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Synthesis and Reactivity of $[(C_2F_5)_2MeP]_2Pt(Me)X$ (X = Me, O_2CCF_3, OTf, OSO_2F): A Reactivity Comparison with Chelate Acceptor Analogues

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A comparative study of new platinum methyl complexes *cis*-$(dfmp)_2Pt(Me)_2$ and *trans*-$(dfmp)_2Pt(Me)X$ (dfmp = $(C_2F_5)_2MeP$; X = O_2CCF_3, OTf, OSO_2F) with previously reported acceptor chelate analogues (dfepe)Pt(Me)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; X = Me, O_2CCF_3, OTf, OSO_2F) is presented. In contrast to $(dfepe)Pt(Me)_2$, which is inert to both H_2 and CO addition, *cis*-$(dfmp)_2Pt(Me)_2$ reacts readily to form $(dfmp)_4Pt$ and *cis*-(dfmp)(CO)-$Pt(Me)_2$, respectively. Similarly, whereas $(dfepe)Pt(Me)_2$ is stable up to 180 °C, thermolysis of *cis*-$(dfmp)_2Pt(Me)_2$ in benzene-d_6 at 80 °C leads to ethane reductive elimination and production of $(dfmp)_4Pt$. Dissolving *cis*-$(dfmp)_2Pt(Me)_2$ in neat trifluoroacetic, triflic, or fluorosulfonic acid at ambient temperature cleanly produces the corresponding *trans*-$(dfmp)_2Pt(Me)(X)$ complexes. Attempted isolation of *trans*-$(dfmp)_2Pt(Me)(O_2CCF_3)$ resulted in dfmp loss and reversible formation of the crystallographically characterized dimer, $[(dfmp)Pt(Me)(\mu\text{-}O_2CCF_3)]_2$. Monitoring the thermolysis of *trans*-$(dfmp)_2Pt(Me)(X)$ complexes by ^{31}P NMR in their respective neat acids reveals a kinetic protolytic stability that is dependent on the nature of the trans X ligand: whereas *trans*-$(dfmp)_2Pt(Me)(O_2CCF_3)$ is less stable than the corresponding $(dfepe)Pt(Me)(O_2CCF_3)$ complex, *trans*-$(dfmp)_2Pt(Me)$-(OTf) and *trans*-$(dfmp)_2Pt(Me)(OSO_2F)$ are significantly more resistant to protolytic cleavage than the chelating analogues. Thermolysis in CF_3CO_2D or DOTf resulted in deuteration of the methyl ligand prior to methane loss, indicating the reversible formation of a methane adduct intermediate.

Introduction

Electrophilic group 10 transition metal complexes have received increased attention over the past decade due to their widespread utility as coupling[1] and polymerization[2] catalysts and as models for electrophilic hydrocarbon activation systems ("Shilov chemistry").[3] A common structural motif in this work has been alkyl complexes $L_2M(R)X$ or $L_2M(R)(solv)^+X^-$, where L is a neutral donor ligand such as a phosphine, amine, or imide, R = alkyl, and X^- is a weakly coordinating anion. We have reported a series of studies involving the chelating acceptor phosphine system (dfepe)Pt(R)X (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$).[4] While such a system in principle can afford an exceptionally electrophilic $(dfepe)Pt(Me)^+$ moiety, in practice we find that an unusually tight binding of anionic X^- ligands limits the observed chemistry. For example, in contrast to analogous donor phosphine compounds (dmpe)Pt(Me)X, which undergo arene C−H bond activation in benzene at 125 °C (and presumably involve the initial dissociation of X^-), no corresponding reaction is observed with (dfepe)-$Pt(Me)O_2CCF_3$ up to 180 °C.[5]

We have recently begun to explore the coordination properties of monodentate fluoroalkylphosphines, $(C_2F_5)_2$-P(R), which afford enhanced ligand labilities, a wider range of steric and electronic tuning, and the additional possibility of trans π-acceptor coordination.[6] A trans acceptor ligand configuration for platinum alkyl complexes $(L)_2Pt(R)(X)$ is of particular interest since this would place the dissociating anionic group trans to a strongly trans-directing alkyl ligand. Moreover, if perfluoroalkylphosphine acceptor ligands indeed have a

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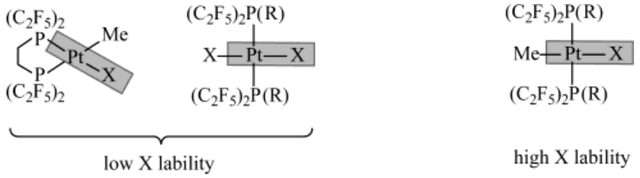
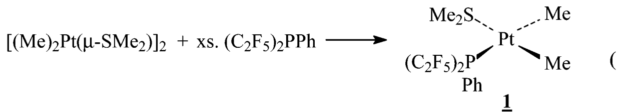
weak trans-influence, the mutually trans acceptor configuration would result in additional complex stability toward phosphine dissociation. In this paper, we report the synthesis of $Me(C_2F_5)_2P$ ("dfmp") derivatives *cis*-$(dfmp)_2Pt(Me)_2$ and *trans*-$(dfmp)_2Pt(Me)(X)$ (X = O_2CCF_3, OTf, OSO_2F) and compare their reactivity properties to the chelate analogues $(dfepe)Pt(Me)_2$ and (dfepe)Pt(Me)(X).



Results and Discussion

Synthesis and Characterization of *cis*-$(dfmp)_2$-$PtMe_2$ (2). The chelate-substituted dimethyl complex $(dfepe)Pt(Me)_2$ has been prepared by alkylation of $(dfepe)PtCl_2$, which is prepared in turn by either ligand exchange of $(cod)PtCl_2$ with dfepe or the direct reaction of dfepe with K_2PtCl_4.[4g,7] Alternatively, $(dfepe)PtMe_2$ is most conveniently obtained by the reaction of $(cod)PtMe_2$ with dfepe. Our initial efforts to prepare nonchelated acceptor phosphine complexes of platinum focused on the phenyl-substituted phosphine $(C_2F_5)_2P(Ph)$. No reaction between excess $(C_2F_5)_2P(Ph)$ and either $(cod)PtCl_2$, $(nbd)PtCl_2$, or $(nbd)PtMe_2$ was observed in refluxing toluene. Treatment of $[(Me)_2Pt(\mu\text{-}SMe_2)]_2$ with 2 equiv of $(C_2F_5)_2P(Ph)$ afforded only the partial substitution product *cis*-$[(C_2F_5)_2PPh](Me_2S)PtMe_2$ (**1**), even after further heating to 80 °C (eq 1).



(1)

1

In light of these observations, we turned our attention to the smaller and (presumably) better donor phosphine, $(C_2F_5)_2P(Me)$ (dfmp). NMR indicated that partial displacement of cyclooctadiene from $(cod)PtMe_2$ in the presence of excess dfmp occurred at ambient temperatures: using 4.2 equiv of dfmp, a 1:0.37 equilibrium ratio of $(dfmp)_2PtMe_2$ to $(cod)PtMe_2$ was observed in benzene after 2.5 h. To surmount this problem, the precursor $(nbd)PtMe_2$ was examined, since norbornadiene is generally considered to be more labile.[8] Reaction of $(nbd)PtMe_2$ with 2 equiv of dfmp in petroleum ether followed by removal of all volatiles cleanly afforded *cis*-$(dfmp)_2PtMe_2$ (**2**) as a low-melting white solid (eq 2). The cis stereochemistry for **2** is clearly indicated by the small observed $^1J_{PtP}$ (1500 Hz), which is diagnostic for a phosphine ligand trans to an alkyl group. In the ^1H NMR spectrum the phosphorus-coupled methyl resonance appears as an apparent triplet ($^3J_{PH}$ = 8.7 Hz) due to virtual coupling.

