mechanical tunneling. Dewar and Merz[2] and Rumpel and Limbach[12] have suggested that tunneling contributions to the automerization rate may occur via vibrationally assisted tunneling, i.e., direct conversion of a vibrationally excited state of **1** to the intermediate **2**.

Further work is in progress to study this reaction mechanism at higher levels of theory. While we do not believe that larger basis sets or more complete allowance for electron correlation will change the potential surface qualitatively, i.e., two-step versus concerted mechanism, they may serve to bring the theoretical and experimental activation barriers into better agreement.

Acknowledgment. We thank H.-H. Limbach for kindly providing us with preprints of ref 11 and 12. This research was conducted using the Merck IBM 3090/200 and the Rohm and Haas Alliant FX/80 computing facilities.

Supplementary Material Available: A table containing AM1 and 3-21G optimized geometries of **1a**–**4a** (2 pages). Ordering information is given on any current masthead page.

Photochemical C-H Bond Activation of Coordinated Propene in $(\eta^5\text{-}C_5Me_5)Re(CO)_2(\eta^2\text{-}C_3H_6)$. X-ray Structure Determination of Exo and Endo Isomers of the Resulting η^3-Allyl(hydrido) Complex $(\eta^5\text{-}C_5Me_5)Re(H)(CO)(\eta^3\text{-}C_3H_5)$

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One mechanism that has been implicated in the transition-metal-catalyzed isomerization of alkenes is the reversible formation of an η^3-allyl (hydrido) intermediate (Scheme I) by oxidative addition of an allylic C–H bond to the metal.[1-3] While a small number of well-characterized η^3-allyl (hydrido) complexes have now been synthesized,[2-11] in no case has the crucial step of allylic C–H activation been observed starting from the well-defined alkene complex. To our knowledge, only one previous study mentions the photochemical formation of an η^3-allyl (hydrido) complex.[6,12] Here we report that photolysis of the propene complex $Cp^*Re(CO)_2(C_3H_6)$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$) results in the formation of the η^3-allyl (hydrido) complex $Cp^*Re(CO)(H)(\eta^3\text{-}C_3H_5)$ (**2**). Furthermore, we have been successful in isolating the exo and endo isomers of **2**, differing in the orientation of the η^3-allyl group, and the structures of both have been determined by X-ray crystallography.

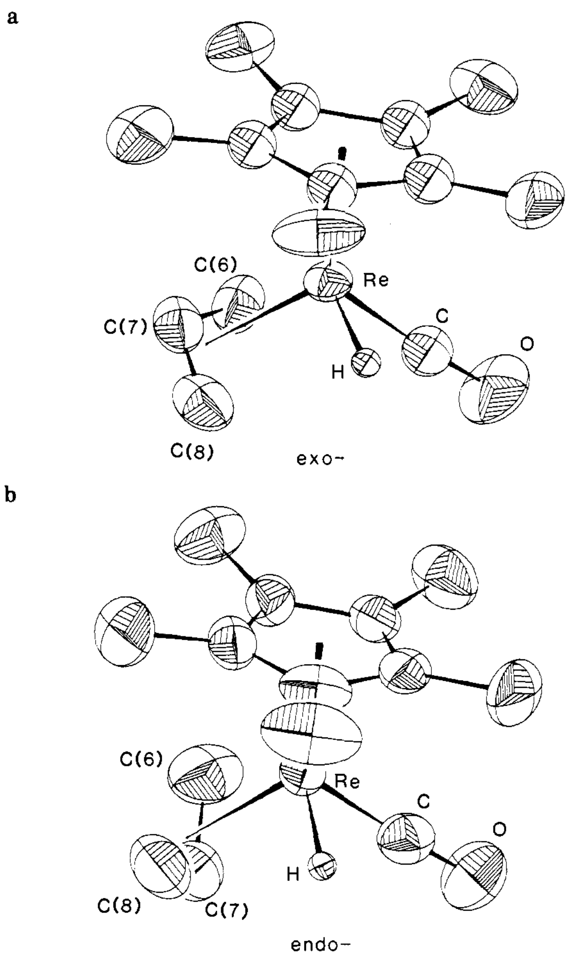
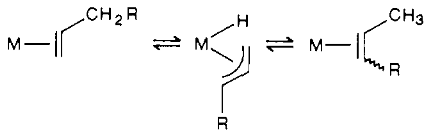
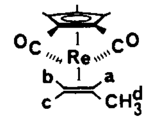


Figure 1. Perspective view of a molecule of *exo*-$(\eta^5\text{-}C_5Me_5)Re(CO)(H)(\eta^3\text{-}C_3H_5)$ (*exo*-**2**) (a) and of *endo*-$(\eta^5\text{-}C_5Me_5)Re(CO)(H)(\eta^3\text{-}C_3H_5)$ (*endo*-**2**) (b).

Scheme I





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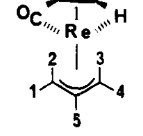
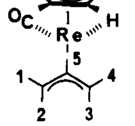


endo-2



exo-2

Irradiation of $Cp^*Re(CO)_3$ in hexane in a quartz tube at 0 °C for 1 h with a propene purge resulted in an IR spectrum having strong absorptions at 1890 and 1961 cm^{-1} for the propene complex **1** and weaker ones at 1904 and 1912 cm^{-1} for *exo*-**2** and *endo*-**2**

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respectively, plus residual absorptions from $Cp^*Re(CO)_3$. Further irradiation intensified the absorptions from **2** relative to **1**. Following chromatography on neutral alumina and crystallization at −78 °C, compounds **1**, *exo*-**2**, and *endo*-**2** (ratio exo:endo = 5:1 at 5 °C) were separated and fully characterized. Irradiation of **1** alone (hexane, quartz tube) under a propene purge gave **2** as the main product, but under a N_2 purge only a low yield of **2** resulted, suggesting that photodissociation of propene from **1** is a competing reaction.

