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# Proton-Catalyzed Oxo−Alkene Coupling: 2-Platinaoxetane Formation

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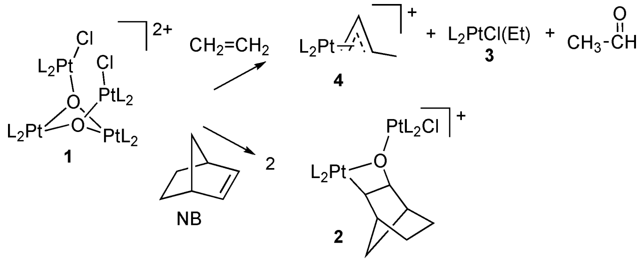
Some 6 years ago we reported alkene oxidation and platinaoxetane formation from Pt oxo complex **1** (Scheme 1).[1] At the time, this was a unique example of 2-metallaoxetane formation from coupling of an alkene and an oxo complex, a potentially important reaction in catalytic alkene oxidations.[2−7] Since then, one other example has been reported along with the closely related formation of 2-metallaoxetanes from a hydroxo complex.[8,9] Herein we describe our mechanistic studies of 2-metallaoxetane formation from **1**. The reaction unexpectedly shows catalytic behavior, which we have traced to a hydroxo complex that reacts directly with norbornene (NB) to form a protonated 2-metallaoxetane.

***Scheme 1.*** Platinaoxetane Formation from **1** ($L_2$ = COD)



A plot of the concentration of 2-platinaoxetane **2** against time for the reaction of **1** with excess NB is shown in Figure 1. The linearity of the plot demonstrates the pseudo-zeroth-order character of the reaction. Further experiments (see the Supporting Information) indicated a first-order dependence on [NB], giving the following rate expression for the reaction: rate = $k_{\mathrm{obs}}$[NB]. Since it is very unlikely that only NB is involved in the rate-determining step, the presence of a catalyst is indicated. Consistent with a catalytic impurity in **1**, the reaction rate varied from batch to batch of **1** and changed with sample age. In addition, the nonzero intercept of the plot suggests "burst kinetics",[10] where there is a rapid reaction of the catalyst or a catalyst complex with **1** to produce product followed by a slower renewal of the catalytic species.

In an effort to discover the nature of the reaction catalyst, small amounts of $BF_3\cdot Et_2O$ (10%), $Pt(COD)(OTf)_2$ (10%),[11] or $HBF_4\cdot Et_2O$ (18%) were added at the beginning of the reaction. Since all three of these species increased the rate of the closely related alkene exchange reaction of **2**,[12] it was anticipated that a similar effect would be observed here. Surprisingly, almost no effect was found for $BF_3\cdot Et_2O$ or $Pt(COD)(OTf)_2$. However, a considerable rate increase was observed for $HBF_4$ (Figure 1), suggesting that $H^+$ or a protonated species is responsible for the catalysis. Consistent with this idea, addition of the polymer base poly(vinylpyridine) (pvp) to **1** followed by addition of NB gave a small amount of **2** but little further progression of the reaction (Figure 1).

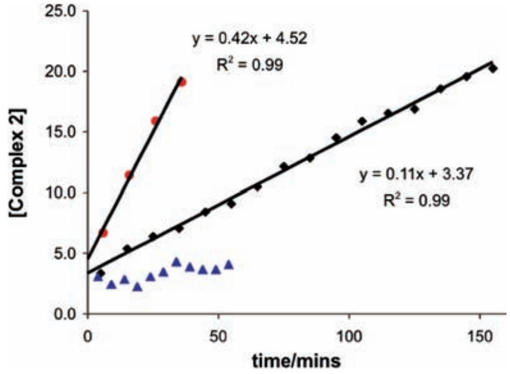
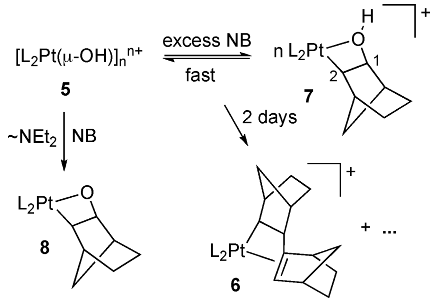


***Figure 1.*** Plots of product concentration [**2**] against time for the reaction of **1** and a 10-fold excess of NB: (◆) no additive; (red ●) 10% $HBF_4$ added (same batch of **1**); (blue ▲) poly(vinylpyridine) added (different batch of **1**).

