7

TUTORIAL CHEMISTRY TEXTS

RSC
ROYAL SOCIETY OF CHEMISTRY

Organotransition Metal Chemistry

by A. F. HILL

TUTORIAL CHEMISTRY TEXTS

7

Organotransition Metal Chemistry

ANTHONY F. HILL

Australian National University, Canberra

RS•C

ROYAL SOCIETY OF CHEMISTRY

Cover images © Murray Robertson/visual elements 1998–99, taken from the
109 Visual Elements Periodic Table, available at www.chemsoc.org/viselements

ISBN 0-85404-622-4

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry, Thomas Graham House, Science Park,
Milton Road, Cambridge CB4 0WF, UK
Registered Charity No. 207890
For further information see our web site at www.rsc.org

Typeset in Great Britain by Wyvern 21, Bristol
Printed and bound by Polestar Wheatons Ltd, Exeter

Preface

Take the crowning achievements of the various sub-disciplines of chemistry, combine them and you have organotransition metal chemistry. First, the organic chemist's shrewd manipulation of functional groups, allowing strategic multi-step synthesis. Add to this the main-group chemist's understanding of reactivity within a framework of periodicity. Apply this to the colourful playground of the transition elements with their enormous variations in oxidation states, ligands, coordination numbers and associated stereochemistries. The scope for intellectual pursuit is staggering, but organometallic chemistry is not simply an academic exercise. It underpins industrial chemical processes on a megatonne scale, providing commodity chemicals from the simplest petrochemicals to the most exotic pharmaceuticals.

This text covers the material I consider appropriate for a core introductory course in organotransition metal chemistry. For all students, such a course will be their first encounter; for some it will be their last, depending on their degree specialization in later years. The material covered here should be seen as the basic tools which any graduate might be expected to call upon. It cannot do justice to the enormous breadth of the subject and the exciting tangential fields (*e.g.*, polymers, metals in catalytic and stoichiometric organic synthesis, industrial chemistry). Tutorial examples, problems and answers are available on the RSC's Tutorial Chemistry Texts website at http://www.chemsoc.org/pdf/tct/organoexamples.pdf, http://www.chemsoc.org/pdf/tct/organoproblems.pdf and http://www.chemsoc.org/pdf/tct/organoanswers.pdf.

I would like to acknowledge the support during the preparation of this text of my partner Mark, to whom it is dedicated.

Anthony F. Hill
Canberra, Australia

TUTORIAL CHEMISTRY TEXTS

This series of books consists of short, single-topic or modular texts, concentrating on the fundamental areas of chemistry taught in undergraduate science courses. Each book provides a concise account of the basic principles underlying a given subject, embodying an independent-learning philosophy and including worked examples. The one topic, one book approach ensures that the series is adaptable to chemistry courses across a variety of institutions.

TITLES IN THE SERIES

Stereochemistry *D G Morris*
Reactions and Characterization of Solids *S E Dann*
Main Group Chemistry *W Henderson*
d- and f-Block Chemistry *C J Jones*
Structure and Bonding *J Barrett*
Functional Group Chemistry *J R Hanson*
Organotransition Metal Chemistry *A F Hill*
Heterocyclic Chemistry *M Sainsbury*
Atomic Structure and Periodicity *J Barrett*
Thermodynamics and Statistical Mechanics *J D Gale and J M Seddon*
Quantum Mechanics for Chemists *D O Hayward*
Mechanisms in Organic Reactions *R A Jackson*

FORTHCOMING TITLES

Molecular Interactions
Reaction Kinetics
Basic Spectroscopy
X-ray Crystallography
Lanthanide and Actinide Elements
Maths for Chemists
Bioinorganic Chemistry
Chemistry of Solid Surfaces
Biology for Chemists
Multi-element NMR

Further information about this series is available at www.chemsoc.org/tct

Orders and enquiries should be sent to:
Sales and Customer Care, Royal Society of Chemistry, Thomas Graham House,
Science Park, Milton Road, Cambridge CB4 0WF, UK

Tel: +44 1223 432360; Fax: +44 1223 426017; Email: sales@rsc.org

Contents

1 Introduction, Scope and Bonding 1

1.1 What is Organometallic Chemistry? 1
1.2 Bonding in Organotransition Metal Compounds 3
1.3 The Bonding of Unsaturated Organic Ligands to a Metal Centre 9
1.4 Thermodynamics of the Metal–Carbon Bond 17
1.5 Accessing the Organometallic Literature 20

2 Co-ligands in Organotransition Metal Chemistry 22

2.1 'Innocent' Co-ligands 22
2.2 Hydride Complexes 30

3 Carbon Monoxide 42

3.1 Introduction 42
3.2 Coordination Modes for Carbon Monoxide 43
3.3 Characterization of Metal Carbonyls 44
3.4 Important Classes of Metal Carbonyls 46
3.5 Synthesis of Metal Carbonyls 53
3.6 Reactions of Metal Carbonyls 58
3.7 Ligands Related to Carbon Monoxide 67

