A new approach to the energetics of clusters and related systems

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by

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To Mum and Dad

A NEW APPROACH TO THE

ENERGETICS OF CLUSTERS

AND RELATED SYSTEMS

" A plausible impossibility is always preferable to an unconvincing possibility."

Aristotle 384-322 B.C.

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MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1976 and September 1979. I declare that this work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

Parts of this work have been published in or submitted for publication to the following Journals:

"Bond Strengths in Metal Carbonyl Clusters"

by Catherine E. Housecroft, Kenneth Wade and Barry C. Smith, J.C.S.Chem.Comm., p.765 (1978)

"Reorganisation Energies and Site Preferences of Carbonyl Ligands: Bond Energies of Bridging and Terminal Carbonyl Groups of the Iron Carbonyls $Fe_2(CO)_9$ and $Fe(CO)_5$"

by Catherine E. Housecroft, Kenneth Wade and Barry C. Smith, J.Organometal.Chem., 170, C1 (1979)

"Bond Length-Based Bond Enthalpies for Nido- and Arachno-Boranes, B_nH_{n+4} and B_nH_{n+6}"

by Catherine E. Housecroft and Kenneth Wade, Inorg.Nucl. Chem.Letters (1979) (in press).

"Bond Enthalpies of Borane Anions $B_nH_n^{2-}$ "

by Catherine E. Housecroft, Ronald Snaith and Kenneth Wade, Inorg.Nucl.Chem.Letters, (1979) (in press)

"The Relationship Between Cyclic Hydrocarbons and Boranes: Cyclobutane as a Hypho-Cluster"

by Catherine E. Housecroft and Kenneth Wade, Tetrahedron Letters, p.3175 (1979)

"Significant Similarities and Differences Between Metal Carbonyl Clusters and Boron Clusters"

by Catherine E. Housecroft and Kenneth Wade, Gazzetta Chimica Italiana, (1979) (in press)

ABSTRACT

The work described in this thesis is concerned with cluster-species and related systems, many of which are electron deficient. The term 'electron deficient' is used to describe a polynuclear species in which there are too few valence electrons to allocate a localised 2-centre 2-electron bond to every pair of atoms which are within normal covalent bonding distance. The bonding in these systems may be rationalised instead in terms of the relationship between the total number of skeletal electrons provided by the skeletal cluster units, and the total number of skeletal atoms.

The aim of this work is to suggest new ways in which bond enthalpy contributions can be allocated to individual 2-centre links in cluster systems. In order to obtain energy terms (E) which reflect changes in bond length, (d), relationships of the form

$$E \propto d^{-k}$$

(where k=constant; $2 < k < 5$)

are proposed. Such empirical correlations are shown to be appropriate for simple main group systems and are applied in turn to boron hydrides, borane anions, transition metal carbonyls and to complexes containing multiple metal-metal bonds. Similar relationships are used to suggest possible bond orders in some systems.

Finally, the extent to which skeletal electron counting methods may be used to rationalise the bonding in boranes, carboranes, transition metal clusters, main group clusters, metal π-hydrocarbon complexes and small cyclic hydrocarbons is discussed.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 Experimental Determinations of Thermochemical Quantities and the Estimation of Bond Energies

Thermochemistry has always been an important branch of chemistry as it provides valuable information about the energy changes which accompany chemical reactions, allowing one to compare the relative stabilities of compounds and predict the ease with which a reaction may occur. Fundamental to all thermochemical calculations is the requirement for accurate values of standard enthalpies of formation of compounds from their constituent elements, all of which must be considered in the gas phase. Accurate determinations of heats of sublimation (or vaporisation) are therefore essential.

The aim of this thesis is to suggest new ways in which experimentally determined thermochemical data may be treated to gain an insight into the allocation of energy to particular bonds in some transition metal and boron-containing systems. Actual methods of measuring thermochemical quantities by experiment are therefore not described; further information on experimental techniques can be found in references 1-11. It is, however, worth commenting on the direct measurement of bond dissociation energies by spectroscopic and electron impact techniques as both methods produce results which must be treated with caution.

Spectroscopic determinations of the heat of formation and bond dissociation energy, D_o, of a diatomic molecule are by the Birge-Sponer extrapolation.[1,2] D_o is given by the approximate expression:

$$D_o \simeq \frac{\omega_o^2}{4 x_o \omega_o} \qquad \omega_o = \text{vibrational frequency} \qquad x_o = \text{vibrational amplitude}$$

Estimates of D_o tend generally to be too high and should only be used as approximate values.

Thermochemical quantities derived from mass spectroscopic electron impact data should also be treated with caution. The method relies on the determination of the appearance potential (A.P.) of an ion, MX_n^+, in the mass spectrum (i.e. the minimum electron energy required to produce the ion from its parent species, MX_{n+1}); equation 1.1. The A.P. is then combined with the ionisation potential (I.P.) of the ion (equation 1.2) to give the appropriate bond dissociation energy, (equation 1.3). The electron impact method measures individual bond dissocation energies for stepwise

$$MX_{n+1} + e^- \xrightarrow{A.P.} MX_n^+ + X + 2e^- \qquad (1.1)$$

$$MX_n + e^- \xrightarrow{I.P.} MX_n^+ + 2e^- \qquad (1.2)$$

$$MX_{n+1} \xrightarrow{D(M-X)} MX_n + X$$
$$D(M-X) = (A.P.) - (I.P.) \qquad (1.3)$$

dissocation of a molecule, (see Section 1.2). These values are NOT equal to the <u>mean</u> bond dissociation energy with which they are sometimes confused.

With the development of new experimental and theoretical methods, bond dissociation energies of many simple molecules are now known with a high degree of accuracy. The use of spectroscopic, photochemical, electron impact and pyrolysis methods have increased the data available regarding individual bond energies, especially in organic compounds[9] and diatomic molecules.[1] However, the allocation of energy to individual bonds in more complex systems, (e.g. transition metal carbonyls, organometallic compounds (other than those of the type $R_{3-x}M_x$ etc.), and cluster or related compounds containing boron), is more difficult. Only a limited number of attempts have been made to solve this problem.

For a diatomic molecule, A_2, the bond dissociation energy is equal to the heat of disruption and can be estimated if the standard enthalpies of formation for both gaseous A and A_2 are known, (equation 1.4).

$$A_2(g) \longrightarrow 2\ A(g)$$

$$\Delta H_{disrupt.}A_2(g) = 2\Delta H^o_{f298}A(g) - \Delta H^o_{f298}A_2(g) \qquad (1.4)$$

For a molecule R_2 (which is NOT diatomic) dissociating into two free radicals R•, the mean dissociation energy D(R-R) is given by equation 1.5. Values of $\Delta H_{disrupt.}R_2(g)$ and $\Delta H_{disrupt.}R\cdot(g)$ are calculated from the appropriate standard enthalpies of formation. (This situation has been simplified.

$$D(R\text{-}R) = \Delta H_{disrupt.}R_2(g) - 2\Delta H_{disrupt.}R\cdot(g) \qquad (1.5)$$

No account has been taken of any changes in hybridisation which might accompany the change $R_2 \longrightarrow 2R\cdot$; see Section 1.2). In some cases however, the necessary thermochemical data ~~is~~ not available. For instance, in a polynuclear metal carbonyl system, bond energies cannot be estimated by considering the type of simple disruption process described above because enthalpies of formation of all possible metal carbonyl fragments have not been determined. Instead, disruption of a metal carbonyl, $M_x(CO)_y$, into metal atoms and discrete carbon monoxide molecules is considered:

$$M_x(CO)_y\ (g) \longrightarrow xM(g) + yCO(g)$$

(This particular process is described fully in Chapter Four). The disruption of any cluster or cyclic system into atoms or small discrete units involves the fission of a variety of bonds of differing strengths. The problem posed is the allocation of a particular percentage of the total heat of disruption to a given bond. A summary of the data already available for each type of system considered in this thesis will be given at the beginning of each chapter.

1.2 Intrinsic Bond Energy Terms and Reorganisation Energies

Allocation of bond enthalpy terms in a molecule XY_n is generally based on the disruption process:

$$XY_n(g) \longrightarrow X(g) + nY(g)$$

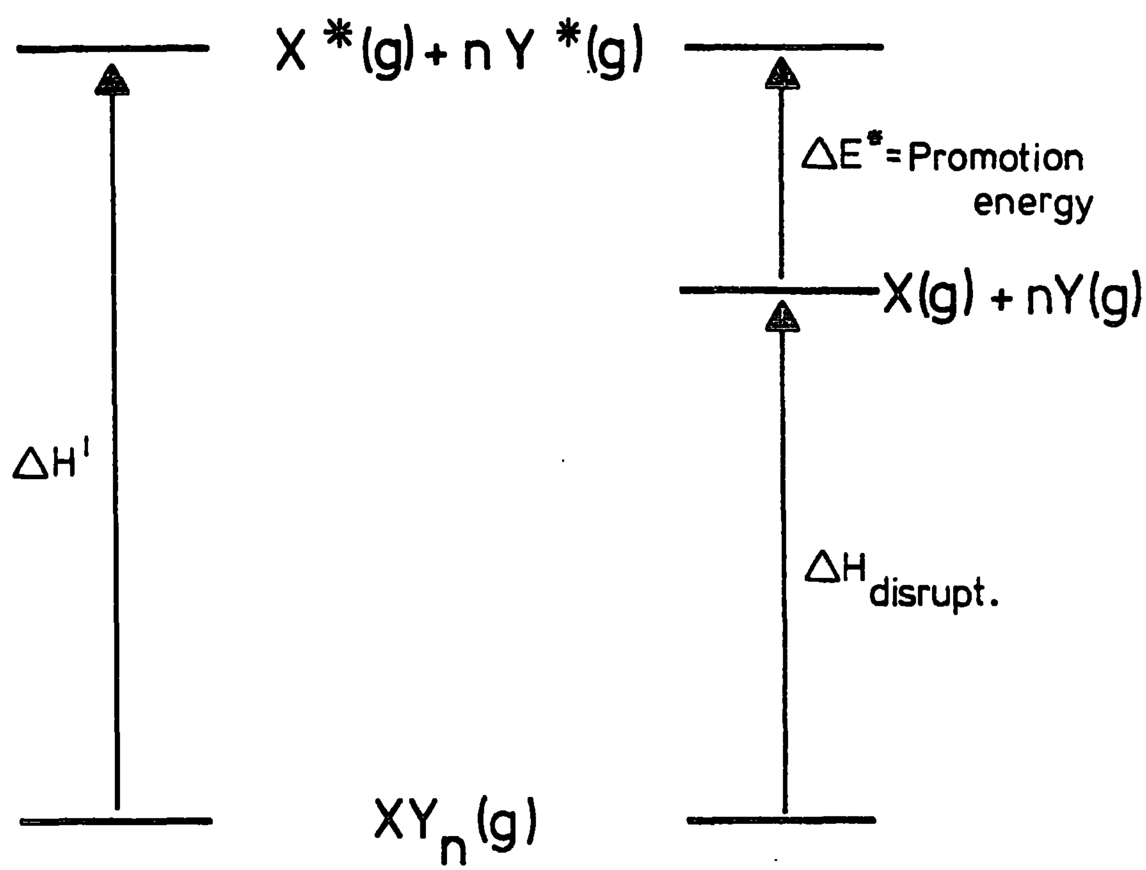
The heat of disruption of XY_n is given by equation 1.6. The standard heats of formation of the gaseous atoms X and Y

$$\Delta H_{disrupt.}XY_n(g) = \Delta H^o_{f298}X(g) + n\Delta H^o_{f298}Y(g) - \Delta H^o_{f298}XY_n(g) \quad (1.6)$$

correspond to values for their ground states. In the molecule XY_n however, X and Y will be in their valence states (X^* and Y^*) and it would therefore be more correct to use the enthalpies of formation $\Delta H^o_{f298}X^*(g)$ and $\Delta H^o_{f298}Y^*(g)$. True, or '<u>intrinsic</u>', bond energy terms are derived from thermochemical quantities which refer to the valence state. As an approximation, it is generally acceptable to consider all the atoms or fragments of disruption in their ground states. Energy terms so derived are the <u>mean bond dissocation energies</u>. It is however worth considering what effects the differences between ground and valence states have on the estimated bond energy contributions.

Figure 1.1 describes the disruption of the molecule XY_n.

Figure 1.1 Disruption of gaseous XY_n.



Initial disruption is to the valence states of the gaseous fragments X and Y, i.e. to $X^*(g)$ and $Y^*(g)$. Such states are unstable with respect to their ground states and spontaneous relaxation will occur with a change of energy, $-\Delta E^*$. ΔE^* is the promotion energy; it cannot be measured directly, but may be calculated by the Slater-Condon theory of atomic spectra.[12-14] The total energy required for the dissociation of XY_n is therefore $(\Delta H_{disrupt.} + \Delta E^*)$.

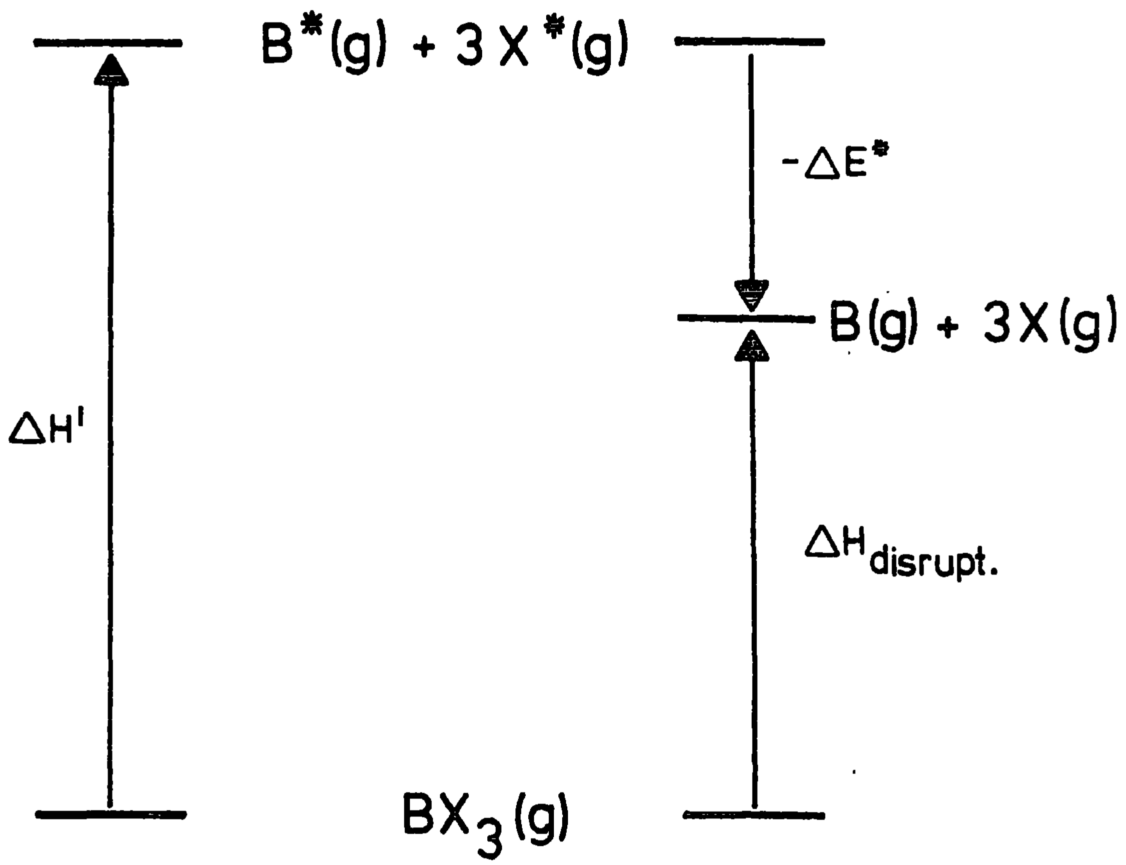
The simplest case for consideration is for atomic X and Y. The major differences between X and X^* or Y and Y^* are hybridisation and spin state. The disruption of e.g. methane into carbon and hydrogen atoms leaves carbon in an sp^3-hybridised valence state, C^*, which, as a result of possessing random relative spins, cannot be detected spectroscopically.[15] The valence state is difficult to define but may, however, be expressed as a mixture of several spectroscopic spin states. The energy of the valence state is then calculable from the weighted mean of the energies of each contributing spectroscopic state. Estimations of the promotion energy of carbon in an sp^3-hybridised valence state gives $\Delta E^* \approx 635 kJ\ mol^{-1}$.[13-14]

An attempt has been made to estimate intrinsic bond energies in boron halides.[16] Figure 1.2 shows the energy changes associated with the disruption of gaseous BX_3 (X = halogen). The total energy, ΔH^1, represents the sum of the intrinsic bond energy terms, $\Sigma E^*(B\text{-}X)$, (equation 1.7).

$$\Delta H^1 = \Delta H_{disrupt.} + \Delta E^* = \Sigma E^*(B\text{-}X) \qquad (1.7)$$

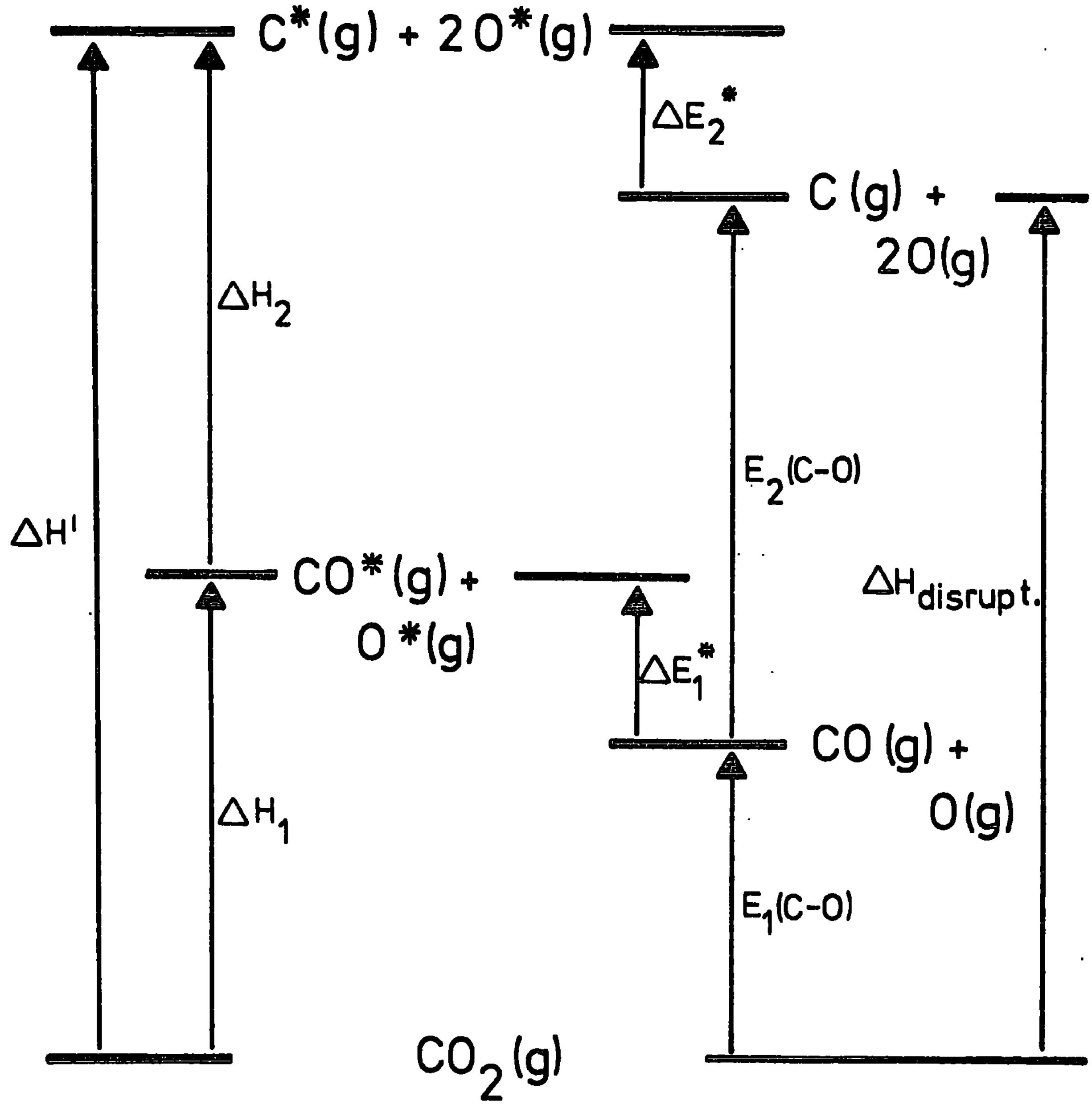
Assuming that the halogen atoms possess sp-hybridised orbitals, the calculated values of ΔH^1 are 2820kJ mol^{-1} for BF_3, 2070kJ mol^{-1} for BCl_3, and 1810kJ mol^{-1} for BBr_3.[16] These values compare with heats of disruption (from which mean bond dissociation energies are determined) of 1929 (BF_3), 1365 (BCl_3) and 1113 (BBr_3) kJ mol^{-1}; (ΔH^o_{f298}(g) B = 590, F = 76.7, Cl = 121.3, Br = 111.6, BF_3 = -1109, BCl_3 = -410, BBr_3 = -188kJ mol^{-1},[16] cf. $\Delta H^o_{f298}B(g)$ = 560kJ mol^{-1} in this thesis, see Chapter Three). The average intrinsic bond energies, $E^*(B\text{-}X)$ are therefore considerably larger than the mean bond dissociation energies, ($D(B\text{-}X) = \frac{1}{3}\Delta H_{disrupt.}$; av.$E^*(B\text{-}X) = \frac{1}{3}\Delta H^1$), and the importance of distinguishing between the two is emphasised.

Figure 1.2 Disruption of gaseous BX_3.



In most cases, calculations of enthalpies of disruption with respect to the ground state, and hence estimation of <u>mean</u> bond enthalpy terms, are adequate and are widely accepted. The energetics of the stepwise removal of atoms, ligands or free radicals are however important exceptions.[4,17] Carbon dioxide provides a useful example, Figure 1.3. In general one might estimate the mean bond dissociation energy with respect to the ground state as $\frac{1}{2}\ \Delta H_{disrupt.}$; this gives D(C-O) = 802kJ mol^{-1}.[8,17] The stepwise dissociation of gaseous CO_2 renders a separate bond dissociation energy for each step, the mean of which is 802kJ mol^{-1}. Removal of one oxygen atom initially gives a carbon-oxygen valence state (CO^*) with sp-hybridised carbon. Reorganisation to the stable

Figure 1.3 Stepwise dissociation of gaseous CO_2.



carbon-oxygen triple bond will be spontaneous, (equation 1.8 and Figure 1.3). The overall energy change is $E_1(C-O)$ = 532kJ mol^{-1}, [17] (i.e. the first bond dissociation energy of

$$CO_2(g) \longrightarrow CO^*(g) + O^*(g) \longrightarrow CO(g) + O(g) \qquad (1.8)$$

carbon dioxide). The second step involves the fission of the carbon-oxygen triple bond, (equation 1.9 and Figure 1.3)

$$CO(g) \longrightarrow C^*(g) + O^*(g) \longrightarrow C(g) + O(g) \quad (1.9)$$

and the overall energy change is $E_2(C\text{-}O) = 1070 kJ\ mol^{-1}$, (i.e. the second bond dissociation energy of carbon dioxide). (It cannot be said that E_2 is always greater than E_1; e.g. in water $E_1(O\text{-}H) > E_2(O\text{-}H)$).

This thesis will generally be concerned with mean bond dissociation energies, (sometimes known as bond enthalpy contributions). Suggested values for such thermochemical quantities should not be confused with individual bond dissociation energies or intrinsic bond energies, both of which require estimates of promotion energies from ground to valence states. In the particular case of transition metal carbonyl compounds, some attempt has, however, been made to estimate the reorganisation energies of terminal and bridging carbonyl ligands on their disruption to free gaseous carbon monoxide (see Chapter Four, Section 4.4).

