Organometallics in Acidic Media: Catalytic Dimerization of Ethylene by (Perfluoroalkyl)phosphine Complexes of Platinum and Palladium in Trifluoroacetic Acid[†]

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Catalytic ethylene dimerization by (dfepe)Pt(Me)X complexes in aprotic and trifluoroacetic acid solvents is described. In CH_2Cl_2, catalyst deactivation due to acid loss and generation of (dfepe)Pt(η^2-C_2H_4) is observed. In contrast, long-term ethylene dimerization activity takes place in trifluoroacetic acid at 80 °C and produces 2-(trifluoroacetato)butane as the sole organic product. Under these reaction conditions, the catalyst resting state is (dfepe)Pt(Et)(O_2CCF_3). At 20 °C, reversible acid elimination from (dfepe)Pt(Et)(O_2CCF_3) and ethylene ligand exchange results in catalytic vinylic H^+/D^+ exchange with CF_3CO_2D ($t_{1/2} \approx 40$ min). Analogous palladium systems exhibit enhanced dimerization activity at 25 °C (340 turnovers/h, 100 psi C_2H_4) and form $(dfepe)_2Pd$ as a catalyst resting state. Inhibition of catalytic activity in the presence of added dfepe was noted. Comparisons between catalytic runs in CF_3CO_2H and CF_3CO_2D gave an apparent solvent kinetic effect of 3.5(2), based on an initial second-order rate dependence on ethylene. In CF_3CO_2D, regioselective acid addition to give only $CH_3CH(O_2CCF_3)CH(D)CH_3$ indicates that isomerization to 2-butene has occurred prior to 1,2-acid addition. A general olefin dimerization mechanism incorporating protonation preequilibria is presented.

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Introduction

There is extensive interest in extending organometallic chemistry and metal-mediated homogeneous catalytic processes to aqueous and other "nontraditional" media.[1−3] Impetus for this work has been the development of desirable environmentally benign chemical conversions, as well as the potential discovery of new reactivity modes which exploit a wider range of solvent properties. One approach taken in aqueous/protic solvent chemistry has been the shift to electrophilic late transition metal systems which form covalent metal−carbon bonds that are more resistant to protonolysis and more tolerant of substrate functionality.

Our research program has focused on the synthesis and properties of (fluoroalkyl)phosphine metal complexes of the middle and late transition metal triads.[4−6] Complexes incorporating the fluorinated phosphine chelate $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe), as well as monodentate phosphines $(C_2F_5)_2(R)P$,[7] generally exhibit greatly enhanced oxidative and thermal stabilities relative to donor phosphine analogues. Compared to corresponding carbonyl systems, (fluoroalkyl)phosphine complexes also closely approximate $(CO)_nM$ electronics while providing increased steric control and thermal stability. In recent reports, we have demonstrated (1) the compatibility of (dfepe)M systems with strongly acidic media and (2) the exceptional resistance of (dfepe)M−alkyl bonds to protonolysis in neat acidic and superacidic media.[4,6] While these preliminary studies have demonstrated the protic compatibility of (dfepe)Pt−alkyl bonds, the question remained whether these compounds would still undergo fundamental organometallic transformations in acidic media (Scheme 1). In this paper, we report that (dfepe)M (M = Pd, Pt) systems function as efficient ethylene dimerization catalysts in trifluoroacetic acid under mild conditions, affording the ester product 2-(trifluoroacetato)butane. Studies concerning the nature of the catalyst resting state for these palladium and platinum systems are also presented, as well as labeling experiments which indi-

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[†] Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

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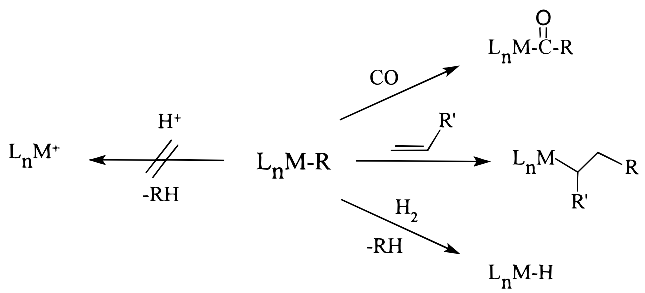
Scheme 1



cate that vinylic-H^+/D^+ exchange with ethylene can occur prior to dimerization.

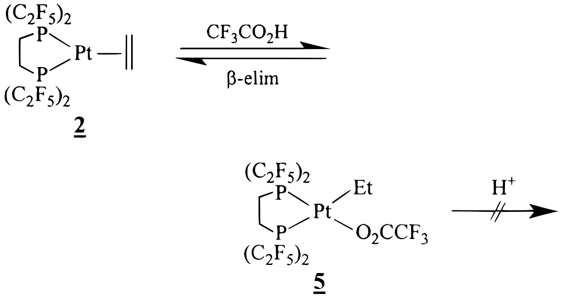
Results

Ethylene Dimerization in Aprotic and Protic Media. Exposure of dichloromethane solutions of (dfepe)-Pt(Me)(OTf) **(1)** to 2 atm of ethylene at 65 °C resulted in ethylene uptake and the generation of 1 equiv of propene and a mixture of *cis*- and *trans*-2-butenes (~1 turnover/h). After several hours, ^{31}P NMR indicated the complete conversion of **1** to an approximately 1:1 mixture of previously characterized (dfepe)Pt(η^2-C_2H_4) (**2**)[5d] and a new species, **3** (Scheme 2). Although **3** was not isolated, ^{31}P NMR spectral data (δ 77.8, $^1J_{PtP} = 1178$ Hz; δ 54.0, $^1J_{PtP} = 5847$ Hz) are consistent with the monoalkyl triflate product, (dfepe)Pt(Et)(OSO_2CF_3). A decrease in catalytic activity correlated with the appearance of **2** as a product.

