Acknowledgment. We are grateful to Dr. Hong-Suk Suh for valuable discussions on the synthesis of compounds used in this study and to Dr. Ralph Nuzzo for communicating results to us prior to publication. Funding for this project was provided by the Texas Advanced Technology Research Program and by the Robert A. Welch Foundation.

Competitive α- and β-Elimination in an Iridium Alkyl

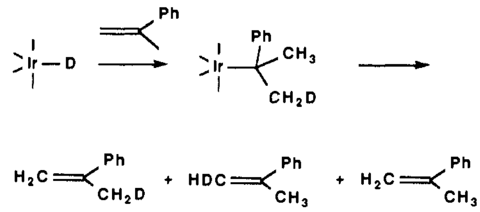
Mark J. Burk, Martin P. McGrath, and Robert H. Crabtree*

Yale University, Department of Chemistry
225 Prospect Street, New Haven, Connecticut 06511

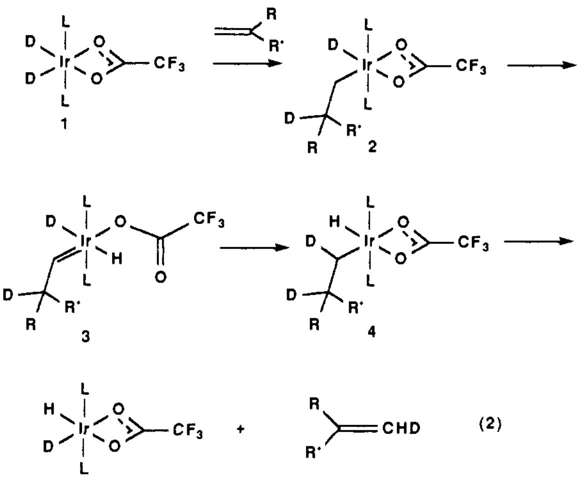
Received July 8, 1987

C–H bond activation is an area of great current interest.[1a] We recently described[1b] thermal alkane dehydrogenation by using $[IrH_2(\eta^2\text{-}O_2CCF_3)(PAr_3)_2]$ (**1**, Ar = $p\text{-}C_6H_4F$) as catalyst in the presence of $t\text{-BuCH}{=}CH_2$ (tbe) as hydrogen acceptor. We now find that **1**-d_2 gives selective H/D exchange with the vinyl hydrogens of various alkenes, including tbe. Direct vinylic C–H activation has recently been reported,[2] but this mechanism is not operating here. Instead, an alkene insertion/β-elimination route is involved. Unexpectedly, rapid α-elimination can also be identified as a pathway leading to exchange.

Monitoring the reaction of **1**-d_2 with tbe-d_0 (15 mol equiv) in C_6H_6 at 25 °C by ^2H NMR showed that D incorporation occurs at the same rate (±5%) for all the vinyl positions; no further incorporation is seen after 2 h at 25 °C. The deuteriated product is ca. 85% tbe-d_2 by GC-MS. Similar rates and selectivities are observed for styrene, stilbene, α-methylstyrene, and ethyl vinyl ether. An insertion/β-elimination mechanism could only account for this result if insertion were taking place twice as fast to give the more hindered branched alkyl than to give the linear alkyl, contrary to what is normally found.[4a] Such a mechanism would tend to give tbe-d_1 as the major product because once one D is incorporated the tbe-d_1 should dissociate; this is rapid on the NMR time scale at 25 °C. Finally, for α-methylstyrene, β-elimination should take place in each of the two possible directions from any intermediate tertiary alkyl, assuming free rotation[4b] about the Ir–C bond (eq 1). We observe D incorporation into the methyl groups at an insignificant (<2%) relative rate, again inconsistent with insertion/β-elimination. $Me_2C{=}CH_2$ behaves similarly. Alternatively, vinyl activation might be taking place at equal rates at all sites. This should give tbe-d_1 as a major product, should give some tbe-d_3, and should give *trans*-$t\text{-BuCH}{=}CHD$ selectively as observed by Faller and Felkin;[2a] none of these features is seen here. The evidence therefore seems to require insertion to give the 1° alkyl followed by α-elimination to account for the deuteriation of the terminal vinyl groups (eq 2). Radical mechanisms can be ruled out because these should give tbe-d_1 as a major product. In addition, the reaction rate is essentially the same in CH_2Cl_2 and toluene, and in no case is D incorporated into the solvents, nor is bibenzyl formed from toluene.



