include the isolation of the product, and processes that involve finely divided supports (clays, silica gel, aluminum oxide) are likely to use excessive amounts of solvents for extraction, filtration, centrifuging, purification, etc. The use of microwave radiation and of supports is elevated to the status of a fetish here. However, the authors fail to check if their reactions may give a higher or even quantitative yield at a lower temperature without a support and without uncontrolled overheating of the pretreated support material. One has to question whether the laborious techniques described are necessary for reactions such as deprotecting, condensations, cyclizations, rearrangements, oxidations, or reductions, as the reactions are then never quantitative, and separating the product from a large quantity of ballast involves procedures that are not environmentally friendly. It is regrettable that ballast-free techniques giving a 100% yield without the need for workup are not mentioned. To take an example, one has to mix 106mg of benzaldehyde and 93mg of aniline with 20mg of montmorillonite K10, then irradiate for 3 minutes with 800–900W microwave power in a bath that heats up to 110°C, followed by extraction with a large quantity of dichloromethane, giving only 98% of impure benzylidene-aniline; the montmorillonite must then be cleaned and reactivated for re-use. Instead, as shown by this reviewer's results, one can simply mix 848g of benzaldehyde with 744g of aniline (both 99.5% pure) in a $31 \times 44\,\text{cm}^2$ flat steel vessel. The temperature does not rise above 35°C. The water of reaction is then evaporated under vacuum from the crystalline product. One obtains 1.436 kg of pure crystalline benzylidene-aniline (100% yield).

In the interest of the subject, the reviewer bears a duty to counteract the dogmatic tendency that appears again and again in this book. It probably arises from the pressure to demonstrate rapid progress in environmentally friendly methods of synthesis, even though the results are unsatisfactory. The potential for a proper balanced evaluation is easily lost when flawed "general principles", for which there is no rational justification, lead to the rejection of good or even better alternatives. The absence of an international input to the US symposium (e.g., by the OECD) also leads to imbalance. This can easily lead to an exclusive circle which attempts to reserve activities in "green" (or "sustainable") chemistry for its members, ignoring the many innovations generated by synthetic chemists in almost all universities and industrial research laboratories throughout the world without any special sponsorship. An example of this damaging dogmatism is the authoritative call in this report for efforts to replace all existing stoichiometric processes by catalytic processes, supported by frequent references to statements by P. T. Anastas (The White House) and T. C. Williamson (Environmental Protection Agency); on page 4 these two refer to "stoichiometric reagents" and "catalytic reagents". Work towards truly environmentally friendly processes should actually emphasize the opposite of that, seeking wherever possible to get away from catalysis towards stoichiometric syntheses that require no workup of the product. The justification for that is provided by over a thousand solid-state reactions, and a few stoichiometric liquid-state reactions in which the product crystallizes during the reaction; these reactions, giving yields of 100%, are not mentioned anywhere in the book. It would be a shame if "green syntheses" became a synonym for complicated and laborious syntheses.

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Computational Organometallic Chemisty.

Edited by *Thomas R. Cundari*. Marcel Dekker Inc., New York 2001. 428 pp., hardcover $ 185.00.—ISBN 0-8247-0478-9

To anticipate the verdict at the outset: this collection of articles about the use of computers in organometallic chemistry by various well-respected research groups is well written. I agree with Thomas Cundari's view, stated in his introduction, that "the time was ripe for a book on computational organometallic chemistry". The volume gives a good overview of the many different methods and their particular advantages, as well as identifying problems that still remain to be solved.

The use of computer methods in organometallic chemistry has become more and more important in recent years. One reason for that is, of course, the enormous increase in computational power. One can now perform even the most demanding calculations using a PC, and the relationship of computing power to cost is very good. A second reason is that many research groups throughout the world have demonstrated that theory can make important contributions to the understanding of experimental results. In the area of organometallic chemistry, density-functional theory naturally deserves to be mentioned. Its significance was recognized in the award of the Nobel Prize for Chemistry in 1998: "… to Walter Kohn for his development of the density-functional theory and to John Pople for his development of computational methods in quantum chemistry".

The chemist working in the field of organometallic chemistry nowadays has access to many different ways of using calculations to yield additional information for his or her research, as can be seen in the 15 chapters of this book, which deal with a wide variety of topics. All the chapters are accompanied by numerous literature references including recent review articles.

In the first chapter Per-Ola Norrby describes his "recipe for an organometallic force field", which he has already used many times with great success. He explains the basic structures of different force fields, the differences between them, and methods for determining their parameters. The discussion covers the automatic generation of force fields, optimization methods such as the Simplex and Newton–Raphson techniques, validation methods, and some commonly encountered problems. Three examples of the application of the "recipe" concept are described.

In the second chapter David White describes methods for the quantitative determination of steric effects, both by the use of molecular mechanics programs (Allinger: MM2, MM3, MM4) and by means of mathematical decriptions (cone angles and solid angles). The most well known among chemists is undoubtedly Tolman's cone angle, which is often used as a measure of space-filling by ligands around a metal center.