Given these observations and the recent report of 2-platinaoxetane formation from a Pt hydroxo complex and alkenes,[9] we began investigating the preparation of $[Pt(COD)(\mu\text{-}OH)]_n^{n+}$ (**5**). Treatment of $Pt(COD)Cl_2$ with $NMe_4OH\cdot 5H_2O$ followed by AgOTf yielded **5** as the triflate salt (**5**-OTf). An X-ray crystal structure analysis gave poor results with severe disorder of the two independent OTf anions but revealed a tetrameric ($n$ = 4) structure for cation **5** (see the Supporting Information). Solution NMR spectra for **5** (see the Supporting Information) showed the expected peaks but did not distinguish the value of $n$, which may be different from that in the solid state.

***Scheme 2.*** Formation of 2-Platinaoxetane **7** ($L_2$ = COD, $\sim NEt_2$ = Polymer-Bound $NEt_2$)



As anticipated, **5** reacted cleanly and rapidly (<10 min) with excess NB to give the new 2-platinaoxetane **7** (Scheme 2). The mixture was not stable, and with time (5 h) the known "ene-yl" complex **6**[14] began to appear along with another unidentified complex. Attempts to isolate **7** immediately after its formation give back **5** or mixtures of **5** and **6**, suggesting that formation of **7** is reversible. Stoichiometric amounts of **5** and NB yield equilibrium mixtures of **5**, NB, and **7** with $K_{\mathrm{eq}} \approx 40$.

Although **7** could not be isolated, its identity is clear from the NMR data (see the Supporting Information). Particularly diagnostic is the $^1$H NMR OH peak at 8.8 ppm that shows coupling to Pt and the adjacent norbornyl H1 proton (Scheme 2). Finally, the reaction of **5** and NB in the presence of polymer-

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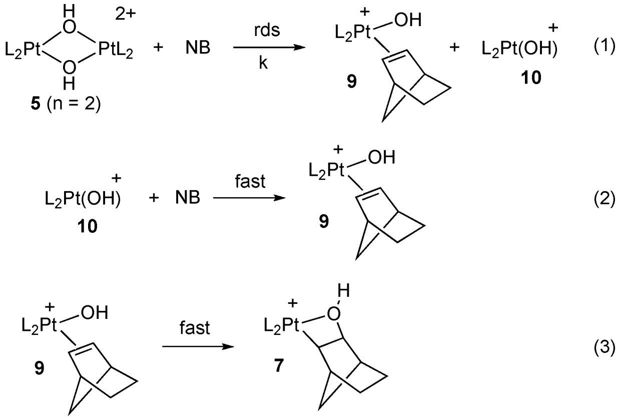
bound diethylamine (~$NEt_2$) yielded known 2-platinaoxetane **8**[15] by deprotonation of **7**.

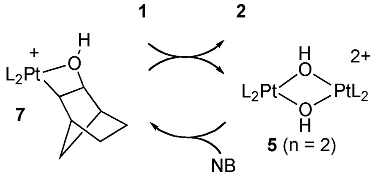
Kinetic data for the reaction of **5** and NB at −10 °C revealed the reaction to be half-order in **5** and first-order in NB, giving the rate expression rate $= k[\mathbf{5}]^{1/2}[\mathrm{NB}]$ (see the Supporting Information). This strongly suggests that the reactive solution species of **5** is the dimer ($n = 2$), the most commonly observed[13] solid-state structure for $[\mathrm{PtL_2}(\mu\text{-OH})]_n^{n+}$ complexes. A proposed mechanism for the reaction, in which breakup of the dimer by NB is rate-determining, is given in Scheme 3. The fragment **10** may be coordinated with solvent or remain bonded to the hydroxo group of **9** until the fast reaction with the second NB in step 2.

