

tions of the art of painting. This disagreement put the advocates of the superiority of line, led by Ingres, against those who chose color, led by Delacroix. As Stevens shows, we now know that these are not entirely aesthetic choices but are intimately involved with the mechanisms by which the brain processes visual information received by the retina. These chapters offer the lay reader tantalizing glimpses of discoveries in brain science that may be just over the horizon. One might hope that these developments ultimately may give some insight into higher cognitive function, among the highest of which we put creativity.

After having read the book, I cannot say that I was conscious of the mental fatigue tempered by exhilaration that one feels after a stimulating symposium. Rather, the afterthoughts were more like those following a good dinner party which one has been privileged to be invited to share with a brilliant company. Such occasions are to be valued, but the opinions expressed in the conversation may be offhand and unsupported. Sometimes, they remain unchallenged because the distinguished guests want to avoid disturbing the air of good fellowship. Also, one must expect that some of them may arrive in an unsociable mood and may not be especially interested in the thoughts of their fellow guests. Nevertheless, those who attend owe thanks to the hosts for making the gathering possible and to the assembled savants for an occasional spark of enlightenment.

Jerome A. Berson

Department of Chemistry
Yale University
New Haven (USA)

Metal Dihydrogen and σ -Bond Complexes. By Gregory J. Kubas. Kluwer Academic/Plenum Publishers, New York 2001. 472 pp., hardcover \$ 95.00.—ISBN 0-306-46465-9

The study of complexes containing nonclassically bound ligands is a flourishing field of research and several hundreds of examples have now been reported. Broadly speaking, these can be defined as complexes in which electron

density from a coordinated $X-Y \sigma$ bond is delocalized onto an otherwise coordinatively and electronically unsaturated metal center, a view going far beyond the classical Lewis concept of localized two-electron bonds. For this reason it is not surprising that, although first postulated more than 30 years ago, such complexes were not unambiguously established until the early 1980s when Kubas reported convincing evidence for the existence of a molecular dihydrogen complex, and Green and Brookhart clearly defined the class of agostic compounds. Several seminal reviews dealing with selected topics (such as $H-H$, $C-H$, and $Si-H$ coordination and activation) within this broad theme have been published since that time. Specifically, those written by Crabtree, Morris, Heinekey, Schubert, Corey, Eisenstein, and Lledos should be mentioned. In particular, in 1993 Crabtree reviewed and generalized in *Angewandte Chemie* the whole field of σ complexation (R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 789). However, the limited scope of that review, and the significant recent progress in studying nonclassical complexes (such as recent studies of the dynamic properties of dihydrogen complexes, the discovery of dihydrogen bonding, and the synthesis of borane $B-H \sigma$ -bond complexes) required a fresher look at this field. It is only now that a comprehensive account covering the whole family of nonclassical complexes, including their synthesis, structures, dynamics, spectral properties, and reactivity, is available from a true expert and the author of the original discovery. There is no doubt that the appearance of such a book is a timely and significant event in the chemical review literature.

As the book's title implies, complexes of molecular hydrogen are the prime focus of Kubas's contribution. This is not only associated with the predominance of dihydrogen complexes in the family of nonclassical compounds, but also reflects the great importance of hydrogen in industrial hydrogenation processes, and the intriguing recognition of how (apparently) easily some naturally occurring systems, such as enzymes, can produce and/or activate H_2 .

The book consists of 13 chapters. The first chapter (Introduction) provides the reader with a concise and clear intro-

duction to the area, establishing a convenient genealogical link with classical Werner complexes, π complexes, and also nonclassical main-group element species such as H_3^+ and CH_5^+ . An account of the relevance of these topics to the activation of small molecules such as dinitrogen, dioxygen, etc. is also given. The comparatively short Chapter 2 gives a historical overview of the discovery and development of the coordination chemistry of dihydrogen. As is often the case with great milestone discoveries, the initial claim for the existence of an intact dihydrogen molecule in the coordination sphere of a tungsten complex met with considerable skepticism. This chapter not only conveys the excitement of scientific discovery, but also nicely illustrates the difficulties in publishing truly paradigm-shifting ideas and getting them accepted by the scientific community. Indeed, four years passed between the first observation of H_2 coordination and the publication of the communication! At this initial stage in the story of dihydrogen complexes theory and experiment developed in parallel. However, the success and recognition that the area enjoys nowadays would not have been possible without the truly synergistic interaction of both approaches as is currently practised. Modern computational techniques, such as MP2 and DFT calculations, not only allow us to explain and predict the experimental results, but also serve as powerful (and, some would say, often even "superior") tools for identification of nonclassical bonding, particularly when the exact position of hydrogen atoms is under consideration.

Chapters 3–9 form the core of the book and deal with the synthesis, theory, problems of identification, dynamics, and reactivity of coordinated dihydrogen molecules. The complexation of σ bonds to a metal is described in this book by a Dewar–Chatt–Duncanson type model, and the crucial role of back-bonding from the metal and the key role of the ligand *trans* to the $H-H$ (or $Si-H$, etc.) bond is emphasized throughout. Apart from the simple (if this term can be appropriate at all!) coordination to a metal, dihydrogen σ complexes are relevant to heterolytic hydrogen splitting and σ bond metathesis reactions. These processes are manifestations of an im-

portant phenomenon called *cis*-interaction, a term which refers to the intramolecular attractive interaction of a coordinated H_2 or silane with another ligand present. In most cases the resultant species are just transient intermediates, but in others the *cis*-interaction determines the molecular geometry. This effect also has a direct relevance to intramolecular hydrogen exchange in transition metal polyhydrides.