The generation of **2** in dichloromethane suggested that loss of HX from a catalytic intermediate (dfepe)-Pt(H)(X) is competitive with ethylene dimerization, and therefore the catalytic activity of (dfepe)Pt(R)(X) systems should be sensitive to acid concentration. Indeed, treatment of either **1** or (dfepe)Pt(Me)(O_2CCF_3) (**4**) with 2 atm ethylene in neat CF_3CO_2H at 80 °C resulted in a single metal monoalkyl product that was tentatively identified as (dfepe)Pt(Et)(O_2CCF_3) (**5**). Under these conditions, however, 1 equiv of 2-(trifluoroacetato)propane and the catalytic production of 2-(trifluoroacetato)-butane (~6 turnovers/h) were observed as products (Scheme 3). No 1-butene or 2-butene products were detected throughout the course of reaction. The propyl and butyl ester products were identified by comparison of ^{1}H and ^{13}C NMR data to authentic samples prepared by the addition of propene and 1- or 2-butene, respectively, to trifluoroacetic acid at 20 °C (see Experimental Section). No ethane or butane protonolysis products were detected by NMR under these reaction conditions.

An independent synthesis of (dfepe)Pt(Et)(O_2CCF_3) was carried out in order to confirm the identify of **5**: Addition of dfepe to (cod)Pt(Et)$_2$ afforded (dfepe)Pt(Et)$_2$, which when treated with excess CF_3CO_2H converted cleanly to (dfepe)Pt(Et)(O_2CCF_3). Essentially identical spectral data for (dfepe)Pt(Et)(O_2CCF_3) and solutions of **5**, as well as nearly identical catalytic activities for CF_3CO_2H solutions of **1** and (dfepe)Pt(Et)(O_2CCF_3) at 80 °C, support the assignment of (dfepe)Pt(Et)(O_2CCF_3) as the catalyst resting state for ethylene dimerization.

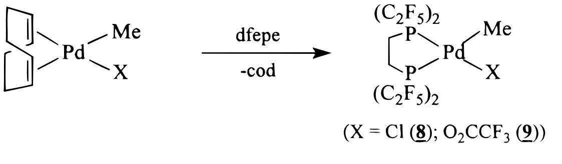
Catalytic Vinyl-H^+/D^+ Exchange. Complexes (dfepe)-Pt(η^2-C_2H_4) and (dfepe)Pt(Et)(O_2CCF_3) are readily interconverted: warming (dfepe)Pt(Et)(O_2CCF_3) in benzene-d_6 to 80 °C cleanly afforded (dfepe)Pt(η^2-C_2H_4) and 1 equiv of CF_3CO_2H, while the addition of excess CF_3CO_2H (~10 equiv) to benzene solutions of (dfepe)-Pt(η^2-C_2H_4) at 20 °C reformed the Pt(II) ethyl complex **5** (eq 1).



(1)

The reversibility of ethylene/ethyl group interchange between **2** and **5** was also apparent in H/D exchange studies between (dfepe)Pt(Et)(O_2CCF_3) and neat CF_3CO_2D: At room temperature, facile conversion of **5** to (dfepe)Pt(Et-d_5)(O_2CCF_3) (**5**-d_5) was indicated by ^{1}H NMR ($t_{1/2} \approx 40$ min). Upon exposure of **5**-d_5 to 1 atm C_2H_4, both the methylene and methyl proton signals increased in intensity, then diminished over the course of several hours. A concomitant decrease in the free ethylene resonance and increase in the CF_3CO_2H protic signal were also observed during this time period. Thus, (dfepe)Pt(Et)(O_2CCF_3) serves as a catalyst for H/D exchange between ethylene and trifluoroacetic acid under mild conditions (Scheme 4).

Palladium Chemistry. The generally low kinetic activity of platinum catalysts prompted us to examine the chemistry of analogous palladium systems. Attempts to prepare (dfepe)Pd(Me)$_2$, either from dfepe addition to (cod)Pd(Me)$_2$ or alkylation of (dfepe)PdCl$_2$ with MeMgBr, were not successful, most likely due to facile reductive elimination of ethane. The presumed instability of (dfepe)Pd(Me)$_2$ led us to investigate approaches to (dfepe)Pd(Me)X systems beginning with (cod)Pd(Me)Cl. Treatment of (cod)Pd(Me)Cl with AgX (X = O_2CCF_3, OSO_2CF_3) in dichloromethane afforded the corresponding (cod)Pd(Me)X complexes **6** and **7**, respectively, in moderate yield. Addition of dfepe to (cod)Pd(Me)Cl or **6** at 20 °C gave the corresponding dfepe monomethyl complexes (dfepe)Pd(Me)X (X = Cl **(8)**; O_2CCF_3 **(9)** (eq 2). Attempts to prepare (dfepe)Pd-(Me)(OTf) from **7** and dfepe gave (dfepe)$_2$Pd (see later) as the only detectable product. Both **8** and **9** are stable in air and in the solid state and, like their platinum analogues, do not undergo protonolysis in neat CF_3CO_2H at ambient temperature. After 2 days at 55 °C, decomposition of **9** occurred to form a mixture of (dfepe)$_2$Pd and several unidentified products.



(2)

Both (dfepe)Pd(Me)X complexes were fully characterized by NMR. The ^{1}H methyl proton resonances of **8** and **9** appear as doublets due to coupling with the trans phosphorus ($^3J_{PH} \approx 7.5$ Hz). For each compound two ^{31}P singlet resonances are observed, a high-field resonance

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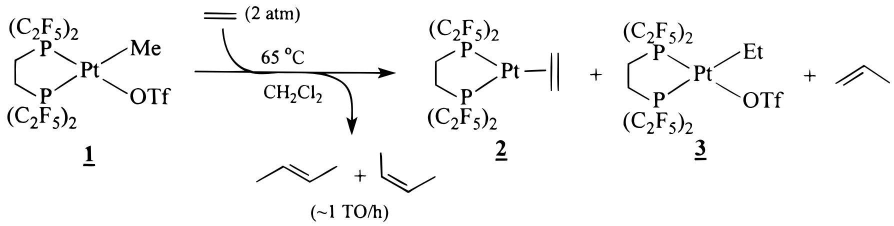
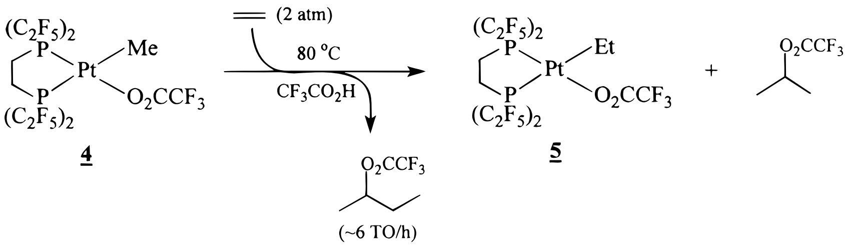
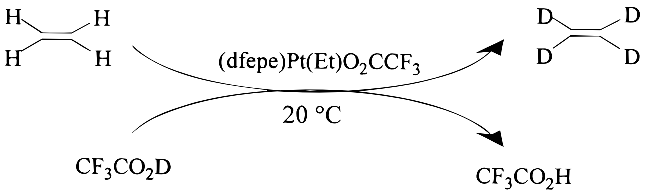
Scheme 2



