

**Table II.** Comparison of the Potential Function Parameters Obtained for Allene with Those for Ethylene (from ref 4)

	ethylene			allene		
	$V_0, \text{cm}^{-1}$	$\epsilon$	$\gamma$	$V_0, \text{cm}^{-1}$	$\epsilon$	$\gamma$
$2\phi$	13920			9674		
$2\phi + 4\phi$	19545	0.094		13400	0.088	
$2\phi + 4\phi + 6\phi$	20920	0.127	0.02	14950	0.137	0.02

A three-term potential fits the allene and ethylene data within experimental error.

The parameters obtained from such fits for allene and ethylene are compared in Table II. In both cases increasing the number of terms in the potential energy function results in a considerable increase in the value of the torsional barrier,  $V_0$ . The value obtained with the three-term potential that seems to be required by the data is, in each case, in reasonable to excellent agreement with the results of theoretical calculations and with the available kinetic data. For example, calculated energies of the perpendicular configuration of ethylene are found to be 20890 and 21860  $\text{cm}^{-1}$ .<sup>14</sup> The value of  $V_0$  for allene is considerably smaller than that for ethylene, as expected. The value of  $V_0$  of 14850  $\text{cm}^{-1}$   $\approx$  43 kcal/mol deduced from our spectra is somewhat smaller than expected on the basis of theoretical calculations (ca. 50 kcal/mol) but is in excellent agreement with the only available relevant experimental data (ca. 46.1 kcal/mol).

The similarity of the values of the coefficients of the higher order  $\cos(4\phi)$  and  $\cos(6\phi)$  terms for ethylene and allene is interesting. In each case the  $4\phi$  term is about 13% and the  $6\phi$  term is about 2% of the  $2\phi$  term. If we assume that this form holds for the next higher member of the cumulene series, butatriene, we can use the torsional frequency of this species, tentatively assigned<sup>21</sup> to a band at 736  $\text{cm}^{-1}$ , to deduce the isomerization barrier. With the value of  $\gamma$  of 0.02 and  $\epsilon = 0.137$ , a value of  $V_0 = 11300 \text{ cm}^{-1}$  (32.4 kcal/mol) results in the observed frequency; for  $\epsilon = 0.147$  (extrapolated) the optimized value of  $V_0$  is 11850  $\text{cm}^{-1}$  (33.9 kcal/mol). We thus estimate a spectroscopic barrier of 33 kcal/mol for butatriene. This is in good agreement with the kinetically determined value of 31.8 kcal/mol determined from the rate of isomerization of 1,4-dimethylbutatriene.<sup>22</sup> This agreement supports the argument that the form of the barrier is substantially the same for this species as for ethylene and allene and also supports the tentative assignment of this vibrational band.

The values of  $V_0$  for ethylene, allene, and butatriene are accurately fit by the simple formula

$$V_0(N) = 150/(N + 1.5) \text{ kcal/mol}$$

where  $N$  is the number of double bonds ( $N + 1$  is the number of carbon atoms).<sup>23</sup> The offset of 1.5 represents an "end effect". The magnitude of this value seems reasonable. If this formula is evaluated for  $N = 4$  and 5 the resulting values of  $V_0$  are 27.3 and 23.0 kcal/mol. The only relevant experimental data appear to be that for the isomerization of the  $\alpha,\omega$ -diphenyl- $\alpha,\omega$ -di-*tert*-butylcumulenes with 4 and 5 cumulated bonds.<sup>24</sup> The kinetic barriers for these compounds are 27.5 and 20.8 kcal/mol, in reasonably good agreement with the extrapolated "spectroscopic" values. This simple formula therefore adequately represents all of the available experimental data and permits modest extrapolation to longer cumulene chains.

**Acknowledgment.** This research was supported by NSF Grant CHE 88-16698. We thank Suzanne Hudson for writing the program used for solution of the torsional Schrodinger problem.

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## Novel Cyclization Reactions on Transition-Metal Templates. The Catalysis of Intramolecular [4 + 2] Cycloadditions by Low Valent Rhodium Complexes

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Received December 18, 1989

The remarkable versatility of the Diels-Alder reaction for the stereospecific construction of six-membered rings has elevated this process to its current status as one of the most widely utilized methods in organic chemistry. Although both inter- and intramolecular variations of this reaction are ubiquitous, almost all cases involve a [4 + 2] cycloaddition event between *electronically dissimilar* components. Indeed, the inherent lethargy of electronically comparable addends to undergo cyclization under all but the most extreme reaction conditions constitutes one of the most prominent limitations of this important annulation method.

