Activation of Aromatic C−H Bonds by (dmpe)Pt(Me)X ($X = Me, O_2CCF_3$, OTf) Systems

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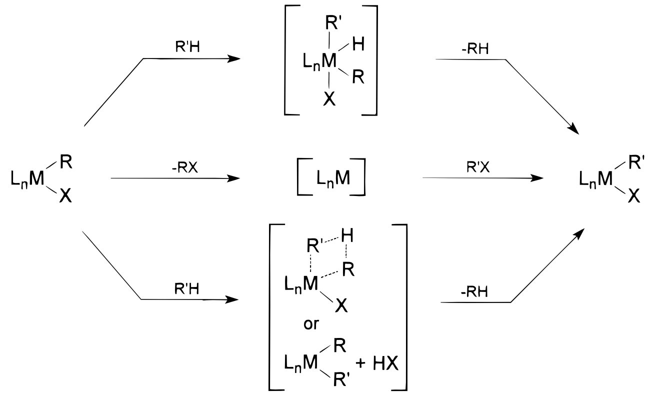
A series of complexes $(dmpe)Pt(X)_2$ ($X = Me, Cl, O_2CCF_3$, OTf) have been prepared and their thermal stabilities examined. In contrast to (dmpe)Pt(Me)(Cl), which is stable up to 150 °C in benzene solution, thermolysis of $(dmpe)Pt(Me)(O_2CCF_3)$ in benzene at 125 °C results in methane loss and the formation of $(dmpe)Pt(Ph)(O_2CCF_3)$ as the major product, along with small amounts of the disproportionation products $(dmpe)Pt(O_2CCF_3)_2$ and $(dmpe)Pt(Ph)_2$ (8−10%). Kinetic studies in C_6H_6 and C_6D_6 indicate that the disappearance of $(dmpe)Pt(Me)(O_2CCF_3)$ is first-order, with an overall kinetic isotope effect of 3.3(2). Methyl/aryl metathesis rates are not inhibited by added $TBA^+O_2CCF_3^-$. Thermolysis of $(dmpe)Pt(Me)_2$ in benzene at 180 °C for 18 h gave a mixture of unreacted $(dmpe)Pt(Me)_2$ (15%), (dmpe)Pt(Me)(Ph) (51%), and $(dmpe)Pt(Ph)_2$ (34%). Thermolysis of $(dmpe)Pt(Me)(O_2CCF_3)$ in either 1,2- or 1,4-difluorobenzene at 125 °C afforded 2:1:1 statistical mixtures of $(dmpe)Pt(Ar)(O_2CCF_3)$, $(dmpe)Pt(Ar)_2$, and $(dmpe)Pt(O_2CCF_3)_2$ ($Ar = 2,3\text{-}C_6H_3F_2$ or $2,5\text{-}C_6H_3F_2$, respectively). Thermolysis of $(dmpe)Pt(Me)(O_2CCF_3)$ in toluene affords a mixture of ortho, meta, and para tolyl products, $(dmpe)Pt(C_6H_4Me)(O_2CCF_3)$. The metathesis rate for polar 1,2-difluorobenzene is not significantly different than that observed for the nonpolar aromatic substrates. Surprisingly, the aryl/aryl exchange rates for $(dmpe)Pt(Ph)(O_2CCF_3)$ in C_6D_6 and C_7D_8 are 10−20 times faster than observed methyl/aryl exchange rates. These data may be accommodated by a mechanism involving a rate-limiting addition of aryl C−H bonds directly to a 4-coordinate (dmpe)Pt(II) or a 3-coordinate (η^1-dmpe)Pt(II) center.

Introduction

The activation of both aliphatic and aromatic C−H bonds by a wide range of transition metal systems is well established.[1] Although the direct detection and/or isolation of initially-formed metal alkyl hydride complexes has been observed in an increasing number of cases,[2] the addition of C−H bonds to metal centers has been more commonly inferred from the isolation of alkyl- or aryl-metathesis products. Four primary reaction mechanisms have been proposed for these types of transformations: (1) oxidative addition of R′−H followed by reductive elimination of R−H, (2) reductive elimination of R−X (X = H, halide, etc.) followed by oxidative addition of substrate R′−X bonds, and (3) concerted (σ-bond metathesis)[3] or stepwise (heterolytic) interchange of R and R′.



In the case of platinum C−H activation chemistry, nearly all of these reaction types have been either demonstrated or suggested. The intermediacy of reactive Pt(0) intermediates in the activation of hydrocarbon substrates has been established by Whitesides and Hoffmann in $[(Cy)_2PCH_2CH_2P(Cy)_2]Pt(R)H$ and $[(Cy)_2PCH_2P(Cy)_2]Pt(R)H$ systems, respectively.[4,5] Alternatively, both the addition of C−H bonds to Pt(II) alkyl complexes to form Pt(IV) alkyl hydride intermediates

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[3] Thompson, M.E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

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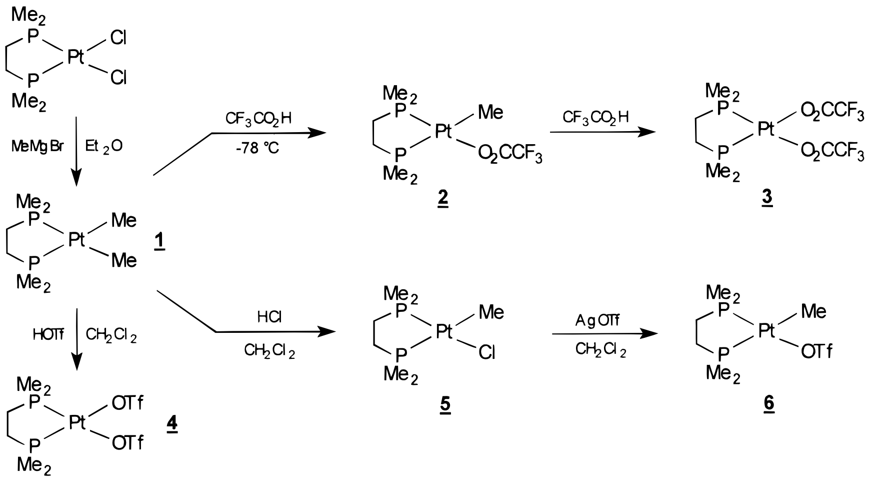
Scheme 1



and alkane heterolysis (nonoxidative) mechanisms have been proposed for “Shilov type” hydrocarbon activation chemistry.[6]

