

19.4 The Various Coordination Numbers⁽¹⁰⁾

In 1893 at the age of 26, Alfred Werner[†] produced his classic coordination theory.^(2,11) It is said that, after a dream which crystallized his ideas, he set down his views and by midday had written the paper which was the starting point for work which culminated in the award of the Nobel Prize for Chemistry in 1913. The main thesis of his argument was that metals possess two types of valency: (i) the primary, or ionizable, valency which must be satisfied by negative ions and is what is now referred to as the "oxidation state"; and (ii) the secondary valency which has fixed directions with respect to the central metal and can be satisfied by either negative ions or neutral molecules. This is the basis for the various stereochemistries found amongst coordination compounds. Without the armoury of physical methods available to the modern chemist, in particular X-ray crystallography, the early workers were obliged to rely on purely chemical methods to identify the more important of these stereochemistries. They did this during the next 20 y or so, mainly by preparing vast numbers of complexes of various metals of such stoichiometry that the number of isomers which could be produced would distinguish between alternative stereochemistries.

The term "secondary valency" has been superseded by the term "coordination number". This may be defined as the number of donor atoms associated with the central metal atom or ion. For many years a distinction was made between coordination number in this sense and in

the crystallographic sense, where it is the number of nearest-neighbour ions of opposite charge in an ionic crystal. Though the former definition applies to species which can exist independently in the solid or in solution, while the latter applies to extended lattice systems, the distinction is rather artificial, particularly in view of the fact that crystal field theory (one of the theories of bonding most commonly applied to coordination compounds) assumes that the coordinate bond is entirely ionic! Indeed, the concept can be extended to all molecules. TiCl_4 , for instance, can be regarded as a complex of Ti^{4+} with 4 Cl^- ions in which one lone-pair of electrons on each of the latter is completely shared with the Ti^{4+} to give essentially covalent bonds.

The most commonly occurring coordination numbers for transition elements are 4 and 6, but all values from 2 to 9 are known and a few examples of even higher ones have been established. The more important factors determining the most favourable coordination number for a particular metal and ligand are summarized below. However it is important to realize that, with so many factors involved, it is not difficult to provide facile explanations of varying degrees of plausibility for most experimental observations, and it is therefore prudent to treat such explanations with caution.

(i) If electrostatic forces are dominant the attractions between the metal and the ligands should exceed the destabilizing repulsions between the ligands. The attractions are proportional to the product of the charges on the metal and the ligand whereas the repulsions are proportional to the square of the ligand charge. High cation charge and low ligand charge should consequently favour high coordination numbers, e.g. halide ions usually favour higher coordination numbers than does O^{2-} .

(ii) There must be an upper limit to the number of molecules (atoms) of a particular ligand which can physically be fitted around a particular cation. For monatomic ligands this limit will be dependent on the radius ratio of cation and anion, just as is the case with extended crystal lattices.

(iii) Where covalency is important the distribution of charge is equalized by the transference

¹⁰ G. WILKINSON, R. D. GILLARD and J. A. McCLEVERTY (eds.), *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, Vol. 1, 1987, 613 pp. D. L. KEPERT, *Inorganic Stereochemistry*, Springer-Verlag, Berlin, 1982, 227 pp. J. A. DAVIES, C. M. HOCKENSMITH, V. YU. KUKUSHKIN and YU. N. KUKUSHKIN, *Synthetic Coordination Chemistry: Principles and Practise*, World Scientific Publ., Singapore, 1996, 452 pp.

¹¹ G. B. KAUFFMAN, *Inorganic Coordination Compounds*, Wiley, New York, 1981, 205 pp.

[†] Born in Mulhouse, Alsace, in 1866, he was French by birth, German in upbringing, and, working in Zürich, he became a Swiss citizen in 1894.

of charge in the form of lone-pairs of electrons from ligands to cation. The more polarizable the ligand the lower the coordination number required to satisfy the particular cation though, if back-donation of charge from cation to ligand via suitable π orbitals is possible, then more ligands can be accommodated. Thus the species most readily formed with Fe^{III} in aqueous solutions are $[\text{FeF}_5(\text{H}_2\text{O})]^{2-}$ for the non-polarizable F^- , $[\text{FeCl}_4]^-$ for the more polarizable Cl^- , but $[\text{Fe}(\text{CN})_6]^{3-}$ for CN^- which, though it is even more polarizable, also possesses empty antibonding π orbitals suitable for back-donation.

(iv) The availability of empty metal orbitals of suitable symmetries and energies to accommodate electron-pairs from the ligands must also be important in covalent compounds. This is probably one of the main reasons why the lowest coordination numbers (2 and 3) are to be found in the Ag, Au, Hg region of the periodic table where the d shell has been filled. However, it would be unwise to draw the converse conclusion that the highest coordinations are found amongst the early members of the transition and inner-transition series because of the availability of empty d or f orbitals. It seems more likely that these high coordination numbers are achieved by electrostatic attractions between highly charged but rather large cations and a large number of relatively non-polarizable ligands.

Representative examples of the stereochemistries associated with each of the various coordination numbers will now be discussed.

Coordination number 2

Examples of this coordination number are virtually confined to linear $D_{\infty h}$ complexes of Cu^{I} , Ag^{I} , Au^{I} , and Hg^{II} of which a well-known instance is the ammine formed when ammonia is added to an aqueous solution of Ag^+ : $[\text{H}_3\text{N}-\text{Ag}-\text{NH}_3]^+$

Coordination number 3⁽¹²⁾

This is rather rare and even in $[\text{HgI}_3]^-$, the example usually cited, the coordination number is

dependent on the counter cation. In $[\text{SMe}_3][\text{HgI}_3]$ the Hg^{II} lies at the centre of an almost equilateral triangle of iodide ions (D_{3h}) whereas in $[\text{NMe}_4][\text{HgI}_3]$ the anion apparently polymerizes into loosely linked chains of 4-coordinate Hg^{II} . Other examples feature bulky ligands, e.g. the trigonal planar complexes $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_3]$, $[\text{Cu}\{\{\text{SC}(\text{NH}_2)_2\}_3\}\text{Cl}]$ and $[\text{Cu}(\text{SPPPh}_3)_3]\text{ClO}_4$.