4 σ-Organyls 69

4.1 Introduction 69
4.2 Selected Classes of σ-Organyls 70
4.3 Reactions of σ-Organyls 79

5 **Metal–Carbon Multiple Bonding** **89**

5.1 Introduction 89
5.2 Carbenes (Alkylidenes) 90
5.3 Carbynes (Alkylidynes) 109
5.4 Vinylidenes (Alkenylidenes) 118
5.5 Cumulenylidenes 120

6 **π-Coordination of C–C Multiple Bonds** **122**

6.1 Introduction 122
6.2 Alkenes 123
6.3 Di- and Polyenes 139
6.4 Allenes 143
6.5 Alkynes 144

7 **η^n-C_nR_n Carbocyclic Polyene Ligands ($n = 3$–8)** **149**

7.1 Introduction 149
7.2 Allyls, η^3-C_3R_5 152
7.3 Pentadienyls, η^5-C_5R_7 156
7.4 Cyclopropenyls, η^3-C_3R_3 (Metallatetrahedranes) 158
7.5 Cyclobutadienes, η^4-C_4R_4 160
7.6 Cyclopentadienyls, η^5-C_5R_5 161
7.7 Arenes, η^6-C_6R_6 169
7.8 Cycloheptatrienyls, η^7-C_7R_7 176
7.9 Cyclooctatetraenes, η^8-C_8R_8 178
7.10 Heteroarenes ('Inorganometallic' Chemistry) 179

Abbreviations **181**

Subject Index **182**

1

Introduction, Scope and Bonding

Aims

By the end of this chapter you should have a feeling for:

- The range of compounds that constitute the important classes of organotransition metal ligands covered in later chapters
- The electronic book-keeping convention (18-electron rule) used to describe such compounds
- The qualitative bonding of transition metals to selected organic fragments

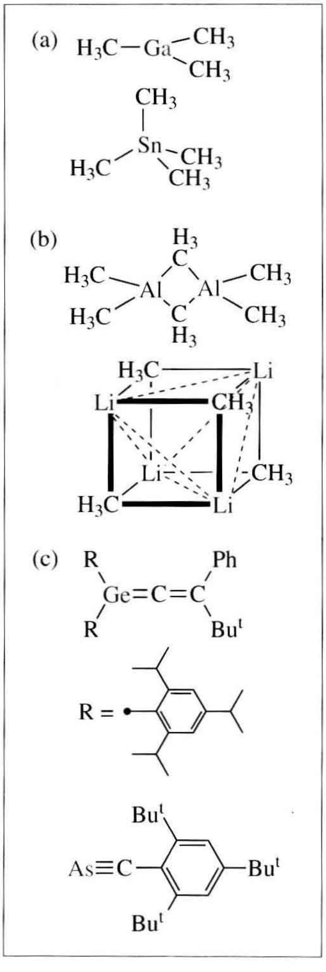


Figure 1.1 Main group M–C bonding

1.1 What is Organometallic Chemistry?

The subdivision of chemistry into inorganic and organic domains reflects history not nature. Organometallic chemistry, the subject of this text, is one unifying point of contact between these two disciplines; it embraces and enriches both. Organometallic chemistry is concerned with the **metal–carbon bond** in all its many and remarkably various forms. Organotransition metal chemistry (compounds featuring bonds between carbon and a transition metal) has matured in the last five decades, in parallel with our general understanding of the bonding of more classical ligands to transition metals. The laboratory curiosities and exotic compounds of yesteryear are today routinely the synthetic organic chemist's reagents, the polymer chemist's catalysts, the industrial chemist's meal-ticket. The eventual exploitation of today's organometallic curiosities provides the challenge and opportunities for this generation of readers.

We shall consider organometallic compounds as those in which the 'metal' has a comparable or lower **Pauling electronegativity** (PE) than that of carbon (2.5). For transition metals, these span the range 1.3

The discussion assumes a familiarity with the basic concepts of transition metal coordination chemistry, as outlined for example in *d- and f-Block Chemistry* (C. J. Jones, RSC Tutorial Chemistry Texts 4).

(hafnium) to 2.5 (gold). These generally increase across a transition period, and less generally down a group. Thus the first transition (3d) elements are more electropositive than the heavier 4d and 5d transition metals. The very electropositive lanthanide and actinide elements (PE 1.1–1.3) also have a rich organometallic chemistry, which will not be dealt with specifically here, however, except where it provides useful illustrative examples.

Main group elements have their own diverse organometallic chemistry, often overlapping with that of the transition metals. Primarily, this is concerned with simple element–carbon σ-bonds (Figure 1.1a). More complex structures arise for electron-deficient organometallic compounds, typically those of Groups 1, 2 and 13 (Figure 1.1b). Multiple bonding between carbon and the heavier p-block elements (pπ–pπ, Figure 1.2a) is less (though increasingly more!) common. For transition metals, multiple bonding (dπ–pπ, Figure 1.2b) is readily achieved and quite commonplace. The nature of a p-block organometallic follows primarily from the characteristics of the central metal: a typical p-block element has a predominant oxidation state [*e.g.* In(III), Sn(IV), Sb(III)], a less common though occasionally accessible oxidation state which differs by two units [*e.g.* In(I), Sn(II), Sb(V)] and a comparatively narrow range of coordination numbers and geometries rationalized by the octet and Gillespie–Nyholm (valence shell electron pair repulsion) rules. Although energetically accessible for hybridization and use in covalent bonding, the d-orbitals of these elements are unoccupied and multiple bonding to carbon, when it does arise, generally involves pπ–pπ orbital combinations. For heavier elements where this is less effective, kinetic stabilization *via* the use of sterically protective substituents is generally required (Figure 1.1c).

