COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

The Synthesis, Reactions and Structures of Organometallic Compounds

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Volume 3

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Preface

Although the discovery of the platinum complex that we now know to be the first π-alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethyl-platinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related π-complexes, the synthesis of a plethora of organometallic compounds containing metal–metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl–titanium chloride systems by Ziegler and Natta and of the Wacker palladium–copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the ele-

ments individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon–metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal–metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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Contents of Other Volumes

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Contents

19

Bonding of Unsaturated Organic Molecules to Transition Metals

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19.1 INTRODUCTION

The rapid development of organometallic chemistry following the discovery of ferrocene in the early 1950s resulted in the isolation of a wide variety of compounds with unusual and at times bewildering bonding modes between transition metals and organic molecules or fragments. The complexity of the structures revealed by an ever increasing number of crystal structure determinations led organometallic chemists to adopt a Baconian approach to the scientific development of the subject,[1] whereby they were content to classify the new compounds in an empirical fashion and relied on only the most rudimentary of bonding concepts, such as the 18-electron rule and Pauling's electroneutrality principle and synergic bonding model, as the basis of a conceptual framework.[2]

In 1956 Longuet-Higgins and Orgel[3] demonstrated the potential of the molecular orbital method as a predictive tool in organometallic chemistry by suggesting the existence of cyclobutadiene complexes two years before they were actually isolated by Criegee and Hubel.[4,5] At that time high speed computers were not generally available and this type of molecular orbital analysis depended heavily on symmetry arguments. Consequently, some erroneous conclusions were also arrived at by this method of analysis.[6] During the last ten years the general availability of high speed computers has led to a renaissance in theoretical organometallic chemistry, and molecular orbital calculations have been reported at various levels of sophistication. Interestingly, the approach which has had most impact on the experimental chemist during this period has not been the very sophisticated *ab initio* calculations, but the approximate semi-empirical molecular orbital calculations based on the extended Hückel method.[7] In particular, the fragment approach to the bonding in organometallic compounds developed so widely by Hoffmann and his coworkers[8] during the last five years has provided a conceptual framework for the experimental chemist which enables him to develop approximate bonding models without having to resort to extensive computing. This chapter illustrates the application of this methodology, which utilises perturbation theory and symmetry arguments extensively,[10] to a wide range of structural and reactivity problems in organometallic chemistry. However, it is recognised that this approach is an approximate one and therefore wherever possible results from more sophisticated computational techniques have been used to check the validity of the conclusions.

19.2. CARBONYL COMPOUNDS

19.2.1 Bonding in Metal Carbonyl Complexes

An understanding of the interactions between carbon monoxide and transition metals is essential to an understanding of the structures and properties of carbonyl complexes and their substituted derivatives. Molecular orbital analyses of the bonding in transition metal complexes have generally been based on two approaches. The approach which is most widely used and simplest to appreciate is based on elementary symmetry and perturbation theory ideas. The second approach which has resulted from the widespread availability of high speed computers is based on the rigorous and quantitative derivation of molecular orbital energies and related observable physical quantities. The high symmetries of carbonyl complexes such as $Cr(CO)_6$, $Ni(CO)_4$ and $Fe(CO)_5$ together with the wealth of photoelectron, vibrational and NMR data which has been accumulated for these complexes have made them an ideal testing ground for the development of sophisticated molecular orbital (and indeed also valence bond) calculations.[11-18] Unfortunately, unlike the situation which pertains to X-ray crystallographic structural analyses, there is no independently based reliability index to judge the reliability of a particular calculation. The tendency of authors to emphasise the merits of their particular mode of calculation makes it difficult for the less specialised reader to make an independent judgement of their validity.

In this section the basic features of the perturbation model of carbonyl bonding will be outlined, and then the more sophisticated calculations will be used to judge its overall reliability. In this context, it is instructive to examine in a little detail the molecular orbitals of the isolated carbon monoxide molecule. Figure 1 illustrates the molecular orbitals of CO.[19] The HOMO is 5σ and the LUMOs are the degenerate set $2\pi^*$. The greater electronegativity of oxygen compared to carbon results in a greater localization of the molecular orbitals 4σ and 1π on the oxygen atom and 5σ and $2\pi^*$ on the carbon atom. Also indicated in Figure 1 are the approximate energies of the metal d-orbitals of the first row transition elements. The precise energies of the metal d-orbitals in a particular complex will depend on the charge on the metal atom, but since the metal charge

