An Introduction to the Chemistry of Molybdenum

M.L.H.Green

Inorganic Chemistry Laboratory,
South Parks Road,
Oxford,
OX1 3QR

AN INTRODUCTION TO THE CHEMISTRY OF MOLYBDENUM

M.L.H.GREEN

2.1 INTRODUCTION

The chemistry of molybdenum is immensely rich and diverse. Molybdenum is essential for life, the element has many important applications in industry, and molybdenum chemistry has often been involved in crucial developments in the understanding of the fundamental principles of the theory and practise of the chemical sciences.

The purpose of this Chapter is to identify the important   physical and chemical properties of molybdenum which combine to give rise to the both the general and the unique features of its chemistry.

The approach adopted will be to present essential properties of molybdenum, to outline the broad features of molybdenum compounds and their reactivity by using a fundamentally new method of classification and, finally, to exemplify some areas of particular interest.

2.2 PROPERTIES OF THE ELEMENT

The position of molybdenum in the periodic table in shown in Figure 2.1. Fundamental properties of molybdenum and the other Group VI metals and other useful data are given in the Table 2.1.

Molybdenum has six valence electrons and nine atomic orbitals of energy suitable for use in chemical bonding, namely the 5 x 4d, 1 x 5s and 3 x 5p = 9 orbitals. Molybdenum has a moderate Pauling electronegativity (1.8) and, in consequence, all six valency electrons are available for formation of chemical bonds contrast the more electronegative and later d-block transition metals,

3	4	5	6	7	8	9	10	11	12
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.995	47.88	51.9415	51.996	54.938	55.847	58.9332	58.69	63.546	65.39
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.9059	91.224	92.9064	95.94	(98)	101.07	102.906	106.42	107.868	112.41
57	72	73	74	75	76	77	78	79	80
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Table 2.1 Some properties of chromium, molybdenum and tungsten

Property		Cr	Mo	W
Atomic number		24	42	74
Electronic configuration		$[Ar]3d^54s^1$	$[Kr]4d^55s^1$	$[Xe]4f^{14}5d^56s^1$
Valency orbitals		3d 4s 4p	4d 5s 5p	5d 6s 6p
Ionisation enthalpies	1st	652.5	685	770
$\Delta H^{\epsilon}_{ion}$ (kJ mol^{-1})	2nd	1592	1558	1710
	3rd	3056	2618	-
	4th	4900	4480	-
Electronegativity		1.6	1.8	1.7
Radius of atom in metal (pm)		128	139	139
Ionic radii for six co-ordination (O.S.), (pm)		44 (VI) - 80 (II)	59 (VI) - 69 (III)	60 (VI) - 66 (III)
MP/°C		1900	1620	3380
BP/°C		2690	4650	5500
Temperature at which evaporation is 1 gh^{-1}cm^{-2},		1480	2610	3320
ΔH_{vap}/ kJ mol-1		342($\pm$ 6)	590 ($\pm$ 21)	824 ($\pm$ 21)
$\Delta H_{formation}$ (monatomic gas)/ kJ mol-1		397 9($\pm$ 3)	664 ($\pm$13)	849 ($\pm$ 13)
Atomic weight		51.009	95.94	183.85

e.g. nickel, palladium and platinum, which normally use up to two electrons, rarely four and only very exceptionally six (PtF_6) of the ten electrons in their nd, (n+1)s and (n+ 1)p shells).

The bonding in all discrete molybdenum molecules or cations and anions containing molybdenum is predominantly covalent and is best described by molecular orbital (M.O.) theory. The bulk properties of molybdenum compounds containing delocalised electronic structures are best discussed using band theory.

Since the energies of the molybdenum valency orbitals are suitable for the formation of bonds there is a marked tendency for molybdenum to fill these orbitals which results in a 2 x 9 = 18 electron environment. In other words, molybdenum in the absence of other constraints has favourable energetic reasons to obey the 18-electron rule. The size of molybdenum is such that for many molybdenum compounds the observed co-ordination number is six. When the six ligands are neither very bulky nor unusually small then a co-ordination number of six is comfortable such that there is neither steric overcrowding of the metal centre, nor a degree of steric unsaturation that would permit low energy barriers to further reaction. Contrast the larger lanthanide elements where co-ordination numbers of seven and eight are common. Lower co-ordination numbers may reflect the requirements of the 18-electron rule, e.g. $Mo(NO)_4$, or, the presence of bulky ligands. Higher co-ordination numbers occur in the presence of small (or compact ligands) and especially when this is combined with an 18-electron environment, e.g. $Mo(PMe)_4H_4$ and $[Mo(CN)_8]^{4-}$.

Molybdenum metal is highly refractory (b.pt 4650°C) which reflects the availability of the valency orbitals and of six electrons for the formation of metal-metal bonds.

2.3 CLASSIFICATION OF MOLYBDENUM COMPOUNDS

This classification is concerned with those compounds of molybdenum which are well described by the covalent model, including infinite lattice compounds such as $[MoO_3]_n$ which may be described as covalent polymers.

In order to gain a broad overview of the dominant features of molybdenum chemistry we have constructed the diagram shown in Figure 2.2.

ELECTRON NUMBER E.N.

VALENCY NUMBER	12	13	14	15	16	17	18
0	MoL_3		MoL_4		MoL_5		MoL_6
1		MoL_3X		MoL_4X	MoL_5X		
2	MoL_2X_2		MoL_3X_2		MoL_4X_2		MoL_5X_2
3		MoL_2X_3		MoL_3X_3		MoL_4X_3	
4	$MoLX_4$		MoL_2X_4		MoL_3X_4		MoL_4X_4
5 (V.N.)		$MoLX_5$		MoL_2X_5		MoL_3X_5	
6	MoX_6		$MoLX_6$		MoL_2X_6		MoL_3X_6
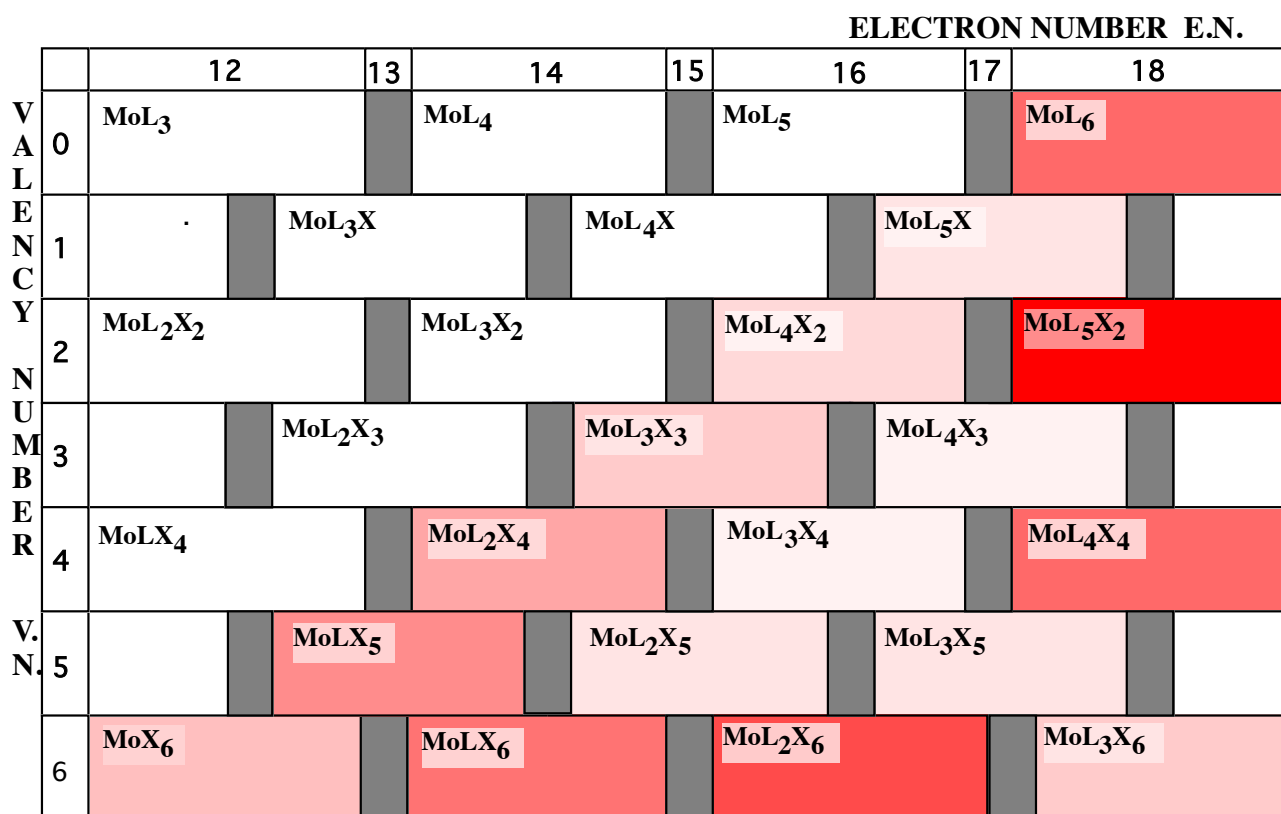
Figure 2.2 The MLX plot for molybdenum

This shows the abundance of different molybdenum compounds according to the nature of the ligand environment about the molybdenum. Before consideration of the implications of this diagram it is necessary to explain how the molybdenum compounds are classified and organised and how the Figure 2.2 is constructed.

The method of classification given below differs in important respects from the normal approach used to organising inorganic compounds. Thus the concept of formal *oxidation state* (or oxidation number) is abandoned, and whilst *co-ordination number* is retained as the 'number of atoms of the ligands which are attached to the central atom' the co-ordination number of a compound is not used for the organisation of the compounds. The use of oxidation state as a classifying principle presents several difficulties in the discussion of the chemistry of an element as complex as that of

molybdenum. Thus, in assigning the oxidation state of a compound any homopolar bonds present are neglected (by definition) and further there is confusion and debate about the inclusion of many other bonds in the determination of oxidation state (O.S.), especially in organometallic compounds. Consider the series of compounds $[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}R]$], where

$$R = \quad Cl \quad Br \quad H \quad CH_3 \quad SiR_3 \quad HgCH_3 \quad \text{and } Mo(\text{or } W)(CO)_3(\eta\text{-}C_5H_5).$$
The O.S. = +2 +2 +2 +2 ?+2 ?+1 and +1(or ?) (by definition), respectively.
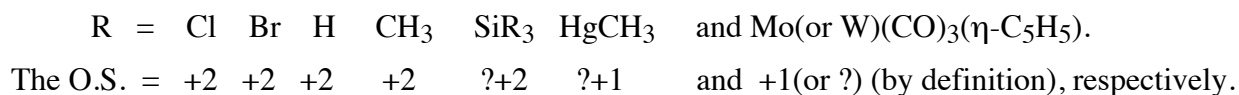
Within the last twenty-five years very many molybdenum compounds with homopolar Mo-Mo bonds have been identified. Similarly, there are many molybdenum compounds with strong covalent bonds to other elements which are defined as metals. The oxidation state principle is not useful for the classification of these compounds anymore than is for the classification of organic compounds and therefore formal oxidation states are not used in this manner in organic chemistry. Thus, consider the series CCl_4 (4), $CCl_3\text{-}CCl_3$ (3), $CCl_2(CCl_3)_2$ (2) and the (hypothetical) $C(CCl_3)_4$ (0!). The O.S. for the identified carbon C in these compounds is given in parenthesis. In the formal definition of oxidation states homopolar metal-metal bonds simply are not counted even though a metal-metal bond is not fundamentally different from any other covalent bond between the metal and another atom.

Likewise the concept of co-ordination number becomes confusing for compounds in which there are ligands which do not bond in a simple 'two-electrons per bond' manner. For example, the series of compounds $Mo(CO)_6$, $Mo(\eta\text{-}C_6H_6)(CO)_3$ and $Mo(\eta\text{-}C_6H_6)_2$ have co-ordination numbers 6, 9, and 12 respectively but the η-benzene ring is often referred to as a 'pseudo three co-ordinate' ligand so that in these three compounds they are deemed to be 'six co-ordinate'. The $\eta^5\text{-}C_5H_5$ (η-cyclopentadienyl) ligand is also referred to as 'pseudo three co-ordinate even when it clearly is has five carbon atoms bonding equally to a metal centre. There are very many molybdenum compounds with otherwise chemically similar features where the co-ordination number does not relate in a simple manner.

The concepts of oxidation state and co-ordination number have been central to the organisation of inorganic compounds since the earliest days when the ionic bonding in simple salts was first recognised. The concept remained useful during the early development of co-ordination chemistry since initially most ligands were relatively simple, e.g. the halogens, CN, O, OH, H_2O, NH_3, etc. In short, the first classifications of inorganic compounds where made on the basis that all compounds could be described as ionic, i.e. as a form of sodium chloride.

For the reasons given above in now seems that a new method of classification which would apply to all molecular compounds and covalent polymers would be more appropriate than the conventional ionic model. This new approach is given below and can be described as a classification and organisation of molybdenum compounds made on the basis that all the compounds can be described as being essentially covalent, i.e. as a form of methane.

A further aspect of the classification reflects the increasing recognition that in many of the diverse ligand environments of molybdenum compounds the 18-electron rule is obeyed. This was not apparent for the historically early ligand environments.

In the new 'covalent based' approach the molybdenum compounds are classified as follows:-

(a) According to the *total number of electrons (E.N.) involved in primary bonding in the molybdenum compound*, i.e. the formal electron count at the metal centre.

Thus, E.N.(for Mo) = 6 (from the Mo atom) + the total number of electrons contributed to the Mo by the ligands. [N.B. Do not confuse E.N. with electronegativity.]

(b) According to the *number of electrons required by the ligands in the formation of the molybdenum-ligand bonds*.

A general classification of many of the atoms and molecular groups which are known to bond as ligands to molybdenum is shown in Table 2.2. The classification shows x, the number of electrons required by each ligand and the total number of electrons donated to the molybdenum by the ligand (denoted L.N.).

The Table 2.2 also assigns the *class* of each ligand (in column 3). The *class* of a ligand is defined in terms of the different *bonding functions* of the ligand, as described below. The identification of the ligand class is crucial to the method of classification. For many ligands the nature of the primary metal-ligand bonding is well understood. In other ligands there may be ambiguities and these, as for the oxidation state formalism, expose the limitations of the formalism. Example of non-innocent ligands are discussed in section 2.3.2.

2.3.1 Definition of the class of a ligand

The atoms of a ligand which are directly involved in primary bonding to the metal centre are called the '*ligating atoms*'. There are three possible *bonding functions* for ligating atom(s) of a ligand and these are designated the X-function, the L-function and the Z-function.

(i) The X-function

This is a singly occupied orbital on the ligand which requires one electron from the molybdenum centre to form a two electron covalent bond. The number of X-functions (written as x) on a ligand is represented by X_x. Normally the subscript when x = 1 is treated as default, i.e. the hydrogen ligand is a monofunctional X ligand. A ligand which has two singly occupied orbitals, i.e. two X-functions is designated as X_2, an example is the carbene ligand $=CR_2$, see Figure 2.3. A X-ligand function most commonly occurs with σ-symmetry (local symmetry). However, π−symmetry X-functions are found, e.g. in the linear NR ligand, in the terminal oxo ligand, and in the singly occupied HOMO of the η-cyclopentadienyl ligand.

(ii) The L-function

This is a filled orbital containing two electrons which are donated to an empty orbital on the metal. The number of L-functions (*l*) on the ligand is represented by L_l . A ligand with a single L-function (lone-pair) is represented as L (subscript taken as default). A ligand with two L-functions,

e.g. $Me_2PCH_2CH_2PMe_2$ is designated as L_2, etc., see Figure 2.4. An L-function can occur with local σ-symmetry (e.g. NH_3), or with π-symmetry (e.g. in the linear imido NR ligand, the planar NR_2 ligand and the degenerate HOMO's in the η-benzene ligand.

 (iii) The Z-function

This is an empty orbital on the metal which can accept the donation of an electron pair from the molybdenum. The number of Z-functions (z) is represented by Z_z. The molecule BR_3 has one Z-function. Compounds of molybdenum containing such σ-bonding Z_z ligands are rare and will not be further discussed in this Chapter. Many ligands have an empty orbital normally of π- or δ-symmetry which can act as an acceptor for a filled orbital of appropriate symmetry on the metal.. Examples are the carbon monoxide ligand (the $p_π{}^*$-orbitals) or, in the η-benzene ligand, the doubly degenerate, empty δ-symmetry molecular orbitals. If this 'back-donation' is thought to contribute a sufficient energy to the metal ligand bond then the ligand orbital should be deemed to be acting as a Z-function. However, normally such back-donation interactions are not regarded as taking part in primary bonding and are ignored in the classification. In the very large majority of cases compounds which appear to contain a Z-ligand also contain an L-ligand. In these cases the class of the compound is defined using the rule $LZ→X_2$. For example, the fragment $H_3N→M→BR_3$ appears to classify as LMZ. However, the correct electron distribution is better represented by H_3N^+- M - B^-R_3, and, therefore, the class of the M centre is MX_2.

