Metallacyclobutanes have been proposed as intermediates in a number of catalytic processes, including olefin metathesis [1], olefin polymerization [2], and alkane isomerization [3]. Due to the intimate involvement of metallacyclobutanes in carbon-carbon bond formation and cleavage reactions, several synthetic routes to isolable metallacyclobutanes have been developed and the reactivity of these compounds has been studied.

Many metal-specific routes to metallacyclobutanes are available, including oxidative addition of cyclopropane [4], reduction of π-allyl complexes [5], γ-H elimination in bis(neopentyl) complexes [6], and olefin reaction with the Tebbe reagent [7]. Recently Bergman and Periana reported the synthesis of a rhodacyclobutane via the rearrangement of a hydridocyclopropylrhodium complex [8]. Recent synthetic developments in the isolation of digrignard and magnesacycle reagents potentially offer a more general route to metallacyclobutanes [9].

With metallacyclobutane complexes in hand, decomposition, isomerization, and reactivity studies have been carried out to gather evidence for the mode of carbon-carbon bond cleavage. Green and coworkers reported that photolytic decomposition of Cp₂W₂CH₂CH₂CH₂ produced ethylene [10]. Their proposed mechanism involved a η⁵ to η³ shift of one cyclopentadienyl ring, followed by cleavage of the metallacycle ring into alkylidene and ethylene fragments, in the manner of the Chauvin mechanism for olefin metathesis [1]. Grubbs and coworkers have studied the isomerization of Cp₂TiCH₂CH₂CH₂ and their results indicate similar metallacycle fragmentation but without the need for the η⁵ to η³ shift [11]. Puddephatt and Casey have separately studied the isomerization of Cl₂L₂PtCH₂CH₂CH₂. Their results are consistent with a concerted mechanism [12].

Titanacyclobutanes do indeed exchange with olefins and catalyze degenerate metathesis [13].
It has also been shown that titanacyclobutanes react with ketones to produce olefins [14]. Analogous reactions with zircona- and hafnacyclobutanes result in carbonyl insertion into a metal-carbon bond rather than cleavage of a metallacycle carbon-carbon bond [9b].

The new synthetic routes may lead to more, diverse metallacyclobutanes and studies of this interesting class of molecules should continue.

References