is likely to lie between 0 and +1, a band can be plotted to indicate the possible d-orbital energy range.[20] A recognition of the relative energies of 4σ and 5σ and their electronic distribution clearly indicates that the metal–carbon σ-bonding interactions will be dominated by donation of electron density from 5σ to a suitable empty orbital on the metal as illustrated in (**1**). The situation is less clear cut for the CO π-levels since although the overlap between the $2\pi^*$ level and the relevant metal d-orbital, as indicated in (**2**), is superior to that between 1π and the metal d-orbital (see (**3**)), the latter is not negligible. In earlier accounts the contribution of (**3**) was largely ignored and the M—CO bonding was described in terms of (**1**) and (**2**) only.[21] The important elements of metal carbonyl π-bonding are better represented by the interaction diagram of Figure 2. This is a common three orbital interaction diagram and indeed if the interactions between 1π and $2\pi^*$ with $3d_\pi$ were identical then the resultant molecular orbitals would approximate to bonding, non-bonding and antibonding, and the non-bonding level would be noded at the central carbon atom as indicated in (**4**).[22] In point of fact the $3d_\pi$–$2\pi^*$ interaction predominates and the highest occupied level in a metal carbonyl complex is better represented by the mixing illustrated in (**5**). The predominance of the $3d_\pi$–$2\pi^*$ interaction also suggests that there will be a net transfer of electron density from the metal to the carbonyl ligand. Therefore, the synergic bonding model as first proposed by Pauling[23] for metal carbonyls whereby the carbonyl metal σ-donation is supplemented by back donation to the $2\pi^*$ (CO) level is essentially corroborated. However, in molecular orbital terms it is also necessary to introduce the suppplementary mixing between 1π and $2\pi^*$ to complete the picture. The essential validity of the three-centre bonding model described above is illustrated by electron contour plots derived from SCF-X$_\alpha$-MSW calculations on Cr(CO)$_6$ by Johnson and Klemperer[19] and illustrated in Figure 3. The $1t_{2g}$ level is primarily CO
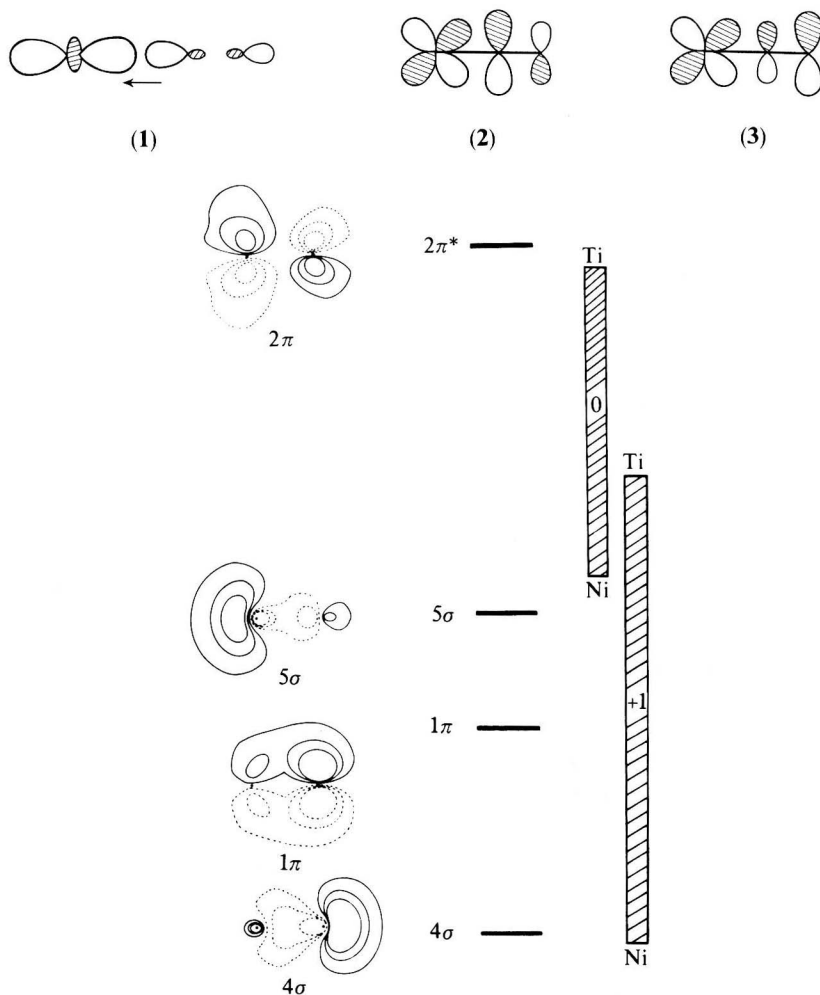