Examples of representative ligands and their class are shown for mono- and poly-functional ligands in Figures 2.3 and 2.4, and for η-bonded hydrocarbon ligands in Figure 2.5. When a single ligating atom has more than one X or L function, e.g., X_2 or LX_2 then these are called *polyfunctional ligand atoms*. Polyfunctional ligand atoms should not be confused with polyfunctional *ligands* , i.e. polydentate ligands with more than one ligating atom.

It should be noted that many ligands can vary in the manner in which they bond to a metal centre in different molecules. For example, the cyclopentadienyl ligand may bond in either the $η^1$, $η^3$ or $η^5$ modes. The amido ligand NR_2 may be pyramidal, and therefore, an X-function ligand, or, planar when it acts as a LX-function ligand. It may be necessary to ascertain the structure of a metal ligand system before allocating a class to the ligand. Indeed, in some cases not only structural data but magnetic, spectroscopic or other physical data may be required to unambiguously identify a ligand class. Even then uncertainties may remain, for example, when is an η-olefin a X_2 or L ligand?

2.3.2 Definition of the class of a molybdenum compound

A general representation of **all** neutral covalent compounds of molybdenum is:-

$$MoL_lX_XZ_Z$$

where l, x, and z are the number (including zero) of L, X, and Z functions of the ligands attached to the molybdenum. The class of a particular compound is said to be defined when the values of l, x and z are specified.

A selection of molybdenum compounds is listed in Table 2.3 where they are organised according to their MLX class, e.g. MoL_6 (i.e. $MoL_6X_oZ_o$), etc.

Figure 2.5. Showing the classification of representative unsaturated hydrocarbon ligands. The Hückel M.O.'s of each ligand are given on an arbitrary energy scale. A M.O. of the ligands which is filled (by two electrons) acts as a two-electron donor to the metal centre and is, therefore, an L-function orbital. An orbital which contains only one electron (half-filled) acts as a one-electron donor. It requires one electron from an appropriate orbital of the metal centre and, therefore, is an X-function orbital. The η-cyclopropenyl and η-cycloheptatrienyl ligands have a doubly degenerate set of orbitals in which there is only one electron. Application of the rule $LZ \rightarrow X_2$, which is discussed in section 2.3.1. (ii), leads to the classification of these ligands as having the classes X_3 and L_2X_3, respectively, i.e. for the cycloheptatrienyl ligand, η-C_7H_7, the apparent class L_3XZ reverts to L_2X_3 and, for η-cyclopropenyl, $LXZ \rightarrow X_3$.

The Table 2.3 also includes cations and anions. The MLX class of cations and anions is identified in exactly the same way as for neutral molecules except that for the purposes of inclusion in the MLX plots the *equivalent neutral class* (E.N.C.) is determined. For many compounds the assignment of the equivalent neutral class can be simply illustrated.
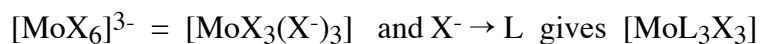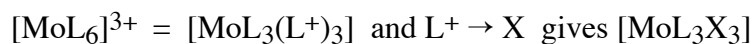Consider the following molybdenum compounds:

$$[MoL_6]^{3+} \; [MoL_5X]^{2+} \; [MoL_4X_2]^+ \; [MoL_3X_3] \;\; [MoL_2X_4]^- \; [MoLX_5]^{2-} \; [MoX_6]^{3-}$$
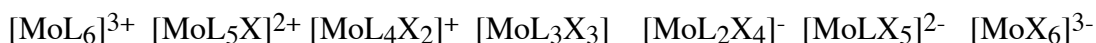
they all have E.N. = 15 and they all have the value $l + x = 6$. Therefore they must **all** be equivalent to the neutral class MoL_3X_3. Indeed, inspection of the MLX plot given in Figure 2.2 shows that compounds with $l + x = 6$ and E.N. = 15 must have V.N. (i.e. x) = 3.
A simple rule which converts most cations to the equivalent neutral MLX class is that $L^+ \rightarrow X$. Correspondingly, most simple anions convert to the equivalent neutral class by the rule $X^- \rightarrow L$.
For example,
$$[MoL_6]^{3+} \; = \; [MoL_3(L^+)_3] \;\text{ and } L^+ \rightarrow X \;\text{ gives } [MoL_3X_3]$$

$$[MoX_6]^{3-} \; = \; [MoX_3(X^-)_3] \;\text{ and } X^- \rightarrow L \;\text{ gives } [MoL_3X_3]$$

There are rare examples of anions which have only L ligands. An example is $[Mo(CO)_5]^{2-}$. For such anions which have no X-function ligands the rule for reduction to the equivalent neutral class in $L^- \rightarrow LX$. Therefore,

$$[Mo(CO)_5]^{2-} \; = \; [Mo(CO)_3(CO^-)_2] \; = \; [MoL_3(L^-)_2] \;\text{ and } L^- \rightarrow LX \text{ gives } \; [MoL_5X_2]$$

This rule may seem surprising at first sight. However, consider the fact that CO^- and NO are isoelectronic. Therefore $[Mo(CO)_5]^{2-}$ and $[Mo(CO)_3(NO)_2]$ are isoelectronic. Since NO is a LX ligand the latter dinitrosyl classifies as $[MoL_5X_2]$.
There are no stable molybdenum cations which have only X-ligands and no L-ligands, i.e. the class $[MX_x]^{n+}$. Rare examples of cations in this class are ammonium cations $[R_4N]^+$, and $[PCl_4]^+$ in $[PCl_4]^+[PCl_6]^-$.

The rule for the reduction to the E.N.C. for such L-free cations is $X^+ \rightarrow Z$. Therefore, $[PCl_4]^+ = [PX_3(X^+)] = [PX_3Z]$.

A more detailed consideration of the reduction of a cation or an anion to the equivalent neutral class is given in the Appendix.

2.3.3 Determination of MLX class of a molybdenum compound containing non-innocent ligands and related aspects

The identification of the MLX class of a molybdenum compounds is normally a straightforward matter of looking up the class of the various ligands in the compounds, as listed in the Table 2.2 . However, not all ligands in a compound may be unambiguously classified without a detailed knowledge of the electronic structure of molecule and this may not be available. Examples where ambiguities arise are shown in the Figure 2.6. These include ligands which are non-innocent, also those polynuclear compounds where the degree of metal-metal bonding in unclear, and the widespread problem of deciding whether donor lone pair (L-functions) of ligating atoms do or do not take part in primary metal-ligand bonding. This problem is especially prevalent for ligating oxygen atoms, as illustrated in Figure 2.6. Where it is not possible to decide the class of a compound unambiguously then this may be indicated by providing a choice or range of values for l/or x in the ML_lX_x class. For example, consider the binuclear compounds $[M_2Cl_3(\mu\text{-}Cl)_3]^{3-}$, where M = Cr, Mo or W, shown in Figure 2.6 (iii). The chromium compound is paramagnetic corresponding to three unpaired electrons. Therefore the class of each chromium is CrL_3X_3 , i.e., d^3 (if the three electrons of the anion are deemed to be located on the three bridging chloro ligands then these become bent L-μ-L ligands (as in bridging R_2S), i.e. the anion may be written as $[X_3CrL_3\text{-}\mu\text{-}L_3CrX_3]$. The tungsten analogue is diamagnetic due to the tungsten-tungsten triple bond. Thus the class of both the tungsten moieties is WL_3X_6. The molybdenum compound is weakly paramagnetic so the Mo-Mo bond order is indeterminate and therefore the class is also indeterminate, e.g. MoL_3X_{4-6}.

For most of the compounds in the classes MoL_lX_6 which have oxo ligands the choice of the value of l depends on whether it is considered that the 'lone pairs' on the oxo ligands contribute to the primary bonding or not (see Section 2.6 and Figure 2.6).

2.3.4 Definition of Electron Number, Valency Number, and Ligand Bond Number

We now identify three quantities I - III which are based on the definition of the general class of all molybdenum compounds as MoL_lX_x. The Z_z ligands are neglected since there are no known compounds of molybdenum for which their representation is appropriate.

$$\text{I Valency Number (V.N.)} = x$$

(where x is the number of X-functions on the ligands).

$$\text{II Ligand Bond Number (L.B.N.)} = l + x$$

(the sum of the number of L- and X-functions).

$$\text{III Electron Number (E.N.)} = \mathbf{Me} + 2l + x$$

$\mathbf{Me}$ is the number of electrons in the valency shell of the element M. For the Group 6 element molybdenum, $\mathbf{Me} = 6$.

We also define the magnitude of the number n of d^n as n = $\mathbf{Me}$ - x (-2z, where appropriate).
A summary of the new definitions given above is given in Table 2.4.

Table 2.4. Summary of new definitions for the classification of covalent compounds

Term	Short Symbol
A one-electron ligand function	X
Number of X ligands	x
A two-electron ligand function	L
Number of L ligands	l
Electron number of ligand of class L_lX_x	L.N. = $2l + x$
A mono-functional X_x -ligand-atom	$X_{x=1}$
A poly-functional X_x -ligand atom	$X_{x>1}$
General representation for the class of a covalent compound	ML_lX_x
Electron Number of Mo in MoL_lX_x	E.N. = 6 (for Mo) + $2l + x$
Valency Number	V.N. = x
Ligand Bond Number	L.B.N. = $l + x$
n of d^n	n = 6(for Mo) - x + (2x)
Number of electrons in the valency shell of the metal	$\mathbf{Me}$
Equivalent Neutral Class	E.N.C.

For many compounds the magnitude of V.N. is the same as that of the formal oxidation state of the metal in the compound. However, they are not always identical, for example the definition of V.N. includes homopolar bonds (e.g. metal-metal bonds). Further, unlike the formal oxidation state, V.N. can not, by definition, be negative. In the rest of this Chapter the value of x for a compound (i.e. the valency number) will be referred to as the x-valency, for example, a compound where x = 4 is referred to as a tetravalent compound.

It can also be seen that the quantity $l + x$, the Ligand Bond Number will be identical to the Co-ordination Number for those compounds which have as ligands *only* those which require one or two electrons per ligating atom (mono-functional ligands). However, the L.B.N. of a compound is different from the classic co-ordination number when the metal ligand bonding is more complex, e.g. for η-hydrocarbon ligands, NO, =O, and generally for poly-functional ligands).

2.4 THE CONSTRUCTION OF E.N. VERSUS V.N. PLOTS (CALLED MLX PLOTS)

The Figure 2.7 consists of a plot of the number of electrons required by the ligands (x) along the abscissa (x-axis) and the total number of electrons in the valency shell of the molybdenum atom (E.N.) along the ordinate (y-axis). This gives a matrix of boxes of which half can be uniquely labelled with a specific MLX class of a molybdenum compound. Thus when x = 0 and E.N. = 18 then the compounds must be MoL_6: when x = 6 and E.N. = 12 then the compounds must be MX_6, etceteras. **All** possible classes of molybdenum compounds for which x = 0 - 6 and E.N. = 12 - 18 are represented in the Figure 2.7. An alternative form for MLX plots which emphasises the 'no-go' areas is given in the Appendix (Figure A.1).

The grey pillars represent boxes for which it is not possible to have a compound. For example, when V.N. is even (x = 0, 2, 4 or 6) and **Me** is even (i.e. 6 for Mo) then the E.N. cannot be odd (since E.N. = 6 + $2l$ + x). Likewise, when V.N. is odd (x = 1, 3 or 5) then since **Me** = 6 the Electron Number must also be an odd number.

Also shown on Figure 2.7 are arrows along the diagonals with constant values for l + x . In other words compounds with the same Ligand Bond Number (L.B.N.) lie on these diagonals. The Ligand Bond Number corresponds to the co-ordination number when all the ligands have monofunctional ligand atoms. It is obvious that the form of MLX plot in Figure 2.7 depends only on the possible given values for x of 0 - 6 and values for E.N. from 12 to 18. Therefore, this plot is equally appropriate for elements which have six valency electrons and nine valency orbitals, i.e. for Cr, Mo and W.

2.4.1 The construction of the MLX plot for molybdenum

The construction of MLX plot specific to molybdenum proceeds by first identifying the individual ML_lX_x class for (in principle) all compounds of molybdenum which have been prepared and suitably characterised. A selection of molybdenum compounds organised according to their MLX class is given in the Table 2.3.

There are probably no known compounds of molybdenum which lie outside the limits given in Figure 2.7. For example, it is doubtful there are any, compounds of molybdenum for which it can be argued that E.N. = 19 or 20.
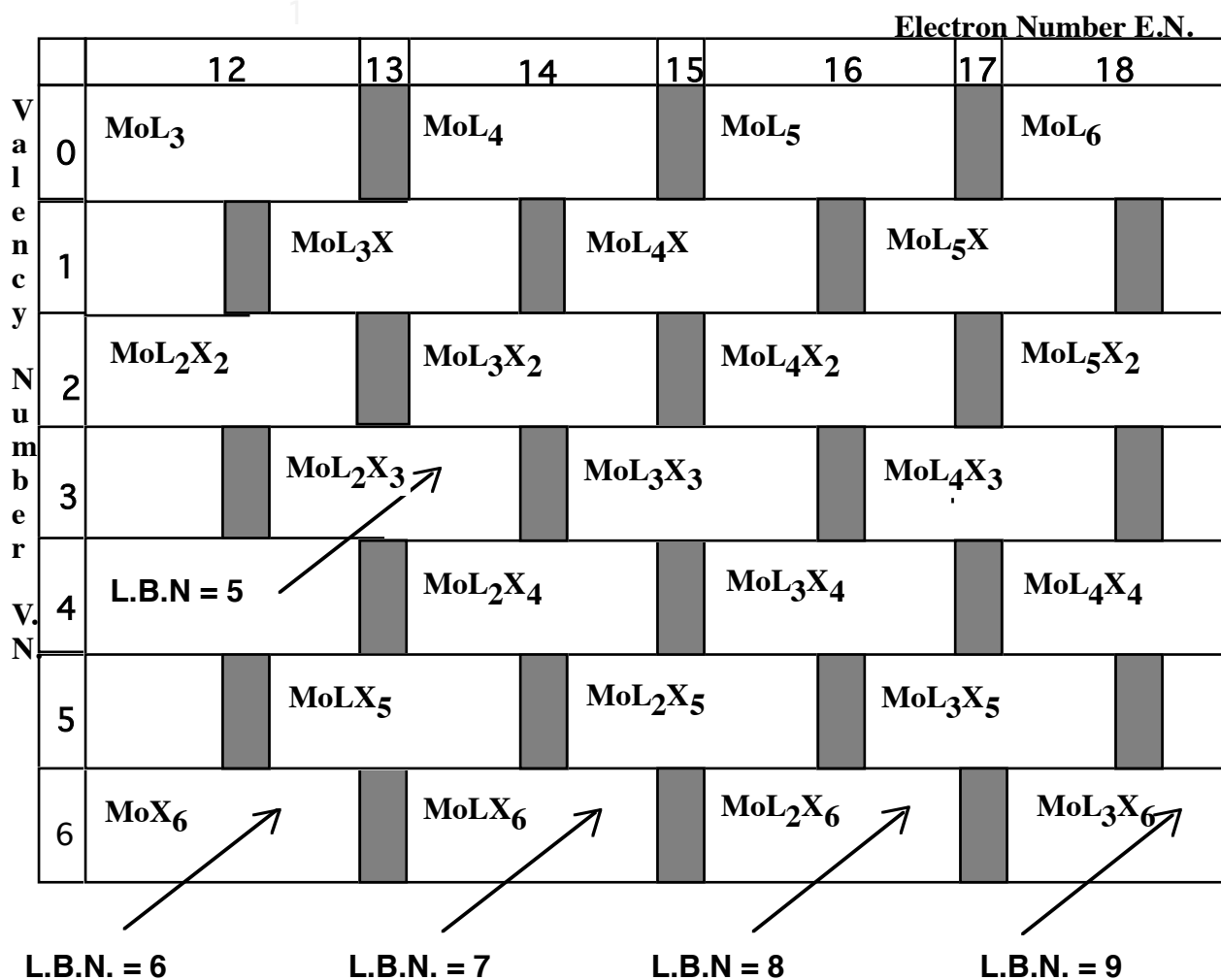
Figure 2.7 The general MLX plot for molybdenum showing possible classes for all available V.N. and for values of E.N. from 12 to 18.

The compound [Mo(η-C_5H_5)$_2$NR] is an example for which the assignment of the E.N. is not straightforward but the evidence indicates that the p_π-lone-pair on the imido nitrogen makes little contribution to the Mo=N bonding but rather it slightly destabilises the Mo-η-C_5H_5 bonding.

Once a list of all appropriate molybdenum compounds and their MLX class has been identified, then the total number of compounds in each class is counted and the relative *populations densities* of each class is represented in the MLX plot by colour intensity (or by shading), as shown in Figure 2.2. The deeper the shading the greater the population density.

