# Decomposition of a Key Intermediate in Ruthenium-Catalyzed Olefin Metathesis Reactions

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The recent development of ruthenium olefin metathesis catalysts such as **1** and **2**, which show high activity and functional group tolerance, has expanded the scope of olefin metathesis.[1] Despite these advances, ring closing of large rings requires high dilution and metathesis of highly substituted or electron-deficient olefins still requires elevated temperatures and extended reaction times. Thus, thermal stability of the catalysts plays a critical role in the catalyst lifetime and turnover numbers, particularly for challenging substrates.[2]


1   **2**   **3**   **4**
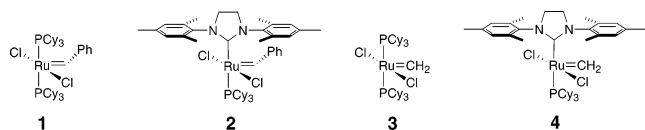
Since methylidenes **3** and **4** serve as critical and least stable intermediates in most metathesis reactions initiated by **1** and **2** such as ring-closing metathesis (RCM), cross metathesis (CM), and acyclic diene metathesis (ADMET) reactions, the understanding of methylidene decomposition and stability is crucial for designing a more stable catalyst system.[3] Previous studies from our group showed that **4** decomposes by a unimolecular pathway similar to **3** and exhibits a longer half-life than complex **3** (5 h 40 min vs 40 min).[3,4] Notably, the decomposition of **3** and **4** is not inhibited by added phosphines, while the decomposition of benzylidenes **1** and **2** is slower and is suppressed by the addition of phosphines.

Despite the information obtained from kinetic studies,[3,4] it has been difficult to understand the decomposition pathway of the ruthenium olefin metathesis catalysts because there has been no report of well-characterized decomposition products generated under typical metathesis conditions. Fortuitously, during the synthesis of **2**, we observed a decomposition product **5**.[5a] In complex **5**, the Ru center has inserted into a C−H bond of one of the mesityl groups. It has also been observed that complexes **1** and **2** decompose into hydrido-carbonyl-chloride complexes **6** and **7** upon treatment with methanol.[5] However, none of these complexes are formed from typical metathesis reaction conditions that employ aprotic solvents such as dichloromethane or benzene. Herein, we report the first well-characterized decomposition products of the N-heterocyclic-based ruthenium olefin metathesis catalyst **4** in benzene.

5   **6**   **7**
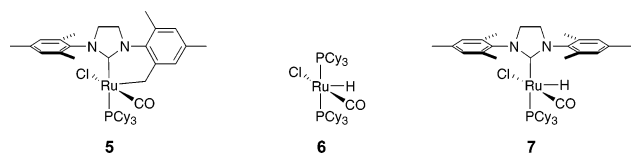
When complex **4** was monitored at 55 °C in C6D6 by 31P NMR spectroscopy, a new peak at δ 34.5 ppm was observed. This peak increased over time, while the peak corresponding to methylidene **4** (δ 38.6 ppm) decreased. An orange-yellow crystalline solid

Scheme 1
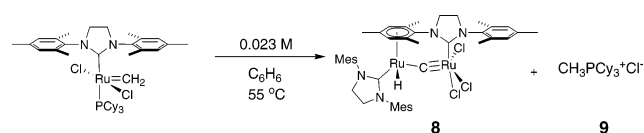
precipitated from the solution as decomposition proceeded, and it was isolated as **8** in 46% yield after 72 h. Formation of complex **8** is reproducible in benzene solution (Scheme 1).

As shown by X-ray crystallography (Figure 1), **8** is a dinuclear ruthenium compound with a bridging carbide between the ruthenium centers and a hydride ligand on Ru2. Also, η^6-binding of Ru2 to one of the mesityl rings in the N-heterocyclic carbene on Ru1 is observed along with complete loss of phosphine ligands. The hydride ligand has a chemical shift of δ −8.6 ppm in the 1H NMR spectrum and was located on the electronic density map from crystallographic data. The location of the hydride on Ru2 was unambiguously confirmed by an NOE experiment, which shows an NOE between the hydride ligand and a proton of the η^6-coordinated mesityl ring. The proton of the mesityl ring has a characteristic 1H chemical shift of δ 5.6 ppm, which is shifted upfield by the η^6-binding of Ru2.[6]
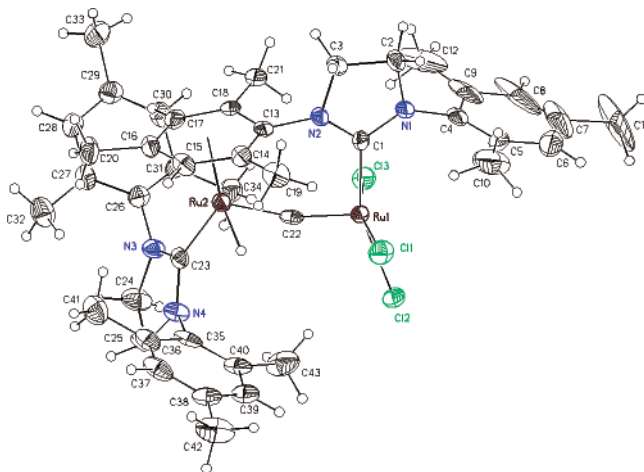

Figure 1. ORTEP drawing of **8** with thermal ellipsoids at 50% probability.

