

The Mechanism of Addition of an Ir–OH bond to Ethylene. Catalytic Tandem Activation by Two $[\eta^5\text{-Cp}^*(\text{Ph})\text{IrPMe}_3]^+$ Complex Fragments

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Received October 23, 1996

The Wacker process is used to make about 4 million tons of aldehydes from alkenes each year.^{1,2} The critical step in this reaction involves the metallohydroxylation of an alkene, although the exact mechanism of this fundamental transformation has been a matter of controversy.^{3–6} Other M–OH + alkene reactions could in principle serve as models for this step. However, the number of isolable mononuclear organometallic hydroxides is small, and examples that undergo insertion of alkenes into the M–OH bond are even more rare.^{7,8} Because of this, our recent synthesis of the iridium hydroxide $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) ($[\text{Ir}] = \text{Cp}^*\text{IrPMe}_3$),⁹ and its reaction with ethylene at 25 °C to give the hydroxyethyl complex $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**), was intriguing, and we felt that this unique process deserved in-depth mechanistic study (Scheme 1). Additional impetus for such an investigation was the perplexing observation that product **2** itself undergoes apparently spontaneous oxidation to iridium-substituted aldehyde **3**. We now report a number of unexpected characteristics of these transformations, the most important of which is that the mechanisms of both processes involve the participation of two metal centers.

When we initiated our study, we noted large differences in insertion reactivity using different batches of hydroxide **1**. Concerned that this process was being catalyzed by a small (and variable) amount of an adventitious impurity, we took advantage of earlier observations¹⁰ and added 2–5 mol % of a phosphine (PMe_3 or PPh_3) to the reaction mixtures. The presence of either phosphine resulted in the dramatic inhibition of insertion rates of “active” batches of hydroxide **1**. Clearly the added phosphine was sequestering some material capable of activating **1** toward reaction with ethylene. In light of the fact that the synthetic precursor to hydroxide **1** was the corresponding triflate $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**) ($\text{OTf} = \text{trifluoromethanesulfonate}$), we considered the possibility that **4** was the activating species. To test this hypothesis, we added 0.4–2% of **4** to an “inactive” mixture of hydroxide **1** and ethylene. This resulted in a reacceleration of the original ethylene insertion reaction. Subsequent addition of PPh_3 to this activated mixture resulted in conversion of **4** to $\text{Ph}[\text{Ir}]\text{PPh}_3^+\text{OTf}^-$ and termination of the conversion. These results demonstrate that the apparent insertion reaction can be “turned on” by small amounts of **4** and “turned off” by added phosphine, which converts triflate **4** into an inactive cationic phosphine complex. Clearly “insertion” of ethylene into the Ir–OH bond of **1** is catalyzed by **4**.

Additional investigation of the role of $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**) in the ethylene insertion reaction yielded the following information.

(1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons, Inc.: New York, 1988.

(2) Wittcoff, H. A.; Reuben, B. G. *Industrial Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1996.

(3) Majima, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1977**, 610.

(4) Stille, J. K.; Divakaruni, R. *J. Am. Chem. Soc.* **1978**, *102*, 1303.

(5) Bäckvall, J.-E.; Akermarck, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(6) (a) Bäckvall, J.-E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369. (b) For earlier references suggesting a cis addition mechanism for the Wacker process, see: Henry, P. M. *Acc. Chem. Res.* **1973**, *6*, 16, and references cited therein.

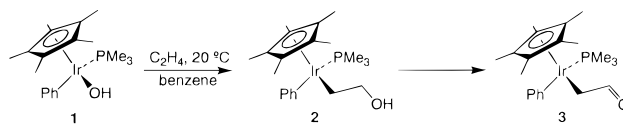
(7) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(8) Bergman, R. G. *Polyhedron* **1995**, *14*, 3227.

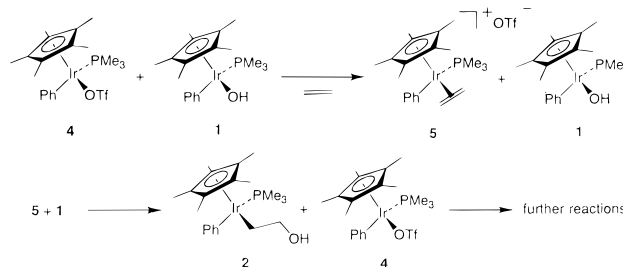
(9) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888.

