $(\text{dfepe})\text{Pt}^0$ center to generate $[(\text{dfepe})_2\text{Pt}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2\text{H}_4)(\text{H})]^+$, followed by $\beta\text{-H}$ elimination to form a $\mu\text{-}\eta^1\text{:}\eta^2$ -vinyl complex which serves as a common intermediate in both Schemes 6 and 7. A number of examples of metal-centered nucleophilic attack on $\text{L}_n\text{M}(\eta^2\text{-C}_2\text{H}_4)$ 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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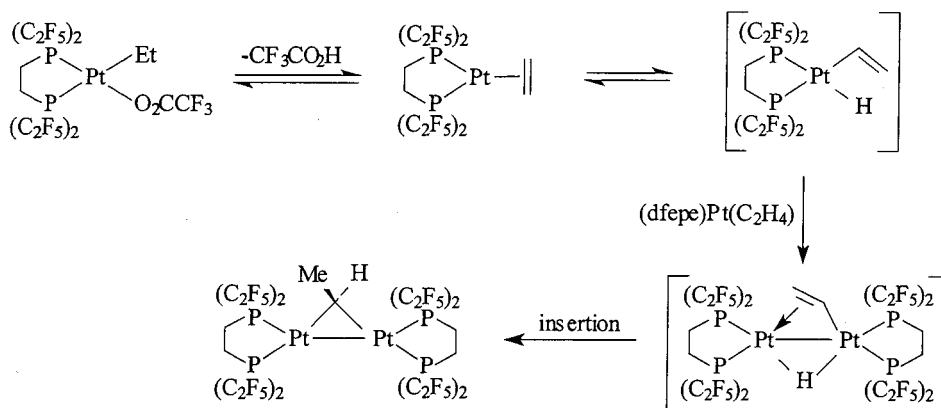
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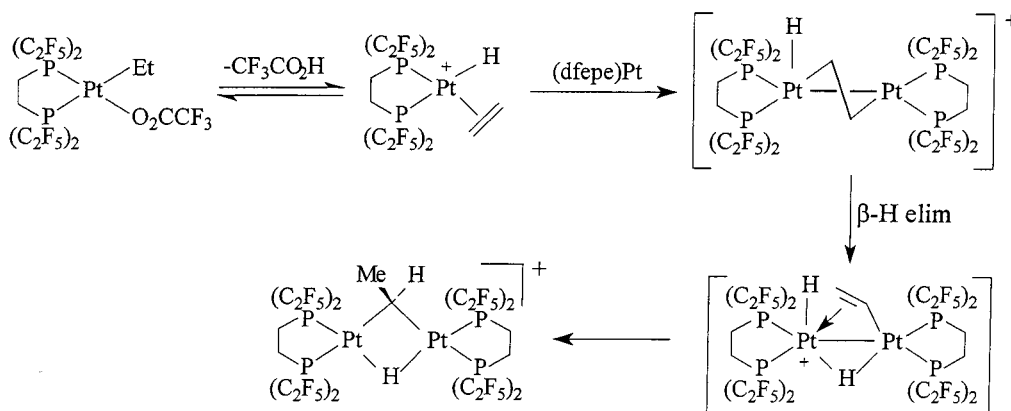
Scheme 5



Scheme 6



Scheme 7



may occur at either $[(\text{dfepe})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{H})]^+$, as shown, or on the neutral $\text{Pt}(0)$ ethylene complex $(\text{dfepe})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$. We believe that the former is most likely, since a $\text{Pt}(\text{II})$ cationic alkene complex is expected to be more reactive and ethylidene formation is only observed under acidic conditions.¹⁷

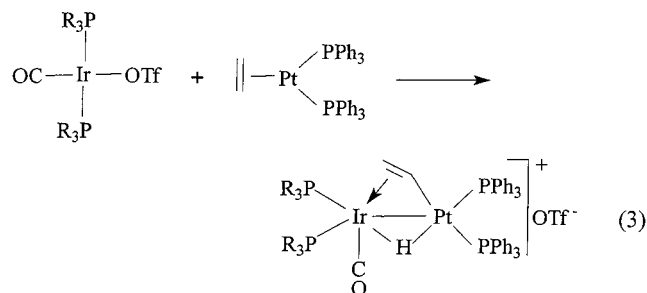
A vinyl-bridged intermediate similar to that proposed in Schemes 6 and 7 has been prepared by the reaction of $(\text{PR}_3)_2\text{Ir}(\text{CO})(\text{OTf})$ with $(\text{PPh}_3)_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ (eq 3).¹⁸ Although this report claimed the first example of intermolecular, homogeneous 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 $\text{Pt}(\text{II})$ alkene complex, $(\text{dfepe})\text{Pt}(\text{H}_2\text{C}=\text{C}(\text{H})\text{Me})(\text{OSO}_2\text{F})^+$: Kalberer, E.; Roddick, D. M. Unpublished observations.

