

ORGANOMETALLIC PHOTOCHEMISTRY

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Organometallic Photochemistry

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Preface

Investigations into the photochemical properties of coordination compounds have been seriously under way for nearly two decades now, and a fairly high level of understanding of their photophysics and excited-state reactivity has begun to emerge. In direct contrast, the photochemical properties of organometallic complexes, with the exception of the metal carbonyls, are very poorly understood. A number of compounds have been studied, but—as will be obvious from the latter chapters in this book—these studies have not constituted a systematic investigation but rather a relatively random sampling. This situation is likely to change rapidly in the near future, what with the growing interest in organometallics in general and with the realization by photochemists that this is a fertile area to study. It is the primary purpose of this book to provide a firm basis upon which these studies can build. This book only deals with *transition-metal* organometallic complexes.

Chapter 1 presents background material on organometallic excited states and excited-state processes and is designed principally to acquaint students or new workers entering the field with these topics. Chapters 2–8 are detailed reviews of those photochemical studies which have been conducted up to the time of the writing. As such, they should provide a useful guide to what has been done and should point out those areas in need of investigation. We have tried to be as comprehensive as possible in our coverage. However, many photochemical studies of organometallics are buried in papers whose principal focus is not on photochemistry, and it is often difficult to find reference to those investigations. It is thus likely that some previous work has been missed, and a person interested in studying a particular compound should conduct a careful literature search on that species before beginning his research. The review chapters are organized according to type of organometallic. Chapter 2 presents a detailed discussion of metal carbonyls, and Chapters 3–8 discuss, in turn, olefin complexes, arene complexes, cyclopentadienyl complexes, isocyanide complexes, hydride complexes, and alkyl complexes. The organization within each chapter is according to the central metal atom and its group in the periodic table.

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Electronic Structure of Organometallic Complexes

I. INTRODUCTION

Transition-metal organometallic chemistry has become an extremely important area of chemistry in recent years, principally due to the usefulness of members of this class of compounds for catalyzing or assisting the transformation of organic substrates. The thermal reactions of a large number of transition-metal organometallics have been examined in detail, and guiding principles have begun to emerge concerning thermal reactivity. Although the last decade has seen a maturation of the field of inorganic photochemistry as restricted to classical coordination compounds in aqueous solution [1,2], relatively few photochemical studies have been conducted on true organometallic complexes, excluding the metal carbonyls [3]. It is likely that organometallic photochemistry will prove to be an area of intensive investigation in the coming years, especially since recent results have shown that irradiation of organometallics can lead to catalytically and synthetically useful transformations. It is the purpose of this book to provide a firm basis from which investigators can conduct these studies.

The bulk of the chemistry of transition-element organometallic complexes has concerned the d-block elements. There is increasing interest in the organometallic chemistry of the f-block elements, but little has been done concerning the photochemistry of such systems. Accordingly, we shall restrict our discussion of the electronic structure and photochemistry to the d-block elements, with the exception of a few isolated cases.

In order to discuss the photochemical properties of specific organometallic compounds in detail, it is necessary to develop an appreciation of the bonding and electronic structure of organometallics and a knowledge of the principles of photochemistry. These topics are discussed in this first chapter. The succeeding chapters critically survey the photochemical properties of those organometallic complexes examined to date. These chapters are organized according to the classes of ligands in the order of carbonyl, olefin, arene, cyclopentadienyl, isocyanide, hydride, and alkyl complexes. Each chapter is then subdivided according to the central metal in the complex with the metals presented in order of their left-to-right position in the periodic table.

This first chapter discusses the bonding of representative members of each of these ligand classes with initial emphasis on the descriptive nature of the orbitals involved in the interaction. The 18-valence-electron rule, of special importance for appreciating the stability and reactivity of organometallics, is described and is followed by a detailed discussion of the electronic absorption spectra and excited states of representative organometallic complexes.

An organometallic compound, as defined throughout this book, is any transition-metal complex which contains at least one direct metal-carbon bond, excluding cyanide and carbonate ligands. In addition, we have chosen to discuss the photochemistry of hydride complexes because of their close relationship to organometallics and because of the critical importance of these compounds in assisting organic transformations. An attempt has been made throughout to follow closely the IUPAC nomenclature rules [4] for coordination complexes.