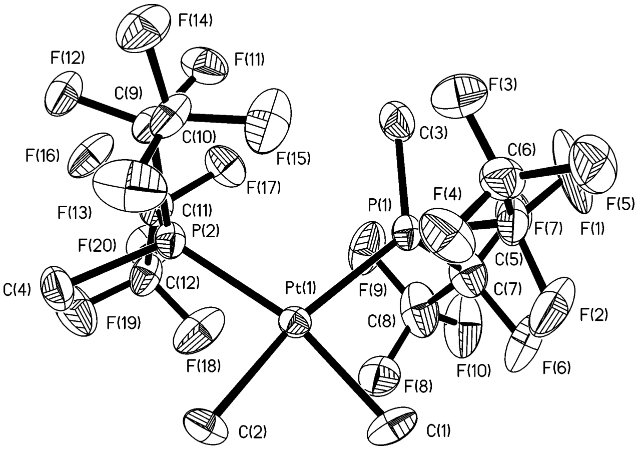
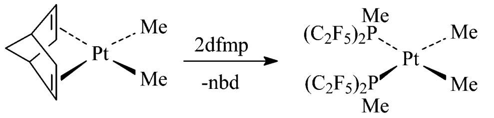


Figure 1. Molecular structure of *cis*-$(dfmp)_2Pt(Me)_2$ (**2**) with atom-labeling scheme (30% probability ellipsoids).



(2)

2

The crystal structure of **2** (Figure 1) was determined in order to provide comparisons with the previously reported X-ray structure of $(dfepe)PtMe_2$[4g] as well as donor phosphine dimethyl analogues.[9,10] A summary of data collection parameters and a listing of selected metrical parameters are presented in Tables 1 and 2, respectively. The observed Pt−C(methyl) average bond length of 2.101(9) Å for **2** falls within the range observed for donor phosphine analogues (2.085−2.129 Å) and is somewhat longer than the Pt−C(methyl) bond length reported for the perfluoroethyl-substituted chelate $(dfepe)Pt(Me)_2$ (2.074(5) Å). The Pt−P bond lengths (2.261(2) and 2.270(2) Å) for the dfmp ligand are substantially shorter than values reported for monodentate alkyl- and aryl-substituted phosphines (2.284−2.337 Å) trans to methyl, comparable to the acceptor *N*-pyrrolylphosphine platinum dimethyl derivative, *cis*-$[(pyrl)_3P]_2PtMe_2$ (2.250(1) Å), and longer than that of $(dfepe)PtMe_2$ (2.233(2) Å). The shortening of metal−phosphorus bond lengths in acceptor phosphine complexes has been ascribed to rehybridization of the phosphorus lone pair.[11]

The disposition and orientation of the phosphine and methyl groups with respect to the square planar coordination geometry about platinum in *cis*-$(dfmp)_2PtMe_2$ is of interest. Reported P−Pt−P angles for *cis*-$(R_3P)_2PtMe_2$ complexes correlate with phosphine steric influence, ranging from 95.0° for Me_2PhP ($\theta = 122°$) to 108.6° for Cy_3P ($\theta = 170°$). The steric influence of C_2F_5 phosphine substituents is comparable to Ph (half-angle, $\theta_i/2$, = 75.5°),[11] with an estimated cone angle for dfmp of 140°. However, the P−Pt−P angle found for **2**, 105.20(8)°, is the second largest observed and is much larger than that reported for *cis*-$(Ph_2PMe)_2PtMe_2$ (97.7°). Despite this difference, the C(methyl)−Pt−C(methyl) angles for these two complexes are essentially equivalent (81.3° for **2** versus 81.9°). This difference in the interphosphorus angle may to be due to differences in

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Table 1. Crystallographic Data for *cis*-(dfmp)$_2$Pt(Me)$_2$ (2) and [(dfmp)Pt(Me)(μ-O$_2$CCF$_3$)]$_2$ (8)

	complex **2**	complex **8**
chemical formula	$C_{12}H_{12}F_{20}P_2Pt$	$C_{16}H_{12}F_{26}O_4P_2Pt_2$
fw	793.25	1214.38
space group	$P2_1/c$	$P2_1/c$
a (Å)	15.265(2)	9.448(3)
b (Å)	12.0422(16)	20.171(4)
c (Å)	12.975(2)	16.265(3)
β (deg)	113.998(10)	98.05(2)
V (Å^3)	2178.9(6)	3069.1(12)
Z	4	4
λ (Å)	0.71073	0.7103
T (°C)	−100	−100
ρ_{calc} (g cm^{-3})	2.418	2.628
R_1 ($I > 2\sigma(I)$)[a]	0.0387	0.0589
R_1 (all data)	0.0456	0.0909

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-(dfmp)$_2$Pt(Me)$_2$ (2) and [(dfmp)Pt(Me)(μ-O$_2$CCF$_3$)]$_2$ (8)

	complex **2**	complex **8**
Pt(1)−P(1)	2.270(2)	2.134(5)
Pt(1)−P(2)	2.261(2)	
Pt(2)−P(2)		2.142(5)
Pt(1)−C(1)	2.102(9)	2.029(17)
Pt(1)−C(2)	2.100(9)	
Pt(2)−C(2)		2.023(16)
Pt(1)−O(1)		2.154(11)
Pt(1)−O(3)		2.070(11)
Pt(2)−O(2)		2.055(11)
Pt(2)−O(4)		2.144(11)
O(1)−C(3)		1.246(19)
O(3)−C(5)		1.25(2)
O(2)−C(3)		1.26(2)
O(4)−C(5)		1.261(19)
C(2)−Pt(1)−C(1)	81.3(4)	
C(2)−Pt(1)−P(1)	168.9(3)	
C(2)−Pt(1)−P(2)	85.7(3)	
C(1)−Pt(1)−P(1)	87.9(4)	
C(1)−Pt(1)−P(2)	166.3(4)	
P(1)−Pt(1)−P(2)	105.20(8)	
P(1)−Pt(1)−C(1)		92.9(6)
P(1)−Pt(1)−O(1)		93.7(3)
P(1)−Pt(1)−O(3)		175.5(4)
C(1)−Pt(1)−O(1)		169.5(6)
C(1)−Pt(1)−O(3)		86.7(7)
O(1)−Pt(1)−O(3)		86.0(4)
P(2)−Pt(2)−C(2)		90.2(5)
P(2)−Pt(2)−O(2)		167.9(3)
P(2)−Pt(2)−O(4)		93.8(3)
C(2)−Pt(2)−O(2)		87.7(6)
C(2)−Pt(2)−O(4)		174.1(6)
O(2)−Pt(2)−O(4)		87.5(4)

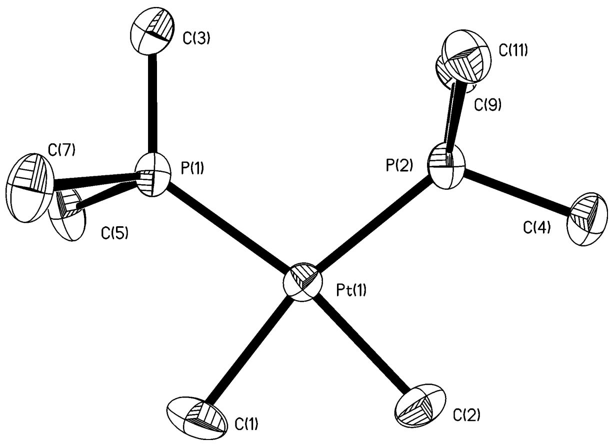

Figure 2. Molecular structure of **2** with fluorines omitted, showing the coplanar disposition of the dfmp methyl substituents C(3) and C(4) relative to the platinum square plane.

preferred Pt−PR$_3$ rotational conformations. In both (Ph$_2$PMe)$_2$PtMe$_2$ and (dfmp)$_2$PtMe$_2$ the phosphorus ligands are rotated with respect to each other such that each phosphine places a substituent essentially eclipsed with the P−Pt−P plane, with one eclipsed group directed centrally between the phosphine groups and the other directed laterally, away from the other PR$_3$ ligand (Figure 2). This "central-lateral" eclipsed bis-phosphine conformation is also adopted by the symmetrical phosphine complexes *cis*-(R$_3$P)$_2$PtMe$_2$ where R$_3$P = Et$_3$P and (pyrrolyl)$_3$P, but not by the bulky Cy$_3$P derivative. For the Ph$_2$MeP complex, the larger phenyl substituents adopt these in-plane positions to minimize steric interactions. However, in the case of the (C$_2$F$_5$)$_2$MeP derivative it is actually the *smaller* methyl groups, C(3) and C(4), that are in the P$_2$PtMe$_2$ plane. This orientational preference most likely reflects a preferred geometry for optimal π-acceptance by the dfmp ligand, resulting in increased phosphine steric interactions and a concomitant increase in the P−M−P angle.

