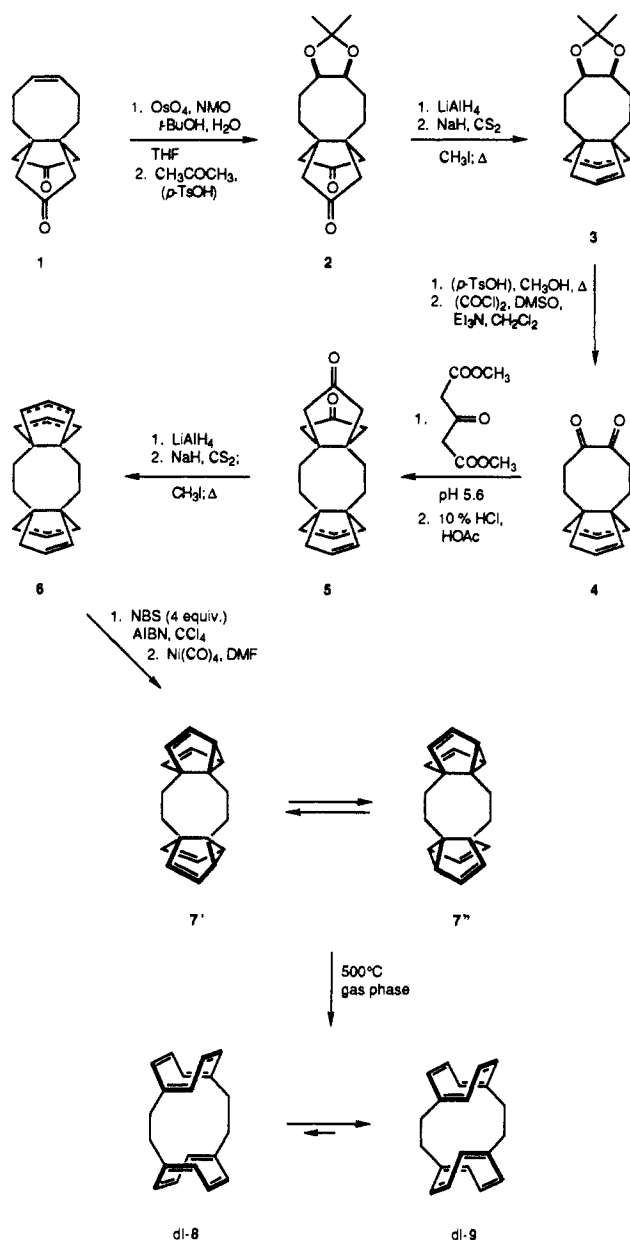


Scheme I



cyclopropane segments.<sup>13</sup> An X-ray analysis of **7** gave results quite similar to the other "averaged" structures reported previously for functionalized semibullvalenes.<sup>14</sup>

Thermal isomerization<sup>15</sup> of **7** at 500–510 °C by dropping an ethereal solution into a vertical quartz tube under nitrogen gave the (1,5)cyclooctatetraenophane as a waxy white solid (32%; 40% based on recovered **7**). The temperature-invariant <sup>1</sup>H and <sup>13</sup>C NMR spectra of the product<sup>16</sup> provide strong suggestion that one bond-shift isomer heavily dominates the *dl* ⇌ *dl* equilibrium. Important insight into this issue was gained by conducting a multiconformer search with the "statistical search" function of the MODEL (version KS 2.94) program.<sup>17</sup> All 124 conformers

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(16) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.89 (dd, *J* = 3.4, 11.3 Hz, 4 H), 5.66 (d, *J* = 11.3 Hz, 4 H), 5.43 (d, *J* = 3.4 Hz, 4 H), 2.13 (s, 8 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): (ppm) 140.17, 133.19, 132.19, 129.67, 36.87.

within 5 kcal/mol of the global minimum were examined for their MM2 energy and ultimately submitted to MMX analysis for final minimization. By this means, the *dl* isomer **9** was found to be 3.1 kcal/mol more stable than *dl*-**8**. The lack of accountability by this computer program of symmetry numbers is of no consequence in this case since either isomer is *d*<sub>2</sub>-symmetric.<sup>18</sup>

Preliminary vacuum-line electrochemical studies on *dl*-**9** using previously developed techniques<sup>19,20</sup> have shown reduction in dry HMPA to give rise to three well-defined irreversible one-electron waves at scan rates of 100–600 mV/s. These appear at –2.65, –2.86, and –3.15 V. The difficulty in adding the first electron is quite striking.<sup>21</sup> While arrival at the tetraanion stage is clearly not achieved,<sup>22</sup> analysis of the precise details of the reduction process awaits completion of additional studies soon to be undertaken.

