Electrophilic Platinum Complexes: Catalytic Reductive Elimination of Ethane from a Tetramethylplatinum(IV) Complex

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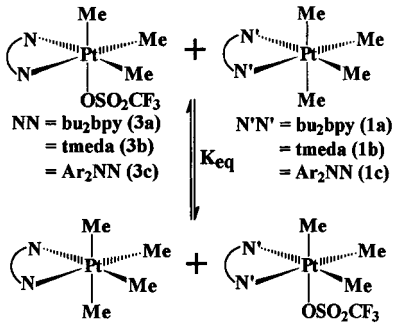
Summary: The reductive elimination of ethane from the thermally stable complex [PtMe$_4$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) is catalyzed by electrophiles such as [PtMe(O$_3$SCF$_3$)(dppe)] by a mechanism involving methyl group abstraction to give [PtMe$_3$(dppe)]$^+$, reductive elimination to give ethane and [PtMe(dppe)]$^+$, and then methyl group return to give [PtMe$_2$(dppe)]. The reactions give insight into potential C−C bond activation mechanisms.

The understanding of reactivity and mechanism in the reductive elimination of ethane from dimethyl complexes is of fundamental interest as a model for the reverse reaction, namely in understanding how the activation of C−C bonds by transition-metal complexes might be accomplished under mild conditions.[1−3] Previous studies of reductive elimination from octahedral methylplatinum(IV) complexes have established that ligand dissociation must precede the reductive elimination, so that complexes [PtMe$_3$XL$_2$] first undergo loss of X$^-$ or L (X = halide or methyl, L = phosphine) before ethane loss. If neither ligand X nor L can easily dissociate, the complexes are thermally stable.[1,2] The complex [PtMe$_4$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) is a good example of a stable complex: it undergoes thermal reductive elimination of ethane at over 100 °C in the solid state and is indefinitely stable at room temperature in solution.[4a,c] This article reports that the reductive-elimination reaction of ethane from this complex can be catalyzed by electrophilic platinum triflate (triflate = SO$_3$CF$_3^-$) complexes by a mechanism involving easy methyl group exchange as a key preliminary step.

Methyl ligand exchange reactions between the electron-rich [PtMe$_4$(N′N′)] (N′N′ = bu$_2$bpy (=4,4′-di-*tert*-butyl-2,2′-bipyridine) (**1a**), tmeda (=Me$_2$NCH$_2$CH$_2$NMe$_2$) (**1b**), Ar$_2$NN (=2,6-*i*-Pr$_2$C$_6$H$_3$N=CHCH=NC$_6$H$_3$-2,6-*i*-Pr$_2$) (**1c**))[4] and the electrophilic [PtMe$_3$(SO$_3$CF$_3$)(NN)] (NN = bu$_2$bpy (**3a**), tmeda (**3b**), Ar$_2$NN (**3c**))[5] occur easily at room temperature (Scheme 1). In these reactions, all platinum(IV) complexes are thermally stable and the reactions reach equilibrium within 1 min at room temperature; this is remarkable in view of the usual kinetic inertness of octahedral platinum(IV) complexes. The position of equilibrium depends on the nitrogen-donor ligand used, favoring [PtMe$_4$(NN)] (and hence disfavoring [PtMe$_3$(SO$_3$CF$_3$)(NN)]) in the same order as the π-accepting properties of the NN ligand; i.e., Ar$_2$NN >> bu$_2$bpy > tmeda.[6] The equilibrium constant (Scheme 1) K_{eq} = [**1b**][**3a**]/[**1a**][**3b**] = 3 × 10^{-2}, while reactions involving the Ar$_2$NN ligand gave equilibrium constants too high to be determined by NMR. It is likely that the reactions proceed by initial dissociation of the SO$_3$CF$_3$ ligand of [PtMe$_3$(SO$_3$CF$_3$)(NN)] to give the five-coordinate intermediate [PtMe$_3$(NN)]$^+$, which then attacks one of the highly nucleophilic mutually *trans* methylplatinum ligands of [PtMe$_4$(N′N′)] to give [PtMe$_3$(SO$_3$CF$_3$)(N′N′)] and [PtMe$_4$(NN)].[7] The presence of the weakly coordinating triflate ligand in complexes **1a**−**c** is essential, and for example, the analogous trifluoroacetato complexes [PtMe$_3$(O$_2$CCF$_3$)(NN)] (where O$_2$CCF$_3$ is a better ligand for platinum than SO$_3$CF$_3$) do not react with [PtMe$_4$(NN)]. The trend in equilibrium constants is readily understood in terms of the decreased nucleophilic character of the methylplatinum ligands of [PtMe$_4$(NN)] (and the increased electrophilic character of [PtMe$_3$(SO$_3$CF$_3$)(NN)]) with the increased π-accepting properties of the NN ligand.