2.4.2 General comments on the MLX plot for molybdenum

The MLX plot represents the relative abundance of the different classes of molybdenum compounds as a function of all the known ligand environments for molybdenum. The pattern of the distribution and relative intensities of the occupations of the various MLX boxes is characteristic for molybdenum and (except for tungsten) differs markedly from the MLX plot of all other elements. The MLX plot for palladium is given in the Appendix to illustrate this point. The MLX plot condenses an enormous amount of factual information and in turn reveals the important major characteristics of molybdenum chemistry.

Before we discuss and interpret the MLX plot for molybdenum we will describe the relationships of the MLX plot to reactivity, to reaction mechanisms and to the functional group properties of the various ligands listed in Table 2.2.

2.4.3 The relationship between the MLX plot and properties of ligands

As mentioned above, the MLX plot for molybdenum is derived from all the known ligand environments. The MLX plots for all the other d-block transition metals contain compounds with many of the same or similar ligand environments as for molybdenum. Close examination of the MLX plots of ALL the d-block metals shows that particular ligand environments occurs in clearly identifiable regions of the MLX plot and they are substantially *independent* of the nature of the metal. The regions for individual ligand environments are called *ligand domains*. For example, the ligand domains of the ligands CO, η-benzene and olefins are very similar. Likewise the oxo and fluorine ligands have similar domains. Five principle ligand domains are illustrated in Figure 2.8. They reflect both steric and electronic properties of the ligands. For example, inspection of the individual compounds (see the data for ML_6 in Table 2.3 and Figure 2.8) which occur in the top right hand corner of the MLX plot shows that ligands such as CO, η-benzene, PF_3, N_2, olefins, PR_3, RNC , and combinations thereof, are dominant. The occurrence of these, at first sight, very disparate compounds in the same ligand domain is associated with the presence on the ligands of empty orbitals which can withdraw electron density from the metal centre by (secondary) bonding These acceptor orbitals normally are of π- or δ-symmetry.
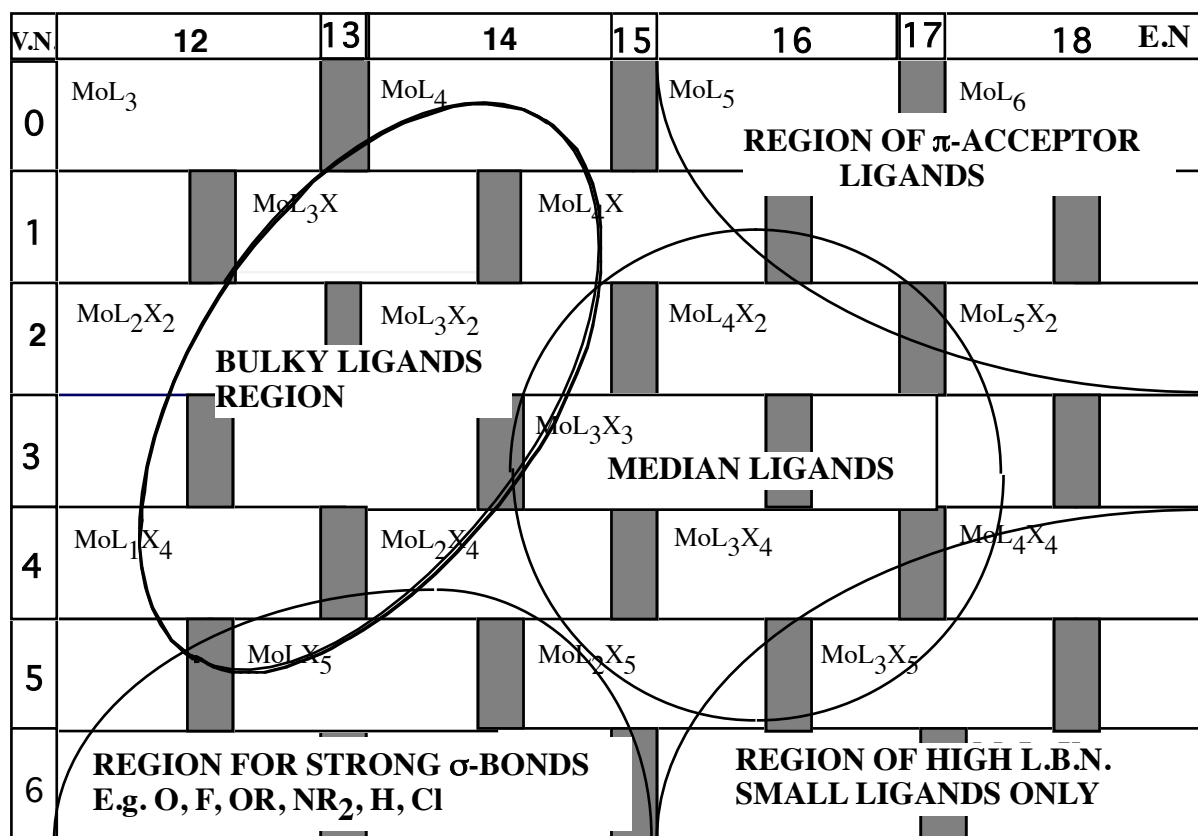

Figure 2. 8 The distribution of major ligand domains

The identification of ligand domains in the MLX plot also relates to aspects of reactivity of (molybdenum) compounds. For example, a compounds will react to give a product whose class lies towards the center of the ligand domain of the product. When the ligand domain of a compound lies on the periphery of a ligand domain then it can undergo reations which will moe it towards the centre of the ligand domain. For example, $[Mo(\eta\text{-}C_6H_6)_2]^+$ readily reduces to $[Mo(\eta\text{-}C_6H_6)_2]$.

2.4.4 A classification of reactions and the use of MLX plots for discussing possible reaction pathways.

All possible reactions of a molybdenum compound MoL_lX_x can be classified in terms of the changes in the values of l and or x in the product. For example,

$$Mo(CO)_4(PR_3)_2 + I_2 \text{ ------>} \quad Mo(CO)_3(PR_3)_2I_2 + CO$$
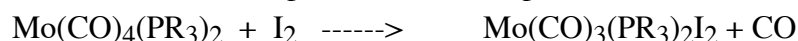
may be represented in terms of the MLX class of the compounds , e.g.

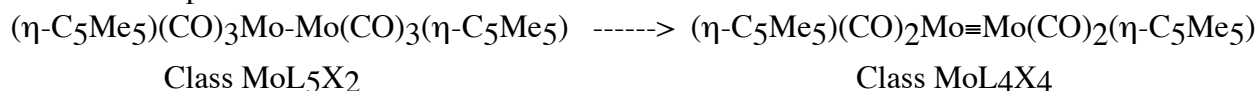$$MoL_6 + X_2 \quad \text{------>} \quad MoL_5X_2 + L$$
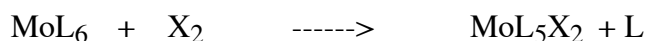
and, therefore, the overall change for the reactant in general terms is the loss of one L-function (ligand) and the gain of 2X-functions (ligand(s)). Thus the reaction may be written as:-
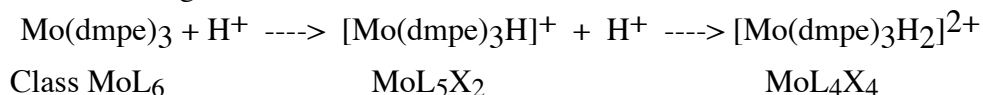
$$ML_l \xrightarrow{-L, +X_2} M_{l-1}X_2$$
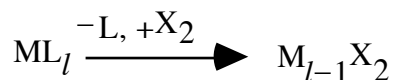
This reaction is called a replacement-addition reaction, i.e. replacement of L by X_2. It should be noted that this reaction is an 'oxidation' reaction since x becomes larger (by 2). However the phrase oxidative-replacement addition becomes too cumbersome.

Another example is the reaction

$(\eta\text{-}C_5Me_5)(CO)_3Mo\text{-}Mo(CO)_3(\eta\text{-}C_5Me_5)$ ------> $(\eta\text{-}C_5Me_5)(CO)_2Mo\equiv Mo(CO)_2(\eta\text{-}C_5Me_5)$

$\qquad\qquad$ Class MoL_5X_2 $\qquad\qquad\qquad\qquad\qquad\qquad$ Class MoL_4X_4

This is also a replacement-addition reaction (-L, +X_2) i.e. loss of CO followed by the addition of two X-bonds to each metal centre.

 The proton addition reaction, which does not increase the electron number E.N., is a also replacement-addition reaction (-L, +X_2). It is a quite general reaction for 18e transition metal compounds with d^n values n = 2 or more providing that the electrons have low ionisation energies. Such compounds are often described as having "electron rich or high energy" metal centres. When the metal centre is exceptionally electron rich then the molecule can undergo a rare consecutive diprotonation reaction, e.g.

$$Mo(dmpe)_3 + H^+ \text{ ---->} [Mo(dmpe)_3H]^+ + H^+ \text{ ---->} [Mo(dmpe)_3H_2]^{2+}$$

$\qquad$ Class MoL_6 $\qquad\qquad\qquad$ MoL_5X_2 $\qquad\qquad\qquad\qquad$ MoL_4X_4

The reactions given below shows the sequential addition of three electrons to MoF_6. Each forward step is a one-electron reduction and this causes the class to change by -X, +L at each step. This reaction is called a reductive-replacement reaction (commonly called a 1-electron reduction),
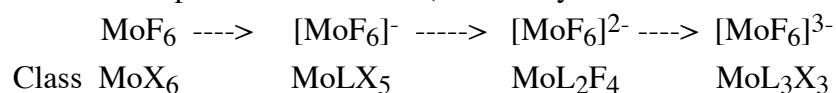
$$MoF_6 \text{ ---->} [MoF_6]^- \text{ ----->} [MoF_6]^{2-} \text{ ---->} [MoF_6]^{3-}$$

$\qquad$ Class MoX_6 $\qquad\qquad$ $MoLX_5$ $\qquad\qquad$ MoL_2F_4 $\qquad\qquad$ MoL_3X_3

Table 2.5. Classification of reactions by the reaction products

Change in L_l and/or X_x	Change in E.N. : V.N.		Name of reaction
$-L_l$ then $+L'_l$	0	0	L_l -substitution
$-X_x$ then $+X'_x$	0	0	X_x -substitution
$+L_l$	$+2l$	0	L_l-addition
$-L_l$	$-2l$	0	L_l-elimination
$+X_x$	$+x$	$+x$	X_x-oxidative-addition
$-X_x$	$-x$	$-x$	X_x-reductive-elimination
$+L$ then $-X$[a]	$+1$	-1	reductive-replacement[a]
$-L$ then $+X$[b]	-1	-1	oxidative-replacement[b]
$-L_n$ then $+X_{2n}$ (n=1)	0	$+2$	replacement-addition[c]
$+L_n$ then $-X_{2n}$ (n=1)	0	-2	replacement-elimination[d]
L goes to new L' or	0	0	L-substitution
X goes to new X'	0	0	X-substitution

[a] When the ligands are unchanged the reaction is a 1-electron reduction.
[b] When the ligands are unchanged the reaction is a 1-electron oxidation.
[c] Assuming n = 1. Generally called n-replacement-addition.
[d] Assuming n = 1. Generally called n-replacement-elimination.

When the class of the product of a compound is the same as that of the reactant compound, i.e. MoL_lX_x -----> MoL_lX_x then this reaction is a substitution reaction and these may be specified as L-substitution (e.g. product is $MoL_{l-1}L'X_x$) or as X-substitution (e.g. product is $MoL_lX_{x-1}X'$).

All possible reactions of a molybdenum compound ML_lX_x which give a product which lies in the nearby (and adjacent) neighbouring MLX classes are shown in Figure 2.9 and these reactions and their proposed names are listed in Table 2.5.

These definitions provide *an unambiguous classification of a reaction in terms of product*. The classification does NOT imply, and is independent of, any particular mechanism. However, the distribution pattern of compounds in the MLX plot of an element, such as the MLX plot of molybdenum, may provide clear indications of the likely mechanism of a particular reaction.
The guiding principle leading to mechanistic insight is

"reaction intermediates resemble known compounds"

This principle can be exemplified for the chemistry of molybdenum by consideration of several regions of the MLX plot in Figure 2.2.

(i) The classes $MoLX_6$, MoL_2X_6 and MoL_3X_6 which lie adjacent on the V.N. = 6 row and all are populated to varying degrees. Therefore it is likely that $MoLX_6$ and MoL_2X_6 will undergo +L-addition reactions and that compounds MoL_3X_6 will undergo -L-elimination reactions.

	12	13	14	15	16	17	18
0					Electron Number, E.N.		
1			MoL_lX_{x-2}	$MoL_{l+1}X_{x-2}$	$MoL_{l+2}X_{x-2}$		
2			MoL_lX_{x-1}		$MoL_{l+1}X_{x-1}$		
3			$MoL_{l-1}X_x$	MoL_lX_x	$MoL_{l+1}X_x$		
4			$MoL_{l-1}X_{x+1}$		MoL_lX_{x+1}		
5			$MoL_{l-2}X_{x+2}$	$MoL_{l-1}X_{x+2}$	MoL_lX_{x+2}		
6							

Valency Number, V.N.

REDUCTIVE ELIMINATION — REPLACEMENT ELIMINATION — REDUCTIVE REPLACEMENT

-L, ELIMINATION — +L, ADDITION

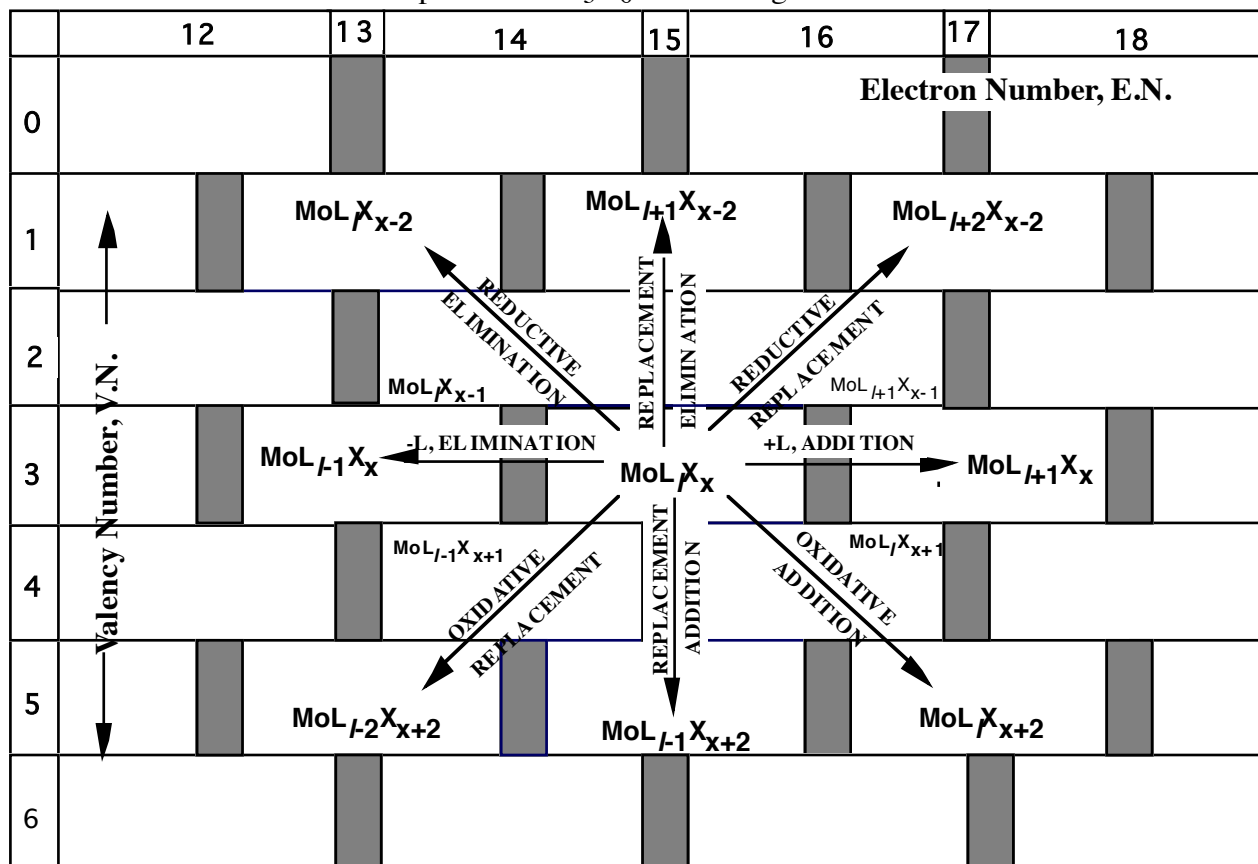OXIDATIVE REPLACEMENT — REPLACEMENT ADDITION — OXIDATIVE ADDITION

Figure 2.9 Classification of reactions by MLX class

Furthermore L-substitution or X-substitution for MoL_3X_6 will certainly proceed in a dissociative manner whilst an associative pathway is indicated for $MoLX_6$.

