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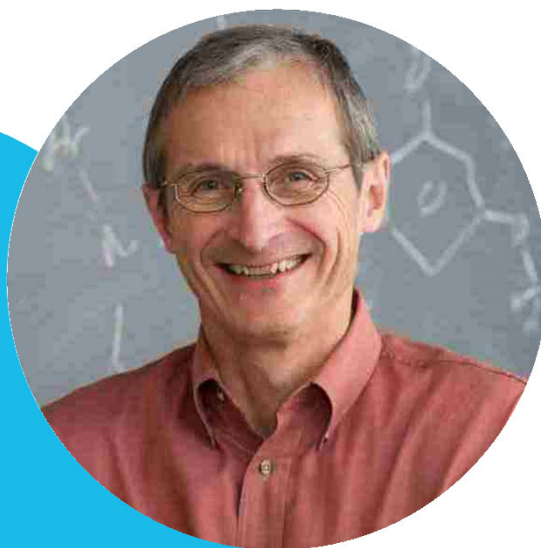
Colloquium of the Collaborative Research Center 1333

Prof. Dr. Richard R. Schrock

MIT, USA

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- **2005 Nobel Laureate
in Chemistry** -



FRIDAY, OCTOBER 14TH, 2022
1:00-2:00 P.M. LH 55.22

Metallacyclopentane Ring- Contraction Yields Olefin Metathesis Catalysts

For almost sixty years an unanswered question in organometallic chemistry and catalysis has been how molybdenum and tungsten olefin metathesis catalysts are formed from olefins. We have now shown that five-coordinate tungstacyclopentane complexes will form from ethylene and "contract" to yield W(VI) methylene complexes. The simplest example is formation of a tungstacyclobutane complex, $W(NAr)(OSiPh_3)_2(CH_2CH_2CH_2)$ ($Ar = 2,6-i-Pr_2C_6H_3$), from a tungstacyclopentane complex, $W(NAr)(OSiPh_3)_2(C_4H_8)$, in the presence of ethylene. The intermediate is an a methyl tungstacyclobutane complex, $W(NAr)(OSiPh_3)_2(MeC_3H_5)$, from which propylene is lost and $W(NAr)(OSiPh_3)_2(CH_2)$ is formed. Ring-contraction takes place in complexes bound to silica, either thermally, or through activation by room or LED (450 nm) light, for a variety of imido complexes (but not all), and for oxo complexes. Disubstituted tungstacyclopentane rings formed from propylene also ring-contrast to form methylene complexes. Finally, ring-contraction has been shown to be a means of forming propylene directly from ethylene (E \rightarrow P) at 85 °C without forming butenes. The metallacyclopentane complex that ring-contracts is proposed to be an unobservable trigonal-bipyramidal complex formed in an observable Berry-type five-coordinate rearrangement process.

