Cleavage of Carbon–Carbon Single Bonds by Transition Metals

Organometallic intermediates generated from carbon–halogen bonds by reaction of metal catalysts have revolutionized organic synthesis. Recently, there has been increased focus on generating such intermediates from comparatively inert bonds, in order to develop new synthetic strategies that are more expeditious and more environmentally friendly, and that sometimes open access to molecules that are otherwise difficult to make. In this context, and despite the remarkable recent progress summarized in *Cleavage of Carbon–Carbon Single Bonds by Transition Metals* by Murakami and Chatani, the metal-catalyzed cleavage of single carbon–carbon bonds is not as developed as the related area of metal-catalyzed activation and functionalization of carbon–hydrogen bonds.

The kinetic and thermodynamic barriers that account for this discrepancy are clearly explained in the first chapter of this book. Accordingly, several classes of substrates (e.g., strained small-ring compounds, tertiary alcohols, and acyclic ketones and nitriles) have emerged in which those barriers are overcome through several modes of activation (e.g., oxidative addition, β-carbon elimination, and retroallylation).

The reactivity of small-ring compounds is described in the two following chapters. Each is organized in sub-sections according to the subclasses of compounds. However, students and researchers unfamiliar with this research area might initially struggle with some of the material presented in Chapter 2. For example, the inclusion of a few more schemes depicting the relevant catalytic cycles would have made the striking rearrangements of bicyclo[1.1.0]butanes (Section 2.3) easier to follow. In contrast, other sections of this chapter (e.g., Section 2.8) are much more detailed and scholarly. Chapter 3 is devoted to four-membered ring compounds, and is also much easier to understand, because the material on each subclass of compounds is organized in sub-sections according to the mechanism at play. Curiously, this chapter covers the literature only up to 2013, and therefore omits a few important developments.[1] Nevertheless, readers will get a good understanding of the field.

In Chapter 4, readers will learn how metal-catalyzed cleavage of single carbon–carbon bonds can be applied to acyclic substrates, and how carboxylic acids and tertiary alcohols are thus used as partners in cross-coupling reactions. Similarly, readers will learn in Chapter 5 how metal-catalyzed retroallylation from allyl alcohols and its variants from homopropargyl alcohols or allenyl alcohols can be applied in carbon–carbon bond-forming reactions. The mechanisms of the reactions are discussed in detail, and depicted using clear three-dimensional diagrams in numerous schemes that are very well suited for advanced undergraduate students and more experienced researchers.

The metal-catalyzed cleavage of single carbon–carbon bonds of ketones and nitriles and its application to synthesis are discussed in Chapter 6. The concepts governing the inherent reactivity of these substrates are very well explained in the introduction of this chapter, which makes it enjoyable and easy to read.

The reactions of diverse substrates are compiled in the penultimate chapter, including some examples of metal-catalyzed cleavage of multiple carbon–carbon bonds. It might be argued that the cross-coupling reactions triggered by metal-catalyzed decarbonylation of aldehydes that are discussed in this chapter could have been included instead in Chapter 4, or that other decarbonylation reactions leading to the formation of heterocyclic compounds[2] might have been covered more explicitly in this chapter or elsewhere in the book. Similarly, the rare examples of ring enlargement of cyclopentane derivatives might have been included in Chapter 3, as a comparison to the studies performed with cyclobutane derivatives.

The metal-catalyzed cleavage of single carbon–carbon bonds can provide unique advantages in total syntheses, as is concisely illustrated in the last chapter of this book. This chapter will appeal to most synthetic organic chemists of all levels, and clearly emphasizes the potential of the methodologies discussed in the previous chapters.

Many challenges remain to be tackled in reactions involving the metal-catalyzed cleavage of single carbon–carbon bonds. A broader scope of substrates, a greater tolerance of different functional groups, and lower catalyst loadings are all needed for the wider adoption and application of those methods. This book gives a good overview of an area of growing interest in homogeneous catalysis, and should inspire a new generation of researchers.

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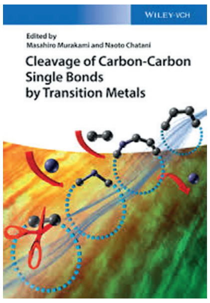

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[1] L. Souillart, N. Cramer, *Chem. Rev.* **2015**, *115*, 9410.
[2] T. Kurahashi, S. Matsubara, *Acc. Chem. Res.* **2015**, *48*, 1703.