(ii) The classes MoX_6, $MoLX_5$, MoL_2X_4 and MoL_3X_3 lie adjacent on the L. B. N. = 6 diagonal and all are populated to varying degrees. Therefore reactions which convert a compound in one class to one of the other classes are expected to occur. The simplest reaction to interchange between these adjacent class is either electron addition, i.e. -X,+L, and electron removal, -L,+X. In other words such a diagonal relationship indicates the likelihood of the occurrence of redox chemistry, as indeed is commonly found for these molybdenum compounds.

(iii) Compound for which there are no adjacent populated compounds in a *row* are expected to be inert to substitution, e.g. MoL_6 and MoL_4X_4.
Further examples of reactivity and mechanism are presented later.

 2.4.5 Further interpretation of the population density pattern in MLX plot for molybdenum
(i) There are two dominant trends observed for compounds with substantial population densities. Those with 18-electrons and those which lie on the diagonal MoL_lX_x, where $l + x = 6$. The preponderance towards 18-electron compounds reflects the favourable energies of the valency

orbitals of molybdenum as discussed earlier. The preference for a six ligand functions (L.B.N. = 6) is a consequence of the fact that relative steric requirements of most ligands are similar and this when coupled with the size of molybdenum gives a sensible degree of steric saturation around the metal. In other words, most ligands are of a similar size in the inner co-ordination sphere. Steric saturation is one of the important factors which leads to kinetic stability towards further reactions both inter and intra-molecular which may lead to decomposition.

(ii) Compounds of molybdenum are found for all six possible values of x

Compounds with x = 1 or 2 occur in the top right hand corner of the plot and are associated with ligands which are capable of back-donation using π- or δ-symmetry acceptor orbitals, for example, CO, PR_3, η-benzene, and N_2. Compounds with x = 5 and 6 occur mostly at the bottom of the MLX plot and towards the left hand corner and thus are associated with strongly σ-bonding ligands such as =O , -OR, =NR, F, Me, i.e. X_x ligands where the ligating atom X is a first row element.

The compounds with values x = 3 and 4 are associated substantially with the less electronegative ligand systems, e.g. Cl, Br, I, CN or strongly donor L ligands, e.g. NR_3. However, for median values of x a variety of *combinations* of ligands can be brought together to satisfy the steric and electronic requirements of the molybdenum.

(iii) Except along the l + x = 6 diagonal there are few compounds for x = 1, 3 or 5. In other words, molybdenum compounds with an odd-number of electron count are most common when steric saturation occurs. This arises since steric saturation of the molybdenum (metal) centre will provide a degree of kinetic stability, for example, it restricts ligand substitution reactions by associative processes.

The continuous population of compounds along the l + x = 6 diagonal is reflected by the characteristic occurrence of redox reactions for the molybdenum compounds which lie along this diagonal. This follows since addition of an electron to MoL_lX_x gives $[MoL_lX_x]^-$, which corresponds to the neutral class $MoL_{l+1}X_{x-1}$. Similarly a one-electron oxidation of MoL_lX_x gives the corresponding neutral class $MoL_{l-1}X_{x+1}$. Examples are given in section 4.4. This ability for molybdenum to take part in redox chemistry over a wide range of ligand environments is a key characteristic and no doubt accounts in part for the catalytic properties of molybdenum, for example, in the molybdenum containing enzyme nitrogenase.

(iv) The oxidative addition reaction ($+X_2$), e.g. the addition of H_2 or MeI to a metal centre, converts a compound in the class MoL_lX_x to MoL_lX_{x+2} and thus increases the value of V.N. by 2. Inspection of the more populus classes in the MLX plot in Figure 2.2 shows that the only portion of the diagram where there are *populated* classes which differ by $+X_2$ occur for the combination of the rare, 16-electron MoL_4X_2 and the common 18-electron MoL_4X_4. Therefore, the MLX plot reflects the rarity of oxidative-addition reactions in molybdenum chemistry but also accounts for the strong tendency for the very rare compounds MoL_4X_2 to undergo such reactions For example,. molybdenocene, which can only exist in isolation and undergoes intermolecular dimerisation by insertion of molybdenum into a C-H bond of another molecule, eventually leading to the red dimer $[(Mo-\eta^5-C_5H_5)_2(\mu-\sigma:\eta^5-C_5H_5)_2])$ This situation is in marked contrast for an element such as

palladium or platinum for which the classes ML_2X_2 and ML_2X_4 are well populated (see the MLX plots for Pd and Pt in the Appendix, Figure A.2).

(v) Addition of a ligand L to a molybdenum compound MoL_lX_x causes an increase of E.N. by 2. Therefore, this reaction will not occur readily for 18-electron compounds and this accounts for the fact that 18-electron compounds of molybdenum are inert to substitution by associative processes. However, where there are populations related by +/-L reactions, e.g. for $[MoL_lX_6]$, where $l = 1$ or 2 substitution reactions by L ligands occur quite readily.

(vi) Finally, we note that stable compounds with L.B.N. less than six are unknown; this reflects the fact that such compounds have empty valency orbitals. (i.e. E.N. < 18e) and also are normally be sterically unsaturated. Further, except for the 18e compounds MoL_5X_2, there are relatively few examples of compounds which have L.B.N. = 7 (or co-ordination number 7). This arises since there is the loss of favourable bonding associated with the more symmetrical L.B.N. = 6 (octahedral or trigonal prismatic co-ordination) and also, there is generally a greater relative increase in steric repulsion energy on changing from L.B.N. = 6 to L.B.N. = 7 than for a change from L.B.N. = 7 to L.B.N. = 8. In other words most of the overall increase of steric repulsion arising from a change of L.B.N. from 6 to 8 is accounted for by the formation of the intermediate with L.B.N. = 7. (Similarly, the increase of steric repulsion from 4-6 co-ordination is mostly accounted for by the change from 4 to 5 co-ordination.)

2.5 DISCUSSION OF INDIVIDUAL MLX CLASSES OF MOLYBDENUM COMPOUNDS

2.5.1 Zerovalent molybdenum compounds, MoL_l

With the exception of the matrix-isolated compound $Mo(CO)_5$, monovalent molybdenum compounds are limited to the 18e class ML_6.

(i) The class ML_6

Illustrative compounds are given in Table 2.3 and Figure 2.10. The colourless, air-stable, octahedral and cheaply available molybdenum hexacarbonyl $Mo(CO)_6$ has been the dominant precursor for compounds in this class. The method of preparation is typical for the monoleptic carbonyls of the more electro-positive transition metals. Thus, a suitably available and soluble metal compound e.g. $[MoCl_5]_2$, in a co-ordinating solvent such as the chelating ether $MeOCH_2CH_2OMe$ is reduced by a suitably strong reducing agent such as Al powder, Mg powder or sodium benzophenone in the presence of carbon monoxide at elevated pressure (150-300 atm.) and temperature (120-160 $^\circ$C).

The substitution of up to four of the carbon monoxide ligands of $Mo(CO)_6$ by other π-acceptor L-class ligands such as R_3P, η-arene, RNC, and mono-, di- and tri-olefins has led to the isolation of a very substantial number of compound in this class. Their study in the earlier days of the development of organotransition metal chemistry contributed to an increased understanding of the various ways in which unsaturated hydrocarbon systems could bond to transition metals. As expected from the absence of stable compounds in the class MoL_5, the compounds MoL_6 are normally fairly inert to substitution. For this reason photochemical methods are often used to

induce L-substitution reactions. Typically, a solution of molybdenum hexacarbonyl in an inert solvent together with the reactant ligand are irradiated using a medium pressure mercury lamp for several hours. This inertness appears to be a limiting factor in their application, for example, as reagents for organic synthesis or in catalysis.

Molybdenum hexacarbonyl has a first ionisation energy in the gas phase of 8.5 e.v. and this is very similar to that of the ionisation energy of the d^1 electron of $[MoCl_5]_2$ (see Table 2.6). It is
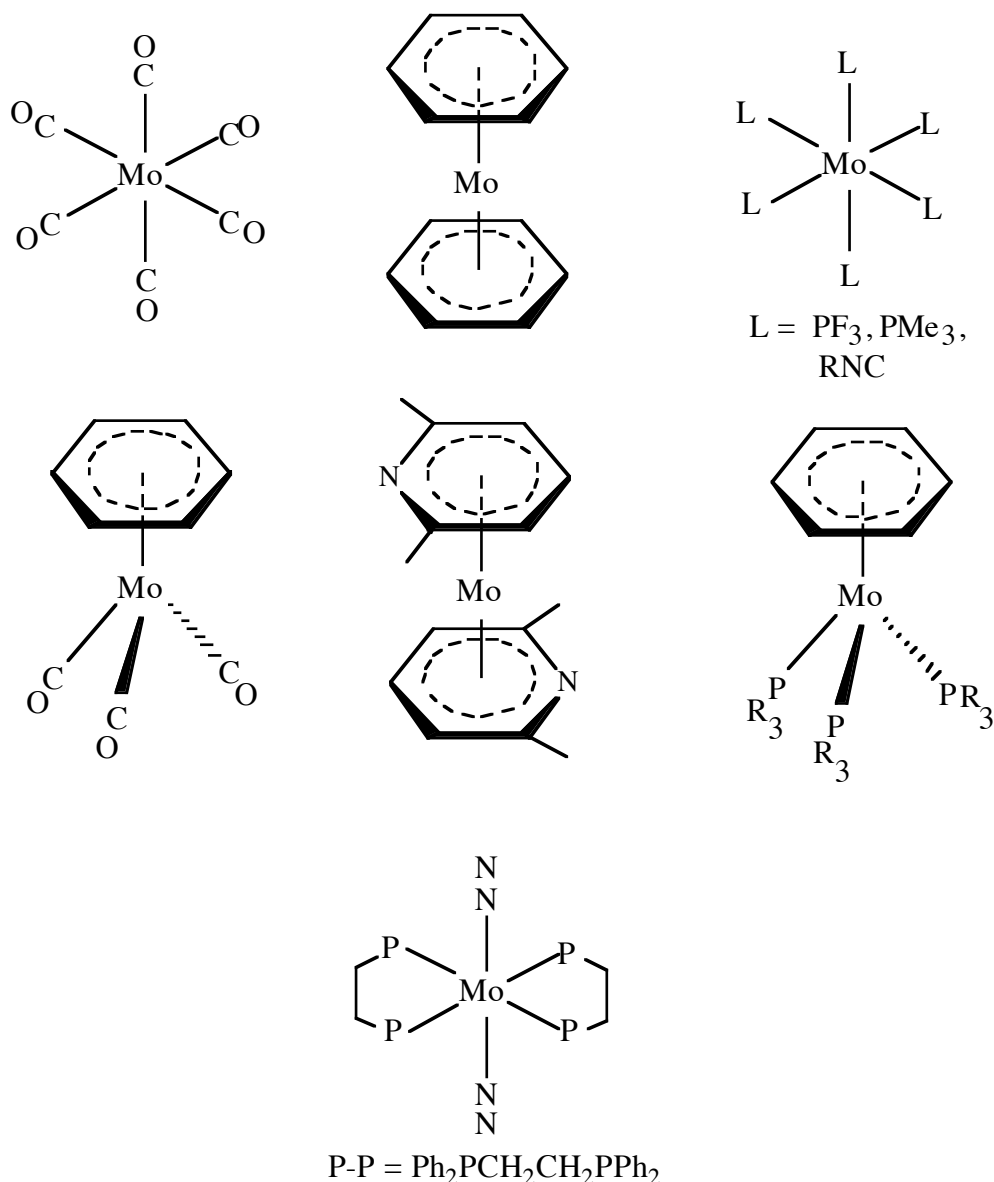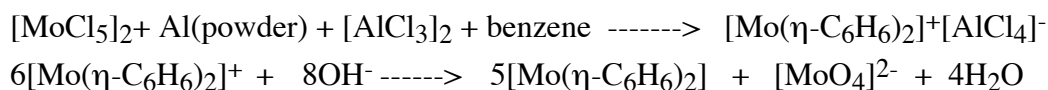

$$L = PF_3, PMe_3, RNC$$

$$P-P = Ph_2PCH_2CH_2PPh_2$$

Figure 2.10 Examples of compounds in the class MoL_6

 the strong π-acceptor role of the empty $p_\pi{}^*$-orbitals of the carbon monoxide ligand that lowers the d^6 t_{2g} electrons of the $Mo(CO)_6$ molecule. Such electrons, which are strongly attached to the central atom, are not readily available for further chemistry.

Another historically important compound in this class is bis-η-benzene molybdenum which has also been used as a precursor for the further development of molybdenum chemistry. It is prepared by the classical reducing Freidel-Crafts procedure, viz:

$$[MoCl_5]_2 + Al(powder) + [AlCl_3]_2 + benzene \ \text{-------}> \ [Mo(\eta\text{-}C_6H_6)_2]^+[AlCl_4]^-$$

$$6[Mo(\eta\text{-}C_6H_6)_2]^+ + \ 8OH^- \ \text{------}> \ 5[Mo(\eta\text{-}C_6H_6)_2] \ + \ [MoO_4]^{2-} \ + \ 4H_2O$$

It may also be prepared by co-condensation of molybdenum atoms and benzene.

Bis-η-benzenemolybdenum has an exceptionally low first ionisation energy of 5.52   e.v. as a consequence of the relatively poor acceptor properties of the δ-orbitals of the η-arene ligand and the compound readily undergoes a reversible one-electron oxidation.

Table 2.6.   First ionisation energies of some molybdenum compounds.

Compound	V.N.	I.E./eV	Compound	V.N.	I.E. /eV
$Mo(\eta\text{-}C_6H_3Me_3)_2$	0	5.13	$Mo_2(CMe_3COO)_4$	6	6.75
$Mo(\eta\text{-}C_6H_6)_2$	0	5.52	$Mo_2(NMe_2)_4$	6	6.76
$Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)$	4	5.87	$Mo(\eta\text{-}C_5H_5)_2Cl_2$	4	6.8
$Mo(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)$	2	6.0	$Mo(\eta\text{-}C_5H_5)_2CO$	2	6.9
$Mo(\eta\text{-}C_5H_5)_2NPr^i$	4	6.09	$Mo(\eta\text{-}C_4H_6)_3$	0	7.23
$Mo(\eta\text{-}C_5H_5)_2Me_2$	4	6.1	$Mo(\eta\text{-}C_6H_3Me_3)(CO)_3$	0	7.24
$Mo(\eta\text{-}C_5H_5)_2H_2$	4	6.4	$Mo(\eta\text{-}C_5H_5)(CO)_3Me$	2	7.78
$Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_3H_5)_2$	2	6.44	$Mo(CO)_6$	0	8.5
$Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$	1	6.46	$Mo_2(CF_3COO)_4$	6	8.67
$Mo(\eta\text{-}C_5H_4Me)_2(O)$	4	6.55	$Mo(PF_3)_6$	0	9.2
$Mo_2(\eta\text{-}C_3H_5)_4$	4	6.72	$MoCl_5$	5	9.27

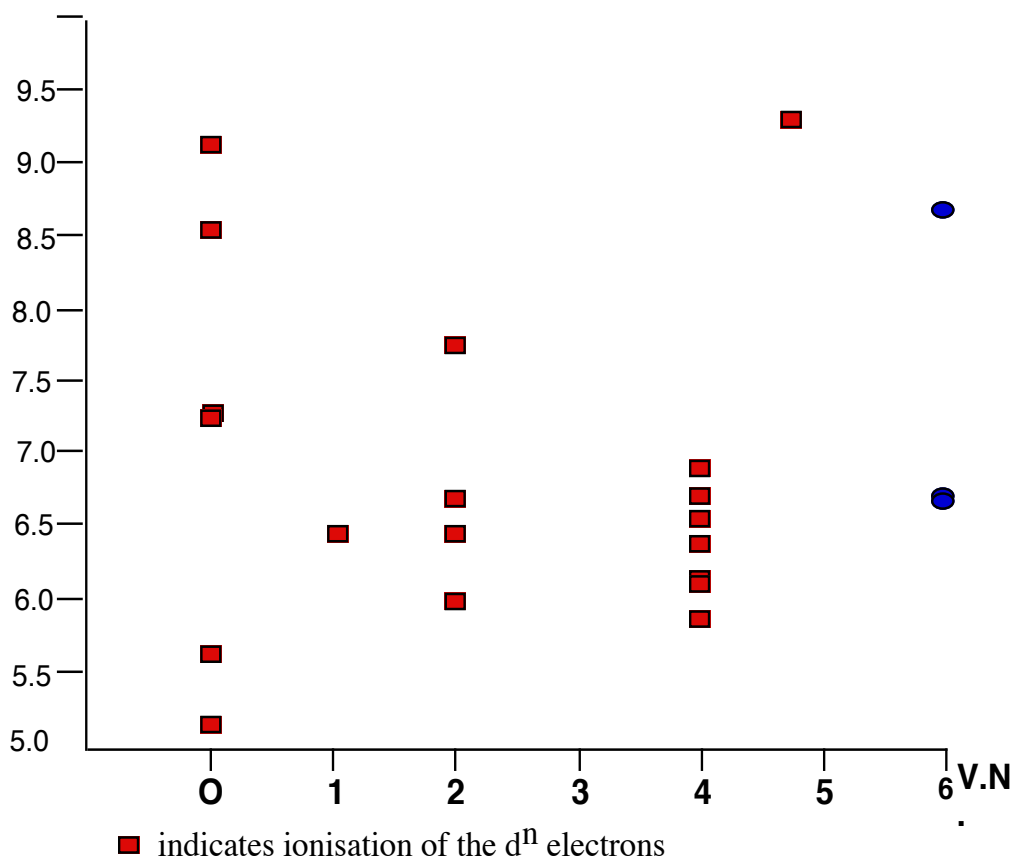
■ indicates ionisation of the d^n electrons

Figure 2.11. Showing the distribution of 1st ionisation energies (eV) of some volatile molybdenum compounds as a function of their valency number (or indeed, their formal oxidation state). It is clear that there is **NO** correlation.