1.3 Use of Empirical Correlations for Estimating Bond Energies

The allocation of energy contributions to individual bonds in a molecule has been a subject of interest for at least the last forty years. Bonds of a given energy are expected to possess other characteristic physical constants, e.g. bond length, bond order, or force constant. It is generally accepted[18] that as bond energy increases, bond length decreases and values of both bond order and force constant increase. It is not surprising, therefore, that many attempts have been made to establish empirical relationships between two or more of these parameters in order to obtain realistic estimates of individual bond strengths. The most commonly studied systems have involved carbon-carbon bonds for the obvious reason that many compounds exist which contain C-C bonds of formal bond order 1, 2 or 3 and which have been fully characterised both structurally and thermochemically. Table 1.1 summarises some of the relationships suggested which relate bond length (d), bond order (n), bond energy (E) and/or force constant (f) for C-C bonds. Several of these relationships have also been tested in other systems e.g. CO, CN, NO, OO and NN bonds, (see column 2 of Table 1.1). Table 1.2 summarises a variety of empirical correlations developed to include other types of bonds, e.g. metal-metal, metal-oxygen, metal-halide and metal-hydride bonds and diatomic molecules. Other attempts have been made to correlate bond order with bond length or bond energy, but specific relationships have not been suggested. (e.g. Smooth curves can be drawn through points plotted for d(M-M) versus n(M-M) for the series $Nb_6X_{12}^{2+}$, $Mo_6X_8^{4+}$, $Re_2Cl_8^{2-}$ and Re_3Cl_9,[49] and for d(M-C) versus n(M-C) for a series of Mo-C bonds.[50])

The mean dissociation energy of a bond, D(A-B), has also been estimated directly from values of D(A-A) and D(B-B) by Pauling's equation:[51]

$$D(A\text{-}B) = [D(A\text{-}A).\ D(B\text{-}B)]^{\frac{1}{2}} + 30(\chi_A - \chi_B)^2 \qquad (1.10)$$

where χ_A and χ_B are the electronegativities of A and B respectively. A method of estimating D(A-B) as the reciprocal mean of D(A-A) and D(B-B) has also been suggested,[52] (equation 1.11)

$$\frac{1}{D(A\text{-}B)} = \tfrac{1}{2}\left[\frac{1}{D(A\text{-}A)} + \frac{1}{D(B\text{-}B)}\right] \qquad (1.11)$$

Empirical methods for estimating bond energies can only be useful if the chosen relationship involves a readily accessible parameter. A bond strength-bond length correlation

TABLE 1.1 Some Suggested Empirical Relationships Connecting Bond Length (d), Bond Order (n), Bond Energy (E), and/or Force Constant (f) for C-C Bonds.

(Units: d = Å, E = kcal mol^{-1}; f = mdyn.$Å^{-1}$ unless stated otherwise).

Relationship*	Comments	Ref.
$E(d^3) = A$ $(n^{2/3})(d^3) = B$	Unreliable $\Delta H_{sublim.}C$	19
$d = A + B(\frac{3}{5})^n$	Unreliable $\Delta H_{sublim.}C$; $\frac{3}{5}$ arises from $\left[\frac{N_1 + N_2 - 1}{N_1 + N_2 + 1}\right]$ where N_1 and N_2 = Principal quantum numbers	20,21
$dZ \;\alpha\; Z^2(\frac{3}{5})^n$	Variation of above; Z = Atomic number	22
$E = Ad^{-k}$	k = constant characteristic of bond type: $k_{C-C} = 3.1$; tested in other systems ($k_{C-O} = k_{C-N} = 4.4$; $k_{N-O} = 4.9$); unreliable $\Delta H_{sublim.}C$	23
$n = Ad^{-2} + B$ $E = Cd^{-2} + D$	Unreliable $\Delta H_{sublim.}C$; equations tested in other systems	24
$d = d_1\left[\frac{2}{3} + \frac{1}{3}\left(\frac{N-1}{N+1}\right)\right]^{n/2}$	d_1 = Single bond distance; N = Principal quantum number; Equation tested in other systems	25

TABLE 1.1 (Continued)

Relationship*	Comments	Ref.
$E = Ad^{-k}$	Development of equation ref.23. Uses $\Delta H_{sublim.}C = 5.888eV \approx 570 kJ\ mol^{-1}$ as best value; k not specified; (E in eV)	26
$E = A - Bd + Cd^2$	Parabolic relationship replaces $E = Ad^{-k}$ suggested previously; Uses $\Delta H_{sublim.}C = 169.8\ kcal\ mol^{-1} \approx 710\ kJ\ mol^{-1}$	27
$d^{-2} = A + Bn$	Similar correlations for C-N and N-N bonds proposed.	28
$E = Ad - Bd^2 + Cd^3 - Dd^4$	Suggested for cycloparaffins; an inverse relationship is suggested for C-H bonds.	29
$E = A - B(4-n)^2$, $n = \left[\frac{C}{d^2}\right] - 2$	Assumes Pauling's scale of empirical bond energies i.e. E(single C-C) = $58.6\ kcal\ mol^{-1} = 245.2\ kJ\ mol^{-1}$	30
$E \propto d$	Tested in other systems	31
$d = A - Bn$	Relation valid for ground AND excited states	32
$d = A - Bn$	Tested for C-O and C-N bonds	33

TABLE 1.1 (Continued)

Relationship*	Comments	Ref.
$E = Ad^5 + Bd^{-4} - Cd^3 - Dd^{-2} + Fd - G$	Confined to hydrocarbons; also proposes: $E(C\text{-}H) = Hd^{-2} + Jd + K$	34
$d = A - B(E)$	Derived from bond length/ energy data in 33 hydrocarbons and derivatives	35,36
$E = Ad^{-3.2}$	Similar relationship assumed for B-N systems; (E in kJ mol^{-1})	37

* A, B, C, D, F, G, H, J, K are constants

TABLE 1.2 Some Empirical Relationships Suggested for Systems Other than C-C Bonds

(Units: d = Å, E = kcal mol^{-1}, f = mdyn.$Å^{-1}$ unless otherwise stated)

Relationship*	Comments	Ref.
$E = A - Bd$	For B-B and B-H bonds in neutral boron hydrides; (see Chapter 3). $\Delta H^{o}_{f298}B(g)$ is taken as 130 kcal mol^{-1} = 543 kJ mol^{-1}.	38
$E \propto f$	For H - X bonds (X = Halogen)	39
$d = \frac{2}{3}d_1 + \frac{1}{3}d_1(\frac{1}{3})^{\frac{n-1}{2}}$	For M-M bonds; application of Bernstein's equation (ref.25)	40
$d^6 = A\left[\frac{m_1 m_2}{p^2 f}\right]$	For diatomic molecule comprising atoms of masses m_1 and m_2; p = group number of diatomic	41
$d \propto \frac{1}{n}$	For Re-Re bonds with n = 1→4	42
$Ed = A + Bd$	For diatomic hydrides	43
$E_s \propto d^{-k}$	For M-O bonds; $2 \leq k \leq 7$ (E_s is defined as "bond strength in valence units")	44,45
$E_s \propto d^{-3.9}$	Above equation adapted for Li-O bonds; (E_s in valence units)	46
$E = f(A + Bd^2 + Cd^4)$	For diatomic molecules	47

TABLE 1.2 (Continued)

Relationship*	Comments	Ref.
$d_o = A - B\nu^{is}$	For C-H bonds; ν^{is} = 'isolated' C-H stretching frequency; force constant data included; $d_o \equiv r_o$ (see Table 1.3)	48

* A, B, C = constants

seems a reasonable choice, since most compounds are characterised structurally. The range of bond energy-bond length relationships suggested in Tables 1.1 and 1.2 is varied. However, by setting the conditions that $dE/_{d(d)} < 0$[34,37], and $d^2E/_{d(d)^2} > 0$[53], (i.e. a plot of E versus d must give a continuous curve of negative slope), several equations can be eliminated. Similarly, the range of bond length-bond order correlations suggested should be considered in the light of the limiting condition $d \longrightarrow \infty$ as $n \longrightarrow 0$. Several relationships can therefore be eliminated.[53] The simplest correlations which satisfy the conditions stated above are given in equations 1.12 and 1.13; the constants

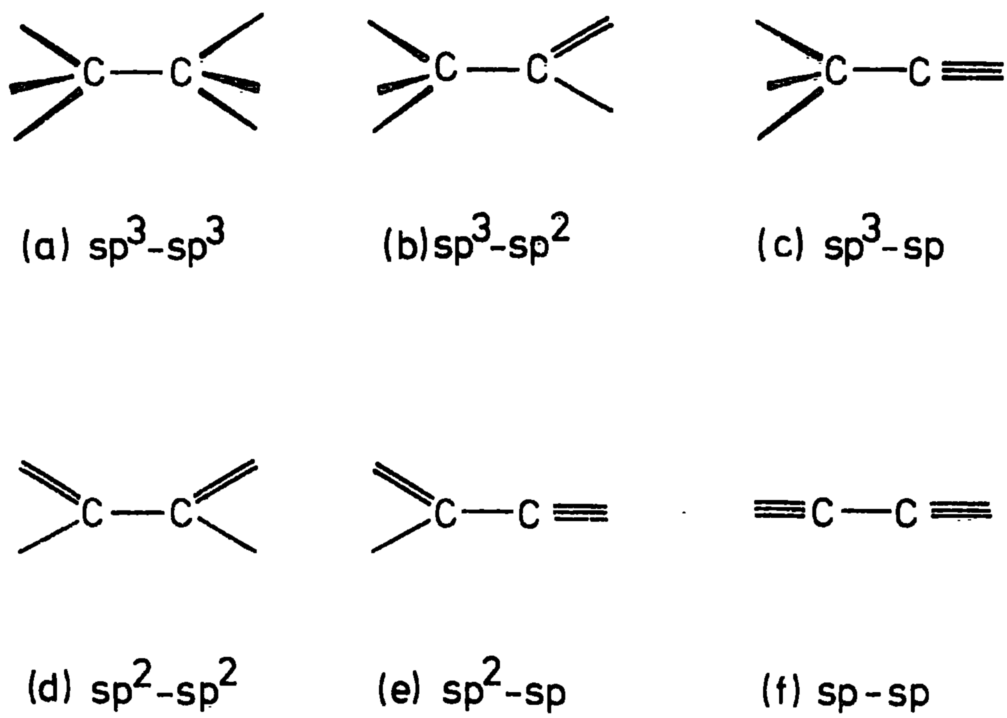
$$E(X\text{-}Y) = A[d(X\text{-}Y)]^{-k} \qquad (1.12)$$

$$d(X\text{-}Y) = B[n(X\text{-}Y)]^{-p} \qquad (1.13)$$

A, B, k and p are characteristic of the bond X-Y.

Empirical relationships involving bond length must be treated with caution, since values of d(X-Y) for bonds in different environments are influenced by a variety of effects; e.g. charge densities of X and Y, inductive effects, differences in hybridisation, conjugative effects, non-bonded and lone-pair interactions, and steric or ring strain effects. Many of these effects, (with the exception of those due to hybridisation), are small and of opposite sign to one another. Appropriate corrections made on d(X-Y) generally give a resultant uncertainty of ca.1pm which is comparable with the estimated experimental error. Hybridisation effects cannot, however, be dismissed as being insignificant. For instance, there are 6 possible environments for a carbon-carbon formal single bond (Figure 1.4) and it has been suggested[54] that the

Figure 1.4 Possible environments for formal single carbon-carbon bonds.



C-C bond length varies over the range 154.4pm (sp^3-sp^3, Figure 1.4a) to 137.4pm (sp-sp, Figure 1.4f). Such variation may well be due in part to conjugation effects, (in which case the formal bond order is no longer unity), but it is argued that the predominant factor is the change in hybridisation of the carbon atom.[54-56] Hence for a bond X-Y, any bond length-bond order relationship should refer specifically to a particular state of hybridisation.[57,58]

The choice of experimental data is also important. Values of d(X-Y) determined by different techniques are not strictly comparable; this problem is discussed in Section 1.4.

It is therefore suggested that relationships of the form shown in equations 1.12 and 1.13 might be appropriate for allocating bond energy contributions and bond orders to bonds of given length. Alternatively, the equations may be combined to give a bond energy-bond order relationship, equation 1.14.

$$E(X\text{-}Y) = C[n(X\text{-}Y)]^{m} \qquad (1.14)$$

(where m = kp from equations (1.12) and (1.13);
C = constant)

1.4 Bond Length : Definitions and Use of Experimental Values

In Section 1.3 it is suggested that empirical relationships connecting bond energy with bond length might be an effective method of estimating bond enthalpy contributions in molecules. Before embarking upon such work, it is necessary to define 'bond length' and point out any possible difficulties in interpreting experimental data.

Bond length is a measure of the distance between two nuclei and can be determined by a variety of methods, the most common of which are spectroscopy (particularly for diatomic molecules), electron diffraction (gas phase), X-ray diffraction and neutron scattering. Each technique involves a different internuclear distance parameter and each has its own symbol. The range of parameters used in spectroscopic and electron diffraction bond length determinations is particularly confusing; these are summarised in Table 1.3. When comparing bond lengths, it is highly desirable that the comparison should be made between internuclear distances derived by the same method. Unfortunately no one parameter is used universally, although electron diffraction results are very

TABLE 1.3 Internuclear Distance Parameters Used in Spectroscopic and Electron Diffraction Methods.[59]

Parameter*	Method†	Definition and Comments
r_e	S and E	Distance between equilibrium positions of nuclei
r_g	E	Average value over the molecular vibrations of internuclear separation for a given temperature
r_a	E	Distance obtained directly from electron diffraction data; r_a is related to r_g by: $r_g \approx r_a + u^2/r_a$ where u = root mean square vibrational amplitude
r_o	S	Distance for diatomic molecule defined by: $r_o^2 = \frac{h}{8\pi^2 \mu B_o}$ where h = Planck's constant; μ = reduced mass; B_o = rotational constant for molecule in a state of zero point vibration
r_s	S	Applied to polyatomic molecules because of inadequacies of r_o model;[60] for a diatomic, r_s is defined as: $r_s \approx \frac{1}{2}(r_o + r_e)$
r_z	S	Distance between mean positions of atoms in ground state; ($r_z \neq r_g$ due to different methods of determination).

TABLE 1.3 (Continued)

Parameter*	Method†	Definition and Comments
r_α	E	Distance between mean positions of atoms at a given temperature; r_α is related to r_g by: $r_\alpha = r_g - \left[\frac{<\Delta x^2> + <\Delta y^2>}{2r_e}\right]$ where $<\Delta x^2>$ and $<\Delta y^2>$ = mean square perpendicular vibrational amplitudes
r_α^o	E	Value of r_α extrapolated to OK
$r_{av.}$	S and E	Distance obtained by simultaneous refinement of spectroscopic and electron diffraction data;[61] (corresponds to refinement of r_z and r_α^o).

* It is conventional to use 'r' for internuclear separation when applied to spectroscopic and electron diffraction values; the symbol 'd' is used elsewhere in this thesis.

† S = Parameter determined by spectroscopic methods.

E = Parameter determined by electron diffraction.

TABLE 1.4 Internuclear Parameters for ^{t}Butyl Chloride[63,64]; d in pm

	r_{α}^{o}	r_z	r_s
d(C-C)	152.5(3)	152.5(5)	153.0(2)
d(C-Cl)	182.5(5)	183.1(15)	180.3(2)
	r_o	r_e	$r_{av.}$
d(C-C)	153.1(7)	152.1(4)	152.5(3)
d(C-Cl)	181.2(19)	182.1(6)	182.7(5)

often presented in terms of r_g, the average internuclear distance. An example of the variation in bond length with differing parameters is given for d(C-C) and d(C-Cl) in ^{t}butyl chloride,[63,64] (Table 1.4).

Structural data for the majority of compounds discussed in this thesis are derived either from electron diffraction or X-ray crystallographic studies. In a few cases the bond length data are the result of neutron diffraction work. The complications arising from the variety of electron diffraction distance parameters have already been discussed. In addition, accurate determinations of bond lengths by electron diffraction techniques are limited to molecules whose symmetry is known. Greater errors in d(X-Y) are incurred for molecules of unknown symmetry. X-ray and neutron diffraction methods measure bond lengths in crystalline solids. Both methods can give accurate measures of internuclear separations although substantial differences can arise when determining the lengths of bonds involving light atoms, (in particular hydrogen). This difference in sensitivity is due to the nature of the diffraction in each case. X-rays respond to accumulations of electrons whilst neutrons are scattered by the nuclei themselves. Hence in a carbon-hydrogen bond, X-ray diffraction peaks from the hydrogen atoms represent the location of the highest electron density and this is generally shifted towards the carbon-atom. Hence a value of d(C-H) ≈ 80pm is typical of X-ray diffraction results. Neutron scattering however gives a realistic measure of d(C-H); values of 100pm $<$ d(C-H) $<$ 110pm are common. The same problem arises with boron-hydrogen bonds. It has been suggested that values of d(B-H) and d(C-H) determined by X-ray diffraction are typically ca. 10pm shorter than values found by neutron scattering.[65,66] Similar corrections are suggested for non-hydrogen bonded N-H and O-H distances.[66]

In this thesis, structural parameters determined by the same experimental technique have been used wherever possible.

1.5 Bond Order

In this work, empirical relationships between bond order and bond length or bond energy will be used. The term '<u>bond order</u>' should therefore be defined. In molecular orbital (MO) theory, formal bond order, n, is defined as the number of electron pairs occupying bonding MO's minus the number of electron pairs occupying antibonding MO's,[67] (e.g. bond orders in He_2, H_2^+, H_2, O_2 and CO are 0, $\frac{1}{2}$, 1, 2 and 3 respectively).

Various interpretations of bond order exist, but in this thesis all values of n are comparable. It is assumed, for example, that in the delocalised benzene ring system each C-C link can be assigned a bond order of 1.5, and that in graphite, the in-plane bonds of the delocalised fused-ring system each have a bond order of ca. $1.33\dot{3}$. (This assumes that bonding between the graphite planes is negligible; this is supported by the two-dimensional electrical conductivity of graphite).

Chapters Two and Three describe the thermochemistry and bonding in some boron-containing species. In its valence state, boron itself has a vacant p-orbital; its ground state electronic configuration is $1s^2 2s^2 2p^1$ (i.e. 3 valence electrons). Hence, sp^2-hybridisation is common leaving a vacant p_z orbital. It is assumed in this thesis that whenever possible the boron atom will accept π-electrons from adjacent atoms in order to completely fill the p_z orbital. Hence in boron trihalides π-electrons are donated from each halogen atom to boron giving a total bond order for each B-X bond of $1.33\dot{3}$. Further discussion can be found in Chapter Two.

1.6 Standard Enthalpies of Formation of Elements

Many calculations in this thesis are concerned with the disruption of compounds into their constituent elements. It is therefore essential that reliable values of the standard enthalpies of formation of the gaseous atoms are used. In most cases, values of $\Delta H_f^o(g)$ are well documented; Table 1.5 summarises data used in this thesis, (values of $\Delta H_f^o(g)$ refer to 25^oC, or 298K, and one atmosphere pressure).

In the case of carbon, many early thermochemical studies suffer from the uncertainty in a value of $\Delta H_{sublimation}$, (see Section 1.3, Table 1.1). However, a value of 716.7kJ mol^{-1} is now accepted. Boron has also created many problems and estimates of its heat of sublimation spread over a range of ca. 120kJ mol^{-1}. The main experimental problems appear to be (a) incorrect measurement of temperature, and (b) the reactivity of boron at high temperature which makes the selection of material for an inert reaction vessel nearly impossible.[68] The weighted mean of all data prior to 1968 gives ΔH^{o}_{f298} B(g) = 556(18) kJ mol^{-1}.[8,68] This has been compared with data published since 1968 and in this thesis a value of ΔH^{o}_{f298} B(g) = 560(12) kJ mol^{-1} is used; (references in Table 1.5 list all sources from which data were considered). (Heats of atomisation of metallic elements will be considered in Chapter Four).

TABLE 1.5 Standard Enthalpies of Formation of Gaseous Atoms, $\Delta H^{o}_{f298}(g)$.

Element	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	References
H	218.0(<1)	8, 69, 70
B	560(12)	8, 68-72
C	716.7(4)	8, 69, 70
N	472.7(4)	8, 69, 70, 73
O	249.2(1)	8, 69, 70
F	79.4(3)	8, 69, 70, 74
Cl	121.3(<1)	8, 69, 70, 74
Br	111.9(1)	8, 69, 70, 74

1.7 Shapes of Cluster Compounds

Boron hydrides, polynuclear transition metal carbonyl compounds and some cyclic hydrocarbon systems adopt structures which are relatable to complete, or nearly complete, triangular-faced polyhedra. These have been classified according to the number of skeletal bonding pairs of electrons,[75-82] (see Chapter Six, Section 6.1).

In estimating possible bond orders and energies in cage compounds (e.g. in the polyhedral anions $B_nH_n^{2-}$ considered in Chapter Three), the theory of skeletal counting becomes an important basis from which to work. The final chapter of this thesis is therefore devoted to the shapes and classification of clusters.

CHAPTER TWO

BOND ENERGY-BOND ORDER AND BOND ENERGY-BOND LENGTH EMPIRICAL CORRELATIONS IN SOME MAIN GROUP SYSTEMS

2.1 Introduction

In this chapter, attempts are made to correlate bond energy with bond order and/or bond length in simple systems containing some main group elements with special emphasis on boron compounds. General relationships suggested in Chapter One, Section 1.3 (equations 2.1 - 2.3) are used.

$$E(X\text{-}Y) = A[d(X\text{-}Y)]^{-k} \qquad (2.1)$$

$$d(X\text{-}Y) = B[n(X\text{-}Y)]^{-p} \qquad (2.2)$$

$$E(X\text{-}Y) = C[n(X\text{-}Y)]^{m} \qquad (2.3)$$

For sp^2-carbon-sp^2-carbon bonds, a plot of log E(C-C) against log n(C-C) gives a good straight line (Figure 2.1)[37] yielding equation 2.4:

$$E(C\text{-}C) = 414.3[n(C\text{-}C)]^{0.4276} \qquad (2.4)$$

The logarithm of 'revised' bond energy terms calculated from equation 2.4 plotted against log d (C-C) also gives a linear correlation (Figure 2.2) (equation 2.5).

$$\begin{aligned} E(C\text{-}C) &= 1425[d(C\text{-}C)]^{-3.2} \quad \text{for d in Å} \\ &\equiv 3.582 \times 10^9 [d(C\text{-}C)]^{-3.2} \quad \text{for d in pm} \end{aligned} \qquad (2.5)$$

Finally, equation 2.6 has been suggested as relating sp^2C-sp^2C bond length with bond order.[37]

$$\begin{aligned} d(C\text{-}C) &= 1.471[n(C\text{-}C)]^{-0.134} \quad \text{for d in Å} \\ &\equiv 147.1[n(C\text{-}C)]^{-0.134} \quad \text{for d in pm.} \end{aligned} \qquad (2.6)$$

Figure 2.1 Log E(C-C) against log n(C-C) for some sp^2-sp^2 carbon-carbon bonds;[37] [E in kcal mol^{-1}].

