Diastereomeric and Isotopic Scrambling in (Hydrido)alkyliridium Complexes. Evidence for the Presence of a Common "Alkane Complex" Intermediate

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Received January 30, 1995

Several studies have implicated the existence of alkane complexes (or σ-complexes)[1] as intermediates along the reaction pathway for alkane C–H bond oxidative addition and reductive elimination reactions. Alkane complexes have been invoked to explain the inverse kinetic isotope effects observed in the reductive elimination of alkanes from certain alkylmetal hydride complexes,[2–5] and they have been observed directly in gas-phase and condensed-phase laser spectroscopy experiments.[6–11] Theoretical investigations of model systems indicate that alkane complexes lie at an energy minimum along the reaction coordinate for C–H bond activation.[12–14]

The rearrangement of deuterium atoms in labeled alkylmetal hydrides has also been explained in terms of alkane complex intermediates (path 1, Figure 1).[2,4,5,15] However, an alternative explanation for the scrambling of isotopic labels in these alkylmetal hydride complexes is the direct dyotropic rearrangement over the transition state pictured in path 2 of Figure 1. In an attempt to clarify the mechanism involved in these deuterium-scrambling reactions we have carried out kinetic investigations of the interconversion of diastereomeric (hydrido)(dimethylcyclopropyl)iridium complexes **1a** and **1b** and the deuterium scrambling of their α-deuterio analogs. Previous work in our laboratories[15] examined the chemistry of the rhodium analogs of **1a**,**b**; however, the thermal instability of the rhodium complexes precluded the isolation and stereochemical characterization of diastereomerically pure materials. A dramatic difference in behavior of the Rh and Ir systems yields significant conclusions regarding the reaction coordinate for alkane oxidative addition reactions to metal centers.

Diastereomeric complexes **1a**,**b** (see Figure 3 for geometrical structures) were synthesized by the photolysis of Cp*(PMe$_3$)IrH$_2$ in neat dimethylcyclopropane followed by thermolysis at 140 °C to convert the methyl-activated side product **2** to **1a**,**b** (eq 1). Alternatively, the synthetic method depicted in eq 2 allows for deuterium labeling of the α-position of the dimethylcyclopropyl group by using the appropriately labeled lithiodimethylcyclopropane. Separation of the diastereomers **1a**,**b** was effected by repeated low-temperature column chromatography.[16]

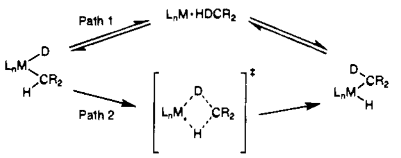
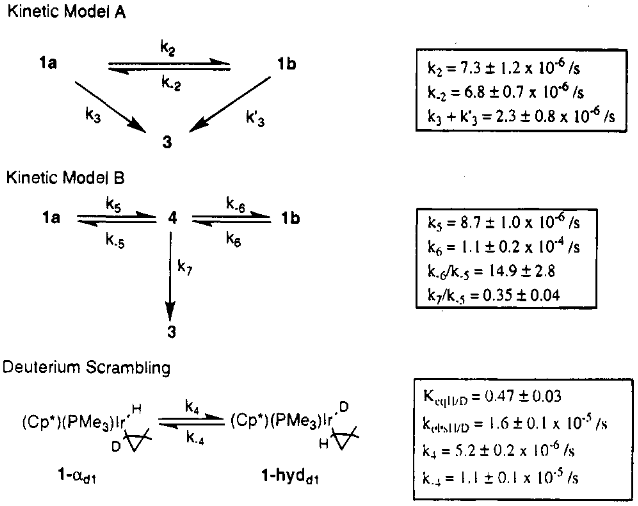


Figure 1. Path 1 illustrates rearrangement via an alkane complex intermediate. Path 2 shows direct 1,2-dyotropic rearrangement (simultaneous migration of hydrogens between iridium and carbon).



