

Figure 1. (a) X-ray structure of 6 and (b) X-ray structure of 7.

ppm) and adenine-2- (0.08 ppm) and 8- (0.05 ppm) proton resonances are seen, reflecting the close approach of the two rings in an aromatic stacking interaction (Chart III).^{2a,b} All of the shifts showed clear saturation behavior, and from these curves

an association constant (K_s) of 3200 M⁻¹ for 7:8 was determined.¹² This value is substantially larger⁴ than related triple hydrogen bonding receptors for thymine,^{2a} guanine,^{2b} and cytosine^{3b} thus confirming that simultaneous Watson-Crick and Hoogsteen interactions are present in complex 7:8. The complementarity and selectivity of this arrangement for adenine is further supported by the weak association between 8 and 1-butylthymine ($K_s < 23$ M⁻¹) or triptanoylguanosine ($K_s < 10$ M⁻¹). Despite the high level of preorganization apparent in Figure 1a, receptor 6 shows much weaker binding to 8 ($K_s = 73$ M⁻¹). This is possibly due to the two intramolecular hydrogen bonds, shown in solution by their downfield shifted NH resonances (δ 9.5 ppm in 6 compared to 8.30 ppm in 7), which block the cavity and must be broken for adenine binding to occur. Thus, the structure of 6 with two *intramolecular* H-bonds between the pyr-NH and the rigid 2,7-dioxynaphthalene provides a model for the conformational change that accompanies the *intermolecular* H-bonding interaction between 7 and 9-alkyladenine 8.

In summary, we have shown that semirigid receptors with oriented hydrogen bonding sites can form strong and selective complexes with complementary substrates. X-ray structural characterization provides important insights into the conformational changes involved in complexation.

Acknowledgment. We thank the National Institutes of Health for partial support of this work and Nalin Pant for helpful discussions.

Supplementary Material Available: Crystallographic details for 6 and 7 including tables of atomic coordinates, thermal parameters, bond angles, and bond lengths (18 pages). Ordering information is given on any current masthead page.

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Catalytic Asymmetric Hydroboration of Styrenes

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We report here novel catalytic asymmetric synthesis of optically active 1-arylalkanols (up to 96% ee) through asymmetric hydroboration of styrenes catalyzed by a chiral cationic rhodium complex, which complements the uncatalyzed asymmetric hydroboration with chiral alkylboranes derived from α -pinene that has been successfully used for internal alkenes.^{1,2}

Since Mannig and Noth reported in 1985 that rhodium complexes catalyze the hydroboration with catecholborane,³ a few reports have appeared on application of the catalyzed hydroboration for organic synthesis, i.e., control of regio- and stereochemistry in the hydroboration of allylic alcohol derivatives⁴ and catalytic asymmetric hydroboration of 1,2- and 1,1-disubstituted alkenes.⁵ We found that the use of a certain cationic phos-

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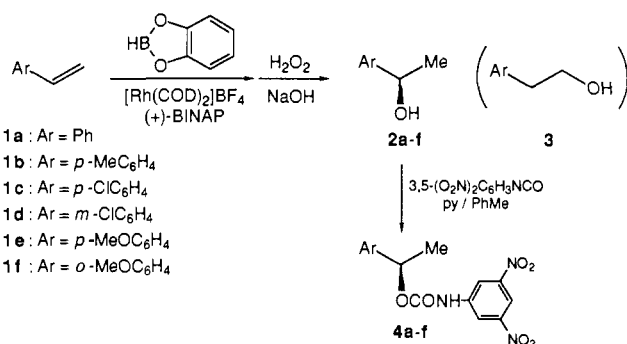
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Table I. Asymmetric Hydroboration of Styrenes **1** with Catecholborane Catalyzed by Cationic Rhodium-(+)-BINAP Complex^a