Coordination number 4

This is very common and usually gives rise to stereochemistries which may be regarded essentially as either tetrahedral T_d or (square) planar D_{4h} . Where a complex may be thought to have been formed from a central cation with a spherically symmetrical electron configuration, the ligands will lie as far from each other as possible, that is they will be tetrahedrally disposed around the cation. This has already been seen in complex anions such as BF_4^- and is also common amongst complexes of transition metals in their group oxidation states and of d^5 and d^{10} ions. $[\text{MnO}_4]^-$, $[\text{Ni}(\text{CO})_4]$ and $[\text{Cu}(\text{py})_4]^+$, respectively, exemplify these types. Central cations with other d configurations, in particular d^8 , may give rise to a square-planar stereochemistry and the complexes of Pd^{II} and Pt^{II} are predominantly of this type. Then again, the difference in energy between tetrahedral and square-planar forms may be only slight, in which case both forms may be known or, indeed, interconversions may be possible as happens with a number of Ni^{II} complexes (p. 1159). In the M_2CuX_4 series of complexes of Cu^{II} , variation of M^{I} and X gives complex anions with stereochemistries ranging from square planar, e.g. $(\text{NH}_4)_2[\text{CuCl}_4]$, to almost tetrahedral, e.g. $\text{Cs}_2[\text{CuBr}_4]$. Figure 19.3 shows that the change from square planar to tetrahedral requires a 90° rotation of one L,L pair and a $19\frac{1}{2}^\circ$ change in the LML angles, and a continuous range of distortions from one extreme to the other would appear to be feasible.

¹² P. G. ELLER, D. C. BRADLEY, M. B. HURSTHOUSE and D. W. MEEK, *Coord. Chem. Revs.* **24**, 1-95 (1977).

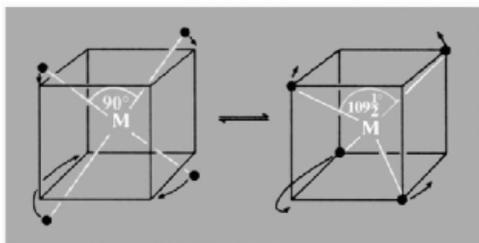
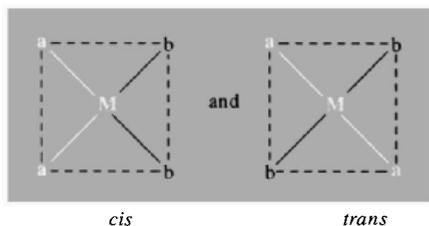


Figure 19.3 Schematic interconversion of square planar and tetrahedral geometries.

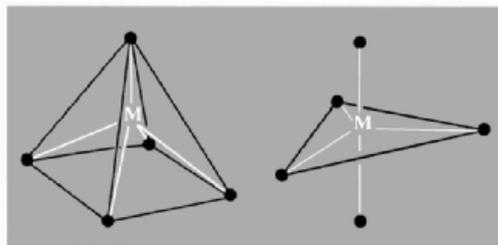
Four-coordinate complexes provide good examples of the early use of preparative methods for establishing stereochemistry. For complexes of the type $[Ma_2b_2]$, where a and b are unidentate ligands, a tetrahedral structure cannot produce isomerism whereas a planar structure leads to *cis* and *trans* isomers (see below). The preparation of 2 isomers of $[PtCl_2(NH_3)_2]$, for instance, was taken as good evidence for their planarity.[†]



Coordination number 5

Five-coordinate complexes are far more common than was once supposed and are now known for all configurations from d^1 to d^9 . Two limiting stereochemistries may be distinguished (Fig. 19.4). One of the first authenticated examples of 5-coordination was $[VO(acac)_2]$ which has the square-pyramidal C_{4v} structure with the $=O$ occupying the unique apical site. However, many of the complexes with this coordination number have structures intermediate between the

[†] On the basis of this evidence alone it is logically possible that one isomer could be tetrahedral. Early coordination chemists, however, assumed that the directions of the "secondary valencies" were fixed, which would preclude this possibility. X-ray structural analysis shows that, in the case of Pt^{II} complexes, they were correct.



Square pyramidal

Trigonal bipyramidal

Figure 19.4 Limiting stereochemistries for 5-coordination.

two extremes and it appears that the energy required for their interconversion is frequently rather small. Because of this stereochemical non-rigidity a number of 5-coordinate compounds behave in a manner described as "fluxional". That is, they exist in two or more configurations which are chemically equivalent and which interconvert at such a rate that some physical measurement (commonly nmr) is unable to distinguish the separate configurations and instead "sees" only their time-average. If ML_5 has a trigonal bipyramidal D_{3h} structure then 2 ligands must be "axial" and 3 "equatorial", but interchange via a square-pyramidal intermediate is possible (Fig. 19.5). This mechanism has been suggested as the reason why the ^{13}C nmr spectrum of trigonal bipyramidal $Fe(CO)_5$ (p. 1104) fails to distinguish two different kinds of carbon nuclei. See also the discussion of PF_5 on p. 499.

Coordination number 6

This is the most common coordination number for complexes of transition elements. It can be seen by inspection that, for compounds of the type (Ma_4b_2) , the three symmetrical structures (Fig. 19.6) can give rise to 3, 3 and 2 isomers respectively. Exactly the same is true for compounds of the type $[Ma_3b_3]$. In order to determine the stereochemistry of 6-coordinate complexes very many examples of such compounds were prepared, particularly with $M = Cr^{III}$ and Co^{III} , and in no case was more than 2 isomers found. This, of course, was only negative evidence for the octahedral structure, though the

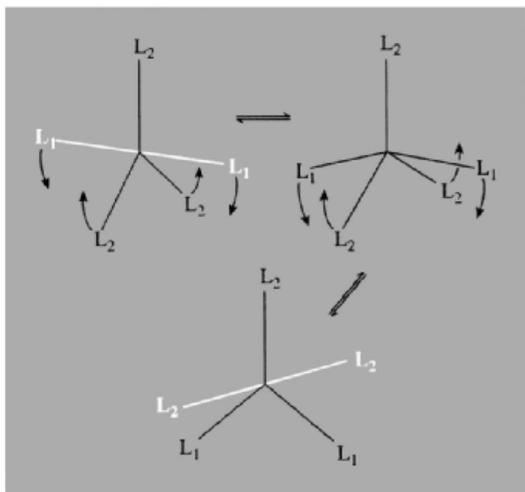
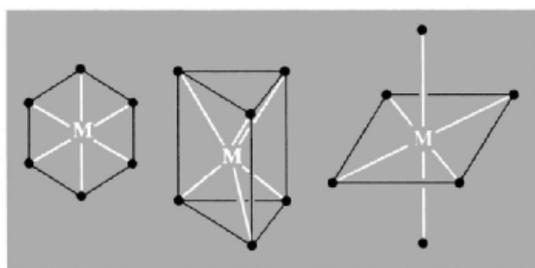