Thermal Stability of *cis*-(dfmp)$_2$Pt(Me)$_2$. The reductive elimination of ethane from palladium dimethyl complexes is relatively facile.[12,13] However, to our knowledge the corresponding elimination of ethane from a platinum(II) dimethyl complex has not been reported. In a previous study we showed that reductive elimination of biphenyl from perfluorinated phosphine complexes was greatly enhanced relative to donor phosphine chelates: clean elimination at 80 °C was observed for [(C$_6$F$_5$)$_2$PCH$_2$CH$_2$P(C$_6$F$_5$)$_2$]Pt(Ph)$_2$, whereas (dfepe)Pt(Ph)$_2$ eliminated biphenyl at subambient temperatures.[7] Despite this increased activity toward reductive elimination, (dfepe)Pt(Me)$_2$ did not undergo elimination of ethane up to 180 °C.

Since reductive elimination in nonchelating palladium systems has been shown to proceed via phosphine ligand loss, we have investigated the propensity of *cis*-(dfmp)$_2$Pt(Me)$_2$ toward reductive elimination. A solution of **2** in C$_6$D$_6$ was monitored by NMR. After 20 h at 80 °C, the phosphorus resonance for **2** was completely replaced by a new resonance at 60.0 ppm ($^1J_{PtP}$ = 4845 Hz). ^{1}H spectra showed a new ligand methyl doublet at 2.01 ppm ($^2J_{PH}$ = 34 Hz) and the presence of free ethane at 0.81 ppm. The new complex was subsequently identified as the Pt(0) elimination product, (dfmp)$_4$Pt (see below). A separate experiment showed that no significant reductive elimination of ethane occurred after warming *cis*-(dfmp)$_2$Pt(Me)$_2$ to 80 °C in benzene for 48 h in the presence of 2 equiv of free dfmp. This inhibition by added phosphine is consistent with a mechanism where rate-determining reductive elimination of ethane is preceded by phosphine loss to form a three-coordinate intermediate (Scheme 1). As we have previously observed for (dfepe)Pt(Ar)$_2$ eliminations,[7] the additional necessary equivalents of dfmp ligand are efficiently

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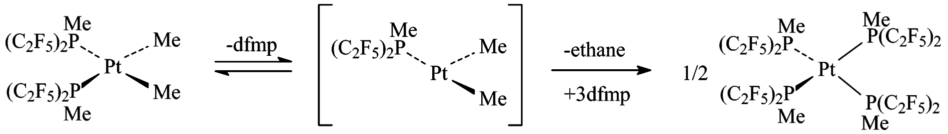
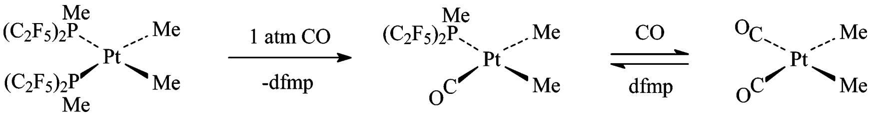
Scheme 1



Scheme 2



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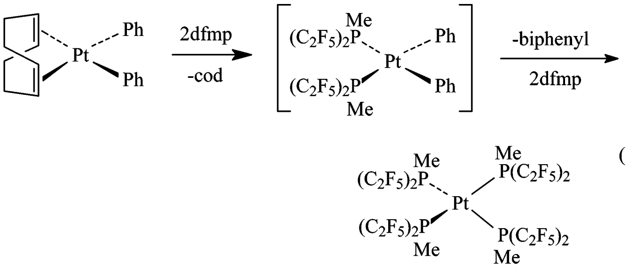
scavenged to cleanly produce $(dfmp)_4Pt$ without visible evidence for the formation of heterogeneous platinum metal.

Synthesis of $(dfmp)_4Pt$ (3). An efficient synthesis and full characterization of the Pt(0) homoleptic phosphine product obtained in the thermolysis of **2** was desired. $(dfmp)_4Pt$ (**3**) may be readily prepared by treatment of $(cod)Pt(Ph)_2$ with excess dfmp at ambient temperature (eq 3). Cyclooctadiene displacement followed by the rapid elimination of biphenyl from thermally unstable *cis*-$(dfmp)_2Pt(Ph)_2$ cleanly produced a mixture of $(dfmp)_4Pt$, cyclooctadiene, and biphenyl. Integration of free cod ^1H resonances relative to the coordinated dfmp methyl doublet confirmed the 4:1 phosphine to platinum stoichiometry. Complex **3** was separated from the nonfluorous byproducts biphenyl and cod by selective precipitation with methanol. The generally hydrophobic nature of perfluorinated phosphine complexes is the key to this separation. Complex **3** exhibited no signs of decomposition after warming to 80 °C for 1 day in benzene.



(3)

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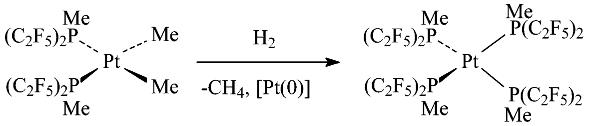
Reactions of *cis*-$(dfmp)Pt(Me)_2$ with H_2 and CO. We have previously noted that the chelating dimethyl complex $(dfepe)Pt(Me)_2$ does not react with H_2 up to 150 °C.[4f] In marked contrast, treatment of *cis*-$(dfmp)_2Pt(Me)_2$ in benzene with 1 atm H_2 resulted in the release of methane and the slow formation of $(dfmp)_4Pt$ over the course of 16 h at ambient temperature, as indicated by ^1H and ^{31}P NMR (eq 4). Again, as found for Scheme 1, there was no visible evidence of platinum metal deposition. A 50% conversion to **3** occurred after 1 h when **2** was exposed to 1250 psi H_2 in a high-pressure 5 mm sapphire NMR cell. Even under high H_2 pressures, no evidence for a hydride complex analogous to $[(dfepe)Pt(\mu\text{-}H)]_2$ was obtained.



(4)

A similar enhanced reactivity of **2** toward carbon monoxide is found. While $(dfepe)Pt(Me)_2$ is unreactive toward 1 atm CO up to 100 °C, addition of 1 atm CO to a benzene solution of *cis*-$(dfmp)_2Pt(Me)_2$ resulted in the rapid loss of 1 equiv of dfmp and formation of the mixed phosphine carbonyl complex *cis*-$(dfmp)(CO)Pt(Me)_2$ (**4**) (Scheme 2). The cis stereochemistry of **4** is clearly indicated by ^1H and ^{31}P NMR. A single ^{31}P resonance is observed at 31.7 ppm with a small platinum coupling ($^1J_{PtP} = 1310$ Hz) that is diagnostic for the disposition of the dfmp ligand trans to methyl. In ^1H NMR spectra, two distinct platinum- and phosphorus-coupled methyl ligand resonances are seen at δ 1.41 ($^2J_{PtH} = 81$ Hz, $^3J_{PH} = 8$ Hz) and 0.80 ($^2J_{PtH} = 72$ Hz, $^3J_{PH} = 12$ Hz). Solution IR data in chloroform reveal a single ν(CO) band at 2101 cm^{-1}. This stretching frequency is lower than that observed for the cationic platinum complex $(dfepe)Pt(Me)(CO)^+$ (2174 cm^{-1}),[4d] but actually higher than the average ν(CO) value reported for *cis*-$(CO)_2Pt(Me)_2$ (2089 cm^{-1}).[14] This comparison lends further support to our assertion that the electronic influence of dfmp and related perfluoroalkylphosphines is very similar to CO. A variable CO pressure NMR study was performed with *cis*-$(dfmp)_2Pt(Me)_2$: under 100 psi CO in C_6D_6, a mixture of **4**, free dfmp, and *cis*-$(CO)_2PtMe_2$ was observed after 40 min. Integration of ^{31}P NMR resonances indicated a 33% conversion of **4** to the dicarbonyl. Under 525 and 1150 psi CO, the conversion to the dicarbonyl was 84% and 88%, respectively. Release of CO pressure resulted in the clean re-formation of *cis*-$(dfmp)(CO)Pt(Me)_2$ after several hours, confirming the reversibility of CO displacement.

