Synthesis of $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$, a Highly Active Ethylene Dimerization Catalyst

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The synthesis of cationic adducts $(dfepe)Pt(Me)(L)^+$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; L = MeCN, CO, C_2H_4, C_5F_5N, μ-Cl) are reported. Treatment of (cod)Pt(Me)Cl with $AgSbF_6$ in acetonitrile followed by the addition of dfepe afforded $(dfepe)Pt(Me)(CH_3CN)^+SbF_6^-$. Addition of $B(C_6F_5)_3$ to (dfepe)Pt(Me)(O_2CCF_3) in methylene chloride afforded the structurally characterized borane association product $(dfepe)Pt(Me)[(O_2CCF_3)B(C_6F_5)_3]$ in high yield. Attempts to displace the $[(O_2CCF_3)B(C_6F_5)_3]^-$ anion with donor ligands resulted in loss of borane and regeneration of (dfepe)Pt(Me)(O_2CCF_3). Addition of the mesitylenium acid $(1,3,5\text{-}C_6H_4Me_3)^+B(C_6F_5)_4^-$ to $(dfepe)PtMe_2$ in methylene chloride at ambient temperatures resulted in chloride abstraction and the precipitation of the chloride-bridged dimeric complex $[\{(dfepe)Pt(Me)\}_2(\mu\text{-}Cl)]^+B(C_6F_5)_4^-$, which has been structurally characterized. In contrast, treatment of $(dfepe)PtMe_2$ with $(1,3,5\text{-}C_6H_4Me_3)^+B(C_6F_5)_4^-$ in pentafluoropyridine at ambient temperature resulted in the precipitation of the structurally characterized pentafluoropyridine adduct $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ in good yield. Exposure of $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ to 1 atm of CO in *o*-difluorobenzene gave the carbonyl complex $[(dfepe)Pt(Me)(CO)]^+B(C_6F_5)_4^-$. In marked contrast to previously reported platinum systems, $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ is a very active ethylene dimerization catalyst at ambient temperature (600 psi ethylene, 22 °C in *ortho*-difluorobenzene, 150 turnovers h^{-1}). The ethylene adduct $[(dfepe)Pt(Me)(\eta^2\text{-}C_2H_4)]^+B(C_6F_5)_4^-$ has been spectroscopically characterized at −20 °C.

Introduction

Cationic group 10 compounds of the general formula $L_2M(alkyl)(L')^+$, $L_2M(L')_2{}^{2+}$, or $L_3M(L')^{2+}$ are of continuing interest due in part to their role in alkene oligomerization,[1] alkene/CO copolymerization,[2] and a wide variety of metal-mediated catalytic organic transformations.[3] A key requirement of many active catalyst systems is the use of very weakly coordinating counteranions (WCAs), solvents, and ancillary neutral donor ligands L′. In our prior work exploring the chemistry of perfluoroalkylphosphine ("PFAP") group 10 systems, we have taken advantage of the remarkable resistance of $(dfepe)M(CH_3)(X)$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) and *trans*-$(dfmp)_2Pt(CH_3)(X)$ (dfmp = $(C_2F_5)_2PMe$) complexes toward protonolysis and have examined their chemistry in acidic and superacidic solvents.[4] Under acidic conditions the anionic ligand X^- is labilized both by virtue of being the conjugate base of a very strong acid, HX, and by homoconjugation (hydrogen bonding) with the neat acid media. This strategy to generate reactive organometallic cations, though fruitful, is limited since the use of increasingly stronger acid media to generate more labile metal cations places restrictions on which coordination substrates can be used. In superacidic media in particular, only extremely weakly basic substrates such as CO and H_2 are stable and readily examined.[4f]

Several years ago we reported that $(dfepe)Pt(Me)O_2CCF_3$ is a modestly active ethylene dimerization catalyst (~6 turnovers h^{-1}) in trifluoroacetic acid at 80 °C.[4e] Although much less active than the corresponding $(dfepe)_2Pd/CF_3CO_2H$ system, this was the first example of catalytic ethylene dimerization by a well-defined platinum complex. Brookhart and Templeton have recently reported ethylene dimerization by $(diimine)Pt(H)(\eta^2\text{-}C_2H_4)^+BAr'_4$ at 100 °C with a slow turnover rate of ~0.1 h^{-1}.[5] A direct comparison of the intrinsic metal−carbon bond insertion reactivity of electron-poor $(dfepe)Pt(R)^+$ and the more electron-rich $(diimine)Pt(R)^+$ moieties is clearly of interest. However, the catalyst resting state for ethylene dimerization by $(dfepe)Pt(Me)(O_2CCF_3)$ in CF_3CO_2H was identified as $(dfepe)Pt(Et)(O_2CCF_3)$, rather than $(dfepe)Pt(Et)(\eta^2\text{-}C_2H_4)^+$ or $(dfepe)Pt(H)(\eta^2\text{-}C_2H_4)^+$, and indicated that trifluoroacetate anion loss was rate-determining. This contrasts with the (diimine)Pt(II)

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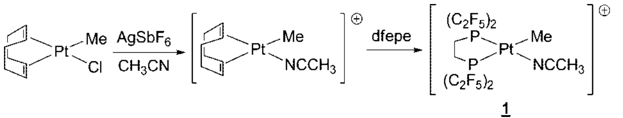
catalyst resting state (diimine)Pt(Et)(η^2-C_2H_4)$^+$, which allowed the barrier to ethylene insertion to be directly determined.[5]

To address this specific issue and to more broadly extend the chemistry of labile PFAP complex metal cations, we have begun to examine routes to isolable, labile complex platinum cations employing WCAs such as fluorinated aryl borates and halocarboranes. In this paper we present the synthesis and characterization of the labile electron-poor methyl cation complex [(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ and a preliminary survey of its reactivity with ethylene. We anticipated that weakly coordinating pentafluoropyridine would be readily displaced by ethylene and that dimerization via a (dfepe)Pt(Et)(η^2-C_2H_4)]$^+$ catalyst resting state would be significantly more facile. Indeed, we find that [(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ reacts with ethylene at low temperatures to form a discrete adduct, [(dfepe)Pt(Me)(η^2-C_2H_4)]$^+$B(C_6F_5)$_4^-$. This platinum system exhibits unusually high catalytic activity for ethylene dimerization at room temperature.

Results and Discussion

Synthesis of [(dfepe)Pt(Me)(MeCN)]$^+$SbF$_6^-$ (1). Conventional halide abstraction has been examined as a route to labile Pt(II) alkyl cation solvates, (dfepe)Pt(Me)(*solv*)$^+$. Treatment of (dfepe)Pt(Me)Cl with AgSbF$_6$ in acetonitrile does not result in halide abstraction, presumably due to strong Pt−Cl binding to the electrophilic (dfepe)Pt(II) moiety. (dfepe)Pt(Me)(MeCN)$^+$ can, however, be prepared via an indirect synthesis: addition of AgSbF$_6$ to (cod)Pt(Me)Cl in acetonitrile followed by the addition of dfepe afforded (dfepe)Pt(Me)(CH_3CN)$^+$SbF$_6^-$ (**1**) (eq 1).