II. STRUCTURE AND BONDING IN ORGANOMETALLICS

A. CARBON MONOXIDE AND ORGANIC ISOCYANIDE LIGANDS

In order to discuss the bonding between a metal and a ligand, it is necessary to consider the metal and ligand orbitals involved and to classify those orbitals according to their symmetry. It is most convenient to illustrate the symmetry properties by referring to the sign of each of the orbital lobes. Orbital interaction then can only occur in those cases which generate a net positive overlap of lobes with the same sign. In bonding to ligands, the metal employs its nd , $(n+1)s$, and $(n+1)p$ orbitals, and the ligand orbitals can be of various types. In considering the metal-ligand interactions we will focus

mainly on the metal d orbitals to illustrate bonding modes. Carbon monoxide and organic isocyanides are quite similar in their bonding properties, and it is appropriate to discuss these ligands together.

Carbon monoxide has a filled σ orbital and two filled π orbitals localized mainly between carbon and oxygen. It also possesses two lone pairs of electrons, localized on the carbon and oxygen atoms but directed away from the molecule. Because of the electronegativity difference between carbon and oxygen, the spatial extent of the carbon lone pair is greater than that of the oxygen lone pair. Carbon monoxide also possesses two mutually perpendicular π -antibonding (π^*) orbitals directed away from the CO internuclear region, and these two orbitals are empty in the ground state. Since oxygen is more electronegative than carbon, the filled orbitals are localized to a greater extent on oxygen than on carbon, and the empty π^* orbitals are more localized on carbon. When CO is bonded to a single transition metal, the M—C—O linkage is invariably linear. If the z direction is chosen along the M—C—O bond, then the d_{z^2} , d_{xz} , and d_{yz} orbitals have the proper symmetry to interact with the carbon lone pair, the π_x^* , and π_y^* orbitals, respectively. This interaction is shown in Fig. 1-1 with positive orbital lobes drawn cross-hatched.

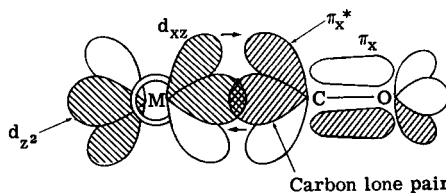


FIG. 1-1. Bonding interactions of CO with transition metals.

The net effect of the bonding is that carbon monoxide donates some electron density to the metal in a σ fashion from its carbon lone pair and accepts electron density from the metal in a π fashion into its π^* orbitals. Carbon monoxide is hence classified as a σ -donor, π -acceptor ligand. It is the σ bonding which contributes principally to the total bond energy, but the π bonding has important ramifications. Both interactions weaken the carbon-oxygen bond, although the π interaction has the greater effect because it directly populates a C—O antibonding orbital. It is this ability of carbon monoxide to accept electron density from the metal which allows it to stabilize metals in low oxidation states.

Isocyanide ligands of the general formula CNR normally bind to metals in a linear fashion through carbon. The bonding picture is very similar to that of carbon monoxide except that the $\equiv\text{O}$ portion is replaced by $\equiv\text{N}-\text{R}$.

Nitrogen is less electronegative than oxygen, and thus isocyanides are in general weaker π acceptors but stronger σ donors than carbon monoxide. The R group of CNR can be varied through a very wide range of organic functional groups, and thus the electronic properties of the ligand can be selectively tuned. Good electron-withdrawing groups such as $p\text{-NO}_2\text{C}_6\text{H}_4$ make CNR a better π acceptor, whereas good electron-releasing groups such as $t\text{-butyl}$ increase its σ -donor ability. Further, the $\pi^*\text{-CN}$ orbitals can conjugate with the π and π^* orbitals of arene substituents; and, as discussed in more detail in Chapter 6, this conjugation has the effect of lowering the energy of one of the $\pi^*\text{-CN}$ orbitals, thus dramatically altering its π -accepting properties.

B. OLEFIN LIGANDS

The bonding of olefins is most conveniently described using what has come to be called the “Dewar–Chatt” bonding model. The bonding picture is quite analogous to CO and CNR except that different ligand orbitals are employed. Olefins normally bond to metals in an edge-on fashion with the carbon–carbon bond perpendicular to the metal–olefin bond. The simplest olefin, ethylene, possesses filled σ - and π -bonding orbitals which are localized principally between the carbons and also corresponding π^* -antibonding orbitals localized mainly on each carbon atom and directed away from the C—C bond (Fig. 1-2). If the z axis lies along the metal–olefin bond, then the filled π orbital has the proper symmetry to give net overlap with the metal d_{xz} orbital; alkenes can donate electron density to the metal in a σ fashion. Likewise, the empty π^* orbital can interact with d_{xz} to accept electron density from the metal, and olefins are considered σ -donor, π -acceptor ligands. In general, the π -accepting ability is much less than that of CO or CNR, primarily because of the relatively low electronegativity of the carbons. The electronic properties can be greatly varied, however, by altering the olefin substituents. Electron-withdrawing groups like CF_3 increase the π bonding

