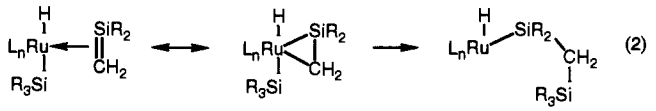
Cleavage of a Si-H bond can be most reasonably accomplished by oxidative addition of a hydrosilane to an unsaturated ruthenium center. Although cleavage of a C-H bond could occur by direct *inter*molecular addition of a free silane methyl group (e.g., H-CH_2SiMe_2H), this process appears unlikely. Catalytic coupling of $HSiMe_3$ in the presence of excess $SiMe_4$ does not yield detectable quantities of $Me_3SiCH_2SiMe_3$, the expected product of quaternary silane C-H activation.[12]

Recent mechanistic studies on related osmium complexes provide a simple alternative to intermolecular C-H activation in the formation of carbosilanes. The osmium silyl complex Os(H)($SiMe_3$)(PMe_3)$_4$ has been found to catalyze the H/D exchange between free $HSiMe_3$ and benzene-d_6 via a mechanism involving an intermediate η^2-silene (η^2-$Me_2Si{=}CH_2$) complex.[13] The η^2-silene ligand is generated through a novel β-hydrogen elimination from a silyl ligand, i.e., an *intra*molecular C-H addition. Note that stable η^2-silene complexes of early and late transition metals have been isolated recently by other synthetic routes.[14] Formation of an η^2-silene ligand by β-hydrogen elimination from a silyl represents the dehydrogenation of a silane molecule containing adjacent Si-H and C-H bonds. The carbosilane products observed in the present study can be viewed as arising from the net addition of the Si—H bond of a free silane across the Si=C unsaturation of the coordinated η^2-silene ligand as shown in eq 2. This is in direct analogy with the metal-catalyzed hydrosilylation of organic olefins.[2] The migration of silyls to organic olefin ligands is well precedented.[15]



(2)

In the present case, carbosilane dimer **2** would result from the net addtiion of $HSiMe_3$ to $Me_2Si{=}CH_2$, the complexed silene generated from a $SiMe_3$ ligand. Furthermore, the distribution of trimeric and tetrameric carbosilanes observed in eq 1 can be readily explained by this model. For example, the trimeric carbosilane **3a** would result from the net addition of $HSiMe_3$ across the silene generated from the dimeric product **2**. In a similar manner, **3b** would arise from the addition of $HSiMe_2CH_2SiMe_3$ (**2**) to the silene generated by dehydrogenation of $HSiMe_3$. Tetramer **4a** would then result from the coupling of two molecules of **2**, and **4b** would arise from the reaction of $HSiMe_3$ with **3a**. In fact, isolated **2** is catalytically coupled to initially yield carbosilane **4a** as the only tetrameric product (eq 3).

$$\underset{\mathbf{2}}{HSiMe_2CH_2SiMe_3} \xrightarrow[150\ ^\circ C,\ C_6H_{12}]{Ru(H)_2(PMe_3)_4} \underset{\mathbf{4a}}{Me_3SiCH_2Si(H)MeCH_2SiMe_2CH_2SiMe_3} + H_2 \quad (3)$$

The first example of a homogeneous dehydrogenative coupling of hydrosilanes to directly produce oligomeric carbosilanes has been described.[16] A mechanism involving the intermediacy of η^2-silene ligands is most consistent with observations obtained thus far and has precedent in a related osmium system.[13] Further exploration of this chemistry is currently in progress.

Acknowledgment. Financial support of this work by the National Science Foundation (Grant No. CHE-8808161) is gratefully acknowledged. Additional support for shared instrumentation was provided by the NSF MRL program (DMR-88-19885). D.H.B. also thanks the University of Pennsylvania Natural Science Association for a Young Faculty Award, and L.J.P. thanks the University of Pennsylvania School of Arts and Sciences for a Dissertation Fellowship.

Supplementary Material Available: Experimental procedures (including spectral and GC data) for the synthesis of **2-4** (4 pages). Ordering information is given on any current masthead page.