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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 $_2$ CCF $_3$) did afford **2** in CF $_3$ CO $_2$ H 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 $_2$ H $_3^+$ induced by ethylene addition is possible, this would simply lead to (dfepe)Pt(Et)O $_2$ CCF $_3$ formation. A likely alternative lower energy pathway involves a dimeric ethylene intermediate, [(dfepe) $_2$ Pt $_2$ (H)(η^2 -C $_2$ H $_4$)] $^+$. Analogous carbonyl complexes have been produced in the reaction of L $_4$ Pt $_2$ H $_3^+$ with CO.¹⁹ Conversion of (dfepe) $_2$ Pt $_2$ (H)(η^2 -C $_2$ H $_4$) $^+$ 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 $_2$ CCF $_3$) and [(dfepe)Pt(μ -H)] $_2$ (H) $^+$ precursors. The chemistry of coordinatively unsaturated bridged-alkene complexes M $_2$ (μ - η^1 : η^1 -C $_2$ H $_4$) 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 $_3$ CO $_2$ D 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 $_3$ PO $_4$ external standard. (dfepe)Pt(Et)(O $_2$ CCF $_3$),¹ (dfepe)Pt(Me)(O $_2$ CCF $_3$),¹⁹ (cod)Pt(benzyl) $_2$ (cod = 1,5-cyclooctadiene),²² and dfepe²³ 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 $_2$ CCF $_3$) (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 $_2$ CCF $_3$) was complete. Spectroscopic data for **2**: ^1H NMR (CF $_3$ CO $_2$ H, 400 MHz, 23 °C) δ 8.93 (br s, 1H; Pt(μ -CHMe), 3.13 (m, 4H, PCH $_2$), 2.90 (m, 4H; PCH $_2$), 2.72 (br s, 3H, Pt(μ -C(H)CH $_3$), 0.26 (tt, 1H, $^1J_{\text{PtH}}$ = 635 Hz, $^1J_{\text{PH}}$ = 163 Hz, Pt(μ -H)); ^{13}C NMR (CF $_3$ CO $_2$ D, 100.6 MHz, 23 °C) δ 151.8 (t, $^2J_{\text{PC}}$ = 130 Hz, $^1J_{\text{PtC}}$ = 491 Hz; Pt(μ -CHMe)), 114.7–124.4 (overlapping mm, 8C, CF $_2$ CF $_3$), 30.2 (s, C(H)CH $_3$), 25.6 (s, 4C, PCH $_2$), 21.8 (s, 4C, PCH $_2$); ^{31}P NMR (CF $_3$ CO $_2$ H, 161.9 MHz, 23 °C) δ 73.2 (m, $^1J_{\text{PtP}}$ = 4866 Hz), 68.0 (m, $^1J_{\text{PtP}}$ = 1845 Hz). Attempts to isolate this protonated dimer from CF $_3$ CO $_2$ H were unsuccessful, due to facile loss of CF $_3$ CO $_2$ H 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 $_4$ Pt $_2$: C, 17.04; H, 0.78. Found: C, 17.08; H, 0.85. ^1H 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)CH $_3$)), 2.44 (m, 2H; PCH $_2$). ^{13}C NMR (acetone- d_6 , 100.6 MHz, 23 °C): δ 157.6 (t, $^2J_{\text{PC}}$ = 139 Hz, $^1J_{\text{PtC}}$ = 814 Hz; Pt(μ -C(H)CH $_3$)), 123.7–112.2 (overlapping mm, 8C, CF $_2$ CF $_3$), 30.3 (s, C(H)CH $_3$), 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, $^1J_{\text{PtP}}$ = 1153 Hz), 74.5 (m, $^1J_{\text{PtP}}$ = 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 $_2$ Cl $_2$, and 30 μL of CF $_3$ -CO $_2$ H was added via microliter syringe. An immediate color change from orange-brown to light yellow was observed. ^1H and ^{31}P NMR indicate complete conversion to a new species assigned as [(dfepe) $_2$ Pt $_2$ (μ -H) $_2$ (H)] $^+$. ^1H NMR (CD $_2$ Cl $_2$, 400.13 MHz, 27 °C): δ 3.02 (m, 8H; PCH $_2$), –2.60 (m, $^1J_{\text{PtH}}$ = 517 Hz, $^2J_{\text{PH}}$ = 50 Hz; 3H; Pt(μ -H)). ^{31}P NMR (CD $_2$ Cl $_2$, 161.97 MHz, 25 °C): δ 85.3 (m, $^1J_{\text{PtP}}$ = 3010 Hz).

