Adduct Studies and Reactivity of *trans*-[$(C_2F_5)_2$MeP]$_2$Pt(Me)X ($X = O_2CCF_3$, OTF, OSO_2F)

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The comparative reactivity properties of previously reported *trans*-(dfmp)$_2$Pt(Me)X (dfmp = $(C_2F_5)_2$MeP; X = O_2CCF_3, OTf, OSO_2F) with small molecules are presented. Anionic ligand displacement by CO depends upon X and the corresponding acid solvent. In trifluoroacetic acid, treatment of *trans*-(dfmp)$_2$Pt(Me)(O_2CCF_3) with CO results in loss of dfmp to form the mixed phosphine/carbonyl product (dfmp)(CO)Pt(Me)(O_2CCF_3). However, in triflic and fluorosulfonic acids *trans*-(dfmp)$_2$Pt(Me)(X) compounds react with CO to form *trans*-(dfmp)$_2$Pt(Me)(CO)$^+$(X)$^-$. *trans*-(dfmp)$_2$Pt(Me)(X) systems react with H_2 under both acidic and aprotic conditions to form *trans*-(dfmp)$_2$Pt(H)(X); *trans*-(dfmp)$_2$Pt(H)(OTf) has been crystallographically characterized. Treatment of *trans*-(dfmp)$_2$Pt(H)(OTf) with CO or dfmp gives *trans*-(dfmp)$_2$Pt(H)(CO)$^+$ or (dfmp)$_3$Pt(H)$^+$, respectively. In contrast to *trans*-(dfmp)$_2$Pt(Me)(OTf), which releases methane in HOTf, *trans*-(dfmp)$_2$Pt(Me)(OSO_2F) in FSO_3H at 80 °C cleanly produces the reductive elimination product $MeOSO_2F$. Carbonylation of *trans*-[(dfmp)$_2$PtMe(CO)]$^+$X$^-$ under 1000 psi CO in turn cleanly produces MeC(O)X at ambient temperatures. The mechanism of reductive elimination from these Pt(II) precursors is discussed.

Introduction

Group 10 complexes of the general form (L)$_2$M(R)(X), where L is a neutral two-electron-donor ancillary ligand and X is a labile anionic group, are of considerable interest due to their use in late transition metal polymerization catalysis and their intermediacy in homo- or cross-coupling reactions.[1,2] Systems with very weakly coordinating X groups afford an incipient source of reactive electrophilic 14-electron (L)$_2$M(R)$^+$ cations, and the tuning of the metal coordination environment by systematic steric variation of donor L ligands continues to be a very fruitful area of investigation.

Our previous work has examined the chemistry of very electron-poor chelating perfluoroalkylphosphine (PFAP) group 10 systems, (dfepe)Pt(R)(X) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$).[3] Because of the remarkable resistance of Pt−alkyl bonds in these compounds to protonolysis, we have explored the chemistry of "(dfepe)Pt(R)$^+$" under aprotic as well as acidic and superacidic conditions. More recently we have reported the synthesis of nonchelating analogues based on $(C_2F_5)_2$PMe ("dfmp"), which exhibit a broader range of reactivity due to phosphine labilization and the availability of both cis and trans (PFAP)$_2$M geometries.[4] *trans*-(dfmp)$_2$Pt(Me)(X) compounds are particularly interesting due to significant trans X ligand effects. In this paper we present an extension of this work that explores the reactivity of *trans*-(dfmp)$_2$Pt(Me)(X) toward CO and H_2 and is an informative comparison to the corresponding (dfepe)Pt(Me)(X) chemistry. Of particular importance is the observation of reductive carbonylation from *trans*-[(dfmp)$_2$Pt(Me)(CO)]$^+$X$^-$ under moderate pressures of CO to cleanly produce MeC(O)X anhydride products.

Results and Discussion

Reactions of *trans*-(dfmp)$_2$Pt(Me)(X) Complexes (X = O_2CCF_3 (1), X = OTf (2), X = OSO_2F (3)) with CO. The syntheses of **1**, **2**, and **3** have been described previously.[4] Complex **1** cannot be isolated because of phosphine ligand loss and subsequent dimerization via acetate bridges. Complexes **2** and **3**, however, are readily isolated. Reaction of **1** with 1 atm of CO in neat trifluoroacetic acid does not result in displacement of the trifluoroacetate ligand by CO, but rather in clean displacement of one dfmp ligand to form the mixed phosphine/carbonyl complex, (dfmp)(CO)Pt(Me)(O_2CCF_3) (**4**). Consistent with *J* trends noted in prior square-planar platinum systems,[4,11]

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[3] (a) Kalberer, E. W.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2004**, *23*, 4112−4115. (b) Kalberer, E. W.; Roddick, D. M. *Organometallics* **2004**, *23*, 4209−4212. (c) White, S.; Kalberer, E. W.; Bennett, B. L.; Roddick, D. M. *Organometallics* **2001**, *20*, 5731. (d) White, S.; Bennett, B. L.; Roddick, D. M. *Organometallics* **1999**, *18*, 2536. (e) Houlis, J. F.; Roddick, D. M. *J. Am. Chem. Soc.* **1998**, *120*, 11020. (f) Peters, R. G.; Bennett, B. L.; Roddick, D. M. *Inorg. Chim. Acta* **1997**, *265*, 205. (g) Bennett, B. L.; Roddick, D. M. *Inorg. Chem.* **1996**, *35*, 4703.

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[6] We have previously reported the isolation of (dfmp)$_4$Pt.[4] When (dfmp)$_4$Pt is recrystallized or (dfmp)$_x$Pt is formed in the absence of excess free phosphine, (dfmp)$_3$Pt is the dominant product. Butikofer, J. L.; Roddick, D. M. Unpublished results.