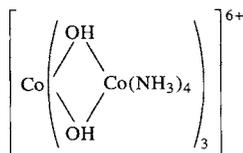
Figure 19.5 The interconversion of trigonal bipyramidal configurations via a square-pyramidal intermediate. Notice that the L_1 ligands, which in the left-hand tbp are axial, become equatorial in the right-hand tbp and simultaneously 2 of the L_2 ligands change from equatorial to axial.



Planar Trigonal prismatic Octahedral

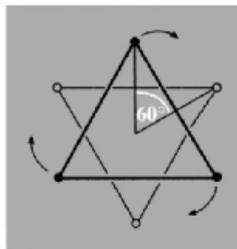
Figure 19.6 Possible stereochemistries for 6-coordination.

sheer volume of it made it rather compelling. More positive evidence was provided by Werner, who in 1914 achieved the first resolution into optical isomers of an entirely inorganic compound, since



neither the planar nor trigonal prismatic structures can give rise to such optical isomers.

Nevertheless, it cannot be assumed that every 6-coordinate complex is octahedral. In 1923 the first example of trigonal prismatic coordination was reported for the infinite layer lattices of MoS_2 and WS_2 . A limited number of further examples are now known following the report in 1965 of the structure of $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$ (Fig. 19.7). Intermediate structures also occur and can be defined by the “twist angle” which is the angle through which one face of an octahedron has been rotated with respect to the opposite face as “viewed along” a threefold axis of the octahedron. A twist angle of 60° suffices to convert an octahedron into a trigonal prism:



In fact the vast majority of 6-coordinate complexes are indeed octahedral or distorted octahedral. In addition to the twist distortion just considered distortions can be of two other types: trigonal and tetragonal distortions which mean compression or elongation along a threefold and a fourfold axis of the octahedron respectively (Fig. 19.8).

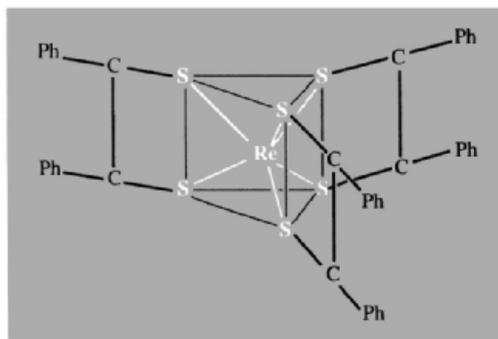
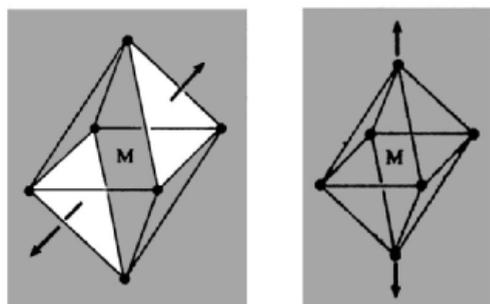


Figure 19.7 Trigonal prismatic structure of $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$.



Trigonal elongation

Tetragonal elongation

Figure 19.8 Distortions of octahedral geometry.

Coordination number 7

There are three main stereochemistries for complexes of this coordination number: pentagonal bipyramidal D_{5h} , capped trigonal prismatic C_{2v} and capped octahedral C_{3v} , the last two being obtained by the addition of a seventh ligand either above one of the rectangular faces of a trigonal prism or above a triangular face of an octahedron respectively. These structures may conveniently be visualized as having the ligating atoms which form the coordination polyhedra on the surfaces of circumscribed spheres (Fig. 19.9).

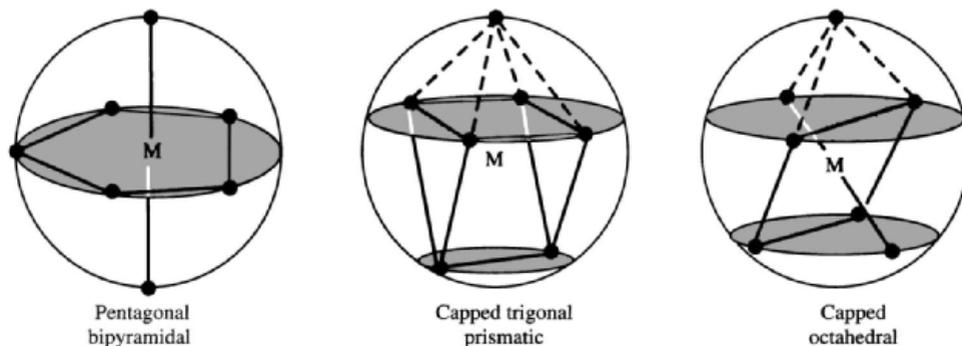
As with other high coordination numbers, there seems to be little difference in energy between these structures. Factors such as the number of counter ions and the stereochemical requirements of chelating ligands are probably decisive and *a priori* arguments are unreliable in predicting

the geometry of a particular complex. $[\text{ZrF}_7]^{3-}$ and $[\text{HfF}_7]^{3-}$ have the pentagonal bipyramidal structure, whereas the bivalent anions, $[\text{NbF}_7]^{2-}$ and $[\text{TaF}_7]^{2-}$ are capped trigonal prismatic. The capped octahedral structure is exemplified by $[\text{NbOF}_6]^{3-}$.

Coordination number 8^(13,14)

The most symmetrical structure possible is the cube O_h but, except in extended ionic lattices such as those of CsCl and CaF_2 , it appears that inter-ligand repulsions are nearly always (but see p. 1275) reduced by distorting the cube, the two most important resultant structures being the square antiprism D_{4h} and the dodecahedron D_{2d} (Fig. 19.10).