(10) Butts, M. D.; Bergman, R. G. *Organometallics* **1994**, *13*, 2668.

Scheme 1



Scheme 2



(1) No change in the ^1H - or $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shifts, or in the shapes of any of the signals in the NMR spectra of the reaction mixture, was observed when $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) and $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**) were dissolved in C_6D_6 or $\text{THF-}d_8$.^{11,12} (2) Addition of 1 equiv of ethylene to these mixtures resulted in the immediate formation of $\text{Ph}[\text{Ir}]\text{C}_2\text{H}_4^+\text{OTf}^-$ (**5**) and rapid formation of $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) (Scheme 2). This was followed by steadily decreasing concentrations of olefin complex **5** and hydroxide **1** and appearance of oxidation product **3**. The cationic olefin complex **5** was synthesized independently from triflate **4** and ethylene. (3) Addition of 1 equiv of hydroxide **1** to a solution of independently-prepared olefin complex **5** in $\text{THF-}d_8$ also led to the formation of **2** along with an approximately equimolar amount of **4** (with respect to **1**) (Scheme 2). We assume that triflate **4** and ion pair **6** are in rapid equilibrium. (4) Olefin complex **5** was observed by NMR to form during the reaction of hydroxide **1** and ethylene in the presence of catalytic amounts of **4** when more than 0.5% of the triflate **4** was used.

To account for these results we postulate the mechanism outlined in Scheme 3, which involves the cooperative participation of two Ir centers. The reaction is initiated when the oxygen atom in the hydroxyl ligand of $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) attacks the metal-bound ethylene¹³ in $\text{Ph}[\text{Ir}]\text{C}_2\text{H}_4^+\text{OTf}^-$ (**5**); we propose that the transition state for this entropically-demanding process is rate-limiting in this reaction. This leads initially to bridged binuclear intermediate **7**, which dissociates by cleavage of the Ir–O bond, generating the “insertion” product **2** and the $\text{Ph}[\text{Ir}]^+$ species **6**.¹⁴ Ion pair **6** reacts rapidly with free ethylene to regenerate **5**.

As mentioned (vide supra), in addition to the hydroxyethyl complex **2** a second product, the formylmethyl complex $\text{Ph}[\text{Ir}]\text{CH}_2\text{CHO}$ (**3**), is formed during the reaction of hydroxide **1** with ethylene. This material is formally a dehydrogenation product of the hydroxyethyl complex **2**. The following information has been obtained on the formation of **3**: (1) As **3** is formed the concentration of hydroxyethyl complex **2** steadily decreases, indicating that **2** is the precursor of **3**. (2) No dihydrogen is observed during this transformation. Instead, a third product, $\text{Ph}[\text{Ir}]\text{H}$ (**10**)¹⁵ is identified albeit in 10–20% smaller concentra-

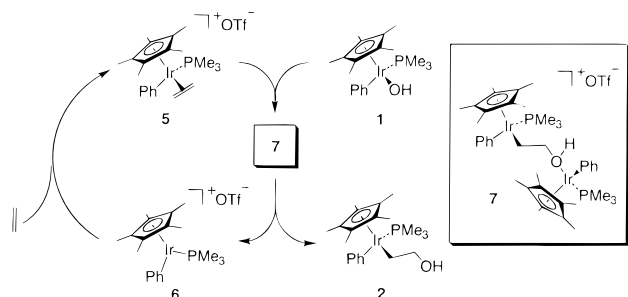
(11) Bimetallic cationic Cp^*Ir -complexes with bridging hydroxy ligands have been reported and characterized spectroscopically: $[\text{Cp}^*\text{Ir}(\mu\text{-OH})_3\text{-IrCp}^*]^+\text{OH}^-$, Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1997. For other related μ -oxo complexes see also ref 14.

(12) Jacobsen, E. N.; Trost, M. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 8092.

(13) This presumably occurs by anti-attack. For the mechanism of nucleophilic addition to olefin complexes, see: Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(14) Iridium-assisted oxygen transfer to phosphines was observed for $\text{Cp}^*\text{Ir}(\mu\text{-O})_2\text{IrCp}^*$: McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543.