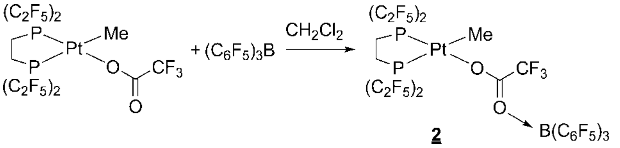


1 (1)

The intermediate (cod)Pt(Me)(CH_3CN)$^+$ was not isolated. However, the formation of (cod)Pt(Me)(CH_3CN)$^+$ was confirmed by ^{1}H NMR, where a 0.08 ppm upfield shift of the methyl resonance relative to the starting material (cod)Pt(Me)Cl was noted. $^1J_{PtP}$ data are diagnostic for the strength of the trans Pt−ligand interaction and is useful for establishing relative trans ligand influences.[6] For **1**, ^{31}P resonances appear at 64.8 ($^1J_{PtP}$ = 4680 Hz) and 81.9 ($^1J_{PtP}$ = 1400 Hz) ppm for the phosphorus atoms trans to the CH_3CN ligand and the methyl group, respectively. The $^1J_{PtP}$ value of 4680 Hz is higher than that reported for [(dppe)Pt(Me)(CH_3CN)]$^+$ ($^1J_{PtP}$ = 4370 Hz),[6] indicating that the acetonitrile ligand is more weakly coordinated in **1**. However, treatment of **1** with 1 atm of CO or ethylene in acetonitrile at ambient temperature does not result in acetonitrile displacement and indicates that **1** is not a sufficiently labile source of the (dfepe)Pt(Me)$^+$ moiety.

Synthesis and Characterization of (dfepe)Pt(Me)[(O_2CCF_3)-B(C_6F_5)$_3$] (2). The Lewis acid B(C_6F_5)$_3$ has been widely used as an alkyl abstraction reagent in coordination chemistry, giving rise to cationic complexes with [RB(C_6F_5)$_3$]$^-$ as the counterion.[7] This reaction has been more commonly employed with more carbanionic early transition metal alkyls, but methyl abstraction from (bu$_2$bpy)PtMe$_2$ has been reported in the presence of trapping ligands.[8] No reaction was observed between (dfepe)PtMe$_2$ and B(C_6F_5)$_3$ in dichloromethane at ambient temperature. No (dfepe)Pt(Me)(CO)$^+$ was formed in the presence of CO as a trapping ligand under these conditions. (dfepe)PtMe$_2$ was similarly unreactive with the trityl reagent Ph$_3$C$^+$B(C_6F_5)$_4^-$.

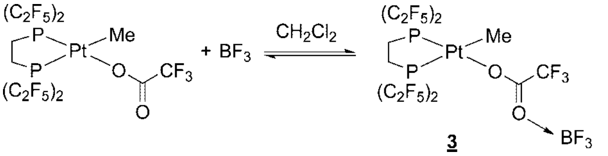
No reaction was also observed between excess B(C_6F_5)$_3$ and the monoalkyl complexes (dfepe)Pt(Me)(OTf) or (dfepe)Pt(Me)Cl. However, when (dfepe)Pt(Me)(O_2CCF_3) was treated with 1.2 equiv of B(C_6F_5)$_3$ in methylene chloride, the association product (dfepe)Pt(Me)[(O_2CCF_3)B(C_6F_5)$_3$] (**2**) was isolated in high yield (eq 2).



2 (2)

NMR data clearly support the formation of a borane adduct: The methyl resonance of **2** is shifted upfield by 0.54 ppm from that of **1**, and the coupling constant for Pt−P trans to the adduct ($^1J_{Pt-P}$= 5220 Hz) is significantly higher than that of the Pt−P trans to O_2CCF_3 in (dfepe)Pt(Me)(O_2CCF_3) ($^1J_{Pt-P}$= 4575 Hz), indicating a weakened interaction of the acetate moiety with the Pt center. ^{19}F NMR spectra exhibit peaks that are characteristic of the presence of a coordinated borane ligand (−134.4, −160.7, −163.5) and are shifted from those of the free borane. Infrared data show a ν(CO) shift from 1704 cm^{-1} in (dfepe)Pt(Me)(O_2CCF_3) to 1653 cm^{-1} in **2**. Spectroscopic evidence is in accord with X-ray crystallographic data (see below).

Treatment of (dfepe)Pt(Me)(O_2CCF_3) in methylene chloride with 2 atm of BF$_3$ similarly resulted in the formation a BF$_3$ adduct, (dfepe)Pt(Me)[(O_2CCF_3)(BF$_3$)] (**3**), as evidenced by a 0.98 ppm downfield shift of the methyl resonance and an increase of the $^1J_{PtP}$ value trans to the trifluoroacetate ligand to 5380 Hz. In contrast to **2**, however, **3** was not isolable and reverted back to the starting complex upon removal of BF$_3$ under vacuum (eq 3).



3 (3)

The large $^1J_{PtP}$ value for **2** indicated that (dfepe)Pt(Me)(O_2CCF_3)B(C_6F_5)$_3$ might be a potential labile source of the 14-electron moiety (dfepe)Pt(Me)$^+$. However, exposure of (dfepe)Pt(Me)[(O_2CCF_3)B(C_6F_5)$_3$] to CO or dissolution in acetone or acetonitrile resulted in regeneration of (dfepe)Pt(Me)(O_2CCF_3). These observations suggest that borane adduct formation in eq 2 is also reversible and [(C_6F_5)$_3$B(O_2CCF_3)]$^-$ is not a sufficiently innocent anion for platinum cation studies.

(dfepe)PtMe$_2$ Protonolysis Studies with (1,3,5-$C_6H_4Me_3$)$^+$B(C_6F_5)$_4^-$: Synthesis and Characterization of [{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C_6F_5)$_4^-$ (4) and [(dfepe)Pt(Me)(L)]$^+$B(C_6F_5)$_4^-$ (L = C_5F_5N (5); CO (6)). Previous research in our group has focused on the formation of (dfepe)Pt(Me)(X) and *trans*-(dfmp)$_2$Pt(Me)X products by HX protonolysis of (dfepe)PtMe$_2$ and *cis*-(dfmp)$_2$PtMe$_2$ with the strong acids CF$_3$CO$_2$H, H$_2$SO$_4$, CF$_3$SO$_3$H, and FSO$_3$H. These conjugate base derivatives, while