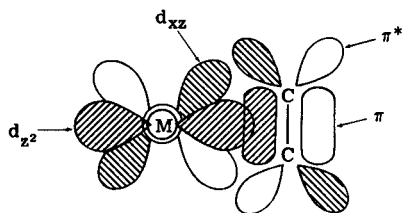
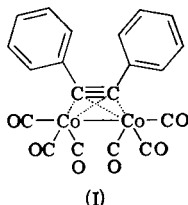


FIG. 1-2. Bonding interactions of olefins with transition metals.

but decrease the σ bonding, whereas alkyl substituents have the opposite effect. The overall strength of the metal-olefin bond appears to increase as the substituents become more electron-withdrawing.

Alkynes bond similarly to transition metals through an exactly analogous orbital interaction. One significant difference, however, arises from the availability of a second π, π^* orbital set perpendicular to the first which allows alkynes to bond to two metals in a bridging fashion, as illustrated in (I) for $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})]$.



C. ARENE LIGANDS

Numerous arene complexes have been prepared and characterized [5], and the normal mode of bonding is one in which the planar arene ring lies above the metal and perpendicular to the metal-arene bond. A variety of arenes have been employed in the preparation of complexes ranging from substituted benzenes to naphthalene, anthracene, and benzonorbornene. The bonding in metal arene complexes is best presented by discussing the most representative ligand benzene. The π -molecular orbitals which can be derived for benzene using the Hückel approximation are shown diagrammatically in Fig. 1-3 along with an energy level diagram.

If the z direction is from the metal to the center of the arene ligand, the filled benzene a_{2u} orbital has the proper symmetry to interact with d_{z^2} . However, the spatial distribution of d_{z^2} and of a_{2u} are not aligned to give a large overlap since d_{z^2} essentially points at the hole in the center of the a_{2u} orbital. The principal donation of electrons to the metal occurs via π interaction between d_{xz} and d_{yz} and the filled e_{1ga} and e_{1gb} orbitals for which the orbital overlap is large. The e_{2u} orbital set does not have the proper symmetry to give strong overlap with any of the metal orbitals although a weak interaction with d_{xy} and $d_{x^2-y^2}$ is possible. Thus, benzene and other arenes are good electron donors but poor electron acceptors. The electronic properties, however, can be altered to a significant extent by varying the nature of the arene substituents.

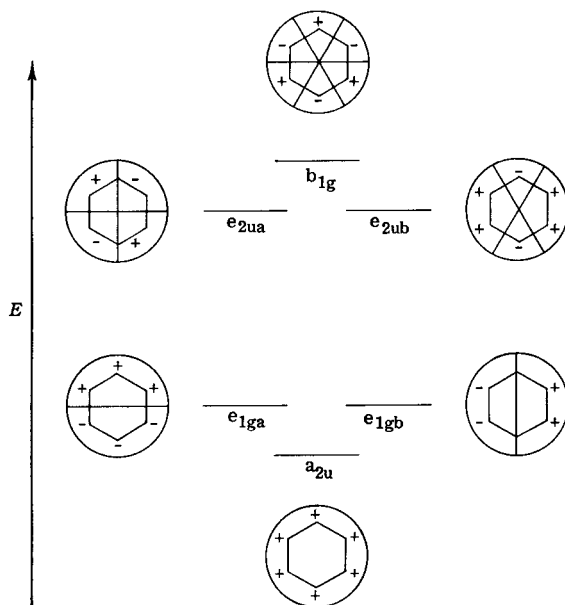


FIG. 1-3. Benzene π -molecular orbitals. The plus and minus signs designate the signs of the molecular orbitals above the plane of the paper. The portion of the orbitals below the plane of the paper has the opposite sign.