entry	styrene	solvent	reaction conditions		product ^b (yield %) ^d	% ee ^c (config)	[α] _D ^e (solvent) ^f
			temp (°C)	time (h)			
1	1a	THF	25	0.5	2a (92)	57 (<i>R</i>)	+29.5° (CH ₂ Cl ₂) ^g
2	1a	THF	-30	0.5	2a (90)	76 (<i>R</i>)	+39.3° (CH ₂ Cl ₂) ^g
3	1a	DME	-78	2	2a (91)	96 (<i>R</i>)	+48.6° (CH ₂ Cl ₂) ^g
4 ^h	1a	DME	-78	2	2a (87)	93 (<i>S</i>)	-46.1° (CH ₂ Cl ₂) ^g
5	1b	DME	-78	6	2b (77)	94 (<i>R</i>)	+51.6° (CHCl ₃) ⁱ
6	1c	DME	-78	6	2c (98)	91 (<i>R</i>)	+46.1° (Et ₂ O) ^j
7	1d	DME	-78	2	2d (99)	85	+36.7° (CHCl ₃) ^k
8	1e	THF	-30	0.5	2e (74)	85 (<i>R</i>)	+44.2° (CHCl ₃) ^k
9	1e	DME/THF ^l	-78	6	2e (54)	89 (<i>R</i>)	+47.2° (CHCl ₃) ^k
10	1f	THF	-30	0.5	2f (84)	82	+22.4° (CHCl ₃) ^k

^a The reaction was carried out in THF. Styrene/catecholborane/catalyst = 1.0/1.1/0.01–0.02. ^b The regioselectivity for the formation of **2/3** is >99/1. ^c Determined by HPLC analysis of 3,5-dinitrophenyl carbamate **4** with a chiral column (Sumitomo Chemical Co., Sumipax OA-4100). ^d Isolated yield by preparative TLC on silica gel. ^e Literature rotations for optically pure (*S*)-**2a**, (*R*)-**2b**, (*R*)-**2c**, and (*R*)-**2e** are [α]_D²⁵ -52.5° (*c* 2.27, CH₂Cl₂) (ref 14), [α]_D²⁵ +56.0° (neat, 1 dm) (Vigneron, J. P.; Jaquet, I. *Tetrahedron* **1976**, *32*, 939. See, also: Kasai, M.; Froussios, C.; Ziffer, H. *J. Org. Chem.* **1983**, *48*, 459), [α]_D²¹ +49.9° (*c* 2, ether) (Ishizaki, T.; Miura, H.; Nohira, H. *Nippon Kagaku Kaishi* **1980**, 1381), and α_D²⁰ +45.2° (neat, 1 dm) (Okamoto, K.; Kinoshita, T.; Takemura, Y.; Yoneda, H. *J. Chem. Soc., Perkin Trans. II* **1975**, 1426), respectively. ^f *c* 0.9–1.1. ^g Rotation at 23 °C. ^h (-)-BINAP was used. ⁱ Rotation at 25 °C. ^j Rotation at 21 °C. ^k Rotation at 20 °C. ^l DME/THF = 3/1. Styrene **1e** was not soluble in DME at -78 °C.

Scheme I

phine-rhodium catalyst for hydroboration of styrene derivatives makes the regiochemistry opposite to the uncatalyzed reaction,⁶ giving rise to benzylboranes exclusively. Thus, the reaction of styrene (**1a**) with catecholborane in THF at 25 °C for 30 min in the presence of 1 mol % of a rhodium catalyst prepared in situ by mixing [Rh(COD)₂]⁺BF₄⁻ and 1,4-bis(diphenylphosphino)butane (dppb) followed by oxidation gave 99% yield of 1-phenylethanol (**2a**) regioselectively (**2a/2-phenylethanol** (**3a**) = >99/1). The high regioselectivity was observed only with rhodium complexes that have tertiary phosphine ligands and a positive charge on rhodium.^{8–10} Representative results obtained for the hydroboration of **1a** with catecholborane in the presence of 1 mol % of rhodium complexes (at 25 °C for 30 min) are as follows: RhCl(PPh₃)₃ (79% yield, **2a/3a** = 10/90), [RhCl(COD)]₂ (37%, 27/73), [Rh(COD)₂]⁺BF₄⁻ (61%, 57/43), [Rh(COD)₂]⁺BF₄⁻ + 2PPh₃ (93%, >99/1), [Rh(COD)₂]⁺BF₄⁻ + dppe¹¹ (84%, 89/11), [RhCl(COD)]₂ + dppb (83%, 45/55), [Rh(COD)₂]⁺BF₄⁻ + dppb

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(99%, >99/1), and [Rh(COD)(dppb)]⁺BF₄⁻ (86%, >99/1). The regioselective formation of benzylboranes with the cationic rhodium catalyst was also observed in the hydroboration of (*E*)-1-phenylpropene (99/1) and 2-phenylpropene (70/30).

