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Book reviews

Inorganic Chemistry in Liquid Ammonia, by David Nicholls, Elsevier Scientific Publ. Co., Amsterdam/Oxford/New York, 1979, x + 238 pp., Dfl. 110.00, \$ 49.00.

This book was written to provide the first English summary of inorganic chemistry in liquid ammonia since the 1935 publication of Franklin's "The Nitrogen System of Compounds." Although Jander's "Anorganische und allgemeine Chemie im flüssigem Ammoniak" (Interscience, 1966) gives a broader and more detailed survey of the subject up through about 1964, Nicholl's book appears to cover the important developments of the last twenty or thirty years very well. It can be heartily recommended as a first reference book for researching a particular topic or as a book for browsing, to spark ideas. Organometallic chemists will be struck by the relative paucity of synthetic work which has been done so far with this useful solvent. The chapter titles are: Introduction to liquid ammonia chemistry, Physical properties of liquid ammonia, Practical techniques in liquid ammonia, Reactions of elements and compounds with ammonia (organized according to the periodic table), Acid-base reactions, Oxidation-reduction reactions, Reactions of alkali metal solutions, and Synthetic reactions involving metathesis or substitution.

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Transition Metal Organometallics in Organic Synthesis; edited by H. Alper, Vol. II, Academic Press, New York/San Francisco/London, 1978, xi + 185 pages, \$ 19.00.

This second (and apparently final) volume on transition metal organometallics in organic synthesis, edited by Howard Alper, contains three reviews. The first concerns reactions where alkynemetal complexes are important (isolated or demonstrated) intermediates and is written by Nicholas, Nestle, and Seyferth, all important contributors to the area. The second chapter surveys reactions of arenemetal complexes emphasizing reactions where the arene ligand is modified. The author is Girard Jaouen, who is part of a vigorous French group working in this area at the University of Rennes. The editor of the series finishes off the effort with a collection of organometallic reactions of interest for synthesis that can be classified only as "miscellaneous."

The first two chapters follow the pattern set by Casey in Volume one (carbene complexes) in that a well-defined and active area is comprehensively reviewed, areas on the verge of sophisticated applications in synthesis. In chapter one, the

required brief introduction to bonding in alkynemetal complexes is accompanied by a useful table of selected preparations of specific examples. The unique function of the $\text{Co}_2(\text{CO})_6$ cluster as a protecting group for alkynes and in stabilizing propargyl cations is brought out with examples, emphasizing selectivities of interest to the synthesis chemist. The longest section concerns special reactivity of the coordinated triple bond, usually involving complexes formed in situ and often efficiently catalytic. It is organized according to reaction type which makes easier reading for the organic chemist and provides the mechanistic generalizations which lie beneath the lists of examples. It is comprehensive enough to indicate reaction types where only one or two examples are known and thus to simulate the reader toward new applications. The summary of alkyne trimerizations is particularly useful because important examples are drawn from different research groups, using different catalysts and producing different end products; important applications include heterocycles and benzocyclobutenes. The final section describes intriguing cluster complexes of methine units, $\text{RCCO}_3(\text{CO})_9$, which are not strictly within the definition of the coverage, but fit the overall purpose of the series. The interconversions of alkylidyne complexes and manipulations into organic products, while primitive from the synthesis viewpoint, are suggestive of an important future. This chapter is concise, filled with well-chosen examples, and strikes the proper perspective to engage the synthesis chemist.

The chapter on arenemetal complexes has a similar perspective and brings to the attention of the reader a range of new aromatic substitution reactions. It is not organized as neatly according to reaction type and certain extraneous material appears. For example, substitution of ring hydrogens by nucleophiles appears on p. 81 (chromium) and again on p. 87 (iron) in a different section. The section on "Arene Complexes as Catalysts" seems not to fit with the theme of the series. Catalytic 1,4-hydrogenation and 1,4-hydrosilylation can be accomplished with benzenechromium tricarbonyl, but other catalysts also work, and the arene ligand seems not to participate in a significant way. An early section on the electronic influence of a $\text{Cr}(\text{CO})_3$ group summarizes a controversial area and introduces a systematic presentation of the special reactivity of arene ligands. Many examples involve side chain reactions where the arenechromium tricarbonyl group is a perturbing substituent. In general, no unique chemistry is involved, but the $\text{Cr}(\text{CO})_3$ group enhances the usual effect of a phenyl substituent. The stereochemical influence of a $\text{Cr}(\text{CO})_3$, blocking one face of the arene ring during side chain reactions, is special; Jaouen summarizes his and related work on stereospecific synthesis of substituted indane and tetralin derivatives.

Nucleophilic addition to arene ligands is probably the new reactivity (since 1959) of most interest in organic synthesis. The applications with $\text{Cr}(\text{CO})_3$ as the activating group are presented briefly: nucleophilic substitution for halogen and the addition/oxidation sequence for nucleophilic substitution for a hydrogen.

Unfortunately, these reactions are separated from a section entitled "Electrophilic Reactivity of Cationic Arene Complexes" which may cause the reader to miss the consistent mechanisms for both neutral and cationic complexes. The section of *ortho*-metalation is particularly welcome, since it brings together diverse examples and some systematic studies to reveal a mechanistically consistent, potentially useful set of reactions. This technique for directly func-

tionalizing positions *ortho* to functional groups is clearly ready for application in complex organic synthesis.

Chapter three "is concerned with useful reactions which have not been discussed in other chapters". This is not a stimulating mandate, so one can sympathize with Alper about the job of organizing the information. The result is primarily a listing of examples with little connection among the short sections. There is essentially no mechanistic discussion nor emphasis on a special role played by transition metals in the reactions. The reader may find an odd reaction of use in his or her research, but more likely the same information will be found in a review of a particular topic. For example, three pages on metal-catalyzed oxidation of alkenes with peroxides is the longest single section but provides only a series of examples, without comparison with classical methods. One of the reviews on oxidation written for synthesis chemists would serve the reader much better.

It is a well-produced volume. The quality of the printing, structure drawing and proofreading is excellent. References are included through late 1977. The price is not out of line for a specialized book, and purchase is recommended to those who work actively in organometallic chemistry. All synthesis chemists will benefit from chapters one (especially) and two, largely from stimulation to develop applications in their own work.

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Inorganic Polymers, by N.H. Ray, Academic Press, New York/San Francisco/London, 1978, 174 pages, \$ 17.35.

At least six books on the general subject of inorganic polymers have been published since 1962. Two of the earliest of these books (by Stone and Graham, and by Lappert and Leigh) were comprehensive accounts that summarized both the purely inorganic and the organic-inorganic aspects of the field. Thus, the two main questions that must be asked about this latest book are: How well does it bring the subject up to date, and to what degree does it emphasize the most important recent developments?

The book emphasizes *mineralogical* polymer chemistry and, within this context, it provides an elementary survey of the traditional topics, such as phosphates, silicates, chalcogenide glasses, borates, etc., with an occasional mention of recent applications, such as electrical "switching" phenomena. Regrettably, those research areas that have produced the most dramatic advances in recent years (those that, for the most part, involve organic-inorganic systems), are badly neglected in this volume. Only ten pages are devoted to poly(sulfur nitrides), polyphosphazenes, and carborane-type polymers, and most of the references are to earlier work. Neither poly(organosiloxanes) nor linear organo-transitional metal coordination systems are discussed. The author promises in his preface "to indicate some of the directions in which future research might be encouraged" but, in fact, no new approaches or underlying principles are developed.