$k_2 = 7.3 \pm 1.2 \times 10^{-6}$ /s
$k_{-2} = 6.8 \pm 0.7 \times 10^{-6}$ /s
$k_3 + k'_3 = 2.3 \pm 0.8 \times 10^{-6}$ /s

$k_5 = 8.7 \pm 1.0 \times 10^{-6}$ /s
$k_6 = 1.1 \pm 0.2 \times 10^{-4}$ /s
$k_{-6}/k_{-5} = 14.9 \pm 2.8$
$k_7/k_{-5} = 0.35 \pm 0.04$

$K_{eq H/D} = 0.47 \pm 0.03$
$k_{obs H/D} = 1.6 \pm 0.1 \times 10^{-5}$ /s
$k_4 = 5.2 \pm 0.2 \times 10^{-6}$ /s
$k_{-4} = 1.1 \pm 0.1 \times 10^{-5}$ /s

Figure 2. Kinetic models and associated rate constants for interconversion of diastereomers **1a** and **1b** and deuterium scrambling of their deuterated analogs.

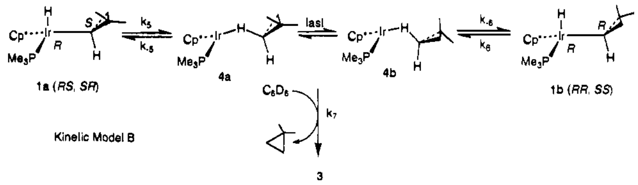
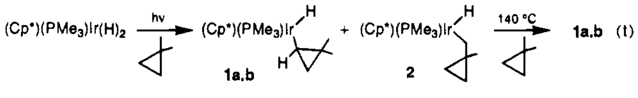
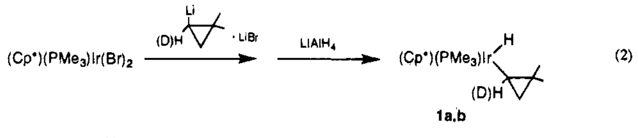


Figure 3. Proposed mechanism for diastereomer interconversion of **1a** and **1b**.

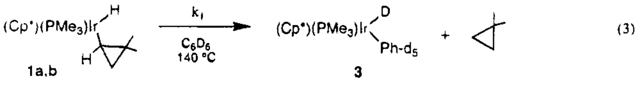
Identification of the relative stereochemistry of the diastereomers **1a** (*RS*,*SR*) and **1b** (*RR*,*SS*) was accomplished using ^{1}H 2D-NOESY NMR experiments.



(1)



(2)



(3)

Upon thermolysis[17] at 140 °C of mixtures of **1a**,**b** in C$_6$D$_6$, reductive elimination of dimethylcyclopropane and oxidative addition of C$_6$D$_6$ to form **3** is observed (eq 3). This reaction

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[1] These terms describe metal complexes that have an alkane ligand interacting with the metal center through an intact C–H σ-bond.

[2] Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

[3] Heinekey, D. M.; Gould, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 5502.

[4] Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

[5] Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897.

[6] Ishikawa, Y.; Brown, C. E.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1988**, *150*, 506.

[7] Xie, X.; Simon, J. D. *J. Phys. Chem.* **1989**, *93*, 291.

[8] Dobson, G. R.; Asali, K. J.; Cate, C. D.; Cate, C. W. *Inorg. Chem.* **1991**, *30*, 4471.

[9] Hop, C. E. C. A.; McMahon, T. B. *J. Am. Chem. Soc.* **1991**, *113*, 355.

[10] Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585.

[11] Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.

[12] Cundari, T. R. *J. Am. Chem. Soc.* **1994**, *116*, 340.

[13] Ziegler, T.; Tschinke, V.; Fan L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

[14] Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118.

[15] Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

[16] **1a**,**b** and the pure diastereomers are isolated and used as racemic mixtures.

[17] Thermolyses in this study were done in sealed 5 mm thin-walled NMR tubes with an external standard capillary containing trimethoxybenzene and (Cp*)(PMe$_3$)IrH$_2$ as integration standards. Approximately 10 mol % of PPh$_3$ was added to inhibit H/D scrambling of the metal complexes with the solvent as previously reported (see ref 5).

