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Book review

Metal dihydrogen and σ-bond complexes. Structure, theory and reactivity

Edited by G.J. Kubas, Kluwer Academic/Plenum Publishers, New York, 2001, pp. xvi + 472. ISBN 0-306-46465-9; € 103.55, US$ 95.00, GB£ 65.55

Real discoveries of great significance, both experimental and conceptual, are rare in modern chemistry. This is what happened in the early 80s with the discovery of dihydrogen coordination by Greg Kubas. After the demonstration of lone-pair coordination to transition metals in the 20s, at the beginning of coordination chemistry and that of π-electrons such as those of ethylene or cyclopentadienyl ion in the 50s, at the beginning of modern organometallic chemistry, the demonstration of coordination of electrons otherwise participating in a σ-bond afforded the third and last category of donated electron pairs able to bring coordinate bond formation. Prior to Kubas' report in1984 of H_2 coordination in a tungsten complex, a few σ-complexes were known but unrecognized as such either by lack of adequate techniques of characterization in the case of dihydrogen complexes or, in the case of silane complexes by lack of a clear picture of the bonding mode (although the concept of 'arrested oxidative addition' developed by Kaesz was clearly correct).

Nevertheless, Kubas' discovery is in no way accidental. The history of the discovery is described in Chapter 2, the reading of which I recommend to all chemists and especially to young researchers. It resulted from a keen sense of observation, in particular of anomalous events. Then the description of the search for a technique which would definitely convince the scientific community of the novel finding is of particular interest. This approach has been extremely creative and resulted not only in the unambiguous characterization of dihydrogen coordination but also in giving chemists the tools to work on the subject and finally in demonstrating the various properties of dihydrogen: vibrational modes, tunnelling modes, access to the rotation barrier of coordinated dihydrogen and also the variability of the H–H distance from consideration of H–D coupling constants. This, together with the NMR T_1 method proposed by Crabtree, permitted the fast growth of the field, rapidly joined by most of 'hydride' chemists who could suddenly understand some peculiar properties of their complexes.

Probably, because of this multidisciplinary start, the field has interested many different communities. It is one of the great qualities of the book to address all aspects of the σ-bond coordination with, of course a special emphasis on dihydrogen coordination, chemistry, theory and physical properties. Chapter 1 is an introduction presenting the field and Chapter 2 describes the background and history of the discovery. Chapter 3 describes the different types of complexes known to date and the different types of syntheses which have been employed. It includes a very useful table giving the stable H_2 complexes classified by generic types.

Chapter 4 describes very clearly all aspects related to the bonding mode of dihydrogen, namely studies related to dihydrogen activation previous to isolation of the first dihydrogen complex, the detailed description of the bonding mode of dihydrogen, its characteristics and its high sensitivity to the electronic effects of the other ligands. This concerns in particular stretched dihydrogen ligands in which the H–H distance is anywhere between 1.6 Å (non-interacting hydrides) and 0.74 Å (free dihydrogen). This fascinating aspect results from the competition between σ-donation and π-back bonding when only two electrons are involved both in a σ-bond and in metal coordination. Different systems are described, with a special emphasis on polyhydride systems which display interesting properties such as *cis*-stabilization of dihydrogen by a hydride, hydride–dihydrogen exchange etc. A useful extension concerns the interaction of dihydrogen with naked metal ions and solid state systems.

The two following Chapters 5 and 6 are devoted to the structures and dynamics of the dihydrogen ligand. The separation between structure and dynamics appears unnecessary in the present case but nevertheless there is a good introduction to techniques not normally used by organometallic chemists, such as Inelastic Neutron Scattering and a summary of the techniques available for the study of dihydrogen complexes. Quantum Mechanical Exchange Couplings which do not necessitate a dihydrogen ground state but which are related to dihydrogen chemistry are also clearly described.

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Chapter 7 summarizes the thermodynamic and kinetic data available on these systems. This is an important basis to understand them and it could also have been included in Chapter 4. Chapter 8 describes vibrational studies of coordinated dihydrogen. Again, this is of importance as a data base and for understanding dihydrogen coordination but it could have been associated to Chapters 5 and 6.

Chapter 9 is of special interest since it describes the chemistry of coordinated dihydrogen and in particular the acidity of such complexes when the coordination mode is predominantly σ-donation. In some cases dihydrogen coordination results in the formation of a superacid and this has obvious consequences in, for example, the mechanism of catalytic hydrogenation reactions.

The chemistry of dihydrogen ligands is not limited to classical organometallic systems. Chapter 10 describes the possible involvement of σ-bond complexes in metallo-enzymes. This appears convincing, and future model studies of such bioinorganic systems will probably involve the coordination of dihydrogen.

Finally Chapters 11, 12 and 13 describe other σ-bond systems able to coordinate to a metal centre, C–H, Si–H as well as Ge–H and Sn–H, and B–H and other M–H. There is no doubt that this is important chemistry in terms of reactivity, and that it implies a modification of our views on many catalytic reactions. It also suggests new ideas for future investigations in organometallic chemistry.

In summary, this book is clear, easy and pleasant to read and gives an up-to-date and complete view of a new aspect of organometallic chemistry that has been developing rapidly in recent years. However, σ-bond coordination proves to be important outside the field of classical organometallic chemistry since it may be involved in catalytic transformations in heterogeneous or gas phase systems. This book is therefore of evident importance for organometallic chemists, and should be of great interest to a variety of researchers, professors and students dealing with chemistry. I recommend it for the evident link it emphasizes between the chemistry and the physical methods necessary to describe it. This last aspect concerns everybody interested in the history and dynamics of science.

Bruno Chaudret
Laboratoire de Chimie de Coordination du CNRS,
205, Route de Narbonne,
31077 Toulouse Cedex 04,
France
E-mail: chaudret@lcc-toulouse.fr