(12) The compound $(Me_3Si)_2CH_2$ is not observed by NMR or GC either (a) when $HSiMe_3$ and $SiMe_4$ are treated with **1** and coupling occurs according to eq 1 or (b) when **1** reacts with excess $SiMe_4$ in the absence of $HSiMe_3$.

(13) Berry, D. H.; Procopio, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 4099.

(14) (a) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558.

(15) (a) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (b) Randolf, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (c) Arnold, J.; Engler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.

(16) To our knowledge, the only other reported example of a metal-mediated dehydrogenative coupling of hydrosilanes producing Si-C bonds involves the reaction of $HSiMe_3$ with the Pd(110) surface under ultrahigh-vacuum conditions, in which c-$(SiMe_2CH_2)_2$ was observed: Gentle, T. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 304.

Microscale CD Method for Determining Absolute Configurations of Acyclic Amino Tetrols and Amino Pentols. Structures of Aminobacteriohopanepolyols from the Methylotrophic Bacterium *Methylococcus luteus*

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The CD exciton chirality method[1] has been applied to numerous compounds including sugars[2] and acyclic polyols with up to five contiguous OH's.[3] In prokaryotic membranes, hopanoids play the reinforcing role of sterols in eukaryotic membranes, and the total organic carbon in fossil hopanoids is estimated to equal the carbon in all living animals, plants, and microorganisms, ca. 10^{12} tons.[4] The CD method developed for acyclic polyols[3] can be extended to amino polyols as demonstrated by its application[5] to a bacteriohopane with an established amino triol moiety.[6] We now extend this method to bacteriohopanoids with amino tetrol **1** and amino pentol **2** moieties of unknown stereochemistry, *despite the lack of authentic hexol corresponding to* **2**.

Amino tetrol **1** and amino pentol **2** were isolated as acetates from *Methylococcus luteus* (NCIMB 11914) and were identical with the corresponding triterpenoids from *Methylococcus capsulatus* and *Methylomonas methanica*.[6] Free amino polyols **1** and **2**, as precipitates that were poorly soluble in solvents, were obtained from acetates by heating at 110 °C for 7 h in 3% KOH/*i*-PrOH.

In the bichromophoric CD method for configurational studies of acyclic polyols[3] and amino polyols,[5] the terminal OH or NH_2 is anthroylated, the remaining OH's are *p*-methoxycinnamoylated, and the 220-340-nm CD spectra are compared with characteristic reference curves. The present *improved* nanomolar-scale deriv-

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(1) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

(2) Wiesler, W. T.; Berova, N.; Ojika, M.; Meyers, H. V.; Chang, M.; Zhou, P.; Lo, L.-C.; Niwa, M.; Takeda, R.; Nakanishi, K. *Helv. Chim. Acta* **1990**, *73*, 509-551.

(3) (a) Wiesler, W. T.; Nakanishi, K. *J. Am. Chem. Soc.* **1989**, *111*, 3446-3447. (b) Wiesler, W. T.; Nakanishi, K. *J. Am. Chem. Soc.* **1989**, *111*, 9205-9213. (c) Wiesler, W. T.; Nakanishi, K. *Croat. Chem. Acta* **1989**, *62*, 211-226.

(4) Ourisson, G.; Rohmer, M.; Poralla, K. *Annu. Rev. Microbiol.* **1987**, *41*, 301-333.

(5) Zhou, P.; Berova, N.; Nakanishi, K.; Rohmer, M. *J. Chem. Soc., Chem. Commun.* **1991**, 256-258.

(6) (a) Neunlist, S.; Rohmer, M. *Biochem. J.* **1985**, *231*, 635-639. (b) Neunlist, S.; Bisseret, P.; Rohmer, M. *Eur. J. Biochem.* **1988**, *171*, 245-252. (c) Neunlist, S.; Rohmer, M. *J. Chem. Soc., Chem. Commun.* **1988**, 830-832.