Again, these forms are energetically very similar; distortions from the idealized structures make it difficult to specify one or other, and the particular structure actually found must result from the interplay of many factors. $[\text{TaF}_8]^{3-}$, $[\text{ReF}_8]^{2-}$ and $[\text{Zr}(\text{acac})_4]$ are square antiprismatic, whereas $[\text{ZrF}_8]^{4-}$ and $[\text{Mo}(\text{CN})_8]^{4-}$ are dodecahedral. The nitrates $[\text{Co}(\text{NO}_3)_4]^{2-}$ and $\text{Ti}(\text{NO}_3)_4$ may both be regarded as dodecahedral, the former with some distortion. Each nitrate ion is bidentate but the 2

**Figure 19.9** The three main stereochemistries for 7-coordination.

¹³ I. G. SHTEREV, G. St. NIKOLOV, N. TRENDAFILOVA and R. KIROV, *Polyhedron*, **10**, 393–402 (1991).

¹⁴ C. W. HAIGH, *Polyhedron*, **15**, 605–43 (1996).

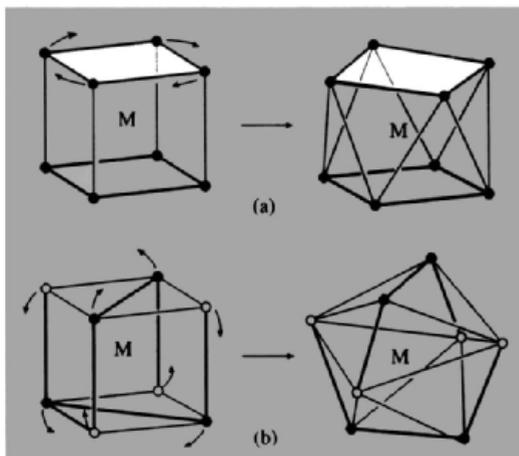
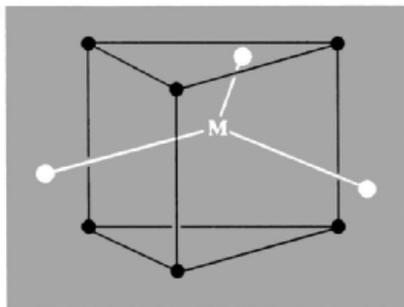


Figure 19.10 (a) Conversion of cube to square antiprism by rotation of one face through 45° (b) Conversion of cube into dodecahedron.

oxygen atoms are necessarily close together so that the structure of the complexes is probably more easily visualized from the point of view of the 4 nitrogen atoms which form a flattened tetrahedron around the metal (p. 966).

Coordination number 9

The stereochemistry of most 9-coordinate complexes approximates to the tri-capped trigonal prism D_{3h} , formed by placing additional ligands above the three rectangular faces of a trigonal prism:

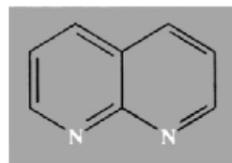


Amongst the known examples of this arrangement are a number of $[M(\text{H}_2\text{O})_9]^{3+}$ hydrates of lanthanide salts and $[\text{ReH}_9]^{2-}$. The latter is

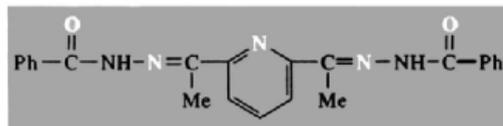
interesting in that it is presumably only the small size of the H ligand which allows such a high coordination number for rhenium. Very occasionally 9-coordination results in a capped square antiprismatic C_{4v} arrangement in which the ninth ligand lies above one of the square faces, e.g. the Cl-bridged $[\{\text{LaCl}(\text{H}_2\text{O})_7\}_2]^{4+}$.

Coordination numbers above 9

Such high coordination numbers are not common and it is difficult to generalize about their structures since so few have been accurately determined. They are found mainly with ions of the early lanthanide and actinide elements and it is therefore tempting to assume that the availability of empty and accessible f orbitals is necessary for their formation. However, it appears that the bonding is predominantly ionic and that the really important point is that these are the elements which provide stable cations with charges high enough to attract a large number of anions and yet are large enough to ensure that the inter-ligand repulsions are not unacceptably high. $\text{K}_4[\text{Th}(\text{O}_2\text{CCO}_2)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (bicapped square antiprism D_{4d}) and $[\text{La}(\text{edta})(\text{H}_2\text{O})_4]$ afford examples of 10-coordination. Higher coordination numbers are reached only by chelating ligands such as NO_3^- , SO_4^{2-} , and 1,8-naphthyridine (8) with donor atoms close together (i.e. ligands with only a small "bite"). $[\text{La}(\text{dapbaH})(\text{NO}_3)_3]$, is a good example (see



(8)



(9)

also p. 1276): in it the 5 donor atoms of the dapbaH, i.e. 2,6-diacetylpyridinebis(benzoic acid hydrazone) (9), are situated in a plane, with the N atoms (but not the donor oxygens) of the 3 bidentate nitrates in a second plane at right angles to the first. $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ contains 12-coordinate Ce in the complex ion $[\text{Ce}(\text{NO}_3)_6]^{3-}$. This has a distorted icosahedral stereochemistry, though it is more easily visualized as an octahedral arrangement of the nitrogen atoms around the Ce^{III} . Another example is $[\text{Pr}(\text{naph})_6]^{3+}$ where naph is 1,8-naphthyridine (8).

Higher coordination numbers (up to 16) are known, particularly among organometallic compounds (pp. 940–3) and metal borohydrides (p. 168).

In addition to coordination compounds in which a central metal atom is surrounded by a polyhedral array of donor atoms, a large and rapidly increasing number of “cluster” compounds^(15–18) is known in which a group of metal atoms is held together largely by M–M bonds. Where more than three metal atoms are involved, they themselves form polyhedral arrays which may be considered as conceptual intermediates between mononuclear classical complexes and the non-molecular lattice structures of binary and ternary compounds of transition metals. A distinction is sometimes made between “clusters” which owe their stability to M–M bonds, and “cages” which are held together by ligand bridges, but the distinction is not rigidly adhered to.