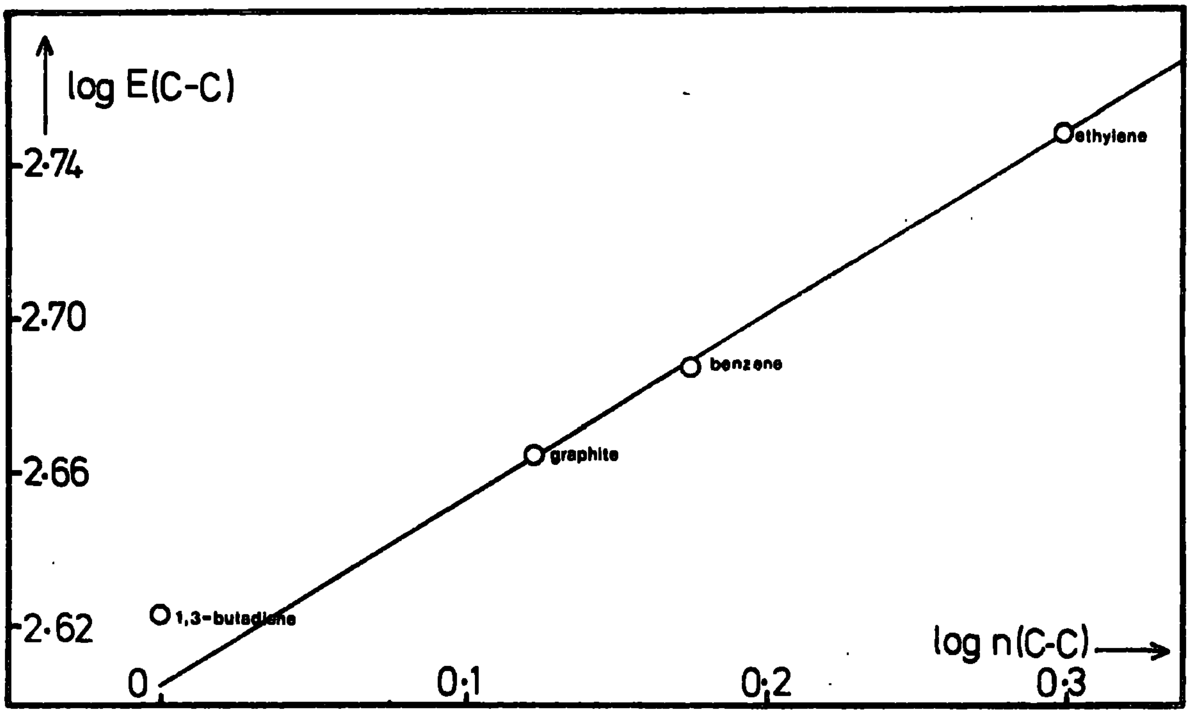
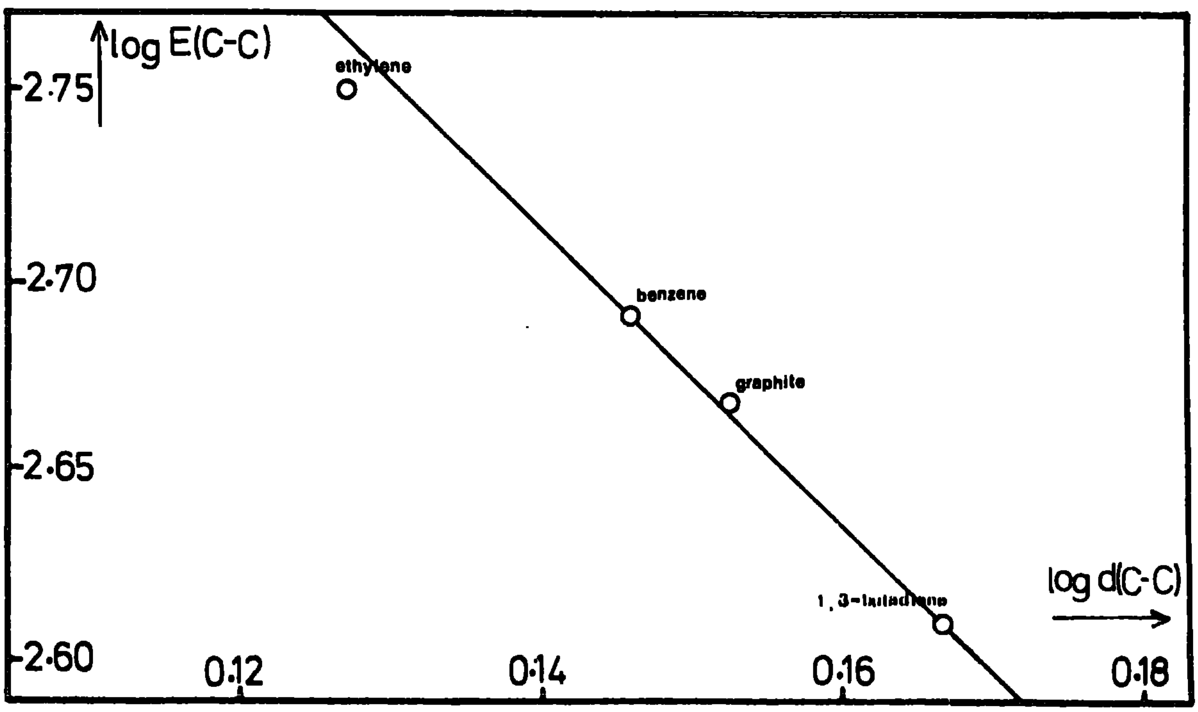


Figure 2.2 Log E(C-C) against log d(C-C) for some sp^2-sp^2 carbon-carbon bonds;[37] [E in kcal mol^{-1}; d in Å].



As boron-nitrogen and carbon-carbon bonds are isoelectronic, it has been postulated that the rate of change of bond energy with bond length should be the same in both cases.[37] Hence, equation 2.7 has been proposed.

$$E(B\text{-}N) \propto [d(B\text{-}N)]^{-3.2} \qquad (2.7)$$

However, it has been noted that for bonds between atoms of unspecified hybridisation, $dE(C\text{-}C)/d[d(C\text{-}C)] \approx 8\text{-}12$ kJ mol^{-1} whereas $dE(B\text{-}N)/d[d(B\text{-}N)] \approx 17$ kJ mol^{-1}.[83]

Relationships of the general form of equation 2.3 were also suggested for boron-halogen bonds, (equations 2.8 and 2.9),

$$E(B\text{-}Cl) = 419.5[n(B\text{-}Cl)]^{0.222} \qquad (2.8)$$

$$E(B\text{-}Br) = 357.2[n(B\text{-}Br)]^{0.146} \qquad (2.9)$$

on the basis of estimated boron-halogen bond enthalpy contributions in the trigonal planar compounds boron trihalide (or trihalogenoborane (BX_3)), phenyldihalogenoborane ($PhBX_2$) and diphenylhalogenoborane (Ph_2BX), (X = Cl or Br). It was assumed that π-electrons from the halogen atoms would be donated to the vacant p_z orbital on boron giving B-X bond orders of $1.\dot{3}\dot{3}\dot{3}$, 1.50 and 2.00 in BX_3, $PhBX_2$ and Ph_2BX respectively. A value of D(B-Ph) was transferred from triphenylboron (Ph_3B) on the assumption that there would be no back donation of π-electrons from carbon to boron in any compound containing a phenyl substituent; (i.e. n(B-C) = 1.00 in all cases).[37] This assumption contrasts with the opinion that in $Ph_{3-x}BX_x$ systems, values of E(B-X) are transferable, implying that the phenyl groups are the primary sources of π-electrons.[84-86] Competition between potential π-electron donors attached to boron is discussed further in Section 2.7.

In relating bond order to either bond length or bond energy in this Chapter, bonds between atoms of the same hybridisation are compared wherever possible. The effects of including atoms of differing hybridisation are discussed.

2.2 Carbon-Oxygen Bonds

Carbon-oxygen formal single, double and triple bonds are well documented and lengths and energies for such bonds are given in Table 2.1. A plot of log E(C-O) against log d(C-O), (Figure 2.3), gives a good straight line, (correlation coefficient = -0.99934), of slope $\approx$ -5 (equation 2.10),

$$E(C\text{-}O) = 1.955 \times 10^{13}[d(C\text{-}O)]^{-5} \qquad (2.10)$$

The values in Table 2.1 include carbon in different states of hybridisation and so attempted correlation of bond energy with bond order might not be expected to be successful. However, a plot of log E(C-O) against log n(C-O), (Figure 2.4), using values listed in Table 2.1 gives an excellent straight line, (correlation coefficient $\approx$ 1.0) and suggests the relationship:

$$E(C\text{-}O) = 335.7[n(C\text{-}O)]^{1.05} \qquad (2.11)$$

In the case of C-O bonds therefore, it appears that hybridisation effects may not be as significant as in C-C bonds.

Combining equations 2.10 and 2.11 gives a bond length-bond order relationship for C-O bonds of the form:

$$d(C\text{-}O) = 142.2[n(C\text{-}O)]^{-0.21} \qquad (2.12)$$

Figure 2.3 Log E against log d for carbon-oxygen bonds; [E in kJ mol^{-1}; d in pm].

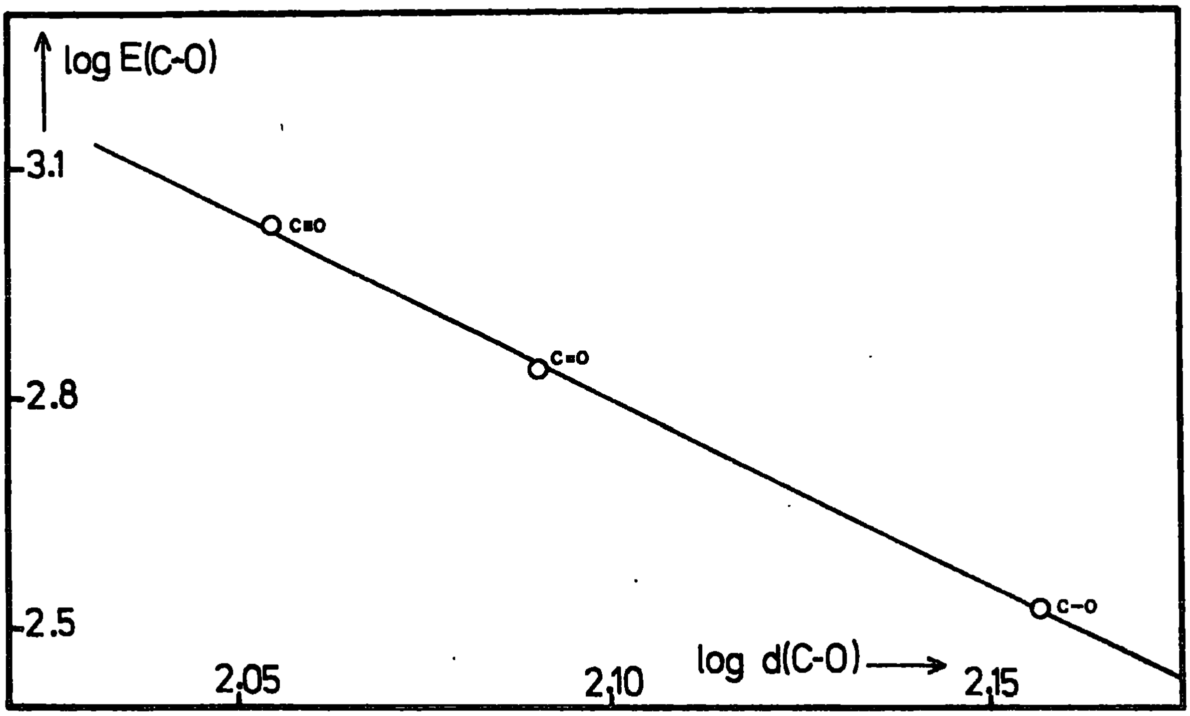


Figure 2.4 Log E against log n for carbon-oxygen bonds; [E in kJ mol^{-1}].

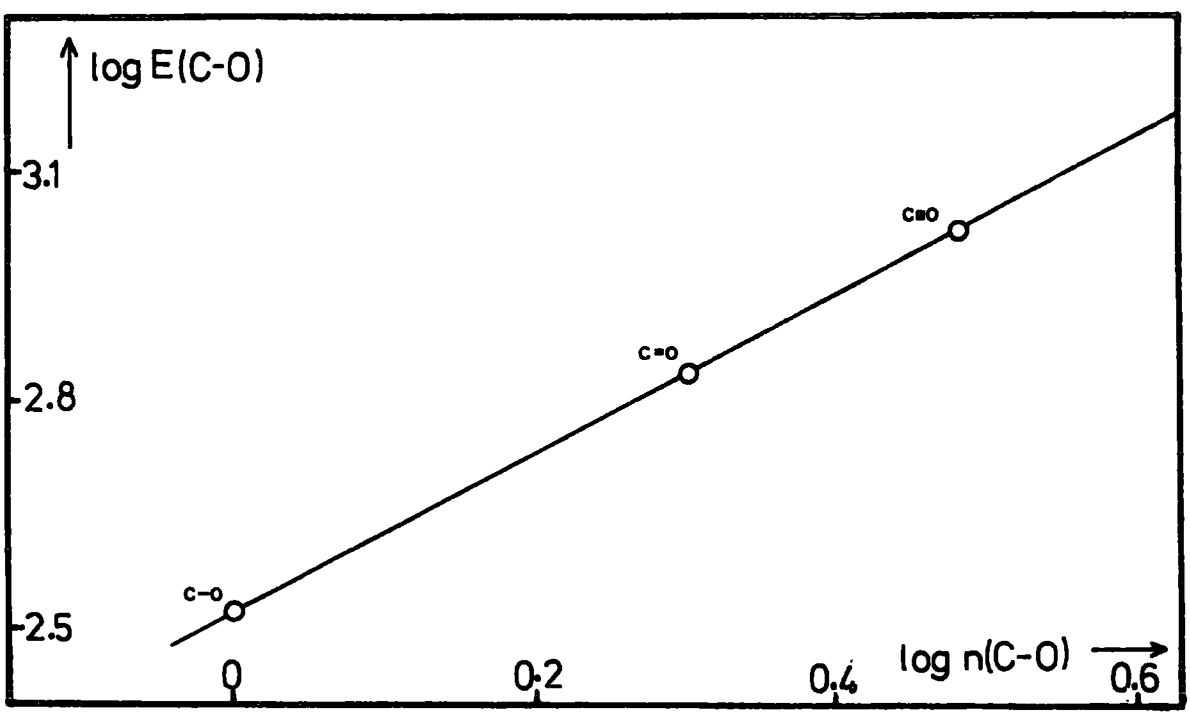


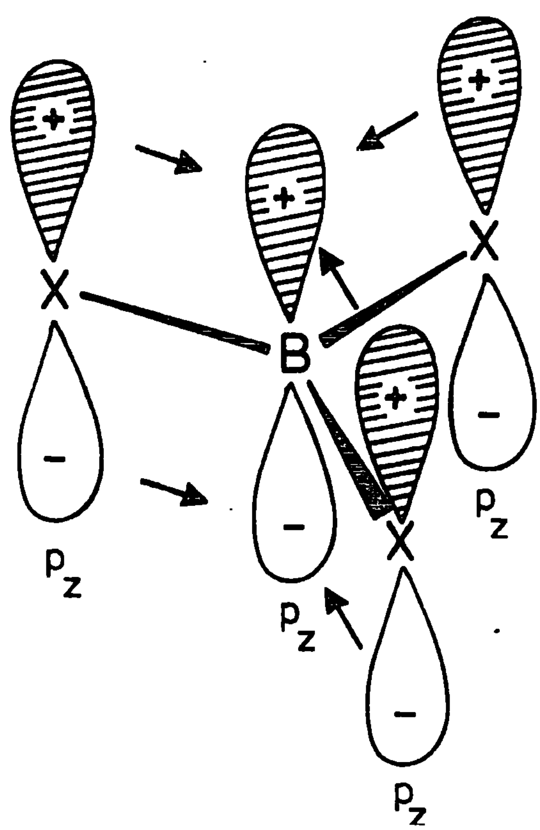
TABLE 2.1 General Carbon-Oxygen Bond Orders, Lengths and Energies.[8, 87, 88]

Bond	Bond Order	Bond Length pm	Bond Energy $kJ\ mol^{-1}$
C ≡ O	3	112.82[89]	1070
C = O	2	123	695
C - O	1	143	336

2.3 Boron-Halogen Bonds

In a large number of its compounds, boron is sp^2-hybridised and is able to accept π-electrons from adjacent atoms to completely fill its vacant p_z orbital, (Chapter One, Section 1.5). Figure 2.5 illustrates the back donation of π-electronic charge from halogen to boron in BX_3 where each B-X bond is expected to have a formal bond order (n) of $1.\dot{3}33$.

Figure 2.5 π-bonding in BX_3.



If other substituents on boron are unlikely to be potential sources of π-electrons, (e.g. hydrogen atom or alkyl group, see Section 2.6), the total π-bonding in the molecule may be assumed to be due to the halogen substituent(s). Hence in HBX_2, n(B-X) = 1.50, and in H_2BX, n(B-X) = 2.00.

Table 2.2 lists thermochemical data for several boron-halogen compounds containing sp^2-boron. For each of boron trifluoride (BF_3), boron trichloride (BCl_3) and boron tribromide (BBr_3), the mean bond dissociation enthalpy, D(B-X), is $\frac{1}{3}\Delta H_{disrupt.}BX_3$; D(B-F) = 644.4, D(B-Cl) = 442.2, and D(B-Br) = 366.9 kJ mol^{-1}. Other compounds in Table 2.2 are of the type R_xBX_{3-x} (x = 1, 2; R = H, alkyl), and an estimate of D(B-R) is therefore required. If it is assumed that D(B-R) is constant along the series $R_3B \longrightarrow RBX_2$ (see Section 2.6), then values of D(B-R) can be transferred directly from the respective trialkylborane compound (R_3B) to the halogeno-substituted derivatives. Table 2.3 gives standard enthalpies of formation and heats of disruption for boron hydride (BH_3) and some trialkylboranes (R_3B) as well as for the free radicals R•. Mean bond dissociation enthalpies for the process:

$$R_3B(g) \longrightarrow B(g) + 3\,R\cdot(g)$$

are also listed in Table 2.3. Finally, Table 2.4 lists bond enthalpy contributions allocated to the B-X bonds with respective values of the bond orders, n(B-X). Bond dissociation energies and bond orders for the gaseous diatomic BX molecules are also included in Table 2.4; ($\Delta H^o_{f298}(g)$ BF = -122.2,[70] BCl = 149.5[70,71], BBr = 238.1[70,71] kJ mol^{-1}).

Plots of log E(B-X) against log n(B-X) for X = F, Cl and Br give good linear correlations (Figure 2.6), and,

TABLE 2.2 Thermochemical Data for Some Boron-Halogen Compounds; (sp^2-B)

Compound	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	Ref.
BF_3	-1136.3	1933.3	8, 70, 71
BCl_3	-402.7	1326.6	8, 70
BBr_3	-205.0	1100.7	8, 68, 70, 71
HBF_2	-738.9	1674.9	71
$MeBF_2$	-832.6*	2921.3	68
$EtBF_2$	-874.4*	4115.8	68
$HBCl_2$	-253.2	1273.8	71
$^{n}Bu_2BCl$	-365.7	10704.6	4, 71, 90
$^{n}Bu_2BBr$	-301.0	10630.5	4, 71, 90

* These values are approximate.[68]

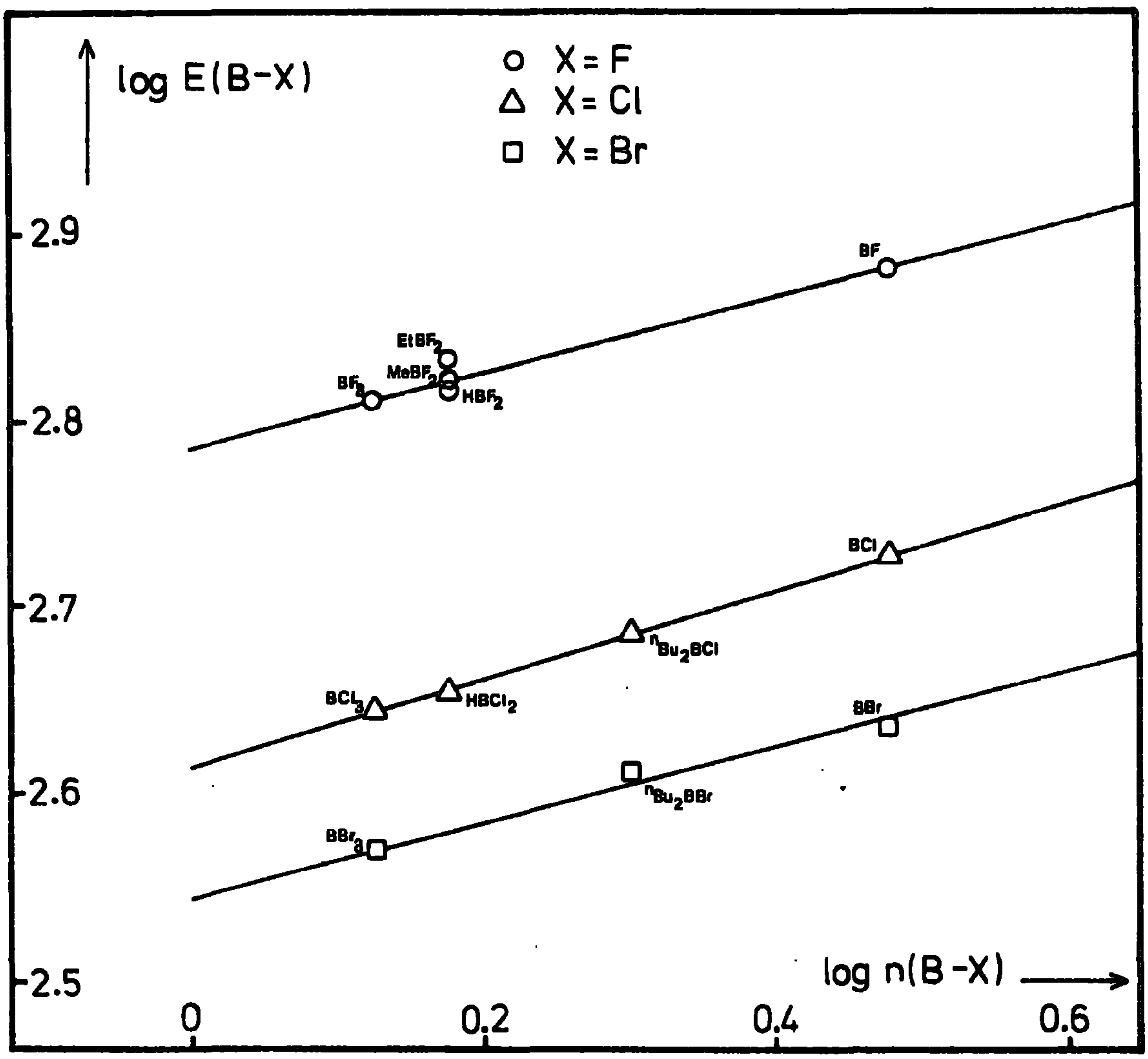
TABLE 2.3 Thermochemical Data for Boron Hydride and Trialkylboranes (R_3B) and for the Radicals R·.

Compound	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	D(B-R) kJ mol^{-1}	Ref.
BH_3	100.4	1113.6	371.2	70
Me_3B	-122.3	4794.4	369.7	4,70,71,90
Et_3B	-152.2	8282.4	345.8	4,70.71,90
$^{n}Bu_3B$	-285.0	15331.4	352.8	4,71,90
Me·	142.3	1228.4	-	9,10
Et·	108.4	2415.0	-	9,10,91
^{n}Bu·	71.1	4757.7	-	9,10

TABLE 2.4 Mean Bond Dissociation Energies and Bond Orders for Some B-X (X = F, Cl, Br) Bonds

Compound	D(B-X) kJ mol^{-1}	n(B-X)
BF_3	644.4	$1.33\dot{3}$
HBF_2	651.9	1.50
$MeBF_2$	661.6	1.50
$EtBF_2$	677.5	1.50
BF	761.2	3.00
BCl_3	442.2	$1.33\dot{3}$
$HBCl_2$	451.3	1.50
$^nBu_2BCl$	483.6	2.00
BCl	531.8	3.00
BBr_3	366.9	$1.33\dot{3}$
$^nBu_2BBr$	409.5	2.00
BBr	433.8	3.00

Figure 2.6 Log E(B-X) against log n(B-X) for X = F, Br, Cl; [E in kJ mol^{-1}].



surprisingly, in each case pass through the point associated with the diatomic, BX. As for C-O bonds therefore, a change in hybridisation of the atoms does not appear to greatly influence any bond energy-bond order correlations. The suggested bond energy-bond order relationships are given in equations 2.13 - 2.15; the correlation coefficients are 0.97825, 0.99942 and 0.98420 for B-F, B-Cl and B-Br bonds respectively.

$$E(B\text{-}F) = 610.6[n(B\text{-}F)]^{0.20} \qquad (2.13)$$

$$E(B\text{-}Cl) = 412.5[n(B\text{-}Cl)]^{0.23} \qquad (2.14)$$

$$E(B\text{-}Br) = 348.8[n(B\text{-}Br)]^{0.21} \qquad (2.15)$$

Equations 2.13-2.15 suggest that the rate of change of bond energy with bond order is much the same for all boron-halogen bonds, and that perhaps the three lines in Figure 2.6 should be parallel. Equation 2.16 is therefore proposed for a general bond energy-bond order relationship covering all B-X bonds.

$$E(B\text{-}X) = A[n(B\text{-}X)]^{0.20} \qquad (2.16)$$

where $A = 608.4$ kJ mol^{-1} for X = F (a)

$A = 417.5$ kJ mol^{-1} for X = Cl (b)

$A = 346.4$ kJ mol^{-1} for X = Br (c)

(Values of the constant A are calculated assuming that each line must pass through the point associated with BX_3).

Bond length data for boron-halogen bonds is both sparse and often inaccurate. It therefore seems unrealistic to attempt to correlate either bond energy or order with bond length.

2.4 Boron-Oxygen Bonds

Table 2.5 lists thermochemical data for some boron-oxygen compounds. The emphasis is on sp^2-hybridised boron, although diatomic BO and triatomic BO_2 are also included for comparison.

The mean boron-oxygen bond dissociation energies in gaseous BO and BO_2 are $\Delta H_{disrupt.}$ BO = 732.2 and $\frac{1}{2}\Delta H_{disrupt.}$ BO_2 = 679.2 kJ mol^{-1} respectively. In all other compounds in Table 2.5, values of D(B-OR) cannot be estimated directly from $\Delta H_{disrupt.}$; additional thermochemical data are required. Firstly, it is assumed that D(B-H) = 371.2 kJ mol^{-1} (Table 2.3) is transferable from gaseous BH_3 to each of gaseous boronic acid ($HB(OH)_2$), dimethoxyborane ($HB(OMe)_2$), boroxine ($(HBO)_3$), and borinic acid ($H_2B(OH)$); (in all species boron is sp^2-hybridised).

Secondly, a value of D(B-^{n}Bu) = 352.8 kJ mol^{-1} (Table 2.3) is assumed to be appropriate in di-n-butylborinic acid ($^nBu_2B(OH)$). Thirdly, standard enthalpies of formation of the radicals ·OR (R = H, Me, Et, ^{n}Pr, ^{n}Bu) are required (Table 2.6). (Unfortunately literature values of ΔH^o_{f298}·OR(g) vary greatly and tend to be inaccurate. Values given in Table 2.6 are the most recent available).