Generation of *trans*-$(dfmp)_2Pt(Me)X$ Complexes ($X = O_2CCF_3$, OTf, OSO_2F). A remarkable feature of $(dfepe)Pt(Me)_2$ chemistry is the exceptional resistance of the initial protonolysis products (dfepe)Pt(Me)(X) toward further reaction in neat HX solutions. Thorn and others have noted enhanced resistance to protonolysis for *trans*-$(R_3P)_2Pt(Me)X$ systems.[15,16] Reaction of *trans*-$(^iPr_3P)_2Pt(Me)(OTf)$ with stoichiometric HOTf in CH_2Cl_2 to produce *trans*-$(R_3P)_2Pt(OTf)_2$ does not occur prior to decomposition,[15] whereas *trans*-$((C_6F_5)_3P)_2Pt(Me)(OTf)$ is moderately stable in HOTf up to 80 °C.[17] Since the perfluoroaryl chelate $[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]Pt$-

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[16] Lucey, D. W.; Helfer, D. S.; Atwood, J. D. *Organometallics* **2003**, *22*, 826.

[17] Thorn, D. L. Personal communication.

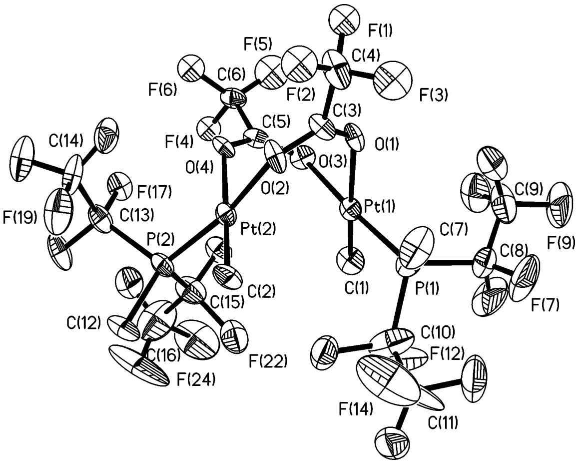
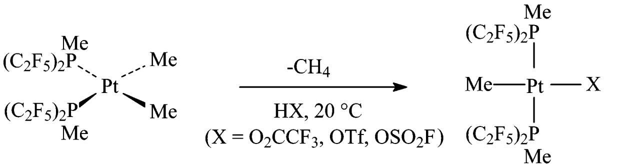


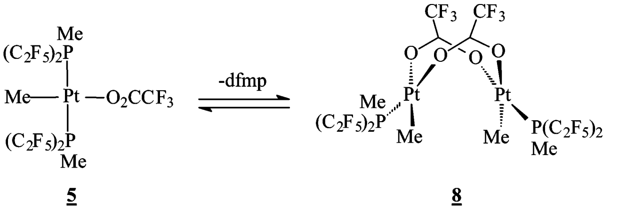
Figure 3. Molecular structure of [(dfmp)Pt(Me)(μ-O_2CCF_3)]$_2$ (**8**) with atom-labeling scheme (30% probability ellipsoids).

(Me)$_2$ is much less resistant to protonolysis than (dfepe)Pt(Me)$_2$,[4b] we anticipated that *trans*-(dfmp)$_2$Pt(Me)(X) would show a commensurately greater resistance to protonolysis than *trans*-(($C_6F_5)_3P)_2$Pt(Me)(X). Dissolving *cis*-(dfmp)$_2$Pt(Me)$_2$ in neat CF_3CO_2H, HOTf, or SFO_3H leads to rapid methane evolution and the formation of *trans*-(dfmp)$_2$Pt(Me)(O_2CCF_3) (**5**), *trans*-(dfmp)$_2$Pt(Me)(OTf) (**6**), and *trans*-(dfmp)$_2$Pt(Me)(OSO_2F) (**7**), respectively (eq 5).



(5)

Complexes **5**−**7** all exhibit characteristic platinum-coupled methyl triplets by ^{1}H NMR due to coupling with equivalent trans-orientated dfmp ligands and single ^{31}P resonances with $^1J_{PtP}$ couplings = 3800 ± 50 Hz that are insensitive to the nature of the cis conjugate base. Attempts to isolate **5** by removal of trifluoroacetic acid resulted in dfmp loss and dimerization to form the trifluoroacetate-bridged complex [(dfmp)Pt(Me)(μ-O_2CCF_3)]$_2$ (**8**) (eq 6). Addition of 1.5 equiv of dfmp to a $CDCl_3$ solution of **8** cleanly regenerated **5**, demonstrating that the displacement of dfmp and competitive coordination of trifluoroacetate is reversible. In contrast, complexes **6** and **7** are isolable without significant dfmp loss, consistent with the lower coordinating and bridging ability of triflate and fluorosulfonate ligands.



(6)

5 **8**

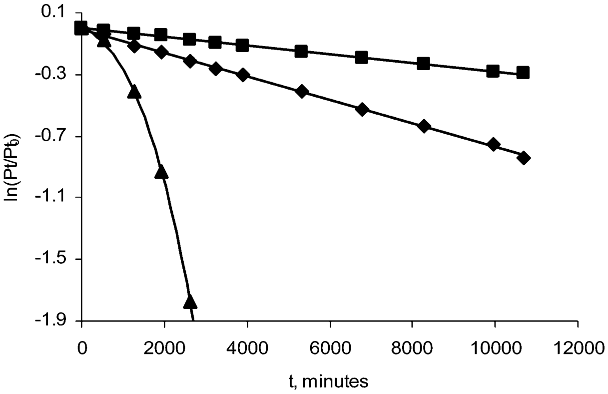


Figure 4. Protonolysis plots for *trans*-(dfmp)$_2$Pt(Me)(X) in neat HX at 80 °C, ■ = CF_3SO_3D solvent, ◆ = CF_3SO_3H solvent, ▲ = FSO_3H solvent.

The molecular structure of **8** is shown in Figure 3, and selected metrical data are presented in Table 2. There is no crystallographically imposed symmetry present within the structure, but the square planar platinum environments are related by a pseudo-C_2 axis normal to the Pt−Pt vector. The Pt−Pt distance (3.264 Å) is longer than that observed in related Pt(II), Pd(II), and Ni(II) acetate bridged structures (2.865−3.079 Å)[18] and considerably longer than that reported for [Pt(Me)$_2$(py)(μ-O_2CMe)]$_2$ (2.530 Å), which has a Pt−Pt single bond.[19] Both the average Pt−Me bond lengths (2.026 Å) and the Pt−P bond lengths (2.138 Å) are significantly shorter than the corresponding Pt−Me and Pt−P values found for **2** (Pt−Me: 2.101 Å, Pt−P: 2.265 Å), in which each dfmp is trans to a methyl group. Pt−O distances to the trifluoroacetate ligands trans to methyl are ~0.09 Å longer than those trans to dfmp. Together, these bond length differences reflect the relative trans-influence ordering of methyl > dfmp > μ-O_2CCF_3.