Scheme 3

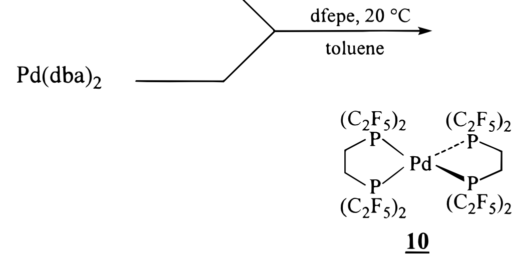


Scheme 4



($\delta = 56.3$, **8**; and 55.6, **9**) for the phosphorus atoms trans to X and a low-field resonance ($\delta = 72.9$, **8**; and 74.3, **9**) for the phosphorus atoms trans to the methyl group. These assignments were made on the basis of the corresponding platinum chemical shifts.

Like the platinum analogue, (dfepe)Pd(Me)(O_2CCF_3) is catalytically active: treatment of **9** with ~2 atm ethylene in trifluoroacetic acid at 25 °C resulted in rapid gas uptake and the clean production of 2-(trifluoroacetato)butane. A qualitatively similar activity was also observed for (dfepe)Pt(Me)Cl. In contrast to platinum, which forms (dfepe)Pt(Et)(O_2CCF_3) as a catalyst resting state, the growth of a new metal species having a single phosphorus resonance at $\delta = 49.1$ ppm was observed during the course of the reaction. In an effort to establish the nature of this symmetrical (dfepe)Pd species, three likely candidates, (dfepe)Pd(O_2CCF_3)$_2$, (dfepe)$_2$Pd, and (dfepe)Pd(η^2-C_2H_4), were considered. Addition of excess dfepe to either (Cp)Pd(allyl) or Pd(dba)$_2$ afforded the bis-chelate (dfepe)$_2$Pd (**10**) in good yield (eq 3).



(3)

10

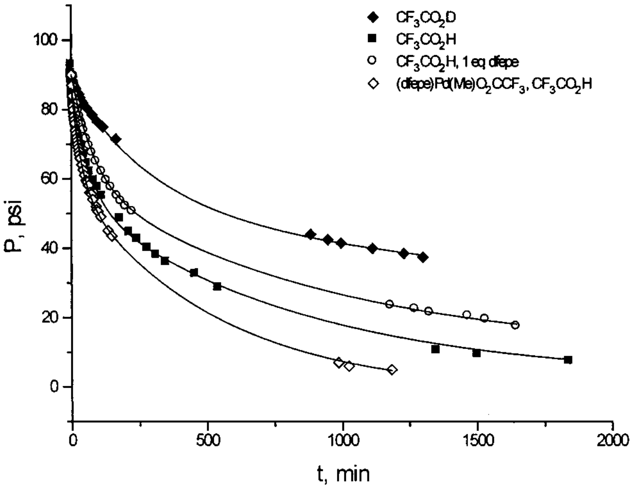


Figure 1. Ethylene consumption in trifluoroacetic acid versus time. Double exponential decay line-fits are shown. Initial parameters: [(dfepe)$_2$Pd] = 1.61 mM, [(dfepe)Pd(Me)(O_2CCF_3)] = 3.23 mM, $P_0 = 90$ psi, $T = 25$ °C.

Attempts to prepare (dfepe)Pd(O_2CCF_3)$_2$ by treatment of (cod)Pd(O_2CCF_3)$_2$ (**11**) with 1 equiv of dfepe resulted only in low yields of (dfepe)$_2$Pd. Similarly, efforts to prepare (dfepe)Pd(η^2-C_2H_4) by the addition of ethylene (~2 atm) to (dfepe)$_2$Pd in aprotic solvents gave no spectroscopic evidence for (dfepe)Pd(η^2-C_2H_4) formation. In addition to exhibiting a single phosphorus resonance for **10** coinciding with that observed in ethylene dimerizations using **9** as the catalyst, (dfepe)$_2$Pd also exhibited essentially identical catalytic activity in trifluoroacetic acid and is therefore the likely dimerization catalyst resting state. Significantly, (dfepe)$_2$Pd was catalytically inactive when acetic acid was used as a solvent.

A series of kinetic experiments were performed to probe the nature of palladium catalysis (Figures 1−3). For each kinetic run, a 100 psi ethylene charge was admitted to a Fisher-Porter bottle containing well-stirred solutions of (dfepe)Pd(Me)(O_2CCF_3) (3.23 mM) or (dfepe)$_2$Pd (1.61 mM) in 5 mL of trifluoroacetic acid at 25 °C. Taking into account an initial 10 psi pressure drop due to gas dissolution, the extent of ethylene dimerization was monitored by following the corresponding decrease in reactor pressure (Figure 1). Considerable deviations from second-order behavior occurred below ~20 psi ethylene. However, inverse pressure plots of ethylene uptake above this threshold for (dfepe)$_2$Pd in CF_3CO_2H and CF_3CO_2D were reasonably

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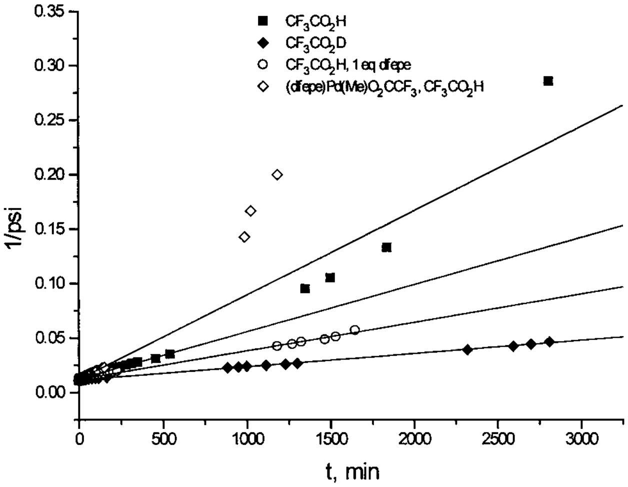


Figure 2. Plots of inverse pressure (psi) versus time at 25 °C. Linear regression fits are for data below a threshold of 0.05 psi^{-1}. Derived second-order rate constants for $(dfepe)_2Pd$ in $CF_3CO_{2x}H$ (1.61 mM), 0.201(4) mol^{-1}·min^{-1}; in CF_3CO_2D (1.61 mM), 0.0570(3) mol^{-1}·min^{-1}; in CF_3CO_2H + 1 equiv dfepe (1.61 mM), 0.122(1) mol^{-1}·min^{-1}; (dfepe)Pd(Me)(O_2CCF_3) in CF_3CO_2H (3.23 mM), 0.356(8) mol^{-1}·min^{-1}.