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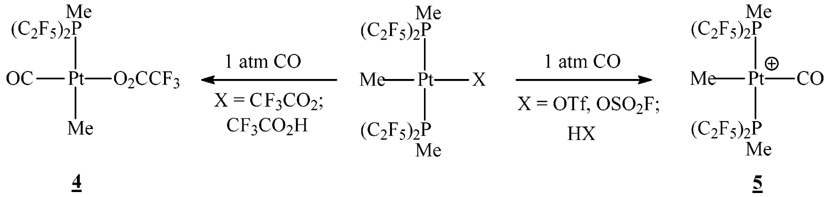
10.1021/om060847p CCC: $33.50

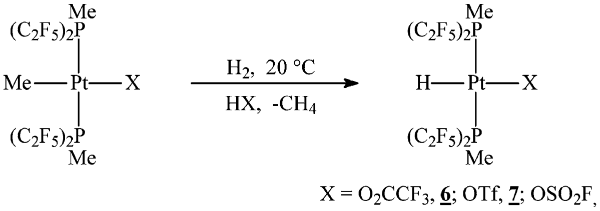
Scheme 1



The low Pt−P coupling observed ($^1J_{PtP}$ = 1230 Hz) clearly indicates that the remaining dfmp ligand is trans to the methyl group; substantially higher $^1J_{PtP}$ values are generally observed in related systems with trans phosphine (∼3800 Hz)[4] and CO (∼3200 Hz).[3e] Exposure of **1** to 200 psi of CO in trifluoroacetic acid resulted in displacement of the remaining dfmp ligand and decomposition of the metal complex. The carbonyl stretching frequency observed for **4** (ν(CO) = 2128 cm^{-1}) falls between that found for (dfepe)Pt(CO) (2044 cm^{-1})[3g] and (dfepe)Pt(Me)(CO)$^+$ (2174 cm^{-1}) and is indicative of the low degree of available π-backbonding in these systems.[3e]

In contrast to **1**, the triflate and fluorosulfonate derivatives **2** and **3** react with 1 atm of CO in their respective neat acid solutions at ambient temperatures to form the corresponding anion displacement products, *trans*-[(dfmp)$_2$Pt(Me)(CO)]$^+$ (**5**) (Scheme 1), due to the higher lability of these anions in conjugate acid media. Similar reactivity has been observed for labile (dfepe)Pt(Me)(X) systems.[3e] A small but significant amount (∼10%) of *trans*-(dfmp)$_2$Pt(H)(CO)$^+$ is also formed in HOTf and FSO$_3$H (see later). Exposure of aprotic solutions of **2** to CO resulted in dfmp loss and decomposition. All attempts to isolate the methyl carbonyl cation **5** by the removal of HOTf under vacuum resulted in an oily residue, which, when taken up in aprotic solvents such as ether, reverted entirely back to the methyl triflate complex **2**. Fluorosulfonic acid solutions of **5** exhibit a CO stretch of 2149 cm^{-1}, which is somewhat lower than that of (dfepe)Pt(Me)(CO)$^+$ (2174 cm^{-1}).

Synthesis and Characterization of *trans*-(dfmp)$_2$Pt(H)(X) Systems. Methyl complexes *trans*-(dfmp)$_2$Pt(Me)(X) react cleanly with 1 atm of H$_2$ in their respective neat acid solutions at ambient temperature to form *trans*-(dfmp)$_2$Pt(H)(X) (X = O$_2$CCF$_3$, **6**; OTf, **7**; OSO$_2$F, **8**) (eq 1). This reactivity differs from (dfepe)Pt(Me)(X) chelate systems, which under analogous conditions form the protonated hydride-bridged dimer {[(dfepe)Pt(μ-H)]$_2$(H)}$^+$.[3g,5] The hydrido trifluoroacetate complex **6** eliminates CF$_3$CO$_2$H when redissolved in benzene to give the Pt(0) disproportionation product, (dfmp)$_3$Pt.[6] In contrast, **7** is stable to acid loss in aprotic solvents and can be isolated as a crystalline solid. Variable-temperature NMR studies of **3** in FSO$_3$H under 1 atm of H$_2$ did not reveal hydrogenation intermediates. However, low-temperature NMR hydrogen adduct studies with *trans*-(dfmp)$_2$Pt(Me)$^+$ in superacidic HF/SbF$_5$ media support the intermediacy of *trans*-(dfmp)$_2$Pt(Me)(η^2-H$_2$)$^+$.[7]



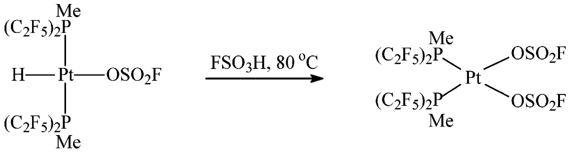
(1)

Spectroscopic data for dfmp platinum hydride complexes in their respective neat acids are presented in Table 1. Chatt and Shaw have noted a decrease in ν(PtH) and an increase in δ(Pt−H) as the donor ability of the X ligand increases.[8,9] Similarly, Green has reported a series of carboxylato complexes where ν(Pt−H) and the hydride chemical shift decrease as the pK_a of the parent carboxylic acid increases.[10] These trends correlate with the donor ability of the trans ligand in *trans*-(R$_3$P)$_2$Pt(H)(X) systems and are also manifested for complexes **6**−**8**.

Table 1. Spectroscopic Data for dfmp Platinum Hydride Complexes

complex	$^1J_{PtH}$ (Hz)	δ(PtH) (ppm)	ν(PtH) (cm^{-1})
trans-(dfmp)$_2$Pt(H)(O$_2$CCF$_3$) (**6**)	1040	−22.14	
trans-(dfmp)$_2$Pt(H)(OTf) (**7**)	1382	−26.32	2292
trans-(dfmp)$_2$Pt(H)(OSO$_2$F) (**8**)	1410	−26.87	
trans-(dfmp)$_2$Pt(H)(CO)$^+$OTf$^-$ (**9**)	700	−8.21	2212
(dfmp)$_3$Pt(H)$^+$OTf$^-$ (**10**)	625	−8.24	

The thermal stability of hydride complexes **7** and **8** in their respective neat acid solutions was also monitored by NMR. *trans*-(dfmp)$_2$Pt(H)(OTf) is extremely stable in HOTf, with no *cis*-(dfmp)$_2$Pt(OTf)$_2$ being observed after several weeks at 100 °C. Complex **7** is similarly stable in benzene: heating to 100 °C for 19 h induced only a slight conversion (7%) to (dfmp)$_3$Pt, while heating for 20.5 h at 120 °C produced a mixture of 8% (dfmp)$_3$Pt, 38% unreacted **7**, and 54% free dfmp. In contrast, fluorosulfonic acid solutions of **8** convert primarily (∼90%) to *cis*-(dfmp)$_2$Pt(OSO$_2$F)$_2$ at 80 °C (∼75% conversion after 2 h) (eq 2).