The catalytic asymmetric hydroboration of substituted styrenes **1** was effected with a cationic rhodium catalyst coordinated with (+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl¹² (BINAP) (Scheme I). The reaction conditions and results are summarized in Table I. The cationic rhodium/BINAP complex was highly active as a catalyst, the hydroboration of styrene (**1a**) being completed in 30 min even at -30 °C with 1 mol % of the catalyst (entry 2). The enantioselectivity was dependent on the reaction temperature: Enantiomeric purities of 1-phenylethanol (**2a**) obtained for the hydroboration at 25 °C, -30 °C, and -78 °C were 57%, 76%, and 96% ee, respectively (entries 1–3). The selectivity attained here giving 96% ee is among the highest of asymmetric reactions by means of chiral transition-metal catalysts,¹³ especially for the preparation of optically active alcohols. The absolute configuration was *R* with (*R*)-(+)-BINAP ligand used. It was found that all of the substituted styrenes **1b–f** were transformed efficiently into optically active 1-arylethanol **2**. The regioselectivity forming 1-arylethylboranes was perfect (>99/1) for all the styrenes examined, irrespective of the electron-releasing or electron-withdrawing nature of the substituent group on the phenyl. The enantioselectivity for substituted styrenes **1b–e** forming (*R*)-1-arylethanol **2b–e** was also high with % ee ranging between 85% and 94% ee (entries 5–9).¹⁴

A typical procedure is given for the reaction of styrene (**1a**) (entry 3). A mixture of 16.2 mg (0.040 mmol) of [Rh(COD)₂]⁺BF₄⁻ and 27.4 mg (0.044 mmol) of (+)-BINAP in 2 mL of 1,2-dimethoxyethane (DME)¹⁵ was stirred under argon at room temperature for 30 min, and 208 mg (2.0 mmol) of styrene (**1a**) was added. Catecholborane (264 mg, 2.2 mmol) was added at -78 °C, and the mixture was kept stirred at the same temperature for 2 h and then quenched with 4 mL of methanol. To the mixture was added 4.8 mL of 3 M NaOH and 0.52 mL of 30% H₂O₂, and it was stirred at room temperature for 3 h. Extraction with ether followed by preparative TLC on silica gel

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(14) α- or β-Substituted styrenes were reluctant to undergo the catalytic hydroboration at low temperature (-30 °C). The reaction of (*E*)-1-phenylpropene with the cationic rhodium-(+)-BINAP catalyst at 25 °C gave (*S*)-1-phenylpropanol of 41% ee.

(15) DME was the solvent of choice for the catalytic asymmetric hydroboration at -78 °C. Catecholborane, styrenes, and the rhodium catalyst are soluble in DME at the low temperature, and the enantioselectivity is usually higher in DME than in THF.

(hexane/ether = 1/1) gave 222 mg (91% yield) of (*R*)-1-phenylethanol (**2a**) ($[\alpha]_D^{23} +48.6^\circ$ (*c* 1.0, dichloromethane)).¹⁶ The regioisomer **3a** was not detected by ¹H NMR analysis of the crude reaction mixture. The enantiomeric purity of **2a** was determined to be 96% by HPLC analysis of 3,5-dinitrophenyl carbamate **4a** (ArNCO/pyridine/toluene) with a chiral stationary phase column (Sumipax OA-4100, hexane/dichloroethane/ethanol = 100/20/1).