***Scheme 3.*** Proposed Mechanism for the Reaction ($L_2$ = COD)



The reaction of **5** with NB to give 2-platinaoxetane **7** even at −10 °C qualifies **5** as a catalytically competent species for the reaction of **1** with NB. This is further supported by the following observations: (1) small amounts of **5** increase the reaction rate of **1** with NB, and (2) the reaction of protonated 2-platinaoxetane **7** with **1** yields a mixture of **5** and 2-platinaoxetane **2**, a critical step in the cycling of **5**. On the basis of these observations, the probable catalytic cycle for the formation of **2** from **1** and NB is given in Scheme 4.

***Scheme 4.*** Probable Catalytic Cycle for the Formation of **2** from **1** and NB ($L_2$ = COD)



In summary, our investigation of 2-platinaoxetane formation from oxo complex **1** has revealed a proton-catalyzed process involving a Pt(II) hydroxo complex that undergoes extremely facile coupling with norbornene. The rate-determining step in the coupling reaction is most likely associated not with C−O bond formation but with breakup of the dimer hydroxo bridge. (Breakup of related Pt and Pd hydroxo dimers by solvent or protonation has recently been found to be important in C−H activation reactions.[16]) The formation of 2-platinaoxetane **7** from hydroxo complex **5** lends further support to the involvement of protonated 2-metallaoxetanes in Wacker alkene oxidation,[17] especially considering the fact that the coordination environment of the Pt(II) center of **5** consists solely of alkene and hydroxo ligands.

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**Supporting Information Available:** Synthetic procedures and characterization data for all new compounds, crystallographic data for **5**-OTf (CIF), and kinetic data and plots. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Szuromi, E.; Shan, H.; Sharp, P. R. *J. Am. Chem. Soc.* **2003**, *125*, 10522–10523.
(2) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* **1990**, *90*, 1483–1506.
(3) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431–458.
(4) Bocquet, M.-L.; Michaelides, A.; Loffreda, D.; Sautet, P.; Alavi, A.; King, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 5620–5621.
(5) Linic, S.; Barteau, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 4034–4035.
(6) Calhorda, M. J.; Lopes, P. E. M.; Friend, C. M. *J. Mol. Catal. A* **1995**, *97*, 157–171.
(7) Madix, R. J.; Roberts, J. T. In *Surface Reactions*; Madix, R. J., Ed.; Springer-Verlag: New York, 1994, p 5−53.
(8) Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6892–6895.
(9) Khusnutdinova, J. R.; Newman, L. L.; Zavalij, P. Y.; Lam, Y. F.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2008**, *130*, 2174–2175.
(10) Logan, S. R. *Fundamentals of Chemical Kinetics*; Longman: Harlow. U.K., 1996.
(11) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2004**, *23*, 4169–4171.
(12) Szuromi, E.; Wu, J.; Sharp, P. R. *J. Am. Chem. Soc.* **2006**, *128*, 12088–12089.
(13) On the basis of a search of the Cambridge Structural Database, version 5.29, Nov 2007:Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.
(14) Szuromi, E.; Sharp, P. R. *Organometallics* **2006**, *25*, 558–559.
(15) Wu, J.; Sharp, P. R. *Organometallics* **2008**, *27*, 1234–1241.
(16) (a) Williams, T. J.; Caffyn, A. J. M.; Hazari, N.; Oblad, P. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 2418–2419. (b) Bercaw, J. E.; Hazari, N.; Labinger, J. A.; Oblad, P. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 9941–9943.
(17) Beyramabadi, S. A.; Eshtiagh-Hosseini, H.; Housaindokht, M. R.; Morsali, A. *Organometallics* **2008**, *27*, 72–79.

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