Bond enthalpy contributions allocated to boron-oxygen bonds are summarised in Table 2.7. They are seen to fall into at least two general series, (a) D(B-OR) for R = H and (b) D(B-OR) for R = alkyl. A plot of log D(B-OR) against log n(B-O) emphasises this fact, (Figure 2.7). Points associated with $B(OH)_3$ (boric acid), $HB(OH)_2$ and $R^1_2B(OH)$ (R^1 = H, ^{n}Bu) lie on one line (equation 2.17; correlation coefficient = 0.99834) whilst a parallel line may be drawn

TABLE 2.5 Thermochemical Data for Some Boron-Oxygen Systems

Compound	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	Ref.
$B(OH)_3$	-991.5	2953.1	70,71
$B(OMe)_3$	-900.0	6319.7	4,70,71,90
$B(OEt)_3$	-1003.0	9880.8	4,70,71,90
$B(O^{n}Pr)_3$	-1077.8	13413.7	4,71,90
$B(O^{n}Bu)_3$	-1147.0	16941.0	4,71,90
$HB(OH)_2$	-640.0	2352.4	71
$HB(OMe)_2$	-579.5	4597.3	4,70,71,90
$(HBO)_3$	-1210.0	4291.6	70,71
$H_2B(OH)$	-290.0	1753.2	71
$^{n}Bu_2B(OH)$	-547.5	11232.3	71
BO_2	-300.0	1358.4	70,71
BO	77.0*	732.2	71

* Value may be unreliable

TABLE 2.6 Standard Enthalpies of Formation and Disruption of Gaseous Radicals, ·OR

Radical	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	Ref.
·OH	38.9	428.3	10, 70
·OMe	17.6	1602.3	92
·OEt	-17.2	2789.8	92
·O^{n}Pr	-41.4	3966.7	92
·O^{n}Bu	-61.5	5139.5	93

through those points associated with $B(OR)_3$ (R = alkyl) and $HB(OMe)_2$ (equation 2.18). Several points lie off the

$$D(B\text{-}OH) = 537.1[n(B\text{-}O)]^{0.12} \qquad (2.17)$$

$$D(B\text{-}OR) = 487.5[n(B\text{-}O)]^{0.12} \qquad (2.18)$$

suggested lines, i.e. $(HBO)_3$, BO_2 and BO. In each case bond enthalpy contributions were allocated assuming disruption into constituent <u>elements</u>, cf. disruption into gaseous boron and hydrogen atoms and radicals for all other systems. In addition, BO_2 and BO do not contain sp^2B.

The rather unsatisfactory picture which has emerged for boron-oxygen systems underlines the cautionary notes made in Chapter One regarding the energetics of disruption of compounds into gaseous radicals rather than atoms. An improvement is however made if revised bond energy terms, D(B-O), are calculated for the process:

$$R^1{}_xB(OH)_{3-x}(g) \longrightarrow xR^1(g) + B(g) + (3-x)O(g) + (3-x)H(g)$$

or:

$$R^1{}_xB(OMe)_{3-x}(g) \longrightarrow x\,R^1(g) + B(g) + (3-x)O(g) + (3-x)C(g) + 3(3-x)H(g)$$

TABLE 2.7 **Bond Orders and Estimated Bond Enthalpy Contributions for Some Boron-Oxygen Bonds**

Compound (gaseous)	D(B-OR) kJ mol^{-1}		n(B-O)
$B(OH)_3$	556.1		$1.33\dot{3}$
$B(OMe)_3$	504.3	mean 505.0	$1.33\dot{3}$
$B(OEt)_3$	503.8		$1.33\dot{3}$
$B(O^nPr)_3$	504.5		$1.33\dot{3}$
$B(O^nBu)_3$	507.5		$1.33\dot{3}$
$HB(OH)_2$	562.3		1.50
$HB(OMe)_2$	510.8		1.50
$(HBO)_3$	529.7		1.50
BO_2	679.2		1.75
$H_2B(OH)$	582.5	mean 582.75	2.00
$^nBu_2B(OH)$	583.0		2.00
BO	732.2		2.50

Figure 2.7 Log D(B-OR) against log n(B-O) for disruption into radicals, •OR; [E in kJ mol⁻¹].

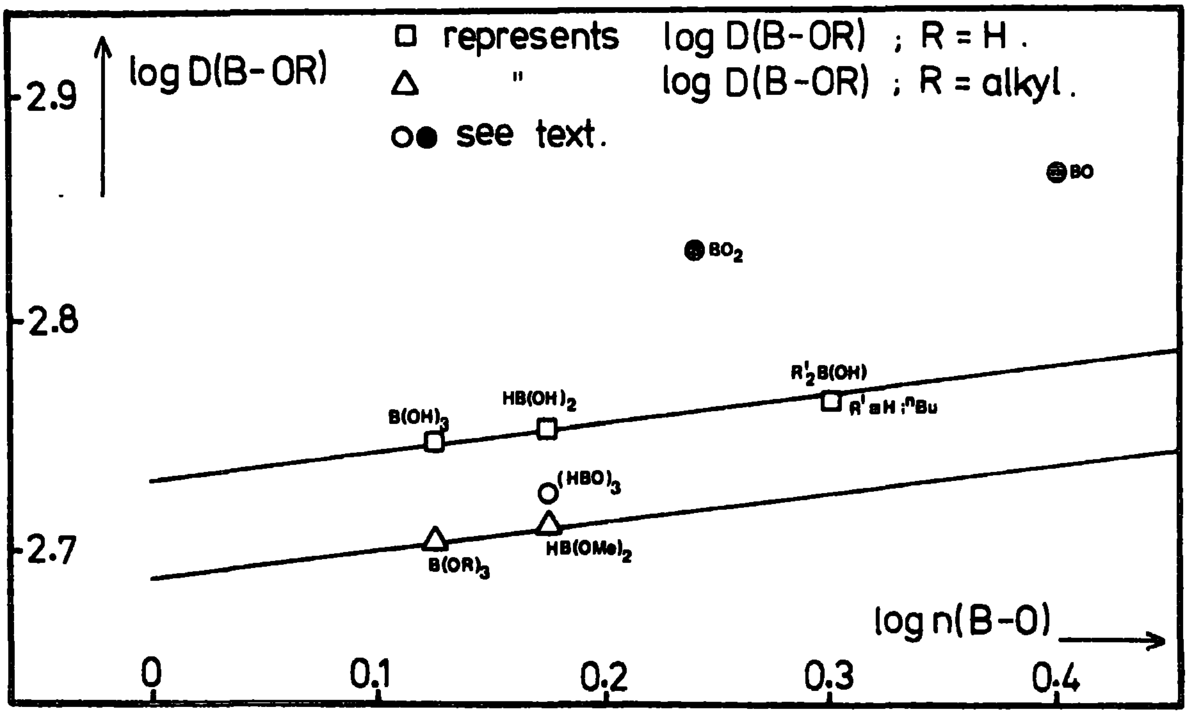
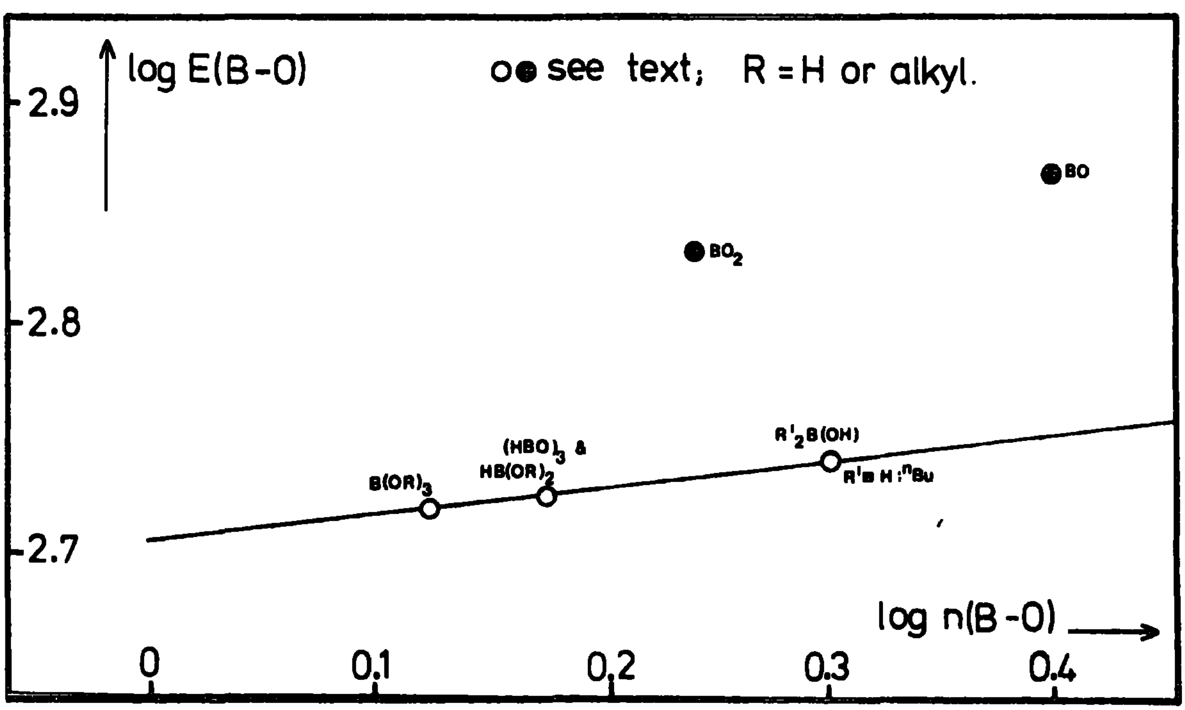


Figure 2.8 Log E(B-O) against log n(B-O) for disruption into atoms; [E in kJ mol⁻¹].



(Compounds involving OEt, O^nPr or O^nBu groups are not considered because of the increasing complexity of assigning C-C and C-H bond enthalpy contributions). Additional thermochemical data required are: $D(C\text{-}H)_{Me}$ = 410 kJ mol^{-1},[10,94,95] D(O-H) = 460.2 kJ mol^{-1},[4,17] and D(O-Me) = 355 kJ mol^{-1} (calculated using $\Delta H^o_{f298} Me_2O(g)$ = -184.1 kJ mol^{-1} [70] and ΔH^o_{f298} ·OMe(g) and ·Me(g) = 17.6 and 142.3 kJ mol^{-1} respectively (Tables 2.6 and 2.3). The revised energy terms D(B-O), are summarised in Table 2.8. A plot of log E(B-O) against log n(B-O) gives a good straight line, (correlation coefficient = 0.99834), with the exception of points due to BO and BO_2 (Figure 2.8). Equation 2.19 relating B-O bond energy to bond order is therefore suggested.

$$E(B\text{-}O) = 503.0[n(B\text{-}O)]^{0.13} \qquad (2.19)$$

Possible reasons for the anamolous behaviour of BO and BO_2 are that (a) the boron atom is not sp^2-hybridised or (b) both systems are odd electron species. It is suggested that whilst both (a) and (b) may be contributory factors to the anomolous behaviour of boron monoxide and boron dioxide, factor (b) may well be of greater significance since changes in the hybridisation of boron (i.e. (a)) had little effect on empirical correlations involving boron-halogen bonds.

The examples given in this Section underline the difficulties affecting the allocation of bond enthalpy contributions based on the disruption of a compound into radical species. However, in simple systems where complete atomisation can be considered, more satisfactory results appear to be forthcoming and a bond energy-bond order relationship for boron-oxygen bonds so derived seems realistic. It is not possible at the present time to correlate B-O bond energy

TABLE 2.8 Bond Orders and Revised Mean Bond Energy Terms for Some Boron-Oxygen Bonds

Compound	D(B-O) kJ mol^{-1}		n(B-O)
$B(OH)_3$	524.2	mean 522.9	$1.33\dot{3}$
$B(OMe)_3$	521.6		$1.33\dot{3}$
$HB(OH)_2$	530.4	mean 529.4	1.50
$HB(OMe)_2$	528.1		1.50
$(HBO)_3$	529.7		1.50
BO_2	679.2		1.75
$H_2B(OH)$	550.6	mean 550.9	2.00
$^{n}Bu_2B(OH)$	551.1		2.00
BO	732.2		2.50

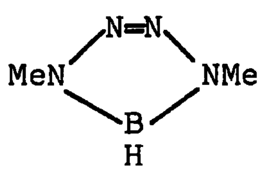
with bond length since accurate values of d(B-O) are not available for many different systems.

2.5 Boron-Nitrogen Bonds

Several compounds containing sp^2-boron attached to nitrogen have been structurally characterised either by electron or X-ray diffraction techniques. Table 2.9 lists such data, along with boron-nitrogen bond orders which are estimated assuming that nitrogen acts as a source of π-electronic charge and that the p_z orbital on boron is completely filled. (Other substituents present are assumed not to be potential π-electron donors). Although diatomic boron nitride does not involve sp^2-B, it is included in the Table to give an indication of the bond length for n(B-N) = 2.00. Some values of d(B-N) do not appear to be consistent with one another (e.g. for a bond order of 1.50, d(B-N) = 139 to 143.55 pm). Indeed, a plot of log d(B-N) against log n(B-N) gives a poor correlation (Figure 2.9; correlation coefficient = -0.93982), and this is attributed to a comparison of bond length data derived from different experimental techniques, (see Chapter One, Section 1.4).

If values of d(B-N) determined by electron diffraction only are taken along with the value of d(B-N) = 128.1 pm for n(B-N) = 2.00, a better correlation is obtained, (Figure 2.10; correlation coefficient = -0.95040). A further improvement is made by using bond lengths determined by X-ray diffraction and spectroscopic methods only, (Figure 2.11; correlation coefficient = -0.98102). This latter plot is therefore used to derive equation 2.20. This suggests a value of 158.7 pm

TABLE 2.9 Bond Lengths and Bond Orders for Some Boron-Nitrogen Bonds

Compound	Method of Structural Determination and Refs. †	d(B-N)* pm	n(B-N)
$B(NMe_2)_3$	E [96]	143.1(12)	$1.33\dot{3}$
Boron nitride (hexagonal)	X [97]	144.6	$1.33\dot{3}$ **
$(HB\text{-}NH)_3$	E [98]	143.55(21)	1.50
$(EtB\text{-}NEt)_3$	X [99]	142.3(15)	1.50
$(MeB\text{-}NH)_3$	X [100]	139	1.50
$(HB\text{-}NMe)_3$	E [101]	142(2)	1.50
	E [102]	141.3(10)	1.50
BN(g)	S [8]	128.1	2.00

† E = Electron diffraction; X = X-ray diffraction;
S = Spectroscopic determination

* Errors included where available

** Bond order of $1.33\dot{3}$ presupposes NO effective bonding between planes in boron nitride as in graphite; (Pauling[103] has suggested n(B-N) = 1.22)

Figure 2.9 Log d(B-N) against log n(B-N) for compounds with sp^2-B and for diatomic BN ; [d in pm].

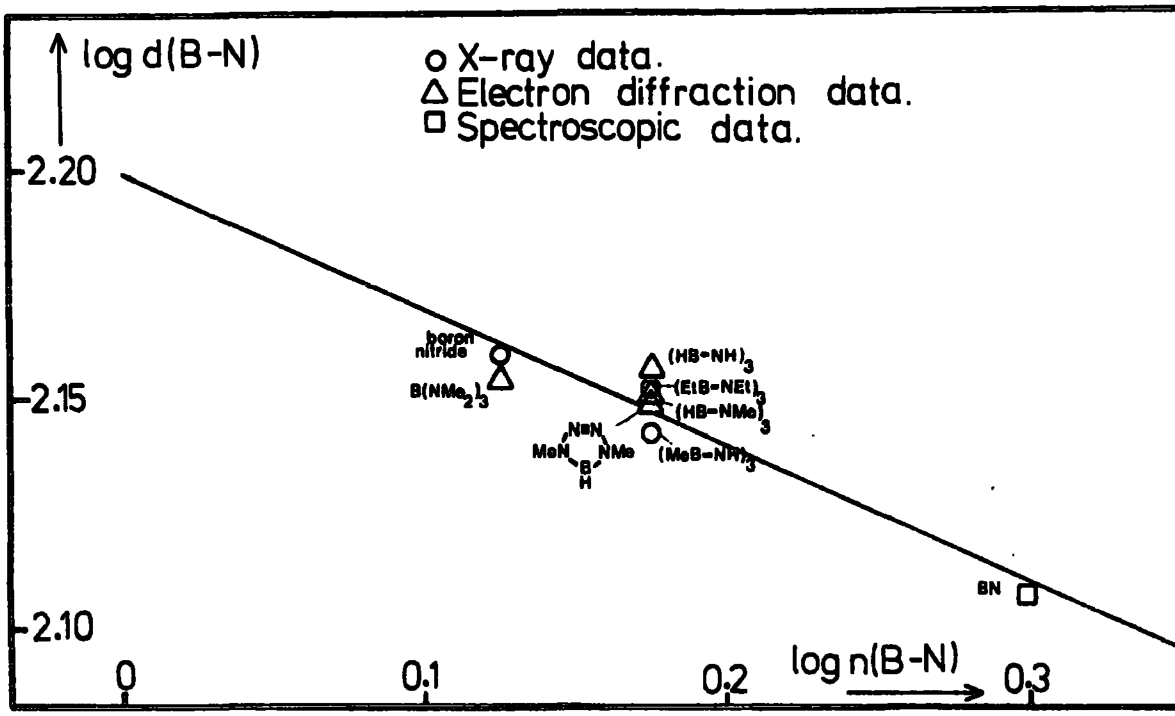


Figure 2.10 Log d(B-N) against log n(B-N) ; electron diffraction and spectroscopic data ; [d in pm].

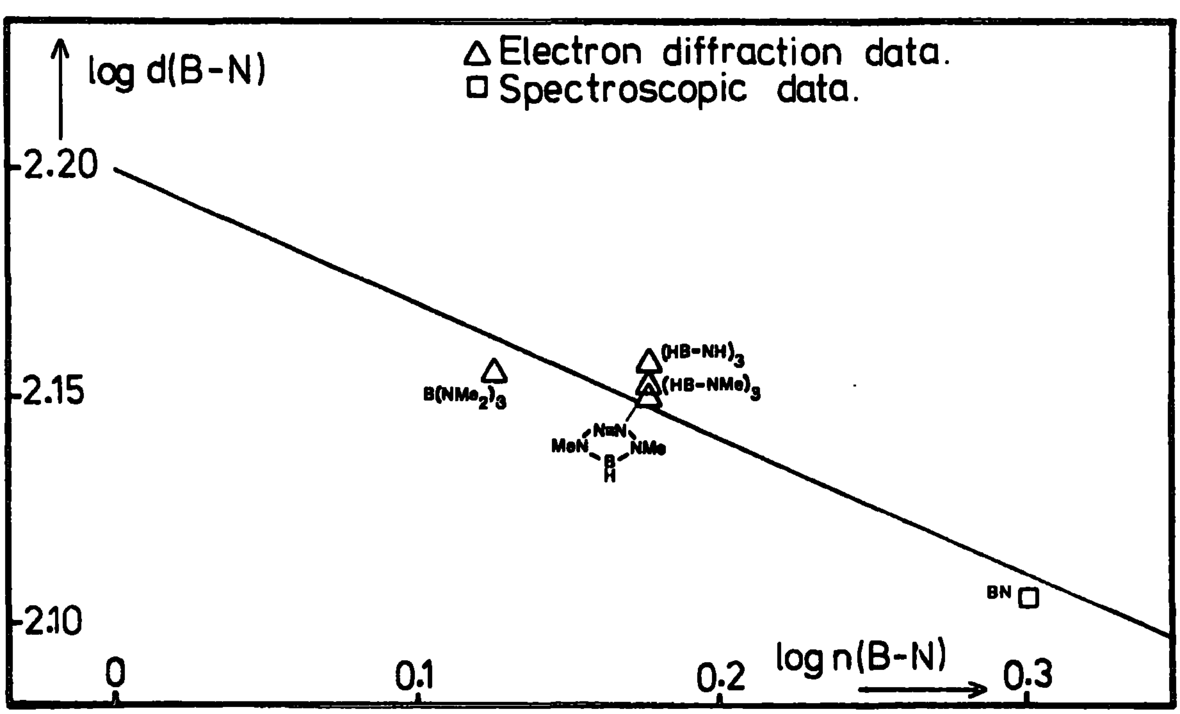


Figure 2.11 Log d(B-N) against log n(B-N); X-ray and spectroscopic data; [d in pm].

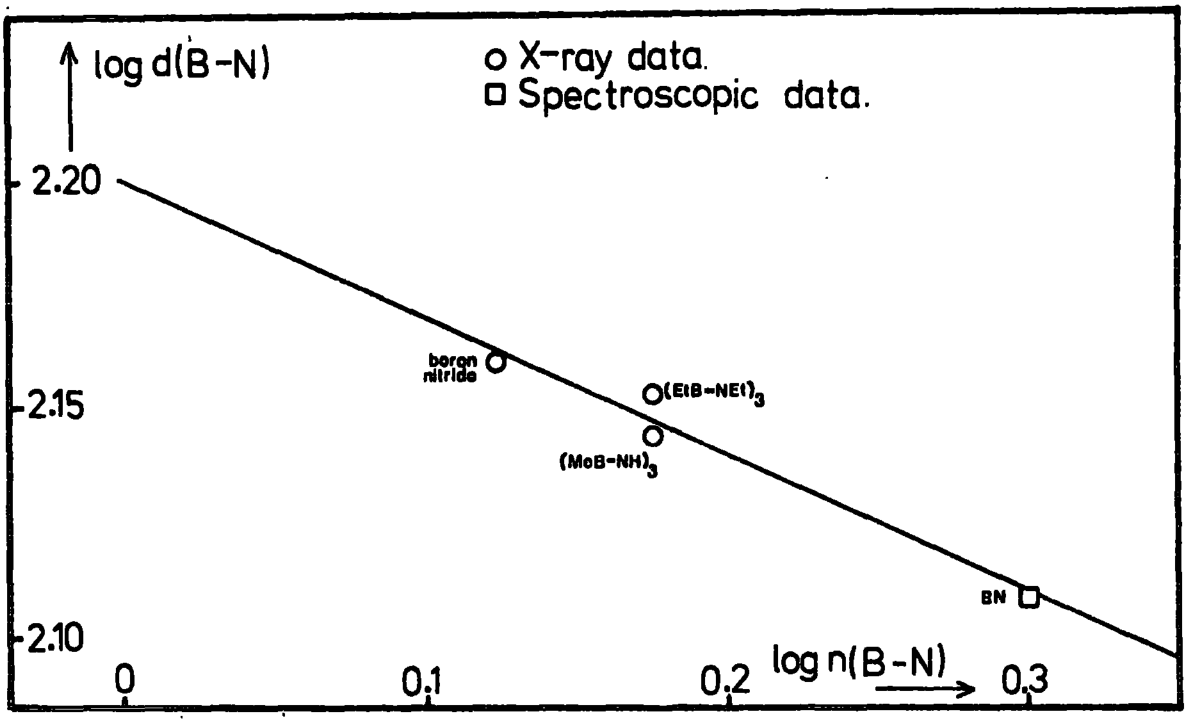
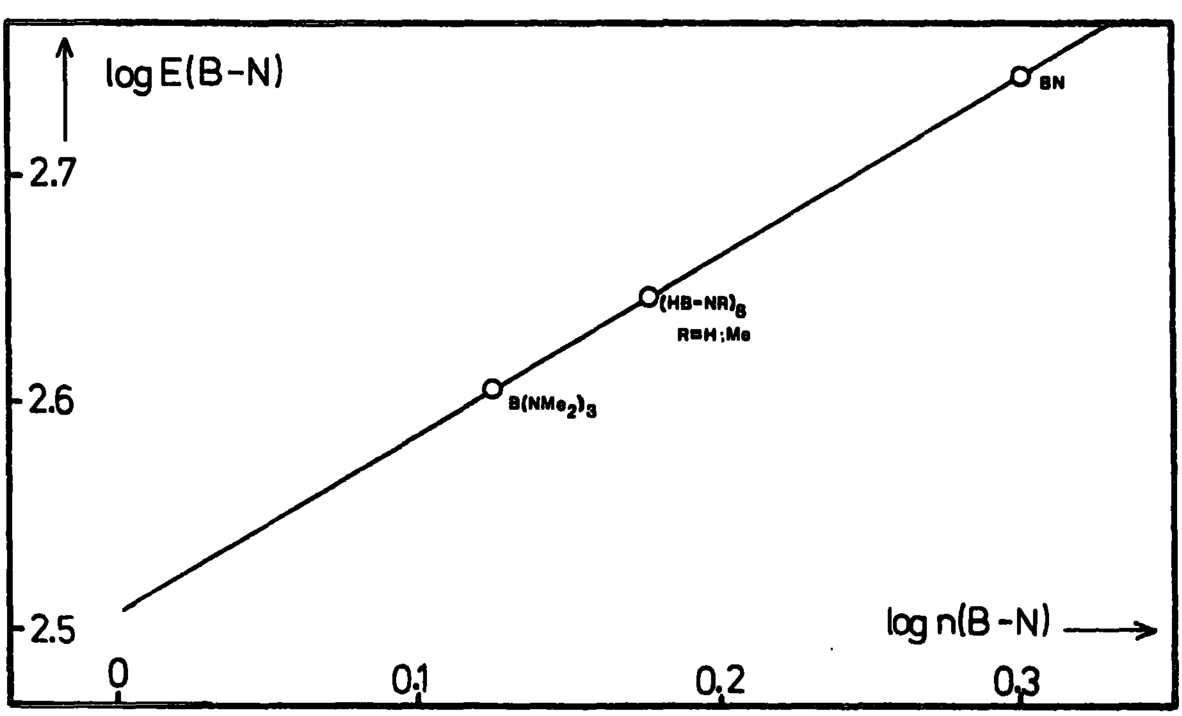