The situation is particularly complicated in Pt(II) systems which contain potentially labile anionic (X^-) ligands, since direct oxidative addition of R′−H to either $L_nPt(R)X$ or $L_nPt(R)^+$ Pt(II) intermediates as well as alkane heterolysis by $L_nPt(R)^+$ are possible. A number of years ago, Whitesides reported the reaction of *trans*-$(Ph_3P)_2Pt(CH_2tBu)(OTf)$ with benzene-d_6 to form *trans*-$(Ph_3P)_2Pt(C_6D_5)(OTf)$ and neopentane-d_1.[7] On the basis of anion dependence studies, a mechanism involving an initial dissociation of triflate and oxidative addition of C_6D_6 to the cationic 14-electron intermediate $(Ph_3P)_2Pt(CH_2tBu)^+$ was proposed. Unfortunately, this study was limited by extensive thermal decomposition of the metal-containing products. More recently, Bercaw has demonstrated C−H bond metathesis between methane and higher alkanes with $(tmeda)Pt(Me)(NC_5F_5)^+BAr_f^-$ in pentafluoropyridine,[8] and Goldberg has trapped and directly characterized a Pt(IV) R−H addition intermediate, (η^3-Tp′)Pt(Me)(H)(R).[9] Aryl C−H bond addition to a Pt(II) diaryl complex has also been recently reported.[10]

During the course of our studies of highly electron-poor (fluoroalkyl)phosphine platinum systems (dfepe)Pt(Me)(X) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$; X = O_2CCF_3, OTf),[11] we observed that, in contrast to reactive $(L)_2Pt(R)(X)$ (L = donor ligand) systems, (dfepe)Pt(Me)X complexes are thermally stable in benzene up to at least 180 °C. This lack of reactivity with aromatic C−H bonds may be due to either the lower lability of X^- in electrophilic (dfepe)Pt(II) systems or the inaccessibility of (dfepe)Pt(IV) intermediates. In an effort to more closely compare (dfepe)Pt chemistry to more electron-rich Pt(II) analogues, we elected to study the chemistry of (dmpe)Pt(Me)X compounds. It was anticipated that the dmpe ancillary ligand would more effectively mimic the innocent nature of the dfepe ligand by avoiding phosphine metalation reactions commonly observed with higher phosphine congeners possessing β or γ C−H groups.[12] In this paper, we report the thermal reactions of a series of (dmpe)Pt(R)(X) (X = O_2CCF_3, OTf; R = Me, aryl) complexes with aromatic C−H bonds, and some observations concerning the mechanism of Ar−H bond activation in this electron-rich ancillary phosphine system.

Results

Synthesis of (dmpe)PtX$_2$ Complexes (X = Me, Cl, O$_2$CCF$_3$, OTf). (dmpe)Pt(Cl)$_2$ serves as a convenient precursor to both (dmpe)Pt(X)$_2$ and (dmpe)Pt(Me)(X) systems. Treatment of (dmpe)PtCl$_2$ with 2 equiv of methylmagnesium bromide in ether afforded (dmpe)PtMe$_2$ (**1**) as a crystalline solid in 77% yield (Scheme 1). Addition of excess triflic or trifluoroacetic acid to solutions of (dmpe)PtMe$_2$ in dichloromethane gave the corresponding (dmpe)PtX$_2$ complexes (X = O_2CCF_3 **3**, O_3SCF_3 **4**), which were isolated as analytically pure solids after solvent removal and repeated washings of the residue with diethyl ether to remove all traces of any excess acid.

Addition of 1 equiv of trifluoroacetic acid to (dmpe)PtMe$_2$ in acetone at −78 °C selectively afforded the monomethyl complex (dmpe)Pt(Me)(O_2CCF_3) (**2**). The triflate derivative (dmpe)Pt(Me)(OTf) (**6**) was prepared using either the procedure reported by Milstein[13a] or from the reaction of (dmpe)Pt(Me)(Cl) (**5**) with 1 equiv of AgOTf. **5** was prepared by the addition of 1 equiv of HCl to (dmpe)Pt(Me)$_2$ in CH_2Cl_2.

The coordination environment of (dmpe)Pt(Me)X compounds is well defined by ^1H and ^{31}P NMR spectroscopy. For example, the ^1H methyl proton resonance of **(6)** exhibits coupling to both the cis ($^3J_{PH}$ = 2 Hz) and trans ($^3J_{PH}$ = 7 Hz) phosphorus atoms, with characteristic platinum satellites ($^2J_{PtH}$ = 48 Hz). The sensitivity of

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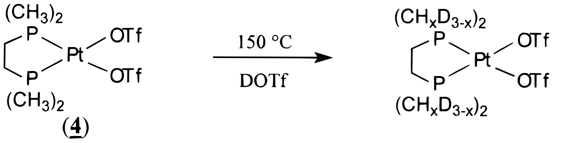
[12] Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

[13] Syntheses of (dmpe)Pt(Me)$_2$[a,b] and (dmpe)Pt(Me)(OTf)[a] have been previously communicated: (a) Goikhman, R.; Aizenberg, M.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 10894. (b) Alcock, N. W.; Brown, J. M.; MacLean, T. D. *J. Chem. Soc., Chem. Commun.* **1984**, 1689.