In our view, the synthetic pathway outlined herein should be amenable to modifications that allow for control of the length, chemical constitution, and location of the interconnective bridges. We hope to report on such developments and on the further chemical modification of **9** at a later date.

**Acknowledgment.** We thank the National Science Foundation for their financial support, Prof. Robin Rogers (Northern Illinois University) for the X-ray analysis of **7**, George Maynard and Eugene Hickey for assistance with the computer calculations, and Stephen D. House for performing the electrochemical measurements.

(17) We thank Professor W. C. Still (Columbia University) for making this program available to us and Professor K. Stellou (University of Montreal) for updates to this software package.

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(22) Such behavior may be a result of homolytic cleavage of one of the ethano bridges. This question is under investigation.

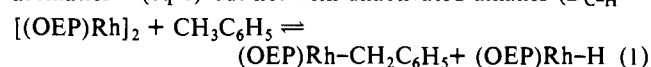
## Metalloradical Activation of Methane

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(Octaethylporphyrinato)rhodium(II) dimer, [(OEP)Rh]<sub>2</sub>, which has a Rh–Rh bond energy of ~16 kcal mol<sup>–1</sup>,<sup>1,2</sup> is observed to react with benzylic C–H bonds (*D*<sub>C–H</sub> ~ 87 kcal mol<sup>–1</sup>) in alkyl aromatics<sup>3,4</sup> (eq 1) but not with unactivated alkanes (*D*<sub>C–H</sub> ~



100–105 kcal mol<sup>–1</sup>). Our approach to extending the range of C–H bond reactions for rhodium(II) porphyrin complexes has been to introduce ligand steric requirements that reduce the Rh<sup>II</sup>–Rh<sup>II</sup> bond energy without seriously weakening the Rh–C bonding. (Tetramesitylporphyrinato)rhodium(II), (TMP)Rh<sup>+</sup>, constitutes a limiting case where ligand steric requirements completely exclude metal–metal bonding.<sup>5</sup> This article reports on the selective reaction of (TMP)Rh<sup>+</sup> with methane in benzene solution and further describes aspects of the thermodynamic and kinetic–mechanistic features for this reaction.

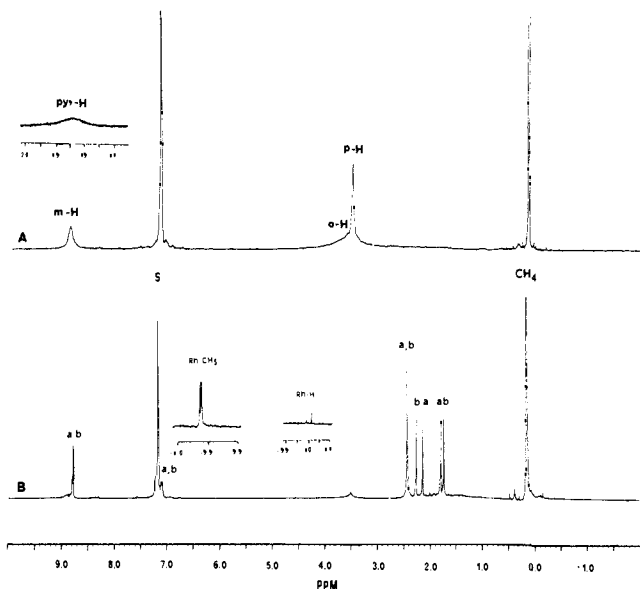
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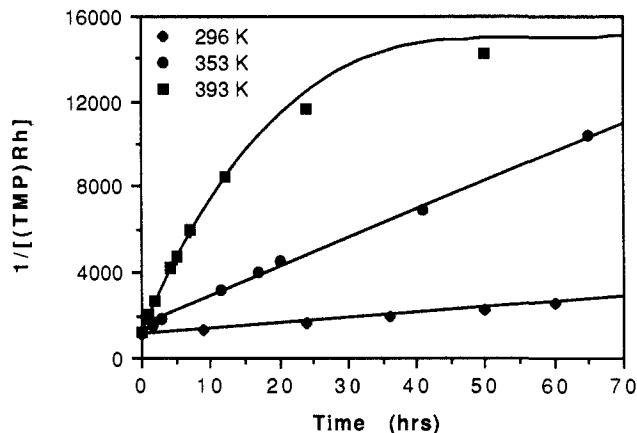
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**Figure 1.** Proton NMR spectra illustrating the reaction of (TMP)Rh<sup>+</sup> with CH<sub>4</sub> ( $P_{\text{CH}_4} = 1.0$  atm) at 353 K in C<sub>6</sub>D<sub>6</sub>. (A) Initial spectrum. (B) Spectrum for the system at equilibrium: (a) resonances assigned to (TMP)Rh-H; (b) resonances assigned to (TMP)Rh-CH<sub>3</sub>.



