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**Structure and Bonding**

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# Structure and Bonding

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# Structure and Bonding

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### Aims and Scope

The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table and addresses structure and bonding issues associated with all of the elements. It also focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of *Structure and Bonding* to the extent that the focus

is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant.

The individual volumes in the series are thematic. The goal of each volume is to give the reader, whether at a university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience. Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented using selected examples to illustrate the principles discussed. A description of the physical basis of the experimental techniques that have been used to provide the primary data may also be appropriate, if it has not been covered in detail elsewhere. The coverage need not be exhaustive in data, but should rather be conceptual, concentrating on the new principles being developed that will allow the reader, who is not a specialist in the area covered, to understand the data presented. Discussion of possible future research directions in the area is welcomed.

Review articles for the individual volumes are invited by the volume editors.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.

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*Dedicated to the memory of Professor  
Herbert Schumann († 2010), a pioneer of  
organolanthanide chemistry*

# Preface

This volume reviews the recent developments in the use of molecular rare-earth metal compounds in catalysis. Most of the applications deal with homogenous catalysis but in some cases, heterogeneous systems are also mentioned. The rare-earth elements, which are the lanthanides and their close relatives – scandium and yttrium – have not been in the focus of molecular chemistry for a long time and therefore have also not been considered as homogenous catalysts. Although the first organometallic compounds of the lanthanides, which are tris(cyclopentadienyl) lanthanide complexes, were already prepared in the 1950s, it was only in the late 1970s and early 1980s when a number of research groups began to focus on this class of compounds. One reason for the development was the availability of single crystal X-ray diffraction techniques, which made it possible to characterize these compounds. Moreover, new laboratory techniques to handle highly air and moisture sensitive compounds were developed at the same time. Concomitant with the accessibility of this new class of compounds, the application in homogenous catalysis was investigated. One of the first applications in this field was the use of lanthanide metallocenes for the catalytic polymerization of ethylene in the early 1980s. In the last two or three decades, a huge number of inorganic and organometallic compounds of the rare-earth elements were synthesized and some of them were also used as catalysts. Although early work in homogenous catalysis basically focused only on the hydrogenation and polymerization of olefins, the scope for catalytic application today is much broader. Thus, a large number of catalytic  $\sigma$ -bond metathesis reactions, e.g. hydroamination, have been reported in the recent years.

This book contains four chapters in which part of the recent development of the use of molecular rare-earth metal compounds in catalysis is covered. To keep the book within the given page limit, not all aspects could be reviewed in detail. For example, the use of molecular rare-earth metal complexes as Lewis acidic catalysts is not discussed in this book. The first two chapters review different catalytic conversions, namely the catalytic  $\sigma$ -bond metathesis (Chapter by Reznichenko and Hultsch) and the polymerization of 1,3-conjugated dienes (Chapter by Zhang et al.). Within these chapters, different catalytic systems and applications are discussed. The final two chapters are more concentrated on recent developments of

catalysts synthesis; but of course catalytic aspects are also mentioned. Therefore, these two chapters are focused on homogeneous catalysis using lanthanide amidinates and guanidinates (Chapter by Edelmann) and the synthesis of rare-earth metal post-metallocene catalysts with chelating amido ligands (Chapter by Li et al.). The organometallic lanthanide catalysts of the first generation, which are the metallocene catalysts of the general composition  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{LnR}]$  ( $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ,  $\text{N}(\text{SiMe}_3)_2$ ,  $\text{H}$ ), are mentioned in the first two chapters, but are not covered in a separate synthetic contribution because a number of excellent reviews on this topic have been published over the recent years.

In summary, the present volume of *Structure and Bonding* shows the substantial activity carried out in recent years in the field of synthesis of inorganic and organometallic rare-earth metal compounds and their use as catalysts for a number of different transformations. The future holds great promise for the rapid growth of this field of chemistry and for new spectacular results.

Karlsruhe  
June 2010

*Peter W. Roesky*

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