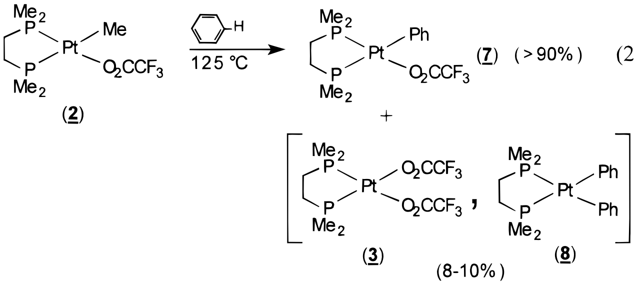
$^1J_{PtP}$ coupling constants to trans ligand donor abilities is well established and is reflected in the progressively higher *trans*-P coupling values observed for X = Cl (3930 Hz), O_2CCF_3 (4111 Hz), and OTf (4572 Hz), consistent with the relative anion donor abilities $Cl^- > O_2CCF_3^- > OTf^-$ in this system. The significant difference between the $^1J_{PtP}$ value found for **6** in CD_2Cl_2 (4572 Hz) and that previously reported in acetone (4305 Hz)[13a] is similar in magnitude to differences observed for (dfepe)-Pt(Me)X systems, and indicates that solvation to form $[(dmpe)Pt(Me)(acetone)]^+OTf^-$ in this solvent is probably occurring.[11]

(dmpe)Pt(X)$_2$ Thermolysis Studies. Intramolecular C−H bond activation (cyclometalation) involving ligand pendant alkyl groups is quite common in organometallic chemistry. H/D exchange into alkylphosphine substituents by protic solvents via metallacycle intermediates in particular has been previously established for Pt(II) systems.[14] To test for the possibility of reversible cyclometalation in (dmpe)Pt(II) compounds, the stability of compounds **3** and **4** in their respective acids was evaluated by ^1H and ^{31}P NMR spectroscopy. (dmpe)Pt(O_2CCF_3)$_2$ did not undergo any significant H/D incorporation into the dmpe methyl groups after 72 hours in trifluoroacetic acid-d_1 at 180 °C. However, in neat DOTf significant H/D scrambling (~25%) into the methyl groups of (dmpe)Pt(OTf)$_2$ was apparent by ^1H NMR spectra after 24 h at 150 °C (eq 1).



(1)

Aromatic C−H Bond Activation Studies. The reactions of (dmpe)Pt(Me)X systems with aromatic substrates are dependent on the nature of X. The chloride derivative **5** is stable in benzene up to 150 °C, while the triflate analogue **6** thermally decomposes in benzene at 80 °C to give an uncharacterized oily residue. In contrast, thermolysis of (dmpe)Pt(Me)(O_2CCF_3) in benzene at 125 °C results in methane loss and the formation of (dmpe)Pt(Ph)(O_2CCF_3) (**7**) as the primary product, together with smaller but significant amounts of both (dmpe)Pt(O_2CCF_3)$_2$ (**3**) and (dmpe)Pt(Ph)$_2$ (**8**) (8−10%) (eq 2). Products **7** and **8** were confirmed by their independent synthesis (see Experimental Section).

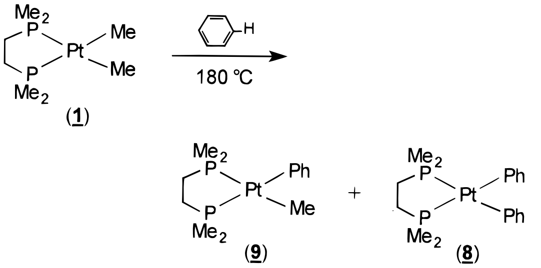


(2)

The origin of the side products **3** and **8** is of interest. Thermolysis of the primary product (dmpe)Pt(Ph)(O_2CCF_3) in benzene at 125 °C does not afford (dmpe)Pt(O_2CCF_3)$_2$ at a rate qualitatively consistent with its appearance in eq 2. However, the amount of the expected accompanying disproportionation product (dmpe)Pt(Ph)$_2$ formed in thermolysis experiments typically ranged between 25 and 66% of that expected from disproportionation. We are unable to account for this consistently low yield of (dmpe)Pt(Ph)$_2$. No (dmpe)Pt(Me)$_2$ was observed in the thermolysis of (dmpe)Pt(Me)(O_2CCF_3), indicating that (dmpe)Pt(O_2CCF_3)$_2$ is not formed from the disproportionation of **2** prior to alkyl metathesis.

When the thermolysis of (dmpe)Pt(Me)(O_2CCF_3) was carried out in C_6D_6, CH_3D as well as significant amounts of CH_4 (CH_3D/CH_4 = 7) were observed by ^1H NMR spectroscopy. The CH_3D:CH_4 ratio remained essentially constant throughout the reaction in both 99.8 and 100 atom% benzene-d_6. Essentially the same CH_3D:CH_4 ratio was found using rigorously flame-dried and silated glassware. Exhaustive thermolysis of (dmpe)Pt(Ph)(O_2CCF_3) in C_6D_6 at 125 °C does not scramble deuterium into the dmpe methyl groups (see below); however, it is possible that the traces of CH_4 observed derive from a minor reaction pathway involving a slightly more favorable dmpe metalation in the methyl derivative. No metal products in the thermolysis of (dmpe)Pt(Me)(OTf) were identified; however, the major methane isotopomer observed using C_6D_6 as a solvent was CH_4 (CH_3D:CH_4 = 1 to 1.3), which suggests that significant metalation and/or H/D exchange with the dmpe ancillary ligand may indeed be occurring in this particular system.

The thermal stabilities of the dialkyl and diaryl complexes **1** and **8** in benzene-d_6 were examined for comparison with (dmpe)Pt(R)(X) systems. (dmpe)Pt(Me)$_2$ was completely unreactive at 150 °C. After 5 h at 180 °C, however, ^{31}P NMR spectra showed the major species remaining in solution to be unreacted dimethyl (67%), together with resonances attributable to (dmpe)-Pt(Me)(Ph) (**9**) (30%) and a small amount of (dmpe)Pt(Ph)$_2$. After 18 h, the major species observed were **9** (51%), diphenyl (34%), and residual dimethyl (15%) (eq 3). ^1H NMR spectra revealed an approximate 1:1 ratio of CH_3D:CH_4 at this point, indicating that phosphine ligand metalation may be occurring at these higher temperatures. (dmpe)Pt(Ph)$_2$ was stable in C_6D_6 at 125 °C, and there was no evidence for C_6D_5 incorporation.