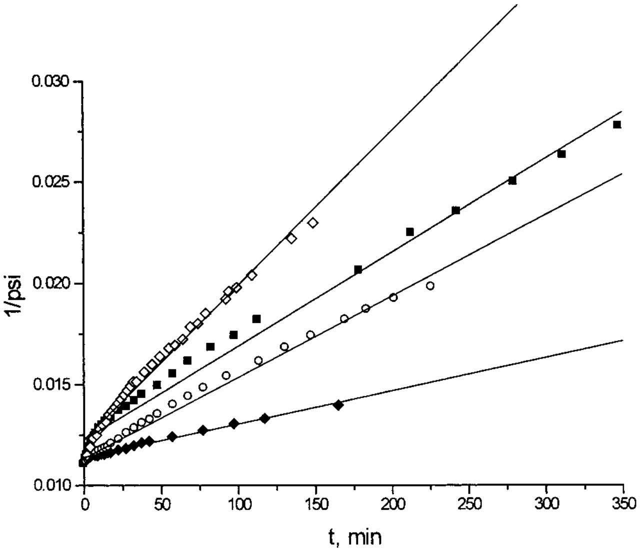
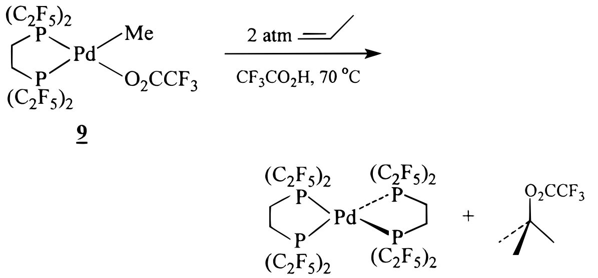


Figure 3. Plot of inverse pressure (psi) versus time at 25 °C, expanded to show data for the initial 350 min.

linear and gave effective second-order rate constants of 0.201(4) mol^{-1}·min^{-1} and 0.0570(3) mol^{-1}·min^{-1}, respectively, corresponding to a solvent kinetic isotope effect of 3.5(2) (Figures 2 and 3). The catalytic activity of $(dfepe)_2Pd$ in CF_3CO_2H at 100 psi is calculated to be 340 turnovers/h. In the presence of 1 equiv of dfepe, a significantly slower (60%) rate constant of 0.122(1) mol^{-1}·min^{-1} was observed in CF_3CO_2H. The initial catalytic activity of (dfepe)Pd(Me)(O_2CCF_3) was calculated to be approximately 300 turnovers/h. ^1H and ^{13}C NMR analysis of the 2-trifluoroacetatobutane product formed in the CF_3CO_2D kinetic run revealed that the sole observable deuterated product produced in this reaction was $CH_3CH(O_2CCF_3)CH(D)CH_3$.

The dimerization of higher olefins by dfepe-substituted platinum and palladium systems was briefly examined. Although propylene readily converts to $^iPr(O_2CCF_3)$ in trifluoroacetic acid, reversible 1,2-acid addition or competitive propylene insertions would allow for dimerization in this solvent. Prolonged thermolysis at 100 °C of (dfepe)Pt(Me)(O_2CCF_3) under ~2 atm propylene gave no evidence for organic products other than $^iPr(O_2CCF_3)$. In contrast, treatment of (dfepe)Pd(Me)(O_2CCF_3) in CF_3CO_2H with 2 atm propylene at 70 °C resulted in the clean formation of $(dfepe)_2Pd$ and 1 equiv of $^tBu(O_2CCF_3)$, as judged by ^1H and ^{13}C NMR spectroscopy. In a separate experiment, no dimerization activity was observed for $(dfepe)_2Pd$ under similar conditions at temperatures up to 80 °C.



9

10

(4)

Discussion

A variety of palladium systems have been well established as olefin dimerization catalysts.[8] In contrast, very few reports of platinum-based olefin dimerization systems have appeared.[9] Lewis or Brönsted acid cocatalysts and/or initiators have been employed in a number of cases to induce activity,[10,11] but to our knowledge the use of an acid as both a solvent medium and a coreactant is not precedented.[12]

The compatibility of (dfepe)M−alkyl bonds with acidic media has been noted in our previous work.[4,6,13] Depending on the specific mechanism of protonolysis (stepwise protonation of the metal center followed by reductive elimination or direct electrophilic attack of the M−C bond), the ease of L_nM−alkyl bond protonolysis should be related to the ease of protonation of available metal lone-pairs and/or the electron density and polarity of the M−alkyl bond.[13,14] For late metal and electron-poor metal systems such as (dfepe)M(R)(X), a "conventional" $M(\delta^+)-C(\delta^-)$ bond polarity is not an accurate description, and therefore proton transfer to a carbanionic alkyl group is not anticipated. Nevertheless, the results of our current study as well as earlier work by Flood[1e,15] clearly show that olefin insertion into these types of M−C bonds is not precluded by such shifts in M−C bond electron density.

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(12) Acetic acid has been used as a solvent for olefin dimerization using Pd(II) salts: see Table 2, in ref 8b.

(13) The mechanism of (dfepe)Pt−R protonolyses has been addressed in more detail: Bennett, B. L.; J. M. Hoerter, J. M.; Roddick, D. M. Manuscript in preparation.