Scheme 3



tions than **3**.¹⁶ (3) In the reaction starting with olefin complex **5**, 2 equiv of **1** are required to completely convert the ethylene complex to formylmethyl complex **3**. Although we have not been able to detect the formation of water directly, we believe that the stoichiometry of the overall reaction in the presence of 1 equiv of ethylene and 0.4–1.0 mol % of triflate **4** must be $2\text{Ph}[\text{Ir}]\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{Ph}[\text{Ir}]\text{H} + \text{Ph}[\text{Ir}]\text{CH}_2\text{CH}=\text{O} + \text{H}_2\text{O}$. (4) If olefin complex **5** and hydroxide **1** are allowed to react in an equimolar ratio both hydroxide **1** and triflate **4** (or ion pair **6**, respectively) show broad ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR signals indicating a slow exchange process on the NMR time scale presumably due to the presence of H_2O .^{17–20}

In addition, (5) Varying the initial concentrations of $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**), $\text{Ph}[\text{Ir}]\text{C}_2\text{H}_4^+\text{OTf}^-$ (**5**), or ethylene strongly affects the ratio of $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) to $\text{Ph}[\text{Ir}]\text{CH}_2\text{CHO}$ (**3**) and $\text{Ph}[\text{Ir}]\text{H}$ (**10**). When the reaction is performed with equimolar amounts of **5** (or triflate **4**) and $\text{Ph}[\text{Ir}]\text{OH}$ (**1**), the concentration of insertion product **2** is lower by one to two orders of magnitude compared to reactions performed with only catalytic amounts (0.4–1 mol %) of triflate **4**, and formyl methyl complex **3** and hydride **10** are observed from the beginning of the reaction. When a catalytic amount of triflate **4** or olefin complex **5** is used, **3** and **10** begin to form detectably (NMR) only after about 60% conversion to hydroxyethyl complex **2**. However, ultimately **2** is completely converted to **3**. (6) Addition of PPh_3 to a reaction mixture in which a substantial amount of hydroxyethyl complex **2** has formed suppresses both the formation of **2** and its further transformation to formyl methyl complex **3**. (7) Treatment of isolated $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) with 1.05 equiv of $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**) led after 10 min to nearly quantitative formation of $\text{Ph}[\text{Ir}]\text{C}_2\text{H}_4^+\text{OTf}^-$ (**5**) and $\text{Ph}[\text{Ir}]\text{OH}$ (**1**).²¹ More slowly, the system then goes on to form formyl methyl complex **3** and hydride **10** via hydroxyethyl complex **2**. (8) Addition of $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) to 1.2 equiv of $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) in the presence of a catalytic amount (1 mol %) of $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**) provides rapid formation of **3** and **10** (Scheme 4).

These observations suggest strongly that $\text{Ph}[\text{Ir}]\text{CH}_2\text{CHO}$ (**3**) and $\text{Ph}[\text{Ir}]\text{H}$ (**10**) are generated by reaction of $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) with $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**). Since all reactions with a minimum initial concentration (0.4 mol %) triflate of **4** go completely to formyl methyl complex **3** and hydride **10**, the transformation of hydroxyethyl complex **2** to give **3** and **10** must also be catalyzed by triflate **4**. We suggest the detailed pathway outlined in Scheme 4 to account for our observations on the formation of **3**. Note that the mechanism in Scheme 3 is abbreviated as

(15) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(16) We ascribe this to the fact that **10** is more labile than **3** in the presence of H_2O and traces of Lewis or Brønsted acids.

(17) Dissociation processes in related systems require the presence of solvents capable of hydrogen bonding: Glueck, D. S.; Newman, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. For further examples see refs 16–18.