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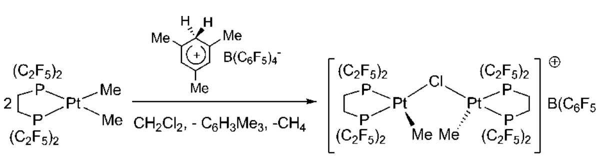
relatively labile, involve significant Pt−X covalent bonding and only form the anion displacement adducts such as [(dfepe)Pt(Me)(CO)]$^+$ and [*trans*-(dfmp)$_2$Pt(Me)(CO)]$^+$ in neat acid solutions for the stronger acids HX = CF$_3$SO$_3$H and FSO$_3$H.[4a,f] Reed and co-workers have reported stable arenium acids (areneH$^+$) with very weakly coordinating counterions such as B(C$_6$F$_5$)$_4^-$ and CB$_{11}$H$_6$Cl$_6^-$, which can serve as protonolysis reagents in organometallic chemistry,[9] although their use for this purpose has only recently been reported.[10] In particular, (1,3,5-C$_6$H$_4$Me$_3$)$^+$B(C$_6$F$_5$)$_4^-$ is a readily prepared arenium acid that is sufficiently stable for protonation studies.[9b] Addition of 1.2 equiv of (1,3,5-C$_6$H$_4$Me$_3$)$^+$B(C$_6$F$_5$)$_4^-$ to (dfepe)PtMe$_2$ in methylene chloride at ambient temperatures resulted in the precipitation of the chloride-bridged dimeric complex [{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C$_6$F$_5$)$_4^-$ (**4**) (eq 4). The reaction of Cp$_2$M(Ph)$_2$ (M = Zr, Hf) with (1,3,5-C$_6$H$_4$Me$_3$)$^+$B(C$_6$F$_5$)$_4^-$ in CH$_2$Cl$_2$ similarly forms [{(Cp$_2$M(Ph)}$_2$(μ-Cl)]$^+$B(C$_6$F$_5$)$_4^-$; this analogous reaction likely proceeds via the intermediacy of a dichloromethane solvate and has been shown to involve the formation of [(arene)CH$_2$Cl]$^+$.[10] ^{31}P NMR spectra of **4** in SO$_2$ display two resonances at δ 82.1 ($^1J_{PtP}$= 1460 Hz) and 62.6 ($^1J_{PtP}$ = 5030 Hz) corresponding to phosphorus groups trans to the methyl and bridging chloride ligands, respectively. ^{19}F spectra resonances for the B(C$_6$F$_5$)$_4^-$ counterion integrate as one B(C$_6$F$_5$)$_4^-$ unit per two dfepe ligands, consistent with a monocation dimeric formulation, which has been verified by X-ray diffraction data (see later). Although **4** may be viewed as a 14-electron (dfepe)PtMe$^+$ unit stabilized by donor base coordination with (dfepe)Pt(Me)Cl, its chemistry does not reflect this description. For instance, treatment of a solution of **4** in CD$_2$Cl$_2$ with CO does not give (dfepe)Pt(Me)Cl and (dfepe)Pt(Me)(CO)$^+$, but instead produces a complex product mixture.



(4)

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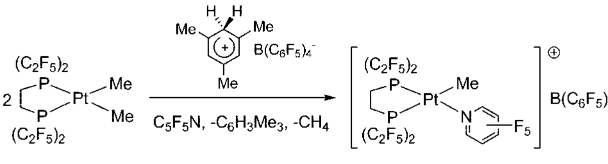
Bercaw and co-workers have reported that pentafluoropyridine is both a weakly coordinating solvent and a ligand for cationic platinum systems such as [(tmeda)Pt(Me)(NC$_5$F$_5$)]$^+$BAr$_f^-$.[11] Accordingly, we have examined pentafluoropyridine as a compatible solvent for our own platinum cation work. Treatment of (dfepe)PtMe$_2$ with (1,3,5-C$_6$H$_4$Me$_3$)$^+$B(C$_6$F$_5$)$_4^-$ in pentafluoropyridine at ambient temperature resulted in the precipitation of [(dfepe)Pt(Me)(NC$_5$F$_5$)]$^+$B(C$_6$F$_5$)$_4^-$ (**5**) in good yield (eq 5).

A promising weakly coordinating polar aprotic solvent for cationic transition metal complexes is *ortho*-difluorobenzene (ODB), which has been previously utilized as an electrochemical solvent.[12] ^{1}H, ^{31}P, and ^{19}F NMR data in ODB, along with X-ray diffraction, have confirmed the formulation of **5**. In addition to a δ 1.33 downfield shift of the methyl proton resonance relative to (dfepe)PtMe$_2$, characteristic phosphorus resonances were observed trans to the methyl group (δ 82.4 ppm, $^1J_{PtP}$ = 1490 Hz) and pentafluoropyridine (δ 60.9 ppm, $^1J_{PtP}$ = 4950 Hz). ^{19}F NMR confirmed the presence of coordinated pentafluoropyridine, whose resonances (ortho: δ −106.8; meta: δ −153.7) were shifted significantly from free pentafluoropyridine (ortho: δ −87.0; para: δ −133.5; meta: δ −161.0). The pentafluoropyridine ligand in **5** is labile: treatment of [(dfepe)Pt(Me)(NC$_5$F$_5$)]$^+$B(C$_6$F$_5$)$_4^-$ with 1 atm of CO in *o*-difluorobenzene gave the carbonyl complex [(dfepe)Pt(Me)(CO)]$^+$B(C$_6$F$_5$)$_4^-$ (**6**) (eq 6). ^{31}P NMR data for **6** show a characteristic $^1J_{PtP}$ (trans to CO) of 3710 Hz, which closely corresponds to the value for [(dfepe)Pt(Me)(CO)]$^+$(OSO$_2$F)$^-$ (3700 Hz).[4f] ν(CO) for **6** is 2174 cm^{-1}, which is also essentially identical to values found for [(dfepe)Pt(Me)(CO)]$^+$(OTf)$^-$ and [(dfepe)Pt(Me)(CO)]$^+$(OSO$_2$F)$^-$ (2176 and 2174 cm^{-1}) in their respective neat acid solutions.



(5)

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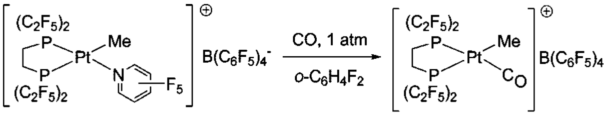

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5 6

Crystallographic Studies. All three structurally characterized compounds **2**, **4**, and **5** contain square-planar (dfepe)Pt(Me)(X) moieties (Figures 1–3). As anticipated, Pt−P bond distances trans to the methyl ligand are all substantially lengthened by the methyl ligand trans influence: 2.312 (av) Å for (**2**), 2.300 (av) Å for **4**, and 2.329(1) Å for **5**. These values are much greater than the 2.233(2) Å value found for (dfepe)Pt(Me)$_2$ and similar to the 2.301(2) Å Pt−P bond distance trans to methyl in (dfepe)Pt(Me)(OTf).[13] There is a corresponding shortening of the Pt−P bond trans to the more weakly coordinating X group relative to (dfepe)Pt(Me)$_2$: 2.158 (av) Å for **2**, 2.166 (av) Å for **4**, and 2.175(1) Å for **5**; the Pt−P bond distance trans to OTf in (dfepe)Pt(Me)(OTf) is 2.149(2) Å.