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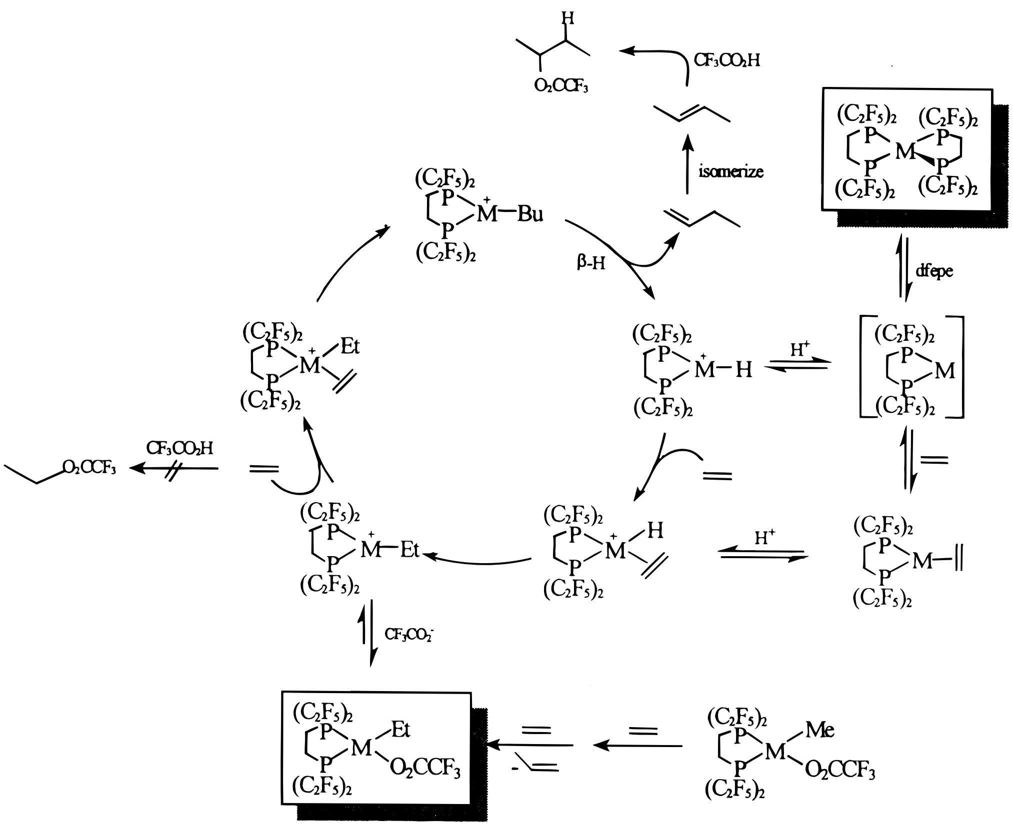
Scheme 5



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A catalytic cycle consistent with all of our observations for both the platinum and palladium systems may be accommodated by the general mechanistic framework shown in Scheme 5. Prior dimerization studies with late transition metal systems have either proposed or directly observed alkyl complexes as reaction intermediates, in accord with a catalytic cycle involving olefin insertion into M−H and M−alkyl bonds. Although an alternative cycloaddition dimerization mechanism may be considered, several observations argue against this potential pathway and support a Cossee−Arlman alkyl insertion mechanism for the systems presented in this study: (1) the decrease in catalytic activity upon formation of (dfepe)Pt(η^2-C_2H_4) during the course of ethylene dimerization in aprotic solvents (Scheme 2), (2) the observation of (dfepe)Pt(Et)(O_2CCF_3) as a catalyst resting state, and (3) the catalytic inactivity of $(dfepe)_2Pd$ in aprotic solvents or in the weaker acid CH_3CO_2H.

In addition to the conventional ethylene dimerization catalytic cycle depicted in Scheme 5, a number of interesting additional features merit consideration. First, despite the presence of both M−ethyl and M−butyl intermediates, no ethane or butane protonolysis products are observed in trifluoroacetic acid after prolonged reaction. From this it can be concluded that the rates of ethylene insertion and β-elimination are much greater than protonolysis side reactions. A second unusual feature in these systems is the role of the acid solvent itself in substrate and product discrimination. For simple alkenes $H_2C{=}CH(R)$, 1,2-addition of trifluoroacetic acid ($pK_a = 0.23$) is favored for all cases where $R \neq H$. As a consequence, only ethylene is stable under the reaction conditions. The absence of any significant quantities of free 1- or 2-butenes throughout the course of dimerization indicates that 1,2-HX addition is fast relative to butene generation. The observation that deuterium is incorporated into only the 3-position of the 2-butyl ester product in $(dfepe)_2Pd$-mediated catalysis in CF_3CO_2D is also quite significant, since it indicates that exclusively 2-butene is intercepted by acid, rather than 1-butene or an equilibrated thermodynamic mixture of 1- and 2-butenes. Thus, not only is olefin isomerization occurring in these systems (as in Scheme 2) but the presence of acid serves to selectively discriminate in favor of 2-butene. An additional conclusion drawn from the selective formation of $CH_3CH(O_2CCF_3)$-$CH(D)CH_3$ is that prior scrambling of deuterons into ethylene is not competitive with dimerization by $(dfepe)_2Pd$ in CF_3CO_2D.

The resistance of (dfepe)Pt−alkyl bonds to protonolysis also leads to catalytic deuteration of ethylene in trifluoroacetic acid under mild conditions (Scheme 4). While this type of exchange should generally be promoted by sufficiently electrophilic late metal systems with reversible olefin insertion/elimination and protonation equilibria, only scattered reports of this reaction mode have appeared in the literature. Cramer, in particular, has reported ethylene deuteration by (acac)-$Rh(C_2H_4)_2$ in DCl/CH_3OD at −24 °C.[10] Although intriguing from a fundamental standpoint, competing ethylene dimerization (especially for palladium) and the limited stability of higher olefins in trifluoroacetic acid place constraints on the utility of this scrambling mechanism.