Protonolysis of *trans*-(dfmp)$_2$Pt(Me)X in HX. The protolytic stabilities of *trans*-(dfmp)$_2$Pt(Me)X systems were monitored by ^{1}H and ^{31}P NMR. Thermolysis of *trans*-(dfmp)$_2$Pt(Me)(O_2CCF_3) in CF_3CO_2D at 150 °C took place over the course of several hours. Disappearance of the ^{31}P resonance for **5** at 32.8 ppm was first-order and was concomitant with the appearance of two new platinum phosphine species at 44.4 ($^1J_{PtP}$ = 3510 Hz) and 22.3 ($^1J_{PtP}$ = 3340 Hz) ppm in a 1:2 ratio after 15 min (45% conversion of **5** to products). On the basis of protonolysis results found for **6** and **7** (see below), we tentatively assign these products as *trans*-(dfmp)$_2$Pt(O_2CCF_3)$_2$ (**9**) and *cis*-(dfmp)$_2$Pt(O_2CCF_3)$_2$ (**10**), respectively. After 75 min (90% conversion) the observed ratio of **9** and **10** was found to be 1.9:1. At later stages of the reaction, a third new ^{31}P resonance was seen at 42.4 ppm, which comprised 23% of the total product at 90% conversion and became the dominant phosphorus-containing species (33%) after thermolysis for an additional 2 h at 150 °C. The remaining phosphorus resonances consisted of free dfmp (~25%) and several minor unidentified products. Since the 42.4 ppm resonance is a well-defined pentet ($^2J_{PF}$ = 79 Hz) lacking ^{195}Pt coupling, we ascribe it to a phosphine decomposition product containing an intact ($C_2F_5)_2$P moiety. The first-order rate constant obtained, 4.7(2) × 10^{-4} s^{-1} (Figure 4), is 23 times greater than that reported for

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(18) (a) Cooper, M. K.; Guerney, H. J.; Goodwin, M.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 757. (b) Hursthouse, M. B.; Sloan, O. D.; Thornton, P.; Walker, N. P. C. *Polyhedron* **1986**, *5*, 1475. (c) Klein, H. F.; Weimer, T.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chim. Acta* **1991**, *189*, 35.

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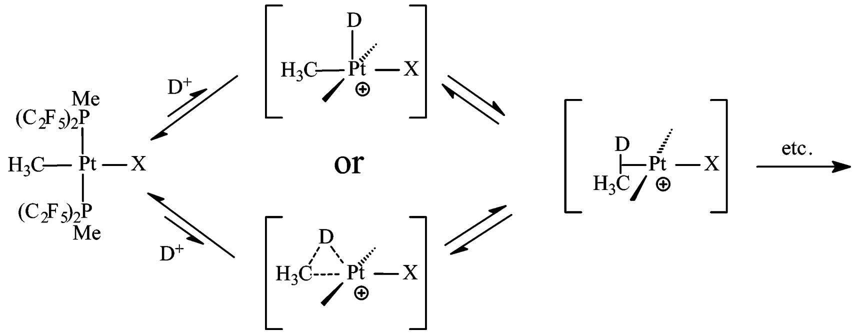
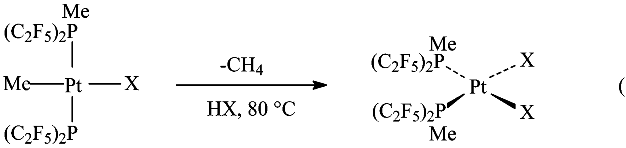
Scheme 3



(dfepe)Pt(Me)(O$_2$CCF$_3$) under identical conditions, so we conclude that **5** is slightly less resistant to protonolysis than the chelating analogue. A protonolysis run with **5** carried out in parallel in the presence of 1 equiv of added dfmp gave a slightly lower first-order rate constant of $1.5(2) \times 10^{-4}$ s^{-1} and indicates that that there is some protonolysis inhibition by added phosphine.

The protolytic stabilities of the triflate and fluorosulfonate derivatives **6** and **7** were also monitored by ^{31}P NMR in their respective neat acids at 80 °C. In contrast to **5**, single platinum products were observed at 17.8 ($^1J_{PtP} = 4250$ Hz) and 14.9 ($^1J_{PtP} = 4340$ Hz) ppm, respectively. The large $^1J_{PtP}$ observed in triflic acid corresponds closely to that found for (dfepe)Pt(OTf)$_2$ ($^1J_{PtP} = 4254$ Hz); thus, we assign the thermolysis products as *cis*-(dfmp)$_2$Pt(OTf)$_2$ (**11**) and *cis*-(dfmp)$_2$Pt(OSO$_2$F)$_2$ (**12**) (eq 7). These protonolysis conversions are cleaner than that observed for **5** at higher temperatures in trifluoroacetic acid. No trans products are observed, and smaller amounts (<10%) of metal-free phosphine decomposition products appear as the reactions approach complete conversion. Isolation of **11** and **12** was not attempted.



(X = OTf, **11**; OSO$_2$F, **12**) (7)

The initial rate kinetics for the protonolysis of *trans*-(dfmp)$_2$Pt(Me)(OTf) in HOTf and DOTf are well-behaved and reproducible. First-order plots (Figure 4) gave a first-order rate constant in HOTf of $1.28(2) \times 10^{-6}$ s^{-1}, a value that is 80 times *slower* than the protonolysis rate for (dfepe)Pt(Me)(OTf) under these conditions. The protonolysis rate obtained for *trans*-(dfmp)$_2$Pt(Me)(OTf) in DOTf ($4.67(4) \times 10^{-7}$ s^{-1}) gave a kinetic isotope effect of 2.7, which is identical to the observed k_H/k_D value found for (dfepe)Pt(Me)(OTf) at 100 °C.[4b]

We have previously reported that (dfepe)Pt(Me)(OSO$_2$F) undergoes complete protonolysis in fluorosulfonic acid within 4 h at ambient temperatures. *trans*-(dfmp)$_2$Pt(Me)(OSO$_2$F) is considerably more resistant: no decomposition is observed under ambient conditions, and only 2% conversion to **12** occurs after 9 h at 80 °C. First-order plots are nonlinear and show that decomposition accelerates with time (87% conversion after 44 h) in this acid media.

Our previous protonolysis study with (dfepe)Pt(Me)X systems in DX solvents showed no significant deuterium scrambling prior to methane loss.[4b] Monitoring the protonolysis of **5** in CF$_3$CO$_2$D by ^{1}H NMR, however, revealed that complete deuteration of the remaining methyl ligand had occurred within 15 min at 150 °C; the extent of the protonolysis reaction at this point was 45%, and a roughly 1:1 mixture of CH$_3$D and CH$_2$D$_2$ was observed in solution. In contrast, complete deuteration of the methyl group in **6** occurred after 9 h at 80 °C, when less than 2% conversion to **11** had occurred. No protio methane isotopomers were observed. Warming (dfmp)$_2$Pt(Me)(OSO$_2$F) in DOTf to 80 °C in the presence of 40 psi methane did not result in any incorporation of deuterium into free methane under these conditions.

For (dfepe)Pt(Me)(X) systems we observed that traces of water induced decomposition to give small amounts of heterogeneous platinum solids, which subsequently catalyzed H/D exchange of the Pt−CH$_3$ group prior to protonolysis. No discernible deposition of heterogeneous platinum was observed in the present work. Moreover, H/D exchange of **6** in DOTf is unaffected by the presence of elemental mercury, so we conclude that H/D exchange in *trans*-(dfmp)$_2$Pt(Me)(X) likely occurs via the reversible formation of a methane complex (Scheme 3).

