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Reversible Alkene Extrusion from Platinaoxetanes

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In 2003, we reported ethylene oxidation by a platinum oxo complex (**1**) and the first isolation of a metallaoxetane (**2**) from the reaction of an oxo complex with an alkene (Scheme 1).[1,2] In following up this chemistry, we investigated the reaction of platinaoxetane **2** with alkenes. In contrast to other metallaoxetanes that insert alkenes into the M−O bond,[3] **2** undergoes an unprecedented alkene exchange by reversible alkene extrusion from the platinaoxetane ring.

We first became aware of the unusual behavior of **2** from its reaction with ethylene. ^{1}H NMR spectroscopic monitoring of the reaction of **2** with excess ethylene revealed the slow formation of acetaldehyde. Analysis of the final mixture (24 h reaction time) by ^{1}H and ^{195}Pt NMR spectroscopy showed acetaldehyde, (COD)Pt(Cl)(Et) **3**, and allyl complex $[(COD)Pt(\eta^3\text{-}CH_2CHCHCH_3)]^+$ **4**, the same products formed in the reaction of oxo complex **1** with ethylene (Scheme 1).[1] The fate of the norbornene (NB) in this reaction is unknown but is presumably associated with broad peaks observed in the ^{1}H NMR spectrum. Oxygen-17 labeled **2** produces labeled acetaldehyde. Similarly, **2** and propylene give the same major products as the reaction of **1** with propylene: acetone, $(COD)PtCl_2$, $[(COD)Pt(\eta^3\text{-}CH_2CHCH_2)]^+$, and $(COD)Pt(Cl)(CH_2C(O)CH_3)$. However, monitoring this reaction reveals the initial formation of free norbornene, which disappears as the reaction progresses.

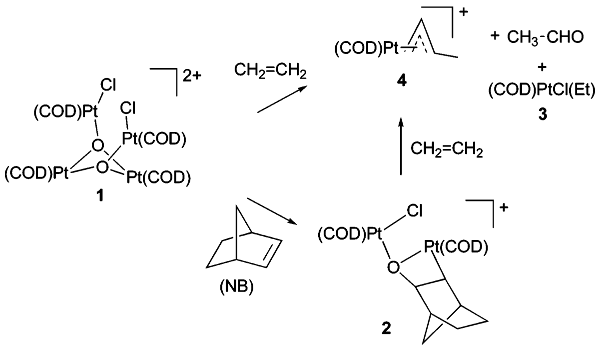
We have previously postulated that the ethylene analogue of platinaoxetane **2** forms as an intermediate in the oxidation of ethylene by oxo complex **1**.[1] The formation of the same products from the ethylene reaction of **2** suggested to us that this same platinaoxetane intermediate forms in the reaction of **2** with ethylene, implying that norbornene is extruded from **2** and replaced by ethylene.[4]

To confirm alkene exchange of platinaoxetane **2**, we sought an alkene that would give a stable platinaoxetane. The new stable platinaoxetane **6** (Scheme 2) is obtained from the reaction of excess substituted norbornene **5** with oxo complex **2**. Monitoring a mixture of a 10-fold excess of norbornene **5** and platinaoxetane **2** shows the release of norbornene and the formation of platinaoxetane **6** with complete conversion of **2** into **6** after 2 days at 25 °C (Scheme 2). The reverse process, conversion of **6** into **2**, is also observed when platinaoxetane **6** is exposed to excess norbornene.