Cluster and cage structures are widespread in the chemistry of main group elements, being particularly extensive in the case of boron (Chap. 6). For transition elements the principal

areas of interest are the lower halides of elements towards the left of the d-block, and carbonyls of elements towards the right of the d-block, the latter being an especially active area. The possibility that metal clusters of high nuclearity might mimic the behaviour of metal surfaces (the “surface-cluster analogy”) has stimulated synthetic chemists to search for materials with high catalytic activity.⁽¹⁹⁾ Such materials, particularly if soluble, should also provide better insight into the catalytic activity of metal surfaces. Unfortunately these objectives have so far proved largely elusive and in only a few cases can catalytic activity be attributed confidently to a cluster itself rather than to its fragmentation products.

These and other classes of cluster compounds will be dealt with more fully in later chapters devoted to the chemistry of the metals involved.

19.5 Isomerism⁽²⁰⁾

Isomers are compounds with the same chemical composition but different structures, and the possibility of their occurrence in coordination compounds is manifest. Their importance in the early elucidation of the stereochemistries of complexes has already been referred to and, though the purposeful preparation of isomers is no longer common, the preparative chemist must still be aware of the diversity of the compounds which can be produced. The more important types of isomerism are listed below.

Conformational isomerism

In principle this type of isomerism (also known as “polytopal” isomerism) is possible with any coordination number for which there is more than one known stereochemistry. However, to actually occur the isomers need to be of comparable stability, and to be separable there

¹⁵ M. MOSKOVITS, *Metal Clusters*, Wiley, New York, 1986, 313 pp.

¹⁶ I. G. DANCE, Chap. 5 in *Comprehensive Coordination Chemistry*, Vol. 1, pp. 135–78, Pergamon Press, Oxford, 1987.

¹⁷ D. F. SHRIVER, H. D. KAESZ and R. D. ADAMS, *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, 439 pp.

¹⁸ D. M. P. MINGOS and D. I. WALES, *Introduction to Cluster Chemistry*, Prentice Hall, New York, 1990, 318 pp.

¹⁹ B. C. GATES, L. GUCZI and H. KNÖZINGER (eds.) *Metal Clusters in Catalysis*, Vol. 29 of *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1986, 648 pp.

²⁰ J. MACB. HARROWFIELD, Chap. 6 in *Comprehensive Coordination Chemistry*, Vol. 1, pp. 179–212, Pergamon Press, Oxford, 1987.

must be a significant energy barrier preventing their interconversion. This behaviour is confined primarily to 4-coordinate nickel(II), an example being $[\text{NiCl}_2\{\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2\}_2]$ which is known in both planar and tetrahedral forms (p. 1160).

Geometrical isomerism

This is of most importance in square-planar and octahedral compounds where ligands, or more specifically donor atoms, can occupy positions next to one another (*cis*) or opposite each other (*trans*) (Fig. 19.11).

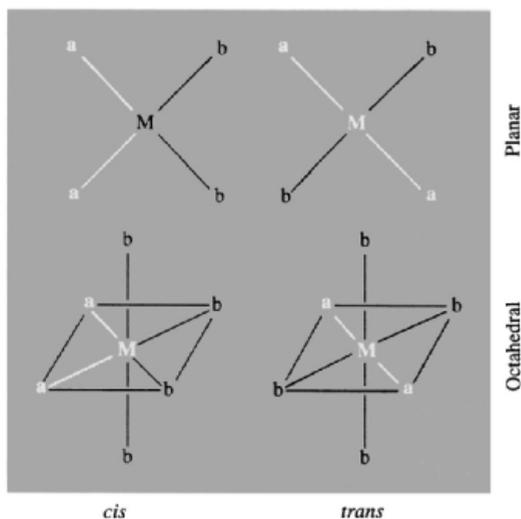


Figure 19.11 *Cis* and *trans* isomerism.

A similar type of isomerism occurs for $[\text{Ma}_3\text{b}_3]$ octahedral complexes since each trio of donor atoms can occupy either adjacent positions at the corners of an octahedral face (*facial*) or positions around the meridian of the octahedron (*meridional*). (Fig. 19.12.) Geometrical isomers differ in a variety of physical properties, amongst which dipole moment and visible/ultraviolet spectra are often diagnostically important.

Optical isomerism

Optical isomers, enantiomorphs or enantiomers, as they are also known, are pairs of molecules

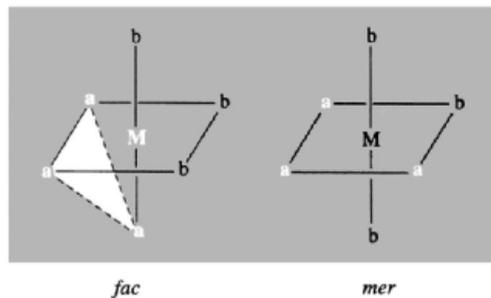


Figure 19.12 Facial and meridional isomers.

which are non-superimposable mirror images of each other. Such isomers have the property of chirality (from Greek $\chi\epsilon\iota\rho$, hand), i.e. handedness, and virtually the only physical or chemical difference between them is that they rotate the plane of polarized light, one of them to the left and the other to the right. They are consequently designated as laevo (*l* or $-$) and dextro (*d* or $+$) isomers.

A few cases of optical isomerism are known for planar and tetrahedral complexes involving unsymmetrical bidentate ligands, but by far the most numerous examples are afforded by octahedral compounds of chelating ligands, e.g. $[\text{Cr}(\text{oxalate})_3]^{2-}$ and $[\text{Co}(\text{edta})]^-$ (Fig. 19.13).

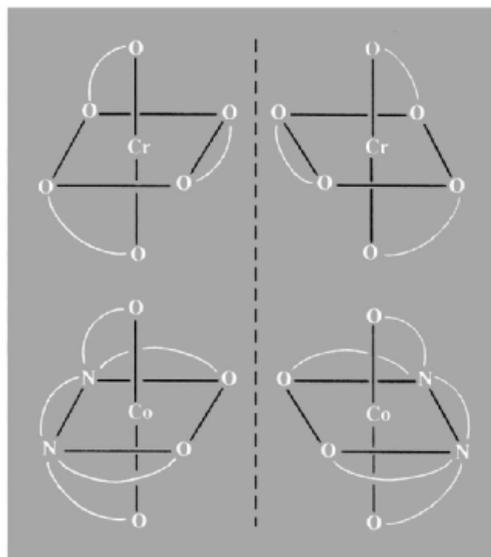
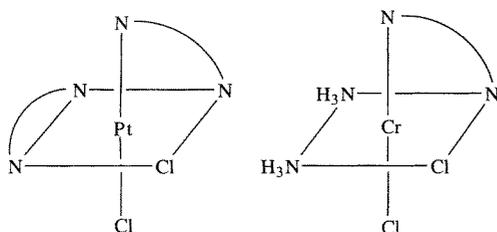


Figure 19.13 Non-superimposable mirror images.