Summary. Extension of chelating dfepe platinum systems to nonchelating analogues results in significant changes in observed reactivity patterns. The ability to access three-coordinate intermediates through phosphine dissociation allows for the reaction of *cis*-(dfmp)Pt(Me)$_2$ with both H$_2$ and CO and also provides the first example of simple reductive elimination of platinum-methyl groups to form ethane. A further difference between (dfmp)$_2$Pt and (dfepe)Pt moieties is in their activity toward H$_2$: while the (dfepe)Pt fragment is known to efficiently scavenge H$_2$ to form the hydride-bridged dimer [(dfepe)Pt(μ-H)]$_2$, (dfmp)$_2$Pt undergoes disproportionation to form (dfmp)$_4$Pt, even in the presence of 1250 psi H$_2$, rather than form products such as (dfmp)$_2$Pt(H)$_2$ or [(dfmp)$_2$Pt(μ-H)]$_2$.

The stereochemical preferences for monodentate dfmp complexes are worth comment. Mixtures of cis and trans geometries for group 10 (R$_3$P)$_2$M(Me)$_2$ complexes have been reported for the small strongly donating phosphine Me$_3$P, while only cis geometries are found for larger and/or more poorly donating phosphines.[20] In general, the observed preferences follow the antisymbiotic effect, where the strong σ-binding alkyl ligand is placed trans to the weakest σ donor.[21] For (R$_3$P)$_2$M(Me)(X) systems, both cis and trans complexes have been observed for

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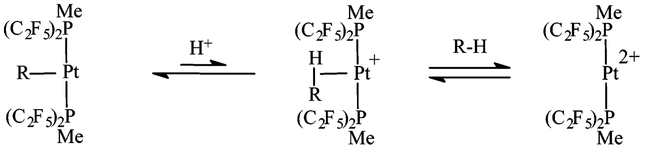
[20] Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1141.

R_3P = phosphite, whereas only trans monomethyl complexes are observed for alkyl and aryl phosphines. A cis preference for aryl phosphite complexes, $[(ArO)_3P]_2Pt(Me)(X)$, has been rationalized in terms of a cis coordination preference for π-accepting phosphines,[22] but we find only trans coordination for the more strongly π-accepting dfmp ligand.

A comparison between the protonolysis reactivities of *trans*-(dfmp)$_2$Pt(Me)(X) with the cis chelating analogues (dfepe)Pt(Me)(X) reveals several interesting features. First, we note that going to a progressively stronger acid medium correlates with increasing relative stability of the trans systems; indeed, *trans*-(dfmp)$_2$Pt(Me)(OSO_2F) is *orders of magnitude* more stable than its dfepe analogue and appears to be the most acid-resistant metal alkyl complex thus far reported. A significant increase in protolytic stability for X = triflate compared to X = chloride has been noted for *trans*-($^iPr_3P)_2$Pt(Me)(X), but the relationship of stability to the relative trans influence of X has not been examined in any detail.[15] We anticipate that further substitution of X with more weakly coordinating anions than OSO_2F^- in poorly solvating media will lead to *trans*-(dfmp)$_2$Pt(alkyl)···X or [(dfmp)$_2$Pt(alkyl)···(*solv*)]$^+$ systems with exceptional stabilities in superacidic media.

Another distinctive difference between (dfepe)Pt(Me)(X) and the trans systems described in this paper is H/D scrambling prior to methane loss for *trans*-(dfmp)$_2$Pt(Me)(X), indicating that reversible protonation to form intermediate methane adducts occurs prior to methane loss. In the case where X = O_2CCF_3, the scrambling and methane loss rates are comparable, whereas when X = the more weakly coordinating triflate ligand, H/D scrambling is significantly faster than methane loss. This observation is in accord with previous work with *trans*-(L)$_2$Pt(Me)(X) systems.[23] Taken together with the observed protonolysis trends, we believe that systems that approach the three-coordinate extreme "*trans*-(dfmp)$_2$Pt(Me)$^+$" will exhibit increasingly unfavorable kinetics for protonation and alkane loss and are therefore good candidates for examining the direct heterolysis reaction of simple alkanes with "*trans*-(dfmp)$_2$Pt^{2+}" to form stable *trans*-(dfmp)$_2$Pt(alkyl)$^+$ products.



accessible?

Experimental Section

General Procedures. All manipulations were conducted under N_2 using high-vacuum line and glovebox techniques. All reactions were carried out under an ambient pressure of approximately 590 Torr (elevation ~2195 m). All solvents were dried using standard procedures and stored under vacuum. Aprotic deuterated solvents as well as CF_3CO_2H and CF_3CO_2D were dried over activated 3 Å molecular sieves. DOTf was prepared from the reaction of excess triflic anhydride with D_2O; DOTf, HOTf, and FSO_3H were distilled prior to use and stored under nitrogen. CF_3CF_2H (Oakwood Products, Inc.) and (Me)PCl_2 (Strem) were used as received. Elemental analyses were performed by Desert Analytics. Infrared spectra were obtained on a Bomem MB100 FTIR instrument. NMR spectra were recorded with a Bruker DRX-400 instrument. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. High-pressure NMR experiments were performed using a 5 mm sapphire NMR cell (Saphikon, Inc.) epoxied to a corrosion-resistant 686 Inconel valve assembly of local design. The compounds (nbd)$PtMe_2$,[24] [$Me_2Pt(\mu$-$SMe_2)]_2$,[25] and (cod)$PtMe_2$ were prepared following published procedures.[26] Alternate synthetic routes to (nbd)$PtCl_2$, $(C_2F_5)_2P(Me)$, and (dfepe)$PtMe_2$ are described below.

Improved Synthesis of (nbd)PtCl$_2$. A direct preparation of (nbd)$PtCl_2$ from K_2PtCl_4 has been developed on the basis of the literature synthesis of (cod)$PtCl_2$;[27] a key modification is the addition of concentrated HCl to prevent lower yields due to extensive decomposition to platinum metal. A 250 mL flask was charged with 2.0 g of K_2PtCl_4 (4.8 mmol), 40 mL of H_2O, 64 mL of glacial acetic acid, and 1 mL of concentrated HCl and brought to reflux under N_2. A 2.0 mL (18.5 mmol) portion of norbornadiene was added, and the solution was allowed to reflux for 45 min, during which time the red color faded to yellow. The reaction mixture was cooled to 0 °C, and the solids were collected on a frit and washed with copious amounts of ice cold water. Drying the resulting tan solid under vacuum for several hours gave 1.27 g (74%) of product, which was judged pure by ^1H NMR.

Alternative Synthesis of Bis(pentafluoroethyl)methylphosphine (dfmp). Synthesis of dfmp following the procedure published for $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ is hindered by the presence of butyl chloride (formed by metal−halogen exchange between C_2F_5Cl and *n*-BuLi), which has a boiling point similar to the dfmp product.[6] Hence, a variation based on metal−hydrogen exchange was developed (*NOTE:* since C_2F_5Cl is no longer commercially available, this alternative method based on C_2F_5H has an additional practical advantage for the synthesis of dfmp, dfepe, and other perfluoroethyl-substituted compounds requiring C_2F_5Li). A 250 mL two-neck flask was charged with 66.7 mL of 2.5 M *n*-BuLi in hexanes (167 mmol). The hexanes were removed under vacuum, and the *n*-BuLi was redissolved in ca. 100 mL of diethyl ether. After cooling to −90 °C, 17.5 mL of C_2F_5H (density ~1.60 g/mL, 234 mmol) maintained at −78 °C in a measured volume was slowly vacuum transferred into the well-stirred *n*-BuLi/ether solution at a rate sufficient to maintain the reaction temperature below −80 °C. Upon completion of the transfer, the solution was maintained at −80 °C and allowed to stir for an additional 85 min. At this point a 5.0 mL aliquot of (Me)PCl_2 (56 mmol) was slowly added via syringe under a nitrogen counterflow to the solution while maintaining the bath temperature below −80 °C. The solution became light orange during the course of the phosphoryl chloride addition. After complete addition, the reaction mixture was allowed to slowly warm to room temperature and the volatiles were vacuum-transferred to a 250 mL RB flask for distillation. Under ambient pressure (590 Torr) diethyl ether was distilled off until the distillate temperature reached 70 °C. NMR analysis of the remaining liquid indicated essentially pure product (7.7 g, d = 1.57 g/mL, 49%). Redistillation of dfmp gave a boiling range of 78−79 °C. Spectroscopic data were in accord with previously reported values.[6]

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Alternative Synthesis of (dfepe)PtMe$_2$. The originally reported synthesis of (dfepe)PtMe$_2$ requires (dfepe)PtCl$_2$, a time-consuming starting material to prepare.[4h] A more practical synthesis uses (cod)PtMe$_2$ as a precursor: To 0.80 g of (cod)PtMe$_2$ dissolved in 60 mL of ether was added 0.75 mL of dfepe (1.5 g, 1.2 equiv) via syringe. After stirring overnight the volatiles were removed and the residue was extracted with petroleum ether. Concentration of the filtrate and cooling to −78 °C afforded 1.61 g (85%) of white crystalline (dfepe)PtMe$_2$.