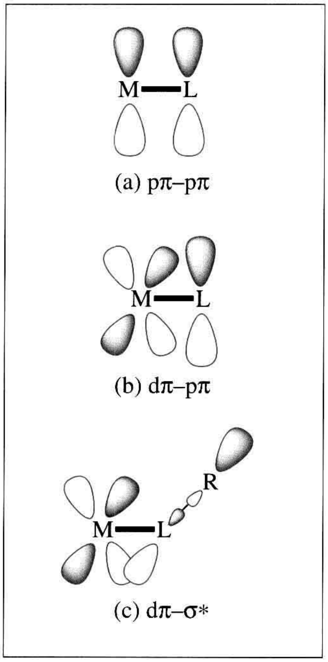


Figure 1.2 Origins of π-bonding

The defiance of these generalizations underpins the intrigue of transition elements. Some transition elements can offer as many as 11 different accessible formal oxidation states {*e.g.* $[Ru(CO)_4]^{2-}$ [Ru(–II)] and RuO_4 [Ru(VIII)]; $[Cr(CO)_4]^{4-}$ [Cr(–IV)] and CrF_6 [Cr(VI)]}; coordination numbers of 1 to 8 are observed, although 4, 5 and 6 remain the most commonly encountered. This breadth arises from the most significant feature of transition elements: the presence of partially filled d-orbitals which may be of suitable energy, symmetry, directionality and occupancy to enter into very effective multiple bonding (dπ–pπ). Indeed, even bonds of δ-symmetry become possible for transition metals. In contrast to p-block elements, the efficiency of this multiple bonding actually increases down a triad. This is due in part to relativistic effects which destabilize d-orbitals for heavy metals, increasing their π-basicity when occupied, a key factor in the bonding of such metals to unsaturated organic molecules which will be discussed later in this chapter. The enormous variation in these characteristic properties would at first glance make the diversity of organotransition metal chemistry appear overwhelming and even intimidating. Fortunately, various guiding principles have emerged help to conceptualize this complexity within generally well-behaved models. The most useful is the 18-electron or effective atomic number (EAN) rule, discussed below.

Two compounds serve to illustrate extremes of complexity in organotransition metal chemistry: nickel tetracarbonyl (Figure 1.3a; see also Chapter 3) and vitamin B_{12} (Figure 1.3b; see also Chapter 4). These exemplary compounds share two features: firstly, both are beautiful, the former for its simplicity, the latter for its complexity. Secondly, both are also useful, the former as an intermediate in the industrial purification of nickel, the latter as a key catalyst (metalloenzyme) in human biochemistry. Figure 1.3c shows a simple organocobalt compound which can serve as a model of the active site of vitamin B_{12}. Chemical models are valuable conceptual tools in understanding the chemistry of more complex chemical systems, which are themselves less amenable to direct study, when appropriate care is taken in making inferences. Many further examples of organometallic model compounds will be met in subsequent chapters.

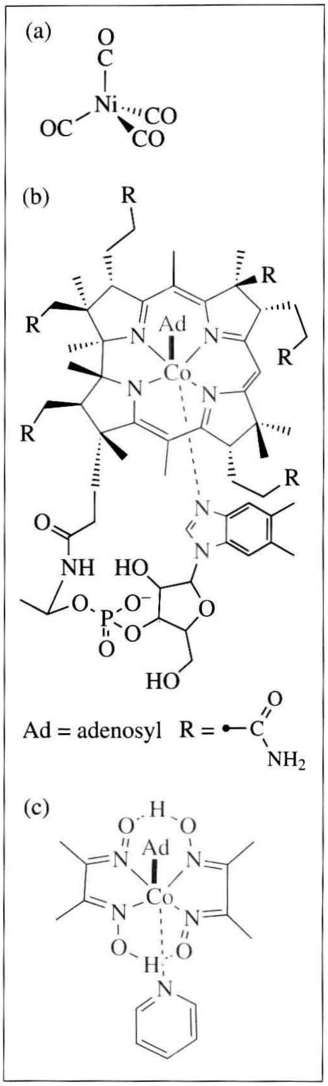


Figure 1.3 Simplicity to complexity

1.2 Bonding in Organotransition Metal Compounds

It is generally accepted that d-orbitals do not play a major role in the bonding of p-block elements to carbon. The diverse chemistry of the transition metals, however, centres on the involvement of partially filled d-orbitals in the bonding to ligands. The basics of simple metal–ligand bonding are dealt with in other texts. The majority of transition metal phenomena can be accommodated by a molecular orbital or 'ligand field' treatment. In addition to providing insights into the symmetry, degeneracy and energy of d-orbitals, such a treatment also concludes that covalency is important in explaining the metal–ligand bond, even for very simple ligands such as halides, water and ammonia. For these classical ligands, however, the large electronegativity difference between the donor atom and the metal would be expected to favour largely ionic character (as is also the case for bonds between carbon and the lanthanides or actinides). For the bonding of carbon to transition metals the electronegativity difference is modest or negligible. Hence the concepts of covalency and electroneutrality become all-important, whilst the concept of oxidation state rapidly loses its usefulness. An organic chemist seldom *explicitly* considers the oxidation state of carbon. Similarly, as organometallic chemists we will only consider this (artificial) concept in the most clear-cut situations where the basic rules can be applied without ambiguity.