(1)



(2)

Our results are consistent with insertion and rapid α-elimination followed by β-elimination. The ca. 1:1:1 regiochemistry of D incorporation is, we propose, the result of a balance between equilibrium isotope effects for the α-elimination equilibrium, which should favor **4** over **2**, and the kinetic isotope effect for β-elimination, which should favor H elimination.[5] At each step the trifluoroacetate can open or close to preserve an 18e configuration at Ir.

The formation of deuteriated alkane by reductive elimination from **2** or **4** is much slower. When this happens, the Ir is irreversibly trapped by the solvent to give $[PhIrH(\eta^2\text{-}O_2CCF_3)(PAr_3)_2]\text{-}d_0$ (**5**). Such adducts have been seen before[6] but never from an alkane conversion catalyst as here. Like **1**, **5** is a thermal alkane dehydrogenation catalyst,[1b] and the alkyl hydride **2** must also be involved in the catalytic cycle. Many alkyl hydrides have been observed and isolated,[6] but in only one case[7] has an alkylidene hydride been detected and then only spectroscopically at low temperatures.

Although α-elimination is rarely observed, it may be a common process for unsaturated alkyls but require isotopic labeling to be detected. Our results suggest that α-elimination must proceed at least as fast as β-elimination and faster than reductive elimination in this system. Shilov et al.[8] have proposed rapid α-elimination to explain multiple H/D exchange in their Pt-based alkane activation chemistry. Shapley et al.[9] have reported faster α- and β-elimination in a cluster alkyl. Schrock et al.[10a] have seen competitive α- and β-elimination and Bercaw and Parkin,[10b] faster α- than β-elimination in some tantalum alkyls. Our results suggest that α-elimination may be more facile for the late metals than previously suspected.

Acknowledgment. We thank NSF (M.J.B.) and DOE (R.H.C.) for support.

---

(1) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Burk, M. J.; Crabtree, R. H.; McGrath, D. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1829–1830. (c) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.*, in press.

(2) (a) Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488–1490. (b) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582.

(3) ^2H NMR peaks are observed for the tbe vinyl positions at 4.84, 4.95, and 5.82 δ. The 1:1:1 intensity ratio is maintained throughout the reaction.

(4) (a) In hydroformylation with Rh catalysts, the formyl group labels the carbon which was attached to Rh in the intermediate alkyl; in aliphatic systems, this is the least hindered carbon: Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660 and 3133. (b) Free rotation has been proposed in a related *tert*-butyl intermediate: Bennett, M. A.; Crisp, G. T. *Organometallics* **1986**, *5*, 1792–1800.

(5) Evans, J.; Schwartz, J.; Urquhart, P. *J. Organomet. Chem.* **1974**, *81*, C37–39. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682. (c) In addition, any IrHD complex would tend to incorporate its D at the α-carbon if $k_H/k_D < 1$ for insertion.

(6) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1563. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725.

(7) (a) Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1979**, 498–499. (b) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589–590.

(8) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97–143.

(9) Cree-Uciyama, M.; Shapley, J. R.; StGeorge, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316–1317.

(10) (a) Fellman, J. D.; Schrock, R. R.; Traficante, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 481–484. (b) Bercaw, J. E.; Parkin, G., personal communication, 1986.

0002-7863/88/1510-0620$01.50/0