(3)

Kinetic Studies. The reaction progress for (dmpe)-Pt(Me)(O_2CCF_3) in C_6H_6 and C_6D_6 at 125 °C was followed by ^{31}P NMR spectroscopy. The disproportionation of initially-formed (dmpe)Pt(Ph)(O_2CCF_3) was taken into account by integration of **2** resonances versus the total (dmpe)Pt species observed in solution. The disappearance of **2** in C_6H_6 followed first-order behavior for over three half-lives, with an apparent rate constant of $1.40(8) \times 10^{-4}$ s^{-1}. The thermolysis rate in C_6D_6 at 125 °C was found to be $4.29(10) \times 10^{-5}$ s^{-1}, correspond-

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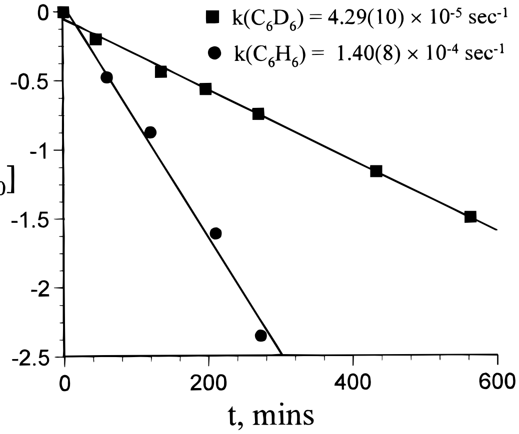
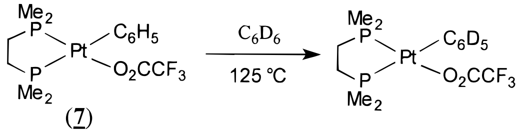


Figure 1. Monitoring of the thermolysis of (dmpe)Pt(Me)(O_2CCF_3) (**3**) in C_6H_6 (●) and C_6D_6 (■) at 125 °C by ^{31}P NMR spectroscopy.

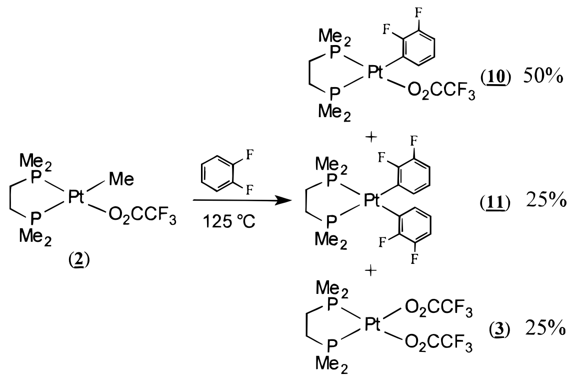
ing to an overall kinetic isotope effect of 3.3(2) (Figure 1). Thermolysis of the aryl platinum complex (dmpe)Pt(C_6H_5)(O_2CCF_3) in C_6D_6 at 125 °C resulted in complete conversion to (dmpe)Pt(C_6D_5)(O_2CCF_3) after 1 h ($t_{1/2}$ ~ 15 min), indicating that degenerate aryl C−H activation also occurs, but at a rate approximately *twenty times* that of aryl C−H bond addition to (dmpe)Pt(Me)(O_2CCF_3) (eq 4). No significant scrambling of deuterium into the ancillary dmpe ligand in the thermolyses of either **2** or **7** was apparent by ^1H NMR spectroscopy under these conditions.



(4)

The role of anion dissociation in the reactions of (dmpe)Pt(R)(X) complexes with aromatic substrates was probed by examining the effect added salts on the rate of Pt−aryl complex formation. Thermolysis of (dmpe)Pt(Me)(O_2CCF_3) in C_6D_6 at 125 °C in the presence of equimolar amounts of either $Bu_4N^+O_2CCF_3^-$ or $Bu_4N^+BF_4^-$ (ca. 0.05 M) was monitored by ^{31}P NMR spectroscopy. In contrast to Whiteside's report of triflate anion inhibition for *trans*-$(Ph_3P)_2Pt(CH_2tBu)$(OTf), the thermal conversion of **2** to **7** with added $Bu_4N^+O_2CCF_3^-$ was approximately *three times faster* (k ~ 1.0 × 10^{-4} s^{-1}) than in the absence of added trifluoroacetate, whereas the observed conversion rate in the presence of $Bu_4N^+BF_4^-$ was essentially unchanged. Investigation of higher added salt ratios was not possible due to limited tetraalkylammonium salt solubilities in benzene.

Substrate Effects. The generation of any cationic platinum intermediates prior to the formation of **7** should be sensitive to solvent polarity effects. To test this, the thermal stability of (dmpe)Pt(Me)(O_2CCF_3) in the polar aromatic solvent 1,2-difluorobenzene (μ = 2.59)[15] was examined. Thermolysis of **2** in 1,2-difluorobenzene at 125 °C cleanly afforded a 2:1:1 statistical mixture of new complexes **10**, **11**, as well as the bis-acetate, (dmpe)Pt(O_2CCF_3)$_2$ (eq 5). This product mixture was not separated; however, we formulated these products as (dmpe)Pt($C_6H_3F_2$)(O_2CCF_3) **10** and (dmpe)Pt($C_6H_3F_2$)$_2$ **11** on the basis of characteristic $^1J_{PtP}$ data. Separate phosphorus resonances for **10** appear at δ 31.9 (dd, J_{PF} = 13, 17 Hz; $^1J_{PtP}$ = 2008 Hz) and δ 11.8 ($^1J_{PtP}$ = 4494 Hz), and a single fluorine-coupled resonance for **11** appears at δ 24.4 (dd, J_{PF} = 12, 18 Hz; $^1J_{PtP}$ = 1950 Hz). At intermediate stages of the thermolysis a set of additional resonances were observed at δ 30.7 (d, J_{PF} ~ 5 Hz; $^1J_{PtP}$ = 1795 Hz) and δ 10.2 ($^1J_{PtP}$ = 4218 Hz) which we tentatively assign as a regioisomer (**10a**) that is thermodynamically unstable with respect to the ultimate product **10**. The regiochemistries of either of these fluoroarylated products could not be unambiguously determined from ^1H and ^{31}P NMR data. However, a thermodynamic preference for C−H bond addition ortho to fluorine has been noted previously[16] and leads us to tentatively assign **10** and **11** as 2,3-$C_6H_3F_2$ aryl products and **10a** as (dmpe)Pt(3,4-$C_6H_3F_2$)(O_2CCF_3).