Recently, it has been found that certain transition-metal complexes can accelerate formal Diels-Alder reactions via metal-mediated  $\eta^3$ -complex formation and subsequent reductive elimination. Although a few intermolecular examples of the above process have been reported,<sup>2</sup> there has been only one account of an intramolecular variation of this reaction.<sup>3</sup> In this communication, we report that several Rh(I) complexes can dramatically accelerate representative intramolecular [4 + 2] cycloaddition reactions (Scheme I).

We initiated our investigation by examining the influence of ligand and solvent effects on the internal [4 + 2] cyclization of 1-(2-propynyloxy)-2,4-hexadiene (**1**) catalyzed by Rh(I). Gentle warming of a THF solution of **1** at 55 °C in the presence of 10 mol% of commercial  $(\text{Ph}_3\text{P})_3\text{RhCl}$  under argon led to the slow consumption of starting material with concomitant production of the anticipated cyclized product **2**.<sup>4,5</sup> Unfortunately, under these conditions, the bicyclic adduct **2** could be obtained in a maximum yield of only 20% after 180 min. The substitution of ethanol for THF as the reaction solvent resulted in a *modest* increase in both the rate and efficiency of cyclization. In sharp contrast to these discouraging results, brief exposure of **1** to  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (10 mol%) in trifluoroethanol (TFE) under Ar led to the formation of **2** in 96% yield after only 15 min at 55 °C.<sup>5,6</sup> Alternatively, the use of 5 mol % of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (TFE, 55 °C) led to complete conversion of **1** within 30 min.

Electronic and/or steric perturbations of the ligand sphere surrounding transition-metal centers frequently result in pronounced enhancements of the rates and selectivities associated with catalysis. Van Leeuwen and Roobeek have reported that the use of electron-deficient phosphite ligands in Ni(0)-catalyzed diene cyclodimerizations<sup>8</sup> and Rh(I)-catalyzed alkene hydro-

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(3) Very recently, the intramolecular [4 + 2] cycloaddition of several nonterminal dienyne catalyzed by Ni(0) has been reported: Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* 1989, 111, 6432.

(4) All new compounds have been fully characterized by IR and 300 MHz NMR spectroscopy and possess satisfactory elemental (C, H) analyses or exact mass.

(5) In a control experiment, the substrate **1** was found to undergo cyclization to the extent of only 20% in TFE at 120 °C after 3 days in the absence of catalyst. It is of stereochemical significance that the product obtained in this manner was found to be identical in all respects with that prepared via Rh(I) catalysis.

(6) The possibility that adventitious HCl [Formed via the reaction of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  with TFE] was functioning as an active catalyst was ruled out by the exposure of **1** to 0.1 molar equiv of HCl in TFE (50 °C, 1 h). Under these conditions, the dienyne **1** was recovered unchanged.

(7) Evidence for the indicated relative stereochemistry of the bicyclic product **2** has been provided by nuclear Overhauser enhancement difference (NOED) spectroscopy.

Scheme I

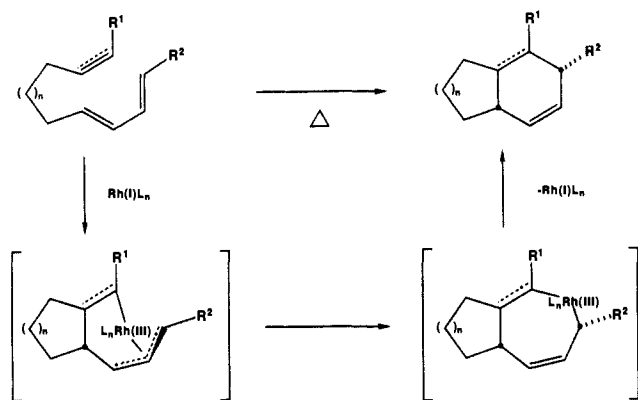


Table I. Rh(I)-Catalyzed [4 + 2] Cycloadditions

Substrate	Product	(yield %)	Reaction Conditions
		(98 %)	(Ph <sub>3</sub> P) <sub>3</sub> RhCl · TFE 55 °C, 15 min
		(83 %)	(Ph <sub>3</sub> P) <sub>3</sub> RhCl · TFE 55 °C, 45 min
		(87 %)	(i-C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P <sub>2</sub> Rh <sup>+</sup> · THF <sup>11</sup> 55 °C, 15 min
		(78 %)	(Ph <sub>3</sub> P) <sub>3</sub> RhCl · TFE 55 °C, 45 min
		(98 %)	(i-C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P <sub>2</sub> RhCl · THF 25 °C, 60 h
		(61 %)	(i-C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P <sub>2</sub> RhCl · THF 55 °C, 16 h

formylations<sup>9</sup> results in dramatic increases in reaction efficiency. Accordingly, several new Rh(I) complexes were generated in situ by the reaction of [RhCl(cyclooctene)]<sub>2</sub> with various phosphite ligands (2 equiv)<sup>10</sup> and examined for efficacy in the intramolecular [4 + 2] cycloaddition reaction. In consonance with the findings of Van Leeuwen and Roobeck,<sup>8,9</sup> a significant enhancement in cyclization efficiency was observed when d<sup>8</sup> rhodium complexes modified by 1,1,1,3,3,3-hexafluoro-2-propoxy bearing phosphite ligands were employed as catalysts. In addition, these highly active catalyst systems were found to be effective in THF solution at temperatures as low as 25 °C.