The important descriptors in oranotransition metal chemistry are the coordination number and the total number of **valence electrons** (VE), independent of where they are 'located' within the metal–ligand bonding framework (the description of which typically requires more sophisticated molecular orbital treatments). The number of valence electrons (nVE) in an organotransition metal complex is crucial to understanding the reactivity of a complex. This is described by the 18-electron rule, which is by no means absolute but provides an effective framework for interpretation.

The octet rule underpins much of the chemistry of the p-block elements, and the origins of deviations when they occur are generally well understood. An analogous generalization also arises for organometallic compounds of the d-block. The octet rule arises from the use of four valence orbitals (s + 3 p) by p-block elements in the majority of their compounds, thereby requiring eight valence electrons (8VE) to attain the effective atomic number of the next heaviest noble gas. Within the transition series it follows that nine valence orbitals are available (s + 3 p + 5 d) and that full use of these will require 18 valence electrons (18VE). Thus the 18-electron (EAN) rule emerges in its simplest form, although later we will look more deeply into the nature of this relationship. The octet rule is not absolute in p-block chemistry and the 18-electron rule has its limitations as well. Fortunately, deviations generally fall within readily understandable situations involving **steric factors** or more subtle **electronic** considerations. Note that the 18-electron rule has no useful application or predictive value in the organometallic chemistry of the f-block elements (in principle, 16 valence orbitals!). In this area, steric and **electrostatic factors** generally hold sway.

We shall first revisit some p-block 'octet' examples as a point of reference. The total number of valence electrons for the atom of interest in a molecule is the sum of the electrons provided by the central element in its **zero-valent** (oxidation state = 0) form and the ligands or substituents, with the charge of the molecule finally subtracted. Table 1.1 collates some of the ligands to be encountered later in this book, according to the number of electrons they provide. An important class of ligands which are ubiquitous in transition metal chemistry are ***polyhapto*** hydrocarbons and their derivatives. These are organic ligands capable of binding through two (Chapter 6) or more (Chapter 7) unsaturated carbon atoms. Each carbon through which the ligand binds provides one valence orbital and accordingly one electron to the valence count. The number of carbon (or other) atoms through which it binds (n) is referred to as the **hapticity** (*monohapto*, *dihapto*, *trihapto* ... *octahapto*) and this is given the symbol 'η^n'. By convention, if all carbons of the unsaturated system are bound to the metal, the superscript is omitted.

A selection of compounds of the simplest p-block element, boron (Figure 1.4), illustrates a number of points. The salt (1.4a) involves two

Table 1.1 Electron counting for commonly encountered ligands

nVE	*Ligands*
1[a]	*Ligands which in the free state would be a radical (one unpaired electron):*[a] H, F, Cl, Br, I, OH, OR, NH_2, NR_2, SR, PR_2, CN, N_3, NCS, bent NO, bent NNR Monodentate carboxylates O_2CR, dithiocarbamates S_2CNR_2, amidates $RC(NR)_2$, alkyl, aryl, vinyl (alkenyl), acetylide (alkynyl), formyl, acyl, aroyl, *etc.*
2[a]	*Ligands which in the free state would have an even number of valence electrons:* OH_2, NH_3, ethers, amines, thioethers, phosphines NR, O, S, PR 'C_1': CO, CNR, CS, CR_2, $C{=}CR_2$, $C{=}C{=}CR_2$, *etc.* 'C_2': alkenes, alkynes; molecules which bind side-on through a multiple bond: O_2, SO_2, CS_2, CSe_2, RP=PR, $R_2Si{=}CR_2$
3	Linear NO, nitride (N), linear NNR, NS, NSe, P *Ligands which can be subdivided into a combination of 1VE and 2VE donations:* *e.g.* η^3-allyl, η^3-cyclopropenyl, bidentate alkenyls, acyls, carboxylates, dithiocarbamates, amidates, β-diketonates, salicylates, glyoximates
4	Dienes, including cyclobutadiene and heteroatom-substituted dienes, *e.g.* vinyl ketones
5	Cyclopentadienyl, pentadienyl, tris(pyrazolyl)borate
6	Arenes, trienes (*e.g.* cycloheptatriene), thiophene, pyrrole
7	η^7-Cyclohexatrienyl ('tropylium')
8	η^8-Cyclooctatetraene
n	η^n-C_nR_x