(5)

A similar result was obtained in the reaction of **2** and 1,4-difluorobenzene: after 12 hrs at 125 °C, clean conversion to a 2:1:1 statistical mixture of (dmpe)Pt(2,5-difluorophenyl)(O_2CCF_3) (**12**), (dmpe)Pt(2,5-difluorophenyl)$_2$ (**13**), and **3** occurred. Despite the considerable difference in solvent polarities and also potential ring substituent effects, there was *no significant difference* in the rate of Pt−aryl product formation for either of these fluorinated substrates relative to the parent benzene system. A more direct comparison of relative aryl C−H bond activation rates was obtained by the thermolysis of **2** in a 1:1 v/v mixture of C_6H_6 and 1,2-difluorobenzene. After 35 min at 125 °C, partial conversion (~8%) to (dmpe)Pt(C_6H_5)(O_2CCF_3) was apparent. After 1 h, however, an approximately equimolar amount of (**10**, **10a**, **11**) compared to **7** had appeared, and after a total of 4 h at 125 products and **3** were present. Thus, activation of C_6H_6 aryl bonds has a modest kinetic preference, while **10** and **11** are thermodynamically favored.

The possibility of electrophilic aryl C−H bond activation was evaluated by examining the regiospecificity of toluene addition. Thermolysis of (dmpe)Pt(Me)(O_2CCF_3) in toluene at 125 °C for 105 min resulted in a ~45% conversion (^{31}P NMR) to a 1:1.4:2.8 mixture of three (dmpe)Pt(C_6H_4Me)(O_2CCF_3) products **14a**, **14b**, and **14c**, respectively, as well as the bis-trifluoroacetate **3** (10%). The observed rate of reaction (k_{obs} ~ 1.3 × 10^{-4} s^{-1}) was essentially identical to that found in C_6H_6.

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[15] O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923, and refs therein.

[16] Selmeczy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, *13*, 522.

Although the specific regioisomers corresponding to **14a**, **14b**, and **14c** were not assigned, the observation of all three possible isomers indicates that there is no pronounced preference for meta, para, or ortho C−H bond addition in this system. Thermolysis of (dmpe)Pt(Ph)(O_2CCF_3) in toluene-d_8 at 125 °C afforded the same relative ratios of (dmpe)Pt($C_6D_5(CD_3)$)(O_2CCF_3). Again, the qualitative rate of aryl/aryl exchange ($t_{1/2} \sim 30$ min) in toluene was significantly faster (∼10 times) than Me/aryl exchange with **2**.

Discussion

The (dmpe)Pt(Me)(O_2CCF_3) alkyl/aryl metathesis results described in this paper are complicated to some extent by (dmpe)Pt(Ar)(X) product disproportionation and also methane label scrambling. The observation of CH_4 product formation in C_6D_6 reactions could be due to a competing phosphine metalation process, but for reactions involving (dmpe)Pt(Me)(O_2CCF_3) the observed CH_4 accounts for only 15−20% of the total methane product and does not significantly perturb the kinetic results. In the case of (dmpe)Pt(Ph)(O_2CCF_3), ∼10% disproportionation is observed during the course of the metathesis, whereas complete ligand redistribution occurs in the thermolysis of (dmpe)Pt(Me)(O_2CCF_3) in 1,2- and 1,4-difluorobenzene. Since these aryl disproportionation reactions appear to be subsequent to rate-determining methyl/aryl exchange, we can address several issues pertaining to aryl C−H bond activation in these systems.

There is a substantial body of evidence which supports the intermediacy of 14-electron unsaturated intermediates in the intra- and intermolecular activation of C−H bonds for group 9 as well as group 10 d^8 metal systems.[8,9,17] A mechanism involving homolysis of Pt−R bonds is deemed unlikely, since the lower stability of aryl radicals is not in accord with the enhanced observed rate of degenerate aryl/aryl exchange and the absence of any radical coupling products. For (dmpe)Pt(R)(X) systems, this would require either the dissociation of X^- or a pre-equilibrium phosphine labilization to form a pendant η^1-dmpe ligand. In our system, (1) the absence of any significant solvent polarity or anion inhibition effects and (2) the observation that (dmpe)Pt(Me_2) also undergoes methyl/aryl ligand metathesis in the absence of potentially labile anionic ligands (albeit at higher temperatures) together suggest that anion dissociation is not a prerequisite for C−H bond activation. We note, however, that the qualitative thermal stability ordering for (dmpe)Pt(Me)(X) of X = Cl > O_2CCF_3 > OTf does in fact follow expected lability trends. Thus, while anion dissociation does not appear likely, the nature of the X group nevertheless is important in determining the ease of Pt−C bond metathesis. The contrasting kinetic behavior of added X^- salts for cis complexes (dmpe)Pt(R)(X) and Whiteside's *trans*-$(Ph_3P)_2Pt(CH_2tBu)(OTf)$ systems may at least be partially ascribed to a stronger trans influence of alkyl ligands relative to phosphorus ligands, which would result in increased anion lability. We are unable to account for the modest rate acceleration observed by us in the presence of $TBA^+O_2CCF_3^-$; in any event, interpretations of added anion effects in strongly ion-paired solvent systems such as benzene should be viewed with some caution.

The possibility of phosphine dissociation to form a reactive (η^1-dmpe)Pt(Me)(O_2CCF_3) intermediate is more difficult to address. Under the conditions of alkyl/aryl metathesis (125 °C), ^{31}P NMR spectra of **2** show no loss in $^1J_{PtP}$ coupling. However, because of the large magnitudes of $^1J_{PtP}$ exchange decoupling would only be manifested for phosphine dissociation rates of greater than 10^3 s^{-1}, which is many orders of magnitude faster than the observed metathesis rates.[18] Young has considered a continuum of possibilities for intramolecular $(L)_2Pt(R)_2$ cyclometalation reactions involving chelating ligands, which range from rate-determining phosphine dissociation ($k_{obs}^H/k_{obs}^D \sim 1$) to direct C−H addition to four-coordinate Pt(II) ($k_{obs}^H/k_{obs}^D \geq 3$).[19] On the basis of our observed $k_{obs}^H/k_{obs}^D = 3.3(2)$, C−H addition to the platinum center is certainly kinetically important, but a preequilibrium involving phosphine dissociation cannot be excluded.

