

Synthesis and Reactivity of Metallacyclobutanes

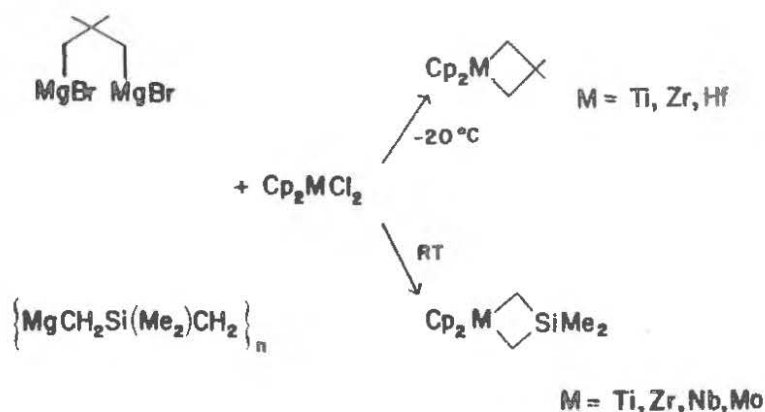
Ann Hermes

Literature Seminar

February 7, 1985

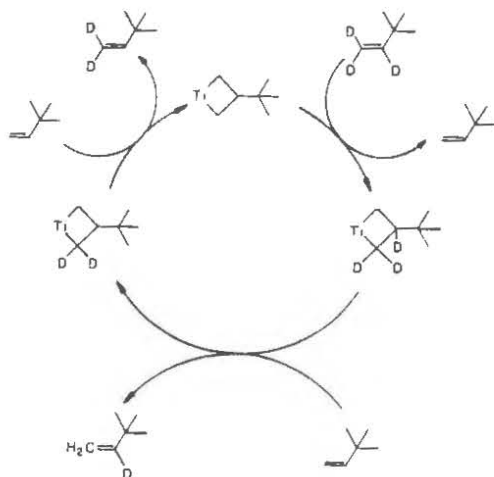
Metallacyclobutanes have been proposed as intermediates in a number of catalytic processes, including olefin metathesis [1], olefin polymerization [2], and alkane isomerization [3]. Due to the intimate involvement of metallacyclobutanes in carbon-carbon bond formation and cleavage reactions, several 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 magnesa-cycle 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 $\text{Cp}_2\text{WCH}_2\text{CH}_2\text{CH}_2$ produced ethylene [10]. Their proposed mechanism involved a η^5 to η^3 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 $\text{Cp}_2\text{TiCH}_2\text{CHPhCH}_2$ and their results indicate similar metallacycle fragmentation but without the need for the η^5 to η^3 shift [11]. Puddephatt and Casey have separately studied the isomerization of $\text{Cl}_2\text{L}_2\text{PtCH}_2\text{CH}_2\text{CHPh}$. 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 metalla-cyclobutanes and studies of this interesting class of molecules should continue.

References

1. Hérisson, J. L.; Chauvin, Y. Makromol. Chem. 1970, 141, 161.
2. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. J. Chem. Soc. Chem. Comm. 1978, 604.
3. Parshall, G. W.; Herskovitz, T.; Tebbe, F. N.; English, D. A.; Zeile, J. V. in "Fundamental Research in Homogeneous Catalysis" 1979, 3, 95.
4. a) Tipper, C. F. H. J. Chem. Soc. 1955, 2045.
b) Adams, D. M.; Chatt, J.; Guy, R. G. Proc. Chem. Soc. 1960, 179.
5. Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. J. Chem. Soc. Dalton 1977, 1131.
6. Foley, P.; DiCosimo, R.; Whitesides, G. M. J. Am. Chem. Soc. 1980, 102, 6713.
7. Howard, T. R.; Lee, J. B.; Grubbs, R. H. J. Am. Chem. Soc. 1980, 102, 6878.
8. Periana, R. A.; Bergman, R. G. J. Am. Chem. Soc. 1984, 106, 7272.
9. a) Seetz, J. W. F. L.; Hartog, F. A.; Böhn, H. P.; Blomberg, C.; Akkerman, O. S.; Bickelhaupt, F. Tet. Let. 1982, 23, 1497.
b) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. Angew. Chem. Int. Ed. Engl. 1983, 22, 248.
c) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. Organometallics 1984, 3, 825.

10. Ephritikhine, M.; Green, M. L. H. J. Chem. Soc. Chem. Comm. 1976, 926.
11. Ikariya, T.; Ho, S. C. H.; Grubbs, R. H. Organometallics 1985, 4, 199.
12. a) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. J. Am. Chem. Soc. 1979, 101, 364.
b) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. J. Am. Chem. Soc. 1979, 101, 4233.
13. Lee, J. B.; Ott, K. C.; Grubbs, R. H. J. Am. Chem. Soc. 1982, 104, 7491.
14. Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. Pure & Appl. Chem. 1983, 55, 1733.