The compounds $Mo(CO)_6$ and $[Mo(\eta\text{-}C_6H_6)_2]$ have very different first ionisation energies (I.E.) even though they are both in the same class ML_6. Clearly there is no simple correlation between the class of a compounds and the electron 'richness 'or 'poorness' of the metal centres. This point is further demonstrated in the Figure 2.11 which shows the total lack of correlation between values of the 1st ionisation energies for a selection of molybdenum compounds. The data for the I.E. versus V.N. plot in Figure 2.11 is given in the Table 2.6, the 1st ionisation energies arise from electrons located in essentially d-orbitals for d^n compounds where $n = 6$ to 1.

The monoleptic tris(η-butadiene)molybdenum, $Mo(\eta\text{-}C_4H_6)_3$ has been prepared by co-condensation of Mo atoms with butadiene as white volatile air-stable crystals. It is not a reactive compound having a first ionisation energy of 7.23 e.v. The structure is shown in Figure 2.6 and the C_2-C_3 bond length corresponds best with a description of the class of the butadiene ligand in this molecule as L_2 rather than LX_2.

2.5.2 Monovalent molybdenum compounds, MoL_lX

Examples are shown in Table 2.3 and Figure 2.12. They are known only for the class ML_5X and even then examples are very rare, as would be expected for such "free radicals" with high ionisation energies. Their chemistry has been little explored.
 The best characterised compounds are the cations $[Mo(\eta\text{-arene})_2]^+$ and the neutral $Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)$. The ability of the 17-electron compound $Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)$ to survive isolation may be associated with the favourable bonding situation for symmetrical sandwich compounds. Dimerisation with formation of a Mo-Mo bond to give an 18e compound is presumably unfavourable for steric reasons. Electron-rich, odd-electron compounds are rare because a single electron in an orbital of valency energy will normally lead to dimerisation. A parallel between $Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)$ and the radical Ph_3C can be made.
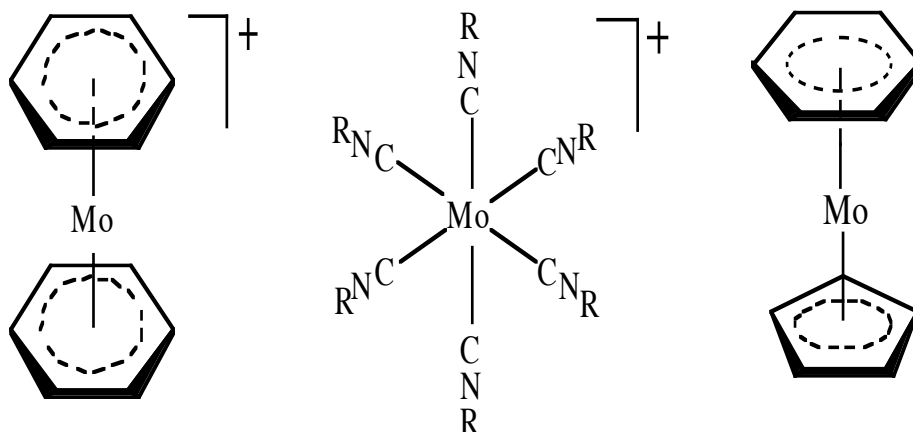
Figure 2.12. Examples of compounds in the very rare class ML5X.

2.5.3 Divalent molybdenum compounds, MoL_lX_2

Examples are shown in Table 2.3 and Figure 2.13.

(i) The class MoL_5X_2

Examples are shown in Figure 2.13. This is by far the most abundant class, despite the relatively rare occurrence of compounds with L.B.N. = 7, and this reflects the strong tendency for molybdenum to attain the 18e configuration. A very substantial proportion of the known examples contain carbonyl ligands and many are prepared by replacement-addition reactions starting from ML_6 derivatives. Derivatives of the $Mo(n-C_5H_5)(CO)_3X$ system have been extensively explored and are particularly dominant, as is exemplified in recent volumes of the Gmelin Handbook of Inorganic and Organometallic Chemistry Parts 6-8, 1990-92 Substitution reactions of these compounds would normally be expected to occur by essentially dissociative processes.
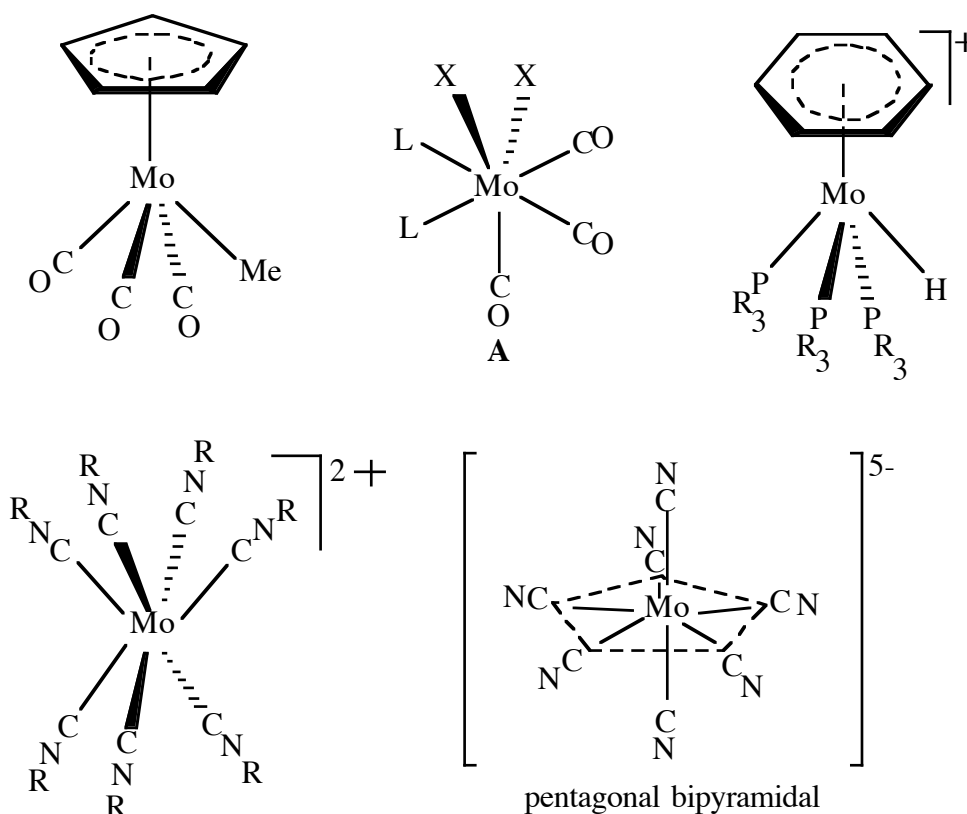

Figure 2.13. Examples of compounds in the class MoL_5X_2. Specific examples of the X and L ligands for **A** are given in Table 2.3.

(ii) The class MoL_4X_2

These 16-electron compounds MoL_4X_2 are rare. The stability of $Mo(diars)_2X_2$ presumably arises from steric saturation due to the bulkiness of the diars ligand; the diars ligand is 1, 2-$(Ph_2P)_2C_6H_4$.

Both the monoleptic cyano anions $[Mo(CN)_6]^{4-}$ and $[Mo(CN)_7]^{5-}$ (which is of class MoL_5X_2) are known and the ability of the latter to dissociate a CN^- anion may be associated with the exceptional negative charge on this anion (penta-negative anions are very rare). It may be noted that there are three 'rules' which concern the stability of a compound with respect to its existence at n.t.p in the absence of other potential reactants, such as O_2 or H_2O. These rules are :

I Filled valency orbitals, the 18-electron rule in the case of molybdenum.

II. Steric saturation. Steric overcrowding leads to ligand dissociation and with steric unsaturation there is space to allow access for reactions at the central atom M. This will lead to low energy barriers to pathways for decomposition to more thermodynamically stable products (very many compounds which may be isolated and stored in bottles are thermodynamically unstable with respects to other combinations of the component atoms and many have only kinetic stability in air.

III. The Electroneutrality Principle. This states that within a covalent system there cannot be a charge separation of greater than +1 or -1 electronic charge.

These rules are mentioned here since rule III explains why the highly electron rich $[Mo(CN)_7]^{5-}$ anion readily dissociates CN^- yet it is not sterically overcrowded and has an 18-electron count. Rule III also explains why the compound $[Mo(NH_3)_6]$ has not been prepared.

Another feature of compounds in the class MoL_2X_4 is that L-substitution reaction are expected to occur by associative processes. The oxidative-addition reaction $(+X_2)$ for the compounds MoL_4X_2 gives the abundant class MoL_4X_4. Thus a high energy compound such as molybdenocene $[Mo(\eta-C_5H_5)_2]$ is known only as an intermediate and as mentioned earlier, it readily undergoes an intermolecular reaction with carbon-hydrogen bonds,

2.5.4 Trivalent molybdenum compounds, MoL_lX_3

Examples are shown in Table 2.3 and Figure 2.14.

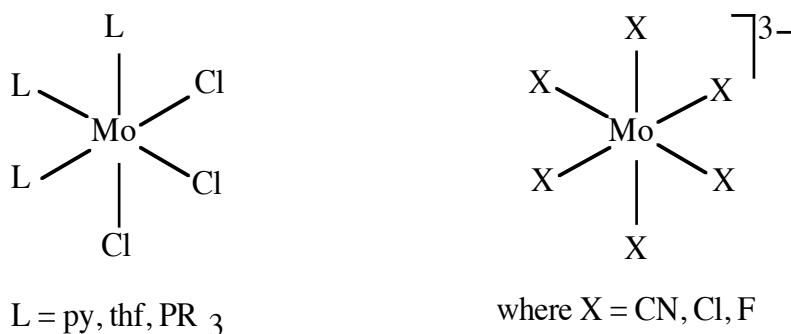$$L = py, thf, PR_3 \qquad where \ X = CN, Cl, F$$

Figure 2.14. Examples of compounds in the class MoL_3X_3.

There are relatively few trivalent compounds presently known. They occur almost exclusively in the class MoL_3X_3. These are paramagnetic (typically $\mu_{eff} = ca.$ 3.8 B.M.) as expected for the essentially octahedral d^3 t_{2g} configuration. The compounds MoL_3X_3 are normally quite inert to substitution but more readily undergo electron loss (oxidation) giving MoL_2X_4 compounds.

The rarity of these compounds contrast strongly with the huge abundance of the substitutionally inert chromium CrL_3X_3 compounds and this observation emphasises the very different functional group properties of chromium and molybdenum (see Figure 2.27).

2.5.5 Tetravalent molybdenum compounds, MoL_lX_4

The MLX plot for molybdenum in Figure 2.2. clearly shows that both the classes MoL_4X_4 and MoL_2X_4 are well represented whilst compounds in the class that lie between them, namely, MoL_3X_4 are virtually unknown. This is another example of unfavourable factors associated with L.B.N. = 7, and indeed with the co-ordination number 7.

(i) The class MoL_4X_4

Compounds in this class must compromise between the desirability of attaining the 18e configuration and the steric overcrowding associated with a L.B.N. of eight. Eight co-ordinate compounds with monofunctional ligands are, in consequence, only found when all or a substantial proportion of the ligands are small or compact. For this reason the disparate ligands CN, F, H and the compact (η-C_5H_5) ligand provide a very substantial proportion known compounds, in this class e.g. the complex anions $[Mo(CN)_8]^{4-}$, $[MoF_8]^{4-}$, the neutral hydrido derivatives $[Mo(PMe_2Ph)_4H_4]$ and the multitudinous bis-η-cyclopentadienyl derivatives, see Table 2.3. A compact ligand is one for which the number of ligand atom functions (L or X) is relatively large compared with the "size" of the ligand, as defined by the Tolman cone angle. Thus the η-cyclopentadienyl ligand (class L_2X) is compact compared to $(PMe_3)_2Me$ which form the class L_2X. There is little energy difference between the two symmetrical structures for the $M(CN)_8$ system, namely, the dodecahedral and the square anti-prism. This is reflected in the observation that the anion $[Mo(CN)_8]^{4-}$ adopts both structures depending on the counter cation (Figure 2.15).

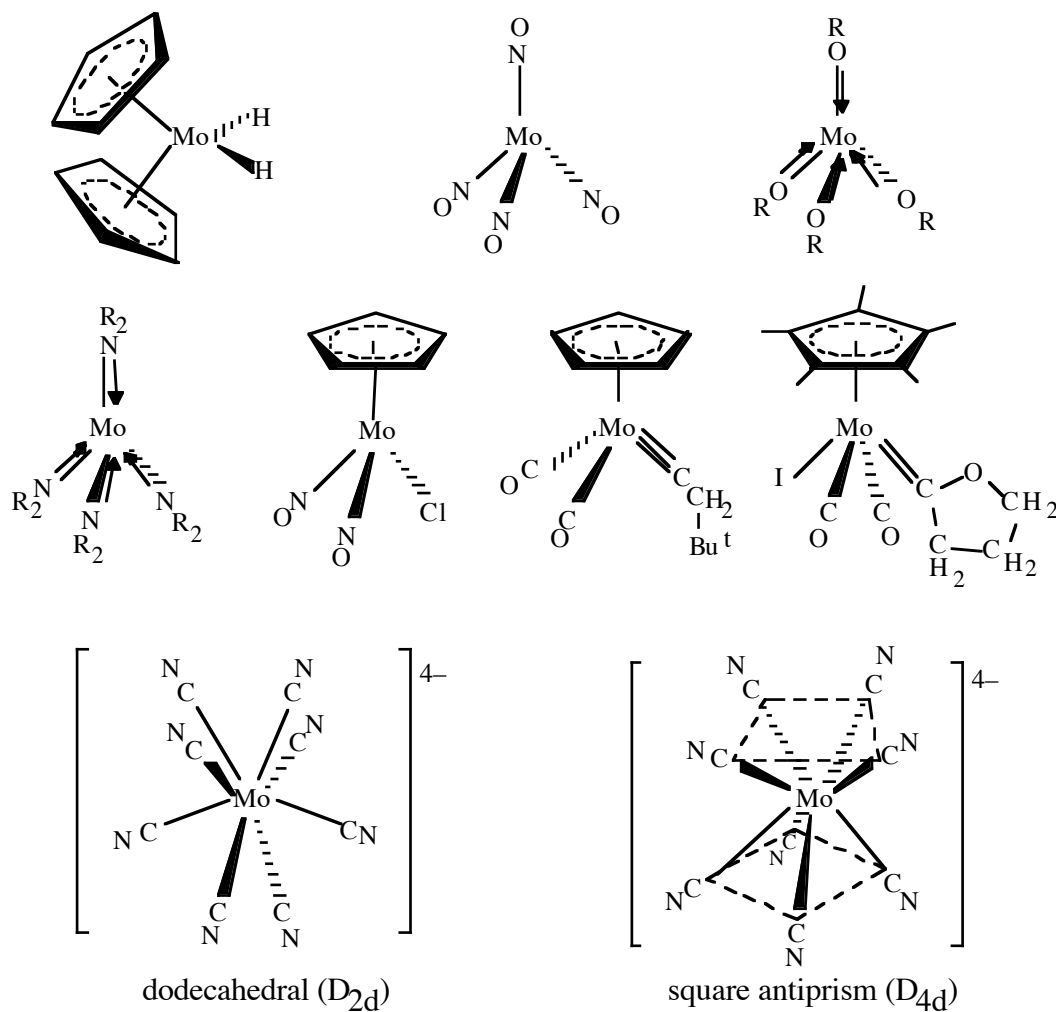dodecahedral (D$_{2d}$)   square antiprism (D$_{4d}$)

Figure 2.15. Examples of compounds in the class MoL$_4$X$_4$.

In fact, [13]C. n.m.r. studies show that in solution this anion is fluxional and rapidly rearranges between the two structures. Photolysis of aqueous solutions of $[Mo(CN)_8]^{4-}$ gives the oxocyano anion $[trans\text{-}Mo(O)_2(CN)_4]^{4-}$. The molybdenum in the co-ordination polymer $[K_2MoF_6]_n$ also has eight co-ordination in a symmetrical anti-prismatic arrangement of the eight F ligands. There is a very extensive chemistry of organo-molybdenum compounds in this class.