Aryl metathesis rates found for benzene, toluene, *o*-difluorobenzene, and *p*-difluorobenzene C−H bonds are all comparable and are inconsistent with electrophilic attack at the aromatic ring. These observations are in accord with earlier studies by Parshall, who reported a modest kinetic preference for fluorinated aromatic C−H bond activation for $Cp_2Nb(H)_3$ but essentially no discrimination by $Cp_2Ta(H)_3$.[20] The fact that ortho toluene C−H bond addition, inferred by the presence of a third tolyl regioisomer, is not observed for *trans*-$(Ph_3P)_2Pt(CH_2tBu)(OTf)$ or Cp*Ir(Me_3P)(Me)(OTf)[21] suggests that steric constraints may not be as severe for (dmpe)Pt(R)(X).[22] The lack of a substrate dependence could be considered support for a rate-determining phosphine dissociation mechanism. However, this is not consistent with the high observed kinetic isotope effect or the qualitative dependence of reactivity for (dmpe)Pt(Me)(X) systems on the nature of X, since dmpe labilization is expected to occur trans to the methyl group rather than the weakly trans-influencing X group, and therefore should be relatively insensitive to the nature of X.

The significantly enhanced rate of aryl/aryl exchange relative to methyl/aryl exchange is a surprising result that we are unable to account for. If the direct oxidative addition of aromatic C−H bonds to (dmpe)Pt(R)(Y) systems is rate-determining, it is not obvious how R = aryl would significantly enhance this process over R = alkyl. Nevertheless, it is clear from the qualitative thermal stability ordering (dmpe)Pt(Me)(OTf) > (dmpe)-

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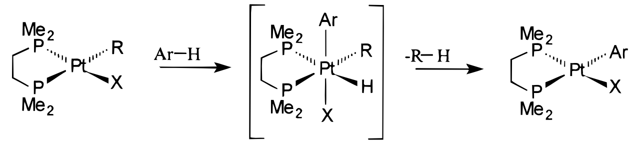
(22) Small (∼8%) amounts of a ortho tolyl C−H addition product have been observed for Cp*Rh(Me_3P)$(H)_2$: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

Pt(Ph)(O_2CCF_3) > (dmpe)Pt(Me)(O_2CCF_3) > (dmpe)Pt(Me)$_2$, (dmpe)Pt(Me)(Cl) that activities are strongly dependent on the nature of both R and X. In light of previous reports concerning the kinetic selectivity of H_2 addition to related d^8 $(L)_2$Ir(X)(CO) systems, it would be worthwhile to probe for similar ancillary ligand effects in group 10 systems.

In summary, given sufficiently labile anionic or neutral ancillary ligands, prior studies have shown that dissociative pathways are generally preferred in square planar d^8 metal systems. Nevertheless, when sufficiently labile ancillary ligands are not present, the more energetically-demanding direct addition of aryl C−H bonds to four-coordinate (dmpe)Pt(II) is a reasonable alternative. Although dmpe chelate dissociation cannot be ruled out, the high observed kinetic isotope effect for aryl C−H addition suggests a direct oxidative addition for the this particular Pt(II) system.



Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of purified nitrogen using high-vacuum, Schlenk, and/or glovebox techniques. Water- and oxygen-free solvents were prepared according to established procedures. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Triflic acid (CF_3SO_3H, Aldrich) was vacuum distilled prior to use and stored at −30 °C under a nitrogen atmosphere. CF_3SO_3D acid was prepared by treatment of triflic anhydride (Aldrich) with D_2O followed by removal of excess anhydride under vacuum. Trifluoroacetic acid (CF_3CO_2H, Aldrich) was dried over activated 3 Å sieves and stored under vacuum. CF_3CO_2D was obtained from Cambridge Isotope Laboratories and was used as received. Elemental analyses were performed by Desert Analytics. Infrared spectrum were obtained on either a Perkin-Elmer 1600 or Bomem MB100 FTIR instrument as Nujol mulls. NMR spectra were recorded with a JEOL GSX-400 or a Bruker Avance DRX-400 instrument. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard and ^{19}F NMR spectra were referenced to CF_3CO_2Et or $CFCl_3$ as external standards. (dmpe)$PtCl_2$ was prepared according to established literature procedures.[23]

(dmpe)Pt(Me)$_2$ (1). To a solution of (dmpe)$PtCl_2$ (2.000 g, 4.88 mmol) in 125 mL of ether was added 3.3 mL of methyl magnesium bromide (3.0 M in diethyl ether, 9.90 mmol). After 3 h the solvent was removed, and the residue was extracted with hexanes. Cooling the concentrated filtrate to −78 °C followed by filtration gave 1.397 g (77%) of **1** as a pure, microcrystalline, white solid. Anal. Calcd for $C_8H_{22}P_2Pt$: C, 25.60; H, 5.91. Found: C, 25.22; H, 5.91. IR (cm^{-1}): 1412 (s), 1282 (s), 1130 (m), 1078 (m), 933 (s), 838 (m), 710 (s). ^{1}H NMR (CD_2Cl_2, 399.65 MHz, 20 °C): δ 1.59 (m, 4H; PCH_2), 1.43 (m, 12H; PCH_3), 0.33 (t, $^2J_{PtH}$ = 68 Hz, $^3J_{PH}$ = 8 Hz, 6H; $PtCH_3$). ^{31}P NMR (CD_2Cl_2, 161.70 MHz, 20 °C): δ 26.6 (s, $^1J_{PtP}$ = 1743 Hz).

(dmpe)Pt(Me)(O_2CCF_3) (2). 20 μL (0.27 mmol) of HO_2CCF_3 was added dropwise via syringe to a flask containing 0.100 g (0.266 mmol) (dmpe)Pt(Me)$_2$ in 15 mL of acetone under nitrogen at −78 °C. After warming to room temperature, the volatiles were removed and the residue was taken up in ca. 15 mL of diethyl ether and filtered. The filtrate volume was reduced to 5 mL, and the white product was precipitated at −78 °C and isolated by cold filtration. The isolated yield of **2** was 0.106 g (85%). Anal. Calcd for $C_9H_{19}F_3O_2P_2Pt$: C, 22.84, H, 4.05. Found: C, 23.16, H, 3.81. IR (cm^{-1}): 1702(vs), 1295(w), 1202(vs), 1179(s), 1121(vs), 1080(sh), 941(s), 842(w), 726 (m). ^{1}H NMR (acetone-d_6, 399.65 MHz, 20 °C): δ 2.08−1.92 (m, 4H: PCH_2), 1.68 (m, 6H; PCH_3), 1.37 (m, 6H; PCH_3), 0.28 (d, $^2J_{PtH}$ = 48 Hz, $^3J_{PH}$ = 2 Hz, 3H; $PtCH_3$). ^{31}P NMR (benzene-d_6, 161.70 MHz, 20 °C): δ 35.5 (s, $^1J_{PtP}$ = 1764 Hz; trans to Pt−CH_3), 12.7 (s, $^1J_{PtP}$ = 4146 Hz; trans to Pt-O_2CCF_3). ^{19}F NMR (benzene-d_6, 376.05 MHz, 20 °C): δ −75.1 (s). ^{13}C NMR (acetone-d_6, 100.40 MHz, 20 °C): 5.03 (td, $^1J_{CH}$ = 126 Hz, $^2J_{PC}$ = 95 Hz; $PtCH_3$), 10.10−15.65 (m; PCH_3).