8
(2)

As noted in our previous work,[11,12] the incorporation of perfluoroalkylated phosphines (PFAPs) into the coordination sphere of Pt(II) complexes imparts significant structural changes relative to donor phosphine systems. *trans*-PFAP systems provide an additional structural comparison to *cis*-(dfepe)Pt(II) complexes as well as trans-donor phosphine systems. The molecular structure of **7** has been determined and is shown in Figure 1. The platinum coordination environment is essentially square planar with a maximum deviation from planarity of 0.047 Å. The hydride ligand was not located; O(1)−Pt(1)−P(1) and O(1)−Pt(1)−P(2) angles are only slightly greater than 90° and are displaced away from the triflate ligand. The dfmp ligand methyl groups are in the complex square plane and are syn with respect to the triflate ligand. This orientation minimizes the steric interactions between the triflate and the C$_2$F$_5$ groups, but may also reflect a preferred geometry for optimal π-acceptance by the dfmp ligands.[4]

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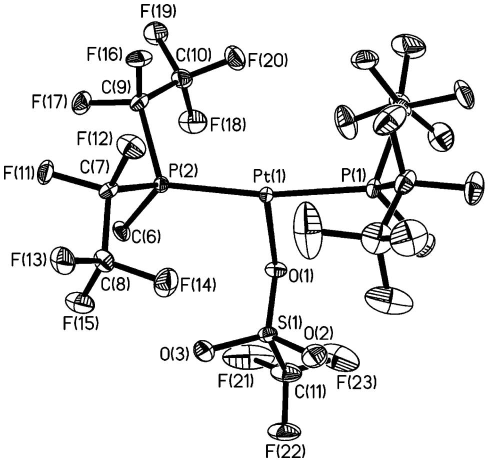


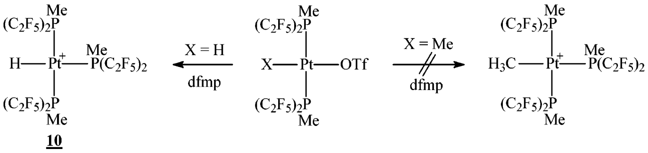
Figure 1. Molecular structure of *trans*-(dfmp)$_2$Pt(H)(OTf) (**7**) with atom-labeling scheme (30% probability ellipsoids). The hydrogen positions were unrefined and are omitted for clarity. Selected metrical data: Pt(1)−P(1) 2.2749(12); Pt(1)−P(2) 2.2590(11); Pt(1)−O(1) 2.179(3); P(1)−Pt(1)−P(2) 170.37(4); O(1)−Pt(1)−P(1) 93.42(10); O(1)−Pt(1)−P(2) 95.48(10).

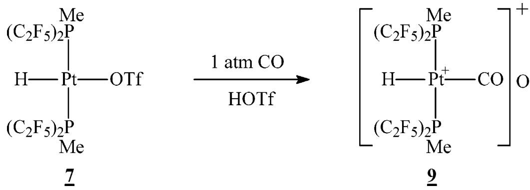
The 2.2749(12) and 2.2590(11) Å Pt−P bond lengths observed for **7** are nearly identical to those reported for *cis*-(dfmp)$_2$Pt(Me)$_2$ (2.270(2) and 2.261(2) Å) despite the bond lengthening expected in the latter complex due to the methyl trans influence.[4] When compared to analogous trans-donor phosphine systems, the observed Pt−P bond distances for **7** are comparable to those of *trans*-(Et$_3$P)$_2$Pt(H)(OPh) (2.261(3) and 2.282(3) Å),[13] *trans*-(Ph$_3$P)$_2$Pt(H)(OPh) (2.257(3) and 2.271(3) Å),[14] and (CH$_3$P)$_3$Pt(H)$^+$(BPh$_4$)$^-$ (2.287(2) and (2.294(2) Å)[15] and shorter than those of *trans*-(^{i}Pr$_3$P)$_2$Pt(H)(THF)$^+$(BAr$^f{}_4$)$^-$ (2.304(3) and 2.310(3) Å) (Ar^f = 3,5-bis(trifluoromethyl)phenyl).[16]

To our knowledge, no other Pt(II) complex with a triflate trans to a hydride has been structurally characterized. The cis complex (dbpp)Pt(H)(OTf) (dbpp = ^{t}Bu$_2$P(CH$_2$)$_3$P^{t}Bu$_2$) has been reported, and the Pt−O bond distances for the two compounds are comparable (2.179(3) Å for **7**, 2.181(9) Å for (dbpp)Pt(H)(OTf)).[17] Other cis-donor phosphine Pt(OTf) complexes exhibit shorter Pt−O bond lengths (2.120(2) to 2.142(4) Å).[18] The Pt−O bond in *cis*-(dfepe)Pt(Me)(OTf) is much shorter (2.090(6) Å) due to the greater trans influence of hydride relative to a PFAP ligand.[11]

Reaction of *trans*-(dfmp)$_2$Pt(H)(OTf) (7) with CO. Triflic acid solutions of **7** react with 1 atm of CO to produce *trans*-(dfmp)$_2$Pt(H)(CO)$^+$(OTf)$^-$ (**9**) (eq 3). The observed CO stretch for **9** (2131 cm^{-1}) is lower than that observed for the methyl carbonyl cation **5** (2149 cm^{-1}). This relative ordering for methyl- and hydride-substituted carbonyl complex ν(CO) values has been reported for *trans*-(R$_3$P)$_2$Pt(R)(CO)$^+$ complexes (R = H, CH$_3$).[19] Attempts to isolate **9** by removal of volatiles followed by dissolution of the residue in aprotic solvents such as 1,2-difluorobenzene resulted in regeneration of **7**. When trifluoroacetic acid solutions of the hydrido trifluoroacetate complex **6** were placed under 1 atm of CO, mixtures of unidentified products and free dfmp were observed.