The generality of the rhodium-catalyzed intramolecular [4 + 2] cycloaddition reaction for the elaboration of 5/6 and 6/6 ring systems was subsequently demonstrated by its application to several representative substrates (Table I).<sup>11</sup>

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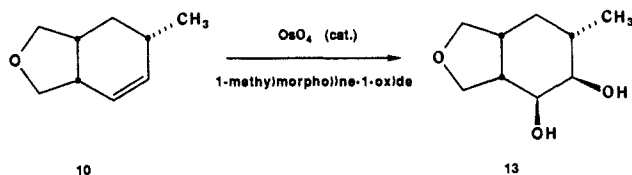
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(11) In a representative experiment, a 12-cm test tube containing [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub> (17.9 mg, 0.025 mmol) was flushed with Ar and then charged with dry THF (4 mL). To the stirred solution was added (*i*-C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>P (53.1 mg, 0.100 mmol) followed by **9** (276 mg, 2.000 mmol). The pale yellow solution was then allowed to stir at 25 °C for 60 h (or, alternatively, was warmed to 55 °C for 2.5 h). The reaction mixture was filtered through 3 g of alumina (30% EtOAc-C<sub>6</sub>H<sub>14</sub> for elution), and the solvents were evaporated. Flash chromatography of the residue on silica gel followed by evaporative distillation provided **10** (270 mg, 98%).

(12) In this instance, cyclization was effected by exposure of **5** to 5 mol % of the cationic complex prepared by the sequential treatment of [(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>RhCl]<sub>2</sub> with AgO<sub>3</sub>SCF<sub>3</sub> (1.0 equiv/Rh)<sup>13</sup> followed by (*i*-C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>P (2.2 equiv).

Several synthetically pertinent features serve to differentiate the reactivity profile of Rh(I) catalysts from their Ni(0) counterparts.<sup>3</sup> Of primary interest is the observation that these cycloadditions are not confined to substrates bearing nonterminal alkynes as [4 + 2] addends. Terminal alkynes and, more importantly, alkenes readily participate in representative cyclizations to provide the corresponding bicyclic products in good to excellent yield. In addition, Rh(I)-catalyzed cycloadditions were found to proceed with excellent levels of diastereoselection. In every instance examined to date, Rh(I)-catalyzed cyclization under optimized conditions led to the formation of an exclusive cycloadduct as determined by GC as well as <sup>1</sup>H and <sup>13</sup>C NMR.<sup>5,7</sup>

In the case of **10**, rigorous proof of relative stereochemistry was provided by single-crystal X-ray diffraction analysis of the corresponding crystalline diol **13**.



The preceding examples indicate that the Rh(I)-catalyzed [4 + 2] cycloaddition reaction is an effective means for the elaboration of a range of bicyclic intermediates from acyclic precursors under exceedingly mild reaction conditions. The utilization of chiral phosphines in enantioselective variations of this novel annulation process as well as its application to problems of synthetic interest will be the topics of future reports from this laboratory.

**Acknowledgment.** Support for this research by grants from the Alfred P. Sloan Foundation and the National Institutes of Health are gratefully acknowledged. The authors thank Ray Larsen of the MSU X-ray facility for obtaining the crystal structure for diol **13**.

**Supplementary Material Available:** Spectroscopic and physical data (<sup>1</sup>H NMR, IR, high-resolution mass spectra, and mp) for the cycloadducts **2**–**12** and the diol **13** (3 pages). Ordering information is given on any current masthead page.

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## Synthesis and Crystal Structure of a Stable Hexacobalt Complex of Cyclo[18]carbon

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Recently, we reported the gas-phase formation of neutral cyclo[18]carbon (C<sub>18</sub>) from a stable precursor prepared by synthesis and characterized by X-ray crystallography.<sup>1,2</sup> We now report the synthesis and the structure of C<sub>18</sub>, stabilized as the transition-metal complex **1** (Scheme I).

Conceptually, the synthesis of **1** originates from the ≡C—C angle bending that occurs in alkynes upon formation of (μ-acetylene)dicobalt hexacarbonyl complexes. The bending angle after complexation lies between 136.2° and 144.4° for complexes of known X-ray crystal structure.<sup>3</sup> Dicobalt hexacarbonyl

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