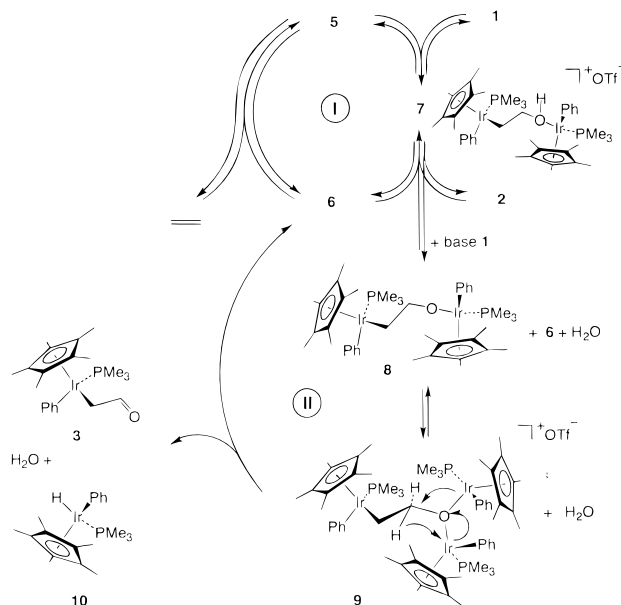
(18) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(19) Strukul, T.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563.

(20) Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478.

(21) Acetaldehyde was never observed during the insertion reaction. Further evidence that acetaldehyde is not an intermediate will be presented in a full paper.

Scheme 4



part I at the top of Scheme 4 to illustrate the interconnection of the two processes. The reaction of hydroxyethyl complex **2** with triflate **4** shows that the C–O bond-forming process is reversible and provides indirect evidence for the intermediacy and reversible formation of the protonated bimetallic complex **7** (part I). Under Lewis acidic conditions, deprotonation of **7** to give its charge-neutral bimetallic analogue **8** is unlikely. However once $\text{Ph}[\text{Ir}]\text{C}_2\text{H}_4^+\text{OTf}^-$ (**5**) and the potentially basic complex $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) are formed, generation of formylmethyl complex **3** and $\text{Ph}[\text{Ir}]\text{H}$ (**10**) can occur. Under overall Lewis basic conditions, the equilibrium shifts toward the formation of the formylmethyl complex **3** and the hydride complex **10**.

To explain the final reaction sequence, the formal β -hydride elimination from **8** to yield **3** and **10**, we assume that this reaction proceeds via a hydride transfer mechanism catalyzed by $\text{Ph}[\text{Ir}]\text{OTf}$ (**4**). In analogy to the Meerwein–Ponndorf–Verley reaction of aluminum alkoxides and ketones, this reaction could take place by a hydride transfer from the electron rich alkoxide **8** to the $\text{Ph}[\text{Ir}]^+$ fragment **6** (part II Scheme 4).²²

In summary we have obtained evidence that the insertion of ethylene into the late metal–OH bond of $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) is catalyzed by trace amounts of complexes capable of generating the cationic species $\text{Ph}[\text{Ir}]^+$. In this reaction both ethylene and OH^- are brought together by two individual $\text{Ph}[\text{Ir}]^+$ fragments. In a second cycle $\text{Ph}[\text{Ir}]^+$ cations catalyze the turnover of $\text{Ph}[\text{Ir}]\text{CH}_2\text{CH}_2\text{OH}$ (**2**) and $\text{Ph}[\text{Ir}]\text{OH}$ (**1**) to give $\text{Ph}[\text{Ir}]\text{CH}_2\text{CHO}$ (**3**), $\text{Ph}[\text{Ir}]\text{H}$ (**10**), and H_2O . The title reaction is an unusual example of a tandem activation of two fragments by identical metal centers. We suggest the possibility that related reactions may occur in Wacker-type systems as well. Further experiments designed to study the scope of this new reaction type are currently underway.

Acknowledgment. We acknowledge the National Institutes of Health (Grant No. R37-GM25459) for generous financial support of this work. J.C.M.R. acknowledges support through a NATO Postdoctoral Fellowship administered through the Deutscher Akademischer Austauschdienst (DAAD).

Supporting Information Available: Spectroscopic and analytic data for **2**, **5**, and $\text{Ph}[\text{Ir}]\text{PPh}_3^+\text{OTf}^-$ (2 pages). See any current masthead page for ordering and Internet access instructions.

JA9636653

(22) (a) March, J. *Advanced Organic Chemistry*; Wiley & Sons, Inc.: New York, 1992. As found for many Meerwein–Ponndorf–Verley reactions, this reaction could also take place by a single electron transfer (SET) mechanism. Further evidence for the intermediacy of **8** and its mechanism of decomposition will be addressed in a full paper. (b) We would like to emphasize that the decomposition of **2** is different from the β -hydride elimination observed in Wacker-type reactions.