Scheme 2





(3)

Reaction of *trans*-(dfmp)$_2$Pt(H)(OTf) with dfmp. Triflic acid solutions of **7** also react readily with 1 equiv of dfmp to produce (dfmp)$_3$Pt(H)$^+$(OTf)$^-$ (**10**) (Scheme 2). ^{31}P NMR data exhibit two resonances in a 2:1 ratio at 39.2 ppm ($^1J_{PtP}$ = 3210 Hz) and 37.6 ppm ($^1J_{PtP}$ = 2200 Hz), respectively. The hydride appears as a broadened doublet at −8.24 ppm ($^2J_{PH}$ = 170 Hz); although cis $^2J_{PH}$ in related (R$_3$P)$_3$Pt(H)$^+$ systems are typically 10−20 Hz,[20] cis coupling was not resolved for **10** (<5 Hz). This may be due to either an anomalously small cis $^2J_{PH}$ or preferential fast exchange of the cis phosphines with traces of free dfmp.[21] Attempts to isolate **10** by removal of HOTf under vacuum resulted in regeneration of complex **7** from loss of dfmp. Reaction of **7** with excess dfmp in C$_6$D$_6$ afforded a mixture of **10** and (dfmp)$_4$Pt. In contrast to hydride complex **7**, *trans*-(dfmp)$_2$Pt(Me)(OTf) does not react with dfmp in HOTf. dfmp is not protonated to any significant extent in this solvent. The complex (Ph$_3$P)$_3$Pt(Me)$^+$(OSO$_2$F)$^-$ has been reported,[22] so it is likely that the formation of (dfmp)$_3$Pt(Me)$^+$ is not prohibited on steric grounds (cone angles: Ph$_3$P = 145°, dfmp = 139°).[23]

Reductive Carbonylation of *trans*-(dfmp)$_2$Pt(Me)(X). As noted previously, small amounts (<10%) of [*trans*-(dfmp)$_2$Pt(H)(CO)]$^+$ were observed at room temperature when *trans*-(dfmp)$_2$Pt(Me)(X) complexes were treated with 1 atm of CO in HX solutions. Exposure of [*trans*-(dfmp)$_2$Pt(Me)(CO)]$^+$ to 1000 psi of CO resulted in complete conversion to the hydride carbonyl complex **9** after 12 h at room temperature (eq 4). Direct reductive elimination products MeX were not observed. However, new ^{1}H methyl resonances appeared at δ 3.14 (HOTf solvent; ^{13}C NMR: δ 7.74 (q, $^1J_{CH}$ = 147 Hz)) and 3.11 (FSO$_3$H solvent), which we have assigned to the mixed anhydrides CH$_3$C(O)OTf and CH$_3$C(O)OSO$_2$F.[24] Mixed anhydride products are most likely derived from either isomerization of **5** to a cis

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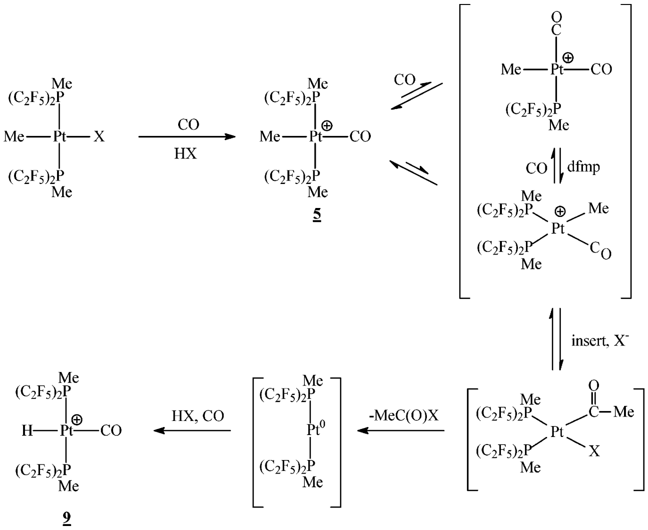
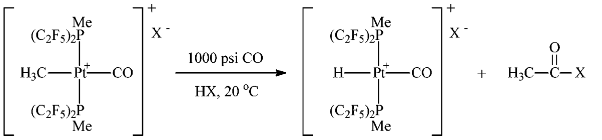
(24) The yield of anhydrides based on integration with respect to the product dfmp methyl resonance varies from 70 to 90%. A spectroscopic reference sample of CH$_3$C(O)OTf was prepared by the addition of acetic anhydride to triflic acid. (a) Germain, A.; Commeyras, A.; Casadevall, A. *Bull. Soc. Chim. Fr.* **1973**, 2527. (b) Germain, A.; Commeyras, A. *J. Chem. Soc., Chem. Commun.* **1972**, *24*, 1345.

Scheme 3

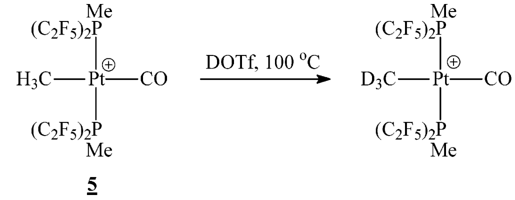


methyl carbonyl complex or substitution of one dfmp by CO, followed by CO migratory insertion, reductive elimination, and then addition of HX and CO (Scheme 3).[25] ^{31}P NMR spectra immediately after CO addition show a ~5 ppm upfield shift from *trans*-$(dfmp)_2Pt(Me)(X)$ to a very broad resonance at 34 ppm ($\Delta\nu_{1/2}$ ~800 Hz) without resolved $^1J_{PtP}$, which is consistent with rapid CO/dfmp ligand exchange. The generally greater propensity for acyl relative to alkyl reductive elimination would favor anhydride products over MeX.[26]



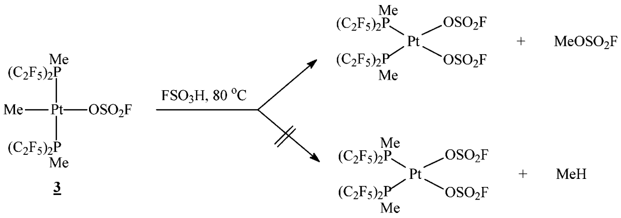
(4)

