$(SiMe_3)_2]_2Ca(THF)$[8] [average Ca–C(η^5) distance 2.68 Å] and $[(C_5Me_5)Ca(\mu\text{-}I)(THF)_2]_2$[9] [average Ca–C($\eta^5$) distance 2.67 Å], but is shorter than that found in the polymeric complex[2] $(C_5H_5)_2Ca$ [average Ca–C(η^5) distance 2.80 Å].

The interatomic distance B(3)···B(8) in **1** is 2.037 (9) Å and is somewhat shorter than the distance 2.166 Å found in the complex 1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$,[19] but is more comparable to the distance 2.082 Å found in the complex 1-(η-C_5H_5)-1,2,4-$CoC_2B_{10}H_{12}$.[20] The B(9)···C(2) distance is 2.789 (7) Å and is somewhat longer than the distance 2.720 Å found in the complex 1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$.[19] The C(2)···B(12) distance is 2.814 (8) Å and is nearly the same (2.841 Å) as found in the complex 1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$.[19] The B(3)···B(10) distance is 2.935 (8) Å, nearly identical with the distance 2.938 Å found in the complex 1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$.[19] The four boron atoms in the top belt (bonding face) of **1** are essentially coplanar (within 0.03 Å) with C(2) lying above (0.277 Å) and C(4) lying below (0.227 Å) this plane. The five boron atoms of the lower belt are coplanar (within 0.07 Å). The planes defined by the top and the bottom belt are nearly parallel (3.4° between their normals).

The molecular structure of **1** raises a number of questions concerning the nature of the interaction of the calcium atom and the carborane unit. The IR spectrum of **1** in the solid state exhibits two broad B–H stretching bands (split pattern), one centered at 2466 cm^{-1} and another at 2419 cm^{-1}. This pattern has previously been observed in lanthanacarborane complexes, viz., *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$ and *closo*-1,1,1,1-$(THF)_4$-1,2,4-$LnC_2B_{10}H_{12}$ (Ln = Sm or Yb), in which the bonding of the metal atom to the carborane fragment is believed to be largely ionic in nature.[17,21] The origin of IR band "splitting" in *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$ (Ln = Sm or Yb) was elucidated by selective deuteration of the carborane cage, and the corresponding deuterated lanthanacarboranes, *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_9D_2$ [Ln = Sm (**2**) or Yb (**3**)], were prepared.[17,22] In these deuterated complexes the two nonadjacent borons [B(4) and B(6)] in the upper belt are bound to deuterium and should exhibit a characteristic low-frequency B–D stretch in the IR spectrum. The solid-state IR spectra of both **2** and **3** indeed exhibited an absorption at ca. 1839 cm^{-1} due to a terminal B–D stretch,[17] and there is a concomitant decrease in the intensity of the low-frequency branch of the terminal B–H absorption.[17] The ratio of ν(BH) to ν(BD) (using the low-frequency branch of the BH absorption) is 1.32 for both **2** and **3**. Given the consistency of $\nu(BH)/\nu(BD)$ ratios[24] using the low-frequency absorption along with the observed decrease in intensity of this stretch due to deuteration, one may assign the low-frequency absorption to the B–H vertices of the top belt and the high-frequency absorption to the B–H vertices of the bottom belt and an apical B–H vertex.[17] Similar arguments can be used to assign the IR spectrum of **1** arising from B–H vertices of the lower belt combined with an apical B–H vertex at 2466 cm^{-1} and another at 2419 cm^{-1} due to B–H vertices of the top belt. It may be concluded from these IR correlations that in complexes **1**, **2**, and **3** strong ionic interactions exist between the cationic metal center and the anionic carborane unit.[26] However, with the data in hand it is impossible to ascertain the relative degree of covalent bonding present. We are currently exploring the chemistry of the alkaline-earth metals with other anionic carborane derivatives.

Acknowledgment. We thank the National Science Foundation (Grant CHE 88-06179) for the support of this work.

Supplementary Material Available: Tables of crystallographic data collection, atom coordinates, bond distances and angles, and anisotropic thermal parameters for **1** (6 pages); table of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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Determination of the Torsional Potential of Allene from Highly Excited Torsional Vibrations Observed by Ultraviolet Resonance Raman Spectroscopy: The Torsional Barrier of Cumulenes

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Resonance Raman spectra of ethylene obtained with excitation in the region of the $\pi\pi^*$ N $\rightarrow$ V transition exhibit considerable intensity in high-level overtone transitions of the torsional mode.[1-3] The frequencies of these transitions follow a remarkably simple pattern, and thus from data of this type it is possible to determine the parameters of a potential energy function representing the torsional motion.[1,4] This is of interest because of the intrinsic importance of the prototypical π-bond, the relevance of this potential to the isomerization reaction of ethylene,[5] and because of the challenge that these data present to quantum chemical theory.