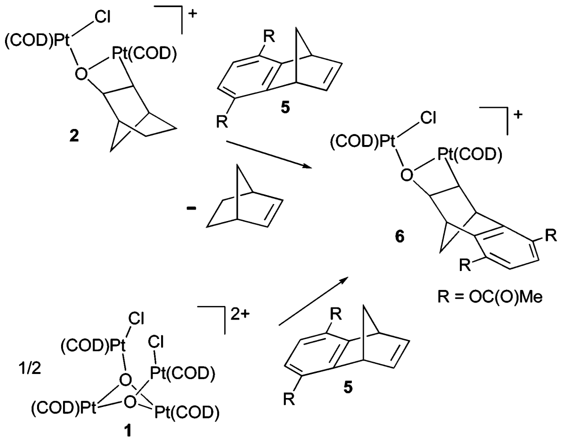
The kinetics of the exchange reaction were investigated by monitoring the growth of platinaoxetane **6** under pseudo-order conditions of ca. 10, 20, and 30 equiv of norbornene **5**. Unexpectedly, plots of the concentration of **6** against time are linear, indicating a zero-order reaction in **2**. Furthermore, a plot of the reaction rates at different concentrations of **5** ([**5**]) against [**5**] shows curvature (Michaelis−Menten plot) indicative of saturation kinetics, which is confirmed by a linear Lineweaver−Burk plot.[6]

These results suggest that the reaction is catalyzed by a small amount of an unknown species, likely an impurity in **2**, with catalyst turnover being rate limiting. To test for the presence of the catalyst in **2**, we examined the rate of the reaction as a function of the *initial* concentration of **2**. The rate for a zero-order reaction in **2** is independent of the concentration of **2** but not the concentration of the catalyst. We observe a rate increase in direct proportion to the initial concentration of **2** consistent with increasing initial concentrations of the catalyst as the amount of **2** is increased.

Scheme 1



Scheme 2



NMR spectroscopy on samples of **2** reveals the presence of trace amounts of $(COD)PtCl_2$ and another platinum-containing compound identified as the hydroxo−oxo complex $[(1,5\text{-}COD)_4Pt_4(\mu^3\text{-}O)_2(\mu^2\text{-}OH)](BF_4)_3$ (**7**). Complex **7** has been independently prepared from $(1,5\text{-}COD)PtI_2$ and $[(Ph_3PAu)_3(\mu^3\text{-}O)]BF_4$. Neither $(COD)PtCl_2$ nor **7** change the reaction rate when added to the reaction mixture. However, the reaction rate is greatly accelerated by addition of the Lewis acids $[(COD)Pt(\mu\text{-}Cl)]_2(BF_4)_2$,[7] $(COD)Pt(OTf)_2$,[8] AgOTf, HOTf, or $BF_3(OEt_2)$.[9] The ether complex of BF_3 is the most efficient with a 10% addition changing the reaction time from 2 days to 10 min. With smaller amounts of **5**, equilibrium between **2** + **5** and **6** + norbornene is established giving an equilibrium constant of ca. 10.

To investigate the role of the BF_3 in the reaction, we treated **2** with $BF_3(OEt_2)$ and obtained platinaoxetane **8**, the BF_3 analogue of **2** (Scheme 3). Like **2**, **8** exchanges alkenes only slowly but experiences a large exchange rate increase with catalytic amounts of BF_3. Furthermore, stoichiometric addition of $BF_3(OEt_2)$ to **8** in

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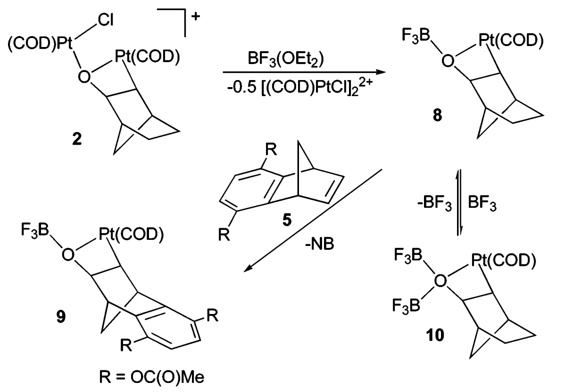
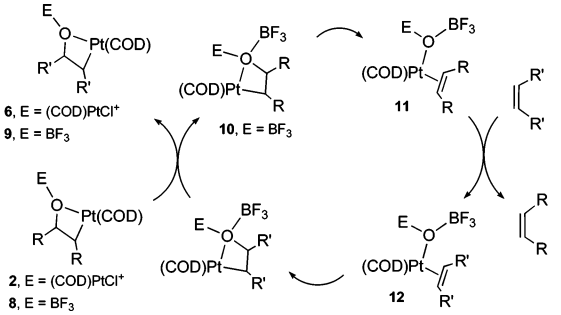
Scheme 3