(dmpe)Pt(O_2CCF_3)$_2$ (3). To a flask containing (dmpe)Pt(Me)$_2$ (0.230 g 0.607 mmol) and 12 mL of CH_2Cl_2 was added 4 mL of CF_3CO_2H at −78 °C. The immediate evolution of methane was observed upon addition. After warming to ambient temperature, the volatiles were removed, and the residue was extracted with dichloromethane. Removal of CH_2Cl_2 and addition of diethyl ether afforded after filtration and drying 0.275 g (79%) of **3** as a white solid. Anal. Calcd for $C_{10}H_{16}F_6O_4P_2Pt$: C, 21.03; H, 2.82. Found: C, 21.31; H, 2.64. IR(cm^{-1}): 1691(vs), 1577(w), 1411(m), 1294(m), 1196(s), 1139(s), 950(m), 913(w), 841(m), 725(s). ^{1}H NMR (CD_2Cl_2, 399.65 MHz, 20 °C): δ 1.86 (m, 4H; PCH_2), 1.81 (m, 12H; PCH_3). ^{19}F NMR (CD_2Cl_2, 376.05 MHz, 20 °C): δ −74.4 (s). ^{31}P NMR (benzene-d_6, 161.70 MHz, 20 °C): δ 23.0 (s, $^1J_{PtP}$ = 3735 Hz).

(dmpe)Pt(OSO_2CF_3)$_2$ (4). To a 25 mL flask charged with 0.210 g (dmpe)Pt(Me)$_2$ (0.561 mmol) and 15 mL of CH_2Cl_2 at −78 °C was added (0.150 mL of $HOSO_2CF_3$ (1.70 mmol) via syringe. The solution was allowed to warm to ambient temperature, the solvent was removed, and **4** was precipitated as a white solid by the addition of diethyl ether. Filtration and repeated washings with ether afforded 0.295 g (82%) of analytically pure **4**. Anal. Calcd for $C_8H_{16}F_6O_6P_2PtS_2$: C, 14.94; H, 2.51. Found: C, 14.98; H, 2.63. IR (cm^{-1}): 1335(s), 1318(m), 1302(m), 1237(s), 1194(s), 1174(s), 1029(m), 1012(m), 950(s), 914(s), 731(m). ^{1}H NMR (CF_3SO_3D, 399.65 MHz, 20 °C): δ 1.47 (m, 4H; PCH_2), 1.32 (m, 12H; PCH_3). ^{31}P NMR (CF_3SO_3D, 161.70 MHz, 20 °C): δ 33.4 (s, $^1J_{PtP}$ = 4114 Hz).

(dmpe)Pt(Me)(Cl) (5). To 0.304 g (0.810 mmol) of (dmpe)Pt(Me)$_2$ and 30 mL of CH_2Cl_2 was added 38.2 mL (390 torr, 0.801 mmol) of hydrochloric acid gas in two 19.1 mL portions at −78 °C. The solution was stirred for 90 min, and the evolved methane was removed before the addition of the second portion. After a further 90 min of stirring, the volatiles were removed and the residue was extracted with dichloromethane. Removal of filtrate solvent and the addition of diethyl ether at −78 °C afforded 0.210 g (66%) of **5** as a white powder. Anal. Calcd for $C_7H_{19}ClP_2Pt$: C, 21.25; H, 4.84. Found: C, 21.22; H, 4.68. IR (cm^{-1}): 1418(s), 1297(w), 1287(s), 1128(w), 1092(w), 939(vs), 919(m), 902(s), 847(s), 796(w), 753(m), 720(s). ^{1}H NMR (acetone-d_6, 399.65 MHz, 20 °C): δ 2.07−1.91 (m, 4H; PCH_2), 1.63 (m, 6H; PCH_3), 1.49 (m, 6H; PCH_3), 0.31 (dd, $^2J_{PtH}$ = 54 Hz, $^3J_{PH}$ = 7.9, 3.6, 3H; $PtCH_3$). ^{31}P NMR (acetone-d_6, 161.70 MHz, 20 °C): δ 37.2 (s, $^1J_{PtP}$ = 1725 Hz, trans to Pt−CH_3), 21.84 (s, $^1J_{PtP}$ = 3930 Hz, trans to Pt−Cl).

(dmpe)Pt(Me)(OSO_2CF_3) (6). A slurry of AgOTf (0.500 g, 1.958 mmol) and 0.740 g (1.870 mmol) of **5** in 50 mL of dichloromethane was stirred under nitrogen in the absence of light. After 24 h the reaction mixture was filtered, and the filtrate volume was reduced to 5 mL. Addition of ether and precipitation at −78 °C gave **6** as an off-white powder in 71% crude yield. Recrystallization from a fluorobenzene/ether mixture yielded analytically pure **6**. Anal. Calcd for $C_9H_{19}F_3O_3P_2PtS$: C, 18.87; H, 3.76. Found: C, 19.01 H, 3.76. IR (cm^{-1}): 1413(s), 1312(s), 1244(vs), 1168(s), 1094(w), 1030(vs), 945(s), 921(m), 906(m), 845(w), 801(w), 755(m). ^{1}H NMR (CD_2Cl_2, 399.65 MHz, 20 °C): δ 1.99−1.81 (m, 2H; PCH_2), 1.70−

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[23] Anderson, G. K.; Lumetta, G.L. *Inorg. Chem.* **1987**, *26*, 1523.