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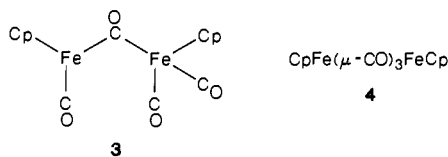
Photochemical Insertion of Alkynes into $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$: A Mechanistic Study by Laser Flash Photolysis

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$\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1**; Cp = $\eta^5\text{-C}_5\text{H}_5$) has a rich and diverse photochemistry, as evidenced by the plethora of synthetic and mechanistic studies of it in the literature.¹ Early photochemical studies of **1** have demonstrated homolysis to the radical Cp(CO)₂Fe* (**2**).² Recent work on metal dimers indicates that a dinuclear species is formed concomitantly. Tyler, Schmidt, and Gray (TSG) first proposed that irradiation of **1** leads to the dinuclear species **3**, which they suggested was the intermediate responsible for phosphine substitution.³ Research by other individuals has indicated that the substitutionally active species is the CO-loss photoproduct **4**.⁴



Our interest in the photochemistry of **1** stemmed from our theoretical studies on piano-stool dimers.⁵ One reaction of particular concern is the photochemical insertion of alkynes into **1** to yield dimetallacyclopentenone **5** (eq 1). On the basis of MO calculations, we proposed a possible "LUMO-controlled" mechanism for this reaction that involved alkyne addition to the TSG transition state **3**, followed by CO loss.^{5b} In this contribution, we report initial experimental studies which demonstrate that **4** is the photochemical intermediate responsible for this reaction. We consider this reaction to be a paradigm for photochemical substitution and insertion reactions in such systems.^{5b,6}

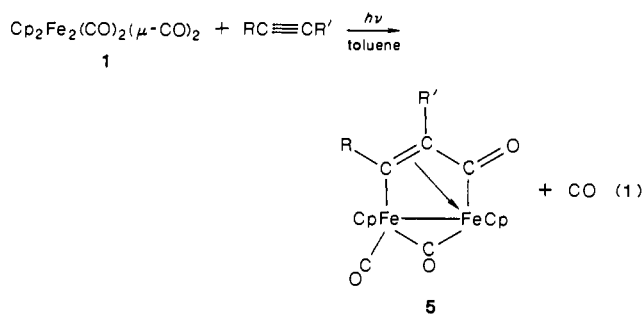
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Laser flash photolysis (LFP)⁷ of **1** in toluene shows the formation of an intermediate with a strong absorbance at 515 nm. This absorption is analogous to that observed in previous flash photolytic and matrix isolation studies^{4a,8} and is readily assigned to the CO-loss photoproduct CpFe($\mu\text{-CO}$)₃FeCp (**4**).

In the absence of alkyne, **4** has a long (ca. 10 ms)^{4a} lifetime. However, in the presence of excess phenylacetylene (PHAC), **4** undergoes a very rapid dark reaction (Figure 1). The decay is pseudo-first-order (inset, Figure 1), with a linear dependence of the observed first-order rate constant (k_{obs}) on PHAC concentration. Similar behavior is observed with 1-hexyne and dimethyl acetylenedicarboxylate (DMAD). Measured second-order rate constants and activation parameters for these alkynes are reported in Table I.⁹ These rate constants are the same order of magnitude as those reported by Poliakov et al. for the reaction of **4** with CO ($6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) to yield **1**,¹¹ but they are somewhat smaller than those for the reaction of **4** with CH₃CN, P(*n*-Bu)₃, and PPh₃.^{4c} The activation parameters for the alkyne reactions, obtained from Eyring plots, are very similar to those found for the simple two-electron ligands; in particular, the large negative ΔS^\ddagger values indicate that the transition state for the reaction of **4** with alkynes has substantial loss in translational and rotational freedom.

The reaction of **4** with L = CO, CH₃CN, and PR₃ is an associative bimolecular process that leads to the substitution photoproducts Cp₂Fe₂($\mu\text{-CO}$)₂(CO)(L) (**6**).^{4c} By analogy, the kinetic data for the reaction of **4** with alkynes are consistent with the same type of process (Scheme I). The similarities between the reported reaction of **4** with CO, CH₃CN, and PR₃^{4c} and those reported here with alkynes suggest the possible formation of an undetected η^2 -alkyne substitution product, **7**,¹² a species similar to the unstable ethylene complex Cp₂Fe₂($\mu\text{-CO}$)₂(CO)($\eta^2\text{-H}_2\text{C}=\text{CH}_2$).¹³ That **7** has not been observed suggests that either the presumed unimolecular transformation **7** → **5** is much faster than the bimolecular process **4** → **7**, at least under the conditions of these studies, or that **7** is a poor chromophore for UV-vis detection.

As a complement to the LFP experiments, we have performed competition reactions between pairs of alkynes to compare product

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