A variety of coordination complexes having the Lewis acid (C$_6$F$_5$)$_3$B ligated to oxo groups,[14] acyls,[15] or amides[16] are known. Most relevant to the (dfepe)Pt(Me)(O$_2$CCF$_3$)B(C$_6$F$_5$)$_3$ structure are (C$_6$F$_5$)$_3$B adducts with carboxylate ligands.[17] The Pt−O bond length in **2** (2.117 (av) Å) is slightly larger than Pt−O bonds

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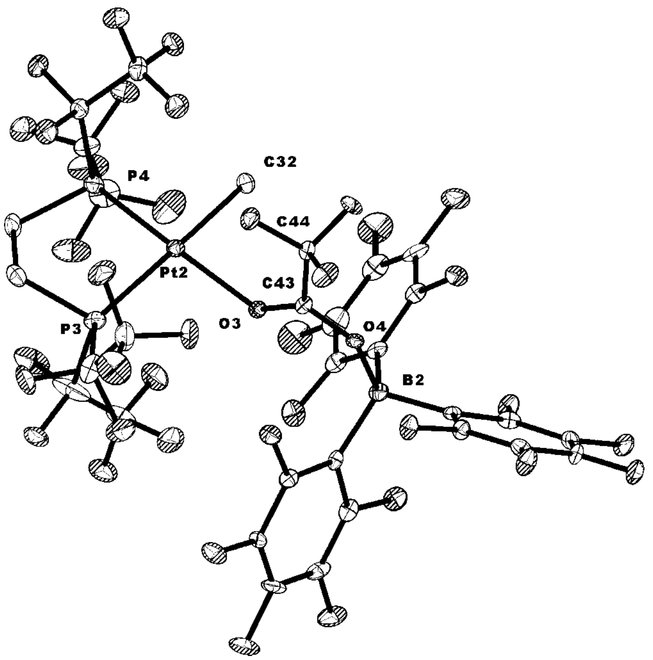

Figure 1. Molecular structure of (dfepe)Pt(Me)(O_2CCF_3)B(C_6F_5)$_3$ (**2**) (hydrogen atoms are omitted for clarity) with atom-labeling scheme (ellipsoids are drawn at 30% probability; only the Pt(2) unit with its associated atoms is shown). Selected metrical data (Å, deg): Pt(2)−P(3) 2.314(2); Pt(2)−P(4) 2.161(2); Pt(2)−O(3) 2.115(5); Pt(2)−C(32) 2.084(7); O(3)−C(43) 1.245(9); C(43)−O(4) 1.258(9); O(4)−B(2) 1.571(10); C(32)−Pt(2)−O(3) 85.4(3); P(3)−Pt(2)−P(4) 85.57(8); C(43)−O(3)−Pt(2) 133.5(5); O(3)−C(43)−O(4) 126.4(7); C(43)−O(4)−B(2) 127.6(6).

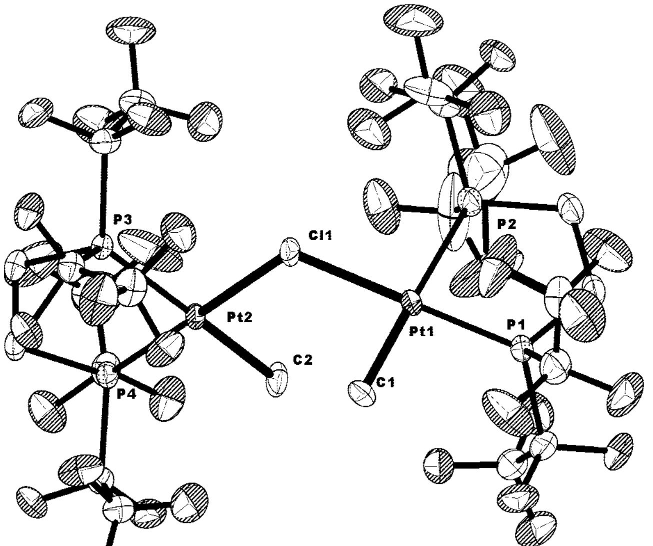

Figure 2. Molecular structure of [{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C_6F_5)$_4^-$ (**4**) (borate anion and hydrogen atoms are omitted for clarity) with atom-labeling scheme (ellipsoids are drawn at 30% probability). Selected metrical data (Å, deg): Pt(1)−P(1): 2.165(3); Pt(2)−P(4): 2.168(3); Pt(1)−P(2): 2.298(3); Pt(2)−P(3): 2.303(3); Pt(1)−Cl(1): 2.381(3); Pt(2)−Cl(1): 2.378(3); Pt(1)−C(1): 2.082(11); Pt(2)−C(2): 2.094(11); Pt(2)−Cl(1)−Pt(1): 122.32(12).

found in (dppe)Pt(O_2CCF_3)$_2$ (2.078(4), 2.096(4) Å),[18] (dfepe)Pt(Me)(OSO_2CF_3) (2.090(6) Å),[13] and [Pt(Me-Duphos)(Ph)]$_2$(μ-CO_3) (2.044(9), 2.079(8) Å)[19] and is consistent with a weakening of the metal−carboxylate ligand interaction. While the

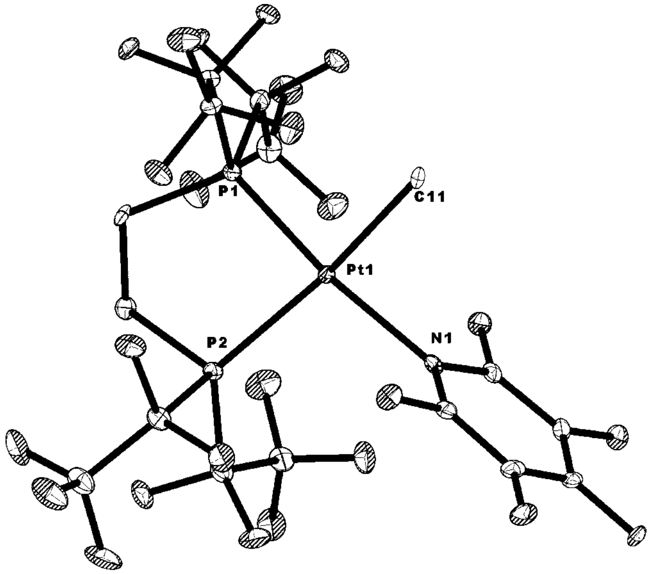

Figure 3. Molecular structure of [(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ (**5**) (borate anion and hydrogen atoms are omitted for clarity) with atom-labeling scheme (ellipsoids are drawn at 30% probability). Selected metrical data (Å, deg): Pt(1)−P(1): 2.1747(10); Pt(1)−P(2): 2.3294(11); Pt(1)−C(11): 2.080(4); Pt(1)−N(1): 2.153(4); C(11)−Pt(1)−N(1): 85.40(14).

