

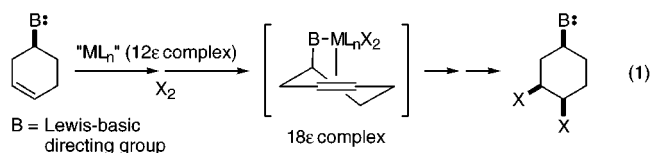
Exploiting η^5 - to η^3 -Indenyl Ring Slippage to Access a Directed Reaction: Ether-Directed, Rhodium-Catalyzed Olefin Hydroboration

Christine E. Garrett and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 11, 1997

Directed reactions, which comprise an important subset of synthetically useful metal-catalyzed processes, are demanding with respect to coordinative unsaturation at the metal.¹ As Crabtree has noted in the context of hydrogenation reactions, access to a 12ϵ (or less) metal complex is often required for a directed olefin addition process (eq 1), due to the need to simultaneously accommodate the directing group (B; 2ϵ), the olefin (2ϵ), and the addend (X_2 ; 2ϵ).² This



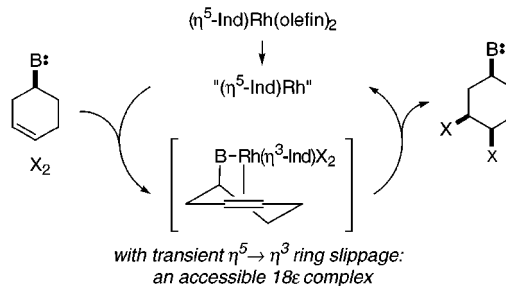
analysis adequately rationalizes the observation that complexes such as $[(\text{bispophine})\text{Rh}]^+$ (12ϵ fragment) are effective catalysts for directed hydrogenation processes, whereas $(\text{phosphine})_2\text{RhCl}$ complexes (14ϵ fragment; e.g., from Wilkinson's catalyst) are not.

The design of catalysts that provide ready access to the requisite coordinative unsaturation should facilitate the development of directed reactions. Toward that end, we have initiated an investigation of complexes that bear ligands prone to coordinative isomerization, a process that can afford a low-energy pathway to an unsaturated metal center. The family of ligands best known for displaying this mode of behavior are cyclopentadienyl derivatives, which can readily interconvert between η^5 - and η^3 -complexation to a metal (ring slippage).³ To the best of our knowledge, coordinative isomerization has never been exploited as a means for effecting a directed reaction. In this report, we furnish evidence, in the context of ether-directed rhodium-catalyzed hydroboration, that this strategy is indeed viable.

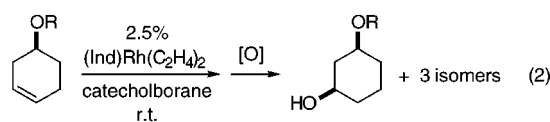
To validate our approach, we chose to examine the chemistry of $(\eta^5\text{-Ind})\text{Rh}$ (Ind = indenyl), a 14ϵ fragment;⁴ we selected the indenyl, rather than the cyclopentadienyl, ligand due to the greater propensity of indenyl to ring slip from η^5 to η^3 .^{3b,5} According to the Crabtree analysis, if ring slippage does not occur, then 14ϵ $(\eta^5\text{-Ind})\text{Rh}$ should not effect a directed olefin addition reaction. Conversely, if a directed process is observed, then it is reasonable to conclude that η^5 to η^3 ring slippage provided the necessary coordinative unsaturation (Scheme 1).

With respect to choice of reaction, we elected to explore the hydroboration of olefins with catecholborane, a process

Scheme 1



that we established is accelerated by $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ (turnovers numbers as high as 1000).^{6,7} One functional group that is known to direct hydrogenations catalyzed by 12ϵ $[(\text{bispophine})\text{Rh}]^+$ is the alkyl ether,^{1,8} and we have determined that this functional group also directs hydroborations catalyzed by $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ (eq 2).^{9–11} This obser-



	cis-1,3 : trans-1,3 : 1,4 (cis + trans)		
R = Bn (79%)	75	8	18
TBS	46	26	28

vation of an ether-directed hydroboration suggests that the ring-slippage strategy outlined above is in fact viable (Scheme 1). As a control experiment, we investigated the hydroboration of the corresponding silyl ether;¹² silyl ethers do not direct $[(\text{bispophine})\text{Rh}]^+$ -catalyzed hydrogenations, and we found that the $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ -catalyzed hydroboration of this substrate proceeds with relatively poor stereoselectivity (eq 2).

To furnish additional evidence that the alkyl ether is directing the $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ -catalyzed hydroboration of 4-(benzyloxy)cyclohexene, we compared the diastereoselection in solvents of high and low Lewis basicity. Consistent

(1) For a review, see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307–1370.

(2) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655–2661.

(3) (a) For the original observation, see: Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. (b) For a review, see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.

(4) CpRhL_2 complexes serve as catalysts for a variety of olefin addition reactions. See: *Dictionary of Organometallic Compounds*, Chapman and Hall: London, 1995.

(5) (a) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403–2407. (b) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208–1209.