***cis*-[(C$_2$F$_5$)$_2$PPh](Me$_2$S)PtMe$_2$ (1).** A 5 mm NMR tube was charged with 10 mg of [Me$_2$Pt(μ-SMe$_2$)]$_2$ (0.017 mmol), 94 μL of (C$_2$F$_5$)$_2$PPh (0.51 mmol), and 0.5 mL of benzene-d_6. NMR spectra indicated the exclusive formation of *cis*-[(C$_2$F$_5$)$_2$PPh](Me$_2$S)PtMe$_2$, with no spectroscopic changes after warming for several hours at 90 °C. No attempt was made to isolate this product. ^{1}H NMR (400 MHz, 27 °C): δ 8.05 (m, 2H; P(C$_6$H$_5$)), 6.96 (m, 3H; P(C$_6$H$_5$)), 1.79 (s, $^3J_{PtH} = 26$ Hz, 6H; S(Me)$_2$), 1.21 (d, $^3J_{PH} = 8$ Hz, $^2J_{PtH} = 73$ Hz, 3H; Pt(CH$_3$)), 1.05 (d, $^3J_{PH} = 9$ Hz, $^2J_{PtH} = 83$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.9 MHz, 27 °C): δ 43.8 (m, $^1J_{PtP} = 1705$ Hz).

***cis*-(dfmp)$_2$Pt(Me)$_2$ (2).** A 25 mL flask was charged with 500 mg (1.58 mmol) of (nbd)PtMe$_2$ and 750 μL of dfmp (3.94 mmol) and placed on a filtration assembly. To this mixture was added 10 mL of petroleum ether at −78 °C, and the solution was warmed to ambient temperature with stirring. After 45 min the volatiles were removed under vacuum and the residue was redissolved in 10 mL of petroleum ether and cooled to −78 °C. The resulting white microcrystalline solid was isolated by cold filtration and dried under vacuum, yielding 0.98 g (79%) of **2** (mp 34−35 °C). Anal. Calcd for C$_{12}$H$_{12}$F$_{20}$P$_2$Pt: C, 18,17; H, 1.53. Found: C, 18.46; H, 1.43. ^{1}H NMR (400 MHz, C$_6$D$_6$, 27 °C): δ 1.53 (m, 6H; P(CH$_3$)), 1.26 (t, $^3J_{PH} = 8.7$ Hz, $^2J_{PtH} = 76$ Hz, 6H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 27 °C): δ 32.9 (m, $^1J_{PtP} = 1500$ Hz).

(dfmp)$_4$Pt (3). A mixture of (cod)Pt(Ph)$_2$ (200 mg, 0.437 mmol) and dfmp (415 μL, 2.19 mmol) was combined in a 25 mL RB flask. After cooling the reactants to −78 °C, 10 mL of diethyl ether was added. Warming the mixture to ambient temperature and stirring 24 h produced a yellow homogeneous solution. Removal of volatiles and addition of ca. 5 mL of methanol produced a light yellow solid, which was collected by filtration and dried under vacuum (0.147 g, 25%). NMR of the filtrate residue indicated the presence of unreacted (cod)PtMe$_2$. Anal. Calcd for C$_{20}$H$_{12}$F$_{40}$P$_4$Pt: C, 18.61; H, 0.67. Found: C, 18.34; H, 1.17. ^{1}H NMR (400 MHz, C$_6$D$_6$, 27 °C): δ 1.53 (s, $^2J_{PH} = 34$ Hz; P(CH$_3$)). ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 27 °C): δ 59.8 (m, $^1J_{PtP} = 4805$ Hz).

***cis*-(dfmp)(CO)Pt(Me)$_2$ (4).** One atmosphere of CO was admitted to a stirred solution of 210 mg of **2** in 5 mL of petroleum ether at ambient temperature. After 20 min, complete displacement of dfmp by CO was confirmed by NMR. Removal of volatiles gave **4** as a volatile colorless oil. IR (chloroform, cm^{-1}): 2101 (vs), 1295 (s), 1218 (s), 1140 (m), 970 (m). ^{1}H NMR (400 MHz, C$_6$D$_6$, 27 °C): δ 1.41 (d, $^2J_{PtH} = 81$ Hz, $^3J_{PH} = 8$ Hz, 3H; Pt(CH$_3$)), 1.21 (d, $^3J_{PtH} = 18$ Hz, $^2J_{PH} = 8$ Hz, 3H; P(CH$_3$)), 0.81 (d, $^2J_{PtH} = 71$ Hz, $^3J_{PH} = 12$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 27 °C): δ 37.9 (m, $^1J_{PtP} = 1310$ Hz).

***trans*-(dfmp)$_2$Pt(Me)(O$_2$CCF$_3$) (5).** Treatment of *cis*-(dfmp)Pt(Me)$_2$ with either a stoichiometric amount of trifluoroacetic acid in CDCl$_3$ or dissolution in neat trifluoroacetic acid cleanly produces *trans*-(dfmp)$_2$Pt(Me)(O$_2$CCF$_3$) in solution. All attempts to isolate **5** resulted in dfmp loss and dimerization to form [(dfmp)Pt(Me)(μ-O$_2$CCF$_3$)]$_2$. Spectroscopic data for **5** in CDCl$_3$: ^{1}H NMR (400 MHz, 27 °C): δ 1.99 (s, br, $^3J_{PtH} = 30$ Hz, 6H; P(CH$_3$)), 0.87 (t, $^2J_{PtH} = 78$ Hz, $^3J_{PH} = 6$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, 27 °C): δ 33.1 (m, $^1J_{PtP} = 3840$ Hz). Spectroscopic data for **5** in CF$_3$CO$_2$H: ^{1}H NMR (400 MHz, 27 °C): δ 1.99 (s, br, 6H; P(CH$_3$)), 0.93 (t, $^2J_{PtH} = 80$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, 27 °C): δ 26.3 (m, $^1J_{PtP} = 3840$ Hz). ^{13}C NMR (100.6 MHz, CF$_3$CO$_2$D, 27 °C): δ 0.7 (q, $^1J_{CH} = 136$ Hz; P(CH$_3$)), −31.7 (q, $^1J_{CH} = 1357$ Hz; Pt(CH$_3$)).

***trans*-(dfmp)$_2$Pt(Me)(OTf) (6).** A mixture of 217 mg (0.274 mmol) of *cis*-(dfmp)$_2$Pt(Me)$_2$ in ca. 3 mL of HOTf was stirred for 10 min, and all volatiles were removed by vacuum. The solid residue was dissolved in 7 mL of diethyl ether and then precipitated at −78 °C and cold filtered to give 185 mg of a white solid (73%). NOTE: since complex **6** decomposes in ether at ambient temperatures, the precipitation step must be carried out quickly. Although NMR indicate isolated **6** to be essentially pure, elemental analysis was low in carbon. Anal. Calcd for C$_{12}$H$_9$F$_{23}$O$_3$P$_2$PtS: C, 15.54; H, 0.98. Found: C, 14.69; H, 1.18. IR (Nujol, cm^{-1}): 1332 (s), 1301 (vs), 1226 (vs), 1142 (s), 992 (s), 974 (s). ^{1}H NMR (400 MHz, C$_6$D$_6$, 27 °C): δ 1.87 (s, br, 6H; P(CH$_3$)), 0.95 (s, br, ($^2J_{PtH} = 82$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 27 °C): δ 36.9 (m, $^1J_{PtP} = 3860$ Hz). ^{1}H NMR (400 MHz, HOTf, 27 °C): δ 1.31 (s, br, 6H; P(CH$_3$)), 0.48 (t, ($^2J_{PtH} = 82$ Hz, $^3J_{PH} = 13$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, HOTf, 27 °C): δ 38.2 (m, $^1J_{PtP} = 3795$ Hz). ^{13}C NMR (100.6 MHz, HOTf, 27 °C): δ 1.3 (q, $^1J_{CH} = 137$ Hz; P(CH$_3$)), −23.8 (q, $^1J_{CH} = 142$ Hz; Pt(CH$_3$)).