[a]Many ligands may also carry a further pair(s) of electrons on the donor atom which may be available (if required) for π-donation, thereby alleviating an otherwise coordinatively unsaturated metal centre. 1VE ligands capable of providing a further electron pair include alkoxides, amides, nitrosyls and diazonium ions. 2VE ligands capable of providing a further two electrons include oxo, imido and alkynes

electron-precise (8VE) boron centres that satisfy the octet rule, and the compound is stable. The molecule BH_3 (1.4b), however, has only 6VE and is therefore electron deficient. In organometallic terms, we describe this as being '**coordinatively unsaturated**' with one (or more) vacant coordination site(s). The molecule cannot be isolated, but rather finds some way of relieving this unsaturation, either by dimerizing to diborane B_2H_6 or by forming adducts with **Lewis bases**, H_3B–L (1.4c; L = diethyl ether), thereby acquiring the 2VE needed to complete the octet. The compound $B(NMe_2)_3$ (1.4d) appears to have the same electron count as BH_3 and yet is stable as a monomer. This introduces the ability of some ligands

(a) $[BH_2(NH_3)_2]^+[BH_4]^-$
B (3)
+ H (2 × 1)
+ NH_3 (2 × 2)
– charge (+1)
= 8VE
B (3)
+ H (4 × 1)
– charge (–1)
= 8VE

(b) BH_3
B (3)
+ H (3 × 2)
= 6VE

(c) $BH_3(OEt_2)$
B (3)
+ H (3 × 1)
+ OEt_2 (1 × 2)
= 8VE

(d) $B(NMe_2)_3$
B (3)
+ NMe_2 (3 × 1)
= 6VE

Figure 1.4 Some boron compounds

(notably those with lone pairs, *e.g.* amides NR_2, alkoxides OR, halides) to provide further electrons *via* π-donation. This phenomenon will also be encountered for such ligands in organotransition metal chemistry, in particular that of the earlier transition metals which typically have suitable vacant orbitals to accommodate π-donation from the ligands.

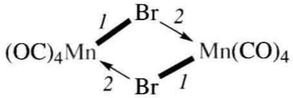
The examples shown in Figure 1.5 illustrate the extension of these ideas to transition metals. The first two examples each obey the 18-electron rule and are stable complexes. The manganese example (1.5c) is, however, coordinatively unsaturated (has a vacant coordination site) and cannot be isolated, but rather dimerizes *via* halide bridges in the same way that $AlCl_3$ dimerizes to $Al_2(\mu\text{-}Cl)_2Cl_4$, with each bridging halide providing three electrons to the overall count. In valence bond terms (1.5d), we can describe this situation as each halide providing a single electron to one metal (covalent bond) and an electron pair (dative bond) to the other metal. The final example (1.5e) is monomeric, although it appears to have less than 18VE. This complex provides an analogy with $B(NMe_2)_3$, in that the presence of strong π-donor oxo ligands helps to stabilize the coordinative unsaturation. Note that in both $B(NMe_2)_3$ and $Re(Me)(=O)_3$ the ligands have more electron pairs available for donation than required for 8VE or 18VE, respectively.

(a) $[Re(CO)_6]^+$
Re (7)
+ CO (6 × 2)
– charge (+1)
= 18VE

(b) $[RuCl_3(CO)_3]^-$
Ru (8)
+ CO (3 × 2)
+ Cl (3 × 1)
– charge (–1)
= 18VE

(c) $MnBr(CO)_4$
Mn (7)
+ CO (4 × 2)
+ Br (1 × 1)
= 16VE

(d)



Mn (7)
+ CO (4 × 2)
+ Br (1 × 1)
+ Br (1 × 2)
= 18VE

(e) $CH_3Re(=O)_3$
Re (7)
+ O (3 × 2)
+ CH_3 (1 × 1)
= 14VE

Figure 1.5 Some transition metal compounds

The examples illustrated above involve simple ligands; however, many more complicated ligands will be encountered. In most cases we can usually subdivide complicated ligands into smaller components so long as we employ reasonable canonical (resonance) forms which each contribute the same overall number of electrons. Thus in Figure 1.6 are shown three-electron ligands, independent of the valence bond descriptions used. Figure 1.7 shows how valence electrons are counted for a range of illustrative examples, including some with metal–metal bonds. Metal–metal bonds also follow the same approach as for multiply bonded p-block compounds, *i.e.* a bond of multiplicity *n* (single, double, triple, quadruple) provides *n*VE to *each* metal.