The article by Diedenhofen, Wagener, and Frenking on the precision of quantum-mechanical methods provides an assessment of the capabilities of modern techniques. The authors give an excellent overview of the best known quantum-chemical programs and the advantages and disadvantages of DFT methods. The importance of the exchange and correlation functions, of ECPs, and of relativistic effects in the field of transition metals is explained clearly, with a wealth of literature references which encourage further reading. Taking carbonyl complexes as an example, the authors discuss how the choice of method affects the results for experimentally measurable quantities such as bond lengths, dissociation energies, and stretching vibrational frequencies. Other examples considered include nitrido complexes and transition-metal-catalyzed processes such as the water-gas shift reaction and the oxidation or epoxidation of olefins. A separate chapter is devoted to the calculation of NMR chemical shifts, a contribution that is likely to be of particular interest to experimentalists. It shows that the 1998 Nobel Committee's statement:"Chemistry is no longer a purely experimental science", is also true for the field of organometallic chemistry!

Kristine Pierloot reports on the use of multireference methods in her article on the importance of non-dynamic correlation in transition metal complexes. However, the choice of the appropriate reference wave-functions and of the active orbitals in the CASSCF or CASPT2 calculations is a difficult problem which requires previous experience with QM methods. The article aims to provide the reader with guidelines for applying such methods, but also points out the limitations that must be kept in mind.

QM/MM methods are an attempt to combine the advantages of molecular mechanics (speed, number of atoms) with those of the QM methods (precision). The molecule is divided into separate regions which are then treated by different methods. The article by F. Maseras describes the application of such a method to three examples: 1) the study of agostic interactions in $[Ir(H)_2(PR_3)_3]$ complexes, 2) porphyrins, and 3) steric effects in asymmetric dihydroxylation.

In another article A. Jolly and co-authors describe the docking of inhibitor molecules on the metal ions of the active center of an HIV integrase.

The next two articles focus on semi-empirical ZINDO calculations. Zhang and co-authors show that calculations for various dienes have enabled them to propose promising candidates for the cyclometalation of dienes. The contribution by Taber and co-authors is concerned with catalytic reactions, in particular with the development and use of a model, and with an investigation of the effect of chiral auxiliaries on the rhodium-catalyzed C–H insertion reaction. The *ee* value of enantioselective reactions is determined in the transition state, which is therefore of crucial importance for optimizing the reaction.

The quality of force-field calculations is very dependent on the choice of parameters. These are much easier to determine for organic molecules than for organometallic compounds, where there is a greater variety of coordination types. Suitably tailored parameterizations have therefore been developed for special problems. In the article "Molecular Mechanics Modeling of Organometallic Catalysts" D. P. White and W. Douglass review studies in the area of catalysis, and also give a useful detailed bibliography of different parameterizations.

The article by M. S. Gordon and co-authors is concerned with titanium compounds, which play an important role as catalysts in many processes, such as hydrosilylation and Ziegler–Natta polymerization. Many titanium compounds have unusual coordination spheres, which often makes the calculations very laborious and requires the use of multi-reference methods. This is discussed for a variety of examples (TiX_2, Ti_2H_6, Ti_2H_8, $H_2Ti=EH_2$).

J. N. Harvey draws attention to a special problem of computational organometallic chemistry, namely that one has to take into consideration different spin states. He takes spin-forbidden reactions as an example, and discusses methods for investigating a change of the potential hypersurface that may occur during the reaction. Several examples are used to describe different possibilities for determining the point where the transition from one potential hypersurface to another occurs.

K. Krogh-Jesperson and co-authors compare the results from density-functional methods with those from MP2 calculations for the oxidative addition of hydrogen to $[M(PH_3)_2Cl]$ ($M=Rh$, Ir). They conclude that the density-functional methods offer the best compromise between precision and effort involved in the calculations.

The article by B. Bursten deals with relativistic effects. Taking actinide complexes as an example, the author discusses the special problems of calculations on these compounds. In particular, the dynamic correlation and the large number of 5f and 6d orbitals with almost equal energies makes the calculations very laborious. The problem can be satisfactorily solved by relativistic DFT calculations (especially with PW91). T. P. Hamilton describes ethene-like compounds with the general formula $H_2M=EH_2$ formed by π-bonding between elements of Groups 13 and 15. Calculations for compounds ranging from $H_2B=NH_2$ to $H_2Ga=AsH_2$ have been carried out using various ab initio methods (HF, MP2, CCSD(T)).

The final article is devoted to metallocenes. The authors describe cp_2E and cpE structures with elements of Main Groups 1, 2, 13, and 14, with different geometries and hapticities. The advantages and disadvantages of semiempirical, ab initio, and density functional methods as applied to population analyses, chemical shift calculations, and ligand effects are discussed and illustrated by various examples. The article also discusses questions of symmetry and level of theory to which one must pay attention when creating inputs for calculations.