Where unidentate ligands are present, the ability to effect the resolution of an octahedral complex (i.e. to separate 2 optical isomers) is proof that the 2 ligands are *cis* to each other. Resolution of $[\text{PtCl}_2(\text{en})_2]^{2-}$ therefore shows it to be *cis* while of the 2 known geometrical isomers of $[\text{CrCl}_2\text{en}(\text{NH}_3)_2]^+$ the one which can be resolved must have the *cis-cis* structure since the *trans* form would give a superimposable, and therefore identical, mirror image:



Ionization isomerism

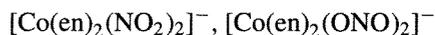
This type of isomerism occurs when isomers produce different ions in solution, and is possible in compounds which consists of a complex ion with a counter ion which is itself a potential ligand. The pairs: $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$ and $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$, $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$, and the series $[\text{CoCl}(\text{en})_2(\text{NO}_2)]\text{SCN}$, $[\text{CoCl}(\text{en})_2(\text{SCN})]\text{NO}_2$, $[\text{Co}(\text{en})_2(\text{NO}_2)(\text{SCN})]\text{Cl}$ are examples of ionization isomers.

A subdivision of this type of isomerism, known as "hydrate isomerism", occurs when water may be inside or outside the coordination sphere. It is typified by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ which exists in the three distinct forms $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (pale green), and $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green). These are readily distinguished by the action of AgNO_3 in aqueous solution which immediately precipitates 3, 2 and 1 chloride ions respectively.

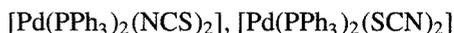
Linkage isomerism

This is in principle possible in any compound containing an ambidentate ligand. However, that

such a ligand can *under different circumstances* coordinate through either of the 2 different donor atoms is by no means a guarantee that it will form isolable linkage isomers with the same cation. In fact, in only a very small proportion of the complexes of ambidentate ligands can linkage isomers actually be isolated, and these are confined largely to complexes of NO_2^- (p. 463) and, to a lesser extent, SCN^- (p. 325). Examples are:



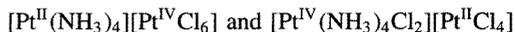
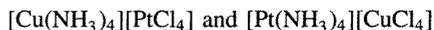
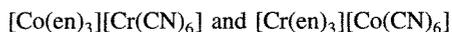
and



It should be noted that, by convention, the ambidentate ligand is always written with its donor atom first, i.e. NO_2 for the nitro, ONO for the nitrito, NCS for the *N*-thiocyanato and SCN for the *S*-thiocyanato complex. Differences in infrared spectra arising from the differences in bonding are often used to distinguish between such isomers.

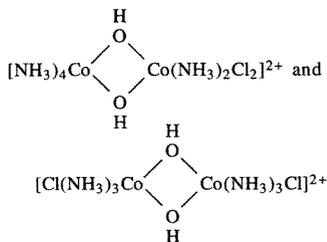
Coordination isomerism

In compounds made up of both anionic and cationic complexes it is possible for the distribution of ligands between the ions to vary and so lead to isomers such as:



It can be seen that other intermediate isomers are feasible but in the above cases they have not been isolated. Substantial differences in both physical and chemical properties are to be expected between coordination isomers.

When the two coordinating centres are not in separate ions but are joined by bridging groups, the isomers are often distinguished as "coordination position isomers" as is the case for:



Polymerization isomerism

Compounds whose molecular compositions are multiples of a simple stoichiometry are polymers, strictly, only if they are formed by repetition of the simplest unit. However, the name “polymerization isomerism” is applied rather loosely to cases where the same stoichiometry is retained but where the molecular arrangements are different. The stoichiometry $\text{PtCl}_2(\text{NH}_3)_2$ applies to the 3 known compounds, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_3(\text{NH}_3)]_2$, and $[\text{PtCl}(\text{NH}_3)_3]_2[\text{PtCl}_4]$ (in addition to the *cis* and *trans* isomers of monomeric $[\text{PtCl}_2(\text{NH}_3)_2]$). There are actually 7 known compounds with the stoichiometry $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$. Again it is clear that considerable differences are to be expected in the chemical properties and in physical properties such as conductivity.

Ligand isomerism

Should a ligand exist in different isomeric forms then of course the corresponding complexes will also be isomers, often described as “ligand isomers”. In $[\text{CoCl}(\text{en})_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me})]\text{Cl}_2$, for instance, the toluidine may be of the *o*-, *m*- or *p*- form.

19.6 The Coordinate Bond⁽²¹⁾

(see also p. 198)

The concept of the coordinate bond as an interaction between a cation and an ion or

molecule possessing a lone-pair of electrons can be accepted before specifying the nature of that interaction. Indeed, it is now evident that in different complexes the bond can span the whole range from electrostatic to covalent character. This is why the various theories which have been accorded popular favour at different times have been acceptable and useful even though based on apparently incompatible assumptions. This dichotomy is reflected in the now obsolete adjectives “dative-covalent”, “semi-polar” and “co-ionic”, which have been used to describe the coordinate bond. The first of these descriptions arises from the idea advanced by N. V. Sidgwick in 1927, that the coordinate bond is a covalent bond formed by the donation of a lone-pair of electrons from the donor atom to the central metal. Since noble gases are extremely unreactive, and compounds in which atoms have attained the electronic configuration of a noble gas either by sharing or transferring electrons also tend to be stable, Sidgwick further suggested that, in complexes, the metal would tend to surround itself with sufficient ligands to ensure that the number of electrons around it (its “effective atomic number” or EAN) would be the same as that of the next noble gas. If this were true then a metal would have a unique coordination number for each oxidation state, which is certainly not always the case. However, the EAN rule is still of use in rationalizing the coordination numbers and structures of simple metal carbonyls.