In the absence of added CO, thermal conversion is significantly slower: the methyl carbonyl complex **5** in HOTf under N_2 at 100 °C forms a 3:1 mixture of *trans*-$(dfmp)_2Pt(H)(CO)^+$ and *trans*-$(dfmp)_2Pt(H)(OTf)$ (47% conversion after 355 h). No *trans*-$(dfmp)_2Pt(OTf)_2$ was observed. Warming **5** in neat DOTf to 100 °C resulted in deuteration of the methyl group prior to formation of *trans*-$(dfmp)_2Pt(D)(OTf)$ (eq 5): after 156 h the extent of deuterium incorporation into **5** was 96%, while the reaction was only 14% completed. As in our previous thermolysis study with *trans*-$(dfmp)_2Pt(Me)(X)$,[4] we ascribe deuterium incorporation into **5** prior to Pt−methyl cleavage to the reversible formation of a methane complex intermediate. Thermolysis of *trans*-$(dfmp)_2Pt(Me)(CO)^+$ in FSO_3H resulted in the formation of a new unidentified platinum product with a ^{31}P resonance at 44.3 ppm (~20% after 2 h). After 16.5 h, the primary identified product (~70%) was *cis*-$(dfmp)_2Pt(OSO_2F)_2$.



(5)

Protonolysis of *trans*-$(dfmp)_2Pt(Me)(OSO_2F)$ Revisited. Our initial report of dfmp platinum chemistry described a notable trans ligand effect on *trans*-$(dfmp)_2Pt(Me)(X)$ protonolysis rates, with X = OTf and OSO_2F systems being substantially more resistant to protonolysis than the corresponding chelating (dfepe)Pt(Me)(X) analogues.[4] The loss of platinum-bound methyl groups (described above) via a mechanism other than protonolysis is unprecedented in our prior neat acid work[3c,11,27] and has prompted a closer examination of the thermal products from *trans*-$(dfmp)_2Pt(Me)(X)$. The clean loss of methane as the sole organic product from *trans*-$(dfmp)_2Pt(Me)(X)$ in HX (X = O_2CCF_3, OTf) has been confirmed by ^{1}H NMR. However, thermolysis of *trans*-$(dfmp)_2Pt(Me)(OSO_2F)$ does *not* produce methane, but rather $MeOSO_2F$ as the only (~95%) organic product (eq 6).[28]



(6)

The formation of $MeOSO_2F$ along with *cis*-$(dfmp)_2Pt(OSO_2F)_2$ is consistent with a reductive elimination mechanism (Scheme 4). A number of Pt(IV) systems have been reported that undergo reductive elimination to form RX products. In these systems, stereochemical and/or kinetic evidence supports an S_N2 mechanism involving external anion attack on the platinum-bound methyl group.[29,30] We have previously observed non-first-order behavior for the thermolysis of *trans*-$(dfmp)_2Pt(Me)(OSO_2F)$ in FSO_3H.[4] In the presence of added FSO_3^-, we find that the reaction remains non-first-order and that there is no significant kinetic effect (Figure 2). The lack of a $[FSO_3^-]$ kinetic independence does not support direct S_N2 attack of FSO_3^- on four-coordinate *trans*-$(dfmp)_2Pt(Me)(OSO_2F)$ as a reaction pathway and is consistent with either prior dissociation of coordinated FSO_3^- followed by S_N2 attack at the platinum-bound methyl or a concerted intramolecular reductive elimination. A concerted elimination could occur either directly from an isomerized *cis*-$(dfmp)_2Pt(Me)(OSO_2F)$ intermediate or from three-coordinate (dfmp)Pt(Me)(OSO_2F). The kinetic dependence on added dfmp cannot be determined under the reaction conditions,[31] but we have observed that ethane reductive elimination from *cis*-$(dfmp)_2Pt(Me)_2$ is inhibited by added dfmp under aprotic conditions,[4] and therefore we favor a three-coordinate elimination mechanism. A possible explanation for the acceleration with time observed in Figure 2 is that the *cis*-$(dfmp)_2Pt(OSO_2F)_2$ product autocatalyzes the formation of a

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(25) Elimination of product from *cis*-$(dfmp)_2Pt(X)(C(O)Me)^+$ is shown in Scheme 3; however *cis*-(CO)(dfmp)Pt(X)$(C(O)Me)^+$ is also a viable intermediate.

(26) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley and Sons: Hoboken, NJ, 2005; p 175.

(27) Bennett, B. L.; Hoerter, J. M.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2000**, *19*, 615.

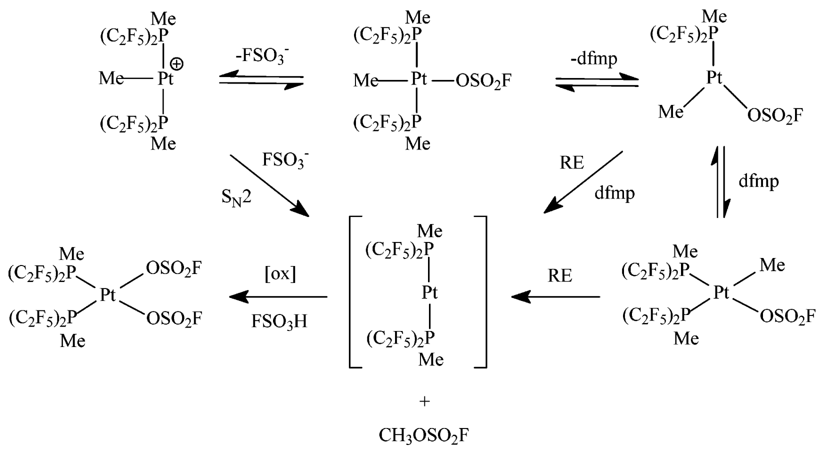
(28) NMR data for CH_3OSO_2F: δ 3.44 (^{1}H), δ 61.4 (q, $^1J_{CH} = 155$ Hz): McGarrity, J. F.; Cox, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 3961.

(29) (a) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75. (b) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004.