C−OB bond length of 1.260 (av) Å and the O−COB bond length of 1.242 (av) Å for **2** fall within the range of reported values,[17] the O−B bond length is 1.58 (av) Å, which is slightly elongated (~0.04 Å) compared to other borane−carboxylate adducts.

Dimeric platinum compounds bridged by a single chlorine atom are not common.[20] The main structural details of chloro-bridged dimeric **4** are in accord with previously reported systems. Observed Pt−Cl bond distances (2.378(3) and 2.381(3) Å) are slightly shorter than values for platinum compounds with trans alkyl and aryl phosphines (range: 2.390−2.421 Å)[20a,c,e] and much longer than the 2.296(1) Å bond length reported for the diimine system {[ArN=C(Me)C(Me)=NAr]Pt(Me)}$_2$(η-Cl)$^+$.[20b] This ordering is consistent with the relative trans influence of diimines, PFAPs, and donor phosphines. The angle between the least-squares planes defined by each platinum square-planar environment (69.8°) falls within the reported range for other [(chelate)Pt(Me)]$_2$(η-Cl)$^+$ structures (65.6−73.4°); the Pt−Cl−Pt angle (122.32(12)°) is slightly greater than the 112.7−120.2° range for these compounds.

Only two other pentafluoropyridine transition metal complexes have been reported.[11,21] The Pt−N bond in [Pt(dfepe)(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ (2.153(4) Å) is significantly longer than the Pt−N bond (2.043(6) Å) of [(tmeda)Pt(Me)(NC_5F_5)]$^+$BAr$_f^-$. This 0.11 Å difference in bond lengths is comparable to the ~0.08 Å bond length increase found for Pt−Cl in **4** compared to {[ArN=C(Me)C(Me)=NAr]Pt(Me)}$_2$(η-Cl)$^+$, and as such could be largely attributed to the greater trans

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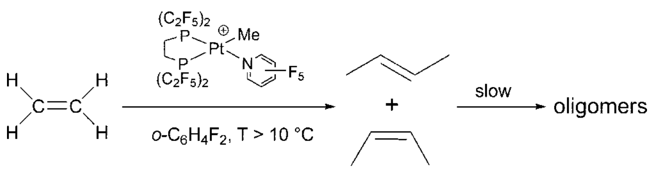
Scheme 1



influence of dfepe relative to tmeda. The twist angle of the NC_5F_5 aryl plane with respect to the Pt-centered square plane is 78°, which is comparable to that found for $[(tmeda)Pt(CH_3)(NC_5F_5)]^+[BAr_f]^-$ (88°).

Dimerization and Oligomerization of Ethylene by $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$. Ni(II) and Pd(II) systems can exhibit very high catalytic activities for ethylene dimerization, oligomerization, or polymerization.[1,22] Only limited catalytic ethylene dimerization activity has been reported for Pt(II) complexes $(dfepe)Pt(Me)(O_2CCF_3)$ (dichloromethane, 65 °C, ~1 turnover h^{-1}; CF_3CO_2H, 80 °C, 6 turnover h^{-1})[4e] and (diimine)$Pt(H)(\eta^2\text{-}C_2H_4)^+BAr_f^-$ (dichloroethane, 100 °C, ~0.1 turnovers h^{-1}).[5] In stark contrast, $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ is *orders of magnitude* more reactive than these related systems: Exposure of a solution of $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ (ca. 0.02 M) to 600 psi of ethylene at 22 °C in *o*-difluorobenzene results in the production of a thermodynamic (~2:1) trans:cis mixture of 2-butenes at an approximate initial rate of 150 turnovers h^{-1} (Scheme 1). In a subsequent slower process, 70% consumption of butenes over a period of 20 h produced an oligomeric product with aliphatic resonances between 0.6 and 2.0 ppm and vinylic resonances between 4.7 and 5.3 ppm in an integrated ratio of 69 to 1. The M_n estimated from ^1H NMR data was ~1000 (about 35 ethylene units).[23] Preliminary GPC measurements on the oily material yielded an approximate M_n value of ~1600.

The reaction between $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ and ethylene in *o*-difluorobenzene was monitored by VT NMR. Addition of 2 atm ethylene at −20 °C resulted in a clean conversion to a new platinum complex with ^{31}P NMR resonances at δ 75.7 ($^1J_{PtP} = 1360$ Hz) and 64.6 ($^1J_{PtP} = 4370$ Hz). Platinum coupling for the upfield resonance is reduced 590 Hz relative to **5**, indicative of replacement of pentafluoropyridine by ethylene to form $[(dfepe)Pt(Me)(\eta^2\text{-}C_2H_4)]^+B(C_6F_5)_4^-$ (**7**). ^1H spectra show dfepe backbone multiplet resonances at δ 1.95 and 1.72 and a platinum-coupled methyl resonance at δ 0.30 ($^2J_{PtH} = 48$ Hz) shifted slightly upfield compared to the methyl resonance in **5**. Under excess ethylene (~2 equiv), an exchanged-broadened ethylene resonance without platinum coupling was observed at 4.4 ppm. The freezing point of *o*-difluorobenzene (−34 °C) does not allow us to determine the slow exchange limit between free and bound ethylene in this solvent. However, solutions of **5** at −20 °C exposed to limiting amounts (<10 mol %) of ethylene showed partial conversion to **7** and a broadened singlet resonance at δ 4.92 with platinum satellites ($^2J_{PtH} = 56$ Hz), which is assigned to the $\eta^2\text{-}C_2H_4$ ligand.

The nature of the catalyst was monitored by ^1H and ^{31}P NMR under the catalytic conditions (*o*-difluorobenzene, 22 °C, 600 psi of ethylene (ca. 125 equiv)). After mixing and warming to ambient temperature, initial ^1H NMR spectra showed 6 equiv of butene products, as well as a downfield shift of the dfepe backbone resonances to δ 2.36 and 2.14. A vinylic resonance consistent with initial production of propene was observed. All platinum-bound alkyl resonances were obscured by a broadened butene aliphatic resonance at 0.8 ppm. ^{31}P NMR revealed a single solution species with resonances at δ 77.3 ($^1J_{PtP} = 1220$ Hz) and 66.0 ($^1J_{PtP} = 4730$ Hz), shifted significantly from those in **7** but consistent with an alkyl alkene complex, $(dfepe)Pt(alkyl)(\eta^2\text{-alkene})^+$ (**8**). After complete consumption of ethylene, resonances for **8** were replaced by broad poorly resolved peaks at 80.0 and 76.3 ppm. After 1 day, three (dfepe)Pt products with resonances at δ 81.7 ($^1J_{PtP} = 3600$ Hz), 75.8 ($^1J_{PtP} = 3940$ Hz), and 73.1 ($^1J_{PtP} = 3920$ Hz) in a 1:3:1.4 ratio were observed. The similarity of $^1J_{PtP}$ magnitudes to that for the previously reported Pt(0) ethylene complex $(dfepe)Pt(\eta^2\text{-}C_2H_4)$ (δ 81.2, $^1J_{PtP} = 3643$ Hz) suggests that these terminal species are $(dfepe)Pt(\eta^2\text{-alkene})$ products. The eventual formation of Pt(0) species from Pt(II) precursors is likely due to proton transfer from acidic $(dfepe)Pt(H)(alkene)^+$ intermediates to the more electron-rich alkene products.

