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Book Review

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Multimetallic catalysts in organic synthesis

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This is a well presented and wide ranging volume, with chapters covering diverse areas of catalysis in organic synthesis and related fields, authored by leading figures in each of those fields. The diverse range of the topics covered makes it difficult to summarise the whole, and although this does not make for a brief and easy-reading review, there is no real option but to address each chapter individually.

The first chapter—'Organic synthesis with bimetallic systems' (Kamijo and Yamamoto)—is subdivided into reactions promoted by one catalytic and one stoichiometric metal, which includes many examples in which the role of the stoichiometric metal is mechanistically simple (e.g. base, or a silver salt acting as a halide abstractor), and a second section covering reactions which have two metals in catalytic quantities. This second section includes both reactions which are traditionally used with single-metal catalysts, describing the improvements which can be obtained the addition of various metals, and also those which are traditionally thought of as bimetallics (e.g. Sonogashira). The details of the systems surveyed are covered well, and the discussion of applications in organic synthesis is good, although in many cases the roles of the individual metals are not discussed in much detail. For instance, the role of copper in the Sonogashira is presented in a very traditional manner, ignoring much of the latest work on the likely mechanisms at play. Similarly the Heck reaction is discussed without any reference to the theories of the importance of palladium nanoparticles. Nevertheless this section gives a good general coverage of some important systems in which mixed metal catalysts have found application. This is the chapter of the book which gives the most general coverage of applications in organic synthesis, and is likely to be of great interest to the organic community at large, although personally I would question if one should really describe a reaction containing a mononuclear palladium species with a stoichiometric second metal acting as a redox cofactor (Wacker) or base as involving 'multimetallic catalysts'.

The second chapter 'Zinc polymetallic asymmetric catalysis' (Kumagai and Shibasaki) is where the true potential of bimetallic catalysts (i.e. molecules which contain two metals) is demonstrated. Here we are introduced *inter alia* to dinuclear zinc complexes which mediate asymmetric aldol condensations, with the metal centres having distinct roles. A mechanistic proposal is presented in which one zinc centre acts as a Lewis acid, binding an aldehyde, and the second centre binding the enolate with which it reacts. The high e.e. observed in these systems can easily be rationalised in terms of the high degree of order in such a complex (especially in the case of hydroxy ketones, which can be double-bound as their enolates. Similar systems are applied in Mannich-type and Michael reactions, again, with good to excellent e.e. The next three chapters 'Group 13-alkali metal heterobimetallic asymmetric catalysis', 'rare earth bimetallic asymmetric catalysis' and 'rare earth-alkali metal heterobimetallic asymmetric catalysis' (all of which also have Shibasaki as one of the authors) have many similarities with the zinc work from Chapter 2. In each case the bimetallic systems are based around polydentate (predominantly) oxo-ligands which bridge two metal centres, allowing each metal to perform a different role (e.g. Lewis acid, Bronsted base) and bring reactants together with a high degree of order, resulting in good selectivities. This section of the book is well structured and the theme is developed well, clearly showing the power of multimetallic catalysts, and hinting at the enzyme-like functions of the more complex examples.

Chapter 6—'Catalytic and stoichiometric transformations by multimetallic rare earth metal complexes' (Hou)—presents and interesting review of recent developments in the area of transformations mediated by multinuclear cyclopenadienyl complexes of the lanthanides. A number of useful transformations mediated by these species is presented and the structural chemistry is itself of great interest. However, these species are not as well developed as those discussed in earlier chapters and, necessarily, this chapter mainly concentrates on the (fascinating) synthesis and reactivity of the complexes themselves and the discussion of the catalysis in terms of the unique features of multimetallic systems is thus limited.

Chapter 7, 'Bimetallic transition metal catalysts for organic oxidation' (Henry) is interesting as it introduces a new theme to the book which is one of the potential real advantages of multimetallics over mononuclear species, which is the multiple electron transformations which are possible when a catalyst contains more than one redox active metal. A series of examples of applications of bimetallic oxidations is presented, with the main focus being upon palladium species. Chapter 8 'Bimetallic oxidation catalysts: hydrogen peroxide generation and its use in hydrocarbon oxidation' (Remias and Sen) continues the oxidation theme, stressing the green aspects of hydrogen peroxide usage, and the possibility of *in situ* generation of hydrogen peroxide over metal catalysts. The work described here is both useful and interesting, but I would question if it is appropriate to this book To my mind it is stretching both the terms to describe some of the catalyst systems here (e.g. a reaction mixture containing dissolved $V(acac)_3$ and solid phase $Pd–Al_2O_3$) as 'multimetallic catalysts' and to describe benzene oxidation as 'organic synthesis'.

Chapter 9—'Two approaches to multimetallic catalysis: combined use of metal complexes and multinuclear complex catalysis' (Ishii and Hidai)—addresses important issues of the synergistic effects of heterobimetallic systems, and the advantages or otherwise of the pre-organisation involved in generating a multinuclear complex, as opposed to allowing reaction to generate a multinuclear intermediate. The studies concentrate on carbonylations and related reactions in the case of simple mixed mononuclear catalysts, then move to multinuclear systems to explore transformations of acetylenes. Chapter 10 'Dirhodium tetraphosphine catalysts' (Stanley) describes one of the classic areas of organometallic catalysis, the rhodium catalysed hydroformylation (and related reactions) of alkenes. An elegant study of the bimetallic reaction mechanism involving Rh–Rh bond formation and cleavage within the catalytic cycle is presented, along with details of the spectroscopic studies that have elucidated this area. This chapter beautifully summarises some of the issues involved in the design of multimetallic catalysts and their applications,

such as the dramatic differences in selectivity seen with the new mechanism at play, and even new reactions.

The final chapter—'Catalysis by homo- and heteronuclear polymetallic systems'—gives a good overview of some fascinating and extremely useful catalysis with such clusters as Pd_{561} $phen_{60}$ $(OAc)_{180}$. The work is presented mainly in terms of the structural studies of the clusters, their activities in various catalytic transformations and the selectivities between different product families. To my mind it is, again, doubtful that many of the reactions discussed (e.g. reductive conversion of cyclohexanone to 11 products) are best considered to be organic synthesis, although this is not to deny the utility of many of the reactions considered. This last point essentially sums up my biggest misgiving about this book. While each of the chapters is a well presented expert review of its area, the extent to which they all combine to a logical whole is questionable. Some of the chapters (e.g. Chapter 11) will be of little or no interest to a target-molecule orientated synthetic chemist wishing to learn how he or she can apply 'multimetallic catalysts in organic synthesis'. Equally, Chapter 1, while going into great detail of the specific organic reactions which a given catalytic system is useful for, pushes the boundaries of what can be defined as a multimetallic catalysts, and does not explore many mechanistic points. While it can be argued that the subject matter here being the applications of multimetallic systems in organic synthesis renders details of the mechanisms irrelevant, when some of the other chapters (notably the excellent chapter ten) focus on these points, it becomes unclear at whom the book as a whole is aimed. However, these are essentially semantic points, and many sections of the book develop a strong theme of how multimetallic systems achieve fundamentally different reactivities and selectivities when compared to mononuclear systems. It was time that this growing field was addressed in such a book and I am pleased that it now has been with this useful and well presented volume which will hopefully stimulate much interest in this area.

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