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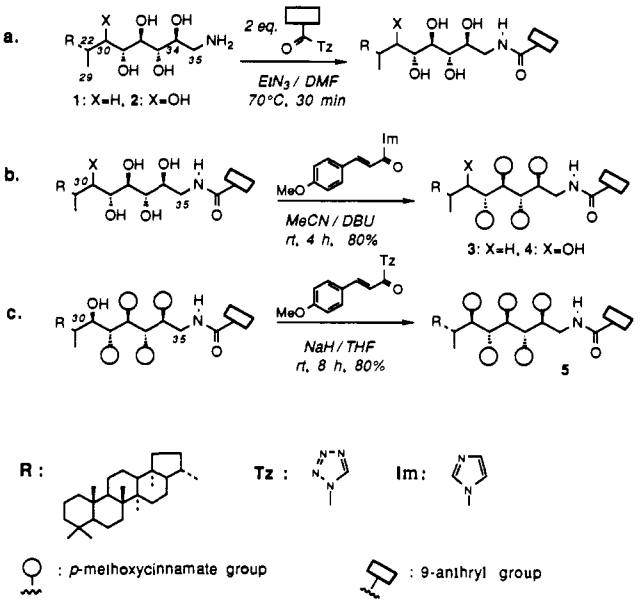
Scheme I. Bichromophoric Derivatizations of 35-Aminobacteriohopane-31,32,33,34-tetrol **1** and 35-Aminobacteriohopane-30,31,32,33,34-pentol **2**



atization for amino polyols is as follows (Scheme I). In a 2 × 30 mm glass tube were added 50–60 μg of amino polyol **1** (~100 nmol), 2 equiv of 9-anthroyltetrazole, excess Et_3N, and 15 μL of DMF. The tube was sealed under N_2, the mixture heated at 70 °C for 30 min with occasional shaking, the tube opened, and the solvent removed in vacuo. The residual anthramide was treated with excess (*p*-methoxycinnamoyl)imidazole[7] and DBU in MeCN at room temperature for 4 h, and the final product was purified by HPLC, CH_2Cl_2/MeOH gradient, 0 → 1%, 5-μm SiO_2, 254–311-nm detection. This gave tetracinnamates of amino tetrol **3** and amino pentol **4**[8] (Scheme I, part b). For complete cinnamoylation of **4**, a longer reaction time or higher temperature had no effect; pentacinnamate **5**, however, was prepared with the more active (*p*-methoxycinnamoyl)tetrazole[7] and stronger base NaH (Scheme I, part c).

Stereochemical assignment of amino tetrol **1** was performed by comparing its CD spectrum with reference spectra.[3b] Figure 1b shows the CD spectra of bichromophorically derivatized tetrols with L-*altro*-**9** and L-*allo*-**10** configurations; the CD spectrum of derivatized amino tetrol **3** (Figure 1c) is almost superimposable with the curve for **10**. The terminal groups of reference polyols and amino polyols are *O*- and *N*-acylates, respectively, but it is known that the CD characteristics of these two are comparable.[1,2,5] The negative Cotton effects in the three curves, due to exciton coupling between the anthroate 253-nm ^1B_b and the cinnamate 311-nm ^1L_a transitions, arise from the identical 34*S* configuration, while similarity in the CD spectra above 250 nm of amino tetrol **3** and L-*allo*-**10** shows that configurations at the remaining three chiral centers are also identical.

Configurational determination of amino pentol **2** is not straightforward due to the lack of reference hexols. However, examination of CD curves of bichromophorically derivatized polyols[3b] reveals a trend in which the assignment of absolute configurations is possible for (amino) polyols having a polyol moiety that is longer than the references. Figure 1a shows that