Figure 2.12 Log E(B-N) against log n(B-N) for disruption into atoms; [E in kJ mol^{-1}].



$$d(B\text{-}N) = 158.7[n(B\text{-}N)]^{-0.31} \quad (2.20)$$

(≈159 pm) for a boron-nitrogen single bond. This compares well with the sum of Pauling's tetrahedral covalent radii (158 pm) and with a value of 155 pm derived from the Stevenson-Schömaker equation.[104] It is also striking that the bond length in borazon, (which is the cubic form of boron nitride and structurally analogous to diamond), is 159 pm for n(B-N) = 1.00.[105] Lengths of other B-N formal single bonds are 161 pm in dimethylaminoborane dimer ($[Me_2NBH_2]_2$),[106] 157.5 pm in trimethylaminoboron trichloride (Me_3N,BCl_3),[107] 159.1 pm in dimethylaminoboron dichloride dimer ($[Me_2NBCl_2]_2$)[108] and 158 pm in trimethylaminoboron trifluoride (Me_3N,BF_3);[109] (all lengths determined by X-ray diffraction). It therefore seems justifiable to extend the applicability of equation 2.20 to bonds involving sp^3-hybridised boron. Indeed, if values of d(B-N) = 159, 161, 157.5, 159.1 and 158 pm for n(B-N) = 1.0 had been included in the original correlation (Figure 2.11), a correlation coefficient of -0.99192 would have been obtained and equation 2.20 revised to give:

$$d(B\text{-}N) = 158.9[n(B\text{-}N)]^{-0.31} \quad (2.21)$$

Boron-nitrogen bond enthalpy contributions can be estimated for several of the simpler compounds considered previously in this Section. Thermochemical data are given in Table 2.10. As with the alkoxy-derivatives of boron, problems arise when considering the disruption of dimethylamino-derivatives, e.g. tris(dimethylamino)borane, ($B(NMe_2)_3$). Firstly, consider the process:

$$B(NMe_2)_3\,(g) \longrightarrow B(g) + 3\cdot NMe_2(g)$$

TABLE 2.10 Thermochemical Data for Some Boron-Nitrogen Compounds

Compound	ΔH^{o}_{f298} kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	Ref.
$B(NMe_2)_3$ (g)	-245.5	10448.8	90
Boron nitride (c)	-251.5	1287.4	8,37,68,70
$(HB\text{-}NH)_3$(g)	-532.4	4939.4	37
$(HB\text{-}NMe)_3$(g)	-524.5	8389.5	37
BN (g)	477.0	556.0*	2,8

* The bond dissociation energy of gaseous boron nitride is controversial. Values of 4eV $< D_o <$ 7eV have been suggested and are summarised in ref. 8 (addendum 1967). The value of ΔH^{o}_{f298} BN(g) = 477 kJ mol^{-1} is based on D_o = 5.7eV.[110]

ΔH^o_{f298} $\cdot NMe_2(g)$ = 123.4 kJ mol^{-1} [9,68] and hence $D(B \text{———} NMe_2)$ = 391.9 kJ mol^{-1}. However for complete atomisation a value of D(B-N)= 402.9 kJ mol^{-1} is obtained;

$$B(NMe_2)_3(g) \longrightarrow B(g) + 3N(g) + 6C(g) + 18\,H(g)$$

(subsidiary thermochemical data are: $D(C\text{-}H)_{Me}$ = 410 kJ mol^{-1} [10,94,95] and D(C-NMe) ≈ 310 kJ mol^{-1} [10]). Mean B-N bond enthalpy contributions for borazine ($(HB\text{-}NH)_3$), N-trimethylborazine ($(HB\text{-}NMe)_3$) and diatomic BN are allocated assuming disruption to gaseous atoms (Table 2.11) and hence for comparison, the value of 402.9 kJ mol^{-1} in $B(NMe_2)_3$ appears more realistic than 391.9 kJ mol^{-1}. (Additional bond enthalpies required in the borazines are D(N-H) = 391 kJ mol^{-1} [9,73] and D(B-H) = 371.2 kJ mol^{-1} (Table 2.3). A plot of log E(B-N) against log n(B-N) gives an excellent straight line, (Figure 2.12; correlation coefficient ≈ 1.0), and suggests the relationship:

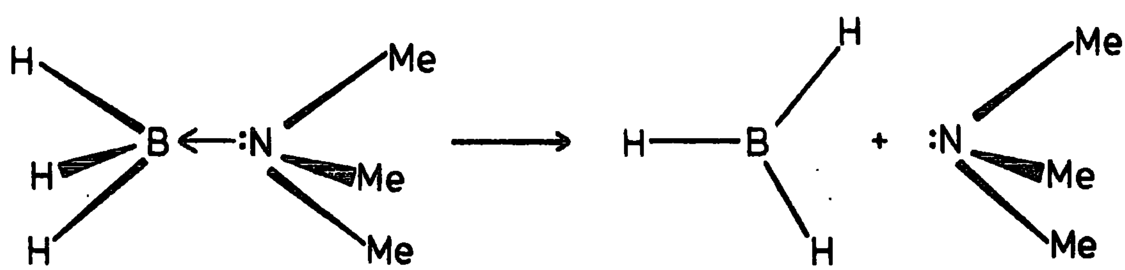
$$E(B\text{-}N) = 320.7[n(B\text{-}N)]^{0.79} \qquad (2.22)$$

The co-ordination complex trimethylaminoborane (Me_3N,BH_3) contains an $sp^3B\text{-}sp^3N$ single bond and, from equation 2.22, would be assigned an energy of 320.7 kJ mol^{-1}. $\Delta H^o_{f298} Me_3N, BH_3(g)$ = -81.4 kJ mol^{-1} [90] and hence $\Delta H_{disrupt.}$ = 5880.5 kJ mol^{-1}. The disruption of gaseous Me_3N,BH_3 into trimethylamine and boron hydride requires not only the fission of the B-N bond, but also the rearrangement of a pyramidal BH_3 unit to a planar molecule, (Figure 2.13). $\Delta H^o_{f298}\ Me_3N(g)$ = -24.3 kJ mol^{-1} [70] giving $\Delta H_{disrupt.}$ = 4609.4 kJ mol^{-1}.

TABLE 2.11 Bond Orders and Estimated Bond Enthalpies for Some B-N Systems

Compound	D(B-N) $kJ\ mol^{-1}$		n(B-N)
$B(NMe_2)_3$	402.9		$1.33\dot{3}$
$(HB\text{-}NH)_3$	442.1	mean 442.4	1.50
$(HB\text{-}NMe)_3$	442.7		1.50
BN (diatomic)	556.0		2.00

Figure 2.13 Rearrangement of BH_3 unit during dissociation of trimethylamino-borane.



Hence:

$$\Delta H_{disrupt.} Me_3N,BH_3 = \Delta H_{disrupt.} Me_3N + D(B\text{-}N) + 3D(B\text{-}H)$$

A value of 316.8 $kJ\ mol^{-1}$ is therefore predicted for a boron-hydrogen bond in trimethylaminoborane giving a reorganisation energy for pyramidal BH_3 in the complex to free planar boron hydride of 163.2 $kJ\ mol^{-1}$. A similar result is obtained for triethylaminoborane (Et_3N,BH_3); $\Delta H^o_{f298}(g)$ Et_3N,BH_3 and Et_3N = -131.6[90] and -95.8 [70] $kJ\ mol^{-1}$ respectively, giving a reorganisation energy for BH_3(pyr.) $\longrightarrow$ BH_3(planar) of 184.5 kJ mol^{-1}. (This assumes again that D(B-N) = 320.7 kJ mol^{-1}). These figures contrast with a value of 55-61 kJ mol^{-1} obtained by molecular orbital calculations for the same reorganisation in NH_3,BH_3.[111,112]

Crystalline boron nitride has not been used in the derivation of equation 2.22. Unlike the other boron-nitrogen systems considered, hexagonal boron nitride vaporises by decomposition and there is no appreciable formation of gaseous boron nitride at high temperatures.[113-115] Any estimation of bond energy contributions must therefore entail use of the standard enthalpy of formation of crystalline rather than gaseous boron nitride. ΔH^{o}_{f298} BN(c) = -254.4 kJ mol^{-1} [70] giving $\Delta H_{disrupt.}$ = 1287.4 kJ mol^{-1}. A value of D(B-N) = 429.1 kJ mol^{-1} is therefore obtained if it is assumed that bonding between the planes of hexagonal BN-units is negligible. This bond energy is higher than the 402.5 kJ mol^{-1} predicted from equation 2.22 for a B-N bond of order $1.\dot{3}\dot{3}\dot{3}$. Borazon has the "diamond-lattice" and so each B-N bond could be allocated an energy of $\frac{1}{4}$ $\Delta H_{disrupt.}$. It may be assumed that the heat of transition from hexagonal boron nitride to borazon is negligible[37] and hence $\Delta H_{disrupt.}$borazon = 1287.4 kJ mol^{-1}. Hence D(B-N) = 321.9 kJ mol^{-1} which is in good agreement with a single-bond strength obtained from equation 2.22. It is possible therefore that the low value obtained for D(B-N) in hexagonal boron nitride results partially from the neglect of interactions between atoms in each plane.

Equations 2.21 and 2.22 may be combined to give the bond energy-bond length relationship:

$$E(B\text{-}N) = 1.022 \times 10^{8}[d(B\text{-}N)]^{-2.5} \qquad (2.23)$$

This suggests that the change in energy with length of boron-nitrogen bonds is less than for carbon-carbon bonds and is not as previously indicated.[37,83]

2.6 Boron-Carbon Bonds

Empirical correlations relating bond energy to bond order and/or bond length have been suggested for BX, BO and BN systems. It seems reasonable to assume therefore that similar relationships should hold for boron-carbon species. Unfortunately little data are available concerning systems in which sp^2-boron is attached to carbon in the absence of any competing π-electron donors, (e.g. in diphenylchloroborane (Ph_2BCl) and phenyldichloroborane ($PhBCl_2$) both substituents are, in principle, capable of donating π-electronic charge to the p_z orbital on boron. This makes it difficult to assign bond orders to each bond). Organoboranes, (R_3B where R = alkyl or aryl), appear to be the only systems in which n(B-C) can be specified. Throughout this work, a value of n(B-C) = 1.00 is assigned to an alkyl-boron bond (e.g. in trimethylborane, Me_3B) although the possibility of stabilisation by hyperconjugation is a point of contention.[116-120]

Bond enthalpy contributions in trimethylborane (Me_3B), triethylborane (Et_3B) and tri-n-butylborane ($^nBu_3B$) have been given in Table 2.4. In addition, tri-n-propylborane ($^nPr_3B$) also contains a formal single B-C bond. $\Delta H^o_{f298}(g)$ $^nPr_3B$ and $^nPr\cdot$ = -236.7[90] and 94.6[91] kJ mol^{-1} respectively. Hence D(B-^{n}Pr) = 360.2 kJ mol^{-1}. In triphenylborane, (Ph_3B), each boron-carbon bond is expected to have a bond order of $1.\dot{3}\dot{3}\dot{3}$.

(The ^{11}B n.m.r. chemical shift for Ph_3B is similar to that for trivinylborane ($(CH_2 = CH)_3B$) for which a bond order of 1.33 has been proposed).[121] $\Delta H^o_{f298}(g)$ Ph_3B and Ph· = 130.0[4,90] and 325.9[122] kJ mol^{-1} respectively; (a value of ΔH^o_{f298} Ph·(g) = 301.2 kJ mol^{-1} has previously been recommended[10] but the slightly higher estimate based on a value of D(Ph-H) = 460 kJ mol^{-1} [122] now appears preferable[86]). A mean bond dissociation enthalpy of 469.2 kJ mol^{-1} is therefore allocated to the B-C bond in Ph_3B.

It is therefore suggested that values of D(B-R) = 357.1 kJ mol^{-1} (average of R = Me, Et, ^nPr and ^nBu) and 469.2 kJ mol^{-1} (R = Ph) are representative energy contributions for B-C bonds of order 1.00 and $1.33\dot{3}$ respectively. Assuming a relationship of the form of equation 2.3, it is proposed that boron-carbon bond energies vary with bond order according to equation 2.24.

$$E(B\text{-}C) = 357.1[n(B\text{-}C)]^{0.95} \qquad (2.24)$$

Trialkylboranes contain sp^2B-sp^3C bonds whilst triarylboranes contain sp^2B-sp^2C bonds. It is anticipated that such changes in hybridisation <u>may</u> influence B-C bond lengths. It is concluded that to suggest a bond length-bond order relationship from the very few data available would be unrealistic.

2.7 Competition Between π-Electron Donors Attached to Trigonal Boron; The Relative Donor Strengths of Phenyl, Dimethylamino and Halogeno Substituents

In Sections 2.3-2.6 compounds containing a single type of π-donating substituent have been considered, and empirical bond energy-bond order/length relationships suggested. In many systems however, boron is attached to different substituents, all of which may be capable of back-donating π-electronic charge to the boron p_z orbital. The relative donor strengths of such substituents, Y, determine the bond orders, n(B-Y). To a first approximation, it may be assumed that the donor properties of one substituent will greatly outweigh those of another (e.g. it is suggested Cl > Ph in $Ph_{3-x}BCl_x$[37]), or that substituents are equivalent with all $n(B-Y) = 1.33\dot{3}$.[84-86] In this Section the relationships derived for BN, BC and BX (X = Cl, Br) systems are used in an attempt to estimate the relative donor strengths of phenyl, dimethylamino and halogeno groups.

Table 2.12 lists standard heats of formation and disruption enthalpies for compounds of the type $Ph_{3-x}BX_x$ (X = Cl, Br) and $(Me_2N)_{3-x}BCl_x$. Firstly consider diphenylchloroborane (Ph_2BCl) and phenyldichloroborane ($PhBCl_2$). Bond orders and energy terms are allocated as shown in Figure 2.14.

For Ph_2BCl therefore:

$$\Delta H_{disrupt.} Ph_2BCl = 2\Delta H_{disrupt.} Ph\cdot + 2E^2_{Ph} + E^3_{Cl}$$

$$\therefore\ 1426.6 = 2E^2_{Ph} + E^3_{Cl} \qquad (2.25)$$

TABLE 2.12 Thermochemical Data for $Ph_{3-x}BX_x$ (X = Cl,Br) and $(Me_2N)_{3-x}BCl_x$ (x = 1,2)

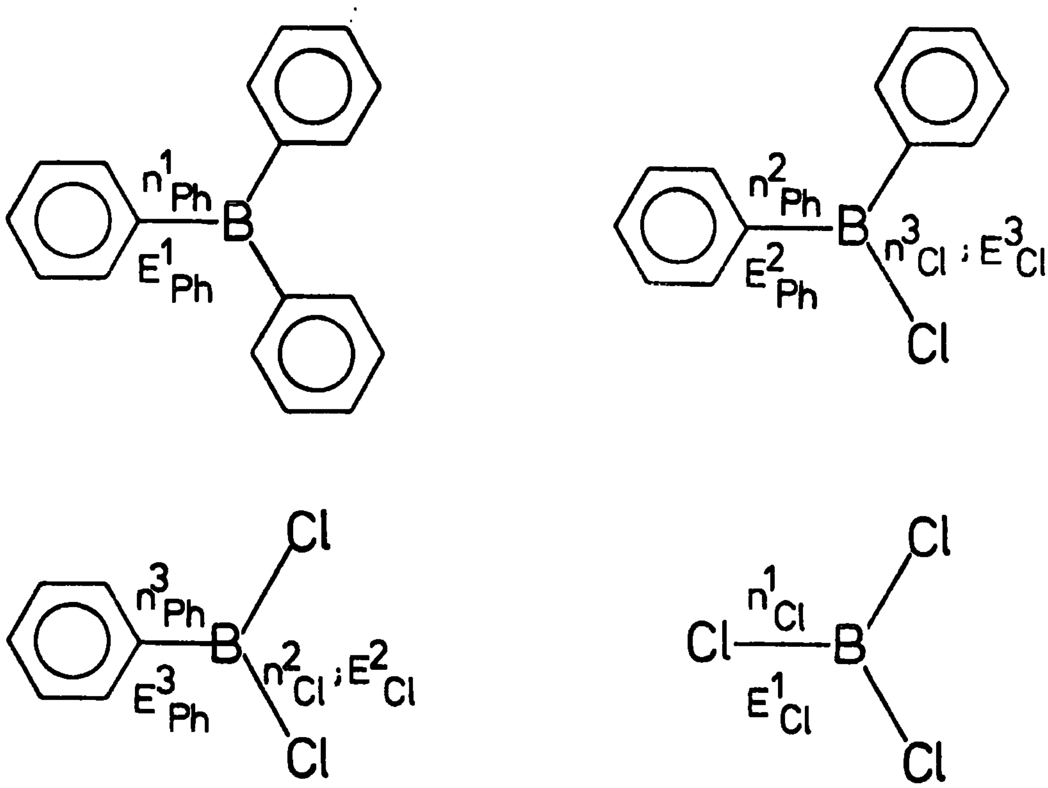
Compound	$\Delta H^o_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	Ref.
Ph_2BCl	-93.5	11555.2	90
$PhBCl_2$	-266.0	6458.7	71,90
Ph_2BBr	-9.4	11461.7	90
$PhBBr_2$	-129.3	6303.3	71,90
$(Me_2N)_2BCl$	-334.8	7444.9	71,90,123
$(Me_2N)BCl_2$*	-401.3	4418.3	71,90,123

*Dimethylaminodichloroborane readily dimerises in liquid phase. The gas phase equilibrium:

$$\text{Dimer} \rightleftharpoons \text{2 Monomer}$$

is in favour of the monomer.[108,124-126] $\Delta H^o_{f298}(g)$ is given for the monomer.

Figure 2.14 Allocation of bond orders and energies in $Ph_{3-x}BCl_x$ [x=0→3].



and for $PhBCl_2$:

$$\Delta H_{disrupt.}PhBCl_2 = \Delta H_{disrupt.}Ph^{\bullet} + E^3_{Ph} + 2E^2_{Cl}$$

$$\therefore 1394.4 = E^3_{Ph} + 2E^2_{Cl} \qquad (2.26)$$

From equation 2.16b:

$$E^2_{Cl} = 417.5\ (n^2_{Cl})^{0.2} \qquad (2.27)$$

$$E^3_{Cl} = 417.5\ (n^3_{Cl})^{0.2} \qquad (2.28)$$

From equation 2.24:

$$E^2_{Ph} = 357.1\ (n^2_{Ph})^{0.95} \qquad (2.29)$$

$$E^3_{Ph} = 357.1\ (n^3_{Ph})^{0.95} \qquad (2.30)$$

For the p_z orbital on boron to be completely filled, the sum of the bond orders of the bonds around the boron atom must equal 4. Hence:

$$\text{in } Ph_2BCl \ : \ 2n^2_{Ph} + n^3_{Cl} = 4 \qquad (2.31)$$

$$\text{in } PhBCl_2 \ : \ n^3_{Ph} + 2n^2_{Cl} = 4 \qquad (2.32)$$

Combining equations 2.25, 2.28, 2.29 and 2.31 gives:

$$1.9975 = \left[\frac{4 - n^3_{Cl}}{2}\right]^{0.95} + 0.5846(n^3_{Cl})^{0.2}$$

$$\text{i.e. } n^3_{Cl} = 1.16$$

Combining equations 2.26, 2.27, 2.30 and 2.32 gives:

$$3.9048 = (4 - 2n^2_{Cl})^{0.95} + 2.3383(n^2_{Cl})^{0.2}$$

$$\text{i.e. } n^2_{Cl} = 1.26$$

It is therefore suggested that in diphenylchloroborane the B-Cl bond is of order 1.16 and so has an energy of 430.1 kJ mol^{-1}. Each B-Ph bond must therefore have a bond order of 1.42 and a mean bond energy of 498.3 kJ mol^{-1}. In phenyldichloroborane, the B-Cl bond order is estimated to be 1.26 and hence an energy of 437.3 kJ mol^{-1} is allocated to each bond. Hence the B-Ph bond is of order 1.48 and energy 518.2 kJ mol^{-1}.

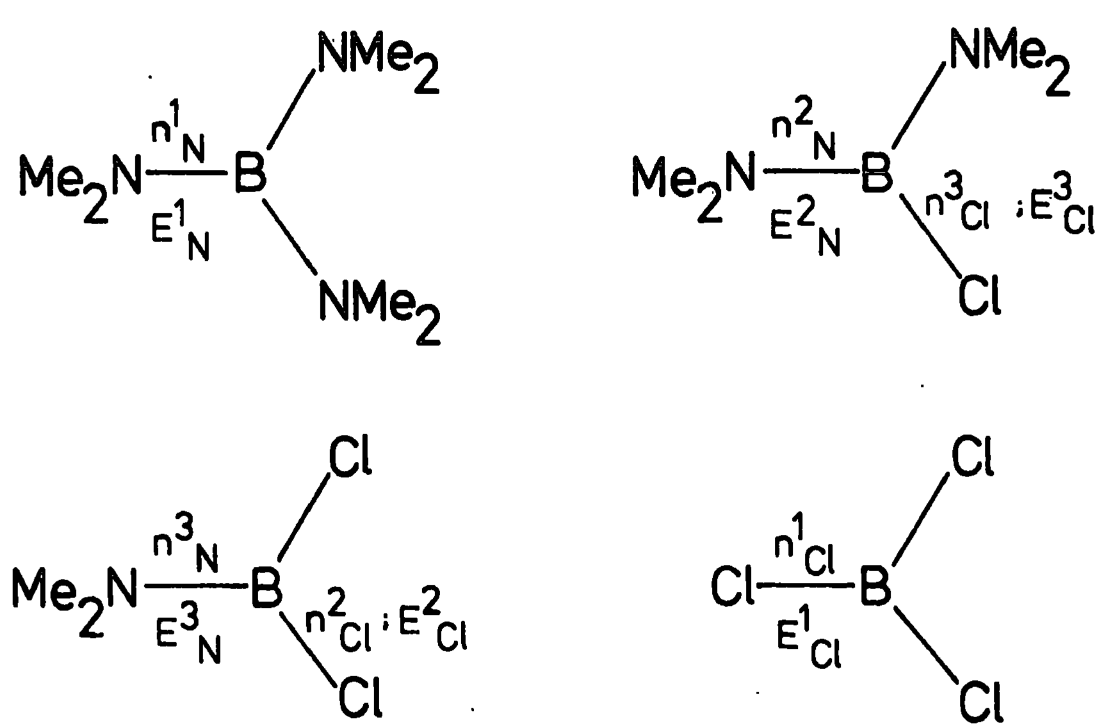
An equivalent calculation can be carried out for diphenylbromoborane and phenyldibromoborane using the relationship for B-Br bonds:

$$E(B\text{-}Br) = 346.4\,[n(B\text{-}Br)]^{0.2} \qquad (2.16c)$$

The results are summarised for both chloro- and bromo-derivatives in Table 2.13.

In bis-(dimethylamino)-chloroborane and dimethylamino-dichloroborane both types of substituents are capable of donating π-electrons to boron. In Section 2.5 it was concluded that consideration of the complete atomisation of the dimethylamino group is preferable to disruption to the $Me_2N\cdot$ radical. Hence, using enthalpies of disruption from Table 2.12 and values of $D(C\text{-}H)_{Me} = 410$ [10,94,95] and $D(C\text{-}NMe) \approx 310$[10] kJ mol^{-1}, equations 2.33 - 2.40 can be written. (Bond orders and energy terms are allocated as shown in Figure 2.15).

Figure 2.15 Allocation of bond orders and energies in $(Me_2N)_{3-x}BCl_x$ [x=0→3].