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follows pseudo-first-order kinetics and gives a pseudo-first-order rate constant for oxidative addition, $k_1 = 1.78 \times 10^{-6}$ s^{-1}. Thermolysis of diastereomerically pure **1a** or **1b** results in its conversion to the other diastereomer (**1b** or **1a**, respectively) at a rate that is somewhat faster than the rate observed for the oxidative addition of C_6D_6. Quantitative analysis of these rate data was accomplished using a nonlinear regression with least squares fitting[18] of NMR integration of resonances from **1a**, **1b**, and **3**. An example of such a fit is available as supporting information.

Fitting the data to kinetic model A (Figure 2) yields the phenomenological rate constants for the system: rate data derived from the fitting of model A to several kinetic trials is summarized in Figure 2. The phenomenological rate constants for the interconversion of **1a** and **1b** (k_2 and k_{-2}) are the same within experimental error and are approximately 3 times faster than the formation[19] of **3**, k_3 and k'_3. The rate constants for formation of **3** derived from the nonlinear least squares fits agrees well with that determined by thermolysis of the 1:1 mixture of **1a**,**b**.

Thermolysis of diastereomerically pure deuterium-labeled **1a**-α_{d_1} (or **1b**-α_{d_1}) results in (1) the scrambling of the deuterium from the α-position of the dimethylcyclopropyl ring to the metal hydride position to generate **1a**-hyd$_{d_1}$ (or **1b**-hyd$_{d_1}$) and (2) conversion to the other diastereomer, **1b**-α_{d_1} and **1b**-hyd$_{d_1}$ (or **1a**-α_{d_1} and **1a**-hyd$_{d_1}$). Deuterium scrambling was evidenced by the disappearance of the hydride resonances and the appearance of the α-proton resonances in the ^{1}H NMR spectrum, the appearance of deuterium-coupled, isotopically shifted PMe_3 resonances in the $^{31}P\{^1H\}$ NMR spectrum, and the appearance of metal deuteride resonances in the $^2H\{^1H\}$ NMR spectrum.[20] Quantitative rate data for the deuterium-scrambling process could be obtained from the first-order log plots of the disappearance of the hydride signal in the ^{1}H NMR spectrum.[21] These data are summarized in Figure 2. The equilibrium constant, $K_{\mathrm{eq}_{H/D}}$, for the deuterium-scrambling reaction as written in Figure 2 was determined by careful integration of the $^{31}P\{^1H\}$ NMR resonances for the hydride compounds **1a**,**b**-α_{d_1} and the deuteride compounds **1a**,**b**-hyd$_{d_1}$ after the deuterium-scrambling reaction had reached equilibrium.[22] From the observed rate constant for the deuterium scrambling, $k_{\mathrm{obs}_{H/D}}$, and $K_{\mathrm{eq}_{H/D}}$ the first-order rate constants for the forward, k_4, and reverse, k_{-4}, reactions depicted in Figure 2 could be determined. Comparison of these results with the analogous rate constants k_2 and k_{-2}, obtained for the diastereomer interconversion[23] reveals that the diasteromeric interconversion process and the deuterium-scrambling process occur at essentially the same rate at 140 °C. This result contrasts with the previously examined deuterium scrambling in the rhodium system: in that system, deuterium scrambling occurs at −50 °C without any change in the diastereomeric ratio of partially enriched mixtures.[15]

Although the rate laws do not allow the analytical differentiation between kinetic model A and kinetic model B (depicted explicitly in Figure 3), we feel that model B is the most reasonable way to account for the close similarity of the rates for diastereomeric interconversion, deuterium scrambling, and reductive elimination of **1a** and **1b**. In this mechanism, **1a** undergoes reductive elimination of dimethylcyclopropane to form an intermediate alkane complex, **4a**, which is in fast equilibrium with the diastereomeric alkane complex **4b**.[24] The metal center can then reinsert into a C−H bond of the ligated dimethylcyclopropane to form either diastereomer. Reinsertion into **4a** re-forms the starting diastereomer, **1a**, and reinsertion into **4b** leads to the second diastereomer, **1b**. Alternatively, the dimethylcyclopropane can be lost into solution and replaced with C_6D_6, which then undergoes oxidative addition to form **3**. Least-squares nonlinear regression analysis of the kinetic data using model B yielded the rate constants[25] summarized in Figure 2.