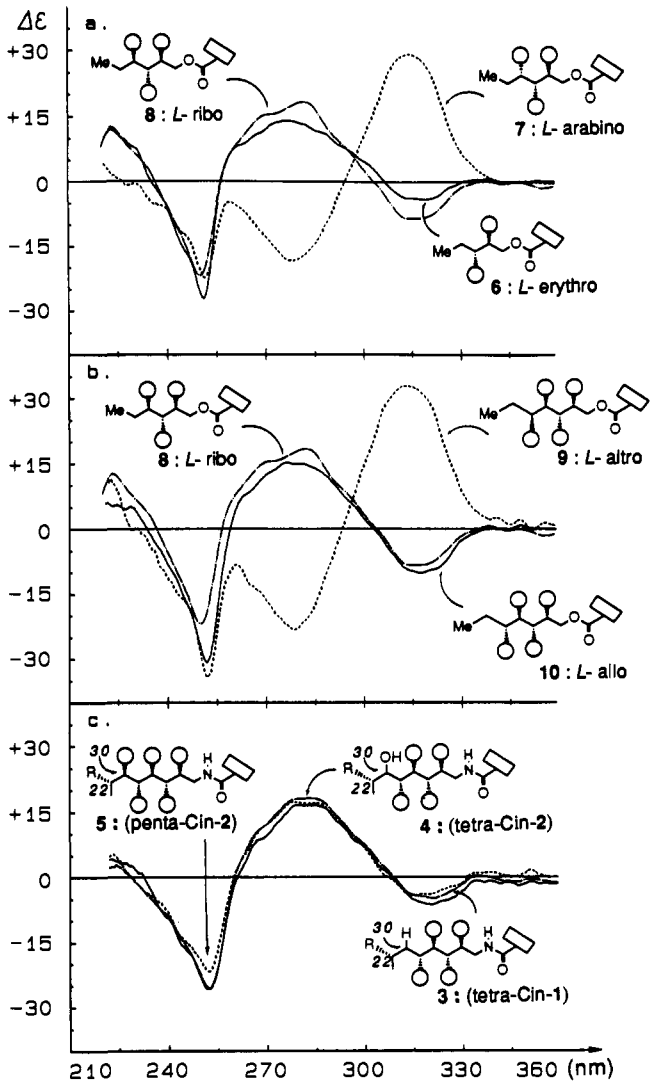


Figure 1. CD spectra (in the *nonpolar* methylcyclohexane[5]) of (a) bichromophorically derivatized triol **6** and tetrols **7** and **8**; (b) tetrol **8** and pentols **9** and **10**; and (c) 35-aminobacteriohopane-31,32,33,34-tetrol **3** and 35-aminobacteriohopane-30,31,32,33,34-pentols **4** and **5**. The molar concentrations were estimated from the 311-nm ε values (in MeCN) of tris(*p*-methoxycinnamate), 72 400, and tetrakis(*p*-methoxycinnamate), 93 400;[3b] the extrapolated ε value of the pentacinnamate is 115 000.

extension of L-*erythro*-**6** to L-*arabino*-**7** and L-*ribo*-**8** inverts the split CD curve around 311 nm when the configuration of the extending OH group is syn, i.e., **6** and **7**, but the 311-nm split CD curves remain unchanged when the configuration of the extending OH group is anti, i.e., **6** and **8**. This can be rationalized qualitatively as follows. When the configuration is 1,2-syn (**7**), the adjacent chromophoric transition moments have a torsional angle of 60° and thus are intensively coupled, whereas when the configuration is 1,2-anti (**8**), the two antiperiplanar chromophores are uncoupled; also, 1,3-chromophoric coupling is large in **7**, but is almost absent in **8**.[1,3b,9]

This trend remains valid when tetrol L-*ribo*-**8** is extended to its two homologous pentols (Figure 1b). Thus, 1,2-syn extension, **8** → **9**, inverts the sign of the 311-nm split CD curve, whereas 1,2-anti extension, **8** → **10**, does not change the sign. The similar curves between amino tetrol **3** (Figure 1c) and partially derivatized amino pentol **4** establish that the absolute configuration of amino pentol **2** is identical with that of amino tetrol **1** at C-31–C-34. The curve of pentacinnamate **5**, prepared by acylating 30-OH with

(7) (*p*-Methoxycinnamoyl)imidazole and (*p*-methoxycinnamoyl)tetrazole were synthesized by reacting *p*-methoxycinnamoyl chloride and imidazole in anhydrous THF at room temperature in 1.2 equiv of Et_2N for 1 h. The yield of the imidazole derivative after flash chromatography, 80% EtOAc in hexane, was >80%; it is stable at room temperature for at least 1 month. (*p*-Methoxycinnamoyl)tetrazole is too unstable to be isolated and was used immediately after generation. Review: Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 351.