The book gives an indication of which areas of research in organometallic chemistry can benefit from computational methods. Due to the broad range of topics covered by the articles, the volume should appeal to a wide readership. However, the promise of a "how to do it" approach should not be taken too literally—the book is not a guide of how to use the programs.

To put together a comprehensive treatment of computational organometallic chemistry is admittedly a difficult task. Nevertheless, it must be mentioned that some aspects are missing: I would have expected to find contributions on ab initio molecular dynamics calculations, on cluster methods, and a separate one on the calculation of “properties”. For many experimental chemists the calculation of molecular properties is of central importance.

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DNA Arrays. Methods and Protocols. Edited by *Jang B. Rampal.* (Series: Methods in Molecular Biology, Vol. 170.) Humana Press, Totowa 2001. 264 pp., hardcover $ 89.50 (ca. € 98).—ISBN 0-896-03822-X

The aim of this book is to give an overview of the current situation in DNA microarray technology, and to provide protocols that will help new starters in the field to set up systems for DNA array analysis, even in laboratories without special facilities for such work. The research field of DNA microarrays, which is still quite new and has a large interdisciplinary element, is described in 17 chapters by authors drawn almost exclusively from industry. This reflects the commercial importance of microarray technology, which is further emphasized by a chapter giving details of the companies engaged in the field and discussing the commercial prospects. A chapter on ethical aspects discusses some of the questions that arise, such as the possibility of compulsory DNA diagnostic tests, the need for individual data protection in view of the ease with which comprehensive genetic data can be communicated electronically, and the possibility that insurance companies and employers may discriminate against higher risk groups. Other chapters dealing with more general aspects are the introduction by Edwin Southern, the brief reviews of confocal fluorescence analysis of DNA arrays, and the chapter on bioinformatics technology, which must assume a key role in the processing of the enormous quantities of raw data on hybridization analyses.

Several chapters are devoted to the preparation of nucleic acid arrays. For example, one of these describes the synthesis of DNA arrays by photolithography. It includes laboratory recipes and NMR data for phosphoramidites with photolabile protecting groups attached, reproduced from the original publications, but one may question how interesting and relevant these are from a practical standpoint, as few laboratories are likely to have facilities for the laborious photolithography. The preparation of gel-immobilized nucleic acid arrays is a simpler procedure. However, the chapters on this technique only describe the coupling chemistry involved in a very general way, and refer one to the original papers for details. Also they do not give protocols for using such arrays, but only schematic diagrams and literature references. Two chapters describe the preparation of DNA arrays by ink-jet and printing methods. Here there are detailed protocols for some of the procedures, but for the average user they are likely to be of little help, as they are very specific to the particular microdispensers and automatic plotters referred to. That criticism applies even more to the chapter on automated genotype classification using mass spectrometry equipment made by Sequenom of the USA.

Six chapters are devoted to describing practical applications of DNA arrays. They contain some useful and widely applicable protocols for the hybridization analysis of RNA and for analyzing nucleic acids by tandem hybridization; these methods could also be useful for some other related investigations. The chapter on “DNA Sequencing by Hybridization” (SBH) describes three variants of the technique, which is still under development. The purpose of the SBH method is to apply DNA arrays to study known gene sequences and mutations, or even to sequence unknown new genes. Several protocols for SBH are given. The chapter on the preparation of oligonucleotide arrays in searching for effective antisense reagents is especially useful, as it not only gives some generally applicable laboratory protocols for procedures such as the surface activation of glass supports, but also contains detailed diagrams of apparatus and reaction vessels. The chapters on applications of DNA microarrays for determining HLA types and for gene expression analysis also contain some useful experimental details.

The appearance of this book on the technology of DNA microarrays is certainly to be welcomed, as the subject is complex and very few well-proven methods are yet available. Unfortunately, however, many of the protocols given here are described in a superficial way, and would only be useful to experts who already have a detailed knowledge of the subject. The book by itself is unlikely to give readers a clear overall impression of this area of research. The arrangement of the subject matter within the chapters is not systematic, and adequate cross-references between chapters are not given. The literature coverage extends only up to 1999, and consequently does not include the most recent developments in this rapidly moving field, so that some parts of the book are already out of date. Nevertheless, it should be of interest to postgraduate students and postdoctoral researchers who have begun work on DNA arrays and need a broader view of the field, together with useful tips for solving practical problems.

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Inorganic and Organometallic Polymers. By *Ronald D. Archer.* John Wiley & Sons Inc., New York 2001. xii + 247 pp., hardcover £ 64.50.—ISBN 0-471-24187-3

This book by Ronald D. Archer reminds us that as well as organic polymers the area of inorganic and organometallic polymers is attracting increasing interest. On page 2 the author defines inorganic polymers as polymers with inorganic repeating units in the backbone, and organometallic polymers as those with a backbone alternating between a metallic element and an organic linkage. But the book also describes examples of polymeric metal complexes in which a metal forms bonds with, for example, oxygen, sulfur, or nitrogen. But these are not organometallic polymers. The author forgot to point out that a field called