The observed catalyst resting states for palladium and platinum catalytic systems differ. This is most likely due to a combination of a lower ethylene binding affinity for (dfepe)Pd(0) relative to (dfepe)Pt(0) and a more unfavorable equilibrium between (dfepe)Pd(η^2-C_2H_4) and (dfepe)-Pd(Et)X for palladium (Scheme 6). While both dfepe displacement by C_2H_4 and protonation are required to

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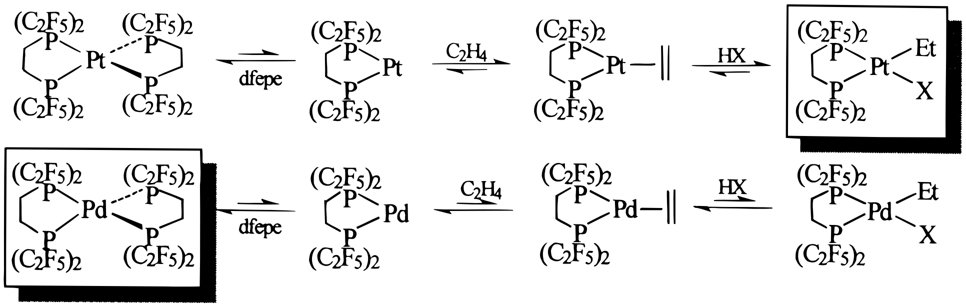
Scheme 6



enter the catalytic cycle from $(dfepe)_2Pd$, the activity of $(dfepe)_2Pd$ is still substantially higher than (dfepe)Pt(R)X. The similar activities of $(dfepe)_2Pd$ and (dfepe)Pd(Me)(O_2CCF_3) indicate that these preequilibria are not severely restrictive; however, the catalytic inactivity of $(dfepe)_2Pd$ in the weaker acid $MeCO_2H$, rate inhibition by added dfepe, and the rate differences observed between CF_3CO_2D and CF_3CO_2H runs indicate that both dfepe dissociation and proton transfer are kinetically important in these systems.

The stoichiometric reaction of propylene with (dfepe)Pd(Me)(O_2CCF_3) and the inactivity of $(dfepe)_2Pd$ in trifluoroacetic acid reflect a lower activity toward higher olefins. While the stoichiometric production of ^tBu(O_2CCF_3) confirms that propylene insertion into a Pd−Me bond has occurred, the lack of any C_6 products suggests that either (1) the insertion of propylene into a Pd−propyl bond is less favorable or (2) (dfepe)Pd(propyl)$^+$ is not accessible from the $(dfepe)_2Pd$ catalyst resting state. The lower binding affinity generally observed for higher olefins relative to ethylene is likely to be the limiting factor in both of these processes.

The number of preequilibria involved in ethylene dimerization by $(dfepe)_2Pd$ complicates the kinetic analysis for this system. If dfepe displacement by ethylene ($K_1 = k_1/k_{-1}$) is rapid relative to CF_3CO_2H addition ($K_2 = k_2/k_{-2}$) and the addition of ethylene to a (dfepe)Pd(Et)O_2CCF_3 intermediate is rate limiting (k_3), then the following rate law can be derived:

$$\text{rate} = \frac{k_1k_2k_3[(\text{dfepe})_2\text{Pd}][\text{CF}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_4]^2}{k_{-1}[\text{dfepe}](k_{-2} + k_3[\text{C}_2\text{H}_4])}$$

Under conditions where $k_{-2} \gg k_3[C_2H_4]$ this expression simplifies to a second-order dependence in ethylene and an inverse dependence on added dfepe, in qualitative agreement with the observed kinetic behavior. Nevertheless, the assumption that the preequilibrium K_1 is established is unsupported, and the deviation from second-order behavior observed in Figure 2 is not explained. A more complete understanding of the underlying mechanism relating to Scheme 5 clearly requires more detailed study.

In summary, we have shown that (perfluoroalkyl)phosphine group 10 systems can serve as useful organometallic catalyst precursors which are compatible with trifluoroacetic acid as a reaction medium. In the case of palladium, a sufficiently high level of acidity is actually required for hydride formation and the initiation of insertion activity. This is in marked contrast with catalysts where adventitious protons are required to initiate catalytic activity. Since we have recently shown that (dfepe)Pt−alkyl bonds are stable in even superacidic solvents such as CF_3SO_3H or FSO_3H for hours at room temperature, the range of potential organometallic transformations based on electrophilic metal systems may in principle be extended even further to extremely acidic media.

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 (Massachusetts) and used as received. AgO_2CCF_3 and MeMgBr were obtained from Aldrich and used as obtained. Elemental analyses were performed by Desert Analytics. High-resolution mass spectrum data were obtained from the Nebraska Center for Mass Spectrometry. IR spectra were recorded on a Perkin-Elmer 1600 FTIR instrument as Nujol mulls using NaCl plates. NMR spectra were obtained with a JEOL GSX-270 or a Brüker DRX-400 instrument. ^{31}P spectra were referenced to an 85% H_3PO_4 external standard. (dfepe)Pt(Me)(X) (X = OTf (**1**), O_2CCF_3 (**4**)),[6] (cod)Pt$(Et)_2$,[16] (cod)Pd(Me)Cl (cod = 1,5-cyclooctadiene),[17] dfepe,[18] CpPd(allyl),[19] and $Pd(dba)_2$[20] were prepared using literature methods.

(dfepe)Pt(Et)$_2$. Approximately 0.5 g of (cod)Pt$(Et)_2$ was dissolved in 20 mL of Et_2O, and 0.95 g (1.68 mmol) of dfepe was added via syringe. After stirring the reaction mixture overnight at ambient temperature, cooling to −78 °C and filtration afforded 1.1 g (~95%) of (dfepe)Pt$(Et)_2$ as an off-white solid. Anal. Calcd for $C_{14}H_{14}F_{20}P_2Pt$: C 20.53, H 1.72. Found: C 20.53, H 1.58. ^1H NMR (CD_2Cl_2, 270 MHz, 27 °C): δ 2.42 (m, 4H; PCH_2), 2.12 (m, $^2J_{PtH} = 86$ Hz, 2H; Pt(CH_2CH_3)), 1.22 (m, $^3J_{PtH} = 82$ Hz, 3H; Pt(CH_2CH_3)). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 27 °C): δ 121.2 (td, $^1J_{CF} = 292$ Hz, $^1J_{CP} = 39$ Hz; CF_2CF_3), 116.9 (qd, $^1J_{CF} = 284$ Hz, $^2J_{CP} = 18$ Hz; CF_2CF_3), 23.4 (t, $^1J_{CP} = 40$ Hz; PCH_2), 15.9 (d, $^1J_{CPt} = 713$ Hz, $^2J_{CP} = 92$ Hz; CH_2CH_3), 15.2 (s, $^2J_{CPt} = 28$ Hz; CH_2CH_3). ^{19}F NMR (CD_2Cl_2, 254.05 MHz, 27 °C): δ −79.87 (s, PCF_2CF_3) (*NOTE:* in all dfepe complexes, there are no observable $^3J_{FF}$ vicinal couplings), −111 (overlapping ABX multiplets, PCF_2CF_3). ^{31}P NMR (CD_2Cl_2, 109.25 MHz, 27 °C): δ −8.70 (m, $^1J_{PPt} = 1095$ Hz). IR (cm^{-1}): 1296(s), 1226(sh), 1200(s), 1146(sh), 1127(s), 1090(sh), 956(s), 871(w), 809(w), 749(m).