Conclusions

The preparation of $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ (**5**) provides an effective labile precursor to the $(dfepe)Pt(Me)^+$ moiety, which can be studied under aprotic conditions in weakly coordinating aprotic solvents. For group 10 nickel and palladium diimine systems, the barriers to ethylene migratory insertion are 13−14 and 17−19 kcal mol^{-1}, respectively, much lower than the corresponding 29.8 kcal mol^{-1} barrier reported for platinum.[5] Details on the underlying mechanism of ethylene dimerization by **5** await further study. However, the clean formation of $[(dfepe)Pt(Me)(\eta^2\text{-}C_2H_4)]^+$ in *o*-difluorobenzene prior to the onset of dimerization activity at 10 °C is consistent with a RDS involving ethylene insertion. From the greatly enhanced observed rate of dimerization for **5** relative to $(diimine)Pt(Et)(\eta^2\text{-}C_2H_4)^+$ we can conclude either (i) the barrier to insertion in electron-poor $(dfepe)Pt(Et)(\eta^2\text{-}C_2H_4)^+$ is significantly lower or (ii) a different mechanism is operative for ethylene dimerization by this more electrophilic system. Alkene oligomerization by electrophilic metal centers may proceed by carbocationic intermediates or metal-stabilized carbenium ion intermediates.[24] Recently Vitagliano et al. have reported that ethylene complexed to dicationic (PNP)Pt(II) is activated toward external nucleophilic attack by electron-rich alkenes to form coupled products.[25] Further studies are underway to determine the operative mechanism of ethylene dimerization and subsequent oligomerization of the butene products by $[(dfepe)Pt(Me)(NC_5F_5)]^+$ and to more broadly explore the reactivity of this and related systems.

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. Deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Desert Analytics. NMR spectra were obtained with a Bruker DRX-400 instrument. IR spectra were taken with a Bomem MB100 instrument as Nujol mulls using KCl plates. ^{31}P

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Table 1. Crystallographic Data for (dfepe)Pt(Me)(O_2CCF_3)B(C_6F_5)$_3$ (2), [{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C_6F_5)$_4^-$ (4), and [(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ (5)

	(dfepe)Pt(Me)(O_2CCF_3)B(C_6F_5)$_3$	[{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C_6F_5)$_4^-$	[(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$
chemical formula	$C_{31}H_7BF_{38}O_2P_2Pt$	$C_{46}H_{14}BClF_{60}P_4Pt_2$	$C_{40}H_7F_{45}P_2Pt$
fw	1401.20	2266.89	1624.31
T, K	100(2)	298(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
space group	$P2_1/c$	$P\bar{1}$	Cc
a, Å	37.2880(7)	13.3406(14)	30.6236(6)
b, Å	11.7590(2)	15.748(2)	10.3226(2)
c, Å	37.4162(7)	17.943(2)	17.6987(4)
α, deg	90	67.388(8)	90
β, deg	91.4960(10)	75.126(9)	122.8130(10)
γ, deg	90	75.726(10)	90
V, Å^3	16400.3(5)	3316.6(7)	4702.13(17)
Z	8	2	4
D_{calc}, Mg m^{-3}	2.270	2.270	2.294
μ, mm^{-1}	3.708	4.556	3.269
$R_1[I > 2\sigma(I)]^a$	0.0407	0.0560	0.0269
$wR_2[I > 2\sigma(I)]^b$	0.0790	0.1448	0.0529

^{a} $R_1 = \sum||F_o - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]\sum w(F_o^2)^2]\}^{1/2}$.

spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F spectra were referenced to CF_3CO_2Et as an external standard (−75.32 ppm vs $CFCl_3$ with downfield chemical shifts taken to be positive). GPC measurements were taken on a Waters SEC equipped with two 300 mm Waters Styrogel columns (molecular weight ranges: 5×10^2 to 3×10^4, 5×10^3 to 6×10^5) and a Waters 2414 refractive index detector. (cod)$PtCl_2$,[25] (dfepe)Pt(Me)$_2$,[26] dfepe, and ($C_6Me_3H_4$)$^+$B(C_6F_5)$_4^-$ were prepared according to literature methods.[9b]

[(dfepe)Pt(Me)(CH_3CN)]$^+$SbF_6^- (1). To a flask charged with (cod)Pt(Me)(Cl) (0.75 g, 2.1 mmol) and $AgSbF_6$ (0.73 g, 2.12 mmol) was added 15 mL of CH_3CN. After 1 h of stirring at ambient temperature the resulting precipitate was filtered off and washed several times with acetonitrile. dfepe (1.44 g, 2.54 mmol) was added to the filtrate, and after stirring the reaction mixture for 1 h, the volatiles were removed and the residue was slurried in 10 mL of methylene chloride. Filtration and washing of the white solid with methylene chloride following by drying under vacuum yielded 1.732 g (80%) of **1**. Anal. Calcd: C, 14.82; H, 0.95; N, 1.33. Found: C, 14.88; H, 0.77; N, 1.30. ^{1}H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 3.60 (m, 2H; PCH_2), 3.30 (m, 2H; PCH_2) 2.93 (s, 3H, CH_3CN), 1.43 (d, $^2J_{PtH}$ = 51 Hz, $^3J_{PH}$ = 7 Hz, 3H, PtCH_3). ^{31}P NMR (161.70 MHz, acetone-d_6, 20 °C): δ 81.9 (P trans to CH_3, m, $^1J_{PtP}$ = 1400 Hz), 64.8 (P trans to CH_3CN, m, $^1J_{PtP}$ = 4680 Hz). ^{19}F NMR (376.5 MHz, acetone-d_6, 20 °C): δ −78.3 (s, 6F; PCF$_2$CF_3), −79.1 (s, 6F; PCF$_2$CF_3), −106 to −110 (overlapping ABX multiplets, 8F; PCF_2CF$_3$).