D. CYCLOPENTADIENYL LIGANDS

The cyclopentadienyl ligand plays a key role in the history of organometallic chemistry since it was employed in the synthesis of many of the first characterized organometallics, including ferrocene and $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}]$. Although the majority of compounds have been prepared using the C_5H_5 ligand, a number have employed substituted derivatives such as $\text{C}_5(\text{CH}_3)_5$. The C_5H_5 ligand is termed *cyclopentadienyl* because it is the name given the C_5H_5 radical in the accepted organic nomenclature. The ligand is derived formally by hydrogen atom abstraction from cyclopentadiene C_5H_6 , although most synthetic applications employ the cyclopentadienide ion $[\text{C}_5\text{H}_5]^-$. The C_5H_5 ligand normally binds to metals in a planar fashion with the plane of the ring perpendicular to the metal–ligand bond and with all five carbon atoms roughly equidistant from the metal. The Greek letter η has been employed to designate ligands bound in this fashion, and the term $\eta\text{-C}_5\text{H}_5$ is used [4]. It is more informative, however, to give a superscript to η to indicate the exact number of carbon atoms equidistant from the metal, and $\eta^5\text{-C}_5\text{H}_5$ is used throughout this book.

The π -molecular orbitals for the C_5H_5 ligand are shown in Fig. 1-4. If the z axis is the metal-ligand axis, the filled a_2'' , e_{1a}'' , and e_{1b}'' orbitals can donate electron density to the metal by interacting with d_{z^2} , d_{xz} , and d_{yz} , respectively. The empty e_2'' orbitals do not have the proper symmetry and spatial distribution to interact appreciably with any of the metal d orbitals, except for a weak interaction with d_{xy} and $d_{x^2-y^2}$. The only π -accepting ability comes through interaction of the half-filled e_1'' orbital with d_{xz} or d_{yz} . In most complexes the ligand is considered to bear a formal negative charge in which a complete electron has been transferred to the e_1'' orbital.

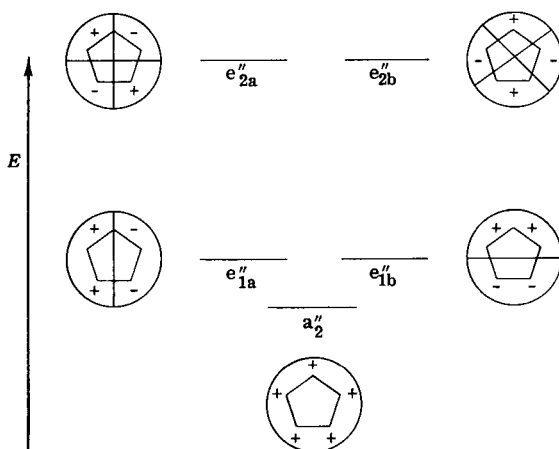


FIG. 1-4. C_5H_5 π -Molecular orbitals.

E. ALKYL, ARYL, AND HYDRIDE LIGANDS

These three ligands are now commonplace in organometallic chemistry, and their bonding properties are well understood. The hydride ligand, formally written as H^- , has a filled s orbital from which electrons are donated in a σ fashion to empty metal orbitals. It, of course, cannot accept electron density from the metal and is simply a σ -donor ligand. It is, however, believed to be the strongest of all σ donors, in part because its small size allows close penetration to the metal (1.55–1.70 Å) and hence gives large orbital overlap. The strong σ donor ability is manifest in the reactivity of hydride complexes since the hydride ligand shows a great tendency to labilize the ligand which is trans to it.

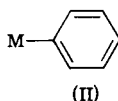
Alkyl ligands are formally considered to be negatively charged, although it is unlikely that a full charge is associated with the ligands in their complexes.

Even so, the bonding is best considered by representation of the ligands as anions such as CH_3^- . The carbon atom is sp^3 -hybridized with a lone pair of electrons in the orbital not bound to a hydrogen. This orbital can interact in a σ fashion with a metal d orbital as illustrated in Fig. 1-5, and alkyl ligands are strong σ -donor ligands but with no π -accepting ability. It must be emphasized, however, that the metal-carbon bond is normally quite covalent in metal complexes, and it is often extremely difficult to deduce the distribution of electron density.



FIG. 1-5. Bonding of alkyl ligands with transition metals.

Aryl ligands bond through a single carbon of the arene, as illustrated in (II),



and the bonding is similar to that of metal alkyls except that the arene π orbitals can also interact with metal d orbitals of the proper symmetry.

III. THE 18-VALENCE-ELECTRON RULE

Unlike coordination compounds, organometallic complexes show a high tendency to achieve the inert-gas electron configuration around the central metal, much as organic compounds strive to obtain an inert-gas configuration around carbon. For transition metals, however, the number of electrons needed to reach the configuration is 18, deriving from two s, six p, and ten d electrons. The stability and reactivity of organometallics can often be rationalized in terms of the number of valence electrons, and hence electron counting has been extremely useful for *predicting* structures and reactivity. Organometallics tend to react in such a way so as to obtain the favored 18-electron configuration, including the formation of single or multiple metal-metal bonds when necessary. In general, complexes with 18 valence electrons are usually quite stable whereas 16- and especially 14-valence-electron complexes are quite reactive. A number of 16-electron complexes of the Group VIIIb metals, however, are exceptions and can be isolated, e.g., *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.

