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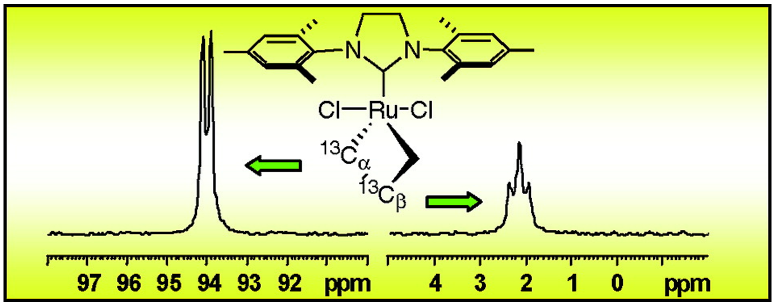

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Direct Observation of a 14-Electron Ruthenacyclobutane Relevant to Olefin Metathesis

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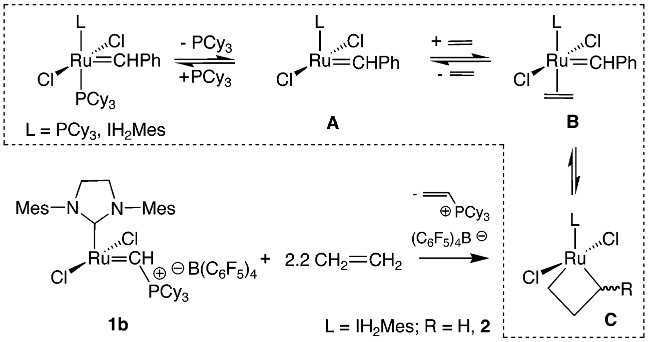
Over the past 10 years, the mechanism of ruthenium-catalyzed olefin metathesis[1] has been the subject of intense experimental[2] and theoretical[3] scrutiny. There is general consensus on the mechanism depicted for the Grubbs generation 1 (L = PCy_3) and 2 (L = IH_2Mes) catalysts in Scheme 1. However, while a large body of kinetic evidence points to the intermediacy of **A**, none of the proposed intermediates along the metathesis reaction coordinate (i.e., **B** or **C**) have been directly observed in the condensed phase.[4] Indirect evidence for the involvement of some of these intermediates has been obtained through the isolation of structural models for **A** and **B**.[5] Particularly important for the outcome of the metathesis reaction is the proposed 14-electron ruthenacyclobutane **C**. The nature of **C** has been the subject of recent theoretical debate since this metallacyclobutane has even been proposed to be a transition state along the reaction coordinate for certain catalysts.[3b] Furthermore, its geometry is unknown, and although the computational studies support the C_{2v} structure shown, other less symmetrical geometries have not been conclusively ruled out. Since metallacyclobutane formation is potentially key in determining the regio- and stereochemical outcomes of metathesis, a more precise definition of ruthenacyclobutane structure in these catalysts is critical for rational ligand design for selective metathesis.

Recently, we reported a new class of highly active 14-electron ruthenium olefin metathesis catalysts, $[(L)Cl_2Ru{=}CH(PCy_3)][B(C_6F_5)_4]$ (L = PCy_3, **1a**; IH_2Mes, **1b**).[6] These air- and moisture-stable phosphonium alkylidene complexes possess a vacant coordination site in direct analogy to the active species **A**, and thus provide rapid metathesis initiation, even at low temperatures. In addition to potential practical benefits, compounds **1a**,**b** also furnish the opportunity to study the intermediates and steps in the metathesis reaction without the bothersome presence of dissociated phosphine.[7] Herein, we report the first observation and characterization of the ruthenacyclobutane **2**[8] via reaction of **1b** with ethylene at low temperature.