(30) (a) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576. (b) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (c) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82. (d) Romero, P.; Valderrama, M.; Contreras, R.; Boys, D. *J. Organomet. Chem.* **2003**, *673*, 102.

(31) Free dfmp in FSO_3H is stable for several hours at ambient temperatures, but when heated to 80 °C converts to a new species (^{31}P NMR: δ 52.2 (p, $^2J_{PF} = 88$ Hz); ^{1}H NMR: δ 1.65 (d, $^2J_{PH} = 16$ Hz)), which we tentatively assign as the phosphine oxide $(C_2F_5)_2P(Me)(O)$.

Scheme 4



three-coordinate reductive elimination intermediate reaction by serving as a "phosphine sponge".[32]

The mechanism outlined in Scheme 4 produces (dfmp)$_2$Pt(0) as the penultimate product, followed by oxidation to form *cis*-(dfmp)$_2$Pt(OSO$_2$F)$_2$. Consistent with this scheme, the thermolysis of (dfmp)$_3$Pt in FSO$_3$H at 80 °C does cleanly produce *cis*-(dfmp)$_2$Pt(OSO$_2$F)$_2$ at a rate qualitatively comparable to the thermal conversion of *trans*-(dfmp)$_2$Pt(Me)(OSO$_2$F) to *cis*-(dfmp)$_2$Pt(OSO$_2$F)$_2$. This conversion may involve successive protonation steps (cf. eq 2) and loss of H$_2$ from a (dfmp)$_2$Pt(η^2-H$_2$)(OSO$_2$F)$^+$ intermediate, or the direct oxidation of Pt(0) by FSO$_3$H. We were unable to observe free H$_2$ under these reaction conditions.

Summary

The reactivity patterns exhibited by (dfmp)$_2$Pt(II) complexes reveal several significant features. First, the potential for PFAP substitution chemistry is dependent on anionic ligand labilities in their respective neat acid solvents, with dfmp substitution by CO preferred when X = O$_2$CCF$_3$ but not when X = OTf or OSO$_2$F. Further substitution of carbonyl cationic adducts by CO most likely plays an important role in reductive carbonylation (Scheme 3). We note that complete and reversible dfmp substitution to form *cis*-(dfmp)(CO)Pt(Me)$_2$ and (CO)$_2$Pt(Me)$_2$ is found for *cis*-(dfmp)$_2$Pt(Me)$_2$,[4] so CO-substituted intermediates in Scheme 3 should also be accessible under higher pressures of CO.

Second, for *trans*-(dfmp)$_2$Pt(Me)(X) there is a surprising transition from Pt−C bond protonolysis to MeX reductive elimination for X = FSO$_3^-$ or, in the presence of added CO, MeC(O)OTf elimination for X = OTf$^-$ and OSO$_2$F. The only reported examples of MeX elimination to date for platinum have been for Pt(IV) systems. The propensity for the electron-poor Pt(II) system *trans*-(dfmp)$_2$Pt(Me)(OSO$_2$F) to undergo reductive elimination is thus more reminiscent of established Pd(II) and Ni(II) chemistry. The sharp changeover in reactivity going from HX = HOTf ($H_0 = -14.1$) to FSO$_3$H ($H_0 = -15.1$) is intriguing and warrants further investigation.[33] This transition in reactivity has intriguing implications for the microscopic reverse of protonolysis, electrophilic alkane activation. A key step in Shilov-type alkane functionalization is S$_N$2 displacement of coordinated alkyl from a Pt(IV) intermediate.[34] The present work demonstrates that RX reductive elimination from Pt(II) systems can be competitive even under highly electrophilic/protic conditions, which sustain cationic metal centers with the potential for alkane activation, and that a Pt(II)/Pt(0) alkane functionalization cycle may also be possible.

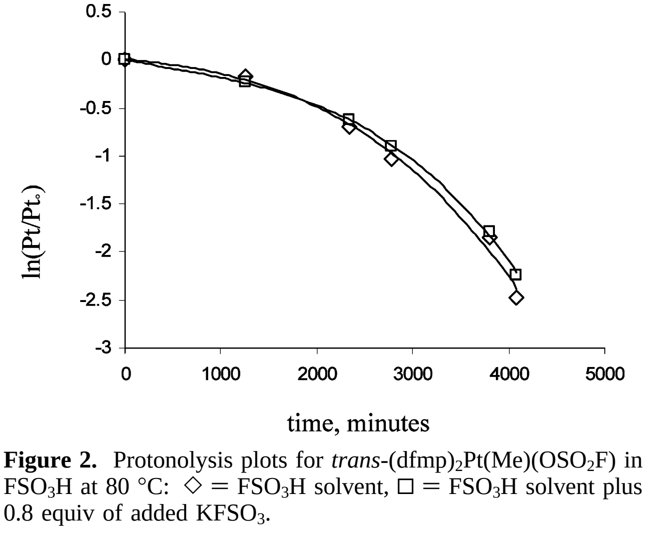


Figure 2. Protonolysis plots for *trans*-(dfmp)$_2$Pt(Me)(OSO$_2$F) in FSO$_3$H at 80 °C: ◇ = FSO$_3$H solvent, □ = FSO$_3$H solvent plus 0.8 equiv of added KFSO$_3$.

Experimental Section

General Procedures. All manipulations were conducted under N$_2$ or vacuum using high-vacuum line and glovebox techniques. All ambient pressure chemistry was carried out under a 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$_3$CO$_2$H and CF$_3$CO$_2$D were dried over activated 3 Å molecular sieves. DOTf was prepared from the reaction of excess triflic anhydride with D$_2$O; DOTf, HOTf, and FSO$_3$H were distilled prior to use and stored under nitrogen. 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$_3$PO$_4$ 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. *cis*-(dfmp)PtMe$_2$ was prepared as described previously.[4]

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(32) A reviewer has suggested that dimerization of intermediate Pt(0) species with Pt(II) centers could facilitate cis/trans isomerization via an associative process and also might account for the non-first-order kinetic behavior observed.

(33) Unlike triflic acid, fluorosulfonic acid can serve as an oxidant and trap the (dfmp)$_2$Pt(0) intermediate produced in Scheme 4. However, he resulting stoichiometric formation of H$_2$O in this redox process is very difficult to discern in neat acid media.

