

Preface

Interactions of π -systems with metals[☆]

It is appropriate to introduce a symposium on the 'Interaction of π -systems with metals' by mentioning briefly a few of the important historical milestones.

The field has its origins in the, presumably accidental, synthesis of Zeise's salt, $\text{KPtCl}_3\text{C}_2\text{H}_4$, during 1827–1830. This compound was the subject of a violent controversy between the Danish chemist W.C. Zeise and Justus Liebig. Liebig had no faith in Zeise's analytical data—he even tried to give him a lesson in analytical chemistry—and suggested that the compound contained a molecule of ether and not of ethylene. Unfortunately, Zeise had died in 1847 before he was vindicated by P. Griess and C.A. Martius in 1861. The bonding situation, with a σ -bond and a π -bond, was formulated by J. Chatt and L.A.J. Duncanson in 1953 using a model suggested by M.J.S. Dewar in 1951 and the structure was established in 1954 by J.A. Wunderlich and D.P. Mellor through X-ray analysis.

A second milestone was the discovery of the catalytic hydrogenation of olefins by P. Sabatier and J.-B. Senderens in 1897 for which Sabatier was awarded the Nobel Prize in 1912. In 1939, Sabatier recalled that the original intention had been to prepare tetrakis-ethylene-nickel in analogy to the preparation of nickel tetracarbonyl by L. Mond et al. However, at 300 °C decomposition occurred liberating, among others, the hydrogenation product ethane. The systematic investigation of this failure led ultimately to the Nobel Prize. Seventy-five years, later we in Mülheim were able to prepare tris-ethylene-nickel by working at low (–30 °C to –78 °C) temperatures. Part of the further development was the discovery of the oxo-synthesis or hydroformylation, as it is now called, by Otto Roelen in 1938, in which both CO and an olefin interact with a metal whereby rhodium displaced cobalt as the metal of choice.

The catalytic synthesis of cyclooctatetraene, which was reported by Walter Reppe in 1948, is one of the most fascinating examples of a reaction involving the interaction of a π -system with a metal and Reppe's discussion of the mechanism is particularly illuminating: "In analogy to the modern representation of the constitution of nickel carbonyl one can assume that four acetylene molecules are bonded coordinatively to a nickel atom or ion" and further "we assume that a bond is formed by a biradical derived from the four acetylene molecules whereby the terminal radical electrons are accepted into the 3d-levels of the nickel". This and the accompanying formulation of the first metallacycle were published 3 years before Dewar's treatment of the bonding.

A further milestone was the discovery of the Ziegler-catalysts and -polymerization in 1953. This process had no economic success and which resulted in the award of the Nobel Prize to Karl Ziegler and Giulio Natta in 1963, is of course based on the interaction of π -systems with a metal even though no well-defined complex could be isolated. It is relevant to mention here a discussion which I had with Karl Ziegler in 1956 following the discovery of the cyclotrimerization of butadiene to cyclododecatriene. On the basis of his experience with the dilution principle in the synthesis of medium rings, Ziegler wanted to formulate the formation of the twelve-membered ring as the head-to-tail coupling of a chain. My suggestion that a π -complex might be involved led to the remark: "You and your modern ideas. If you could only show me a π -complex." The challenge was effective: the first π -complex isolated in our institute was pentamethylcyclopentadienyl-hexamethylbenzene-chromium from 2-butyne and a chromium catalyst active for the cyclotrimerization of butadiene and this was followed by complexes such as $(\text{CDT})\text{Ni}$, $(\text{COD})_2\text{Ni}$ and $(\pi\text{-allyl})_2\text{Ni}$. We chose the reaction with chromium as a model because in 1955 E.O. Fischer and W. Hafner had opened up a whole new area with the isolation of dibenzene-chromium and we hoped that the metal atom of the catalyst could

[☆] A symposium held on the occasion of the termination of the Sonderforschungsbereich 247 'Organisation and reorganisation of π -systems with metals', which was supported by Deutsche Forschungsgemeinschaft

be trapped by the cyclotrimer formed from butyne. What we did not anticipate, however, was that the dichotomy of a butyne molecule would also occur.

In 1959, we were able to convert the cyclotrimerization of butadiene into a cyclodimerization reaction by introducing auxiliary ligands such as phosphines and were able to show for the first time that the nature of the ligand has an influence upon the structure of the product. This influence, which can have both a steric and an electronic origin, enables the catalytic reaction to be directed towards a particular product.

The discovery of ferrocene in 1951 and the elucidation of the structure and bonding in 1952 introduced the metallocene-age which celebrates its 50th jubilee in this year and which culminated in the award of the Nobel Prize to G. Wilkinson and E.O. Fischer in 1973. Though ferrocene was long regarded as an undesired side product, the compound is now prepared on a large technical scale using an electrochemical procedure developed in our institute and it is used as an additive to control the combustion of diesel fuel.

E.O. Fischer is responsible for a further important discovery: in 1964, he reported the first metal–carbene complexes whereby examples containing chromium, e.g. $(OC)_5Cr=C(OLi)CH_3$, have attracted particular attention. Carbene complexes are also believed to be involved in the so-called metathesis reaction, which was discovered by R.L. Banks and G.C. Bailey in 1964. From both the scientific and technical standpoint, this highly unusual reaction, together with the Ziegler–Natta polymerization, has become one of the most important catalytic reactions involving π -complexes.

One of the most challenging objectives in catalysis is the development of enantioselective processes, i.e. asymmetric synthesis. An early indication of the potential was reported by S. Akabori in 1956 but the real breakthrough came in 1968 when L. Horner et al. and W.S. Knowles et al. reported the use of the so-called Horner-phosphines in homogeneous, catalytic hydrogenation. At the same time, we discovered the homogeneous, catalytic C–C-coupling reaction using phosphines having optically active substituents derived from readily available natural products and this led

eventually to an enantioselective synthesis of the pharmacologically important product ibuprofen through the hydrovinylation of a styrene derivative.

Soon after the discovery of the Ziegler-catalysts, attempts had been made to carry out an isotactic polymerization of propene in a homogeneous phase. The initial results were discouraging and it was not until 1984–1985 that J.A. Ewen as well as W. Kaminsky and H.H. Brintzinger et al. were successful. The key to their success lay in the use of chiral titanocene and zirconocene complexes and, although originally of academic interest only, this approach is becoming of increasing technical importance.

From this personal and selective review of the historical development, it is clear that many different areas of chemistry—inorganic, organic, physical, theoretical and even pharmaceutical and biochemistry—have been involved in the investigation of the interaction of metals with π -systems. This diversity emphasised the importance of creating a ‘Sonderforschungsbereich’ devoted to the ‘Organization and reorganization of π -systems with metals’, which has been supported by the Deutschen Forschungsgemeinschaft for the last 12 years. Although much had already been done, it was clear that much more could be accomplished by applying modern methodology and the scope and significance of the results obtained in this period are certainly the best justification for the extensive financial support.

W. Siebert
*Anorganisch-Chemisches Institut,
Universität Heidelberg,
Im Neuenheimer Feld 270,
69120 Heidelberg,
Germany*
E-mail: ci5@ix.urz.uni-heidelberg.de

G. Wilke
*Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1,
45470 Mülheim an der Ruhr,
Germany*

22 August 2001