Metal Amide Chemistry

As one of the main pillars of coordination chemistry, metal amide complexes are a flourishing class of compounds. They are also widely exploited by nature, and the electronic and steric versatility of amido ligands has led over the past 25 years to seminal discoveries in such diverse areas as enantioselective organic transformations (e.g., hydroamination), polymerization catalysis ("postmetallocene" or non-cyclopentadienyl catalysts for polyolefin and polylactide generation), small-molecule activation (e.g., N_2 or N_2O), and materials chemistry (metal–organic chemical-vapor deposition, nanochemistry). In particular, custom-made metal amide complexes have emerged as formidable synthesis precursors for the generation of pure alkoxide and alkyl derivatives through protonolysis and amide elimination reactions, respectively. This book is a very timely summary of the metal amide chemistry that has surfaced over the past three decades since the comprehensive treatise *Metal and Metalloid Amides* by M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, published by Ellis Horwood in 1980.

The present book by Michael F. Lappert and Philip P. Power, together with their former postdoctoral fellows Andrey V. Protchenko and Alexandra L. Seeber, comprehensively (but not exhaustively) covers the post-1980 literature up to 2007, and is divided into ten chapters. Following a brief introduction that highlights important developments in the field, there are nine chapters which are subdivided according to the Periodic Table. All the chapters relate to the preceding book and often document the "advances" made in the field through the use of numbers, e.g., that the bibliographic citations for amide complexes comprised of Group 3 and 4f/5f as well as d transition metals increased from 317 (1980) to 1110 (post-1980). The emphasis is clearly put on the synthesis, structure (as determined by X-ray diffraction analysis), and reactions/reactivity of neutral, cationic, and anionic metal amide derivatives.

The variety of amido ligands employed is very large, and it is the bulky variants, in particular, which lead to intriguing structural features and reactivity. Prominent examples are the sterically demanding monodentate ligand $[N(SiMe_3)(2,6\text{-}Mes_2C_6H_3)]$ (Mes = 2,4,6-$Me_3C_6H_2$), which allowed for the isolation of a monomeric Ga^{I} complex, and a super-bulky hexaisopropylterphenyl-substituted triamido ligand, which provided a suitable scaffold for studying the reduction ("activation") of N_2 at a Mo^{III} center. However, well-established silylamido ligands have also proved unique in stabilizing less-common metal oxidation states, as evidenced by monomeric $[Ce^{IV}\{N(SiMe_3)_2\}_3Br]$ and the fascinating anionic metalloid clusters $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ and $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$, or promoting unusual metal amide reactivity and the formation of unusual complexes, as shown for mixtures of $[K\{N(SiMe_3)_2\}]$ and $[Zn\{N(SiMe_3)_2\}_2]$, which can deprotonate toluene and form so-called "inverse crowns" $[\{M_2Zn_2\{N(SiMe_3)_2\}_4(O_2)\}_\infty]$ (M = Na, K) in the presence of trace amounts of O_2/H_2O.

While tetradentate encapsulating ligands such as biologically relevant porphyrinato ligands are outside the scope of the book, parent NH_2^- and imido derivatives are covered, as well as a diverse range of functionalized mono-, di-, and triamide complexes. It is immediately apparent that the authors could not give a comprehensive treatise of the plethora of d-transition-metal amide complexes, but the two tables on structurally characterized derivatives of nonchelating diorganoamido ligands do indeed provide the readers with a rough guide of the activity of each metal.

Regrettably, the structure of the predecessor book was not fully adopted, with the former part II, which deals with properties and applications of metal amide complexes (ca. 150 pages), having been abandoned. Although the authors attempted to include some of this valuable information into each of the chapters, it is not readily visible among the numerous formulas and labels. The readers would no doubt have appreciated a well-arranged summary on the current status in the application of metal amides in catalysis and material science.

On balance, the venture is an indisputable success: I can recommend this book to all colleagues and students who are actively pursuing research in the fields of coordination, organic, and inorganic chemistry. However, the book is not of the caliber of a standard textbook as was the predecessor book (and the authors never claim it to be so), but rather falls into the category of a most valuable reference book, providing in-depth knowledge and visions for one of the most important and successful classes of coordination compounds.

Reiner Anwander
Institut für Anorganische Chemie
Universität Tübingen (Germany)

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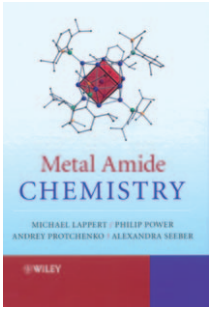

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