***trans*-(dfmp)$_2$Pt(Me)(OSO$_2$F) (7).** A mixture of 211 mg (0.266 mmol) of *cis*-(dfmp)$_2$Pt(Me)$_2$ in ca. 3 mL of FSO$_3$H was stirred for 10 min, and all volatiles were removed by vacuum. The resulting oil was dissolved in 7 mL of diethyl ether and then precipitated at −78 °C and cold filtered to give 127 mg of a white solid that was contaminated by 0.7 equiv of fluorosulfonic acid. Reprecipitation from ether yielded acid-free product. NOTE: as with complex **7**, the precipitation from ether must be carried out quickly to avoid decomposition in this solvent. Anal. Calcd for C$_{11}$H$_9$F$_{21}$O$_3$P$_2$PtS: C, 15.06; H, 1.03. Found: C, 14.78; H, 1.21. ^{1}H NMR (400 MHz, C$_6$D$_6$, 27 °C): δ 1.78 (s, $^3J_{PtH} = 28$ Hz, 6H; P(CH$_3$)), 0.92 (br s, $^2J_{PtH} = 82$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 27 °C): δ 36.5 (m, $^1J_{PtP} = 3870$ Hz). ^{1}H NMR (400 MHz, FSO$_3$H, 27 °C): δ 1.29 (br s, $^3J_{PtH} = 35$ Hz, 6H; P(CH$_3$)), 0.46 (t, ($^2J_{PtH} = 87$ Hz, $^3J_{PH} = 14$ Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, FSO$_3$H, 27 °C): δ 38.2 (m, $^1J_{PtP} = 3760$ Hz). ^{13}C NMR (100.6 MHz, FSO$_3$H, 27 °C): δ 116.9 (qm, $^1J_{CF} = 288$ Hz; CF$_2$C*F*$_3$), 114.5 (tm, $^1J_{CF} = 294$ Hz; C*F*$_2$CF$_3$), 0.4 (q, $^1J_{CH} = 138$ Hz; P(CH$_3$)), −22.6 (q, $^1J_{CH} = 140$ Hz; Pt(CH$_3$)).

[(dfmp)Pt(Me)(μ-O$_2$CCF$_3$)]$_2$ (8). A flask was charged with 0.208 g (0.262 mmol) of **2**, and ca. 3 mL of trifluoroacetic acid was condensed in at −78 °C. Upon warming to ambient temperature, the evolution of methane was noted and the reaction mixture was stirred for 20 min. The solution volume was reduced to ∼1 mL, and 10 mL of methanol was added in an effort to precipitate initially formed **5**. No precipitation was observed down to −78 °C, so the volatiles were removed and the resulting white solid was suspended in ∼5 mL of petroleum ether, cooled to −78 °C, and isolated by filtration. The obtained product (52.5 mg, 33%) was identified by NMR as not **5**, but compound **7**. Anal. Calcd for C$_{16}$H$_{12}$F$_{26}$P$_2$Pt$_2$: C, 15.82; H, 1.00. Found: C, 16.00; H, 0.94. IR (Nujol, cm^{-1}): 1667(s), 1629(vw), 1418(vw), 1307(s), 1224(vs), 1199(w), 1148(vs), 1120(w), 974(m), 904(m), 883(m), 860(w), 749(m), 731(m). ^{1}H NMR (400 MHz, CDCl$_3$, 27 °C): δ 1.93 (d, $^3J_{PtH} = 52$ Hz, $^2J_{PH} = 11$ Hz, 6H; P(CH$_3$)), 1.03 (s, $^2J_{PtH} = 70$ Hz, 6H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, CDCl$_3$, 27 °C): δ 24.3 (ps pentet, $^2J_{PF} = 69$ Hz, $^1J_{PtP} = 6005$ Hz). ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 27 °C): δ 2.6 (dq, $^1J_{CH} = 136$ Hz, $^1J_{PC} = 34$ Hz; P(CH$_3$)), −19.7 (q, $^1J_{CH} = 136$ Hz; Pt(CH$_3$)).

Crystal Structure of *cis*-(dfmp)$_2$Pt(Me)$_2$ (2). Colorless prismatic crystals suitable for X-ray analysis deposited from an oily sample of impure **2** upon standing for several days at ambient temperature. A crystal of suitable size was affixed onto a glass fiber with epoxy. Data were collected using a Siemens P4 diffractometer using monochromatic molybdenum radiation and an LT-2 nitrogen stream low-temperature apparatus operating at 173 K. A summary of crystal data is presented in Table 1. A monoclinic cell was determined based on 31 reflections in the 2θ range of 10−24°. A total of 4784 reflections were gathered, the octants collected being $\pm h$, $\pm k$, $+l$, using omega scans in the 2θ range 4−50°. The data were integrated and averaged to yield 3808 independent reflections. Three standard reflections monitored after every 100 data collected showed no systematic variation; the R for averaging 976 redundant data was 3.79%. $P2_1/c$ symmetry deduced from a statistical analysis of all collected data was confirmed by successful refinement in this space group. Data were corrected for absorption using an empirical ellipsoidal model based on ψ-scans for 12 reflections with $10° < 2\theta < 35°$.

The structure was solved by direct methods and standard difference Fourier techniques (SHELXTL 5.04).[28] The maximum and minimum residual electron densities were 1.580 and −1.043 Å^3. Selected metrical parameters for **2** are presented in Table 2.

Crystal Structure of [(dfmp)Pt(Me)(μ-O$_2$CCF$_3$)]$_2$ (8). Colorless prismatic crystals suitable for X-ray analysis were grown from hexanes at −50 °C. A crystal of suitable size was affixed onto a glass fiber with epoxy, coated with Paratone-N oil, and cooled to 173 K. A summary of crystal data is presented in Table 1. A monoclinic cell was determined from 33 reflections in the 2θ range of 10−25°. A total of 5082 unique reflections were gathered over the ranges $\pm h$, $+k$, $+l$ using omega scans in the 2θ range 4−50°. $P2_1/c$ symmetry deduced from a statistical analysis of all collected data was confirmed by successful refinement in this space group. In the absence of suitable ψ-scan data, data were corrected for absorption using XABS2.[29]

The structure was solved by direct methods using the SHELXTL software package. Hydrogen atoms were added in ideal calculated positions with $d(\mathrm{C-H}) = 0.96$ Å with isotropic thermal parameters set to 1.5 times the attached carbon atom. The fluorine atoms of the bridging CF$_3$CO$_2$ moieties exhibited disorder and were accounted for using a model populating two sets of fluorine positions which refined to SOFs of 0.53/0.47 for the C(4) CF$_3$ group and 0.57/0.43 for the C(6) CF$_3$ group. Positional disorder was noted for C(11), and the C(10)−C(11) bond distance was therefore restrained to 1.50 ± 0.03 Å. The maximum and minimum residual electron densities were 2.51 and −2.46 Å^3 and are associated with the Pt(2) and Pt(1) atoms, respectively. Selected metrical parameters for **8** are presented in Table 2.

Supporting Information Available: Complete tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **2** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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