Addition of 2.2 equiv of $CH_2{=}CH_2$ to a 0.01 mol/L solution of **1b** in CD_2Cl_2 at −50 °C results in clean and quantitative generation of **2** after 2−3 h, along with the vinyl phosphonium salt, $[CH_2{=}CHPCy_3][B(C_6F_5)_4]$ (^{31}P NMR, $\delta = 33$ ppm).[6] No intermediates are observed, indicating that formation of the initial phosphonium-substituted metallacyclobutane is rate limiting. The ruthenacyclobutane is characterized by the appearance of two unresolved multiplets at δ 6.6 (H_α) and −2.6 ppm (H_β) in a 4:2 ratio in the 400 MHz ^1H NMR spectrum.[9] Despite the unresolved multiplicity pattern for H_α and H_β, ^1H homodecoupling and $^1H{-}^1H$ NMR correlation experiments clearly showed them to be mutually coupled. Unlike the spectrum for **1b** at −50 °C, in which the mesityl groups are diastereotopic due to restricted rotation about the Ru−C bond, the pattern of signals for the IH_2Mes ligand in **2** is indicative of a symmetrical structure in which the mesityl groups are fully equivalent.

Scheme 1



When **1b** was reacted with isotopically labeled $^{13}CH_2{=}^{13}CH_2$, the resonances for H_α and H_β in the ruthenacyclobutane, **2**-$^{13}C_3$, split due to coupling with the ^{13}C nucleus, while the rest of signals for the IH_2Mes ligand remained unperturbed. From these experiments, ^1J $^{13}C{-}^1H$ coupling constants of 165.4 and 154.8 Hz for H_α and H_β, respectively, were obtained. Corroborating evidence for the formation of **2**-$^{13}C_3$ came from the $^{13}C\{^1H\}$ NMR spectrum. As shown in Figure 1, when the reaction was monitored at −50 °C, clean formation of **2**-$^{13}C_3$ was observed along with the expected resonance for $[^{13}CH_2{=}CH{-}PCy_3]^+$ ($\delta = 143.5$ ppm). C_α and C_β appeared as a doublet and a triplet, respectively, due to $^{13}C{-}^{13}C$ coupling ($^1J_{CC} = 15.0$ Hz); a $^1H{-}^{13}C$ HMQC experiment[9] showed the expected correlation between these signals and those for H_α and H_β. Taken together, these data require the highly symmetrical C_{2v} structure depicted in Scheme 1 to be the geometry of this ruthenacyclobutane.

In comparison to typical platinum group metallacyclobutanes,[10] the chemical shifts for the proton and carbon nuclei of the ruthenacyclobutane moiety in **2** are unusual. However, the low field shifts for C/H_α and high field C/H_β resonances are in line with those observed in both titanium[11] and molybdenum or tungsten[12] metallacyclobutanes that are active in olefin metathesis. These distinctive chemical shift patterns appear to be reflective of flat metallacyclobutane rings with a significant degree of $C_\beta{-}M$ interaction. Recent computations have indicated a short $Ru{-}C_\beta$ contact of 2.227 Å in a model of the Grubbs generation 1 14-electron metallacyclobutane that is absent in the much less active phosphine-ligated 16-electron species.[13] Schrock et al. have utilized the parameter $\delta(C_\alpha){-}\delta(C_\beta)$ as a measure of the $M{\cdots}C_\beta$ distance for a series of metallacyclobutanes, with large $\delta(C_\alpha){-}\delta(C_\beta)$ values being associated with a short $M{\cdots}C_\beta$ distance.[12b] In the case of **2**, $\delta(C_\alpha){-}\delta(C_\beta) = 92$ ppm, a rather large value comparable to those found for metallacyclobutanes of molybdenum and tungsten, and well outside the range from those of 18-electron platinum group metallacyclobutanes.[14] Finally, the $^1J_{CH}$ values for **2** are 20−25 Hz larger than typical values for metallacyclobutanes with no $M{\cdots}C_\beta$ interactions;[15] increased $^1J_{CH}$ values could be a consequence of the compression of the ruthenacyclobutane ring into a kite shape as

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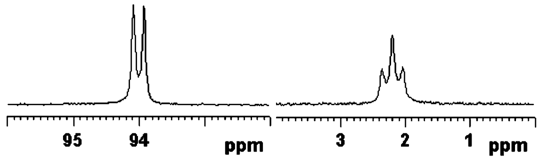


Figure 1. ^{13}C NMR resonances for C_α (left) and C_β (right) in the ^{13}C-enriched metallacyclobutane **2**-$^{13}C_3$.