1.65 (m, 2H; PCH_2), 1.70 (m, 6H; PCH_3), 1.65 (m, 6H; PCH_3), 0.47 (dd, $^2J_{PtH} = 40$ Hz, $^3J_{PH} = 7$ Hz, 1.5 Hz, 3H; $PtCH_3$). ^{31}P NMR (CD_2Cl_2, 161.7 MHz, 20 °C): δ 41.1 (s, $^1J_{PtP} = 1789$ Hz P trans to Pt−CH_3), 14.9 (s, $^1J_{PtP} = 4572$ Hz P trans to Pt−OTf). ^{19}F NMR (CD_2Cl_2, 376.05 MHz, 20 °C): δ −77.3 (s, 3F; SO_3CF_3).

(dmpe)Pt(Ph)(O_2CCF_3) (7). A 23 μL (0.30 mmol) amount of HO_2CCF_3 was added dropwise via syringe to a flask containing 0.158 g (0.300 mmol) of (dmpe)Pt$(Ph)_2$ in 23 mL of dichloromethane at room temperature. The reaction mixture was extracted with dichloromethane, and the filtrate volatiles were removed. The residual was slurried in an ether/petroleum ether mixture (2 mL/3 mL) and filtered at −78 °C, yielding 0.138 g of **7** (86%). Anal. Calcd for $C_{14}H_{21}F_3O_2P_2Pt$: C, 31.41; H, 3.95. Found: C, 31.30; H, 3.88. IR(cm^{-1}): 3049 (m), 1696 (vs), 1567 (m), 1412 (m), 1285 (w), 1196 (vs), 1138 (vs), 939 (s) 907 (m), 834 (m), 794 (w), 742 (m), 723 (s). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 20 °C): δ 7.40 (t, $J_{HH} = 13$ Hz, $^3J_{PtH} = 38$ Hz, 2H; *o*-Pt(C_6H_5)), 7.09 (t, $^3J_{HH} = 15$ Hz, 2H; *m*-Pt-(C_6H_5)), 6.96 (t, $^3J_{HH} = 15$ Hz, 1H; *p*-Pt(C_6H_5)), 1.90-1.50 (m, 4H; PCH_2), 1.65 (m, 6H; PCH_3), 1.45 (m, 6H; PCH_3). ^{19}F NMR (benzene-d_6, 376.49 MHz, 20 °C): δ −77.1 (s). ^{31}P NMR (benzene-d_6, 161.99 MHz, 20 °C): δ 32.8 (s, $^1J_{PtP} = 1696$ Hz; trans to Pt−Ph group), 12.0 (s, $^1J_{PtP} = 4100$ Hz; trans to Pt−O_2CCF_3).

(dmpe)Pt$(Ph)_2$ (8). To a solution of (cod)Pt$(Ph)_2$ (0.158 g, 0.345 mmol) and 10 mL of petroleum ether was added 60 μL of dmpe at room temperature under a nitrogen atmosphere. Immediate precipitation occurred and collection by filtration afforded 0.158 g (92 %) of **8** as a flaky white powder. Anal. Calcd for $C_{18}H_{26}P_2Pt$: C, 43.29; H, 5.25. Found: 42.83; H, 5.05. IR (cm^{-1}): 3045(s), 1572(s), 1416(m), 1280(s), 1136(m), 1021-(w), 993(w), 935(vs), 900(s), 835(m) 741(vs), 706(s), 652(m). ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 7.33 (t, $J_{HH} = 15$ Hz, $^2J_{PtH} = 56$ Hz, 2H; *o*-Pt(C_6H_5)), 6.95 (t, $^2J_{HH} = 15$ Hz, 2H; *m*-Pt-(C_6H_5)), 6.72 (t, $^2J_{HH} = 15$ Hz, 1H; *p*-Pt(C_6H_5)), 1.69 (m, 4H; PCH_2), 1.28 (m, 12H; PCH_3). ^{31}P NMR (benzene-d_6, 161.99 MHz, 20 °C): δ 21.8 (s, $^1J_{PtP} = 1638$ Hz).

Thermolysis Products of (dmpe)Pt(Me)(O_2CCF_3) in 1,2- and 1,4-$C_6H_4F_2$. Approximately 10 mg samples of **2** in 0.5 mL of 1,2- and 1,4-difluorobenzene were sealed off in flame-dried 5 mm NMR tubes. After 4 h at 125 °C, ^{31}P NMR spectra showed 2:1:1 statistical mixtures of (dmpe)Pt(aryl)(O_2CCF_3), (dmpe)Pt$(aryl)_2$, and **3** as products, which were not separated. ^{31}P NMR data (benzene-d_6, 161.99 MHz, 20 °C) for **10**: δ 31.9 (dd, $J_{PF} = 13$, 17 Hz; $^1J_{PtP} = 2008$ Hz), 11.8 ($^1J_{PtP} = 4494$ Hz). ^{31}P NMR data for **10a**: δ 30.7 (d, $J_{PF} \sim 5$ Hz; $^1J_{PtP} = 1795$ Hz), 10.2 ($^1J_{PtP} = 4218$ Hz). ^{31}P NMR data for **11**: δ 24.4 ((dd, $J_{PF} = 12$, 18 Hz; $^1J_{PtP} = 1950$ Hz). ^{31}P NMR data for **12**: δ 26.2 (d, $J_{PF} = 13$ Hz; $^1J_{PtP} = 1960$ Hz), 14.3 ($^1J_{PtP} = 4570$ Hz). ^{31}P NMR data for **13**: δ 34.4 (d, $J_{PF} = 14$ Hz; $^1J_{PtP} = 2020$ Hz).

Thermolysis Products of (dmpe)Pt(Me)(O_2CCF_3) in Toluene. Thermolyses were carried out as described above for **10**−**13**. After 2 h at 125 °C, a 1:1.4:2.8 mixture of tolyl products **14a**, **14b**, and **14c** were observed, along with ∼10% of **3**. This mixture was not separated and was characterized by ^{31}P NMR. ^{31}P NMR data for **14a**: δ 33.3 ($^1J_{PtP} = 1705$ Hz), 12.5 ($^1J_{PtP} = 4090$ Hz). ^{31}P NMR data for **14b**: δ 32.7 ($^1J_{PtP} = 1690$ Hz), 12.0 ($^1J_{PtP} = 4110$ Hz). ^{31}P NMR data for **14c**: δ 32.5 ($^1J_{PtP} = 1680$ Hz), 11.9 ($^1J_{PtP} = 4110$ Hz).

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