Scheme 4



the absence of alkene **5** reveals rapid exchange between coordinated and "free" BF_3 at 25 °C and the formation of a new species, observed at low temperature and tentatively identified as the double BF_3 adduct **10** (Scheme 3).

These results suggest that coordination of two Lewis acids to the platinaoxetane oxygen atom is required for alkene extrusion and exchange. A proposed catalytic cycle for alkene exchange of **2** and **8** catalyzed by BF_3 is given in Scheme 4. The need for two strong Lewis acids bonded to the oxygen atom can be understood in terms of the stabilization of the oxo complexes **11** and **12**. This is supported by DFT (B3LYP) studies (gas phase), which show strong stabilization of the model double BF_3 oxo complex **13** relative to the model single BF_3 oxo complex **14** and a corresponding reduction in the alkene coupling transition state energy (Figure 1).

In summary, we report reversible alkene extrusion from platinaoxetanes catalyzed by Lewis acids. The reactions are catalyzed by coordination of the platinaoxetane oxygen atom to Lewis acids. A single Lewis acid appears to be inadequate for stabilization of a proposed intermediate oxo complex, and two Lewis acids are needed for stabilization and for the reaction to occur.

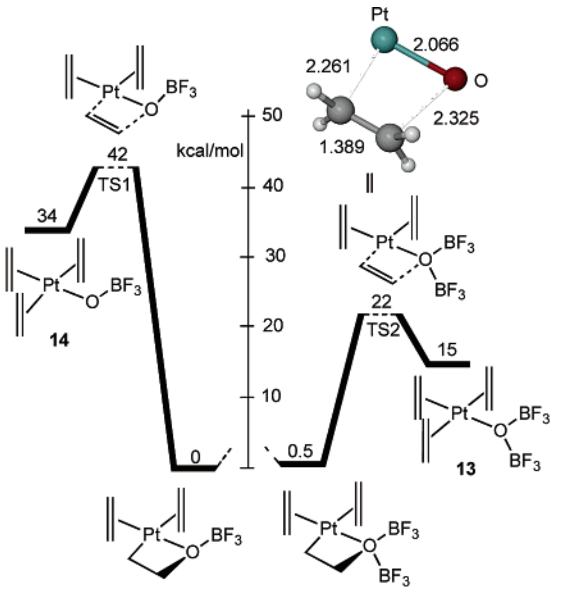


Figure 1. Calculated (DFT) enthalpy changes for alkene extrusion.

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Supporting Information Available: Experimental data for the reaction of **1** with norbornene **5**, structural data for (COD)Pt(Cl)($CH_2C(O)CH_3$), **6**, **8**, and **9**, synthetic and spectroscopic data for **7**, **8**, **9**, and **10**, kinetic data for the reactions of **5** with **2**, and DFT experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Szuromi, E.; Hui, S.; Sharp, P. R. *J. Am. Chem. Soc.* **2003**, *124*, 10522−10523.
(2) A recent report of an auraoxetane from a Au oxo complex and an alkene: Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6892−6895.
(3) de Bruin, B.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4142−4157.
(4) Irreversible alkene extrusion from metallaoxetanes: (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344−3362. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234−3236. (c) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062−1067.
(5) Ketone extrusion from a metallaoxetane: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079−3080.
(6) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, NJ, 1989.
(7) Eaborn, C.; Farrell, N.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 289−292.
(8) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2004**, *23*, 4169−4171.
(9) Irreversible Lewis acid induced alkene extrusion from a ruthenaoxetane has been reported (refs 4a,b).

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