

## Rhodium(I)-Catalyzed Hydroboration of Olefins. The Documentation of Regio- and Stereochemical Control in Cyclic and Acyclic Systems

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The hydroboration reaction has had a profound impact on the field of organic synthesis.<sup>1</sup> In spite of numerous variants of the basic process which have been developed, it has only been within the last several years that the possibility has been raised that transition-metal catalysis might significantly extend the utility of this reaction.<sup>2,3</sup> Within this context, the recent report by Mannig and Noth<sup>2</sup> that certain metal complexes, such as Rh-(PPh<sub>3</sub>)<sub>3</sub>Cl (1), effectively catalyze the hydroboration of simple alkenes by catecholborane (CB), a reaction which normally requires elevated temperatures (70–100 °C),<sup>4</sup> complements the seminal observation made 10 years earlier by Kono that this catalyst rapidly undergoes an oxidative insertion into the B–H bond of catecholborane.<sup>5</sup> Since the transition-state stoichiometries and (presumably) the rate-determining steps of the two reactions are not the same, the stereochemical consequences of the catalyzed and uncatalyzed processes could well be different. The purpose of this communication is to provide the first documentation that this is indeed the case. In addition to the catalysts previously reported,<sup>2</sup> we have found a variety of other complexes which catalyze this process with varying levels of efficiency.<sup>6</sup> Finally, we have documented the first examples of a *directed*, metal-catalyzed hydroboration reaction.

The following discussion provides an overview of olefin reactivity for the catalyzed hydroboration of various olefin classes with catecholborane (CB). In the presence of Wilkinson's catalyst (2 mol%) monosubstituted olefins (0.07–0.10 M, 3 equiv of CB, THF) undergo hydroboration within 30 min at –20 °C, while 1,1-disubstituted alkenes require up to 5 h at 25 °C for complete reaction. Whereas cyclic 1,2-disubstituted alkenes react completely within 12 h (25 °C), the corresponding acyclic alkenes (both E and Z) are hydroborated more slowly, and olefin isomerization and hydrogenation are observed as significant side reactions. Finally, the hydroboration of trisubstituted alkenes is sluggish, affording less than 10% conversion after 24 h (25 °C).

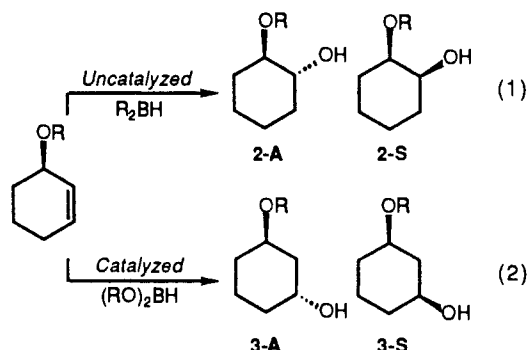
Hydroboration of 1-decene with catecholborane and Wilkinson's catalyst proceeds with high regioselectivity in favor of the primary alcohol (>99.5% at –40 °C, 99% at 25 °C),<sup>7</sup> comparable to the

Table I. Hydroboration of Cyclohexenol Derivatives (Eq 1 and 2)

R	conditions <sup>a</sup>	yield <sup>b</sup> %	2-A	3-A	3-S	2-S <sup>c</sup>
H	uncatalyzed	86	83	5	10	2
	catalyzed	84	18	72	9	1
CH <sub>2</sub> Ph	uncatalyzed	73	68	13	19	0
	catalyzed	87	7	72	13	8
Si <sup>t</sup> BuMe <sub>2</sub>	uncatalyzed	70	74	13	13	0
	catalyzed	79	2	86	11	1

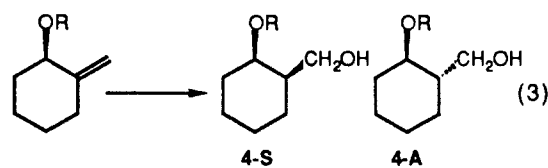
<sup>a</sup>Uncatalyzed reaction: 3 equiv of 9-BBN, THF, 25 °C; catalyzed reaction: 3 equiv of catecholborane, 3% 1, 25 °C. <sup>b</sup>Combined, isolated yields of diastereomeric mixture. <sup>c</sup>Ratios determined by capillary GLC.

reaction with hindered dialkylboranes such as 9-BBN (>99.5% at 25 °C).<sup>8</sup> On the other hand, the same reaction catalyzed by the cationic rhodium complex, [Rh(nbd)(diphos-4)]BF<sub>4</sub>, is significantly less selective (97% at –40 °C, 90% at 25 °C). In the hydroboration of cyclic 1,2-disubstituted allylic alcohol derivatives, the regioselectivity of the catalyzed reaction is opposite to that of the uncatalyzed variant (eq 1 and 2). In contrast to the



9-BBN hydroborations,<sup>9</sup> which appear to be dominated by electronic effects favoring the anti 1,2 diols 2-A, the catalyzed reaction favors the anti 1,3 diols 3-A (Table I). In both reactions, the yields and diastereoface selectivities ( $\Sigma$  A:S) are comparable, with each reaction occurring predominantly anti to the allylic oxygen. The inversion of the regioselectivity in the two reactions is difficult to explain in the absence of additional mechanistic data; however, one should not rule out the possibility that boron, rather than hydrogen, might be preferentially transferred in the olefin insertion step.