(**1**)   (**2**)   (**3**)

Figure 1 Electron density plots of the frontier molecular orbitals of carbon monoxide, adapted from J. B. Johnson and W. G. Klemperer, *J. Am. Chem. Soc.*, 1977, **99**, 7132. Also shown in the figure are the energies of these molecular orbitals relative to those of the first row transition elements in their zero and singly charged states
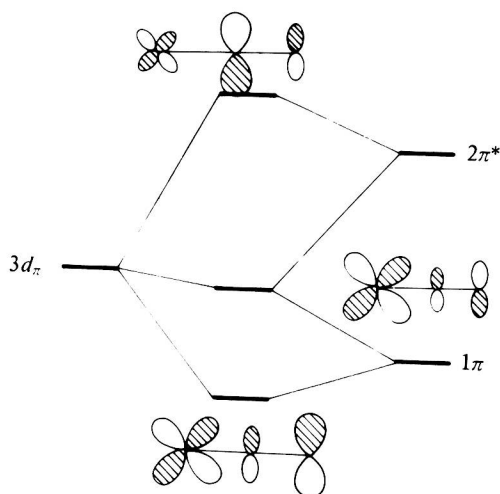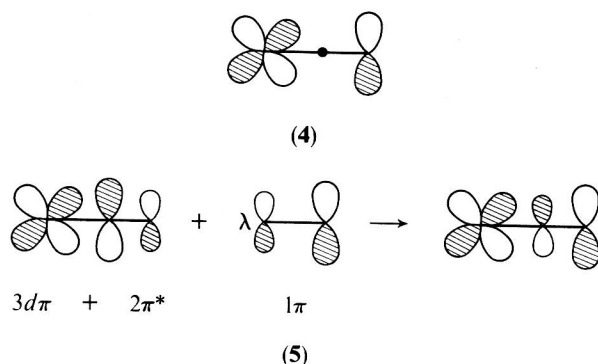
(4)

$$3d\pi \quad + \quad 2\pi^* \qquad\qquad 1\pi$$

(5)

Figure 2 A schematic illustration of the three-centre orbital interaction which occurs as a result of the overlap of the carbon monoxide 1π and $2\pi^*$ molecular orbitals with the d-orbital of a transition metal with π-pseudosymmetry, $3d_\pi$

1π in character, with a small bonding contribution from $3d_\pi$. The $2t_{2g}$ level is primarily a $3d_\pi$-orbital perturbed by a bonding interaction with $2\pi^*$ (CO) and an antibonding interaction with 1π (CO); and $3t_{2g}$ is primarily $2\pi^*$ (CO) in character with an antibonding interaction with $3d_\pi$.

In thiocarbonyl and thionitrosyl complexes the lower electronegativity of sulphur compared to oxygen and the smaller $1\pi-2\pi^*$ energy separation results in an equalization of the $3d_\pi-2\pi^*$ and $3d_\pi-1\pi$ interactions and consequently a closer similarity to the bonding, non-bonding, antibonding situation described above and illustrated in (**4**). Lichtenberger and coworkers have compared CO, CS and NO and NS as ligands using Fenske–Hall molecular orbital calculations and the reader is referred to refs. 24–27 for a full discussion of the implications of this three-centre model to the interpretation of UV photoelectron, IR and electron impact studies on complexes of these ligands.