(34) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.

(dfmp)(CO)Pt(Me)(O_2CCF_3) (4). A 5 mm NMR tube fitted with a Teflon valve was charged with approximately 20 mg of *cis*-(dfmp)$_2$Pt(Me)$_2$ dissolved in 0.4 mL of trifluoroacetic acid, and the solution was placed under 1 atm of CO. After 1 h complete displacement of dfmp was confirmed by NMR. Removal of volatiles gave **4** as colorless oil, which was unstable under prolonged exposure to vacuum. IR (neat oil, cm^{-1}): ν = 2128 (vs), 1294 (s), 1216 (s), 1139 (m), 969 (w). ^{1}H NMR (400 MHz, CF_3CO_2H, 27 °C): δ 1.46 (d, $^{2}J_{PH}$ = 8 Hz, 3H; P(CH$_3$)), 0.83 (d, $^{2}J_{PtH}$ = 55 Hz, $^{3}J_{PH}$ = 8 Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, CF_3CO_2H, 27 °C): δ 51.9 (p, $^{1}J_{PtP}$ = 1230 Hz, $^{2}J_{PF}$ = 62 Hz). ^{1}H NMR (400 MHz, C_6D_6, 27 °C): δ 1.37 (d, $^{2}J_{PH}$ = 8 Hz, 3H; P(CH$_3$)), 1.22 (d, $_{2}J_{PtH}$ = 55 Hz, $^{3}J_{PH}$ = 8 Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, C_6D_6, 27 °C): δ 52.0 (p, $^{1}J_{PtP}$ = 1200 Hz, $^{2}J_{PF}$ = 61 Hz).

***trans*-(dfmp)$_2$Pt(Me)(CO)$^+$ (5).** *trans*-(dfmp)$_2$Pt(Me)(CO)$^+$ (**5**) was generated by dissolution of *cis*-(dfmp)$_2$Pt(Me)$_2$ in either HOTf or FSO_3H to generate **2** and **3**, respectively, followed by treatment with 1 atm of CO. Anion displacement by CO was complete after 1 h, as judged by NMR. Attempts to isolate **5** from HOTf by removal of volatiles followed by precipitation from ether resulted in complete conversion back to **2**. Spectroscopy for **5** in HOTf: ^{1}H NMR (400 MHz, HOTf, 23.2 °C): δ 1.56 (br s, $^{3}J_{PtH}$ = 36 Hz, 6H; P(CH$_3$)), 0.33 (t, $^{2}J_{PtH}$ = 58 Hz, $^{3}J_{PH}$ = 8 Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, HOTf, 23.2 °C): δ 37.4 (m, $^{1}J_{PtP}$ = 3220 Hz). Spectroscopy for **5** in FSO_3H: IR (FSO_3H, cm^{-1}): ν(CO) = 2149. ^{1}H NMR (400 MHz, FSO_3H, 23.2 °C): δ 1.56 (br s, $^{3}J_{PtH}$ = 41 Hz, 6H; P(CH$_3$)), 0.33 (t, $^{2}J_{PtH}$ = 58 Hz, $^{3}J_{PH}$ = 9 Hz, 3H; Pt(CH$_3$)). ^{31}P NMR (161.7 MHz, FSO_3H, 23.2 °C): δ 37.5 (m, $^{1}J_{PtP}$ = 3220 Hz). ^{13}C NMR (100.6 MHz, FSO_3H, 27 °C): δ 122−113 (overlapping CF_2CF_3 resonances), 0.7 (q, $^{1}J_{CH}$ = 139 Hz; P(CH$_3$)), −4.6 (q, $^{1}J_{CH}$ = 135 Hz; Pt(CH$_3$)).

***trans*-(dfmp)$_2$Pt(H)(O_2CCF_3) (6).** Complex **6** was generated by dissolution of *cis*-(dfmp)$_2$Pt(Me)$_2$ in CF_3CO_2H to generate **1** followed by placement of this solution under 1 atm of H_2. Product formation was complete after 24 h, as judged by NMR. Attempts to observe **6** under aprotic conditions by removal of volatiles followed by redissolution in C_6D_6 resulted in formation of (dfmp)$_3$Pt. ^{1}H NMR (400 MHz, CF_3CO_2H, 27 °C): δ 1.56 (br m, 6H; P(CH$_3$)), −22.14 (t, $^{1}J_{PtH}$ = 1040 Hz, $^{2}J_{PH}$ = 14 Hz, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, CF_3CO_2H, 27 °C): δ 43.5 (m, $^{1}J_{PtP}$ = 3580 Hz).

***trans*-(dfmp)$_2$Pt(H)(OTf) (7).** A mixture of 351 mg (0.443 mmol) of *cis*-(dfmp)$_2$Pt(Me)$_2$ in ca. 5 mL of HOTf was stirred for 15 min and was then placed under 1 atm of H_2. The solution was stirred for 2 h, and all volatiles were removed. The solid residue was dissolved in 10 mL of diethyl ether and then precipitated at −78 °C and cold filtered to give 332 mg of an off-white solid (82%) that was contaminated by 0.3 equiv of triflic acid. Reprecipitation from ether yielded acid-free product. NOTE: since complex **7** decomposes in ether at ambient temperatures, the precipitation step must be carried out quickly. Anal. Calcd for $C_{11}H_7F_{23}O_3P_2PtS$: C, 14.47; H, 0.77. Found: C, 14.73; H, 0.69. IR (Nujol, cm^{-1}): 3023 (m), 2292 (w), 1414 (w), 1298 (s), 1217 (s, br), 1143 (s, br), 976 (s, br), 892 (s, br), 752 (s), 651 (m), 614 (m). ^{1}H NMR (400 MHz, C_6D_6, 23.2 °C): δ 1.75 (m, 6H; P(CH$_3$)), −22.88 (t, $^{1}J_{PtH}$ = 1170 Hz, $^{2}J_{PH}$ = 13 Hz, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, C_6D_6, 23.2 °C): δ 48.2 (m, $^{1}J_{PtP}$ = 3560 Hz). ^{1}H NMR (400 MHz, HOTf, 23.2 °C): δ 1.43 (br s, 6H; P(CH$_3$)), −26.32 (t, $^{1}J_{PtH}$ = 1382 Hz, $^{2}J_{PH}$ = 13 Hz, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, HOTf, 23.2 °C): δ 46.2 (m, $^{1}J_{PtP}$ = 3515 Hz).