Scheme 1



In an attempt to study the effect of changing the chelating ligand from an N donor to a P donor on the

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(1) Goldberg, K. I.; Yan, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

(2) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121.

(3) (a) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1996**, 2167. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(4) (a) Lashanizadehgan, M.; Rashidi, M.; Hux, J. E.; Puddephatt, R. J.; Ling, S. S. M. *J. Organomet. Chem.* **1984**, *269*, 317. (b) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (c) Goldberg, K. I. Personal communication. Complexes [PtMe$_4$(LL)] were prepared by reaction of [Pt$_2$Me$_8$(μ-SMe$_2$)$_2$][4a] and LL. LL = tmeda (**1b**), NMR in acetone-d_6: δ(^{1}H) −0.31 [s, 6H, ^2J(PtH) = 41 Hz, *trans* to Me]; 0.53 [s, 6H, ^2J(PtH) = 73 Hz, PtBMe *trans* to N]. LL = Ar$_2$NN (**1c**), NMR in acetone-d_6: δ(^{1}H) = −0.06 [s, 6H, ^2J(PtH) = 44 Hz, *trans* to Me]; 0.59 [s, 6H, ^2J(PtH) = 73 Hz, PtBMe *trans* to N].

(5) Complexes [PtMe$_3$(SO$_3$CF$_3$)(NN)] were prepared by reaction of [PtMe$_2$(NN)] with CH$_3$OSO$_2$CF$_3$.[4b] NN = tmeda (**3b**), NMR in acetone-d_6: δ(^{1}H) 0.96 [br s, 9H, ^2J(PtH) = 72 Hz, PtBMe]. NN = Ar$_2$NN (**3c**), NMR in acetone-d_6 (300.1 MHz): δ(^{1}H) 1.06 [br s, 9H, ^2J(PtH) = 74 Hz, PtBMe]. The broadness of the NMR signals is due to fluxionality involving intramolecular methyl group exchange within the five-coordinate intermediate formed by triflate dissociation (see also ref 11).

(6) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

(7) (a) Kondo, Y.; Ishikawa, M.; Ishihara, K. *Inorg. Chim. Acta* **1996**, *241*, 81. (b) Hux, J. E.; Puddephatt, R. J. *Inorg. Chim. Acta* **1985**, *100*, 1.

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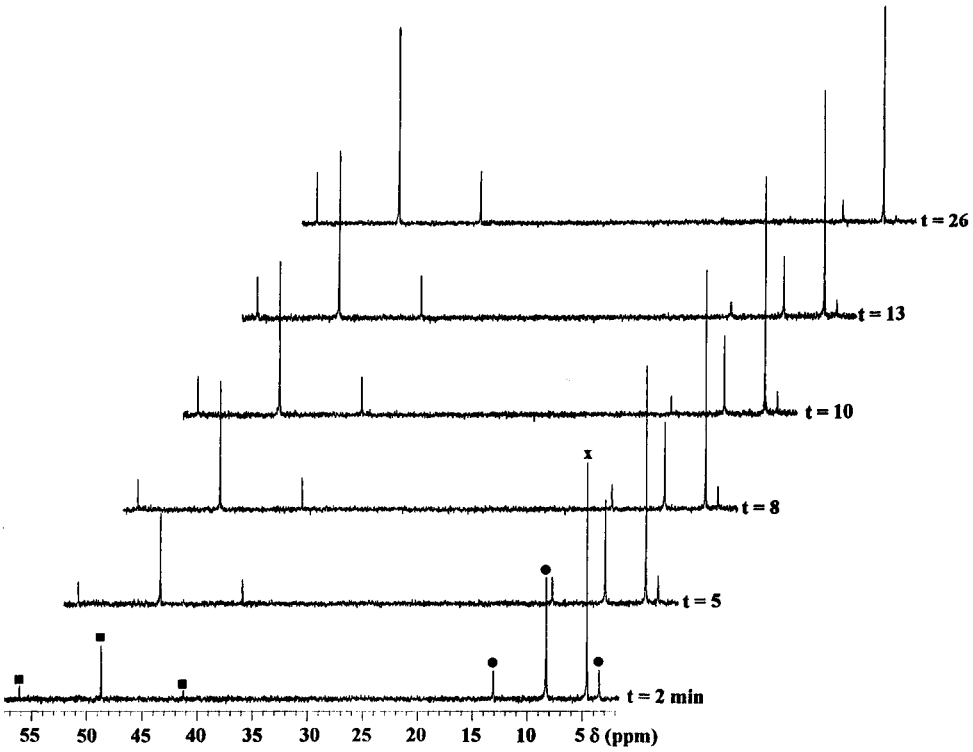