There has been some controversy in the literature recently concerning the relative importance of the σ-donation and π-back donation components of the synergic bonding model. Part of this controversy originates from an absence of unambiguous techniques for allocating in a precise fashion the charge associated with metal and carbonyl within the complex and the precise degree of build-up of electron density in the internuclear regions.[19,28–30] Johnson and Klemperer[19] have estimated on the basis of X_α–SCF–MSW calculations that in $Cr(CO)_6$ the σ-donation represents approximately 80% of the bonding contribution compared with 20% for π-back donation. These
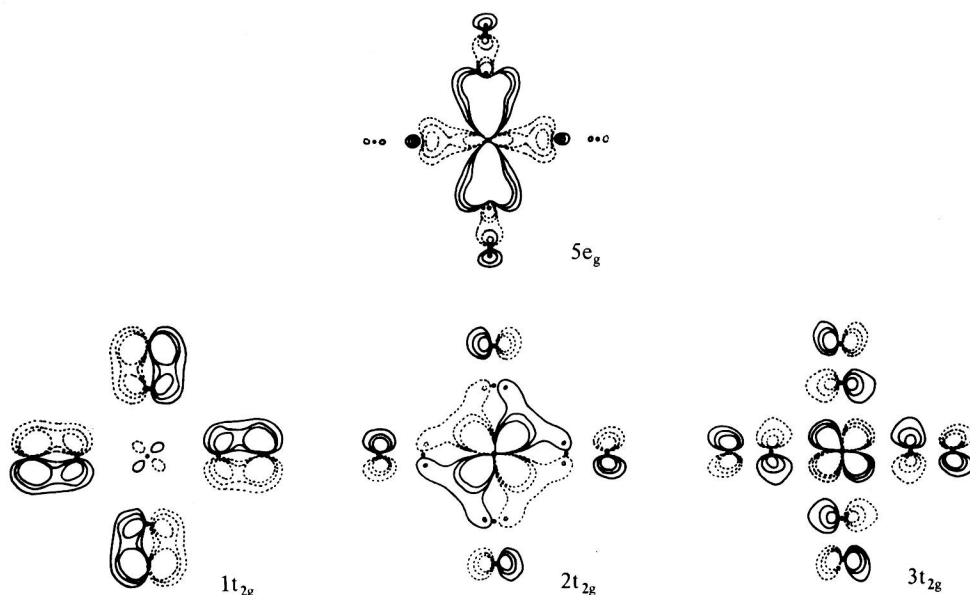
Figure 3 Electron density contour plots of the $5e_g$, $1t_{2g}$, $2t_{2g}$ and $3t_{2g}$ molecular orbitals in $Cr(CO)_6$ derived from SCF-X_α-MSW molecular orbital calculations (reproduced with permission from J. B. Johnson and W. G. Klemperer, *J. Am. Chem. Soc.*, 1977, **99**, 7132). The $1t_{2g}$, $2t_{2g}$ and $3t_{2g}$ molecular orbitals can be related to the three molecular orbitals illustrated schematically in Figure 2. The $5e_g$ molecular orbital corresponds to the lowest unoccupied set of molecular orbitals in $Cr(CO)_6$

estimates were based on charge density comparisons in $(CO)_6$ and $Cr(CO)_6$ and must be treated with some caution in view of changes in atomic sphere sizes in the independent calculations on the $(CO)_6$ and $Cr(CO)_6$ entities. Although the strength of bonding represented by these components differs by a large amount, Johnson and Klemperer[19] have suggested that the weaker π-interaction is able to charge compensate for the strong σ-interaction since Cr d_π to CO $2\pi^*$ bonding leads to far more charge transfer than CO 5σ to Cr d_σ bonding of an equivalent magnitude. Sherwood and Hall's[29] Fenske–Hall parameter free molecular orbital calculation on $Cr(CO)_6$ suggests that the bonding contributions are more equally balanced — 55% for σ-donation and 45% for π-back donation. They suggest that their results are in general agreement with the low temperature X-ray and neutron diffraction study of Rees and Mitschler.[31] Electron population analyses showed 1.52 electrons in the 5σ-orbitals and 0.51 in the $2\pi^*$-orbitals of each carbonyl while the experimental values are 1.65 and 0.38, respectively. The gross atomic charge on Cr was 0.306 compared to the experimental value of 0.15 ± 0.12.[31]

Bursten, Freier and Fenske's[30] results using the projected X_α (PX_α) technique also indicate that the estimates of Johnson and Klemperer undervalue the importance of the back donation component. The PX_α technique has permitted the authors to avoid the ambiguities inherent in the interpretation of X_α–SW charge distributions by not relying on the contour plot technique utilized by Johnson and Klemperer.[19] Their calculations suggest that 1.42 electrons are donated and 1.25 electrons back donated in $Cr(CO)_6$. Therefore, in summary there appears to be a consensus of opinion that metal–carbonyl bonding leads to electroneutrality as originally proposed by Pauling[23] although the relative strengths of σ-bonding and π-bonding components remain a matter of some debate. A delineation of these relative contributions is of course experimentally very demanding if not impossible.

19.2.2 UV Photoelectron Spectral Studies of Metal Carbonyls

The UV photoelectron[32,33] spectra of metal carbonyls and related species have been extensively investigated during the last few years. There is general agreement concerning the important spectral features and especially those associated with ionizations from molecular orbitals localized predominantly on the metal. However, there has been a considerable debate concerning the assignment of the lower lying carbonyl based orbitals. These compounds have proved to be an important testing ground for the more sophisticated theoretical calculations[11-17] and for evaluating