(8) Hopanoid **4** was identified by FAB-MS. The pentaacetate of amino pentol **2** with a free 30-OH has been reported (ref 6a).

(9) Harada, N.; Saito, A.; Aoki, K.; Uda, H.; Sato, H. *Proceedings of the F.E.C.S. Second International Conference on Circular Dichroism*; Kajtár, M., Ed.; Inst. Organic Chemistry, L. Eötvös University, Budapest, 1987; pp 209–214.

(*p*-methoxycinnamoyl)tetrazole,[7] is similar to that of tetracinnamate **4**; *30-OH must thus be anti to adjacent 31-OH*. It follows that amino tetrol **1** is 31*R*,32*R*,33*S*,34*S*, and amino pentol **2** is 30*R*,31*R*,32*R*,33*S*,34*S*.

Acknowledgment. The studies were supported by NIH Grant GM34509 and Centre National de la Recherche Scientifique (Unitē de Recherche Associē 135).

Amide-Directed, Iridium-Catalyzed Hydroboration of Olefins: Documentation of Regio- and Stereochemical Control in Cyclic and Acyclic Systems

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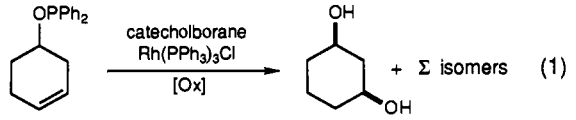
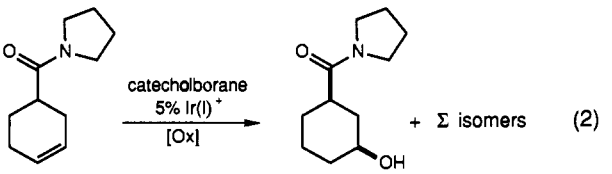
A "directed reaction" is a process in which a functional group transiently binds a reagent and delivers it to a second functionality within the molecule. High levels of regio- and stereocontrol often result from the multiple contact points that are established between the reacting partners in the transition structure. Recent examples of directed hydrogenation and ketone reduction serve to illustrate this point.[2]

Although a number of reactions have been shown to be directable, no general approach to effecting a directed olefin hydroboration with BH_3 or alkylboranes has been reported.[3,4] The lack of success in this area may well arise from constraints inherent to the uncatalyzed hydroboration process.[5] The discovery of a rhodium-catalyzed variant by Mannig and Noth[6] revived the prospects for the development of a directable olefin hydroboration. Indeed, we reported in 1988 that phospinites are capable of delivering the rhodium-mediated reaction (eq 1);[7] however, because *stoichiometric* quantities of $Rh(PPh_3)_3Cl$ are required, this method fell short of accomplishing our goal of developing a *catalytic* directed hydroboration. In this communication we report that amides effectively direct the $[Ir(cod)(PCy_3)(py)]PF_6$[2c]-catalyzed hydroboration of olefins with catecholborane (CB), an observation that represents a fulfillment of our original objective.

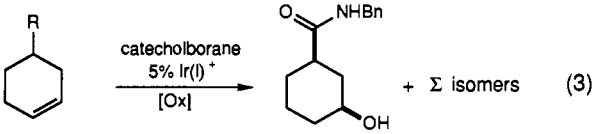


diastereoselection 98 : 2 (82%)

A number of functional groups known to direct metal-catalyzed olefin hydrogenation were screened for participation in the analogous hydroboration process with catecholborane.[8] From this survey, amides were found to be quite effective at actively participating in the hydroboration process.[9] For example, $[Ir(cod)(PCy_3)(py)]PF_6$-catalyzed hydroboration[7] of pyrrolidinyl amide **1** (2 equiv of CB, 5% catalyst, 11 h, 20 °C, $ClCH_2CH_2Cl$) affords the syn-1,3 hydroxy amide (eq 2) with good control of both regio- and stereoselectivity (95:5).[10,11] Competitive reduction of the tertiary amide moiety, the origin of the modest yield observed in this reaction, is readily avoided through the use of more reduction resistant secondary amides (**2a**; 5 equiv of CB, 5% catalyst, 10 h, 20 °C, $ClCH_2CH_2Cl$) as the directing group (eq 3).



