

Book Reviews

Organosilicon Chemistry: From Molecules to Materials
N. Auner and J. Weis (eds.), VCH, Weinheim, 1994,
349 pages, DM128.00.
ISBN 3-527-29061-3

This volume is a compilation of the lectures and posters (or in some cases seemingly brief summaries of them) presented during a meeting entitled "Munich Silicon Days '92" held in Munich in 1992. They are organized under five headings, viz.: Tetravalent organosilicon compounds: chemistry and structure; Subvalent and unsaturated organosilicon compounds: formation and structure; Hypervalent organosilicon compounds: formation and chemistry; Organosilicon–metal compounds: coordination chemistry and catalysis; Silicon polymers: formation and application.

A good number of the best known names in the field are represented among the authors. Much of the material has appeared elsewhere, but overall the volume gives a fair idea of the current scope of organosilicon chemistry.

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Oxygenates by Homologation or CO Hydrogenation with Metal Complexes
G. Braca (ed.), Kluwer, Dordrecht 226 pages, £64.00,
ISBN 0-7923-2628-8.

The book is the 16th volume in the series *Catalysis by Metal Complexes* from the same publisher.

The escalating oil prices in the 1970s and early 1980s have given a strong impetus to the development of new catalytic chemistry for the production of industrial chemicals from syngas. This book gives an overview of advances in this field but limited to homogeneously metal-complex catalyzed hydrocarbonylation reactions with syngas, which were described in papers and patents appearing mainly after 1982.

The review is organized in three chapters. The first deals with CO hydrogenation for the direct conversion of syngas into oxygenates and is titled "Monoalcohols, glycols, and their ethers and esters by CO hydrogenation" (with 136 references). The second chapter deals with the indirect synthesis of oxygenates from syngas via homologation of alcohols and their derivatives ("Alcohols and derivatives by homologation with syngas"; with 226 references) and the third with their synthesis via aldehyde hydrocarbonylation ("Hydrocarbonylation of aldehydes and their derivatives; with 85 references). The first two chapters (88 and 101 pages, respectively) are written by G. Braca, A.M. Raspolli Galletti and G. Sbrana and the last chapter (30 pages) by M. Marchionna.

The authors did not have an easy task in collecting and systematically organizing the large body of results on the subject, and at the same time giving a meaningful interpretation of catalytic phenomena underlying the experimental data. Often the experimental results cited, and not only those in patent literature, are conflicting and incomplete. In many cases selectivity data towards the various products are unreliable; for instance, hydrocarbon formation in syngas reactions is almost never accounted for.

Nevertheless, the authors have attempted to discuss the subject systematically in terms of a common scheme, first presenting the catalytic performance of the various metal complexes and then a general discussion of the reaction mechanisms, involving the various successive steps in the proposed catalytic cycles. Since most catalytic systems consist of complicated mixtures of metal complexes (and often of more than one metal) with so-called promoters, a discussion of reaction mechanisms, involving simultaneous and/or sequential carbonylation and hydrogenation reaction steps, is bound to be rather speculative. Rarely can direct experimental evidence for postulated intermediate metal complexes be given.

The review shows that selective and efficient formation of target oxygenate chemicals, such as the C₂-chemicals ethylene glycol and ethanol, via direct or indirect hydrocarbonylation reactions with syngas, is still an elusive goal. In addition to the effect of the fall

in crude oil prices in the mid 1980s, the selectivity problems in hydrocarbonylation reactions together with the severe reaction conditions generally required and the corrosive nature of the catalyst components (e.g. iodide promoters) have certainly also contributed to the decision of many industrial and academic research groups to discontinue the study of this type of syngas chemistry. However, oil prices may escalate again and even if this does not happen, syngas will become abundantly available from emerging new technologies for the relatively inexpensive syngas manufacture from widely available sources such as natural gas. Industrial interest in syngas as a feedstock for chemicals will therefore certainly remain, provided highly active and selective, non-corrosive catalyst systems can be developed for syngas conversions.

I value the book for two reasons. First, as an overview of the present state of the art of hydrocarbonylation syngas chemistry, the book may function as starting point for further studies and inspire the industrial chemical community to look at existing chemical and technological problems in this field with renewed creativity and enthusiasm. Second, for organometallic and theoretical chemists the review offers many challenges to contribute towards a better understanding of catalytic syngas chemistry by organometallic complexes. Together with the traditional organometallic chemistry approach, the increasing applicability to organometallic systems of the newly emerging techniques of computer-aided molecular modelling and molecular mechanics, in combination with quantum mechanical calculations, may prove instrumental in achieving this understanding. Such studies could bear fruit in designing (rather than finding by the trial and error approach mainly used so far) of highly active and selective catalysts for the desired selective and efficient conversions of syngas.

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The Organometallic Chemistry of the Transition Metals
R.H. Crabtree, Wiley, New York, 2nd edn., 1994, 487
+ xvii pages, £49.50
ISBN 0-471-59240-4

This book is an expanded, corrected, and amended version of the first edition which appeared in 1988. Although it keeps essentially to the same pattern as the first edition, it seems altogether a more polished production, reflected in its appearance (hard back, rather

than paper) and its price (£49.50 rather than £16.50). Whether students will still buy it at such a price is open to question, even though the author says in his preface that "this is what you need to know to get started in the field". Started for what? Perhaps the answer should be – for passing examinations.

This is a good text book. It is designed for senior undergraduate and graduate courses in organometallic chemistry, and for that it seems to function very well. It starts with an introduction and first chapter covering the basic coordination chemistry principles that are required for an understanding of organometallic chemistry but are sometimes not taught in that context. Each chapter includes problems (with solutions) and selected references. However, it is a pity that the author does not use full IUPAC notation (such as square brackets, etc.), because this is the basic language of chemistry; but he is not alone in that. If he had done so, some minor solecisms, such as $\text{Rh}(\text{PPh}_3)_3^+$ rather than $[\text{Rh}(\text{PPh}_3)_3]^+$ might have been avoided. Thereafter, organometallic compounds are treated in classes: alkyls, aryls and hydrides; carbonyls, phosphine complexes (with a long discussion of substitution reactions); and alkene and alkyne complexes (including dienes, cyclopentadienyls, arenes, etc.).

It is refreshing that the emphasis is placed upon practical characterisation and reactions rather than on structure, which has often been the case in the past. The presentation of structural types is succeeded by chapters on oxidative addition and reductive elimination, on insertion and elimination, and on nucleophilic and electrophilic reactions.

The last group of chapters deals with application: homogeneous catalysis, alkyne metathesis, activation of small molecules, organic synthesis, and so on. There is a final chapter on bioorganometallic chemistry. However, even if one admits that nitrogen fixation involves organometallic chemistry, the brief discussion of the subject does contain the occasional error (apart from omitting the reviewer's name from one reference!).

This book presents the information in a very easily digestible form, and is written in a very relaxed style. It covers the whole field of organometallic chemistry of the transition metals in a way likely to appeal to student and professor alike. It should provide strong competition for the texts already in the field. With minor reservations, I recommend it warmly.

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