The nonclassical nature of the H–H bonding in H_2 complexes raises the question of its identification. The scope and limitation of the available techniques is thoroughly discussed and nicely illustrated in the book. The picture is, however, further complicated by the range of bonding distances observed, spanning a continuum from 0.82 Å in unstretched H_2 complexes to 1.6 Å in classical dihydrides. Furthermore, the potential energy surface for $H\cdots H$ interactions in some cases is remarkably flat, and even simple libration motions can drastically affect the results. The importance of intramolecular dynamics finds further manifestations in the intriguing phenomenon of quantum-mechanical exchange couplings (QECs), which has been a subject of considerable debate and intense study. The origin of this effect is now reasonably well understood, and the story is beautifully presented in Chapter 6 along with other intramolecular dynamic properties of hydride and dihydrogen complexes.

Another recently discovered phenomenon, namely dihydrogen bonding, is not considered in a separate subsection; rather the discussion is spread over Chapters 4, 6, 7, and 9. This is not convenient for the reader who is a newcomer in the field, but is partly justified because dihydrogen bonding is not a type of σ -bond coordination. Rather, it denotes the interaction of a hydride ligand with a proton donor, which can be considered as an initial step in the formation of a dihydrogen ligand. It has been shown that dihydrogen bonding is the first step in the interaction of a transition metal hydride with a proton, leading either to dihydride or coordinated dihydrogen complexes. Also dihydrogen bonding modulates QECs and is relevant to the intramolecular heterolytic cleavage of dihydrogen.

A separate short, but impressive, Chapter 10 is dedicated to the exciting field of bio-organometallic chemistry. Its appearance in a book about nonclassical compounds is at first sight surprising. However, for researchers working in inorganic and organometallic chemistry it will be instructive to compare how nature has designed sophisticated and extremely effective systems for the activation of dinitrogen, dihydrogen, and methane. There is growing evidence coming from the studies of model compounds that these activation steps proceed by H–H and C–H bond complexation to metal centers.

The rest of the book considers coordination of other E–H (e.g., E = B, C, Si, Ge, Sn) and related X–Y bonds. Although silane Si–H complexes are among the oldest known, and probably the second best studied class of σ complexes, the corresponding chapter is relatively short. The reason for this is apparently the availability of a recent comprehensive review by Corey and Braddock-Wilking. Chapter 12 outlines the important topic of the coordination and activation of C–H bonds. Although no species with C–H bond σ coordination to a metal unsupported by any other interaction have been isolated so far, strong spectroscopic and theoretical evidence for the intermediacy of such compounds in alkane oxidative addition reactions has been accumulated. C–H agostic complexes, the earliest examples of nonclassical bonding, are considered here as well, and are treated as having 3c–2e coordination of C–H bonds to metals supported by back-bonding, which is a universal view accepted in this book. Regrettably, the recent experimental and theoretical studies of Scherer and of McGrady et al. showing that at least some β -agostic alkyl complexes have predominantly β -C \cdots M interactions (and a lesser contribution from $M\cdots H$ –C interactions) are not discussed. Nor is there a mention of earlier theoretical work by Eisenstein proposing that α -C–H \cdots M agostic interactions are mainly the result of the electronic reorganization of the M–C σ bond. This is the only place in the book that can be a cause for criticism.

Following a short discussion of metal borohydride complexes, an important earlier class of 3c–2e species, the final

Chapter 13 proceeds with a consideration of the most recent findings, and in particular the coordination of B–H bonds unsupported by any other interaction or chelate-type effect. These are found in complexes of borane adducts, such as $H_3B^*PMe_3$ (isoelectronic with alkanes) and in borane σ complexes such as Hartwig's $[Cp_2Ti(\eta^2-HBR_2)L]$ ($L = HBR_2, PMe_3, HSiPh_3$). The latter species are of great importance because of their relevance to catalytic hydroboration reactions.

Although the overall coverage of the field is astonishingly huge, it is not exhaustive. Clearly, it is not the goal of the author to list all of the known nonclassical complexes; this has already been mostly achieved in a number of recent specialized reviews cited in the book. Instead, Kubas thoroughly discusses the ideas and basic principles of σ -bond coordination and activation, while the abundant literature references serve to support and illustrate the author's conclusions. Although the topics described are relatively specialized ones, and certainly demand some background knowledge, the presentation in the book is remarkably clear and vivid. The author has achieved an excellent balance between a detailed and accurate discussion and the ease of understanding by readers who are not necessarily specialists in the field. Undoubtedly, this book will be very helpful to undergraduate-level students studying advanced courses of organometallic and inorganic chemistry, as well as to PhD, postdoctoral, and other advanced researchers in the area.

Overall, this is a long-awaited monograph of impressive and monumental character. It is very well organized and is a real joy to read. Undoubtedly, this book should be on the shelves of any serious chemistry library, and must be recommended to researchers from both industry and academia working in the fields of inorganic and organometallic chemistry and catalysis.

Georgii Nikonov
Chemistry Department
Moscow State University
Moscow (Russia)