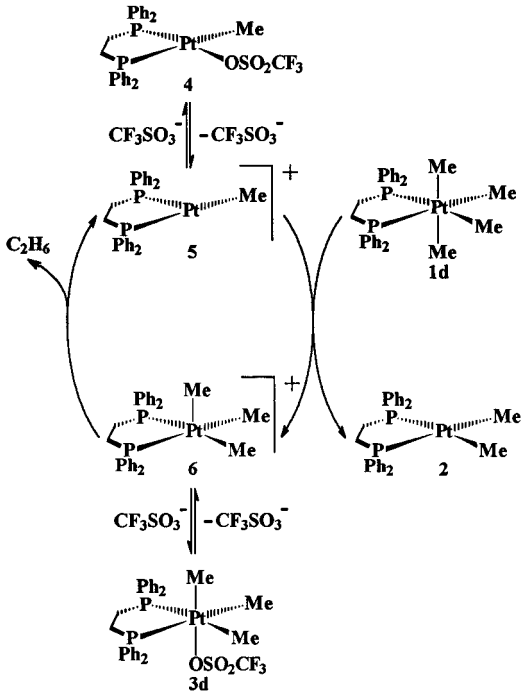
Figure 1. Selected $^{31}P\{^1H\}$ NMR spectra (acetone-d_6, 121.4 MHz, 22 °C) for the conversion of [$PtMe_4$(dppe)] (**1d**, ●) to [$PtMe_2$(dppe)] (**2**, ■) catalyzed by [$PtMe(SO_3CF_3)$(dppe)] (**4**). The resonances due to **4** are not visible due to the low concentration of **4** and the broadness of the peaks at 22 °C. The **x** denotes the resonances of the $OP(OMe)_3$ internal standard. $[\mathbf{1d}]_0 = 34$ mM, $[\mathbf{2}]_0 = 0$, and $[\mathbf{4}]_0 = 1.8$ mM.

reactions in Scheme 1, [$PtMe_4$(dppe)] (**1d**) was reacted with a stoichiometric amount of [$PtMe_3(SO_3CF_3)$(NN)] (NN = bu_2bpy (**3a**), tmeda (**3b**), Ar_2NN (**3c**)) in acetone-d_6 solution but, in place of the expected products, the reaction rapidly gave 1 equiv each of [$PtMe_2$(dppe)] (**2**), ethane, and unchanged [$PtMe_3(SO_3CF_3)$(NN)]. The reaction is truly catalytic in [$PtMe_3(SO_3CF_3)$(NN)] and can be very fast. For example, the reaction reaches completion (by ^1H and $^{31}P\{^1H\}$ NMR) within *ca.* 60 min with *ca.* 5 mol % catalyst and within seconds when reacted stoichiometrically.