For $(Me_2N)_2BCl$:

$$\Delta H_{disrupt.}(Me_2N)_2BCl = 12D(C\text{-}H)_{Me} + 4D(C\text{-}NMe) + 2E^2_N + E^3_{Cl}$$

$$\therefore 1284.9 = 2E^2_N + E^3_{Cl} \qquad (2.33)$$

For $(Me_2N)BCl_2$:

$$\Delta H_{disrupt.}(Me_2N)BCl_2 = 6D(C\text{-}H)_{Me} + 2D(C\text{-}NMe) + E^3_N + 2E^2_{Cl}$$

$$\therefore 1338.3 = E^3_N + 2E^2_{Cl} \qquad (2.34)$$

From equation 2.22:

$$E^2_N = 320.7\ (n^2_N)^{0.79} \qquad (2.35)$$

$$E^3_N = 320.7\ (n^3_N)^{0.79} \qquad (2.36)$$

From equation 2.16b:

$$E^2_{Cl} = 417.5\ (n^2_{Cl})^{0.2} \qquad (2.37)$$

$$E^3_{Cl} = 417.5\ (n^3_{Cl})^{0.2} \qquad (2.38)$$

Assuming Σ bond orders = 4:

$$\text{in } (Me_2N)_2BCl \ : \ 2n^2_N + n^3_{Cl} = 4 \qquad (2.39)$$

$$\text{in } (Me_2N)BCl_2 \ : \ n^3_N + 2n^2_{Cl} = 4 \qquad (2.40)$$

Combining equations 2.33, 2.35, 2.38 and 2.39 gives:

$$2.0033 = \left[\frac{4 - n^3_{Cl}}{2}\right]^{0.79} + 0.6509(n^3_{Cl})^{0.2}$$

$$\text{i.e. } n^3_{Cl} = 1.10$$

Combining equations 2.34, 2.36, 2.37 and 2.40 gives:

$$4.1731 = (4-2n^2_{Cl})^{0.79} + 2.6297(n^2_{Cl})^{0.2}$$

$$\text{i.e. } n^2_{Cl} = 1.20$$

The B-Cl bond energy contributions so obtained are listed in Table 2.13 along with the boron-nitrogen bond orders and enthalpies.

It is concluded that both chloro- and bromo-substituents are <u>less</u> powerful π-electron donors than either phenyl or dimethylamino groups. From a comparison of $Ph_{3-x}BCl_x$ and $Ph_{3-x}BBr_x$ systems it is also concluded that a bromo-substituent donates π-electrons more strongly than a chloro-group, and by comparing $(Me_2N)_{3-x}BCl_x$ and $Ph_{3-x}BCl_x$, dimethylamino groups are shown to off-load π-electronic charge more readily than phenyl groups. Overall, the relative donor strengths of phenyl, dimethylamino, chloro and bromo groups are:

$$Me_2N > Ph \gg Br > Cl$$

This suggestion supports conclusions drawn from electron impact studies.[127,128]

It has been proposed that allowance should be made for the differing donor strengths of substituents attached to boron. However, comparison of the B-Cl bond order and energy terms in Ph_2BCl and $PhBCl_2$ or of the B-Br enthalpies in Ph_2BBr and $PhBBr_2$ (Table 2.13) indicate that the estimated differences in bond orders are so small as to make only slight differences to the bond energy values. It can be concluded that to a first approximation it <u>is</u> possible to allow transferance of D(B-X) between Ph_2BX and $PhBX_2$. However, the energy most appropriate is less than in BX_3 itself and it is <u>not</u> therefore

TABLE 2.13 Suggested Bond Orders and Bond Enthalpy Contributions for $Ph_{3-x}BX_3$ (X = Cl,Br) and $(Me_2N)_{3-x}BCl_x$ (x = 1,2)

Compound	Bond	Estimated Bond Order	Estimated Bond Energy kJ mol^{-1}
Ph_2BCl	B-Cl	1.16	430.1
	B-Ph	1.42	498.2
$PhBCl_2$	B-Cl	1.26	437.3
	B-Ph	1.48	518.2
Ph_2BBr	B-Br	1.23	361.0
	B-Ph	1.385	486.6
$PhBBr_2$	B-Br	1.27	363.4
	B-Ph	1.46	511.6
$(Me_2N)_2BCl$	B-Cl	1.10	425.5
	B-N	1.45	430.1
$(Me_2N)BCl_2$	B-Cl	1.20	433.0
	B-N	1.60	464.9

realistic to transfer one value of D(B-X) between all members of the series $BX_3 \longrightarrow Ph_2BX$ as has previously been suggested.[84-86] The estimated values of boron-phenyl bond energies in Ph_2BX and $PhBX_2$ also indicate that transferance of D(B-Ph) from Ph_3B to each halogeno-derivative is not really valid, although reasonably satisfactory results can be obtained if this approximation is made.[37]

2.8 Conclusion

The studies in this Chapter have shown that empirical bond energy-bond order/length relationships of the type:

$$E \propto d^{-k}$$

$$d \propto n^{-p}$$

$$E \propto n^{m}$$

can be applied successfully to CO, BF, BCl, BBr, BO, BN and, by analogy, to BC systems. Changes in hybridisation of boron from sp to sp^2 or sp^3 states do not appear to seriously affect such correlations.

The type of disruption process under consideration is important. Bond enthalpy terms calculated for the disruption of a system into free radical species may not necessarily be the same as energy contributions estimated for the total atomisation of the system. It is suggested that more consistent sets of bond energy contributions can be derived from consideration of total atomisation processes wherever this is possible.

Bond energy-bond order/length relationships can be utilised to gain an insight into the relative π-donor strengths of various substituents. This has been exemplified using the systems $Ph_{3-x}BX_x$ and $(Me_2N)_{3-x}BX_x$ and the relative donor strengths of the various groupshave been successfully predicted.

CHAPTER THREE

BOND ENTHALPIES AND BOND ORDERS IN BORONE HYDRIDES, B_nH_{n+x} (x=4,6) AND IN BORANE ANIONS, $B_nH_n^{2-}$.

3.1 Introduction

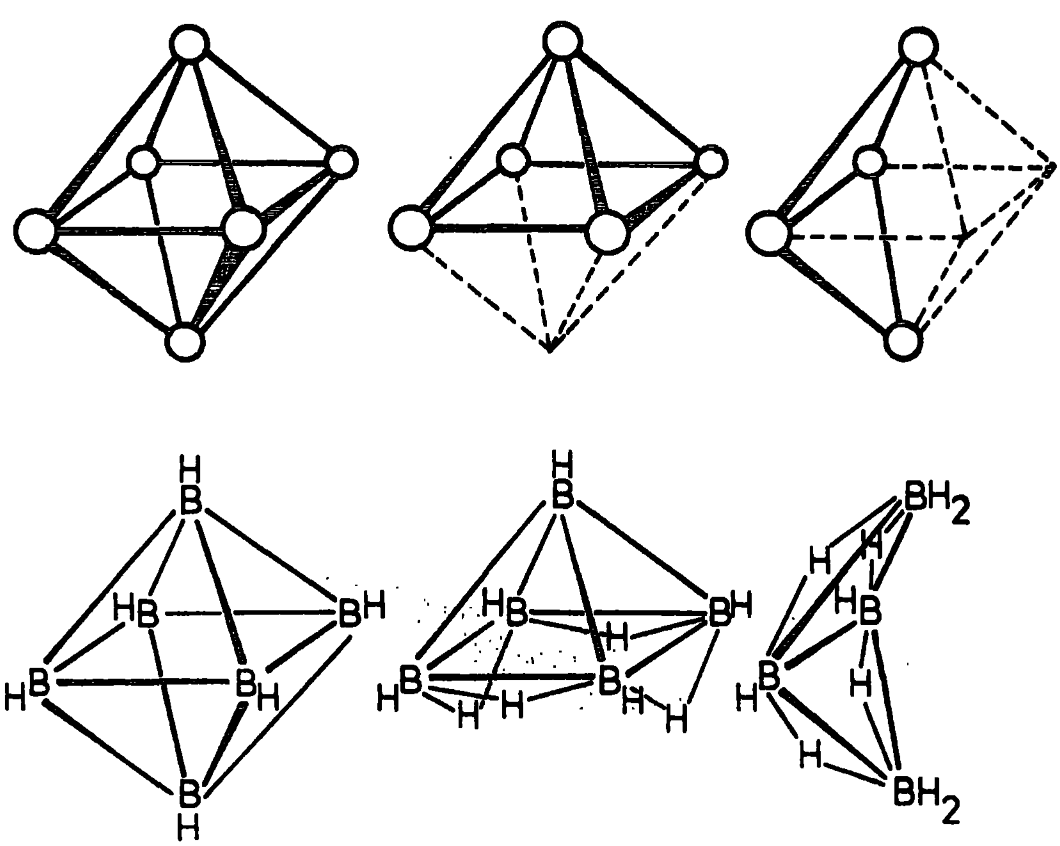
Boron hydrides of the general form B_nH_{n+x} (x = 4,6) or borane anions $B_nH_n^{2-}$ are systems in which there are too few valence electrons to allocate a pair of electrons to every pair of adjacent atoms which are within usual covalent bonding distance. The bonding in these compounds has been described in terms of 2-centre 2-electron (2c2e) and 3-centre 2-electron (3c2e) bonds.[129] A skeletal electron counting approach has also been used[76,78-82] in which each BH unit is regarded as a source of 2 skeletal bonding electrons. Further electrons are provided by additional H-atoms or negative charges associated with the cluster species. A detailed account of skeletal electron counting schemes is given in Chapter Six, but Table 3.1 and Figure 3.1 summarise the application to boron hydride systems.

Several attempts have been made to estimate bond enthalpy contributions in the neutral boranes. Treatments have generally used the 2- and 3-centre electron pair bonding approach and have assumed transferability of energy terms between similar bonds in a series of compounds,[130-132] (Table 3.2). The weakness of such treatments is the basic neglect of changes in bond energies indicated by varying bond lengths; (in the series B_4H_{10} to $B_{18}H_{22}$, 160pm $<$ d(B-B) $\leqslant$198pm). Although this weakness has been recognised,[131] it has been assumed that errors so incurred will be self-cancelling.

TABLE 3.1 Classification of Boron Hydride Systems by Skeletal Electron Counting; (see Figure 3.1)

Number of Atoms	Number of Skeletal Bonding Pairs of Electrons	Number of Vertices of Parent Polyhedra	Class Name	General Borane Type	Example	Figure
n	n + 1	n	Closo	$B_nH_n^{2-}$	$B_6H_6^{2-}$	3.1a
n	n + 2	n + 1	Nido	B_nH_{n+4}	B_5H_9	3.1b
n	n + 3	n + 2	Arachno	B_nH_{n+6}	B_4H_{10}	3.1c

Figure 3.1 Boron hydrides with 7 skeletal pairs of electrons based on the octahedron.



(a) $B_6H_6^{2-}$ (b) B_5H_9 (c) B_4H_{10}

TABLE 3.2 Previously Suggested Bond Enthalpy Terms in Some Boron Hydrides

Parameter *	Enthalpy Contribution kJ mol^{-1} Prosen[130]	Gunn[131]	Wade[132]
B-B (2c2e)	347.7	332.0	310
B-B-B (3c2e)	408.8	379.4	380
B-H (2c2e) (Terminal)	389.5	381.4	375
B-H-B (3c2e) (Bridge)	448.5	441.1	450
Assumed $\Delta H^o_{f298}B(g)$	585.8	565.8	563

* 2c2e = 2-centre electron pair bond

3c2e = 3-centre electron pair bond

Standard enthalpies of formation of the boron hydrides, B_nH_{n+p}, have been predicted from a plot of $(\Delta H^o_f/_n)$ against $(1 + p/_n)$ for known values of ΔH^o_{f298} relating to gaseous boron, diborane (B_2H_6), pentaborane-9 (B_5H_9) and decaborane-14 $(B_{10}H_{14})$.[133] This method suffers from the use of inaccurate values of ΔH^o_{f298} B(g) and $B_{10}H_{14}$(g). In addition, 'tetragonal' boron was used as the basis for estimating an average boron-boron bond enthalpy contribution. It has recently been shown that this so-called 'allotrope' is in fact NOT pure elemental boron, but incorporates either carbon or nitrogen atoms in the lattice (i.e. $B_{50}C_2$ or $B_{50}N_2$).[134,135]

One attempt has been made to allow for variation in bond energy with bond length.[38] The linear relationships:

$$E(B\text{-}B) = 228.10 - 103.63\ d(B\text{-}B) \quad (3.1)$$

$$E(B\text{-}H) = 177.92 - 90.20\ d(B\text{-}H) \qquad (3.2)$$

$$(E \text{ in kcal mol}^{-1};\ d \text{ in Å})$$

are assumed. Equation 3.1 was derived using values of d(B-B) and E(B-B) from diatomic B_2 and 'tetragonal' boron. Equation 3.2 was based on values of d(B-H) and E(B-H) from gaseous BH and BH_2. The method is unsatisfactory because of (a) the use of 'tetragonal elemental boron' and (b) reliance on inaccurate values of d(B-H) in BH and BH_2. (Estimated bond energy terms in the neutral boranes lie in the approximate ranges

$$280 < E(B\text{-}H)_{terminal} < 300 \text{ kJ mol}^{-1},$$

$$200 < E(B\text{-}H)_{bridge} < 245 \text{ kJ mol}^{-1}, \text{ and}$$

$$150 < E(B\text{-}B) < 220 \text{ kJ mol}^{-1}).$$

In the previous Chapter, bond energy-bond length relationships of the form:

$$E(B\text{-}Y) = A[d(B\text{-}Y)]^{-k} \qquad (3.3)$$

were suggested for Y = N, and bond energy-bond order correlations of the type:

$$E(B\text{-}Y) = A'[n(B\text{-}Y)]^{m} \qquad (3.4)$$

were proposed for Y = F, Cl, Br, O, N, C. It is reasonable to assume that similar relationships will apply to boron-boron and boron-hydrogen bonds. This Chapter is therefore devoted to the estimation of possible bond enthalpy terms and bond orders in a variety of boron hydride systems.

3.2 The Development of Bond Energy-Bond Length Relationships for Boron-Boron and Boron-Hydrogen Bonds

The neutral nido- and arachno-boranes, B_nH_{n+4} and B_nH_{n+6}, form a series of closely related compounds, the structures of which have been determined for many species in the range $2 \leq n \leq 18$. Thermochemical data are however only available for diborane (B_2H_6), tetraborane-10 (B_4H_{10}), pentaborane-9 (B_5H_9), pentaborane-11 (B_5H_{11}), hexaborane-10 (B_6H_{10}) and decaborane-14 ($B_{10}H_{14}$). Standard enthalpies of formation and disruption are listed in Table 3.3. The enthalpy of disruption of gaseous B_nH_{n+x} into boron and hydrogen atoms will have contributory bond energy terms, E(B-B) and E(B-H), and it is assumed that these are dependent on the corresponding bond lengths, d(B-B) and d(B-H), according to equations 3.5 and 3.6.

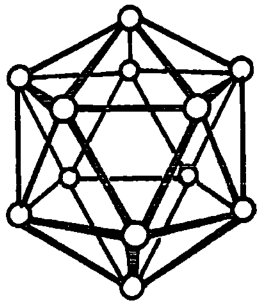
$$E(B\text{-}B) = A[d(B\text{-}B)]^{-k} \qquad (3.5)$$

$$E(B\text{-}H) = C[d(B\text{-}H)]^{-k^1} \qquad (3.6)$$

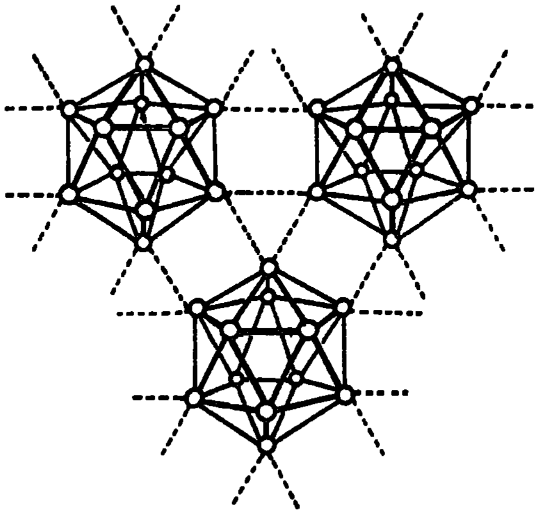
(A, C, k and k^1 = constants)

Pure elemental boron exists in the α-rhombohedral crystalline form between temperatures of 800°C and 1100°C, and in the β-rhombohedral form above 1300°C.[136] Precise structural details are known for each allotrope. α-rhombohedral boron possesses the simpler structure. It consists of discrete icosahedral B_{12}-units, (average d(B-B) = 176.7pm), which are linked in a manner which is rationalised using 2c2e-bonds, (d(B-B) = 171pm), and 3c2e-bonds, (d(B-B) = 202.5pm).[137] There are a total of 39 bonds of average d(B-B) = 180.2pm linking the 12 boron atoms of the unit cell, (Figure 3.2). The average boron-boron bond enthalpy contribution is estimated as $\frac{1}{39}$ $(12\ \Delta H^{o}_{f298}B(g)) = 172.3$ kJ mol^{-1}. (β-rhombohedral boron has a complex structure with 105 atoms and a total of 336 B-B bonds varying in length from 167 to 191pm per unit cell. It is therefore unrealistic to use this allotrope initially for estimating an average value of E(B-B); a detailed analysis of

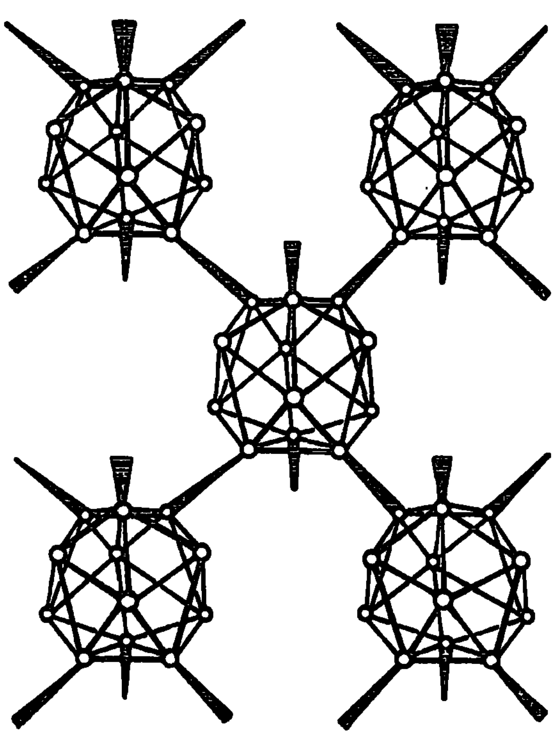
Figure 3.2 Structural units and bond types in α-rhombohedral boron.



(a) Icosahedral B_{12} - unit



(b) Basal xy - plane showing 3c 2e links.



(c) Vertical yz - plane showing 2c 2e links.

TABLE 3.3 Standard Enthalpies of Formation and Disruption of Some Gaseous Boranes[70,90]

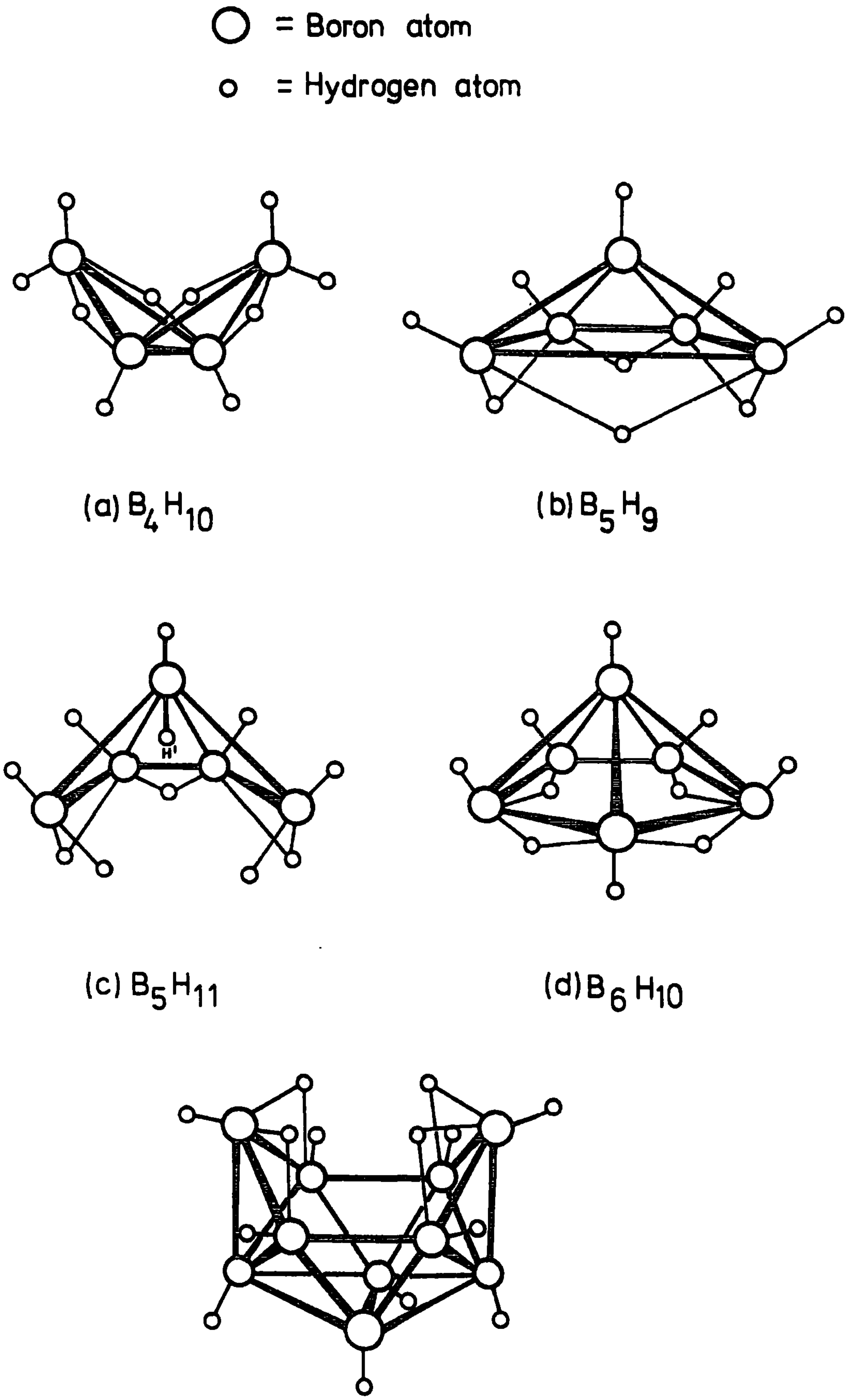
Compound	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}
B_4H_{10}	66.1	4354
B_5H_9	73.2	4689
B_5H_{11}	103.3	5095
B_6H_{10}	94.6	5445
$B_{10}H_{14}$	31.5	8620

the structure is considered later in this Section). Hence, from α-rhombohedral boron, an average B-B bond of length ca.180pm will have an energy of ca.172 kJ mol^{-1}.

The terminal hydrogen atoms in boron hydrides may generally be considered to have d(B-H) = 119pm[138-140]; problems regarding location of H-atoms have already been noted (Chapter One, Section 1.4). Previously,[130-132] values for $E(B\text{-}H)_{term.}$ have been transferred directly from BH_3, i.e. ≈370 - 380 kJ mol^{-1}. Since, however, BH_3 contains sp^2-boron, (which is NOT generally its hybridised state in borane systems), and since d(B-H) in BH_3 = 116pm [8,141,142], it is anticipated that $E(B\text{-}H)_{term.} < 370$ kJ mol^{-1}. The lowest value of $E(B\text{-}H)_{term.}$ previously proposed for $d(B\text{-}H)_{term.}$ = 119pm is 295 kJ mol^{-1}.[38] Hence it is suggested that $300 \leq E(B\text{-}H)_{term.} \leq 370$ kJ mol^{-1}.

Before equations 3.5 and 3.6 can be used to estimate B-B and B-H bond enthalpies, values of k and k^1 must be found. Detailed structural data are available for B_4H_{10} [143-147], B_5H_9 [148], B_5H_{11} [138,139,144,149], B_6H_{10} [150, 151], and

Figure 3.3 Structures of some boranes.