The carbide between the ruthenium centers has a distinctive 13C chemical shift of 414.0 ppm, coupled with the hydride ($J_{HC} = 10.4$ Hz); this falls within the range of 211−446.3 ppm known for other μ-carbide complexes.[7] The single-carbon bridge between two ruthenium centers is slightly bent with a Ru1−C22−Ru2 angle of 160.3(2)°. The Ru1−C22 distance in **8** is 1.698(4) Å and is slightly longer than in other reported μ-carbide ruthenium complexes such as in $(PCy_3)_2(Cl)_2Ru\equiv C-Pd(Cl)_2(SMe_2)$ (1.662(2) Å)[7a] and $[(PPr^i_3)_2(Cl)(CF_3CO_2)Ru\equiv CCH_2Ph][BAr_4]$ (1.660(4) Å).[8] The Ru2−C22 distance of 1.875(4) Å is much shorter than the usual Ru−C

single bonds in ruthenium complexes with carbide ligands that generally range from 2.00 to 2.09 Å[9] such as in [(Me₃CO)₃W≡C−Ru(CO)₂(Cp)] (2.09(2) Å).[9d] Although the allylidene alternative [Ru=C=Ru] is possible on the basis of bond lengths, we assign the Ru1−C22 interaction as a triple bond and the Ru2−C22 interaction as a single bond on the basis of the electron distribution on the ruthenium atoms.[10]

Characterization of the major phosphine byproduct with a ³¹P chemical shift of δ 34.5 ppm was also attempted. Since complex **8** has one less carbon atom than expected, we speculated that the phosphine byproduct might be methyltricyclohexylphosphonium chloride, **9**, or a phosphine ylide, CH₂=PCy₃. Upon treatment of the decomposition mixture with pentane, we isolated the phosphine product along with some unidentified decomposed ruthenium species. The ¹H, ¹³C, ³¹P NMR spectra and HRMS data of the product match exactly those of an independently prepared sample of the methyltricyclohexylphosphonium salt.[11] The formation of **9** from complex **4** occurs even at room temperature. Light gray crystals of **9** were observed with yellow-orange crystals of **4** from a saturated benzene solution of **4** at room temperature after two weeks under an N₂ atmosphere.

On the basis of the significant formation of **9**, we propose that the decomposition of **4** occurs mainly by attack of dissociated tricyclohexylphosphine on the methylidene of **10** (Scheme 2). This type of phosphine attack on the carbene carbon atom of Ru-alkylidenes was also reported by Hofmann and co-workers.[12] The 12 electron species **12** formed upon elimination of phosphine ylide **11** would bind one of the mesityl rings of **10**. Through two chloride bridges between two ruthenium centers and HCl abstraction by **11**, terminal alkylidyne complex **13** could be formed with generation of **9**. Formation of **8** can be explained by oxidative addition of the terminal alkylidyne in **13** with migration of two chlorides. However, none of these intermediates has been observed by NMR spectroscopy.

Scheme 2. Proposed Mechanism
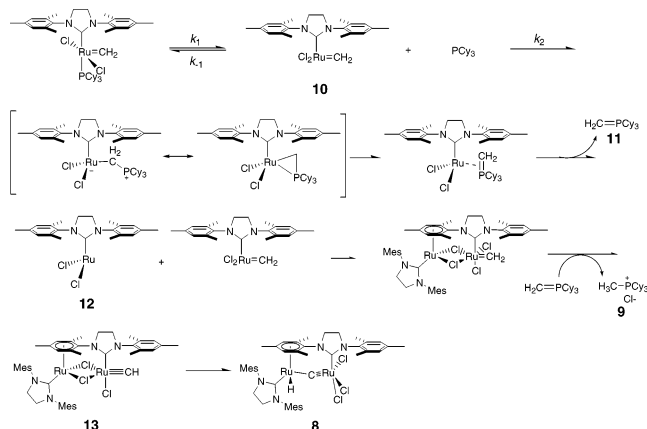
Application of the steady-state approximation to **10** affords the decomposition rate expression (eq 1), assuming the phosphine-attacking step is rate determining. This expression is consistent with the independence of phosphine concentration and the first-order kinetic observation on the decomposition of **4**.[3,4]

$$\text{rate of decomposition} = k_2[\mathbf{10}][\text{PCy}_3] = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{4}] \quad (1)$$

The formation of a hydridic species has important implications for olefin metathesis processes. Olefin isomerization is one of the side-reactions observed during olefin metathesis.[13] While not common, olefin isomerization can significantly alter the product distribution in certain metathesis reactions. Suppressing this side

reaction is thus an important goal. There have been some reports on olefin isomerization with catalyst **2**, although it is generally highly selective for olefin metathesis.[14] We believe that this process is catalyzed by either a hydride decomposition species, observable by ¹H NMR spectroscopy, or by impurities remaining from catalyst synthesis, as reported by Snapper and co-workers.[15] We have found that complex **8** catalyzes isomerization under metathesis conditions (Scheme 3). This observation implies that decomposition of catalyst **2** via methylidene **4** could be responsible for the undesirable isomerization reaction during difficult olefin metathesis reactions.

Scheme 3

76 %
(trans:cis=8:1)
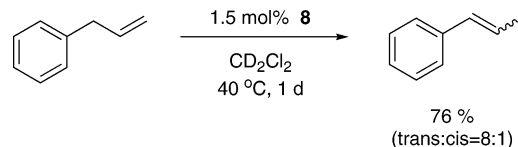
In conclusion, the dinuclear ruthenium complex **8** and methyltricyclohexylphosphonium chloride **9** result from thermal decomposition of olefin metathesis catalyst **4** in benzene. We have proposed that dissociated phosphine is involved in the decomposition of **4**. In addition, we have shown that **8** has catalytic olefin isomerization activity, which can be responsible for competing isomerization processes in certain olefin metathesis reactions.

Supporting Information Available: Crystallographic data of **8**, experimental details, and characterization data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) See Supporting Information for NOE and ¹H NMR spectra of **8**.

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