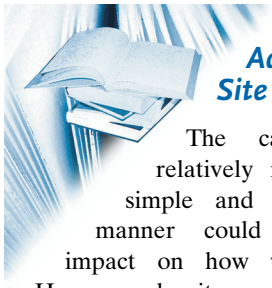


Alkane C–H Activation by Single-Site Metal Catalysis

The catalytic activation of relatively inert C–H bonds in a simple and technologically feasible manner could have a tremendous impact on how we produce chemicals. However, despite some initial optimism, this "Holy Grail" quest has been on-going for several decades, and has proven to be extremely difficult. For evidence of this initial optimism one need look no further than Chatt, who in 1976 wrote "… *I believe that in twenty-five years methane will be the most popular ligand in coordination chemistry*." This book gives a comprehensive overview of the various strategies that have been developed for C–H activation, with a strong emphasis on the mechanistic insights that have accumulated over time. The three functionalization strategies discussed are: 1) replacement of a hydrogen atom by a more useful group, 2) formation of a C–C double bond, and 3) insertion of a fragment into the C–H bond, while retaining the hydrogen atom.

In Chapter 1, Brent Gunnoe gives an overview of the most important transition metal systems for alkane functionalization. The scientific challenges presented by the chemistry of the kinetic and thermodynamic activation of C–H bonds are weighed against the huge potential for catalytic enhancement of the value of alkanes.

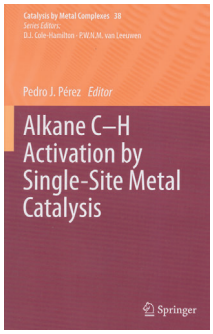
The second chapter reviews the formation of metal–carbon bonds by the electrophilic activation of C(sp^3)–H bonds. The chronological overview starts with the seminal work on chloroplatinum complexes by Shilov in the early 1970s, and continues through to more recently discovered systems based on palladium, iridium, gold, and mercury. Although the focus is on the mechanistic insights, the practical feasibility is also critically reviewed. Jay Labinger summarizes, in an excellent manner, the importance of well-designed kinetic experiments, together with advanced computational tools, to provide valuable insights.

Unlike alkanes, organoboron compounds can be easily converted into a variety of valuable chemicals. In Chapter 3, Chulsung Bae reviews the borylation of alkane C–H bonds, starting from stoichiometric chemistry, then moving on to catalytic reactions, based on mechanistic insights. The high degree of regioselectivity towards the less sterically hindered primary C–H bonds of reactive 16-electron transition-metal systems formed by σ-bond metathesis opens up unique opportunities to preferentially functionalize the more reactive primary bonds over the more abundant and reactive secondary C–H bonds. Unfortunately, the scope of available substrates, as well as the turnover frequency, would need to be improved to make the approach of broad synthetic interest.

Olefins are, besides aromatics and synthesis gas, some of the most important platform molecules in the chemical industry, and are currently manufactured in high-temperature energy-intensive processes—conditions under which one will always be severely challenged to prevent cracking and olefin isomerization as undesired side-reactions. Alkane dehydrogenation under benign conditions could be an interesting alternative, and is the topic of Chapter 4 by Goldman and Brookhart. Special emphasis is given to iridium pincer complexes, which afford reasonable turnover frequencies for both transfer hydrogenations and acceptorless dehydrogenations. Another advantage, offering interesting possibilities, is that they can easily be immobilized on supports, thus bridging between homogeneous and heterogeneous catalysis. This could at least compensate for one of the remaining problems of such systems, namely the high catalyst cost. Indeed, to develop cheaper catalytic systems with higher turnover frequencies remains a challenge. Combining such dehydrogenation catalysts with olefin metathesis catalysts offers interesting perspectives for bifunctional alkane metathesis.

The direct oxyfunctionalization of C–H bonds, without organometallic interaction, is the topic of Chapter 5 by Miquel Costas. In addition to the thermodynamic problem of C–H bond activation, one faces the kinetic challenge of preventing overoxidation of the intrinsically more reactive oxygenate. This leads to an inherent problem regarding selectivity, as one needs a reactive species in order to attack the stable C–H bond in the substrate, while preventing such a species from reacting with other functional groups in the substrate, or with the product. Such a reactive species can be one of metal–oxo or metal–peroxo form, or an oxygen-centered organic free radical. In most cases, this leads to the homolytic cleavage of the C–H bond. This might result either in a free-radical chain oxidation (e.g., Fenton chemistry), or, in the case of a rapid rebound, in the formation of C–O bonds with stereoretention. Various examples of both pathways are discussed. Despite significant progress in this field, finding a compromise in stereo- and regioselectivity remains a challenge. Progress on enantioselective C–H oxidations trails far behind that on other enantioselective oxidation reactions, and applications of C–H oxidations are at present almost exclusively limited to enzymatic systems.

In the sixth and final chapter, Pedro Pérez (also the editor) summarizes the current state of the art in catalytic alkane functionalization by carbene and nitrene insertion. Despite several promising examples, and continuing mechanistic studies, here too



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there remains a challenge regarding regio- and enantioselectivity.

In summary, this book allows one to gain an appreciation of the challenges facing us, and of the in-depth mechanistic studies that have been performed thus far. I thoroughly enjoyed reading the book, and would encourage both the homogeneous and heterogeneous catalysis communities to explore it.

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