**Figure 2.** Kinetic studies for reaction 2 at a series of temperatures;  $P_{\text{CH}_4} = 1.0$  atm. Points on the graph represent experimental data. Solid lines are calculated for a pseudo-second-order process approaching equilibrium (see refs 7b,c).

Benzene solutions of (TMP)Rh<sup>+</sup> ( $\sim 1 \times 10^{-3}$  M) in contact with methane ( $P_{\text{CH}_4} = 1-10$  atm,  $T = 296-393$  K) react reversibly to form (TMP)Rh-CH<sub>3</sub> and (TMP)Rh-H (eq 2; Figure 1), which

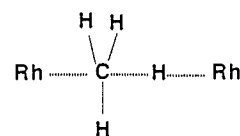
$$2(\text{TMP})\text{Rh}^+ + \text{CH}_4 \rightleftharpoons (\text{TMP})\text{Rh}-\text{CH}_3 + (\text{TMP})\text{Rh}-\text{H} \quad (2)$$

are identified by comparisons with authentic samples synthesized by alternate independent routes.<sup>6</sup> Solutions of (TMP)Rh<sup>+</sup> in benzene fail to give observable aromatic C-H bond reaction over a period of weeks at 353 K.

(6) (TMP)Rh-CH<sub>3</sub> and (TMP)Rh-H were independently prepared by addition of CH<sub>3</sub>-I and CH<sub>3</sub>COOH, respectively, to (TMP)Rh(I) anion, using established methodology (see: Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461). (TMP)Rh-CH<sub>3</sub>: <sup>1</sup>H NMR ( $\delta$  in C<sub>6</sub>D<sub>6</sub>) 8.75 (s, 8 H, pyrrole), 2.26 (s, 12 H, *o*-CH<sub>3</sub>), 1.73 (s, 12 H, *o'*-CH<sub>3</sub>), 7.20 (s, 4 H, *m*-phenyl), 7.07 (s, 4 H, *m'*-phenyl), 2.43 (s, 12 H, *p*-phenyl), -5.25 (d, 3 H, Rh-CH<sub>3</sub>), <sup>2</sup>J(Rh-H) = 2.9 Hz; FAB MS, *m/e* = 898. (TMP)Rh-H: <sup>1</sup>H NMR ( $\delta$  in C<sub>6</sub>D<sub>6</sub>) 8.77 (s, 8 H, pyrrole), 2.14 (s, 12 H, *o*-CH<sub>3</sub>), 1.79 (s, 12 H, *o'*-CH<sub>3</sub>), 7.03 (s, 4 H, *m*-H), 6.95 (s, 4 H, *m'*-H), 2.43 (s, 12 H, *p*-CH<sub>3</sub>), -39.99 (d, 1 H, hydride), J(Rh-H) = 43.9 Hz; [R (Nujol mull)]  $\nu$ (Rh-H) = 2095 cm<sup>-1</sup>; FAB MS, *m/e* = 884. (TMP)Rh<sup>+</sup> is prepared by photolysis of (TMP)Rh-CH<sub>3</sub> in benzene or toluene solution ( $\lambda \geq 350$  nm): <sup>1</sup>H NMR ( $\delta$  in C<sub>6</sub>D<sub>6</sub>,  $T = 296$  K) 18.25 (br s, 8 H, pyrrole), 3.57 (br s, 24 H, *o*-CH<sub>3</sub>), 8.87 (s, 8 H, *m*-phenyl), 3.51 (s, 12 H, *p*-CH<sub>3</sub>); EPR (90 K, toluene glass)  $g_{x,y} = 2.65$ ,  $g_z = 1.9158$ ,  $A^{103}\text{Rh}(g_{xy}) = 197$  MHz,  $A^{103}\text{Rh}(g_z) = 158$  MHz; FAB MS, *m/e* = 883.