(dfepe)Pt(Et)(O_2CCF_3) (5). A 100 mL flask was charged with 1.100 g (1.343 mmol) of (dfepe)Pt$(Et)_2$ and 1 mL of CF_3CO_2H under a nitrogen atmosphere. Rapid evolution of gas indicated the reaction was essentially complete upon dissolu-

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tion of the solid (1−2 min). All volatiles were removed, and 15 mL of diethyl ether was added. Filtration of the resulting slurry and drying under vacuum afforded 1.017 g of white solid (84% yield). Anal. Calcd for $C_{14}H_9F_{23}O_2P_2Pt$: C, 18.62; H, 1.00. Found: C, 18.61; H, 0.99. ^1H NMR (CD_2Cl_2, 400 MHz, 27 °C): δ 2.70 (m, 2H; PCH_2), 2.44 (m, 2H; PCH_2), 2.32 (q, $^2J_{HPt} = 53$ Hz, $^3J_{HH} = 6$ Hz, 2H; Pt(CH_2CH_3)), 1.16 (t, $^3J_{HH} = 6$ Hz, $^3J_{HPt} = 29$ Hz Pt(CH_2CH_3)). ^{19}F NMR: (CD_2Cl_2, 376.5 MHz, 27 °C): δ −78.6 (s, 6F, PCF_2CF_3), −77.9 (s, 6F; PCF_2CF_3), −108.4 (m, overlapping ABX multiplets, 8F; PCF_2CF_3), −73.2 (s, 3F; CF_3CO_2). ^{31}P NMR (CF_3CO_2H, 109.25 MHz, 27 °C): δ 76.7 (m, $^1J_{PPt} = 1171$ Hz), 57.4 (m, $^1J_{PPt} = 5302$ Hz). In acetone-d_6: δ 79.8 (s, $^1J_{PPt} = 1135$ Hz), 60.73 (s, $^1J_{PPt} = 4861$ Hz). IR (cm^{-1}): 1704(m), 1408(w), 1295(s), 1191(s), 1136(s), 963(m), 751(w).

(cod)Pd(Me)(O_2CCF_3) (6). A flask charged with 0.50 g (1.9 mmol) of (cod)Pd(Me)(Cl), 0.50 g (2.3 mmol) of AgO_2CCF_3, and 20 mL of CH_2Cl_2 was stirred at 20 °C in the absence of light for 5 h. The resulting brown-gray slurry was filtered, and the CH_2Cl_2 was removed from the filtrate. Addition of 20 mL of Et_2O yielded a yellow solution, which upon cooling to −78 °C formed a white precipitate. Filtration and drying under vacuum yielded 0.48 g (74%) of (cod)Pd(Me)(O_2CCF_3) (**6**). **6** is thermally sensitive and was stored at −40 °C to prevent plating of Pd^0 metal; no elemental analysis was obtained. ^1H NMR (C_6D_6, 270 MHz, 20 °C): δ 5.54 (s, 2H, olefinic cod), 4.07 (s, 2H, olefinic cod), 1.61 (m, 4H, aliphatic cod), 1.44 (m, 4H, aliphatic cod), 1.02 (s, 3H, $PdCH_3$). IR (cm^{-1}): 1685(s), 1581(w), 1415(m), 1194(s), 1179(s), 1160(s), 1137(s), 1087(w), 1020(w), 1003(w), 986(w), 906(w), 840(m), 790(w), 771(w), 748(w), 726(s), 668(w).

(cod)Pd(Me)(OTf) (7). To a flask charged with 0.500 g (1.89 mmol) of (cod)Pd(Me)(Cl) and 0.484 g (1.89 mmol) of AgOTf (OTf = O_3SCF_3) was added 25 mL of CH_2Cl_2. After stirring at room temperature for 24 h in the absence of light, a gray solid was filtered off to give a yellow-brown filtrate, which was concentrated to ca. 5 mL and precipitated with Et_2O to yield white crystalline **7** (0.716 g, 74%). The solid was isolated by cold filtration, dried under vacuum, and stored at −40 °C under nitrogen. **7** was not sufficiently stable for elemental analysis. ^1H NMR (CD_2Cl_2, 400 MHz, 20 °C): δ 6.14 (s, 2H, olefinic cod), 5.50 (s, 2H, olefinic cod), 2.71 (m, 8H, aliphatic cod), 1.40 (s, 3H, $PdCH_3$). ^{19}F NMR (CD_2Cl_2, 400 MHz, 23 °C): δ −77.12 (s, O_3SCF_3). IR (cm^{-1}): 1311(m), 1231(s), 1208(m), 1156(m), 1017(s), 906(s), 853(s), 815(s).

(dfepe)Pd(Me)(Cl) (8). To a flask charged with 0.345 g (1.30 mmol) of (cod)Pd(Me)(Cl) and 25 mL of CH_2Cl_2 was added 0.550 mL (1.95 mmol) of dfepe via syringe at 20 °C. After 24 h the solution was concentrated to 10 mL and cooled to −78 °C. The resulting white solid, **8** (0.64 g (68%)), was collected by filtration and dried under vacuum. Anal. Calcd for $C_{11}H_7ClF_{20}P_2Pd$: C, 18.27; H, 0.98. Found: C, 17.91; H, 0.75. IR (cm^{-1}): 1459(m), 1377(w), 1301(m), 1228(s), 1135(m), 963(m), 866(w), 808(w), 752(m). ^1H NMR (acetone-d_6, 270 MHz, 20 °C): δ 3.33 (m, 2H, PCH_2), 3.03 (m, 2H, PCH_2), 1.63 (d, $^3J_{PH} = 7$ Hz, 3H, $PdCH_3$). ^{31}P NMR (acetone-d_6, 270 MHz, 20 °C): δ 72.9 (m), 56.3 (m).