In his *valence bond theory* (VB), L. Pauling extended the idea of electron-pair donation by considering the orbitals of the metal which would be needed to accommodate them, and the stereochemical consequences of their hybridization (1931–3). He was thereby able to account for much that was known in the 1930s about the stereochemistry and kinetic behaviour of complexes, and demonstrated the diagnostic value of measuring their magnetic properties. Unfortunately the theory offers no satisfactory explanation of spectroscopic properties and so was

²¹ B. N. FIGGIS, Chap. 7 in *Comprehensive Coordination Chemistry*, Vol. 1, pp. 213–80, Pergamon Press, Oxford, 1987. S. F. A. KETTLE, *Physical Inorganic Chemistry*, A

Coordination Chemistry Approach, pp. 95–237, Spektrum, Oxford, 1996.

eventually superseded by *crystal field theory* (CF).

About the same time that VB theory was being developed, CF theory was also being used by H. Bethe, J. H. van Vleck and other physicists to account for the colours and magnetic properties of hydrated salts of transition metals (1933–6). It is based on what, to chemists, appeared to be the outrageous assumption that the coordinate bond is entirely electrostatic. Nevertheless, in the 1950s a number of theoretical chemists used it to interpret the electronic spectra of transition metal complexes. It has since been remarkably successful in explaining the properties of M^{II} and M^{III} ions of the first transition series, especially when modifications have been incorporated to include the possibility of some covalency. (The theory is then often described as *ligand field theory*, but there is no general agreement on this terminology.)

In order to take full account of both ionic and covalent character, recourse must be made to *molecular orbital theory* (MO) which, like the VB and CF theories, originated in the 1930s. It has gained increasing ground with the development of powerful high-speed computers and the ready accessibility of software programmes which enable either semi-empirical or complex *ab initio* calculations to be carried out reliably and rapidly. There is still a place, however, for the pictorial representation of localized two-centre or three-centre bonds in elementary descriptions of bonding.

The fundamental assumption of MO theory is that metal and ligand orbitals will overlap and combine, providing they are of the correct symmetries to do so and have similar energies. In one approximation the appropriate AOs of the metal and atomic or molecular orbitals of the ligand, are used to produce the MOs by the linear combination of atomic orbitals (LCAO) method. Since combination of metal and ligand orbitals of widely differing energies can be neglected, only valence orbitals are considered.

In the case of an octahedral complex ML_6 , the metal has six σ orbitals, i.e. the e_g pair of the nd set, together with the $(n+1)s$ and the three $(n+1)p$. The ligands each have one

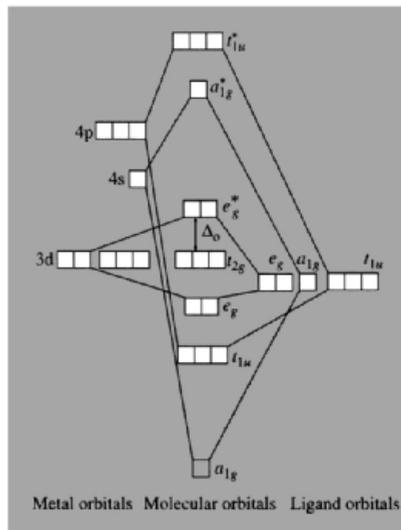


Figure 19.14 Molecular orbital diagram for an octahedral complex of a first series transition metal (only σ interactions are considered in this simplified diagram).

σ orbital (containing the lone-pair of electrons) and these are combined to give orbitals with the correct symmetry to overlap with the metal σ orbitals (Fig. 19.14). The 6 electron pairs from the ligands are placed in the six lowest MOs, leaving the non-axial, and hence non- σ -bonding, metal t_{2g} and the antibonding e_g^* orbitals to accommodate the electrons originally on the metal. This central portion of the figure is the same as the e_g/t_{2g} splitting defined in CF theory, with the difference that the e_g^* orbitals now have some ligand character which implies covalency. The lower in energy the ligand orbitals are with respect to the AOs of the metal the nearer is the bonding to the electrostatic extreme. Conversely, the nearer in energy the ligand orbitals are to the AOs of the metal the more nearly can the bonding be described as electron pair donation by the ligand as in VB theory. Indeed, the metal character of the bonding MOs is derived from just those metal orbitals used in VB theory to produce the d^2sp^3 hybrids which accommodate the electron pairs donated by the ligands.

If the ligand possesses orbitals of π as well as σ symmetry the situation is drastically changed

because of the overlap of these orbitals with the t_{2g} orbitals of the metal. Two situations may arise. Either the ligand π orbitals are empty and of higher energy than the metal t_{2g} , or they are filled and of lower energy than the metal t_{2g} orbitals (Fig. 19.15). The former in effect increases Δ_o , the separation of the t_{2g} and e_g^* orbitals, and is the more important case, including ligands such as CO, NO^+ and CN^- . This type of covalency, called π bonding or back bonding, provides a plausible explanation for the stability of such compounds as the metal carbonyls (pp. 926–9).

If Δ_o is large enough then electrons which would otherwise remain unpaired in the e_g

orbitals may instead be forced to pair in the lower t_{2g} orbitals. For metal ions with d^4 , d^5 , d^6 and d^7 configurations therefore two possibilities arise depending on the magnitude of Δ_o . If Δ_o is small (compared with electron–electron repulsion energies within one orbital) then the maximum possible number of electrons remain unpaired and the configurations are known as “spin-free” or “high-spin”. If Δ_o is large then electrons are forced to pair in the lower t_{2g} set and the configurations are known as “spin-paired” or “low-spin”. This is summarized in Fig. 19.16.