***trans*-(dfmp)$_2$Pt(H)(OSO_2F) (8).** Complex **8** was generated by dissolution of *cis*-(dfmp)$_2$Pt(Me)$_2$ in FSO_3H to generate **3** followed by treatment of this solution with 1 atm of H_2. Formation of **8** was complete after 3 h, as judged by NMR. Isolation of **8** was not attempted. ^{1}H NMR (400 MHz, FSO_3H, 21.2 °C): δ 1.43 (br m, 6H; P(CH$_3$)), −26.87 (t, $^{1}J_{PtH}$ = 1410 Hz, $^{2}J_{PH}$ = 14 Hz, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, FSO_3H, 21.2 °C): δ 45.7 (m, $^{1}J_{PtP}$ = 3500 Hz).

Table 2. Crystallographic Data for *trans*-(dfmp)$_2$Pt(H)(OTf) (7)

chemical formula	$C_{11}H_7F_{23}O_3P_2PtS$
fw	913.26
space group	$P2_12_12_1$
a (Å)	9.9400(10)
b (Å)	11.8053(12)
c (Å)	21.397(2)
β (deg)	90
V (Å^3)	2510.9(4)
Z	4
λ (Å)	0.71073
T (°C)	−173
ρ_{calc} (g cm^{-3})	2.416
R_1 ($I > 2\sigma(I)$)	0.0289
R_1 (all data)	0.0301

***trans*-(dfmp)$_2$Pt(H)(CO)$^+$OTf$^-$ (9).** *trans*-(dfmp)$_2$Pt(H)(CO)$^+$-(OTf)$^-$ was generated by dissolution of **7** in HOTf followed by introduction of 1 atm of CO. Formation of **9** was complete after 2 h, as judged by NMR. Attempts to isolate **9** by removal of volatiles followed by dissolution in 1,2-difluorobenzene resulted in complete conversion back to **7**. IR (HOTf, cm^{-1}): ν(CO) = 2131 cm^{-1}; ν-(Pt−H) = 2211 cm^{-1}. ^{1}H NMR (400 MHz, HOTf, 23.2 °C): δ 1.80 (br m, 6H; P(CH$_3$)), −8.21 (t, $^{1}J_{PtH}$ = 700 Hz, $^{2}J_{PH}$ = 13 Hz, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, HOTf, 23.2 °C): δ 39.0 (m, $^{1}J_{PtP}$ = 3070 Hz).

(dfmp)$_3$Pt(H)$^+$(OTf)$^-$ (10). A 5 mm NMR tube fitted with a Teflon valve was charged with 26 mg (0.029 mmol) of **7**, which was then dissolved in 0.4 mL of HOTf. To the solution was added 11 μL of dfmp (0.058 mmol). After 20 min complete displacement of (OTf)$^-$ by dfmp was confirmed by NMR. Attempts to isolate **10** by removal of volatiles resulted in complete conversion back to **7**. ^{1}H NMR (400 MHz, HOTf, 21.2 °C): δ 1.71 (br m, 6H; P(CH$_3$)), 1.67 (br m, 3H; P(CH$_3$)), −8.24 (d, $^{1}J_{PtH}$ = 625 Hz, $^{2}J_{PH}$ = 170, 1H; Pt(H)). ^{31}P NMR (161.7 MHz, HOTf, 21.2 °C): δ 39.2 (m, $^{1}J_{PtP}$ = 3070 Hz, 2P; *trans*-dfmp), 37.6 (m, $^{1}J_{PtP}$ = 2200 Hz, 1P; *cis*-dfmp).

Crystal Structure of *trans*-(dfmp)$_2$Pt(H)(OTf) (7). Colorless prismatic crystals suitable for X-ray analysis were grown by slow cooling of a saturated hexanes solution to 4 °C. X-ray diffraction data for *trans*-(dfmp)$_2$Pt(H)(OTf) were collected on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator) (Table 2). A colorless rectangular prismatic crystal of approximate dimensions 0.30 mm × 0.28 mm × 0.20 mm in a glass capillary was used for data collection. A total of 5979 [R_{int} = 0.0444] independent reflections were gathered in the 2θ range of 3.94° to 56.66° with the data collected having $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-27 \leq l \leq 27$. Standard Bruker control (SMART) and integration (SAINT) software[35,36] were employed, and Bruker SHELXTL software[37] 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 the SADABS program.[38] The structure was solved by Patterson methods and refined (on F^2 using all data) by a full-matrix, weighted least-squares process.

The compound crystallizes in the orthorhombic space group, $P2_12_12_1$. All non-hydrogen atoms were located in the difference maps during successive cycles of least-squares and refined anisotropically. The two sets of methyl hydrogen atoms were placed in

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(35) *SMART* V. 5.631, Software for the CCD Detector System; Bruker AXS: Madison, WI, 1997.

(36) *SAINT-NT* V.5/6.0, Software for the CCD Detector System; Bruker AXS: Madison, WI, 1997.

(37) Sheldrick, G. M. *SHELXS97* and *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(38) Sheldrick, G. M. *SADABS*, A Program for Area Detector Absorption Corrections; University of Göttingen: Göttingen, Germany, 1966.

calculated positions and refined by a riding model. The hydrido H atom was neither located nor placed in a calculated position. The final refinement parameters were $R_1 = 0.0289$ and $wR_2 = 0.0687$ for data with $F > 4\sigma(F)$, giving a data to parameter ratio of 16. The refinement data for all data were $R_1 = 0.0301$ and $wR_2 = 0.0690$. The absolute configuration of the molecule is satisfactorily determined by refining the Flack parameter to 0.070(6).

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE-0457435) and the DOE-EPSCoR Lab Partnership Program (Grant DE-FG02-05ER46185).

Supporting Information Available: Complete tables of atomic coordinates, thermal parameters, and bond distances and angles for complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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