We have now applied the ultraviolet resonance Raman technique[6-8] to allene, $H_2C{=}C{=}CH_2$. We also observe highly excited torsional excitations. The experimental methods used are described elsewhere.[2,6] The results to be presented here demonstrate the general utility of this technique for observing highly excited torsional excitations of alkenes.

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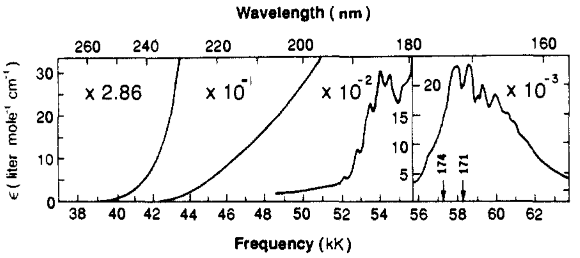

Figure 1. The absorption spectrum of allene (from ref 10). The wavelengths used to obtain the resonance Raman spectra of Figure 2 are indicated.

The electronic spectrum of allene (Figure 1) is quite complex.[9-12] The spectrum begins with a weak, broad band in the 44000–52000-cm^{-1} region followed by a structured absorption from 52000 to 55000 cm^{-1}, which is either the $^1A_1 \rightarrow {}^1E$ valence transition or one component of the $\pi 2e \rightarrow 3s$ Rydberg excitation.[9-12] A strong, complex transition begins at 56000 cm^{-1}; this is followed by a series of Rydberg transitions. The ^1E state is expected to be distorted by the Jahn–Teller effect as is the limiting ion of the Rydberg series. Twisting appears to be the primary active symmetry-lowering motion based on a tentative vibronic analysis.[9]

There has been considerable theoretical work on allene concerning both the excited electronic states[11,12] and the ground-state potential energy surface[13-19] with emphasis on the pathway and energetics of torsional isomerization. One of the most interesting aspects of the isomerization is that the transition state for this process with a planar disposition of the atoms appears to be an open-shell configuration. There is a curve crossing as a function of torsional angle such that in the planar D_{2h} geometry the A_u excited state (which correlates with an excited state of D_{2d} geometry) is lower than the A_g closed-shell state. Singlet and triplet states are nearly degenerate. The most stable geometry for the transition state also appears to be somewhat bent due to the occupied in-plane orbital. The kinetic barrier for isomerization is estimated from these theoretical calculations to be about 50 kcal/mol (17500 cm^{-1}). The torsional barrier per se (i.e., without bending relaxation) would be estimated to be somewhat higher, in the range of 55–60 kcal/mol (19200–21000 cm^{-1}).

The only experimental evidence concerning the barrier to isomerization of allene appears to be that derived from the isomerization kinetics of 1,3-dimethylallene and 1,3-di-*tert*-butylallene.[20] The values for the barrier of 46.2 and 46.9 kcal/mol (16100–16400 cm^{-1}) are consistent with the somewhat higher theoretical results for allene.

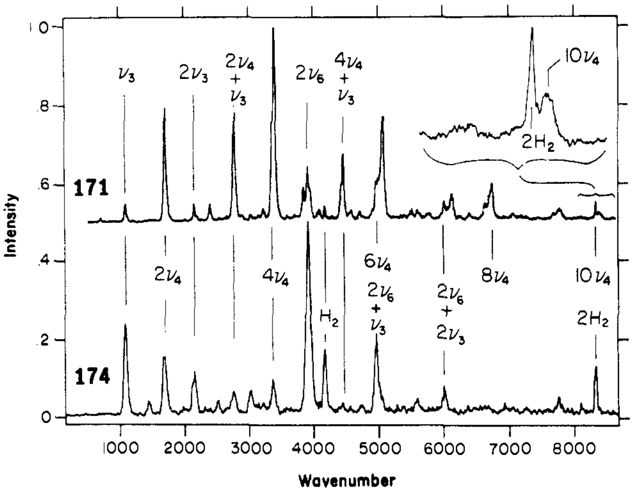

Figure 2. Resonance Raman spectra of allene obtained with excitation at 174 nm (bottom) and 171 nm (top). The lines labeled H_2 and $2H_2$ are due to lower order shifts in the hydrogen stimulated Raman shifting process used to produce the excitation radiation. The $12\nu_4$ transition could not be identified in the 171-nm spectrum.