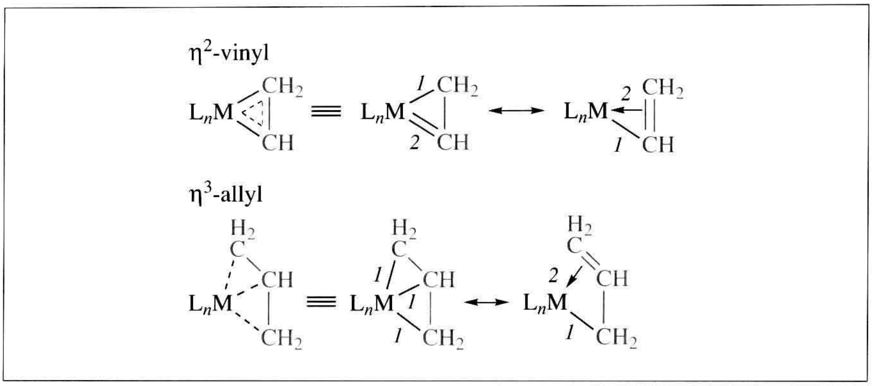


Figure 1.6 Deconstructing complicated ligands

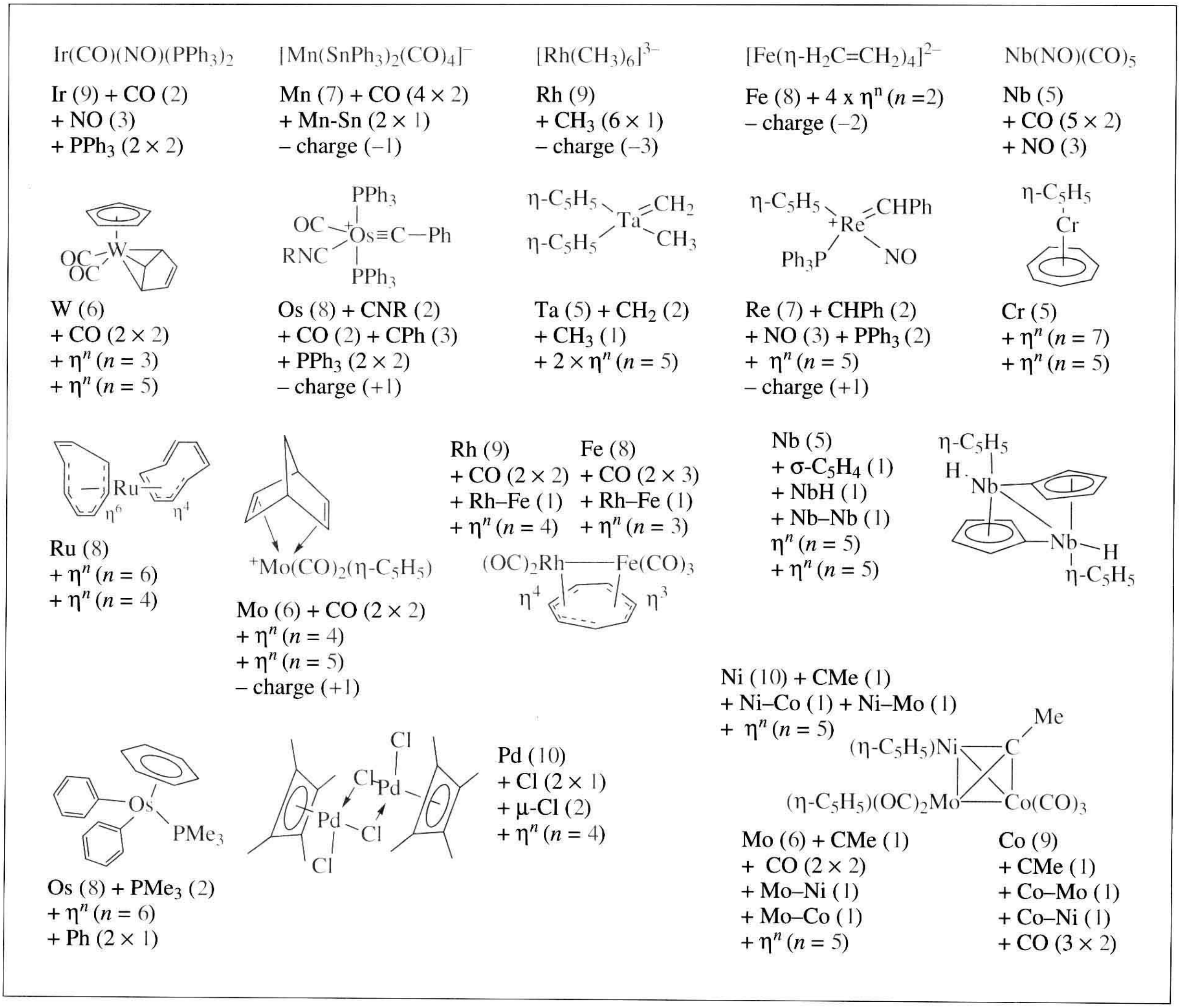


Figure 1.7 The 18-electron rule: illustrative examples

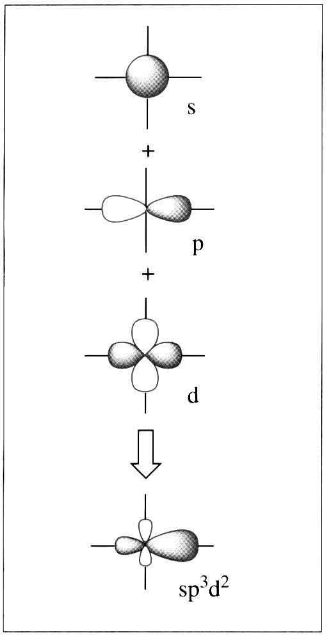


Figure 1.8 sp^3d^2 hybridization

1.2.1 Limitations of the 18-Electron Rule

The 18-electron rule follows in its simplest form from the requirement to fully populate nine metal valence orbitals with 18VE. This is a convenient working simplification which is generally borne out by more sophisticated treatments. We can delve more deeply into the nature of the bonding, however, through a simplified molecular orbital treatment, taking for illustrative purposes an octahedral sp^3d^2 hybridized (Figure 1.8) metal centre. This perspective provides six empty sp^3d^2 orbitals, each of which is directed along *one* metal–ligand vector. This may interact with the lone pair of a ligand (σ_L) in a bonding (Figure 1.9a; M–L σ) and antibonding (Figure 1.9b; M–L σ^*) combination. The remaining three orbitals ($t_{2g} = d_{xy}, d_{xz}, d_{yz}$) protrude *between* the metal–ligand vectors and may only interact with ligand orbitals which have π-symmetry with respect to these vectors (Figure 1.9c). In the absence of ligand π-orbitals, these t_{2g} orbitals remain non-bonding in nature. Combining these interactions leads to the orbital scheme shown in Figure 1.10a. For an octahedron, therefore, the most stable configuration will require a d^6 metal configuration (6VE), in addition to the six lone pairs (12VE) (reassuringly) providing a total of 18VE.

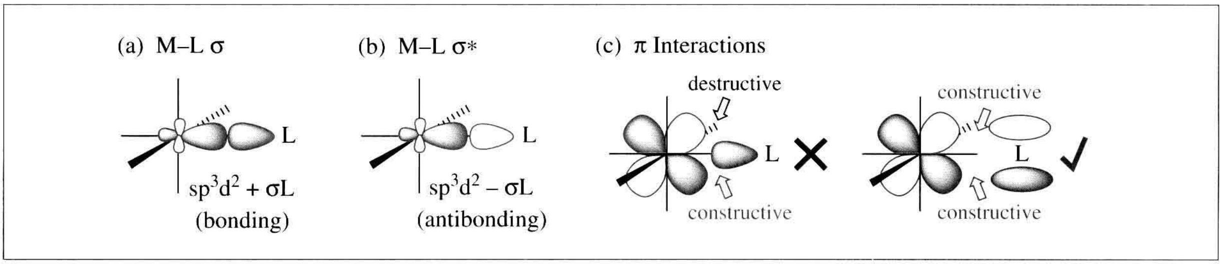


Figure 1.9 Metal–ligand orbital interactions

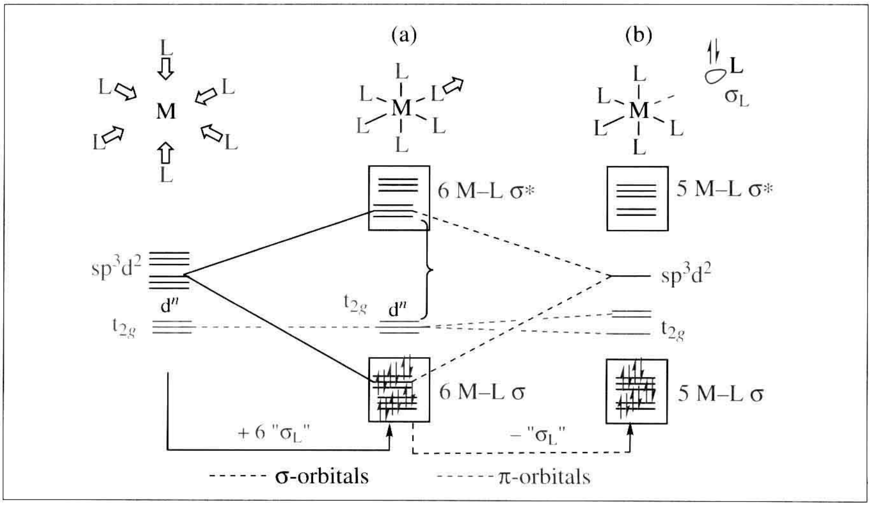


Figure 1.10 Molecular orbitals for octahedral and square-based pyramidal complexes