In the hydroboration of exocyclic cycloalkenes under the conditions described in Table I, the uncatalyzed reactions with 9-BBN show only marginal levels of stereocontrol, whereas the catalyzed hydroborations provide the syn isomers 4-S with excellent diastereoselection (eq 3).



R	Conditions <sup>11</sup>	Yield, %	4-S	4-A
H	Uncatalyzed	83	50	50
	Catalyzed	93	90	10
S <sup>t</sup> BuMe <sub>2</sub>	Uncatalyzed	81	39	61
	Catalyzed	88	96	4

The diastereoselective hydroboration of acyclic 1,1-disubstituted allylic alcohols with various alkylboranes has been investigated by Still and Barrish, who have reported that high levels of anti-selectivity are achieved when hindered boranes such as 9-BBN

(8) For the regioselectivity of some common boranes, see: Zweifel, G.; Brown, H. C. *Org. React.* 1963, 13, 1. Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* 1975, 97, 5249.

(9) Satisfactory spectral data and elemental analyses were obtained on all compounds reported herein.

(1) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973. Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

(2) Mannig, D.; Noth, H. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 878.

(3) For leading references in this area, see: (a) Catalytic hydroboration with rhodium carboranes: Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 5757. (b) Transition-metal-promoted reactions of polyhedral boranes and carboranes: Sneddon, L. G. *Pure Appl. Chem.* 1987, 59, 837. (c) Rhodium-catalyzed addition of borazine to alkynes: Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* 1987, 109, 5867.

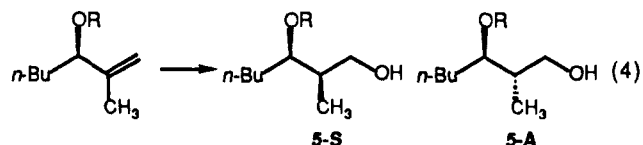
(4) For a review of the chemistry of catecholborane, see: Lane, C. F.; Kabalka, G. W. *Tetrahedron* 1976, 32, 981. See, also: Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* 1983, 48, 5080.

(5) Kono, H.; Ito, K. *Chem. Lett.* 1975, 1095.

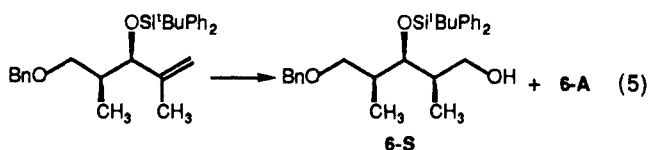
(6) In addition to catalysts reported by Mannig and Noth (1), RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, RhCl(CO)(AsPh<sub>3</sub>)<sub>2</sub>, and [RhCl(cod)]<sub>2</sub><sup>2</sup> we have found that (C<sub>6</sub>Me<sub>6</sub>)RhCl<sub>2</sub>(PPh<sub>3</sub>), F(CO)Rh(PPh<sub>3</sub>)<sub>2</sub>, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, [Rh(nbd)(diphos-4)]BF<sub>4</sub>, and [Ir(cod)(PCy<sub>3</sub>)(py)]PF<sub>6</sub> are also active catalysts for the hydroboration of 1-decene with catecholborane at 25 °C. A variety of other transition-metal catalysts (Ru, Rh, Pd, Pt, Ni, Ti, Zr, Fe), both heterogeneous and homogeneous, were screened. Olefin hydrogenation as a side reaction was frequently observed; similar behavior has been observed in transition-metal-catalyzed hydrosilylation reactions: Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* 1983, 48, 5101. Abbreviations: cod = 1,5-cyclooctadiene; nbd = norbornadiene; diphos-4 = 1,4-bis(diphenylphosphino)butane; py = pyridine.

(7) All the hydroboration reactions described in this communication include the usual oxidative workup (NaOOH). See the Supplementary Material for experimental details.

are employed, affording a >10:1 preference for 5-A (eq 4).<sup>10,11</sup> In contrast, the Rh(PPh<sub>3</sub>)<sub>3</sub>Cl-catalyzed hydroboration of 1,1-disubstituted allylic alcohol derivatives also takes place with high levels of stereoselectivity but in the complementary sense to that observed with dialkylboranes with the major product being the syn diastereomer 5-S. The related hydroboration illustrated in eq 5 illustrates the potential utility of these complementary reactions in the synthesis of polypropionate-derived natural products.<sup>12</sup> Although space limitations preclude the presentation of the analogous data for other catalysts, we have found the cationic catalyst, [Rh(nbd)(diphos-4)]BF<sub>4</sub>, to be decidedly less regio- and diastereoselective than Rh(PPh<sub>3</sub>)<sub>3</sub>Cl. Collectively, these experiments suggest that the catalyzed and uncatalyzed reactions may well have different product-determining steps, and deuterium-labeling experiments to be described at a later date support this position.