(e) $B_{10}H_{14}$

$B_{10}H_{14}$ [152,153], (Figure 3.3; Table 3.4). Since each borane contains bonds of differing lengths and, presumably, differing strengths, an expression for the heat of disruption in terms of individual bond enthalpy contributions will contain a large number of unknown quantities; e.g. equations 3.7 and 3.8 for B_5H_9. However by comparison with other main group systems (Chapter Two) it is anticipated that k and k^1 will lie in the range $2 \leqslant k$ or $k^1 \leqslant 6$. The variables in equations 3.7 and 3.8 can therefore be given suggested limits or else be inter-

For B_5H_9: $d_1(B\text{-}B) = 169pm$; $d_2(B\text{-}B) = 180pm$

$d_1(B\text{-}H) = 119pm$; $d_2(B\text{-}H) = 136pm$

$$\Delta H_{disrupt.}B_5H_9 = 4E_1(B\text{-}B) + 4E_2(B\text{-}B) + 5E_1(B\text{-}H) + 8E_2(B\text{-}H) \quad (3.7)$$

$$\text{i.e. } \Delta H_{disrupt.}B_5H_9 = 4A[d_1(B\text{-}B)]^{-k} + 4A[d_2(B\text{-}B)]^{-k} + 5C[d_1(B\text{-}H)]^{-k^1} + 8C[d_2(B\text{-}H)]^{-k^1} \quad (3.8)$$

related:

$$E_1(B\text{-}H) \equiv E(B\text{-}H)_{term.} = 300\text{-}370 \text{ kJ mol}^{-1}$$

$$E_2(B\text{-}H) = \left[\frac{d_1(B\text{-}H)}{d_2(B\text{-}H)}\right]^{-k^1} \cdot E_1(B\text{-}H) \quad (3.9)$$

$$E_1(B\text{-}B) = \left[\frac{d_{av.}(B\text{-}B)}{d_1(B\text{-}B)}\right]^{k} \cdot E_{av.}(B\text{-}B) \quad (3.10)$$

$$E_2(B\text{-}B) = \left[\frac{d_{av.}(B\text{-}B)}{d_2(B\text{-}B)}\right]^{k} \cdot E_{av.}(B\text{-}B) \quad (3.11)$$

where $E_{av.}(B\text{-}B) \simeq 172 \text{ kJ mol}^{-1}$

$d_{av.}(B\text{-}B) \simeq 180pm$

and $2 \leqslant k$ or $k^1 \leqslant 6$

Using appropriate expressions for each of the hydrides B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$, and substituting in values for the variables, $\Delta H_{disrupt.}$ can be estimated for each compound. Figures 3.4a-3.4f give graphical representations of some of the results obtained in terms of the difference between $(\Delta H_{disrupt.})_{calc.}$ and $(\Delta H_{disrupt.})_{expt.}$ for different combinations of the suggested values of the variables k, k^1, $E(B\text{-}H)_{term.}$, E(B-B) and d(B-B); (d(B-B) and E(B-B) are varied only slightly). The best fit to the published thermochemical data is found when:

$$E(B\text{-}B) = 1.766 \times 10^{11} [d(B\text{-}B)]^{-4.0} \quad (3.12)$$

$$E(B\text{-}H) = 4.476 \times 10^{11} [d(B\text{-}H)]^{-4.4} \quad (3.13)$$

These equations correspond to values of E(B-B) = 172 kJ mol^{-1} for d(B-B) = 179pm, and E(B-H) = 330 kJ mol^{-1} for d(B-H) = 119pm.

Table 3.4 gives individual bond enthalpies, estimated using equations 3.12 and 3.13, and also calculated enthalpies of disruption (with experimental values for comparison) for nido- and arachno-boranes with $4 \leq n \leq 10$. B_5H_{11} contains a unique endo terminally bound hydrogen atom, H^1 (indicated in Figure 3.3c), which is also involved in partial bridge bonding to two basal boron atoms; $d(B\text{ --- }H^1)_{br.} \approx 175$pm and $d(B\text{-}H^1)_{term.} > 119$pm. In this work, H^1 is treated as a normal terminal atom with d(B-H) = 119pm. Allowance for partial-bridging character would add ca. 30-40 kJ mol^{-1} to the calculated value of $\Delta H_{disrupt.}$, (††in Table 3.4). For all the boranes in Table 3.4 there is good agreement between calculated and literature values of the disruption enthalpy.

Equations 3.12 and 3.13 can also be applied successfully

Figure 3.4 Trial estimates of $\Delta H_{disrupt.}$ from bond length data for boranes.

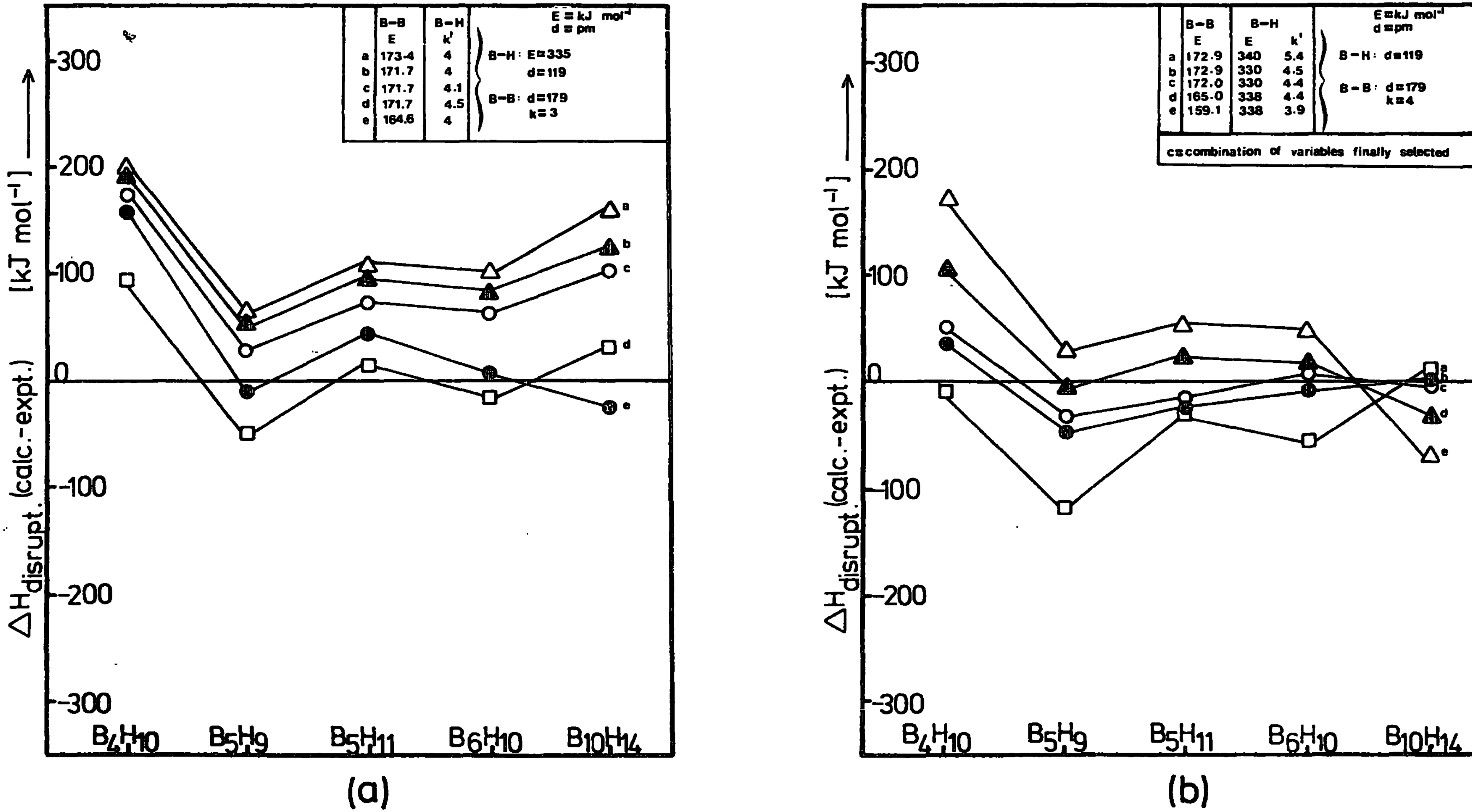


Figure 3.4 (contd.)

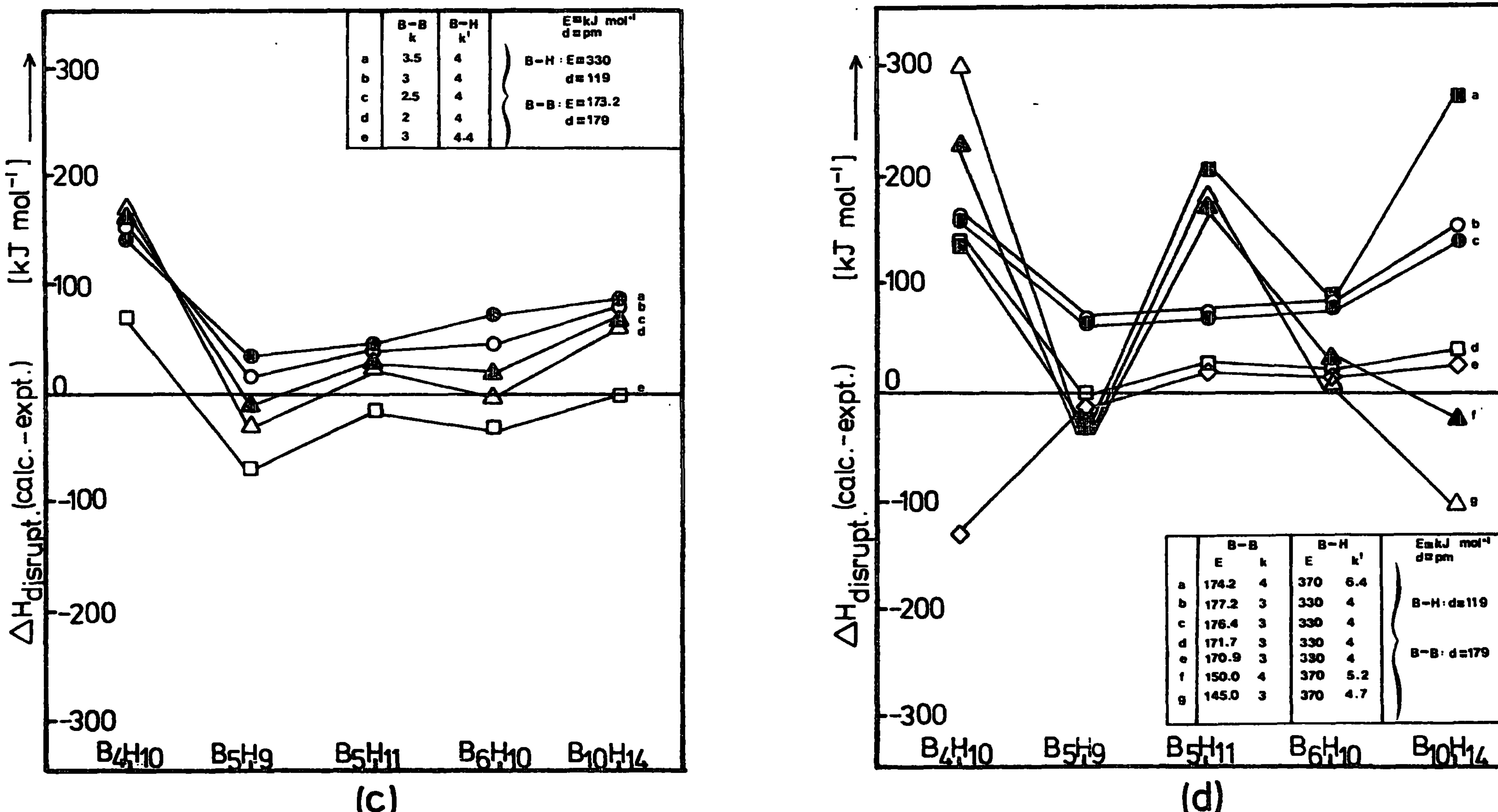
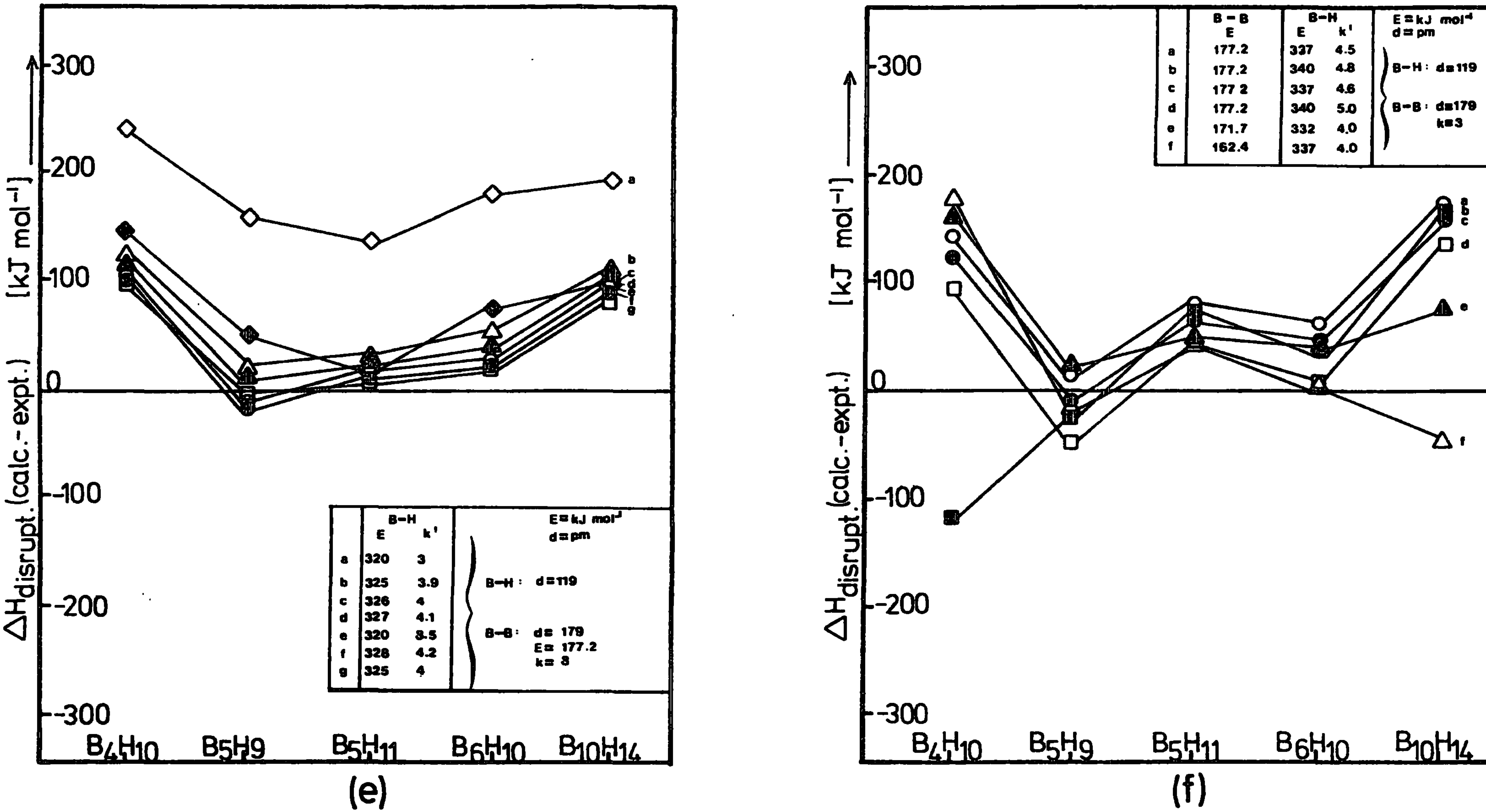


Figure 3.4 (contd.)



Compound	d(B-B)* pm	E(B-B)† kJ mol^{-1}	d(B-H)* pm	E(B-H)† kJ mol^{-1}	Calc. $\Delta H_{disrupt.}$ kJ mol^{-1}	Expt. $\Delta H_{disrupt.}$ kJ mol^{-1}
B_4H_{10}	172x1	203x1	119x6	330x6	4403	4354
	185x4	151x4	133x8	202x8		
B_5H_9	169x4	217x4	119x5	330x5	4656	4689
	180x4	168x4	136x8	183x8		
B_5H_{11}	172x2, 176x2	203x2, 184x2	119x8	330x8	5081 ††	5095
	177x1, 187x2	180x1, 144x2	132x2	209x2		
			134x4	195x4		
B_6H_{10}	160x1, 174x3		119x6	330x6	5450	5444
	175x2, 179x2		134x8	195x8		
	180x2					
$B_{10}H_{14}$	172x2, 176x4		119x10	330x10	8617	8620
	177x5, 178x4		130x4	224x4		
	179x4, 197x2		135x4	189x4		

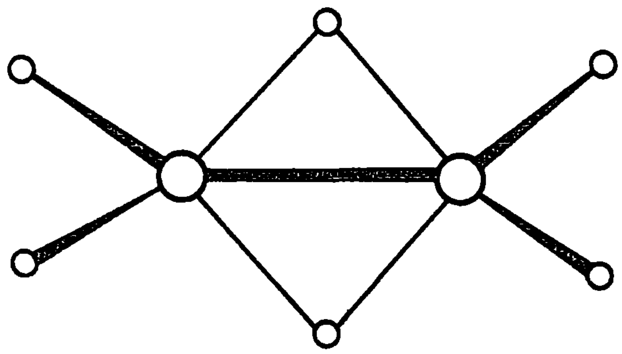
* Structural refs. given on p.72 ; Mean e.s.d. in d(B-B) and d(B-H) ≈ 1pm.

† Values of E(B-B) quoted as integers to correspond to degree of accuracy of d(B-B); Mean e.s.d. in E(B-B) ≈ 5 kJ mol^{-1}; Mean e.s.d. in E(B-H) ≈ 8kJ mol^{-1}.

†† See text

to other systems. Equation 3.12 predicts a bond dissociation energy of 275(5) kJ mol^{-1} for the diatomic molecule B_2, (d(B-B) = 158.9pm[8]), cf. literature values of 280(39) kJ mol^{-1} [1] and 289 kJ mol^{-1}.[70] Equation 3.13 suggests a disruption enthalpy of 1110(20) kJ mol^{-1} for BH_3, (d(B-H) = 116pm), cf. literature value of 1114 kJ mol^{-1}. [70] In diborane, the agreement is not quite as good: d(B-B) = 177pm giving E(B-B) = 180 kJ mol^{-1}, $d(B\text{-}H)_{term.}$ = 119pm giving $E(B\text{-}H)_{term.}$ = 330 kJ mol^{-1}, and $d(B\text{-}H)_{br.}$ = 133pm giving $E(B\text{-}H)_{br.}$ = 202 kJ mol^{-1}. [154,155] Hence, estimated $\Delta H_{disrupt.}$ B_2H_6 = 2310(60)kJ mol^{-1}, cf. literature value of 2392 kJ mol^{-1}. [70] This discrepancy may be due to the unique doubly-bridged B-B bond which is unparalleled in other borane structures; each boron is co-ordinated to 4 H-atoms, (Figure 3.5)

Figure 3.5 Structure of diborane.



◯ = boron ; ○ = hydrogen

α-rhombohedral boron was used to estimate an <u>approximate</u> average boron-boron bond energy term for a given bond length. Equation 3.12 can now be applied to the <u>detailed</u> structure of

TABLE 3.5 Bond Lengths and Strengths in α-Rhombohedral Boron

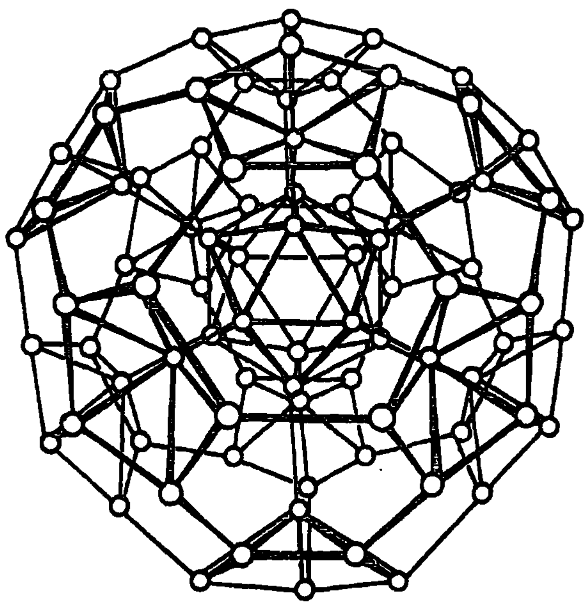
Type of Bond	Number per Unit Cell	d(B-B) pm	E(B-B) $kJ\ mol^{-1}$
Icosahedral B_{12}	30	176.7	181.1
Inter-icos. 2c2e	3	171.0	206.5
Inter-icos. 3c2e	6	202.5	105.0

this allotrope. Suggested bond enthalpy contributions for individual types of bonds are given in Table 3.5. They give a value of ΔH^{o}_{f298} α-B(g) = 557(4) kJ mol^{-1}, cf. literature value of 560(12) kJ mol^{-1}, (assuming negligible heat of transition between the allotropes of boron).

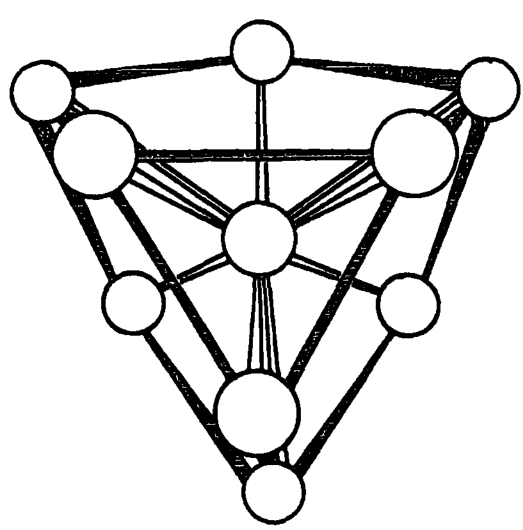
β-rhombohedral elemental boron consists of a complex lattice with 105 atoms per unit cell.[156] There is a basic B_{84} unit in which a central icosahedral B_{12} unit (average d(B-B) = 176.2pm) is surrounded by an icosahedron of icosahedra, Figure 3.6Aa. Adjacent B_{84} units are linked either by direct B-B bonds or via B_{10} sub-units, Figure 3.6Ab. Finally a 6-coordinate boron atom is sited at the centre of symmetry of two adjacent B_{10} units. The B-B links may be categorised as shown in Figures 3.6A and 3.6B and Table 3.6. Individual bond enthalpy terms estimated using equation 3.12, (summarised in Table 3.6) suggest a standard enthalpy of formation of gaseous boron of 540(6) kJ mol^{-1}. Although this is 3.6% lower than the literature value of 560 kJ mol^{-1}, it is a satisfactory result considering that the value depends upon the estimation of energies of a total of 336 bonds.

Equations 3.12 and 3.13 therefore appear to give consistent results for a variety of boron and boron-hydrogen systems.

Figure 3.6A β-Rhombohedral boron unit cell structures.

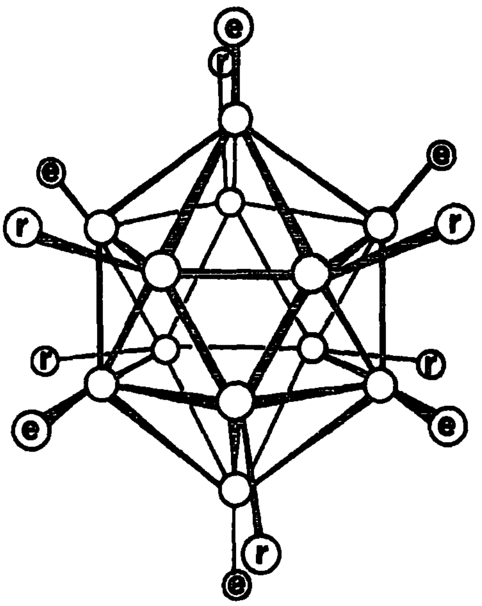


(a) B_{84}-unit

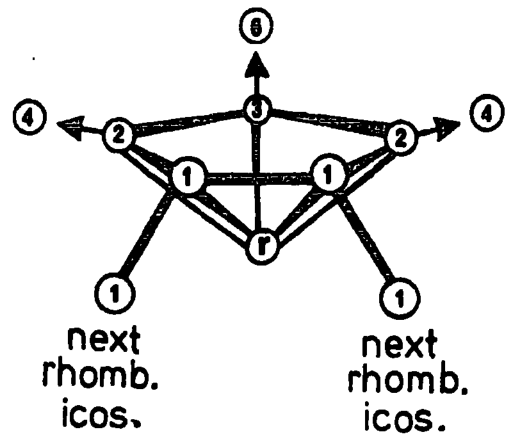


(b) B_{10}-unit

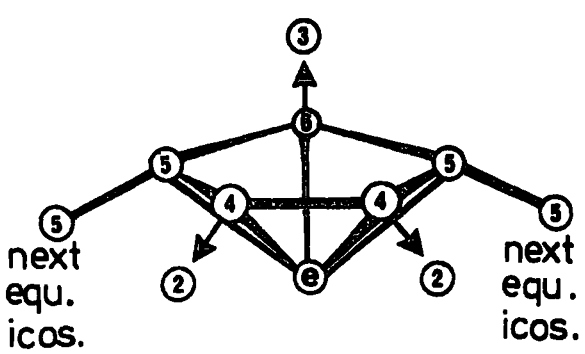
Figure 3.6B Structural units and bond types in β-rhombohedral boron.



