# Reducing Them Down To Charge Them Up: Low Temperature Catalyst Activation

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<th>Citation</th>
<th>Schrock, Richard R. “Reducing Them Down To Charge Them Up: Low Temperature Catalyst Activation.” ACS Central Science 2, 8 (August 2016): 495–496 © 2016 American Chemical Society</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1021/ACSCENTSCI.6B00223">http://dx.doi.org/10.1021/ACSCENTSCI.6B00223</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Chemical Society (ACS)</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Fri Mar 29 00:14:11 EDT 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/113413">http://hdl.handle.net/1721.1/113413</a></td>
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Reducing Them Down To Charge Them Up: Low Temperature Catalyst Activation

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The largest industrial application of olefin metathesis today is the synthesis of propylene from ethylene and butenes employing WO$_3$ on SiO$_2$, a relatively long-lived and regenerable catalyst that operates at 350–400 °C. It is widely proposed that high temperatures are required because the percentage of metal sites actually involved in the metathesis reaction is extremely low, or the reaction that generates alkylidenes is not a high yield reaction, or both. A recent paper by Copéret, Mashima, and co-workers tackles head-on the question concerning how in WO$_3$/SiO$_2$ catalysts the alkylidene is formed from an olefin alone. Hundreds of papers have attempted to answer this question, although one has to admit that there may not be a single answer for all supported oxide catalysts or all olefins.

Copéret and Mashima employ Me$_4$BTDP to reduce four-coordinate (SurfO)$_2$WO$_2$ sites on silica in the absence of olefins to give 2,3,5,6-tetramethylpyrazine, hexamethyldisiloxane, and M(IV) sites (eq 1). Analogously, five-coordinate (SurfO)$_4$WO sites are also reduced to (SurfO)$_4$W(IV) sites. When the purple solid containing a high percentage of W(IV) sites produced in this manner is then exposed to cis-4-nonene and heated to 70 °C, 1000 equiv of the alkene are metathesized in 6 h. When instead ethylene is added to the purple solid, solid-state NMR studies reveal that propene is formed along with unsubstituted square pyramidal metallacyclobutane and metallacyclopentane complexes. A variety of experiments led the authors to conclude that above 70 °C, metathesis activity can be ascribed to a relatively efficient contraction of a metallacyclopentane ring to a metallacyclobutane ring, from which loss of propylene generates an initial methylidene complex (eq 2). Ultimately, rearrangement of a metallacyclobutane complex to an olefin results in reduction to W(IV) and reformation of a metallacyclopentane and subsequently another methylidene.

“Ring-contraction” was discovered in the process of exploring reactions between tantalum(III) olefin complexes and terminal olefins to give two dimers of the terminal olefins, not metathesis products. This reaction turned out to be a good model for nonmetathetical steps in alkylidene/metallacycle chemistry of Mo and W. It was recognized at the time that “the MC$_4$ to MC$_3$ ring contraction is a straightforward and reasonable way of forming an alkylidene ligand from olefins—assuming that some MC$_3$ complexes which form in this manner will cleave to give metathesis-type products instead of rearranging.”

Although unsubstituted d$^9$ metallacyclopentane (MC$_4$) complexes of Mo and W (especially) have been observed as the end products of a decomposition “cascade” in the presence of ethylene, there is little hard evidence in homogeneous systems that alkylidenes arise from M(IV) olefin complexes through ring-contraction of metallacyclopentanes in homogeneous...
metathesis reactions at 22 °C. Virtually the only exception in Mo-based or W-based olefin metathesis systems is the catalytic homologation of vinyltributylstannane to allyltributylstannane in the presence of ethylene,8 which can so far only be explained through a ring-contraction mechanism. An alternative to ring-contraction as a mechanism of forming an alkylidene is a mechanism in which an allyl hydride is formed through allylic CH activation in an olefin. Allyl hydrides are intermediates in rearrangement of a metallacyclobutane to an olefin and consequent reduction of a d0 complex to a d2 olefin complex with loss of metathesis activity, so formation (to some degree) of a metallacyclobutane from an alkenyl hydride also seems feasible.

The work by Copéret and Mashima may revolutionize the synthesis and use of inexpensive supported metathesis catalysts for hydrocarbons on an industrial scale by allowing the use of much lower temperatures than currently employed. It also may open up opportunities for regenerating catalysts in flow systems. However, it remains to be seen to what extent functional groups are tolerated as metathesis substrates or whether C=CH bond isomerization7 becomes a complication at the temperatures employed. Finally, it also must be noted that the level of selectivity found in homogeneous catalysts today9 may be difficult to match in a heterogeneous catalyst since the latter are unlikely to contain true (100%) “single sites” that can be tuned with the high level of molecular precision as soluble catalysts.

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REFERENCES

NOTES
Updated to correct an editorial error in the element named in the deck.