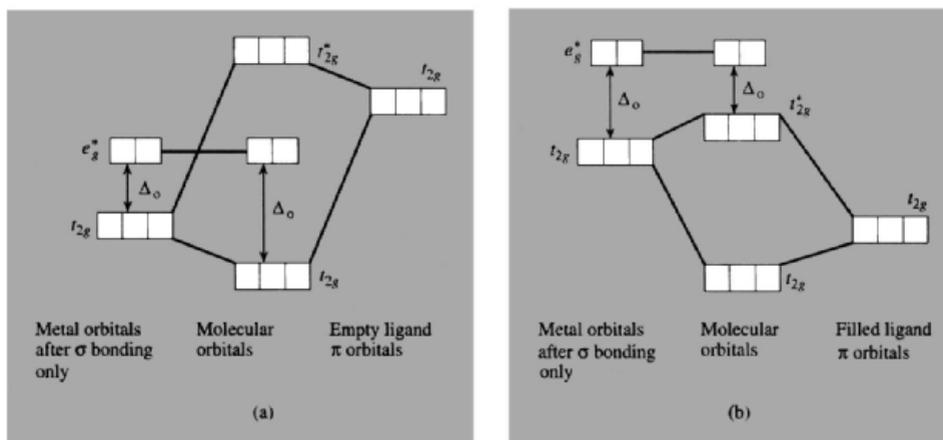


Figure 19.15 Possible effects of π bonding on Δ_o : (a) when ligand π orbitals are empty, and (b) when ligand π orbitals are filled.

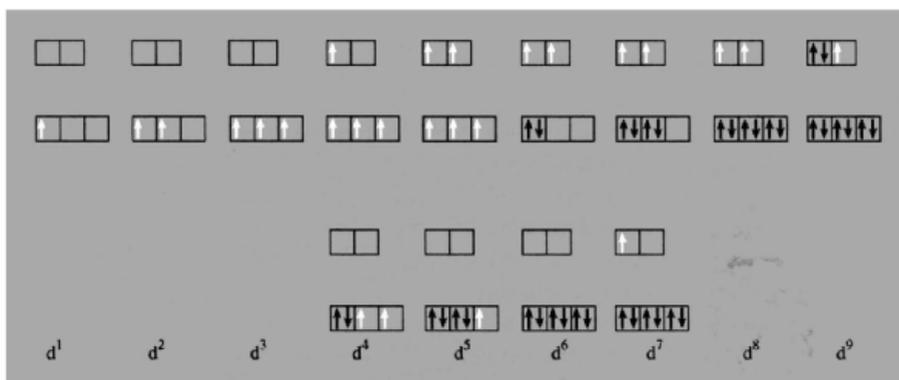


Figure 19.16 The possible high-spin and low-spin configurations arising as a result of the imposition of an octahedral crystal field on a transition metal ion.

Similar MO treatments are possible for tetrahedral and square planar complexes but are increasingly complicated.

19.7 Organometallic Compounds

This section gives a brief overview of the vast and burgeoning field of organometallic chemistry. The term *organometallic* is somewhat vague since definitions of *organo* and *metallic* are themselves necessarily imprecise. We use the term to refer to compounds that involve at least one close M–C interaction: this includes metal complexes with ligands such as CO, CO₂, CS₂ and CN[−] but excludes “ionic” compounds such as NaCN or Na acetate; it also excludes metal alkoxides M(OR)_n and metal complexes with organic ligands such as C₅H₅N, PPh₃, OEt₂, SMe₂, etc., where the donor atom is not carbon. A permissive view is often taken in the literature of what constitutes a “metal” and the elements B; Si, Ge; As, Sb; Se and Te are frequently included for convenience and to give added perspective. However, it is not helpful to include as metals all elements less electronegative than C since this includes I, S and P. Metal carbides (p. 297) and graphite intercalation compounds (p. 293) are also normally excluded. Further treatment of organometallic compounds will be found throughout the book under each individual element.

No area of chemistry produces more surprises and challenges and the whole field of organometallic chemistry continues to be one of great excitement and activity. A rich harvest of new and previously undreamed of structure types is reaped each year, the rewards of elegant and skilful synthetic programmes being supplemented by an unusual number of chance discoveries and totally unsuspected reactions. Synthetic chemists can take either a buccaneering or an intellectual approach (or both); structural chemists are able to press their various techniques to the limit in elucidating the products formed; theoretical chemists and reaction kineticists, though badly

outpaced in predictive work, provide an invaluable underlying rationale for various aspects of the continually evolving field and just occasionally run ahead of the experimentalists; industrial chemists can exploit and extend the results by developing numerous catalytic processes of immense importance. The field is not new, but was transformed in 1952 by the recognition of the “sandwich” structure of dicyclopentadienyliron (ferrocene).^(22,23) Compendia and extended reviews^(24–27) are available on various aspects, and continued progress is summarized in annual volumes.^(28,29)

The various classes of ligands and attached groups that occur in organometallic compounds are summarized in Table 19.2, and these will be briefly discussed in the following paragraphs. Aspects which concern the general chemistry of carbon will be emphasized in order to give coherence and added significance to the more detailed treatment of the organometallic chemistry of individual elements given in other sections, e.g. Li (p. 102), Be (p. 127), Mg (p. 131), etc.

²² G. WILKINSON, M. ROSENBLUM, M. C. WHITING and R. B. WOODWARD, *J. Am. Chem. Soc.* **74**, 2125–6 (1952). For some personal recollections on the events leading up to this paper, see G. WILKINSON, *J. Organometallic Chem.* **100**, 273–8 (1975).

²³ J. S. THAYER, *Adv. Organometallic Chem.* **13**, 1–49 (1975).

²⁴ G. WILKINSON, F. G. A. STONE and E. W. ABEL (eds.), *Comprehensive Organometallic Chemistry*, 9 Vols., Pergamon Press, Oxford, 1982, 9569 pp. E. W. ABEL, F. G. A. STONE and G. WILKINSON (eds.), *Comprehensive Organometallic Chemistry II*, 14 Vols, Pergamon Press, Oxford, 1995, approx. 8750 pp.

²⁵ F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, particularly Chaps. 22–29, pp. 1021–334.

²⁶ *Dictionary of Organometallic Compounds*, Chapman and Hall, London, Vols. 1–3, (1984), J. BUCKINGHAM (ed.); Supplement 1 (1985)–Supplement 5 (1989), Index (1990), J. F. MACINTYRE (ed).

²⁷ *The Chemistry of the Metal–Carbon Bond*, Wiley, Chichester, Vols. 1–3 (1985), F. R. HARTLEY and S. PATAI (eds.); Vol. 4 (1987), Vol. 5 (1989), F. R. HARTLEY (ed.).

²⁸ F. G. A. STONE and R. WEST (eds.), *Advances in Organometallic Chemistry*, Academic Press, New York, Vol. 1 (1964)–Vol. 40 (1996).

²⁹ *Organometallic Chemistry Reactions*, Wiley, Vol. 1, (1967)–Vol. 12 (1981).