Due to the similarity of rates of the deuterium-scrambling process and the diastereomer interconversion, we believe that the deuterium-scrambling process occurs by the same mechanism: the metal center of the intermediate complexes **4a**,**b**-d_1 is capable of activating either the C−H bond or the C−D bond of the dimethylcyclopropane-d_1 ligand.[26] Although the deuterium scrambling for this system could still occur through a concerted dyotropic rearrangement, such a pathway should result in simultaneous inversion of both stereocenters in the molecule and thus is not a likely mechanism for the diastereomer interconversion.

Comparison of the results from the iridium system discussed here and the analogous rhodium system studied earlier[15] with respect to model B yields the following interesting conclusion: with iridium, the barrier for interconversion of **4a** and **4b** is comparable to the barrier for C−H insertion to re-form **1a**,**b** whereas the corresponding barrier for interconversion of the rhodium analogs of **4a** and **4b** is high compared to the barrier for C−H insertion.[27] This difference may be caused by the different temperatures at which the two reactions are run; another possibility, however, is that deuterium scrambling in the rhodium system occurs by a dyotropic rearrangement. Studies with other isotopically and stereospecifically labeled complexes[27] will be required to obtain evidence on this question.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. T.A.M. thanks the National Science Foundation for a predoctoral fellowship.

Supporting Information Available: Spectral data for **1a**,**b** and deuterated analogs, a description of the low-temperature chromatography, and a representative kinetic fit of NMR integration data (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(18) Three Fortran programs were used to fit the data using numerical integration and least squares nonlinear regression: Gear (version 2.1) and Git (version 2.1) were written by R. J. McKinney and F. J. Weigert at E. I. DuPont de Numours and Co. and Calkinetics (version 1.0) was written by J. Krom (currently at Cornell University). The results obtained using Gear and Git agreed with those using Calkinetics.

(19) Only the sum of the rate constants, k_3 and k'_3, leading to **3** can be determined. This fact is indigenous to the analytical solution for this mechanism and manifested itself in the variability of the relative magnitudes of k_3 and k'_3 produced by the fit.

(20) At extended reaction times a slower process exhibiting deuterium scrambling into the β-cyclopropyl positions could be observed by $^2H\{^1H\}$ NMR spectroscopy.

(21) The integration of the hydride signal was corrected to account for the loss of compound to the oxidative addition process forming **3** by using the integration of the $P(CH_3)_3$ resonance of **3** as an estimate for the amount of material consumed.

(22) The value obtained from this analysis agreed with the value obtained from the $^{31}P\{^1H\}$ NMR data; however, due to signal overlap in the α-proton region of the spectrum these data were not as precise as those given in Figure 2.

(23) The diastereomer interconversion rate constants k_2 and k_{-2} determined in experiments using deuterium-labeled materials are the same within experimental error as those determined using unlabeled materials.

(24) The alkane complexes **4a**,**b** are not meant to suggest specific structures but are drawn merely to indicate an interaction between the metal center and the alkane. Theoretical evidence (refs 12−14) supports end-on or near end-on structures. In this case, diastereomeric **4a** and **4b** as drawn in Figure 3 each represent one of the two possible enantiomeric end-on structures.

(25) The regression analysis predicts that interconversion of the *RR* and *SS* enantiomers of diastereomer **1b** should occur at a rate approximately 1 order of magnitude faster than the *RS* and *SR* enantiomers of diastereomer **1a** ($k_6 > k_5$). Future work may include the study of optically active materials to determine if this is true.

(26) Scrambling of deuterium atoms into the β-positions (see footnote 20) in the cyclopropyl ring involves a higher energy 1.2-shift of the iridium center prior to oxidative addition.

(27) Formation of intermediate **4a** from **1a**. followed by reoxidative addition of the (original) cyclopropyl C−H bond without leakage to **4b**. is essentially the dyotropic reaction process; this would result in inversion at both stereocenters in **1a**. Examination of deuterium scrambling in optically active **1a**-α_{d_1} would be required to determine if deuterium scrambling occurs by this double-inversion pathway.