(ii) The class MoL$_2$X$_4$

Examples are given in Table 2.3 and Figure 2.16. Only recently have useful synthetic routes to these compounds been established. It is interesting to note that MoCl$_5$ is readily reduced, for example, by alkylnitriles, by an unknown mechanism, giving Mo(RCN)$_2$Cl$_4$ derivatives.

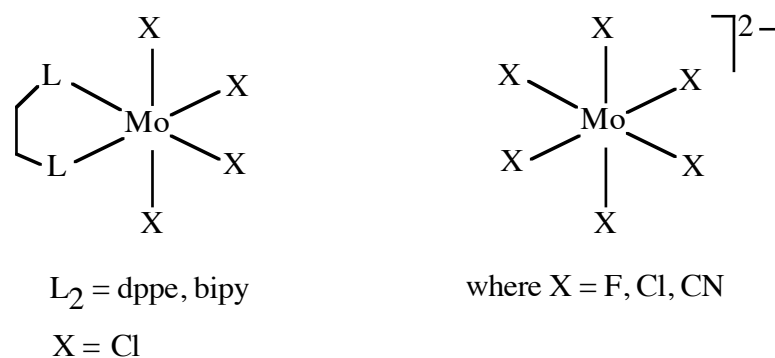L_2 = dppe, bipy

X = Cl

where X = F, Cl, CN

Figure 2.16. Examples of compounds in the class MoL_2X_4.

2.5.6 Pentavalent molybdenum compounds, MoL_lX_5

Examples are given in Table 2.3. Presently, the chemistry of compounds in this class is very largely concerned with molybdenum-oxygen derivatives for which, as indicated in Section 2.6.1, the unambiguous assignment of the values of l for L_l is not straight forward. Examples are shown in Figure 2.24 and the oxo chemistry of molybdenum compounds in this class is discussed further in Section 2.6.1. The occurrence of these oxo compounds MoL_lX_5 for l = 1 and 2 may be associated with facile ligand exchange reactions and would be expected to occur via essentially associative processes .

Molybdenum-oxo compounds are common in both the penta- and hexa-valent states and in consequence redox equilibria between these two valencies occur readily.
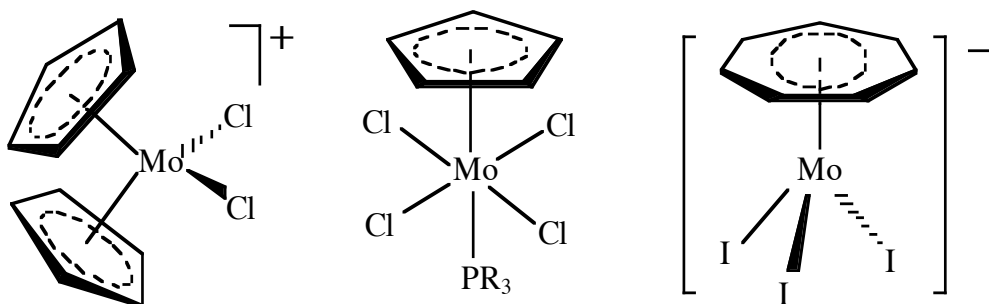

Figure 2.17. Examples of compounds in the class MoL_3X_5

Rare examples of compounds in the class MoL_3X_5 include the bis- and mono-η-cyclopentadienyl compounds shown in Figure 2.17. The paucity of compounds in this class reflects the demanding steric requirement for L.B.N. = 8 coupled with the 17-electron (open shell) count.

2.5.7 Hexavalent molybdenum compounds, MoL_lX_6

There is a very extensive chemistry for this class. Examples broadly divide into those where ligating atoms such as oxygen, nitrogen or the halogens play a decisive role and those where potential problems of excessive positive charge on the metal and of steric overcrowding are avoided by the presence of molybdenum-molybdenum multiple bonds. The Mo-Mo triple and quadruple bonds mean that with respect to one molybdenum the other molybdenum is a very compact ligand.

The extensive variety of compounds in this class is illustrated by the compounds in Figures 2.18 and 2.19. Many other examples are shown in the Figures 2.21, 2.22, 2.24 and 2.25.

It is not possible to identify the value of l for many of the compounds with oxygen ligand atoms since the degree participation of the oxygen lone pairs in primary bonding is not determined.
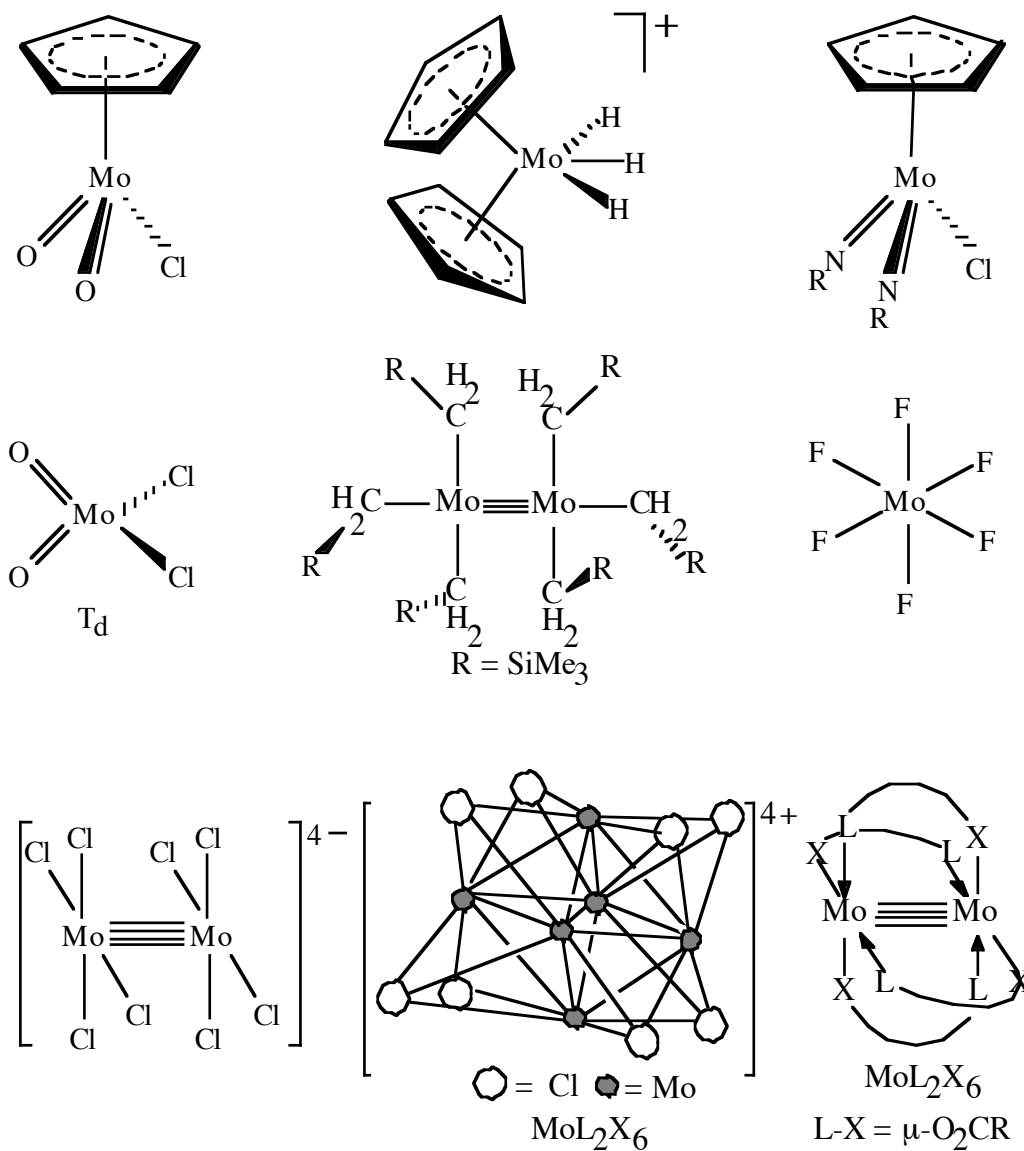

Figure 2.18 Examples of compounds in the classes MoL_lX_6 (see also Figures 2.19 - 2.20). The eclipsed configuration of the dimer $[Mo_2Cl_8]^{4-}$ provides convincing for the presence of a quadruple bond. The classification of the $[Mo_6Cl_8]^{4+}$ cluster is discussed in Section 2. 6.1 ii.

General features of the chemistry of oxo and related compounds in this class are:

(*a*) Ligands *trans* to a M=O ligand system are labile.

(*b*) The systems $Mo(=X_2)_2$, e .g. MoO_2, $Mo(=CR_2)$, $Mo(=NR)$ adopt a *cis* configuration (see Figure 2.24).

(*c*) Whilst the L.B.N. number varies from 6-9 the co-ordination number rarely rises above six. This reflects the fact that the oxo ligand is very compact, especially when it is donating four electrons to the metal in the LX_2 class, see Figure 2.3

(*d*) As noted earlier, the compounds in the classes MoL_lX_6, where $l = 1$-3 readily and variously undergo addition, elimination, and substitution reactions as would be expected from the relative abundance's of these adjacent classes.

Some of the extensive aqueous and oxo chemistry of compounds in this class is detailed in Section 2.6.1.

(i) Molybdenum compounds with multiple bonds.

The fragments [Mo≡Mo] and [Mo≡Mo] are stable and relatively unreactive in a wide range of chemical environments. Starting from compounds such as $Mo(\mu\text{-}O_2CMe)_4Mo$ and $(R_2N)_3Mo≡Mo(NR_2)_3$ it is possible to prepare a very extensive range of derivatives, see Figure 2.19.

(ii) Comment on molybdenum halide cluster compounds

The long known cluster cation $[Mo_6Cl_8]^{4+}$ has the structure shown in Figure 2.18. In this cation the molybdenum atoms classify as MoL_2X_6, i.e. as 16e. There are eight μ^3-Cl ligands each of which contribute one X function and two L functions giving a total of 16L and 8X for the 6 Mo atoms. The 4+ charge means that four of the 16L become X (since $L^+ = X$). Therefore there is a total of 12L and 12X ligands, i.e. L_2X_2 for each or the six Mo atoms. The X-ray structure shows that there are four single bond joining each molybdenum atom to four adjacent atoms in the octahedron; these give a further 4X per Mo atom. Thus each Mo centre in the cation classifies as MoL_2X_6. In the structurally related anions $[Mo_6Cl_{14}]^{2-}$ the molybdenum centres classify as MoL_3X_6, as does Mo_6Cl_{12}. Thus the electron count , E.N., for each molybdenum centre in these latter compounds is 18.

2.6 A DISCUSSION OF THE CHEMISTRY OF MOLYBDENUM IN VARIOUS LIGAND ENVIRONMENTS

It is beyond the scope of this introductory chapter to discuss molybdenum chemistry in a detailed and comprehensive manner. However, an introduction should identify exceptional features and in this Section several ligand environments of particular dominance in molybdenum chemistry are presented. The treatment of these topics is made in a broad and descriptive manner.

2.6.1 The aqueous solution and other oxygen chemistry of molybdenum

The chemistry of molybdenum with the varieties of the ligand systems present in aqueous media is very extensive, complex, rich and fascinating and even now there remains much to unravel. Figure 2.20 exemplifies many of the various possibilities for ligand systems which can be derived from water, all are found in molybdenum compounds and to a much greater extent than for most of the

other earlier and later transition elements. We shall include in this section a brief summary of molybdenum-oxo chemistry which includes ligands other than those derived from solely water since their rigorous exclusion would introduce and imply artificial divisions to a common chemistry for molybdenum.

Terminal ligands   Bridging two atoms $- \mu^2-$ Bridging three atoms $- \mu^3=$
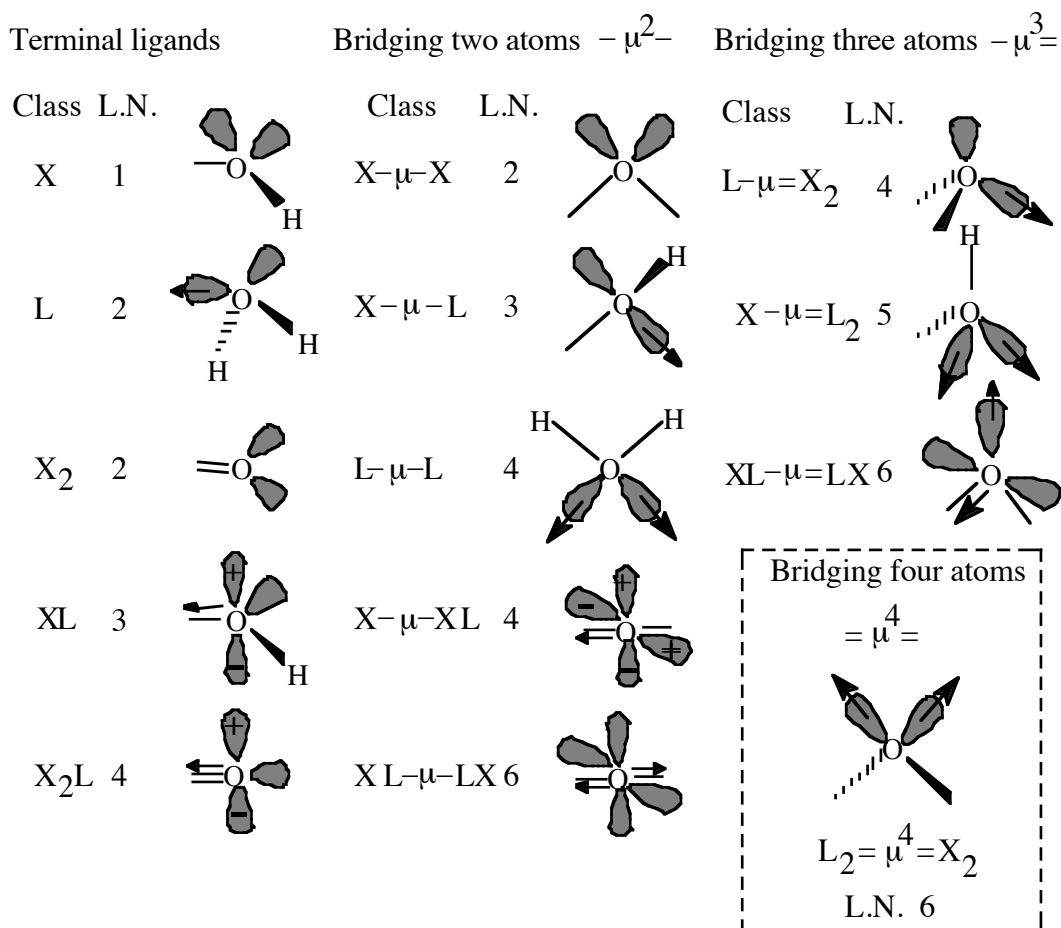

Figure 2.20. Examples of ligands which are present in the aqueous environment. They are listed by their MLX class and by L.N., the total number of electrons donated to the metal centre by the ligand. Pure p-orbitals (filled) are indicated by + and - symmetry assignments. Orbitals (filled) which are sp$^{1-3}$ hybrids (shaded lone pairs) have no sign given.

Molybdenum oxygen derivatives may be broadly classified into those which contain stoichiometric discrete molecular entities and those which exist as infinite lattices, layered or otherwise, and which may be non-stoichiometric.

Figure 2.21 exemplifies the equilibria and structural relationship between some discrete covalent monomeric, binuclear and trinuclear aquo-oxo compounds. Some of the equilibria given in the Figure 2.21 are postulated rather than experimentally established. They are presented in order to help provide an image of the possible processes by with the complex polynuclear species may be derived. Many of the molybdenum-aquo-oxo species which have been unambiguously identified under various conditions (e.g. of pH) are shown in Figure 2.21.

The Figure 2.21 also shows: (i) the change of species on addition of H^+ to aqueous molybdate. (ii) a hypothetical sequence which suggests how the tri-aquo species **A** might isomerise to the octahedral $Mo(OH)_6$ molecule. (iii) Protonation of **A** might give **B** and reduction could lead to **C**. (iv) **B** and **C** could then dimerise by cocondensation forming water and the dimers **D** and **E** respectively. (v) Shows further reactions of **E** which lead to other dimers and trimers all of which have been structurally characterised. An excellent detailed discussion of the aqueous solution chemistry of molybdenum may be found in Gmelin 3a, Supplementary volume B 1987 and B, 3b, 1989.