Some insight into the mechanism was obtained by monitoring the reactions by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in acetone-d_6, using the catalyst in stoichiometric amount to facilitate detection of minor species. At room temperature, only the catalyst, starting complex **1d**, products **2**, and ethane were detected. However, at −70 °C, the complexes [$PtMe_4$(NN)] and [$PtMe_3(SO_3CF_3)$(dppe)] (**3d**) were also detected, the rate of formation of these intermediate products of methyl−triflate exchange being competitive with the rate of formation of **2** and ethane.[8] A mechanism can then be envisaged in which **3d** undergoes rapid C−C bond reductive elimination to give [$PtMe(SO_3CF_3)$(dppe)] (**4**)[8] and C_2H_6, followed by a second methyl-triflate exchange between either [$PtMe_4$(NN)] (**1a**−**c**) or [$PtMe_4$(dppe)] (**1d**) and **4** to give the product [$PtMe_2$(dppe)] (**2**) with regeneration of the catalyst [$PtMe_3(SO_3CF_3)$(NN)] (**3a**−**c**) or [$PtMe_3(SO_3CF_3)$(dppe)] (**3d**), respectively. Independent experiments show that this second methyl−triflate exchange occurs easily.

If this proposed mechanism is correct, it can be argued that complex **4**, **3d**, or any reagent (such as triflic acid) that could easily form **4** or **3d** from **1d** should be a catalyst for the decomposition of **1d**, thus greatly simplifying the proposed mechanism (Scheme 2). This

Scheme 2



(8) [$PtMe_3(SO_3CF_3)$(dppe)] (**3d**), NMR in acetone-d_6 (−70 °C): $\delta(^1H)$ 0.09 [br t, 3H, $^2J(PtH) = ca.$ 75 Hz, $^3J(PH) = ca.$ 5 Hz, PtBMe *trans* to SO_3CF_3]; 1.22 [br t, 6H, $^2J(PtH) = ca.$ 55 Hz, $^3J(PH) + {}^3J(P/H) = ca.$ 5 Hz, PtBMe *trans* to dppe]; $\delta(^{31}P)$ 20.5 [s, $^1J(PtP) = 1115$ Hz, dppe]. [$PtMe(SO_3CF_3)$(dppe)] (**4**), prepared by reaction of [$PtMe_2$(dppe)] with MeO_3SCF_3 with elimination of ethane, NMR in acetone-d_6: $\delta(^1H)$ 0.37 [br dd, 3H, $^2J(PtH) = ca.$ 48 Hz, $^3J(P^aH) = ca.$ 2 Hz, $^3J(P^bH) = ca.$ 8 Hz, PtBMe]; $\delta(^{31}P)$ 36.0 [br s, 1P, $^1J(PtP) = 4646$ Hz, P *trans* to SO_3CF_3]; 56.0 [br s, 1P, $^1J(PtP) = 1853$ Hz, P *trans* to Me].

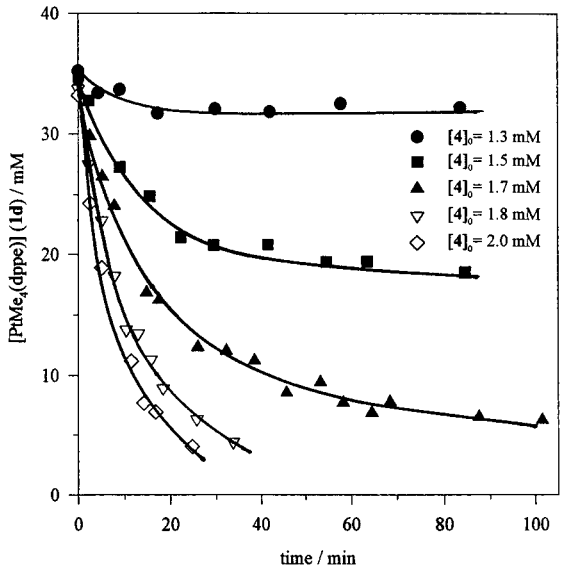


Figure 2. Graphs of the concentration of $[PtMe_4(dppe)]$ (**1d**) versus time (acetone-d_6, 22 °C) using various initial concentrations of catalyst as measured by $^{31}P\{^1H\}$ NMR spectroscopy. The catalyst = $[PtMe(SO_3CF_3)(dppe)]$ (**4**). In all cases $t = 0$ is the time of initial mixing.

prediction was upheld and it was shown that treatment of **1d** with either **4** or $HOSO_2CF_3$ (which reacts with **1d** to give methane and **3d**) in acetone-d_6 solution gave rapid catalytic production of $[PtMe_2(dppe)]$ and C_2H_6. The kinetics of the reaction of $[PtMe_4(dppe)]$ (**1d**) with $[PtMe(SO_3CF_3)(dppe)]$ (**4**) (Scheme 2) in acetone-d_6 were studied by $^{31}P\{^1H\}$ NMR spectroscopy (121.4 MHz) at 22 °C, and a typical set of spectra showing the conversion of **1d** to **2** is shown in Figure 1.