Kinetic studies for reaction 2 at a series of methane concentrations were followed by <sup>1</sup>H NMR and used in determining that the rate is second order in (TMP)Rh<sup>+</sup> and first order in CH<sub>4</sub> (rate<sub>2</sub>) =  $k_2[(\text{TMP})\text{Rh}^+]^2[\text{CH}_4]$ ;  $k_2$  (296 K) = 0.132 L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>).<sup>7a,b</sup> Temperature dependence of the forward rate constant yields the activation parameters for reaction 2 ( $\Delta H^\ddagger_2 = 7.5 \pm 1.5$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger_2 = -37 \pm 5$  cal K<sup>-1</sup> mol<sup>-1</sup>) (Figure 2). Substituting CD<sub>4</sub> for CH<sub>4</sub> in reaction 2 produces large deuterium isotope effects ( $k_{\text{H}}/k_{\text{D}}$  (296 K) = 8.6  $\pm$  1.5;  $k_{\text{H}}/k_{\text{D}}$  (353 K) = 5.0  $\pm$  1.0). Equilibrium constants were determined at 353 K (7300) and 393 K (1300)<sup>7c</sup> and used in estimating thermodynamic values for reaction 2 ( $\Delta H_2^\circ \sim -12$  kcal mol<sup>-1</sup>,  $\Delta S_2^\circ \sim -15$  cal K<sup>-1</sup> mol<sup>-1</sup>).<sup>7c</sup>

The rate law for reaction 2 is compatible with either a set of bimolecular steps involving rapid formation of an intermediate methane complex or a single termolecular step. An important feature of either mechanism is that the transition state is trimolecular and proposed to involve the interaction of a metalloradical at both the carbon and hydrogen sites, in a four-centered linear array. The observed activation entropy ( $\Delta S^\ddagger_2$ ) of -37 cal K<sup>-1</sup>



mol<sup>-1</sup>) and deuterium kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$  (296 K) = 8.6) are compatible with the proposed highly ordered linear transition state. Linear four-centered transition states have been previously proposed for reactions of H<sub>2</sub> with radicals<sup>8-11</sup> and may