The Figure 2.22 presents the structures of fully characterised binuclear molybdenum-oxo compounds which a clearly related to some of the dimeric compounds shown in Figure 2.21.

trans, LX = acac, S_2COEt, S_2CNR cis, L = $S_2P(OEt)_2$,
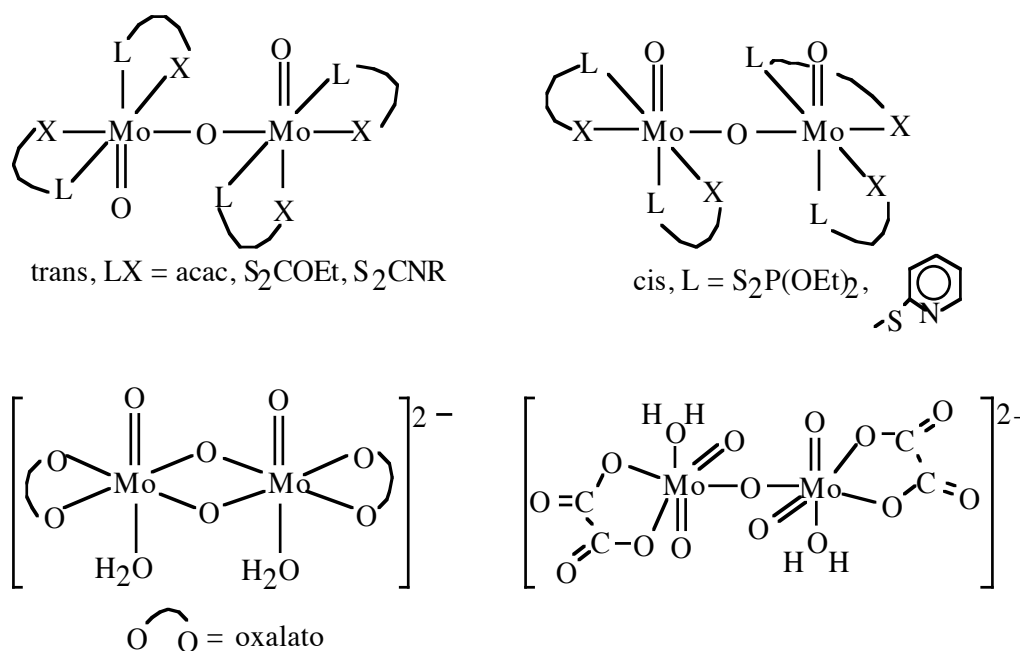

$O \frown O$ = oxalato

Figure 2.22. Examples of molybdenum-oxo-dimers with a variety of chelate ligands.

The formation of the more complex iso- and hetero-polymolybdates from simple aquo-molybdenum species is exemplified in Figure 2.23. The structures of these poly-anions will not be discussed here but the dominant structural feature of these polymolybdates is the occurrence of fused octahedral MoO_6 units. The favourable bonding of the linear Mo-O-Mo moiety is believed to be a major factor contributing to the formation of these octahedral Keggin structures. Figure 2.22 shows the equilibria between the $[MoO_4]^{2-}$ and $[Mo(OH)_6]$, the latter readily undergoes condensation reactions which cause elimination of water and give the polymolybdate structures. Molybdenum forms discrete octahedral alkoxide compounds $[Mo(OR)_6]$ which are close analogues of the proposed $Mo(OH)_6$.

A broadly similar aquo-oxo chemistry is found for tungsten but not for chromium for which the linear Cr-O-Cr system is rarely found. It is thought that the 3d orbitals of chromium in the six valent oxygen atom environment are not sufficiently extensive to overlap favourably in octahedral Cr-O-Cr units.

Examples of infinite lattice solid oxides and their formation from $[MoO_3]_n$ and the tetrahedral anion $[MoO_4]^{2-}$ are given in Figure 2.24. These include the non-stoichiometric oxo-hydroxy compounds

with the characteristic blue colour (the hydrogen bronzes) and MoO_2 which has multiple Mo-Mo bonding as indicated by some Mo-Mo distances of 2.51Å.

The long known molybdenum blues are formed by hydrogen reduction of $[MoO_3]_n$, which has a layer structure. These may be viewed as intercalation compounds of the hydrogen atom which transfers an electron to a lattice molybdenum and the resulting proton bonds to an oxo ligand in the covalent polymer forming an OH ligand at the molybdenum.
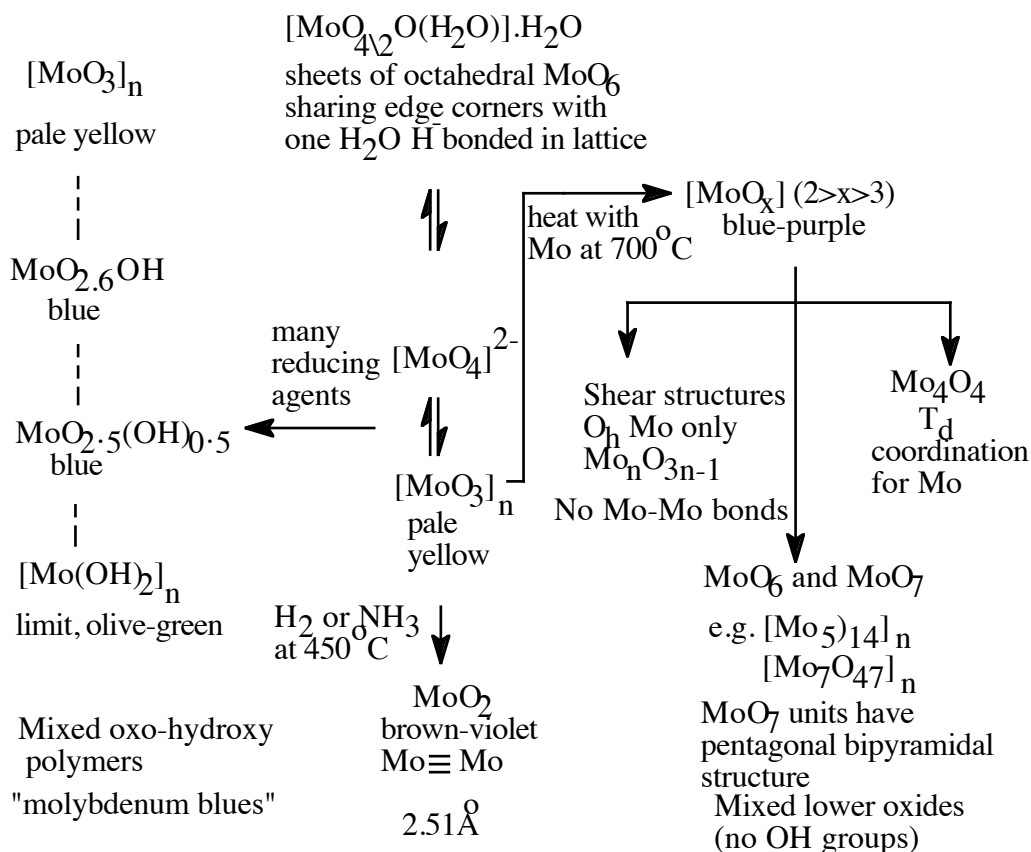
$[MoO_3]_n$
pale yellow

$MoO_{2.6}OH$
blue

$MoO_{2.5}(OH)_{0.5}$
blue

$[Mo(OH)_2]_n$
limit, olive-green

Mixed oxo-hydroxy polymers
"molybdenum blues"

$[MoO_{4\backslash 2}O(H_2O)].H_2O$
sheets of octahedral MoO_6 sharing edge corners with one H_2O H bonded in lattice

many reducing agents $[MoO_4]^{2-}$

$[MoO_3]_n^-$
pale yellow

H_2 or NH_3 at 450°C

MoO_2
brown-violet
Mo≡Mo
2.51Å

heat with Mo at 700°C

$[MoO_x]$ (2>x>3)
blue-purple

Shear structures
O_h Mo only
Mo_nO_{3n-1}
No Mo-Mo bonds

Mo_4O_4
T_d coordination for Mo

MoO_6 and MoO_7
e.g. $[Mo_5)_{14}]_n$
$[Mo_7O_{47}]_n$
MoO_7 units have pentagonal bipyramidal structure
Mixed lower oxides (no OH groups)

Figure 2.24. An overview of the occurence of infinite lattice, polymeric molybdenum-oxo, and oxo-hydroxy compounds. Some of these are non-stoichiometric unlike the discrete systems shown in Figure 2.23. The archetypal molybdenum trioxide $[MoO_3]_n$ has an interesting layer structure in which each molybdenum is surrounded by six oxygens in a distorted octahedral arrangement. The interlayer region between the MoO_3 sheets can be intercalated and take up guest cations such as Na^+ (e.g. the "bronzes" Na_xMoO_3, or even bulky organometallic cations such as the molybdenum cubane cluster cation $[Mo_4(\eta-C_5H_5)_4(\mu-S)_4)]^+$ (see Figure 2.26).

The blue colour in these non-stoichiometric "hydrogen bronzes" is thought to arise from the presence of trinuclear molybdenum systems containing both five- and six-valent molybdenum, which are more or less randomly distributed into the fragmenting $[MoO_3]_n$ lattice.

The lower molybdenum oxo compounds, formed by heating $[MoO_3]_n$ with molybdenum powder at 700°C are known with stoichiometries MoO_x, where $2 < x < 3$, and within this range they adopt a wide variety of structures.

2.6.2 Molybdenum-oxo-chloro chemistry

The combination of oxo and chloro ligands is a very common combination in the inorganic chemistry of most transition metals and compounds with these ligands are very extensive for molybdenum. A synopsis of the synthesis and structures of some covalent molybdenum-oxo-chloro molecules and molecular ions is shown in Figure 2.25.

2.6.3 Molybdenum compounds with sulphur ligand environments

There is an especially rich chemistry of molybdenum-sulphur systems. Indeed molybdenum shows a strong affinity for sulphur, as exemplified by the occurrence of molybdenum as the ore molybdenite, $[MoS_2]_n$. The affinity of molybdenum for sulphur ligands seems close to that for analogous oxygen ligands so that there is an extensive molybdenum-oxo-sulphur chemistry. Where applicable, sulphur adopts a bridging position in preference for oxygen. Some representative examples of molybdenum sulphur compounds are shown in Figure 2.26.

2.7 COMPARISON OF GENERAL TRENDS IN THE CHEMISTRIES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

The MLX plots for chromium, molybdenum and tungsten are given in Figure 2.27. Inspection of these enable important similarities and differences in the chemistries of the three elements to be identified.

(i) The 18-electron rule is well obeyed by all three elements.

(ii) Compounds with L.B.N. < 6 are almost unknown (a possible exception is CrR_4, where R = alkyl, L.B.N. = 4 in the absence of agostic bonds).

(iii) Compounds with L.B.N. = 6 are well represented and a similar pattern for this diagonal relationship is found for all three elements.

(iv) The regions of the MLX plots at the bottom left hand side are clearly similar for molybdenum and tungsten but these differ markedly from that of chromium. In this high valency region the ligands are the more highly electronegative and form strong σ-bonds to the metals. Therefore these ligand environments develop a partial positive charge at the metal centre. Since the sensitivity of 3d-orbitals to such a partial charge is much greater than for the more highly shielded 4d- and 5d-orbitals it is correspondingly more difficult for chromium in a given ligand environment to achieve higher valencys than for molybdenum or tungsten.

(v) The regions where the values for V.N. are 0 - 2 are very similar for all three elements. This arises since the donor-acceptor nature of the ligand environments in this region do not cause a

substantial increase or decrease in the energies of the unused d^n electron on the metal centre in the compounds. Therefore, the different sensitivities to partial charge of the 3d,4d and 5d orbitals, a detailed above, are not interrogated.

(vi) When V.N. > 3 the precise distribution of the population densities are very closely similar for molybdenum and tungsten but the population densities for all classes of chromium where x > 3 are much smaller. In other words compounds where V.N. > 3 are much more abundant for molybdenum than chromium and slightly more abundant for tungsten compared to molybdenum. The increasing stabilisation of higher valency numbers in the sequence 6d>5d>3d is a well-known trend which, as noted above, reflects the greater availability of the d-electrons of the heavier elements as a consequence of subtle differences in the shielding which arise from the filled 3d shell (for Mo) and the 4d and 4f shell (for W). For example, the highest values of V.N. for the binary chlorides are $CrCl_4$, $MoCl_5$ and WCl_6. Typically for a first row transition metal such as chromium, the high valency compounds with electronegative ligands are highly oxidising, e.g. CrO_3 compared to MoO_3.

(vii) The historically important and classically inert octahedral chromium compounds in the class CrL_3X_3 have no equivalence in molybdenum or tungsten chemistry. The inertness of CrL_3X_3 compounds to substitution is reflected by the virtual absence of compounds in the adjacent class CrL_2X_3 and CrL_4X_3. The absence of the former can be associated with the undesirable steric unsaturation and partially filled valency shell (13-electrons). Whilst the paucity of the CrL_4X_3 can be associated with the general steric disadvantages of seven co-ordination. The relatively smaller size of Cr (compared to Mo and W) and the loss of crystal field stabilisation energy (CFSE) and exchange energy compared to that for d^3 t_{2g} chromium compounds. The MLX plot for chromium shows that the class CrL_4X_2 which is diagonally related to CrL_3X_3 has a modest population density. Therefore, redox chemistry is expected to occur between these two classes, as is observed.

2.8 CONCLUSION

We have introduced a new method of classification of the covalent compounds of molybdenum. The classification leads to the construction of the MLX plot for molybdenum. This plot provides a broad overview of the different classes of compounds which molybdenum forms and enables the major characteristic trends of molybdenum chemistry to be readily identified.

APPENDIX TO CHAPTER 2.

Further comments on the Classification of Covalent Compounds by Valency Number, Electron Number and Ligand Bond Number.

A.1 An alternative form for MLX plots.

The Figure A.1 shows an form of MLX plot which differs from that shown in Figure 2.2 insofar that the boxes which have no possible compound class are the same size as the boxes which do have a compound class.

ELECTRON NUMBER E.N.

		12	13	14	15	16	17	18
V A L E N C Y N U M B E R V. N.	0	ML_3		ML_4		ML_5		ML_6
	1		ML_3X		ML_4X		ML_5X	
	2	ML_2X_2		ML_3X_2		ML_4X_2		ML_5X_2
	3		ML_2X_3		ML_3X_3		ML_4X_3	
	4	MLX_4		ML_2X_4		ML_3X_4		ML_4X_4
	5		MLX_5		ML_2X_5		ML_3X_5	
	6	MX_6		MLX_6		ML_2X_6		ML_3X_6

Figure A.1 An alternative presentation of an MLX plot for which the element M has six valency electrons. The dark grey boxes which have no ML_lX_x class shown are those for which compounds cannot by definition exist. The boxes with compounds classes given are shaded as for the distribution of population densities found for molybdenum compounds. These are the same as those given in Figure 2.2 in Chapter 2.

A. 2 Definitions of ligand functionality and denticity

When a ligand bonds to the central atom using only one-ligating atom and one orbital then the ligating atom is called a mono-dentate, mono-functional ligating atom. The orbital may contain two, one or zero electrons..

When a ligand bonds to the central atom using only one-ligating atom and more than one orbital then the ligating atom is called a mono-dentate, bi-, tri-,. or, in general, a poly-functional ligating atom. Each orbital may contain two, one or zero electrons.

When a ligand bonds to the central atom using more than one atom and each ligating atom uses only one orbital in the formation of the metal-ligand bond then it is called a bi-, tri,...(generally) a poly-dentate, mono-functional ligand.

When a ligand bonds to the central atom using more than one ligating atom and at least one of the ligating atoms is poly-functional then the ligand is classed as a poly-dentate, poly-functional ligand.

A.4 Definition of d^n

In the Crystal Field theory or the Ligand Field theory of transition metal compounds the term d^n is used and it indicates the *number of electrons n remaining in essentially d-orbitals on the metal*. We define d^n similarly using the MLXZ formalism by

for d^n, $n = Me-x-2z$

For elements where the unused valency electrons are not in d-orbitals then the general symbol v^n can be used to indicate there are n unused valency electrons remaining in the valency orbitals of the element M of $ML_lX_xZ_z$.

Examples are,

$$[Mo(\eta-C_5H_5)_2H_2] = L_4MX_4 \qquad\qquad n = 6-4 = 2; \quad d^2$$
$$[Mo(\eta-C_5H_5)_2H_2(AlMe_3)] = L_4MX_4Z \qquad\qquad n = 6-4-2 = 0; \, d^o$$
$$NH_3 = MX_3, \qquad\qquad n = 5-3; \qquad v^2$$
$$NH_4^+ = MX_3Z, \qquad\qquad n = 5-3-2; \qquad v^0$$
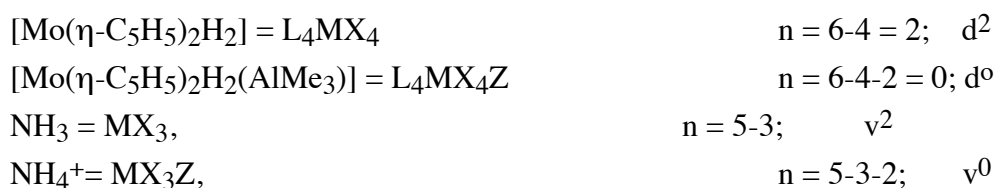
A.5 The classification of covalent anions

The central atom and all ligands are treated in the first place as <u>neutral</u>. Thus chlorine as a ligand is regarded as Cl not as Cl⁻, similarly the nitrosyl ligand is regarded as NO and not as NO⁺ One advantage of this approach is that it is not necessary to make any decision about the partial charge on the ligand A molecular ion is therefore <u>first</u> classified as though there was no charge and the total charge is placed outside the bracket.