It is often useful to consider how this scheme would change if one ligand was then removed to provide a hypothetical 16VE complex, since this allows us to consider how one individual ligand might interact with a typical metal centre (a '**fragment orbital**' approach). The departing ligand takes its lone pair of electrons with it, leaving a vacant (Lewis acidic) sp^3d^2 orbital directed towards a vacant coordination site, flanked in the d^6 case by two occupied t_{2g} orbitals of π-symmetry with respect to the M–L vector. We will return to this hypothetical situation later when considering how the molecules CO, CH_2 and C_2H_4 might bond to such a d^6 ML_5 metal centre. Similar schemes may also be constructed for other geometries and coordination numbers; however, the d^6 octahedral case is the simplest to visualize.

The 18-electron rule loses dominance at the extremes of the transition series. At the left-hand side (Groups 3 and 4) the metal centre contributes fewer electrons to the valence count, and thus more electrons are required from ligands. This may not always be easily possible simply due to the steric pressures of accommodating more ligands, *e.g.* the metallocenes MCl_2Cp_2 (M = Ti, Zr, Hf, Nb, Ta; Cp = η-C_5H_5; see Chapter 7) are stable with <18 VE (chloride is a π-donor). This also accounts for the prevalence of π-donor ligands in isolable organometallic compounds of these metals, *i.e.* ligands capable of providing extra electrons to the overall count from 'lone' pairs. Steric factors in general provide a useful method of kinetically stabilizing coordinative unsaturation (preventing bimolecular decomposition routes, which generally require vacant coordination sites), and this approach will be encountered often.