(7) (a) All methane reactions were performed in sealed NMR tubes with C<sub>6</sub>D<sub>6</sub> solvent. Relative concentrations of (TMP)Rh<sup>+</sup>, (TMP)Rh-H, and (TMP)Rh-CH<sub>3</sub> were determined by using <sup>1</sup>H NMR and comparing the integrated intensities of the *p*-CH<sub>3</sub> resonances for the metalloradical with the *o*-CH<sub>3</sub> resonances for the diamagnetic products. Absolute concentrations were obtained by using methane as an internal standard. Accuracy of this method was limited by comparison of broad, overlapping resonances of (TMP)Rh<sup>+</sup> ( $s = 1/2$ ) with sharp resonances for the diamagnetic complexes (TMP)Rh-H and (TMP)Rh-CH<sub>3</sub>. The molar concentration of methane in benzene as a function of temperature and methane pressure is given by the following expression:  $[\text{CH}_4]_{T,P} = [3.817 \times 10^{-2} \text{ mol L}^{-1} - (5.143 \times 10^{-5})T_2](T_2/T_1)_{(296)}(P/1 \text{ atm})$  where  $P$  is the CH<sub>4</sub> pressure in atmospheres at temperature  $T_1$  (296 K) and  $T_2$  is the temperature at which the experiment is performed. Solubility data are taken from Evans and Battino (Evans, F. C.; Battino, R. *J. Chem. Thermodyn.* **1971**, *3*, 753), and the temperature dependence of the density of benzene is from Brunel and VanBibber (Brunel, R. F.; VanBibber, K. *Int. Crit. Tables* **1928**, *3*, 27.) (b) Kinetic experiments were performed at  $P_{\text{CH}_4}$  such that reaction 2 is pseudo zero order in CH<sub>4</sub>: rate<sub>2</sub> =  $-1/2 d[(\text{TMP})\text{Rh}^+]/dt = k_2[(\text{TMP})\text{Rh}^+]^2[\text{CH}_4] = k_2'[(\text{TMP})\text{Rh}^+]^2$ . Representative kinetic studies at 1.0 and 10.0 atm of CH<sub>4</sub>(g) illustrate that the rate for reaction 2 is adequately described as first order in methane (at 1.0 atm,  $[\text{CH}_4] = 2.36 \times 10^{-2} \text{ mol L}^{-1}$ ,  $k_2' \approx 3.12 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_2 = 0.132 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ; at 10.0 atm,  $[\text{CH}_4] \approx 2.36 \times 10^{-1} \text{ mol L}^{-1}$ ,  $k_2' \approx 2.88 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_2 = 0.122 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ). Deviations from linearity in the kinetic plots are ascribed to the reverse reaction [(TMP)Rh-H + (TMP)Rh-CH<sub>3</sub> → 2(TMP)Rh<sup>+</sup> + CH<sub>4</sub>], which becomes significant at higher temperatures. We have independently observed that the reverse of reaction 2 proceeds at a finite rate at temperatures above 350 K. Final analysis of the kinetic data was obtained by treating reaction 2 as a pseudo-second-order process approaching equilibrium and using the experimentally determined equilibrium constants at 353 and 393 K. Simulations of the concentration versus time profiles were obtained by use of the computer program GEAR adapted by T. E. Beukelman and F. G. Weigert from HAVCHM, written by R. N. Stabler and J. Chesick (*Int. J. Chem. Kinet.* **1978**, *10*, 461-469). The PC version (1.1) was converted to Microsoft Fortran (v. 3.31) by R. J. McKenney. (c) Equilibrium constants for reaction 2 were determined by integration of the <sup>1</sup>H NMR spectra for solutions equilibrated at 353 and 393 K. The progress of reaction 2 was monitored over a period of at least seven half-lives and the concentration quotient observed to be constant for a period of at least 2 weeks prior to the final equilibrium constant measurements. The solutions investigated had first half-life times between 2 and 10, h, which, for a pseudo-second-order process, requires reaction times from 15 to 60 days to achieve equilibrium. Equilibrium constants at 353 K [(7.3  $\pm$  1.3)  $\times 10^3$ ] and 393 K (1.3  $\pm$  0.2)  $\times 10^3$  were used in deriving thermodynamic values for reaction 2 ( $\Delta H^\circ = -11.7 \pm 1.0$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = -15 \pm 5$  cal K<sup>-1</sup> mol<sup>-1</sup>).

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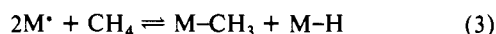
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be broadly operative in oxidative additions and reductive eliminations that involve metalloradicals.

Selective reaction of methane with (TMP)Rh<sup>+</sup> in benzene solvent is a distinctive feature of this system in that other reported metal complexes have manifested a preference for aromatic C-H bond reactivity.<sup>12-17</sup> Aromatic C-H bond reactions are favored thermodynamically because the difference in M-phenyl and M-CH<sub>3</sub> bond energies (10-25 kcal mol<sup>-1</sup>)<sup>15-19</sup> more than compensates for the difference in C-H bond energies (C-H<sub>(C<sub>6</sub>H<sub>6</sub>)</sub> = 110 kcal mol<sup>-1</sup>, C-H<sub>(CH<sub>3</sub>)</sub> = 105 kcal mol<sup>-1</sup>). Oxidative addition of C-H bonds to a single metal center usually occurs under thermodynamic control, which results in a preference for reactions with aromatics.<sup>15,16</sup> Reaction of a phenyl C-H bond with two metalloradicals requires a nonlinear Rh-C-H-Rh transition state, which places the two sterically demanding (TMP)Rh<sup>+</sup> groups in an untenable proximity. We currently believe that the absence of (TMP)Rh<sup>+</sup> reactivity with benzene is a kinetic effect arising from unfavorable steric interactions in the transition state.