Table I. Torsional Potentials and Resulting Calculated Frequencies for Allene[a]

exp	cos (2ϕ)	cos (2ϕ) + cos (4ϕ)	cos (2ϕ) + cos (4ϕ) + cos (6ϕ)
1694	+1	-5	+2
3380	-78	+11	-4
5056	-243	+24	-1
6727	-513	+10	-1
8378	-893	-37	+3
V_0, cm^{-1}	9674	13400	14950
ϵ		0.088	0.137
γ			0.02

[a] The experimental frequencies are in cm^{-1}. The entries under each form for the potential are calculated frequencies minus observed frequencies. The reduced moment of inertia used for the calculations is 0.84545 amu Å^2. In a previous publication[1] an incorrect value was used for this parameter (see ref 4).

Resonance Raman spectra of allene obtained with ultraviolet radiation exhibit considerable intensity in the even overtones of the torsional mode ν_4. With excitation at 171 nm, near the peak of the strong structured absorption band, these bands become particularly strong (Figure 2). The transition corresponding to $4\nu_4$ is the strongest band in this spectrum; transitions corresponding to $2\nu_4$, $4\nu_4$, $6\nu_4$, $8\nu_4$, and $10\nu_4$ are clearly seen at 1694, 3380, 5056, 6727, and 8378 cm^{-1}. Using these frequencies we can adjust the parameters of a torsional potential to determine the barrier height.[1,4] Such a potential energy function can be represented as a sum of terms of the form $a_n \cos(n\theta)$, where n is even, θ is the torsional angle, and the amplitudes a_n are parameters to be adjusted to fit experiment. For convenience in interpretation and comparison with the results for ethylene we put this potential function in the form[4]

$$V(\phi) = [V_0/2(1 + \gamma)]\{[1 + \cos(2\phi)] - \epsilon[1 - \cos(4\phi)] + \gamma[1 + \cos(6\phi)]\}$$

where, for allene, $\phi = \theta + \pi/2$, V_0 represents the torsional barrier and ϵ and γ represent the fractional contributions of the terms beyond the minimum cos (2ϕ) term. The transition frequencies resulting from optimized potentials of this form of increasing complexity are given in Table I. It is found that a single cos (2ϕ) term potential with V_0 adjusted to fit the $2\nu_4$ transition frequency results in calculated values for the higher transitions that are much too low in frequency. This is also true for ethylene. For allene, the value of V_0 that results from a single cos (2ϕ) term is unacceptably low from the point of view of the known kinetic and theoretical results and because with such a low barrier the observed transitions would be split.

When a two-term potential function form is used and the parameters are optimized in a least-squares sense, the resulting deviations are greatly reduced but remain well outside the error of the experimental values and, more importantly, exhibit a systematic variation. This behavior has also been observed for the corresponding two-term fit to the ethylene torsional spectrum.[4]

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

	ethylene			allene		
	V_0, cm^{-1}	ϵ	γ	V_0, cm^{-1}	ϵ	γ
2ϕ	13 920			9 674		
$2\phi + 4\phi$	19 545	0.094		13 400	0.088	
$2\phi + 4\phi + 6\phi$	20 920	0.127	0.02	14 950	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 21 860 cm^{-1}.[14] The value of V_0 for allene is considerably smaller than that for ethylene, as expected. The value of V_0 of 14 850 cm^{-1} 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 (4ϕ) and cos (6ϕ) terms for ethylene and allene is interesting. In each case the 4ϕ term is about 13% and the 6ϕ term is about 2% of the 2ϕ 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[21] to a band at 736 cm^{-1}, to deduce the isomerization barrier. With the value of γ of 0.02 and $\epsilon = 0.137$, a value of $V_0 = 11\,300$ cm^{-1} (32.4 kcal/mol) results in the observed frequency; for $\epsilon = 0.147$ (extrapolated) the optimized value of V_0 is 11 850 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.[22] 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).[23] 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 α,ω-diphenyl-α,ω-di-*tert*-butylcumulenes with 4 and 5 cumulated bonds.[24] 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.

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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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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 η^3-complex formation and subsequent reductive elimination. Although a few intermolecular examples of the above process have been reported,[2] there has been only one account of an intramolecular variation of this reaction.[3] 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 $(Ph_3P)_3RhCl$ under argon led to the slow consumption of starting material with concomitant production of the anticipated cyclized product **2**.[4,5] 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 $(Ph_3P)_3RhCl$ (10 mol%) in trifluoroethanol (TFE) under Ar led to the formation of **2** in *96% yield after only 15 min at 55 °C*.[5,6] Alternatively, the use of 5 mol % of $(Ph_3P)_3RhCl$ (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[8] and Rh(I)-catalyzed alkene hydro-

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[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 $(Ph_3P)_3RhCl$ 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 **12** has been provided by nuclear Overhauser enhancement difference (NOED) spectroscopy.