Thus the general representation of a molecular cation or anion is $[ML_lX_xZ_z]^{n+ \text{ or } n-}$. In order to determine the E.N., V.N. or L.B.N. and for convenience in classifying molecular ions in V.N./E.N. (i.e. M.L.X.) plots the general representation for a molecular ion has to be transposed to the *Equivalent Neutral Class* (E.N.C) The general rules for this procedure are given in Table A.2. Although, at first sight, these may seem to be complex, the procedure, in fact, is extremely simple and is exemplified in Table 3.

A summary of the rules used in the Table 3 is

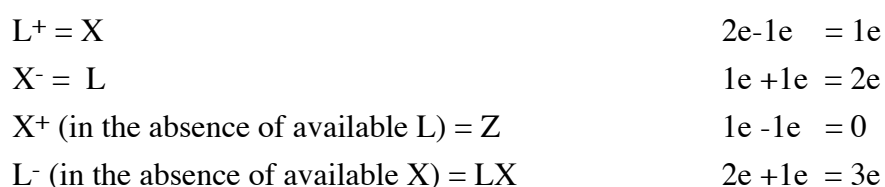|	
$L^+ = X$	2e-1e $\ = 1e$
$X^- = L$	1e +1e $= 2e$
X^+ (in the absence of available L) $= Z$	1e -1e $\ = 0$
L^- (in the absence of available X) $= LX$	2e +1e $= 3e$

Table A.2 Rules for classification of covalent molecules and molecular ions

Initial class	Rule for reduction to E.N.C.	V.N. given by	L.B.N. given by	Limits
MX_X neutral	-	x	x	$x \leq$ **Me**
$[MX_X]^{m-}$ anions	$X^- \rightarrow L$	x - m	x	$m \leq x$
$[MX_X]^{m+}$ cations	$X^+ \rightarrow Z$	x - m	x	$m \leq x$
ML_l neutral	-	x = 0	l	availability of M orbitals, 18e rule
$[ML_l]^{m-}$ anions	$L^- \rightarrow LX$	m	$l + m$	availability of ligand orbitals
$[ML_l]^{m+}$ cations	$L^+ \rightarrow X$	m	l	$m \leq n$
ML_lX_X neutral	-	x	$l + x$	$x \leq$ **Me**, availability of M orbitals
$[M_lX_X]^{m-}$ anions	$X^- \rightarrow L$, then $L^- \rightarrow LX$	x-m $(m \leq x)$ m - x $(l+x > m > x)$	$l + x$ $l + m + x$	As for $[ML]^{m-}$ and $[MX]^{m-}$ anions
$[ML_lX_X]^{m+}$ cations	$L^+ \rightarrow X$, then $X^+ \rightarrow Z$	x + m $(m < l)$ $2l$ + x - m $(m>l)$	$l + x$ $l + x$	As for $[ML]^{m+}$ and $[MX]^{m+}$ cations

Table A.3 Examples of conversion of the classes of ions to the Equivalent Neutral Class

Compound	Molecular ion	Rearrange	Rule applied	Equiv.Neutral Class E.N.C.
$[Co(NH_3)_6]^{3+}$	$[ML_6]^{3+}$	$[ML_3(L^+)_3]$	$L^+ = X$	ML_3X_3
$[CoF_6]^{3-}$	$[MX_6]^{3-}$	$[MX_3(X^-)_3]$	$X^- = L$	ML_3X_3
$[Co(NH_3)_4Cl_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[Mn(CO)_5]^-$	$[ML_5]^-$	$[ML_4(L^-)]$	$L^- = LX$	ML_5X
$[Mn(CO)_6]^+$	$[ML_6]^+$	$[ML_5(L^+)]$	$L^+ = X$	ML_5X
$[Co(\eta-C_5H_5)_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[NiCl_4]^{2-}$	$[MX_4]^{2-}$	$[MX_2(X^-)_2]$	$X^- = L$	ML_2X_2
$[Pt(NH_3)Cl_3]^-$	$[MLX_3]^-$	$[MLX_2(X^-)]$	$X^- = L$	ML_2X_2
$[Cr(CO)_5]^{2-}$	$[ML_5]^{2-}$	$[ML_3(L^-)_2]$	$L^- = LX$	ML_5X_2
$[Ir(PR_3)_2H_6]^+$	$[ML_2X_6]^+$	$[ML(L^+)X_5$	$L^+ = X$	MLX_7

Very occasionally, the question of the order of precedence of these rules arises, see Table 2.

A.5.1 Classification of molecular anions which contain polyfunctional ligating atoms

It is necessary to distinguish between ligands with monofunctional ligating atoms and those with polyfunctional ligating atoms because the rules for reduction of a molecular anion to the Equivalent Neutral Class differ for the two cases.
Examples of the more common ligands with polyfunctional co-ordinating atoms are given in Table 4. By far the most commonly encountered polyfunctional ligand is the oxygen atom.

Table A. 4 Examples of ligands with poly-functional ligating atoms.

Ligand	Class	Representation	Examples.
O	2	$M = O$	CO_2, $[Mo(\eta\text{-}C_5H_5)_2O]$, OsO_4, $MoCl_2O_2$
S	2	$M = S$	$[MoS_4]^{2-}$, CS_2
NR	2	$M = NR$	$RC = NR$
CR_2	2	$M = CR_2$	$H_2C = CH_2$, $[Ta(\eta\text{-}C_5H_5)_2(=CH_2)Me]$
CR	3	$M \equiv C$	$HC \equiv CH$, $Mo(\equiv CR)Br(CO)_4$
N	3	$M \equiv N$	N_2, $(PR_3)_4Re(\equiv N)Cl_2$[a]
NO	L[b]	$M—NO$	NO in $Cr(NO)_4$, $Co(CO)_3NO$
Cl_4Re	4	$M \equiv M$	$[Cl_4Re \equiv ReCl_4]^{2-}$

[a] $Re\text{-}N = 1.79\text{Å}$ [b] For reduction to E.Q.N. is $L \to L_2$

The classification of neutral oxo-compounds such as OsO_4, $[Mo(\eta\text{-}C_5H_5)_2O]$ and CrO_2Cl_2. proceeds in an identical manner as for other neutral compounds. The representations MX_8 and $M(X_2)_4$ for the neutral OsO_4 are equivalent. In each case each oxygen requires two electron from the metal and contributes a p_π-lone pair, as discussed in Chapter 2.
However for a molecule anion such as the carbonate ion $[CO_3]^{2-}$ if we define the class as $[M(X_2)_3]^{2-} = [MX_6]^{2-}$ and then use the normal rule, $X^- \to L$, for reduction to the equivalent neutral class, this leads to the E.N.C. class MX_4L_2. This assigns an electron number of 12 to the carbon which is clearly absurd since carbon in its vast range of compounds *never* exceeds an electron number of eight. i.e. MX_4.

We can achieve this desired class for carbon in the carbonate anion in the following manner. The bi-functional oxo ligand atom O is represented not as X_2 but as $\bar{X}_2$, the notation with the bar above the ligand class serves to identify the ligating atom as being poly-functional. The rule for reduction of anions with poly-functional ligands to the E.N.C. is $\bar{X}_2^- \to X$

Using this rule we may classify the carbonate ion as follows;

$$[CO_3]^{2-} = [M(\bar{X}_2)_3]^{2-} = [M(\bar{X}_2)(\bar{X}_2)_2^-] = [M(\bar{X}_2)X_2] = MX_4$$
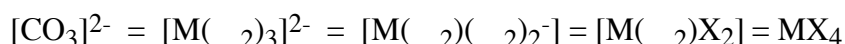
Once all the charges on the anion have been dealt with there is no longer any need to distinguish between the classes $\bar{X}_2$ and X_2 so that the final step is $[M(\bar{X}_2)X_2] = MX_4$, as shown above.

The general rule for the reduction of ions containing L_x ligands to the equivalent neutral class is

$$(L_x)^- \to L_{x-1}$$
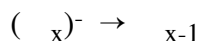
When both poly- and mono-functional atoms are present then the electron is added first to the polyfunctional atoms. For example the anion $[CrO_3Cl]^-$ is treated as follows

$$[CrO_3Cl]^- = [M(L_2)_3X]^- = [M(L_2)_2(L_2^-)X] = [M(L)_2X_2] = MX_6$$
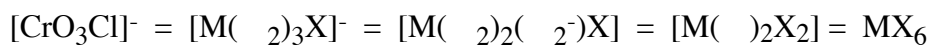
Further examples of the classification of covalent oxides and oxyanions are given in Table A.5.

Table A.5 Determination of MLXZ class and reduction to the neutral class of oxygen derivatives; where 0 is a L_2 class ligand.

Molecular or Ion	Class	Rule	Equivalent Neutral Class
CO_2	$M(L_2)_2$	--	MX_4
CO_3^{2-}	$M L_2(L_2^-)_2$	$L_2^- \to X$	MX_4
MoO_2Cl_2	$M(L_2)_2X_2$	--	$MX_6 b$
SO_3	$M(L_2)_3$	--	MX_6
SO_2Cl_2	$M(L_2)_2X_2$	--	MX_6
Me_2CO	$[M(L_2)_2X_2]$	--	MX_4
MoO_4^{2-}	$[M(L_2)_2(L^-)_2]$	$L_2^- \to X$	$MX_6 b$
ReO_4^-	$[M(L_2)_3(L^-)_2]$	$L_2^- \to X$	$MX_7 b$
NO_2^-	$[M(L_2)(L_2^-)]$	$L_2^- \to X$	MX_3
PHO_3^{2-}	$[M(L_2)(L_2^-)_2X]$	$L_2^- \to X$	MX_5
$[VO(H_2O)_4]^{2+}$	$[M(L_2)L_2(L^+)_2]$	$L^+ \to X$	$ML_2X_4 b$
$[VO(H_2O)_4]^{2+}$	$[M L_2L_2(L^+)_2]$	$L^+ \to X$	$ML_2X_4 b$
$VO(acac)_2$	$[M L_2(LX)_2]$	--	$ML_2X_4 b$
$[VO(SCN)_4]^{2-\,a}$	$[M(L_2)^- X_3X^-]$	$L_2^- \to LX$ $X^- \to L$	$ML_2X_4 b$

[a] The V = O distance = 1.62Å so O is classified as $(L_2)^-$. [b] The metal centre has empty d-orbitals, if p_π-lone pair electrons on the oxygen donate to the metal the number of L-functions. increases by one or more according to symmetry considerations.

A simple aid-memoir for determining the equivalent neutral class of an anion containing poly-functional ligands is to envisage protonation (or methylation) of the poly-functional ligand. The class of the resulting neutral molecule will be the same as that of the anion. For example protonation of $[SO_4]^{2-}$ gives $SO_2(OH)_2$ (sulphuric acid) which has the class MX_6.

The reduction of the molybdate anion $[MoO_4]^{2-}$ to the E.N.C. also gives the class with V.N. = 6. However, in this case there are empty valency (d) orbitals on the molybdenum centre. Therefore the class is MoL_lX_6 where l remains to be determined. In the tetrahedral symmetry of the molybdate anion the six X-function bonds are formed by the molybdenum five 4d-orbitals and the single 5s-orbital which are in combination with the e, $1t_2$ and a_1 combinations of orbitals formed by the four oxygen ligands. There remain six electrons arising from the four oxygen ligands which form the $2t_2$ set. and these can donate into the corresponding $2t_2$ molybdenum based orbitals. Therefore, if we deem that the $2t_2$ electrons on the oxygens take part in primary bonding to the molybdenum centre then the class of the $[MoO_4]^{2-}$ anion is $MoL_3X_6.$ In which case, the anion has an electron count of E.N. = 18. The six electron in the t_1 set of oxygen-based orbitals cannot donate to the molybdenum since there are no orbitals of appropriate symmetry on the molybdenum.

A.6 Comments on the Table 2.2.

In this Table NH_3 is classified as L whilst ethylenediamine $H_2NCH_2CH_2NH_2$ is classified as L_2. Clearly such a distinction is trivial and in chemical terms can only have significance in terms of possible consequences of pre-organisation, such as the entropy based chelate effect. In any event, this distinction is lost in the final statement of the class of a molybdenum compound when the only information required is the total number of L- or X-functions without regard to the particular ligands from which they are derived. Therefore it is reasonable to ask why such a distinction is made which seems at first sight to unnecessarily complicate the Table. The reason is that for some poly-dentate ligand systems and poly-functional ligands the class is sometimes less obvious, e.g. the η-unsaturated hydrocarbon ligands and the linear imido NR ligand (class X_2L). Therefore to help those who wish to identify the class of a compound which contains such ligands it is sensible to indicate their classes. In which case, for the sake of consistency, the trivial distinctions fall better into the organisation than to let them lie outside. Once you explain that $Mo(CO)_6$ is class ML_6, that MoF_6 is MX_6 and $Mo(PR_3)_3Cl_3$ is MoL_3X_3 then most chemistry students can immediately classify most ligands without the need for the elaborate Table 2.2. It is the less obvious ligands which introduce the need for a more rigorous classification, albeit rather pedantic.

It may also ne noted that ligands which have very different bondiong properties occur in the same class, for example, the molecules NH_3 and the π-acid CO. However, the difference of properties of these ligands are striking manifested by the very different ligand domains for the two ligands. For example, the compounds $[Mo(NH_3)_6]$ and $[Mo(CO)_6]^{3+\cdot}$are unknown.

A. 7. MLX plots for nickel, palladium and platinum

The title plots are shown in Figure A.2. These plots have been provided to demonstrate the similarities and substantial differences between the chemistries of the Group VI metals Cr, Mo and

W and the Group 10 metals. Inspection of the MLX plots of molybdenum and palladium clearly leads to the following observations:

(i)   18- and 16-electron compounds dominate palladium chemistry. The favourable stability of square-planar, 16-electron, d^8 compounds of the Group 10 elements is self evident from their MLX plots.

(ii)   Odd-electron compounds, i.e. where V.N. = 1 or 3 are very rare indeed. There are no consecutive diagonal sequences of compounds with constant L.B.N. and palladium shows little redox chemistry in marked contrast to molybdenum

(iii) In contrast to molybdenum there are two well populated classes related by +/-X_2 reactions; these are the classes PdL_2X_2 and PdL_2X_4. Therefore, oxidative-addition and reductive elimination reactions are expected to be a dominant feature of the chemistry of palladium, as is observed. As noted in Chapter 2, oxidative-addition reactions are rare for molybdenum.

(iv) Palladium shows a limited chemistry for V.N. > 2 as a consequence of the higher ionisation potentials for the element (compared to molybdenum)

(v) Since **Me** = 10 for Pd the highest observed ligand bond numbers are 6 and these occur when the electron number is 18. Contrast molybdenum which has compounds with values of L.B.N of 6-9. However, palladium compounds are found with L.B.N. = 3 (rare) and commonly 4 and these are unknown for molybdenum. Such low ligand bond numbers means that ligand addition reactions (and hence ligand substitution by associative processes) will have low steric barriers.

The MLX plot for nickel.

ELECTRON NUMBER E.N.

VALENCY NUMBER V.N.	14	15	16	17	18	19	20
0	NiL_2		NiL_3		NiL_4		NiL_5
1		NiL_2X		NiL_3X		NiL_4X	
2	$NiLX_2$		NiL_2X_2		NiL_3X_2		NiL_4X_2
3		$NiLX_3$		NiL_2X_3		NiL_3X_3	
4	NiX_4		$NiLX_4$		NiL_2X_4		NiL_3X_4
5			NiX_5		$NiLX_5$		NiL_2X_5
6				NiX_6		$NiLX_6$	NiL_2X_6

The MLX plot for palladium.

ELECTRON NUMBER E.N.

VALENCY NUMBER V.N.	14	15	16	17	18	19	20
0	PdL_2		PdL_3		PdL_4		PdL_5
1	·	PdL_2X		PdL_3X		PdL_4X	
2	$PdLX_2$		PdL_2X_2		PdL_3X_2		PdL_4X_2
3		$PdLX_3$		PdL_2X_3		PdL_3X_3	
4	PdX_4		$PdLX_4$		PdL_2X_4		PdL_3X_4
5			PdX_5		$PdLX_5$		PdL_2X_5
6				PdX_6		$PdLX_6$	PdL_2X_6

The MLX plot for platinum.

ELECTRON NUMBER E.N.

VALENCY NUMBER V.N.	14	15	16	17	18	19	20
0	PtL_2		PtL_3		PtL_4		PtL_5
1	·	PtL_2X		PtL_3X		PtL_4X	
2	$PtLX_2$		PtL_2X_2		PtL_3X_2		PtL_4X_2
3		$PtLX_3$		PtL_2X_3		PtL_3X_3	
4	PtX_4		$PtLX_4$		PtL_2X_4		PtL_3X_4
5			PtX_5		$PtLX_5$		PtL_2X_5
6				PtX_6		$PtLX_6$	PtL_2X_6

Figure A.2 MLX plots for nickel, palladium and platinum.