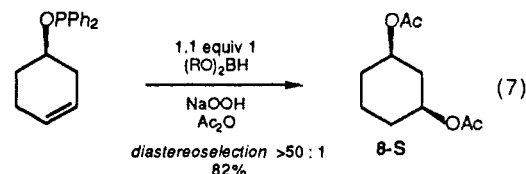
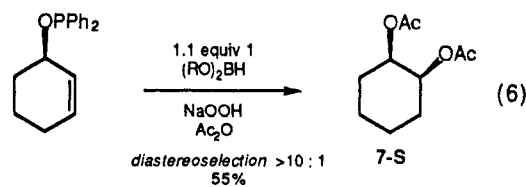
R	Conditions <sup>11</sup>	Yield, %	5-S	5-A
H	Uncatalyzed	80	8	92
	Catalyzed	77	75	25
s <sup>t</sup> BuMe <sub>2</sub>	Uncatalyzed	94	11	89
	Catalyzed	80	96	4
s <sup>t</sup> BuPh <sub>2</sub>	Uncatalyzed	92	14	86
	Catalyzed	96	97	3



Conditions <sup>11</sup>	Yield, %	6-S	6-A
Uncatalyzed	82	14	86
Catalyzed	80	95	5

We have also addressed the notion that proximal functional groups might be employed to direct the stereochemical course of the hydroboration reaction. Because of the rapid reaction of catecholborane with alcohols to form borates, direction of the reaction by complexation of the hydroxy group to the catalyst is precluded. However, we have discovered that suitably disposed phosphinites<sup>13</sup> may effectively serve as directing groups in the metal-catalyzed hydroboration reaction (eq 6 and 7). Thus, in contrast to the aforementioned silyl ethers (eq 2), hydroboration of the illustrated allylic phosphinite selectively affords the syn 1,2-diol diastereomer 7-S. Hydroboration of the analogous homoallylic phosphinite affords the syn 1,3-diol with high regio- and stereocontrol, whereas reaction of the corresponding silyl ether results in a statistical mixture of 1,3- and 1,4-diols.<sup>14</sup>

The previously described experiments illustrate the expanded scope which is provided by the rhodium-catalyzed hydroboration process. Additional studies regarding the metal-catalyzed hydroboration reaction continue in these laboratories.



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**Supplementary Material Available:** Detailed procedure for the catalyzed hydroboration reaction (3 pages). Ordering information is given on any current masthead page.

### The Preparation and Structure of a Dinuclear $\eta^2\text{-H}_2$ Complex (P-N)( $\eta^2\text{-H}_2$ )<sub>2</sub>Ru( $\mu\text{-Cl}$ )<sub>2</sub>( $\mu\text{-H}$ )Ru(H)(PPh<sub>3</sub>)<sub>2</sub>, P-N = Fe( $\eta\text{-C}_5\text{H}_3(\text{CHMeNMe}_2)\text{P}(i\text{-Pr})_2$ , 1,2)( $\eta\text{-C}_5\text{H}_5$ )

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A number of mononuclear complexes containing an  $\eta^2$ -hydrogen ligand have been described recently,<sup>2</sup> and  $\eta^2\text{-H}_2$  has been established in the two known solid-state structures.<sup>3</sup>

(1) NRC publication no. 29296.

(2) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (e) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (f) Vergamini, P. J.; Wasserman, H. J.; Koetzle, T.; Kubas, G. J., manuscript in preparation, quoted in ref 1e. (g) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113. (h) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (i) Crabtree, R. H.; Lavin, M.; Bonnevot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (j) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (k) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (l) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794. (m) Crabtree, R. H., personal communication. (n) Morris, R. M.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (o) Bautista, M. T.; Earl, K. A.; Morris, R. M.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (p) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.*, in press. (q) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowich, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674. (r) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598. (s) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124. (t) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (u) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (v) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

(10) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. For related work on vinyl ethers, see: McGarvey, G. J.; Bajwa, J. S. *Tetrahedron Lett.* **1985**, *26*, 6297.

(11) See the conditions defined in Table I for the catalyzed and uncatalyzed hydroboration reactions.

(12) A large number of 1,1-disubstituted allylic alcohols were examined, and all show similar levels and patterns of diastereoselection.

(13) For examples of phosphine-directed hydroformylation, see: Burke, S. D.; Cobb, J. E. *Tetrahedron Lett.* **1986**, *27*, 4237. Jackson, W. R.; Perlmutter, P.; Suh, G.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 724.

(14) Stoichiometric quantities of catalyst are required for high yields, probably due to the instability of the uncatalyzed phosphinite to catecholborane.