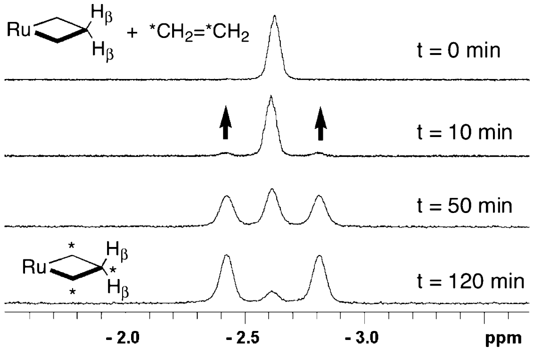
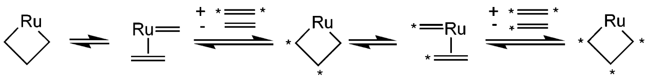


Figure 2. ^1H NMR spectra showing the resonance for H_β in the unlabeled ruthenacyclobutane **2** under an atmosphere of $^{13}CH_2{=}^{13}CH_2$.

Scheme 2



the M···C_β interaction engages. Thus, while more precise structural data for **2** (i.e., an X-ray structure) are necessary to fully answer this question, the NMR data are consistent with significant flattening of the ring through a Ru···C_β interaction.

The reversibility of ruthenacyclobutane formation in **2** was demonstrated to be significant on the chemical time scale by generating unlabeled **2** with a stoichiometric amount of ethylene at −50 °C and then exposing this solution to an excess of $^{13}CH_2{=}^{13}CH_2$. Under these conditions, smooth conversion of **2** into **2**-$^{13}C_3$ was observed, as evidenced by the spectral changes seen for H_β in Figure 2. A plausible mechanism is shown in Scheme 2; we are unsure if the exchange with free olefin from the methylidene/ethylene intermediate takes place via an associative or dissociative mechanism, but kinetic experiments designed to probe this question are underway.

Interestingly, addition of $CH_2{=}CH_2$ to the phosphine-supported **1a** showed that, unlike **1b**, this complex did not furnish a ruthenacyclobutane over a range of −50 to +20 °C. We also attempted the formation of substituted ruthenacyclobutanes by using *cis*- and *trans*-2-butene. These olefins do not react with **1b** to form ruthenacyclobutanes, and further warming is accompanied by isomerization to cis/trans mixtures as a consequence of the onset of metathesis processes. Clearly, the energetic factors that allow for generation and observation of **2** are subtle.

Samples of **2** are stable below −40 °C for at least several hours, but decomposition ensues when the sample is warmed to −10 °C in CD_2Cl_2 solution. Preliminary studies of this decomposition process using **2**-$^{13}C_3$ indicate that $^{13}C_3$−propylene is cleanly formed as a byproduct when the reaction is performed under an atmosphere of ethylene in accord with a recent report.[16] The ruthenium products in this reaction are unknown at this point. In the presence of diethyldiallylmalonate, **2** is a competent ring closing metathesis catalyst (5%) even at −50 °C, with the reaction going to completion upon warming the reaction mixture to room temperature.[6]

In conclusion, we have presented convincing evidence that the 14-electron ruthenacyclobutane intermediate **2** is an observable intermediate in NHC-stabilized Grubbs catalysts, where the strongly σ donating carbene ligand is able to stabilize this Ru(IV) species. The spectroscopic data obtained indicate it has a symmetrical C_{2v} structure. Further studies aimed at probing the kinetics of formation of this species and its mode of decomposition are currently in progress.

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Supporting Information Available: Detailed experimental procedures and complete set of NMR plots for **2** and **2**-$^{13}C_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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