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# Organometallic Oxidation Catalysis

Volume Editors: Franc Meyer · Christian Limberg

With contributions by

M. A. Ciriano · C. Freund · W. A. Herrmann · F. E. Kühn  
C. Limberg · F. Meyer · B. V. Popp · D. Schröder · H. Schwarz  
S. S. Stahl · T. Strassner · C. Tejel · K. H. Theopold  
J. I. van der Vlugt

The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structure, properties and mechanisms increases, new ways are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being achieved that are of significance to a larger scientific audience.

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## Preface

For 80% of all compounds produced in chemical and pharmaceutical industry at least one *catalytic* step is essential during their synthesis. At the same time the use of hydrocarbons as feed-stock for commodity and fine chemicals typically requires an *oxidation* step, which is usually mediated by a transition metal compound. Consequently, *oxidation catalysis* is a major research field in chemistry, both in academia and in industry. This volume “Organometallic oxidation catalysis” deals with catalytic oxidation processes where metal-carbon bonds occur in one way or the other, for instance in key intermediates formed as part of the catalytic cycle. This is the case in homogeneous oxidative conversions mediated by palladium complexes, as described by S. S. Stahl et al., or by rhodium and iridium complexes, as outlined by C. Tejel et al. It also applies to the heterogeneous Mo/Bi-based SOHIO process, and C. Limberg describes recent advances with respect to the modelling of crucial organometallic intermediates in this process by molecular compounds. On the other hand, the contribution of D. Schröder et al. highlights the oxidation chemistry of basic organometallic species in the gas phase, as this may reveal fundamental characteristics inherent to oxidation catalysts. A further important aspect that is covered by some of the experts is the use of suitable organic ligands – and their resulting organometallic complex fragments – to achieve efficient oxidation catalysis. Hence, one article by T. Strassner summarises recent developments in the field of N-heterocyclic carbene complexes that proved surprisingly robust under oxidative conditions. It has not been self-evident that organometallic complexes can survive the conditions necessary for polar oxygen-transfer reactions, but research of the last decade concerning oxo and peroxo complexes that are functionalized by organic ligands – as described by K. H. Theopold for organometallics of early transition metals – has clearly shown that relatively non-polar M–C bonds can be quite stable in the presence of oxidants and protic media. They may even be essential for the favourable activity and life-time of a catalyst, so that extensive efforts were made to heterogenise such compounds by linking them to the most different surfaces. The review by F. E. Kühn and W.A. Herrmann outlines results obtained for immobilised organorhenium and organomolybdenum catalysts. In a complementary approach, the active site structures of metal containing oxidase and oxygenase enzymes have provided great inspiration for the development of novel oxidation catalysts. Although

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those systems in most cases are not strictly organometallic, selected examples of homogeneous copper-catalyzed oxidations are described in a chapter by J.I. van der Vlugt and F. Meyer to build a bridge to the rapidly expanding field of bioinspired catalysis. We hope that the readers enjoy reading this multi-faceted volume as much as we did.

January 2007

Franc Meyer  
Christian Limberg



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