(dfepe)Pt(CH $_2$ Ph)(O $_2$ CCF $_3$) (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 $_2$ Pt: C, 23.64; H, 1.15. Found: C, 23.25; H, 1.03. ^1H NMR (C $_6$ D $_6$, 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, $^2J_{\text{PtH}}$ = 28 Hz; Pt–CH $_2$ Ph), 1.62 (m, 2H, PCH $_2$), 1.41 (m, 2H, PCH $_2$). ^{31}P NMR (C $_6$ D $_6$, 161 MHz, 23 °C): δ 76.8 (m, $^2J_{\text{PtP}}$ = 1200 Hz), 56.4 (m, $^2J_{\text{PtP}}$ = 4830 Hz). NMR data for (dfepe)Pt(benzyl)(O $_2$ CCF $_3$) in CF $_3$ CO $_2$ D: ^1H NMR δ 7.97 (t, $^3J_{\text{CH}}$ = 7.7 Hz, 2H; *m*-C $_6$ H $_5$), 7.49 (m, 1H; *p*-C $_6$ H $_5$), 6.71

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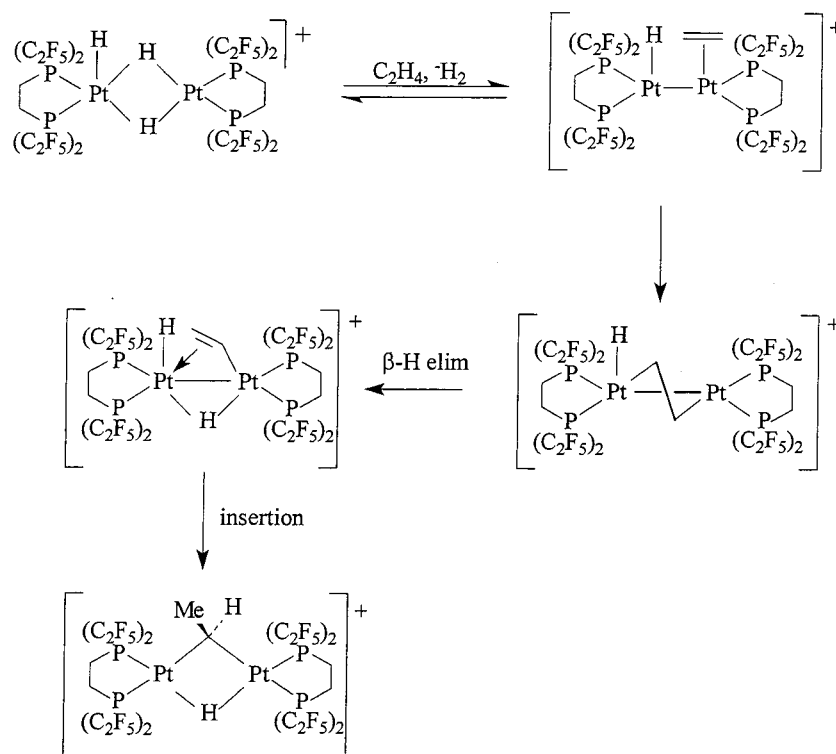
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Scheme 8



(m, 2H; *o*-C₆H₅), 3.66 (AB pattern, ²J_{PH} = 9.7 Hz, 2H; PtCH₂-Ph), 2.94 (m, PCH₂), 2.72 (m, PCH₂); ³¹P 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(η³-CH₂Ph)][(CF₃CO₂)SbF₅] (6). SbF₅(SO₂) (5 mg, 0.012 mmol) was added to a solution of (dfepe)Pt(CH₂Ph)-(O₂CCF₃) (15 mg, 0.012 mmol) in 1 mL of pentafluoropyridine. Immediate conversion to **6** was observed by ³¹P NMR spectroscopy. Isolation of this compound was not accomplished. ¹H NMR (pentafluoropyridine, 400 MHz, 23 °C): δ 7.99 (t, ³J_{CH} = 6.0 Hz, 2H; *m*-C₆H₅), 7.51 (m, 1H; *p*-C₆H₅), 6.75 (m, 2H; *o*-C₆H₅), 3.70 (AB pattern, ²J_{PH} = 9.1 Hz, 2H; PtCH₂Ph), 2.91 (m, PCH₂), 2.67 (m, PCH₂). ³¹P 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)₂Pt₂(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 *R*1 = 0.0767 and *wR*2 = 0.1374 for 7682 data with *F* > 4σ(*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 Å³. Selected metrical parameters for **3** are presented in Table 2.

Acknowledgment. This work has been supported by the National Science Foundation (Grants CHE-9615985 and CHE-009049), and the Wyoming DOE-EPSCoR Program.

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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