(dfepe)Pt(Me)(O_2CCF_3)B(C_6F_5)$_3$ (2). To a flask charged with (dfepe)Pt(Me)(O_2CCF_3) (0.19 g, 2.2×10^{-4} mol) and B(C_6F_5)$_3$ (0.135 g, 2.64×10^{-4} mol) was added 15 mL of methylene chloride. After 3 h of stirring the resulting white solid **2** was collected by filtration, washed, and dried under vacuum to yield 0.33 g of borane adduct (82%). Crystals suitable for diffraction analysis were grown by slowly cooling a warm, saturated dichloromethane solution. Anal. Calcd for $C_{31}H_7F_{38}BO_2P_2Pt$: C, 26.57; H, 0.50. Found: C, 26.20; H, 0.33. IR (cm^{-1}): 1653(s), 1226(br, s), 1156(m), 984(s). ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 2.82 (m, 2H; PCH_2), 2.52 (m, 2H; PCH_2), 0.78 (d, $^2J_{PtH}$ = 40.17 Hz, $^3J_{PH}$ = 7.07 Hz, 3H, PtCH_3). ^{31}P NMR (161.70 MHz, CD_2Cl_2, 20 °C): δ 81.9 (P trans to CH_3, m, $^1J_{PtP}$ = 1530 Hz), 62.1 (P trans to (O_2CCF_3)B(C_6F_5)$_3$, m, $^1J_{PtP}$ = 5220 Hz). ^{19}F NMR (376.5 MHz, CD_2Cl_2, 20 °C): δ −78.0 (s, 6F; PCF$_2$CF_3), −79.0 (s, 6F; PCF$_2$CF_3), −106 to −110 (overlapping ABX multiplets, 8F; PCF_2CF$_3$), −134.4 (br s, 8F; *o*-ArF), −160.7 (br s, 4F; *p*-ArF), −163.5 (br s, 8F; *m*-ArF).

(dfepe)Pt(Me)(O_2CCF_3)(BF_3) (3). A 20 mg amount of (dfepe)Pt(Me)(O_2CCF_3) and 5 mL of CD_2Cl_2 were placed in a Teflon valve NMR tube that was pressurized with ca. 2 atm of BF_3. NMR data for the resulting solution were consistent with the formation of (dfepe)Pt(Me)(O_2CCF_3)(BF_3). ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 2.85 (m, 2H; PCH_2), 2.54 (m, 2H; PCH_2), 0.33 (t, 3H, PtCH_3). ^{31}P NMR (161.70 MHz, CD_2Cl_2, 20 °C): δ 81.8 (P trans to CH_3, m, $^1J_{Pt-P}$ = 1530 Hz), 56.2 (P trans to O_2CCF_3(BF_3), m, $^1J_{Pt-P}$ = 5380 Hz). ^{19}F NMR (376.5 MHz, CD_2Cl_2, 20 °C): δ −77.8 (s, 3F; O_2CCF_3), −78.7 (s, 6F; PCF$_2$CF_3), −78.9 (s, 6F; PCF$_2$CF_3), −107 to −110 (overlapping ABX multiplets), −139.0 (s, 3F; BF_3).

[{(dfepe)Pt(Me)}$_2$(μ-Cl)]$^+$B(C_6F_5)$_4^-$ (4). To a flask charged with 0.263 g of (dfepe)Pt(Me)$_2$ (3.32×10^{-4} mol) and 0.32 g of ($C_6Me_3H_4$)$^+$B(C_6F_5)$_4^-$ (4.0×10^{-4} mol) was added 15 mL of CH_2Cl_2. After 2 h of stirring, the resulting white solid was collected by filtration, washed, and dried under vacuum to yield 0.31 g (23.4%) of **4**. Crystals suitable for diffraction analysis were grown by slow diffusion of *m*-difluorobenzene into a solution of {[Pt(dfepe)Me]$_2$(μ-Cl)}$^+$[B(C_6F_5)$_4$]$^-$ in *o*-difluorobenzene. Anal. Calcd for $C_{46}H_{14}F_{60}BClP_4Pt_2$: C, 24.40; H, 0.62. Found: C, 23.54; H, 0.68. ^{1}H NMR (SO_2, 400.13 MHz, 20 °C): δ 3.31 (m, 2H; PCH_2), 3.02 (m, 2H; PCH_2), 1.66 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 45 Hz, 3H, PtCH_3). ^{31}P NMR (161.70 MHz, SO_2, 20 °C): δ 82.1 (P trans to CH_3, m, $^1J_{PtP}$ = 1460 Hz), 62.6 (P trans to μ-Cl, m, $^1J_{PtP}$ = 5030 Hz). ^{19}F NMR (376.5 MHz, SO_2, 20 °C): δ −79.1 (s, 6F; PCF$_2$CF_3), −79.6 (s, 6F; PCF$_2$CF_3), −107 to −111 (overlapping ABX multiplets), −132.0 (br s, 8F; *o*-ArF), −162.9 (t, $^3J_{FF}$ = 20 Hz, 4F; *p*-ArF), −166.5 (t, $^3J_{FF}$ = 20 Hz, 4F; *m*-ArF).

[(dfepe)Pt(Me)(NC_5F_5)]$^+$B(C_6F_5)$_4^-$ (5). To a flask charged with (dfepe)Pt(Me)$_2$ (0.25 g, 3.2×10^{-4} mol) and ($C_6Me_3H_4$)$^+$B(C_6F_5)$_4^-$ (0.33 g, 4.1×10^{-4} mol) was added 25 mL of pentafluoropyridine. After 2 h of stirring the resulting white solid **5** (0.45 g, 88%) was collected by filtration, washed, and dried under vacuum. Crystals suitable for diffraction analysis were grown by slow diffusion of *m*-difluorobenzene into a solution of [(dfepe)Pt(Me)(NC_5F_5)]$^{+-}$B(C_6F_5)$_4^-$ in *o*-difluorobenzene. Anal. Calcd for $C_{40}H_7F_{45}BNP_2Pt$: C, 29.57; H, 0.43. Found: C, 29.56; H, 0.71. ^{1}H NMR (400.13 MHz, *o*-difluorobenzene, 20 °C): δ 2.01 (m, 2H; PCH_2), 1.71 (m, 2H; PCH_2), 0.17 (br s, $^2J_{PtH}$ = 43 Hz, 3H, PtCH_3). ^{31}P NMR (161.70 MHz, *o*-difluorobenzene, 20 °C): δ 82.4 (P trans to CH_3, m, $^1J_{PtP}$ = 1490 Hz), 60.9 (P trans to NC_5F_5, m, $^1J_{PtP}$ = 4950 Hz). ^{19}F NMR (376.5 MHz, *o*-difluorobenzene, 20 °C): δ −77.9 (s, 6F; PCF$_2$CF_3), −78.4 (s, 6F; PCF$_2$CF_3), −105 to −109 (overlapping ABX multiplets, 8F; PCF_2CF$_3$), −115.2 (p, J = 20 Hz, 1F; *p*-C_5F_5N), −130.8 (br s, 8F; *o*-B(C_6F_5)$_4$), −153.7 (br s, 2F; *meta*-

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C_5F_5N; *ortho*-C_5F_5N obscured by solvent resonance at −139 ppm), −162.0 (t, $^3J_{FF}$ = 20 Hz, 4F; *p*-$B(C_6F_5)_4$), −165.9 (m, 8F; *m*-$B(C_6F_5)_4$).