Towards the right-hand side of the transition series, electronic factors are usually associated with coordinative unsaturation. We assumed above that it will be energetically advantageous to employ all nine metal valence orbitals. For this to be true, it is necessary that these are all of comparable energy. However, on moving from Ca to Zn there is a progressive relative increase in the energy gap between the $(n-1)$d and the *n*s and *n*p orbital energies. This separation is further increased by increasing positive charge (or oxidation state) at the metal centre. For late transition metals, the *n*p orbitals are generally less likely to participate significantly in bonding. Furthermore, as in classical coordination chemistry, the characteristic stability associated with the **square planar** geometry for d^8 metal centres (high energy but vacant $d_{x^2-y^2}$ orbital) extends to organometallic examples of Groups 9 and 10.

1.3 The Bonding of Unsaturated Organic Ligands to a Metal Centre

For simple σ-ligands, *e.g.* alkyls (sp^3 hybridized carbon), there are no orbitals of appropriate π-symmetry with respect to the metal–ligand vector and so the metal t_{2g} orbitals remain non-bonding in character. There are, however, many unsaturated organic ligands which do have orbitals of appropriate π-symmetry, be they associated with one carbon atom ['C_1': carbenes, carbynes, vinylidenes (Chapter 5), acyls (Chapter 4)] or two or more carbon atoms ['C_n': alkenes, alkynes (Chapter 6), η^n-hydrocarbons (Chapter 7)]. We will deal with three illustrative cases here: carbon monoxide (CO), methylene (CH_2) and ethene ($H_2C{=}CH_2$) (Figure 1.11). These basic principles can then be modified and refined in later chapters for more complex ligands.

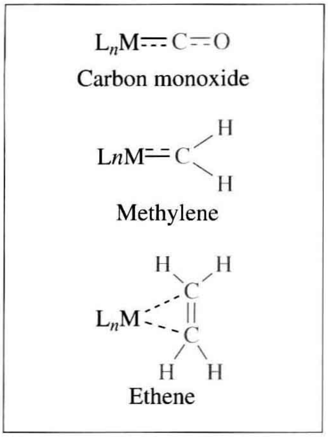


Figure 1.11 Representative π-ligands

1.3.1 Carbon Monoxide

Carbon monoxide shows very little basicity or nucleophilicity within p-block chemistry, although some Lewis acid adducts *are* known, *e.g.* $H_3B–CO$. In contrast, there are many thousands of known complexes of CO with transition metals (metal carbonyls; Chapter 3). The simple classical two-electron dative interaction from the lone pair on carbon, although important, is seldom sufficiently strong to bind CO firmly to a transition metal. Accordingly, comparatively few d^0 or d^{10} metal carbonyl complexes are known. The key lies in the presence of electrons housed in d-orbitals of π-symmetry with respect to the metal–carbon vector (t_{2g}). We begin by considering the frontier orbitals of CO (Figure 1.12).

The HOMO (3σ) is primarily based on carbon, and the degenerate set of antibonding π* orbitals (2π LUMO) also have their greatest contribution from carbon p-orbitals. The most important component of the bonding involves the combination of occupied metal t_{2g} orbitals with the

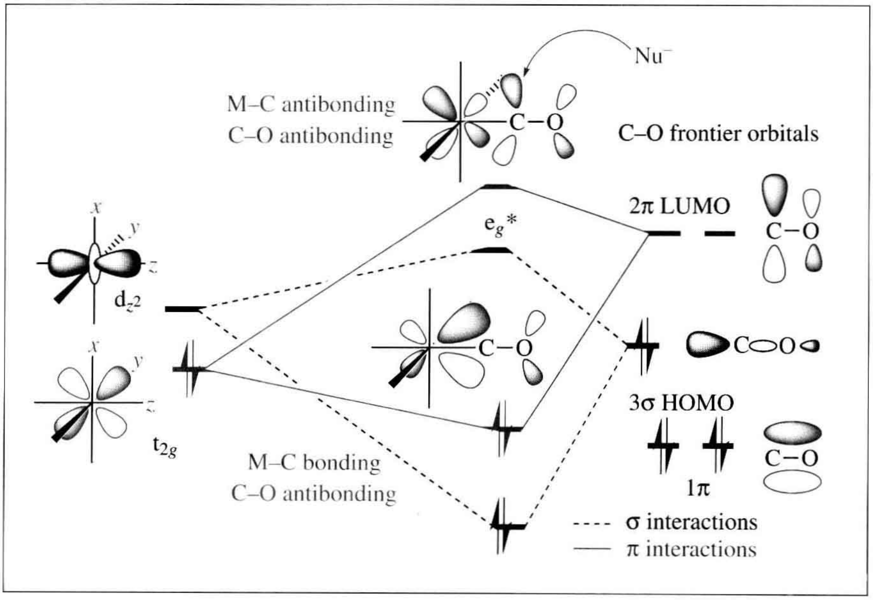


Figure 1.12 Synergic bonding of CO to a transition metal; implications for nucleophilic (Nu⁻) attack