Crystals of *exo*-**2** and *endo*-**2** are composed of equal amounts of the *R*- and *S*- enantiomers (Figure 1). In both cases the hydride position was located. The η^3-allyl group is symmetrically bonded to Re in *exo*-**2** with distances Re–C(6) = 2.260 (9) Å and Re–C(8) = 2.257 (10) Å to the terminal carbons and Re–C(7) = 2.179 (9) Å to the central carbon atom; however, in *endo*-**2** the allyl group is somewhat asymmetrically bonded, with distances Re–C(6) = 2.191 (9) Å and Re–C(8) = 2.242 (9) Å to the termini and Re–C(7) = 2.215 (9) Å. This is reflected in the carbon–carbon bond lengths of the allyl group which are equal within error in *exo*-**2** (C(6)–C(7) = 1.374 (16) Å; C(7)–C(8) = 1.363 (17) Å) but differ in *endo*-**2** (C(6)–C(7) = 1.446 (13) Å; C(7)–C(8) = 1.386 (13) Å). The carbon atom C(6) that is pseudotrans to hydride ligand is the one having shorter Re–C and longer C–C bond lengths in *endo*-**2**.

Two previous X-ray structures of (η^3-allyl) hydrido compounds have been published,[2,5] but only for $IrHCl(\eta^3\text{-}CH_2CHCHPh)(PPh_3)_2$ has the hydride been located and full structural details published.[2] The allyl ligand is asymmetrically bonded in this complex, but this may be partly a consequence of the phenyl group. The existence of two isomers of the allyl(hydrido) complex $[Ir(H)(C_3H_5)(PMe_3)_3]^+$, postulated to involve different rotational orientations of the allyl group, was not confirmed.[7]

Exo and endo isomeric forms for the allyl ligand in cyclopentadienyl complexes with piano-stool structures like **2** have been amply studied, notably by Faller and co-workers.[13] While X-ray structures have been determined for either exo or endo forms of several such compounds,[14] in the present case structures have been obtained on both exo and endo forms of the same compound, providing the opportunity for a detailed comparison of the ligand in its two orientations.[14h] Although the ligand is slightly asymmetrically bound in the endo isomer, there is no doubt that it is nevertheless a true η^3-allyl group rather than a σ–π allyl as found, for example, for the very asymmetrically bound group in *endo*-$CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$ and its tungsten analogue.[14f,g]

The ^1H NMR spectra of the two isomers have been completely assigned by decoupling and NOE procedures, and these also show interesting differences. For the symmetrically bound η^3-allyl ligand in *exo*-**2** the resonances of all five inequivalent hydrogens are in the range 1.76–2.57 ppm. For the endo isomer the resonances occur either side of this range; anti hydrogens H_2 and H_3 have smaller δ values (0.25 and 0.65 ppm, respectively), while the syn hydrogens H_1 and H_4 have larger δ values (2.67 and 3.26 ppm, respectively), and H_5 (4.01 ppm) is greatest. This contrasts with results for exo and endo isomers of $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ where the most prominent difference was a shift of the anti protons of the endo isomer to larger δ compared with the exo isomer.[13a] It also differs from results for the very asymmetrically bound allyl group in $CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$ where in both exo and endo isomers both protons of one terminus (the allylic protons) resonate at low δ, well separated from the vinylic protons at higher δ values.[14f,g]

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Supplementary Material Available: Analytical and spectroscopic data for **1** and **2** and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and selected bond distances and angles for *exo*-**2** and *endo*-**2** (12 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Graph Theoretical Approach to Carbon-13 Chemical Shift Sum in Alkanes

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In structural chemistry molecules can conveniently be viewed as graphs. A wide variety of different graph theoretical indices have been devised[1-4] and used in structure-property and structure-activity studies.[5-10] In the present study we have found that an integer graph theoretical index L which is a simple linear combination of molecular path counts of length one, p_1, length two, p_2, and length three, p_3, for carbon atoms of alkanes is well correlated with a summation of carbon-13 atomic chemical shifts.

In an earlier study, Wiener[11] first introduced a path number W and a polarity number p_3 to find a correlation for the boiling points of alkanes. W was defined as the total number of bonds between all pairs of carbon atoms in an alkane molecule. p_3 was defined as the number of ways in which an alkane C–C–C–C fragment can be superimposed on the alkane molecule and is equal to the path counts of length three. Wiener applied his analysis also to molecules having heteroatoms. The Gordon–Scantlebury[12] index p_2 was proposed to characterize molecular branching in hydrocarbons. p_2 is equal to the path count of length two. Randić and Wilkins[13] reported that the regular variations in numerous thermodynamic properties of alkane isomers have been demonstrated by considering only p_2 and p_3.

Grant and Paul[14] and Lindeman and Adams[15] found the additivity expression for carbon-13 chemical shifts for atoms in alkanes. In contrast to the additivity of the chemical shift study,

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