(dfepe)Pd(Me)(O_2CCF_3) (9). To a flask charged with 0.206 g (0.601 mmol) of (cod)Pd(Me)(O_2CCF_3) (prepared as described above) and 20 mL of toluene was added 0.25 mL (0.90 mmol) of dfepe via syringe at 20 °C. An immediate reaction took place to give a tan solid. Removal of toluene and addition of a petroleum ether/Et_2O (ca. 2:1, 30 mL) gave **9** (0.345 g (72%), which was isolated by filtration and dried under vacuum. **9** was stored at −40 °C under nitrogen. Anal. Calcd for $C_{13}H_7F_{23}O_2P_2Pd$: C, 19.50; H, 0.88. Found: C, 19.13; H, 0.81. ^1H NMR (CF_3CO_2D, 270 MHz, 20 °C): δ 2.99 (m, 2H, PCH_2), 2.67 (m, 2H, PCH_2), 1.84 (d, $^3J_{PH} = 8.1$ Hz, 3H, $PdCH_3$). ^{31}P NMR (C_6D_6, 270 MHz, 20 °C): δ 74.3 (m), 55.6 (m). ^{19}F NMR (C_6D_6, 400 MHz, 20 °C): δ −72.39 (s, O_2CCF_3), −78.27 (s, PCF_2CF_3), −78.91 (s, PCF_2CF_3), −107.82 (overlapping ABX multiplets, PCF_2CF_3). IR (cm^{-1}): 1693(s), 1420(w), 1298(m), 1234(s), 1196(m), 1137(s), 962(s).

$(dfepe)_2Pd$ (10), Method A. To a flask charged with 0.05 g (0.2 mmol) of (Cp)Pd(allyl) was added 20 mL of toluene and 0.2 mL (0.7 mmol) of dfepe. The reaction mixture was stirred at room temperature for 1 h, and the solution was then cooled to −78 °C, upon which a white precipitate formed. The solid was collected by cold filtration and dried under vacuum to yield 0.20 g (80%) of **10**. Anal. Calcd for $C_{20}H_8F_{40}Pd$: C, 19.40; H, 0.651. Found: C, 19.14; H, 0.40. ^1H NMR (C_6D_6, 400 MHz, 23 °C): δ 1.82 (m). ^{31}P NMR (C_6D_6, 400 MHz, 23 °C): δ 48.7 (m).

$(dfepe)_2Pd$, Method B. To a flask charged with 0.25 g of $Pd(dba)_2$ (0.04 mmol) was added 30 mL of CH_2Cl_2 and 0.35 mL (0.11 mmol) of dfepe. The reaction mixture was stirred at room temperature for 3 h and evaporated to dryness. CH_3OH (10 mL) was added to precipitate a white solid, which was collected by filtration and dried under vacuum to yield 0.35 g (66%) of $(dfepe)_2Pd$.

(cod)Pd(O_2CCF_3)$_2$ (11). To a flask charged with 0.26 g (0.89 mmol) of (cod)$PdCl_2$ and 0.394 g (1.78 mmol) of AgO_2CCF_3 was added 25 mL of CH_2Cl_2. After stirring at room temperature for 24 h in the absence of light a red-brown solid was filtered. The yellow filtrate was concentrated and precipitated with petroleum ether to give a light yellow powder (0.393 g (73%)). **7** was isolated by filtration, dried under vacuum, and stored at −40 °C under nitrogen. **7** was not sufficiently stable for analysis. ^1H NMR (CD_2Cl_2, 400 MHz, 20 °C): δ 6.36 (s, 4H, olefinic cod), 3.05 (s, 4H, aliphatic cod), 2.54 (s, 4H, aliphatic cod). ^{19}F NMR (CD_2Cl_2, 400 MHz, 23 °C): δ −73.64 (s). IR (cm^{-1}): 1785(s), 1670(s), 1203(w), 1150(w).

2-(Trifluoroacetato)butane Synthesis. To 10 mL of CF_3CO_2H in a 3 oz Fisher-Porter bottle was admitted 45 psi 1-butene. After complete reaction, as judged by ^1H and ^{13}C NMR, the solution was quenched with H_2O (100 mL) and the ester product was extracted with 100 mL of CH_2Cl_2. Removal of the CH_2Cl_2 under vacuum gave essentially pure 2-(trifluoroacetyl)butane as a light brown liquid (crude yield 1.78 g). High-resolution mass spectrum (CI, isobutane) for MH^+ ion: 176.0637 (176.0633 calcd, −2.3 ppm). ^1H NMR (CF_3CO_2H, 400 MHz, 20 °C): δ 5.07 (m, 1H; CH(O_2CCF_3)), 1.66 (m, 2H; CH_2), 1.29 (d, 3H; CH_3), 0.87 (t, 3H; CH_3). ^{13}C NMR (CF_3CO_2H, 400 MHz, 20 °C): δ 82.7 (d, $^2J_{CH} = 150$ Hz; $CH_3CH(O_2CCF_3)CH_2CH_3$), 31.1 (t, $^2J_{CH} = 123$ Hz; $CH_3CH(O_2CCF_3)CH_2CH_3$), 20.5 (q, $^2J_{CH} = 128$ Hz; $CH_3CH(O_2CCF_3)CH_2CH_3$), 10.9 (q, $^2J_{CH} = 115$ Hz; $CH_3CH(O_2CCF_3)CH_2CH_3$).

Ethylene Dimerization Studies. A typical experiment was as follows: 5 mL of CF_3CO_2H and $(dfepe)_2Pd$ (20 mg, 0.016 mmol) were placed in a 3 oz Fisher-Porter bottle fitted with a magnetic stirbar, gas inlet valve, and 160 psi pressure gauge (1 psi increments); 100 psi was admitted at 25 °C, and after the initial pressure drop due to the equilibration of ethylene into solution, the uptake of gas was monitored by following the pressure drop as a function of time.

Reaction of (dfepe)Pd(Me)(O_2CCF_3) with Propylene. Trifluoroacetic acid (1 mL) and (dfepe)Pd(Me)(O_2CCF_3) (20 mg, 0.025 mmol) were placed in an NMR tube fitted with a Teflon valve, pressurized with ∼2 atm propylene, and heated to 70 °C. After 24 h, ^1H and ^{13}C NMR indicated the formation of $^iPr(O_2CCF_3)$, 1 equiv of $^tBu(O_2CCF_3)$, and $(dfepe)_2Pd$.

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