Book Reviews

Advances in Carbene Chemistry. Volume 2. Edited by Udo Brinker (Universität Wien, Austria). JAI Press: Stamford, CT. 1998. x + 295 pp. $109.50. ISBN 1-55938-837-4.

As stated by the Editor in his preface, carbene chemistry has "advanced dramatically" in the past decade, primarily due to improvements in technology for examining short-lived carbenes as reactive intermediates. This volume provides excellent articles by leaders in the carbene field that summarize a variety of recent advances.

The articles in the volume focus on a wide variety of topics and include discussion of rearrangements of alkyl- and heteroatom-substituted carbenes as well as their thermochemistry. Recent (and historical) information is presented by Bonneau and Liu as well as by Platz on migratory processes in carbenes and the role of carbene−olefin complexes as well as excited states of the carbene precursors. Recent results are presented that demonstrate the important role of how the carbene is generated for understanding the product distribution of the true carbene intermediate.

Carbenes have been studied in a variety of "conditions" in order to modify the product distribution as well as to characterize the short-lived intermediate. Brinker discusses the study of carbenes in cyclodextrin and zeolite hosts and reveals modified pathways for reaction without chemical modification of the actual reactive intermediate but only by its environment. Kozankiewicz and Platz discuss high-resolution spectroscopic approaches to understanding triplet aromatic carbenes in Shpolskii (hydrocarbon) matrixes. In particular, the first application of hole-burning spectroscopy to carbenes has determined the zero-field splitting parameters for a triplet carbene.

Toscano presents a summary of laser-flash photolysis studies on carbonyl carbenes and the corresponding Wolff rearrangement. In particular, the role of the precursor conformation has a profound effect on the final photochemistry, and the *anti* conformer of the diazocarbonyl precursor yields more carbene production.

Chen presents thermochemical information for predicting the ΔH_f of small- to medium-sized carbenes via an additivity approach. These methods validate the use of additivity approximations even for reactive intermediates such as carbenes, and as presented by Chen, the singlet−triplet splitting is indicative of potential deviations in these approximations.

Persistent triplet carbenes are reviewed by Tomioka, and new results are presented for long-lived persistent carbenes. Substituent effects at multiple positions are discussed for extending the lifetime of triplet carbenes. In particular, bromine as a "protecting" group appears to be very promising.

Warkentin presents an exhaustive review of heteroatom-substituted carbenes (with N, O, and/or S attached to the carbene center) in both the gas and the condensed phases. The generation and reactivity of these carbenes are discussed, and data consistent with their nucleophilic character are presented. These carbenes are truly unique in their reactivity patterns, and a wealth of information is presented on oxy-, amino-, and thio-substituted carbenes.

Carbenes as intermediates in the generation of bridgehead double bonds are discussed by Jones. This chapter presents a vast array of information on the migratory aptitude in carbene rearrangement of different ring sizes, and once again Jones brings up the topic of the role of the carbene precursors.

Overall, this volume presents a wealth of information for the practicing carbene chemist as well as for novices to the field. This book is a necessary reference for the practicing chemist's library.

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Advances in Metal and Semiconductor Clusters: Cluster Materials. Volume 4. Edited by M. A. Duncan. JAI Press: New York. 1998. 402 pp. $109.50. ISBN 0-7623-0058-2.

Volume 4 of this series contains 11 articles and has as its focus the measurement of properties of cluster materials that relate to realized or potential applications. Because of the great diversity of cluster materials as a class of chemical substances, a brief summary of each contribution will be provided below.

Alivisatos et al. discuss the synthesis, characterization, and optical properties of InAs and InP nanocrystals (67 references). Synthetic strategies for preparing III−V nanocrystals are reviewed. Enhanced quantum confinement effects are not observed for these cluster materials, in contrast to expectations predicted from the effective mass approximation. Magnetization reversal in nanoparticles is reviewed by Majetich (35 references). An excellent introduction to magnetic properties and the size dependence of magnetic properties is provided. Magnetically hard materials, such as nano-$SmCo_5$ or nano-Co, are discussed in more detail. A comprehensive overview of how the combination of electron diffraction and electron imaging techniques can be used to structurally characterize individual nanoparticles is presented by Cowley (87 references). A wide range of nanoparticulate materials is discussed, including metals, alloys, metal oxides, semiconductors, with special emphasis on single-walled and multiwalled carbon nanotubes. El-Shall and Li summarize the vapor-phase synthesis of metal and semiconductor nanoparticles using pulsed laser vaporization with controlled condensation (141 references). An overview of the synthetic method is provided, along with specific discussion of the synthesis and characterization of several metal oxides, a few metal carbides, and silicon.

Three chapters summarize advances in fullerene or fullerene-like materials. Compton et al. (97 references) and Shinohara (45 references) independently review the synthesis and characterization of endohedral metallofullerenes. The relative chemical stability of various $M@C_n$ substances is mentioned, particularly with respect to problems associated with the isolation and purification of metallofullerenes. Results of STM, NMR, and synchrotron X-ray diffraction studies are included in the contribution by Shinohara. Tenne et al. review the synthesis and properties of encapsulated or intercalated inorganic fullerene-like structures (45 references). Layered structures, such as MoS_2 or WS_2, are unstable as nanoclusters relative to hollow cage structures resembling nested fullerenes and nanotubes. Metals intercalate into these nanocages and impart photovoltaic properties to these materials. Fullerene-like MoS_2 can be prepared from amorphous MoS_3 using electrical pulses produced by a STM tip.

Two chapters report results of principally theoretical studies. Maclagan and Scuseria compare ab initio calculations of met-car clusters to determine the level of calculation required to produce reliable comparative results (41 references). The B3LYP density-functional method is recommended. Omeltchenko et al. present the results of large-scale molecular dynamics simulations of several structural and mechanical properties for nanophase silicon nitride (132 references). Crack propagation and fracture processes, the effects of porosity and grain size on the bulk and shear moduli, and other properties are modeled.

Wang and Wu probe the electronic structure of selected first-row transition metal clusters using photoelectron spectroscopy to determine size dependence on the change from molecular to bulklike electronic structure (148 references). Size-selected anion clusters are studied, with cluster sizes ranging from one to 33−70 atoms. The onset of bulklike behavior occurs with relatively small clusters for the lighter metals (eight atoms for Ti) and with larger clusters for the heavier metals (greater than 25 atoms for Cr). A concluding contribution by Kreibig et al. reviews the effect of embedding medium on the optical absorption spectra of silver nanoclusters (39 references). The effect of a nanocluster/medium interface is determined for a variety of matrix materials, including silica and other metal oxides, solid triphenylphosphine, and solid C_{60}.

Overall, each contribution is well written and provides the reader with both a general introduction to the topic of interest and a more detailed summary of recent research results. This volume will serve as a useful reference work for the materials chemistry community due to the broad range of cluster materials and properties covered in these contributions.

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