$[(\mathrm{dfepe})\mathrm{Pt(Me)(CO)}]^+\mathrm{B(C_6F_5)_4}^-$ (6). To a flask charged with $[(\mathrm{dfepe})\mathrm{Pt(Me)}(\mathrm{NC_5F_5})]^+\mathrm{B(C_6F_5)_4}^-$ (**5**) (0.11 g, 6.8×10^{-5} mol) was added 10 mL of *o*-difluorobenzene. After 2 h of stirring at room temperature under 1 atm of CO, the solution was concentrated and precipitated with methylene chloride to give a white solid, which was isolated by filtration and dried under vacuum (0.51 g, 50%). Anal. Calcd for $C_{36}H_7F_{40}BOP_2Pt$: C, 29.15; H, 0.48. Found: C, 28.81; H, 0.76. IR (*o*-difluorobenzene): 2174 cm^{-1}. ^{1}H NMR (*o*-difluorobenzene, 400.13 MHz, 20 °C): δ 2.16 (m, 2H; PCH_2), 2.03 (m, 2H; PCH_2), 0.66 (t, $^2J_{PtH}$ = 59.3 Hz, $^3J_{PH}$ = 10.7 Hz, 3H, $PtCH_3$). ^{31}P NMR (161.70 MHz, *o*-difluorobenzene, 20 °C): δ 84.7 (P trans to CH_3, m, $^1J_{PtP}$ = 1350 Hz), 70.9 (P trans to CO, m, $^1J_{PtP}$ = 3710 Hz).

Preparation of $[(\mathrm{dfepe})\mathrm{Pt(Me)}(\eta^2\text{-}\mathrm{C_2H_4})]^+\mathrm{B(C_6F_5)_4}^-$ (7). In a typical experiment, a 5 mm NMR tube fitted with a Teflon valve (Chemglass CG-512 or New Era NE-CAV-VBP) was charged with ca. 20 mg of **5** and 0.5 mL of *o*-difluorobenzene and cooled to −80 °C. Approximately 2 atm of ethylene was added via syringe, and the solution was warmed to −20 °C with stirring. Low-temperature NMR data confirmed the clean formation of $[(\mathrm{dfepe})\mathrm{Pt(Me)}(\eta^2\text{-}\mathrm{C_2H_4})]^+\mathrm{B(C_6F_5)_4}^-$. ^{1}H NMR (400.13 MHz, *o*-difluorobenzene, −20 °C): δ 1.95 (m, 2H; PCH_2), 1.72 (m, 2H; PCH_2), 0.30 (br. s, $^2J_{PtH}$ = 48 Hz, 3H, $PtCH_3$). ^{31}P NMR (161.70 MHz, *o*-difluorobenzene, -20 °C): δ 75.7 (P trans to CH_3, m, $^1J_{PtP}$ = 1360 Hz), 64.6 (P trans to ethylene, m, $^1J_{PtP}$ = 4370 Hz).

X-ray Crystallographic Studies. X-ray diffraction data were collected for $(\mathrm{dfepe})\mathrm{Pt(Me)}[(\mathrm{O_2CCF_3})\mathrm{B(C_6F_5)_3}]$ (**2**) on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator) at 173 K. Standard Bruker control (SMART, 1997) and integration (SAINT, 1997) software were employed, and Bruker SHELXTL software (Sheldrick, 1997) was used for structure solution, refinement, and graphics.[27] The unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. Intensities were integrated from a series of frames (0.3° ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied using SADABS (Sheldrick, 1996).[28] Compound **2** crystallizes in the monoclinic space group *C2/c*. The asymmetric unit contains two well-separated independent molecules. One molecule (Pt(1) and its associated atoms) exhibits some disorder in the difluoromethylene carbon atoms (C8 and C10), as reflected in their high thermal parameters. The remainder of this molecule and the second molecular unit are well-ordered. All non-hydrogen atoms were located in the Fourier maps and refined anisotropically. The H atoms were placed in calculated positions and were refined isotropically by a riding model.

X-ray diffraction data were collected for $[\{(\mathrm{dfepe})\mathrm{Pt(Me)}\}_2(\mu\text{-}\mathrm{Cl})]^+\mathrm{B(C_6F_5)_4}^-$ (**4**) on a Bruker P4 diffractometer equipped with a molybdenum tube and a graphite monochromator at 298 K. A colorless crystal of approximate dimensions 0.64 mm × 0.48 mm × 0.20 mm in a sealed glass capillary was used for data collection. A total of 11 469 (R_{int} = 0.0590) reflections were gathered in the 2θ range of 3.68° to 50.00° with the data collected having $-1 \le h \le 15$, $-17 \le k \le 17$, $-20 \le l \le 21$ using the XSCANS program.[29] Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity. The structure was solved by direct methods and refined by least-squares techniques adapting the full-matrix weighted least-squares scheme, $w^{-1} = \sigma^2 F_o^2 + (0.0851P)^2 + 20.4914P$, where $P = (F_o^2 + 2F_c^2)/3$, on F^2 using the SHELXTL program suite.[27,30] The asymmetric unit consists of discrete well-separated $[\{(\mathrm{dfepe})\mathrm{Pt(Me)}\}_2(\mu\text{-}\mathrm{Cl})]^+$ and $\mathrm{B(C_6F_5)_4}^-$ ions located on general positions. All non-hydrogen atoms were located in the difference maps during successive cycles of least-squares and refined anisotropically. The (C11−C12) perfluoroethyl group is partially disordered with no satisfactory model; therefore, the two carbon atoms and their associated fluorine atoms were assigned fixed positional and thermal parameters. All hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The final refinement parameters were $R_1 = 0.0560$ and $wR_2 = 0.1448$ for data with $F > 4\sigma(F)$ and $R_1 = 0.0767$ and $wR_2 = 0.1591$ for all data with the data to parameter ratio of 12.

X-ray diffraction data were collected for $[(\mathrm{dfepe})\mathrm{Pt(Me)}(\mathrm{NC_5F_5})]^+\text{-}\mathrm{B(C_6F_5)_4}^-$ (**5**) on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator) at 100 K. Standard Bruker control and integration software were employed, and Bruker SHELXTL software was used for structure solution, refinement, and graphics. The unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. Intensities were integrated from a series of frames (0.3° ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied using TWINABS.[31] **5** crystallizes in the monoclinic space group *Cc*. The asymmetric unit consists of well-separated and well-ordered $[(\mathrm{dfepe})\mathrm{Pt(Me)}(\mathrm{NC_5F_5})]^+$ and $\mathrm{B(C_6F_5)_4}^-$ ions. All non-hydrogen atoms were located in the Fourier maps and refined anisotropically. The H atoms were placed in calculated postions and refined isotropically using a riding model. The final refinement parameters were $R_1 = 0.0269$ and $wR_2 = 0.0529$ for data with $F > 4\sigma(F)$ and $R_1 = 0.0312$ and $wR_2 = 0.0552$ for all data with the data to parameter ratio of 13. The absolute configuration of the formula unit was verified satisfactorily by refining the Flack parameter close to zero (−0.003(3)).[32] Crystallographic data collection parameters and refinement data for compounds **2**, **4**, and **5** are summarized in Table 1.

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Supporting Information Available: Complete tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs. acs.org.

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