The general reaction of two metalloradicals with methane and the corresponding enthalpy-bond energy relationship are given by eqs 3 and 4. Evaluation of eq 4 using ΔH<sub>2</sub><sup>°</sup> (-12 kcal mol<sup>-1</sup>)



$$\Delta H_2^{\circ} = (H_3C-H) - [(M-CH_3) + (M-H)] \quad (4)$$

and H<sub>3</sub>C-H (105 kcal mol<sup>-1</sup>) results in an estimate of 117 kcal mol<sup>-1</sup> for the sum of the (TMP)Rh-H and (TMP)Rh-CH<sub>3</sub> bond energies.<sup>7c</sup> IR data suggest that the Rh-H bond energy in (TMP)Rh-H is somewhat smaller than the 62-kcal value observed for (OEP)Rh-H<sup>1,2</sup> (ν((OEP)Rh-H) = 2220 cm<sup>-1</sup>, ν((TMP)Rh-H) = 2095 cm<sup>-1</sup>). Estimating the Rh-H bond energy for (TMP)Rh-H at ~60 kcal mol<sup>-1</sup> places the Rh-CH<sub>3</sub> bond energy at ~57 kcal mol<sup>-1</sup>.

Bimolecular reductive eliminations of methane from reactions of metal hydride and methyl complexes provided early evidence that thermodynamic rather than kinetic factors were responsible for limiting the reactions of methane with transition-metal complexes.<sup>20</sup> More recent studies have provided examples of homogeneous metal complexes that react with alkanes by oxidative addition to a single metal center,<sup>13-16,21-26</sup> σ-bond metathesis of M-X units,<sup>27-29</sup> and addition to M=X groups.<sup>30-33</sup> Mechanistic

studies have illustrated the importance of alkane C-H σ-bond donation in oxidative additions<sup>34</sup> and four-centered cyclic interactions in reactions of M-X and M=X units.<sup>27-30</sup> The reaction of (TMP)Rh<sup>+</sup> with methane expands the mechanistic versatility for alkane reactions by providing an example of oxidative addition of a methane C-H unit with two metalloradicals through a probable linear four-centered transition state. The reaction of (TMP)Rh<sup>+</sup> with methane is also unusual in permitting the direct observation of the reactive metal species, (TMP)Rh<sup>+</sup>, complete selectivity for reaction of CH<sub>4</sub> in benzene solvent, and the exclusion of undesirable intramolecular C-H bond reactions. We are currently refining and extending the kinetic and thermodynamic measurements for the methane reaction, examining the reactivity of a series of alkanes, and extending this work to iridium porphyrins.

**Acknowledgment.** We gratefully acknowledge helpful discussions of this work with Professor Donald H. Berry and partial financial support by the National Science Foundation through Grant CHE-87-16691.

**Registry No.** (TMP)Rh, 121393-39-3; CH<sub>4</sub>, 74-82-8; (TMP)RhCH<sub>3</sub>, 121471-27-0; (TMP)RhH, 124535-65-5; (TMP)Rh<sup>+</sup>, 124535-66-6; D<sub>2</sub>, 7782-39-0.

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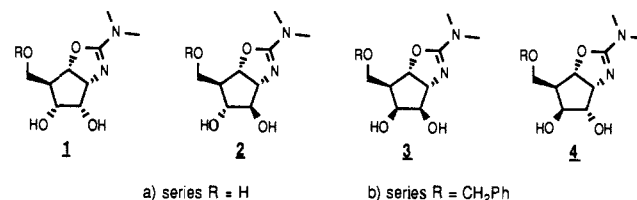
## Template-Directed Synthesis of (±)-Allosamizoline and Its 3,4-Epipimers

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The importance of chitin as one of the main structural components of insect cuticles<sup>1</sup> and fungal cell walls<sup>2</sup> generates interest in discovering agents that may interact with its biosynthesis. A screen for chitinase inhibitors revealed the presence of a novel pseudotrisaccharide allosamidin in the mycelial extract of *Streptomyces* sp. no. 1713.<sup>3</sup> Its structure derives from its hydrolysis, which produces 2 equiv of D-allosamine and 1 equiv of a new aminocyclitol, named allosamizoline, whose structure was initially suggested to be the cis diol **1a**<sup>4</sup> and later revised to the trans diol **2a**.<sup>5</sup> Since the structural assignment rests on inter-



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