There are several methods which can be used to count valence electrons. Of course, it makes no difference how one counts as long as the correct number of electrons is reached. Since it is often difficult to assign a definite oxidation state to the central metal, we prefer to use the counting scheme which always considers the metal neutral *for the purposes of counting*. The rules which can be written for counting by this method are given as follows:

Rule 1: Consider the metal to have an oxidation state of zero and count the number of electrons it contributes.

Rule 2: Each ligand shown in Table 1-1 contributes the number of electrons shown.

TABLE 1-1
Electron-Counting Rules for Selected Ligands

Ligand	Number of valence electrons to be added to the count
H, Cl, Br, I, CN, alkyl, aryl, η^1 -allyl	1
CO, PR_3 , $\text{P}(\text{OR})_3$, AsR_3 , olefins, nonbridging alkynes	2
η^3 -Allyl, NO	3
Bridging alkynes, η^4 -dienes	4
η^5 - C_5H_5	5
η^6 - C_6H_6 , other η^6 -arenes	6

Rule 3: Add one electron to the count of each metal for each metal-metal bond that is formed.

Rule 4: For anionic complexes, add to the electron count the number of negative charges the *complex* has; for cationic complexes, subtract from the electron count the number of positive charges the *complex* has.

Rule 5: Bridging hydrides contribute $\frac{1}{2}$ electron to the count of each metal; doubly bridging carbonyls contribute 1 electron to the count of each metal.

It must be emphasized that these are only rules to aid in counting valence electrons; they imply nothing about the actual electron density distribution in the complex. For illustration, several examples are worked as follows:

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$	$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$	$[\text{Mn}_2(\text{CO})_{10}]$
Fe = 8	Ir = 9	Mn = 7
$2 \times (\eta^5\text{-C}_5\text{H}_5) = 10$	Cl = 1	$5 \times (\text{CO}) = 10$
Total = 18	CO = 2	Mn - Mn = 1
	$2 \times (\text{PPh}_3) = 4$	Total = 18 for each Mn
	Total = 16	

IV. EXCITED STATES OF ORGANOMETALLIC COMPLEXES

Organometallic complexes have a variety of low-lying excited states. By low-lying states we mean those which can be populated by optical irradiation in the near-infrared, visible, and ultraviolet region. This region corresponds to wavelengths approximately in the range 200–1100 nm. It has been very useful to identify the low-lying excited states according to the one-electron excitation involved. Table 1-2 lists the types of one-electron excitations which have been identified in organometallics. A discussion of key examples in each category follows in the subsequent sections. It is important to recognize that characterization of excited states according to one-electron considerations can be, and often is, a gross oversimplification because of the complete neglect of electron repulsion effects. However, such considerations lead to relatively straightforward chemical expectations.

TABLE 1-2
Types of One-Electron Excited States in Organometallic Complexes

Excited state	Common abbreviation	Example
Ligand field (metal-centered)	"d-d," LF	[W(CO) ₅ (piperidine)]
Intraligand (ligand-centered)	IL	<i>fac</i> -[ReCl(CO) ₃ (3-styrylpyridine) ₂]
Ligand-to-metal charge transfer	LMCT	[Fe(η^5 -C ₅ H ₅) ₂] ⁺
Metal-to-ligand charge transfer	MLCT	[W(CO) ₅ (4-formylpyridine)]
Metal-to-solvent charge transfer	MSCT	[Fe ₄ (CO) ₄ (η^5 -C ₅ H ₅) ₄] · CCl ₄
Metal-metal (metal-centered over ≥ 2 metals)	$\sigma_b \rightarrow \sigma^*$ $d\pi \rightarrow \sigma^*$	[Co ₂ (CO) ₆ (PPh ₃) ₂]

A. INTRALIGAND EXCITED STATES

Ligands which can be coordinated to metals have their own set of excited states. For organic ligands the study of such excited states comprises the field of organic photochemistry. *A priori*, coordination of an organic ligand to a metal will result in perturbation of its electronic structure. If the free ligand has one-electron transitions which terminate or originate in an orbital centered on the ligating atom, the perturbation can be so great that it is inappropriate to refer to the transition in the complex as an intraligand (IL) transition. On the other hand, coordination of certain ligands involves relatively small perturbation of the electronic structure, and we can expect