1 *diastereoselection 95 : 5 (44%)*



2a, R = CONHBn *diastereoselection 91 : 9 (77%)*
2b, R = COOMe
2c, R = OSi(*tert*-Bu)Me_2

The following observations support the assertion that these reactions are amide-directed:

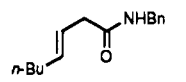
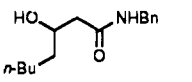
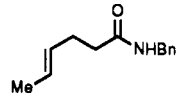
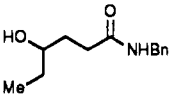
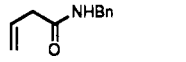
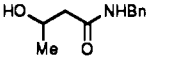
Stereoselectivity. The catalyzed hydroboration of a variety of other 4-substituted cyclohexenes, which include derivatives such as **2b** or **2c**, furnish an essentially statistical mixture of the four isomeric reaction products. Predominant formation of the syn-1,3 isomer (eqs 2 and 3) is consistent with the expectation of a directed reaction.[12]

Table I. Solvent Effect on the Stereoselectivity of the Amide-Directed Hydroboration (Eq 2)

solvent	syn-1,3: Σ(other 3 isomers)[a]
THF	45:55
ether	52:48
$ClCH_2CH_2Cl$	95:5

[a] Ratios determined by GLC on derived acetates.

Table II. Amide-Directed, Catalyzed Hydroboration: Acyclic Cases[15]

entry	substrate	product	selectivity[a] (% yield)
1			>99:1 (73)
2			99:1 (78)
3			1.2:1 (78)

[a] Ratio of proximal:distal hydroxylation, as determined by GLC.

(1) National Science Foundation Predoctoral Fellow.
(2) Directed hydrogenation: (a) Brown, J. M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 190-203. (b) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866-3868. (c) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655-2661. Directed ketone reduction: (d) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560-3578. (e) Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 6447-6449.
(3) Several workers have proposed reaction pathways involving the delivery of a boron hydride in order to explain anomalous regio- and stereoselectivities observed in uncatalyzed olefin hydroboration reactions. For example, see: (a) Suzuki, K.; Miyazawa, M.; Shimazaki, M.; Tsuchihashi, G.-i. *Tetrahedron* **1988**, *44*, 4061-4072. (b) Welch, M. C.; Bryson, T. A. *Tetrahedron Lett.* **1989**, *30*, 523-526.
(4) (a) For a report of an unsuccessful attempt to achieve a hydroxyl-directed hydroboration, see: Smith, A. B., III; Yokoyama, Y.; Huryn, D. M.; Dunlap, N. K. *Tetrahedron Lett.* **1987**, *28*, 3659-3662. (b) For a discussion of the likelihood of directivity in the hydroboration of a homoallylic alcohol with borane, see: Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243-246.
(5) For a discussion of the mechanism of the uncatalyzed hydroboration reaction, see: Wang, X.; Li, Y.; Wu, Y.-D.; Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 2601-2609.
(6) Mannig, D.; Noth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878-879.
(7) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917-6918.
(8) For a review of directed hydrogenation reactions, see ref 2a.
(9) Schultz, A. G.; McCloskey, P. J. *J. Org. Chem.* **1985**, *50*, 5905-5907.
(10) The cited selectivities refer to the ratio of the illustrated isomer to the sum of all other isomers. Product analyses were carried out by capillary GLC on the derived acetates.
(11) We have also examined the utility of $Rh(PPh_3)_3Cl$ and $[Rh(nbd)(diphos-4)]BF_4$ (nbd = norbornadienyl) as catalysts for amide-directed hydroboration. In some cases, use of these complexes affords selectivity comparable to that observed with $[Ir(cod)(PCy_3)(py)]PF_6$. In general, however, significantly lower selectivities are obtained.
(12) For example, see: Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090-6093.

0002-7863/91/1513-4042$02.50/0