(6) (a) For the first report of transition metal-catalyzed hydroboration of olefins with catecholborane, see: Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878–879. (b) For a review, see: Fu, G. C.; Evans, D. A.; Muci, A. R. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI: Greenwich, CT, 1995; Vol. 1, pp 95–121.

(7) For a report of amide-directed, metal-catalyzed olefin hydroboration, see: Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 4042–4043.

(8) Brown, J. M.; Hall, S. A. *Tetrahedron* **1985**, *41*, 4639–4646.

(9) The *cis*-1,3-diol derivative, rather than the *cis*-1,4 isomer, should be the predominant product in a directed reaction wherein the directing group is bound to the metal in the regioselectivity-determining step.¹

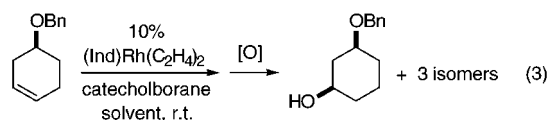
(10) (a) In the absence of $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ under otherwise identical conditions, less than 10% conversion is observed. The product that is generated is an approximately equimolar mixture of four isomeric alcohols.

(b) We have established through ¹¹B NMR studies that catecholborane does not disproportionate in the presence of alkyl ethers and that the preoxidation product of the $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ -catalyzed hydroboration is an alkylboronate ester. For leading references to potential complications in hydroborations of olefins with catecholborane, see: Garrett, C. E.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 3224–3225. (c) We have found that commercially available catecholborane is sometimes contaminated with SME_2 -derived impurities that can affect catalyst activity and reaction diastereoselectivity. (d) This $(\text{Ind})\text{Rh}(\text{C}_2\text{H}_4)_2$ -catalyzed hydroboration proceeds with comparable rate and diastereoselectivity in the presence of mercury (a test for homogeneous catalysis: Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725).

(11) In contrast, hydroborations of 4-(benzyloxy)cyclohexene in the presence of catecholborane/ $\text{ClRh}(\text{PPh}_3)_3$ or $\text{BH}_3\text{-THF}$ are not selective (approximately statistical mixture of products).

(12) For a discussion of the low Lewis basicity of silyl ethers, see: Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697–703.

with the behavior expected for a directed process, we observed higher selectivity in solvents that cannot compete effectively with the benzyl ether for binding to rhodium (eq 3). Thus, hydroborations in CH_2Cl_2 and hexane preferentially afford the *cis*-1,3 isomer, whereas the reaction in THF is relatively unselective.



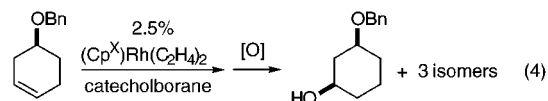
	<i>cis</i> -1,3	<i>cis</i> -1,4	<i>trans</i> -1,3	<i>trans</i> -1,4
hexane	75	7	7	11
CH_2Cl_2	74	5	8	13
THF	47	15	23	15

Our investigation of the catalyzed hydroboration of 4-(benzyloxy)cyclohexene by a family of Cp^XRh catalysts (Cp^X = a cyclopentadienyl-derived ligand) provides support for the suggestion that ring slippage plays a pivotal role in making a directed reaction possible. Literature data establish the following order for the relative propensity of cyclopentadienyl-derived ligands to ring slip:¹³



We have determined that each of the rhodium complexes that bear these ligands serves as a catalyst for olefin hydroboration, and we have observed a correlation between the propensity of the ligand to ring slip and the preference for generating the product of a directed reaction (the *cis*-1,3 isomer, eq 4).

(13) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, 198–200, 219–231 and references therein.



	<i>cis</i> -1,3	<i>cis</i> -1,4	<i>trans</i> -1,3	<i>trans</i> -1,4
$\text{Cp}^X = \text{Ind}$	75	7	8	11
1,2,3-trimethylindenyl	65	10	12	13
Cp	30	28	30	12
Cp^*	26	29	33	12

propensity to ring slip: Ind > 1,2,3-trimethylindenyl >> Cp > Cp^*

To the best of our knowledge, this study provides the first report that an alkyl ether can direct a metal-catalyzed olefin hydroboration. This process relies upon the capacity of an indenyl ligand to transiently ring slip, thereby affording access to the necessary level of coordinative unsaturation at the metal. We anticipate that this ring-slippage approach to directed reactions may be extendible to other systems.¹⁴

Acknowledgment. Support has been provided by the Alfred P. Sloan Foundation, the American Cancer Society, the Camille and Henry Dreyfus Foundation, Eli Lilly, Firmenich, Glaxo Wellcome, the National Science Foundation (predoctoral fellowship to C.E.G.; Young Investigator Award to G.C.F., with funding from Procter & Gamble, Merck, Bristol-Myers Squibb, DuPont, Pfizer, Rohm & Haas, Pharmacia & Upjohn, and Bayer), and the Research Corporation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research.

Supporting Information Available: Experimental procedures and compound characterization data (9 pages).

JO9720647

(14) Preliminary results indicate that esters also direct the $\text{IndRh}(\text{C}_2\text{H}_4)_2$ -catalyzed hydroboration of olefins.