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Citation: 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

As Published: <http://dx.doi.org/10.1021/ACSCENTSCI.6B00223>

Publisher: American Chemical Society (ACS)

Persistent URL: <http://hdl.handle.net/1721.1/113413>

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

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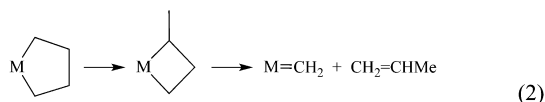
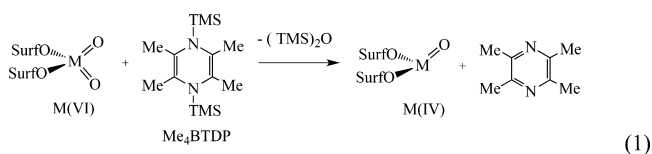
Reducing Them Down To Charge Them Up: Low Temperature Catalyst Activation

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The largest industrial application of olefin metathesis today is the synthesis of propylene from ethylene and butenes¹ 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-workers² 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_4BTDP to reduce four-coordinate $(\text{SurfO})_2\text{WO}_2$ 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



$(\text{SurfO})_4\text{WO}$ sites are also reduced to $(\text{SurfO})_4\text{W(IV)}$ 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

Copéret, Mashima, and co-workers use silyl reduction of tungsten metathesis catalysts to activate them for use at much lower temperatures.

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. It is not yet known whether only TBP $(\text{SurfO})_2\text{W(O)}(\text{C}_4\text{H}_8)$ sites undergo this “ring-contraction” to give a 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.^{3,4} 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

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.

which form in this manner will cleave to give metathesis-type products instead of rearranging.”³ Although unsubstituted d^0 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,^{5,6} there is little hard evidence in homogeneous systems that alkylidenes arise from M(IV) olefin complexes⁷ through ring-contraction of metallacyclopentanes in homogeneous

Published: August 16, 2016

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.

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=C 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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NOTES

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