Figure 2 shows plots of the concentration of $[PtMe_4(dppe)]$ (**1b**) versus time using various initial concentrations of $[PtMe(SO_3CF_3)(dppe)]$ (**4**). At higher concentrations of catalyst, the reactions go to completion but, at low concentrations of catalyst, the reactions go only partway. Similar results were obtained using **3c** as catalyst. Two possible explanations of this effect were considered. The first possibility is that the methyl exchange step of Scheme 2 is reversible, with the result that the product $[PtMe_2(dppe)]$ would retard the reaction. This was disproved by independent study and by isotopic labeling studies; thus, if the methyl group exchange were reversible, reaction of $[Pt(CD_3)_4(dppe)]$ with $[PtMe(SO_3CF_3)(dppe)]$ according to Scheme 2 should lead to formation of some $[Pt(CD_3)_3(CH_3)(dppe)]$ and $[Pt(CD_3)_2(CH_3)(SO_3CF_3)(dppe)]$ at intermediate stages of reaction and to some CH_3CD_3 in the products, but neither was detected when the reactions were monitored by low-temperature ^1H NMR though, as predicted by Scheme 2, methyl group incorporation in the product **2** was observed.[9] The second possible explanation is that the catalyst is short-lived, giving only a finite turnover number before being destroyed, and this is favored by the process of elimination.[10]

A key step in the mechanism of Scheme 2 is the easy reductive elimination of ethane from complex **3d**. This step has been confirmed independently. Thus, as monitored by ^1H and $^{31}P\{^1H\}$ NMR in acetone-d_6 at −70 °C, the reaction of $[PtMe_2(dppe)]$ (**2**) with $CH_3OSO_2CF_3$ gave $[PtMe_3(SO_3CF_3)(dppe)]$ (**3d**) by C−O oxidative addition and, on warming to room temperature, **3d** rapidly underwent reductive elimination of ethane to give **4**. It is explicit in Scheme 2 that the "active" complexes in the catalytic cycle are the coordinatively unsaturated and highly electrophilic cations **5** and **6** and the triflate ligand is critical in allowing their easy formation and hence giving low activation energies for both the methyl ligand exchange and the reductive elimination.[11] Neither $[PtMe_4(dppe)]$ nor $[PtIMe_3(dppe)]$ can easily form the cation **6**, and so they are indefinitely stable in solution at room temperature and require high temperatures for their thermolysis. In all these platinum(IV) complexes the C−C reductive elimination is thermodynamically favored, and so the reverse activation of unstrained C−C bonds by platinum(II) cannot be expected. However, if systems can be found where the C−C oxidative addition is thermodynamically favored, the reverse reaction of Scheme 2 offers a potential low-activation-energy route. The easy switching of methylplatinum complexes from nucleophilic to electrophilic character by methyl for triflate exchange is an important factor in the present system.

Acknowledgment. We thank the NSERC of Canada for financial support and for a graduate fellowship to G.S.H.

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(9) Note that the labeling experiment also proves that simple exchange of Me^- for triflate occurs, rather than the type of redox exchange observed in related compounds: (a) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 5713. (b) Aye, K-T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518.

(10) The catalyst concentrations in the experiments in which the plateau effect is observed are too low to allow direct detection of the catalyst or its decomposition products by NMR. Note the added difficulty that the triflate complexes give broad resonances due to fluxionality.[5,11] In separate experiments, the triflate complex **4** is shown to have a limited lifetime in solution.[11]

(11) A further complicating factor, not shown in Scheme 2, is the trapping of the cationic species **5** and **6** by solvent or traces of water in solution. There is a detectable quantity of such species in acetone solution in equilibrium with the triflate complexes, as shown by low-temperature NMR studies.[9c] Both methyl exchange and reductive-elimination steps are retarded by free anion.