Journal of Organometallic Chemistry, 81 (1974) C37–C39

Preliminary communication

THE MECHANISM OF β-HYDRIDE ELIMINATION FROM TRANSITION METAL ALKYLS (d^8): KINETIC DEUTERIUM ISOTOPE EFFECT

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(Received August 26th, 1974; by publisher October 11th, 1974)

Summary

The kinetic isotope effect for β-hydride elimination from alkyliridium(I) complexes has been found to be $k_H/k_D = 2.28 \pm 0.20$.

Although β-elimination from metal alkyls and addition of metal hydrides to olefins are central processes in many organic transformations involving transition metal complexes, very little is known about this process mechanistically. The kinetic deuterium isotope effect (k_H/k_D) for β-hydride elimination can clearly provide useful mechanistic information, and several studies concerning it have been reported [1-3]. These determinations have not, however, afforded readily interpretable values for k_H/k_D due either (1) to β-hydride elimination not being rate determining in the process studied [3], (2) to equilibrium effects which scramble deuterium labels [1-3], or (3) to an inability to rule out special cluster effects which may be important in β-elimination from clustered transition metal alkyls [3b]. In contrast to these studies, we have found that alkyliridium(I) complexes provide an excellent opportunity to measure k_H/k_D in a clear-cut fashion; by this process, β,β-dideuteriooctyliridium(I) species Ia gives 1-octene-d_1 as the sole olefinic product and with no scrambling of the deuterium labels [4].

Octyliridium(I) complex Ib was prepared[**], its decomposition was studied (eqn. 1), and the ratio for deuterium incorporation in the olefinic product, 1-octene-d_1/1-octene-d_0, was measured[***]. Two limiting kinetic schemes can be

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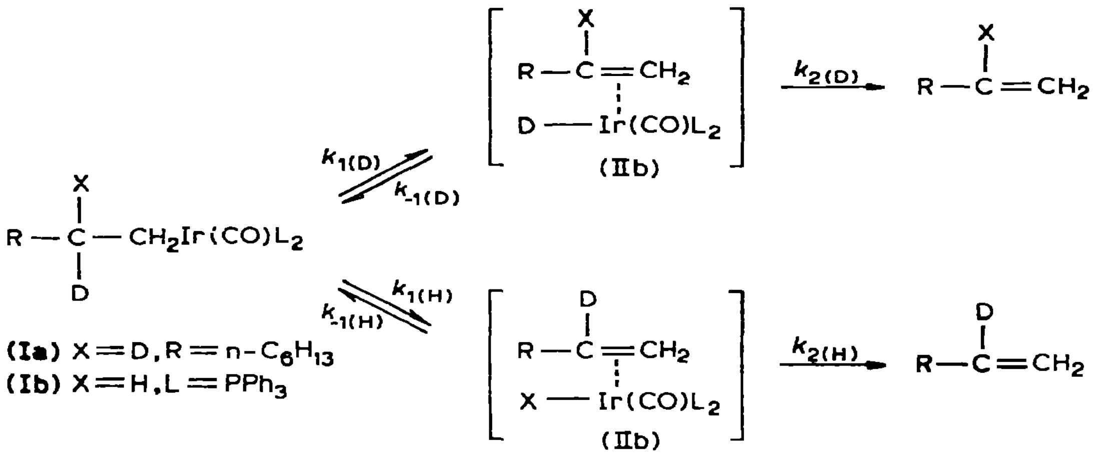
[**] The synthesis of Ib from *trans*-$L_2Ir(CO)Cl$ and n-$C_6H_{13}CHDCH_2Li$ was as reported [4]. The lithium reagent was prepared from the chloride (95 % d_1), itself synthesized employing standard procedures as shown:

$$RCH_2CO_2H \xrightarrow{\substack{1.\ Br_2/PCl_3 \\ 2.\ CH_3OH/H_2SO_4 \\ 3.\ Zn/D_2O/DME}} RCHDCO_2CH_3 \xrightarrow{\substack{1.\ LiAlH_4/THF \\ 2.\ H_2O \\ 3.\ PPh_3/CCl_4}} RCHDCH_2Cl$$

[***] Amounts of octene-d_1 and octene-d_0 produced from Ib were as follows (correcting for deuterium incorporation in the chloroalkyl): 67.3% d_1, 32.7% d_0; k_H/k_D = 2.06. 71.5% d_1, 28.5% d_0; k_H/k_D = 2.51. 67.5% d_1, 32.5% d_0; k_H/k_D = 2.08.



(1

envisioned for the decomposition of I based on a steady state assumption for II. Case 1: If $k_{-1} \ll k_2$, then the ratio octene-d_1/octene-d_0 is, itself, the desired kinetic isotope effect k_H/k_D. Case 2: If $k_{-1} \gg k_2$, then the observed ratio of olefins represents the ratio of equilibrium constants for rapid H versus D elimination and readdition, This latter situation is incompatible with the observation [4] of no label scrambling for IIa unless readdition (II→I) occurs regiospecifically to place the metal only at the terminal carbon,and this possibility is negated by the fact that label is scrambled rapidly by nonspecific readdition of M—H in isoelectronic alkylplatinum(II) complexes [3]. β-Hydride elimination in alkyliridium(I) complex I must therefore be rate determining in its decomposition; case 1 must be correct.

The measured isotope effect for β-hydride elimination from Ib, k_H/k_D = 2.28 ± 0.20, suggests a transition state for β-elimination in which the iridium atom inserts into the β-C—H bond of the alkyl group (or, C—Ir and H—Ir bond formation are both important in the transition state). This interpretation is formally an oxidative addition of C—H to Ir^I* and is one of several possibilities which have recently been suggested for β-elimination in connection with a general discussion of reactivity of organo-transition-metallic complexes [6].

Acknowledgments

The authors wish to acknowledge John B. Cannon for his helpful comments and Matthey—Bishop, Inc., for a generous loan of iridium. They also give special thanks to Hoffman La Roche, Inc., for performing the mass spectral determinations of deuterium content in octene products of the reactions described herein.

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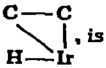
*Note that the species formed by this process,  is just a limiting representation for back-bonding in an hydridoiridium(I) (olefin) complex. This procedure has been discussed in some detail for oxidative addition to Ir^I of an *ortho*-C—H bond of coordinated triphenylphosphine [5].

Analogous square planar d^8 metal alkyl complexes [e.g., those of Rh^I and Pt^{II}] may β-eliminate by the same mechanism.

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