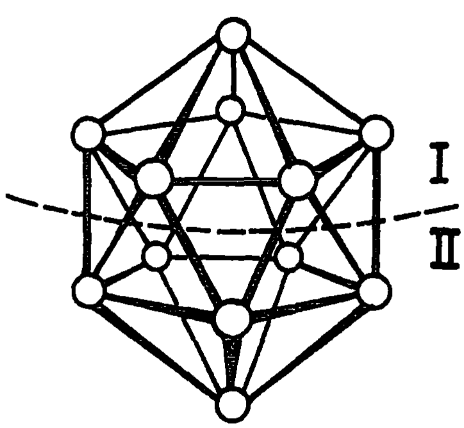
(a) Central icosahedron with links to rhombohedral (r) and equatorial (e) ½-icosahedra.



(b) Rhombohedral ½-icosahedron with links to adjacent icosahedral units.



(c) Equatorial ½-icosahedron with links to adjacent icosahedral units.



(d) Links between B_{84} and B_{10} units:

I = B_{84} , II = next B_{84}

or I = B_{84} , II = B_{10}

TABLE 3.6 Bond Lengths and Strengths in β-Rhombohedral Boron				
Type of Bond	Figure	Number per Unit Cell	d(B-B) pm	E(B-B) kJ mol^{-1}
Central icosahedral B_{12}	3.6Ba	30	176.2	183.2
Rhombohedral $\frac{1}{2}$-icos.	3.6Bb	60	184.0	154.0
Equatorial $\frac{1}{2}$-icos.	3.6Bc	60	180.8	165.2
Central-adjacent icos.	3.6Ba	12	167.6	223.8
Rhomb.-rhomb.icos.	3.6Bb	6	191.2	132.1
Rhomb.-equat.icos.	3.6Bb	18	171.3	205.1
Equat.-equat.icos.	3.6Bc	6	167.8	222.7
Intra-B_{10} unit (i)	3.6Ab	18	176.8	180.7
Intra-B_{10} unit (ii)	3.6Ab	30	186.2	146.9
Inter-B_{10}-B_{84}	3.6Bd	60	180.8	165.2
Inter-B_{84}-B_{84}	3.6Bd	30	184.1	153.7
Octahedrally sited B	-	6	168.6	218.5

3.3 Predictions of Enthalpies of Disruption of Some Higher Boranes

There are a number of higher boranes the structures of which have been determined but the thermochemistry of which is, as yet, unexplored. Equations 3.12 and 3.13 can be used to calculate enthalpies of disruption from bond length data for octaborane-12 (B_8H_{12}),[157,158] nonaborane-15 (B_9H_{15}),[159] tridecaborane-19 ($B_{13}H_{19}$),[160,161] and octadecaborane-22 ($B_{18}H_{22}$),[147,162,163] (Figure 3.7). Suggested boron-boron and boron-hydrogen bond enthalpy contributions are summarised in Table 3.7 along with calculated enthalpies of disruption. (The degree of accuracy inherent in this method of calculation means that $(\Delta H_{disrupt.})_{calc.}$ can only realistically be quoted to the nearest 10 kJ). Predicted values of standard enthalpies of formation can be estimated from the disruption enthalpies but, owing to the uncertainties in estimated values of $\Delta H_{disrupt.}$ (typically $\pm$ 100 to 150 kJ mol^{-1}), such predictions are untenable.

In general, standard enthalpies of formation of nido- and arachno-boranes are positive and negligibly small in comparison to values of $\Delta H_{disrupt.}$, (see Table 3.3). This feature allows $\Delta H_{disrupt.}$ to be predicted by an alternative method. Consider the atomisation process:

$$B_nH_{n+x}(g) \longrightarrow n\ B(g) + (n+x)\ H(g)$$

The disruption enthalpy is given by:

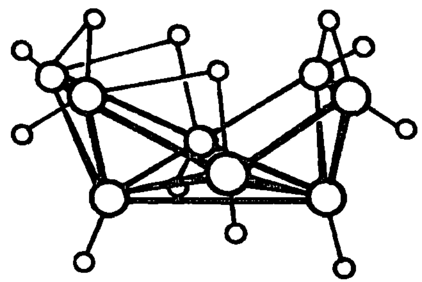
$$\Delta H_{disrupt.} = n\Delta H^o_{f298}B(g) + (n+x)\Delta H^o_{f298}H(g) - \Delta H^o_{f298}B_nH_{n+x}(g) \quad (3.14)$$

Substituting $\Delta H^o_{f298}B(g) = 560$ and $H(g) = 218$ kJ mol^{-1} gives:

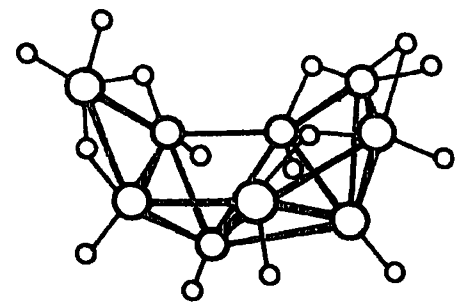
$$\Delta H_{disrupt.} + \Delta H^o_{f298}B_nH_{n+x}(g) = 778n + 218x \quad (3.15)$$

Generally, the left-hand side of equation 3.15 will be over-

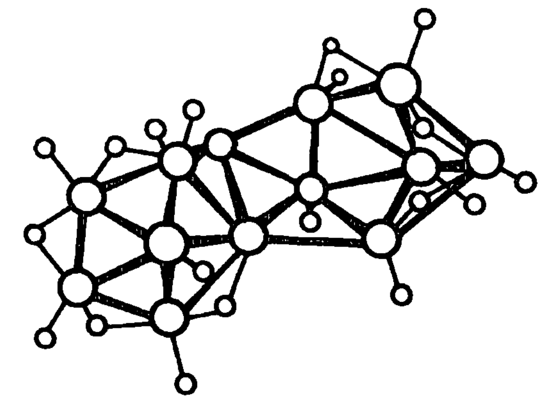
Figure 3.7 Structures of some higher boron hydrides.



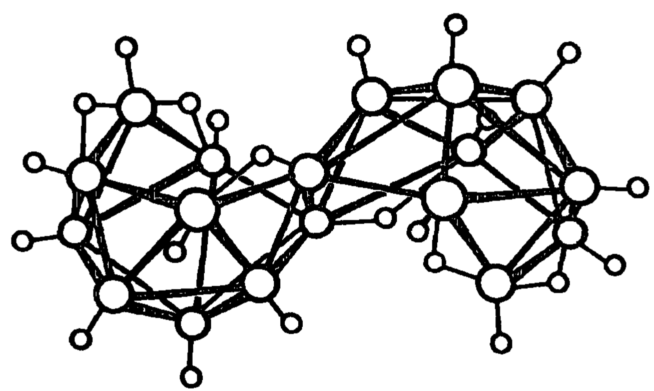
(a) B_8H_{12}



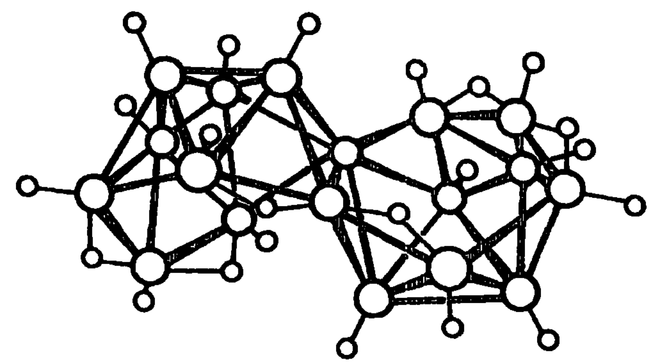
(b) B_9H_{15}



(c) $B_{13}H_{19}$



(d) $^{n}B_{18}H_{22}$



(e) $^{iso}B_{18}H_{22}$

TABLE 3.7 Structural and Thermochemical Data for Some Higher Boranes

Compound	d(B-B)* pm	E(B-B)† kJ mol^{-1}	d(B-H)* pm	E(B-H)† kJ mol^{-1}	Calc.** $\Delta H_{disrupt.}$ kJ mol^{-1}
B_8H_{12}	167x2, 173x4	227x2, 197x4	119x8, 129x2	330x8, 231x2	6920 (80)
	180x3, 182x6	168x3, 161x6	148x2, 132x4	126x2, 209x4	
B_9H_{15}	176x7, 179x2	184x7, 172x2	119x10	330x10	8130 (110)
	184x6, 195x2	153x6, 122x2	133x10	202x10	
$B_{13}H_{19}$	170x3, 173x7	212x3, 197x7	119x12	330x12	11380 (140)
	176x2, 179x6	184x2, 172x6	134x14	195x14	
	180x2, 183x4	168x2, 157x4			
	187x2	144x2			
$B_{18}H_{22}$ ††	172x2, 176x12	203x2, 184x12	119x16	330x16	14700 (180)
	179x16, 181x6	172x16, 165x6	133x12	202x12	
	182x1, 198x4	161x1, 115x4			

* Mean e.s.d. in d(B-B) and d(B-H) = 1pm.

† Mean e.s.d. in E(B-B) = 3-5 kJ mol^{-1}; mean e.s.d. in E(B-H) = 8 kJ mol^{-1}; all estimated enthalpies quoted to nearest integer.

** Calculated $\Delta H_{disrupt.}$ quoted to nearest 10 kJ.

†† Structural data is ca. equivalent for both isomers i.e. for n-$B_{18}H_{22}$ and iso-$B_{18}H_{22}$.

whelmingly dominated by $\Delta H_{disrupt.}$ and hence, equation 3.15 approximates to equation 3.16. A plot of

$$\Delta H_{disrupt.} \approx 778n + 218x \qquad (3.16)$$

$\Delta H_{disrupt.}$ against n will be effectively linear for constant x. For nido-boranes x=4 and hence:

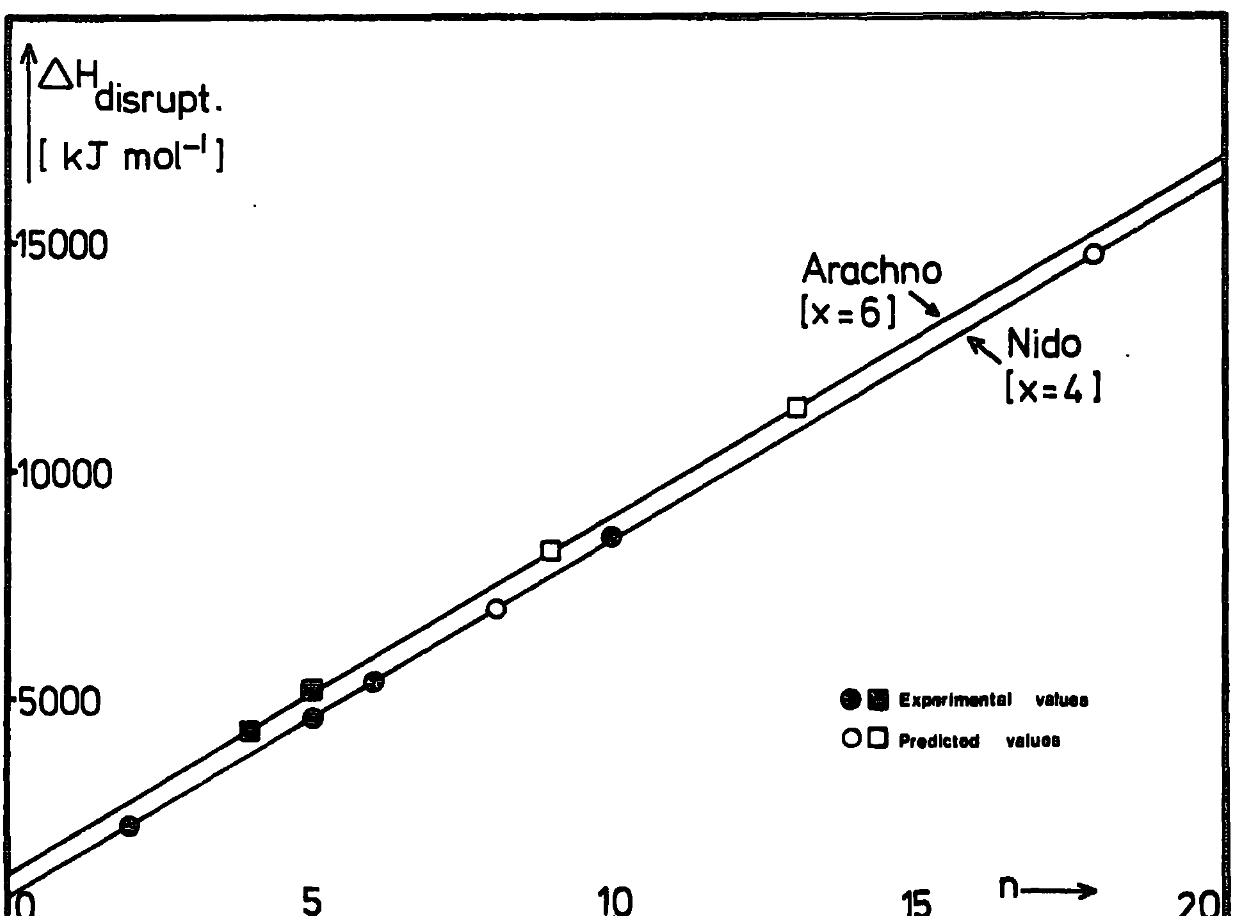
$$\Delta H_{disrupt.}\ (NIDO) \approx 778\ n + 872 \qquad (3.17)$$

and for arachno-boranes x=6, giving:

$$\Delta H_{disrupt.}\ (ARACHNO) \approx 778n + 1308 \qquad (3.18)$$

Figure 3.8 shows plots for equations 3.17 and 3.18 (two parallel lines) using experimentally determined enthalpies of disruption

Figure 3.8 $\Delta H_{disrupt.}$ for boranes B_nH_{n+x}.



for the nido-boranes B_2H_6, B_5H_9, B_6H_{10} and $B_{10}H_{14}$ and for the arachno-boranes B_4H_{10} and B_5H_{11}. Predictions of enthalpies of disruption for the higher boranes from Figure 3.8 give $\Delta H_{disrupt.}$ B_8H_{12} $\approx$ 7000, B_9H_{15} $\approx$ 8200, $B_{13}H_{19}$ $\approx$ 11400, $B_{18}H_{22}$ $\approx$ 14700 kJ mol^{-1}. There is good agreement between these values and the values in Table 3.7 and it is therefore concluded that equations 3.12 and 3.13 can be applied successfully to boranes B_nH_{n+x} (x=4,6) over a wide range of n.

3.4 Skeletal Bond Enthalpies and Relative Stabilities of Borane Anions, $B_nH_n^{2-}$

In Sections 3.2 and 3.3 bond energy-bond length relationships have been successfully employed in estimating boron-boron and boron-hydrogen bond enthalpy contributions in nido- and arachno-boranes. In view of the close relationship that exists between closo-, nido-, arachno-, and hypho-clusters, (see Chapter Six), it seems reasonable to assume that the same energy/length correlations will hold for closo- and hypho-systems.

The triangular-faced polyhedral structures of the closo-hexahydrohexaborate(2-) ($B_6H_6^{2-}$),[164] octahydrooctaborate(2-) ($B_8H_8^{2-}$),[165] nonahydrononaborate(2-) ($B_9H_9^{2-}$),[166] decahydrodecaborate(2-) ($B_{10}H_{10}^{2-}$),[167] and dodecahydrododecaborate(2-) ($B_{12}H_{12}^{2-}$)[168] anions have been established by X-ray crystallography, (Figure 3.9). Skeletal boron atoms in these clusters are either 4-coordinate (filled circles in Figure 3.9) or 5-coordinate (open circles) and the B-B links are classified according to these coordination numbers (i.e. 4-4, 4-5, or 5-5 bond types). The polyhedral edge lengths vary markedly with the bond type (Table 3.8) and hence a variation in bond strengths is expected. Equation 3.12 (restated below) is used to suggest possible enthalpy contributions for the

$$E(B\text{-}B) = 1.766 \times 10^{11}[d(B\text{-}B)]^{-4.0} \qquad (3.12)$$

skeletal B-B bonds. These are summarised in Table 3.8 along with the total skeletal bond enthalpy, $\Sigma E(B\text{-}B)$, for each cluster. As would be expected, $\Sigma E(B\text{-}B)$ increases as the number of skeletal electron pairs (n+1) increases.

Figure 3.9 Closo-$B_nH_n^{2-}$ skeletons for n=6,8,9,10 and 12.

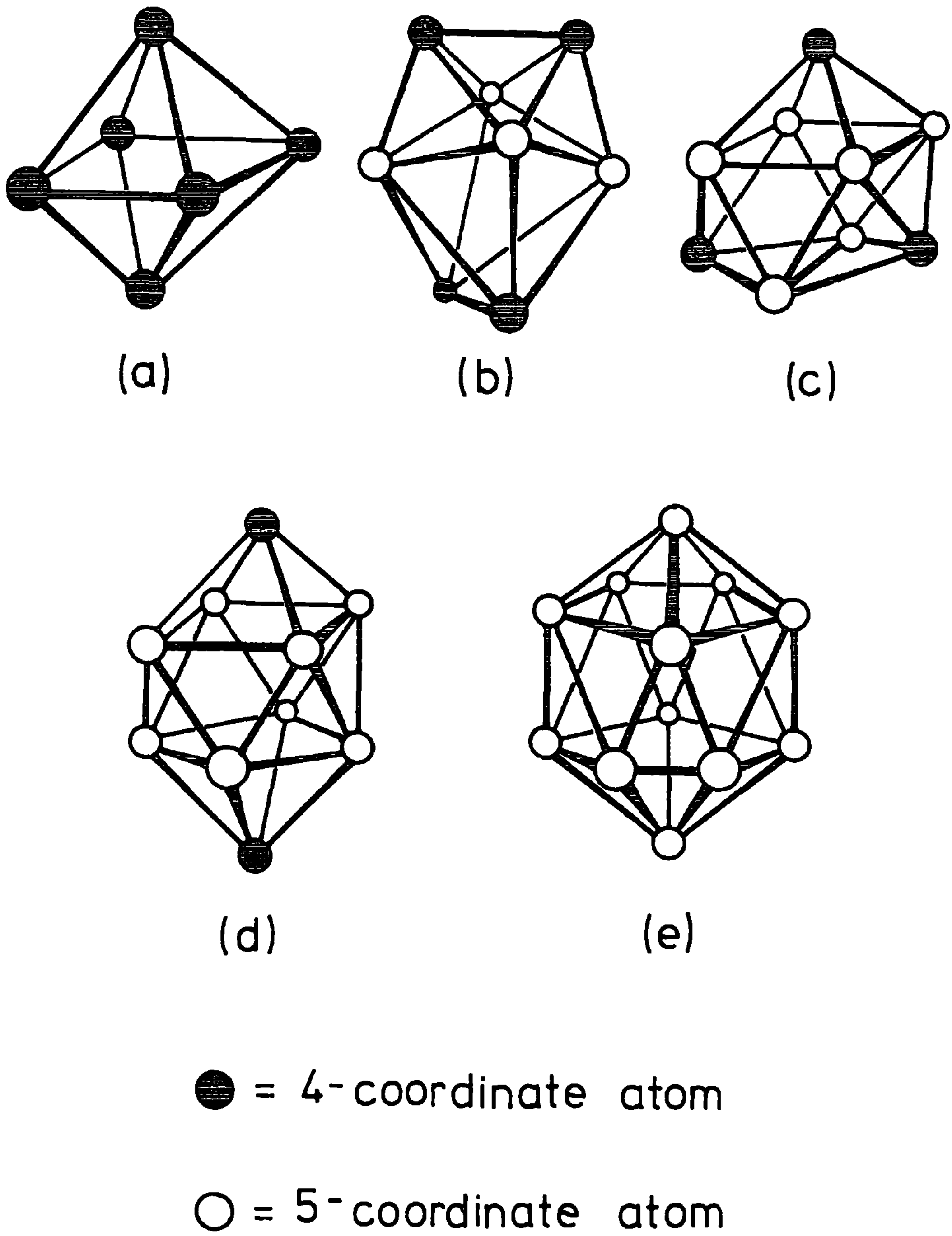


TABLE 3.8 Structural Data and Suggested Bond Enthalpies for Skeletal Bonds in $B_nH_n^{2-}$ Anions

Anion	Figure	Edge Type	d(B-B)* pm	E(B-B)† kJ mol^{-1}	ΣE(B-B)** kJ mol^{-1}
$B_6H_6^{2-}$	3.9a	4-4	169x12	217x12	2600(60)
$B_8H_8^{2-}$	3.9b	4-4	156x2	298x2	3390(40)
		4-5	172x4	203x4	
		4-5	176x8	184x8	
		5-5	193x4	127x4	
$B_9H_9^{2-}$	3.9c	4-5	168x4	222x4	3780(40)
		4-5	171x4	207x4	
		4-5	173x4	197x4	
		5-5	181x1	165x1	
		5-5	185x4	151x4	
		5-5	193x4	127x4	
$B_{10}H_{10}^{2-}$	3.9d	4-5	168x8	222x8	4410(60)
		5-5	180x8	168x8	
		5-5	182x8	161x8	
$B_{12}H_{12}^{2-}$	3.9e	5-5	176x6	184x6	5330(100)
		5-5	178x24	176x24	

*Mean e.s.d. in d(B-B) ≈ 1pm

†Mean e.s.d. in E(B-B) ≈ 3-5 kJ mol^{-1}

**ΣE(B-B) quoted to nearest 10 kJ

Table 3.9 gives the average enthalpy per polyhedron edge bond ($\Sigma E(B\text{-}B)/_{(3n-6)}$), the average enthalpy per skeletal electron pair ($\Sigma E(B\text{-}B)/_{(n+1)}$), the average enthalpy per boron atom ($\Sigma E(B\text{-}B)/_n$), and the average enthalpy per skeletal atom of given coordination number, x, ($E_{B(x=4)}$ and $E_{B(x=5)}$).

Table 3.9 Average Skeletal Bond Enthalpies per Bond, per Electron Pair and per Boron Atom in $B_nH_n^{2-}$ Anions

Anion	$\frac{\Sigma E(B\text{-}B)}{(3n-6)}$ kJ mol^{-1}	$\frac{\Sigma E(B\text{-}B)}{(n+1)}$ kJ mol^{-1}	$\frac{\Sigma E(B\text{-}B)}{n}$ kJ mol^{-1}	$E_{B(x=4)}$ kJ mol^{-1}	$E_{B(x=5)}$ kJ mol^{-1}
$B_6H_6^{2-}$	217	371	433	433	-
$B_8H_8^{2-}$	188	376	423	434	412
$B_9H_9^{2-}$	180	378	420	417	421
$B_{10}H_{10}^{2-}$	184	401	441	443	440
$B_{12}H_{12}^{2-}$	178	410	445	-	445

The following trends emerge from Table 3.9:

(a) The average strength of the edge bonds ($\Sigma E(B\text{-}B)/_{(3n-6)}$) decreases as n increases, i.e. as the number of skeletal electron pairs available per edge bond $(n+1)/_{(3n-6)}$[169] decreases; (the bonds in $B_9H_9^{2-}$ appear weaker than might have been expected).

(b) Values of $\Sigma E(B\text{-}B)/_{(n+1)}$ increase slightly from n=6 ⟶ 9 and quite substantially from n=9 ⟶ 12. This suggests that the higher borane anions make more effective use of their skeletal bonding electrons than do the lower species.

(c) Values of $\Sigma E(B\text{-}B)/_n$ decrease in the sequence $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_6H_6^{2-} > B_8H_8^{2-} > B_9H_9^{2-}$, (Figure 3.10, solid line), indicating the greater thermodynamic stability of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. This result is consistent with the thermal interconversions of $B_nH_n^{2-}$ species[170] and observed high stability of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$,[171] as well as with trends in resonance energies of the three dimensional aromatic cages.[172] (Again $B_9H_9^{2-}$ appears to be less stable than previously suggested).

(d) With the exception of $B_9H_9^{2-}$, values of the average enthalpy per boron atom for (i) x=4 and (ii) x=5 generally increase with n (Figure 3.11). For $B_8H_8^{2-}$ and $B_{10}H_{10}^{2-}$, the enthalpy per 4-coordinate atom is greater than that per 5-coordinate atom. This supports the suggestion that boron atoms of lower coordination number have a greater share of the available skeletal electrons and are therefore negatively charged relative to other skeletal atoms.[169,170]

In several instances, $B_9H_9^{2-}$ appears to be anomolous. In Figure 3.11 smooth curves can be drawn through points for n=6,8 and 10 when x=4 and for n=8, 10 and 12 when x=5. Revised enthalpies per boron atom for n=9 can be predicted from the plots giving $E_{B(x=4)} \approx 438$ kJ mol^{-1} and $E_{B(x=5)} \approx 431$ kJ mol^{-1}. This gives an <u>average</u> energy per skeletal atom of ca. 433 kJ mol^{-1}. The sequence of relative stabilities of the borane anions is therefore revised to $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_6H_6^{2-} \approx B_9H_9^{2-} > B_8H_8^{2-}$, (Figure 3.10, broken line). It is probable that the anomolous value of $\Sigma E(B\text{-}B)_{n=9}$ is a consequence of the tricapped trigonal pris-

Figure 3.10 Average enthalpy per boron atom in $B_nH_n^{2-}$ cages.

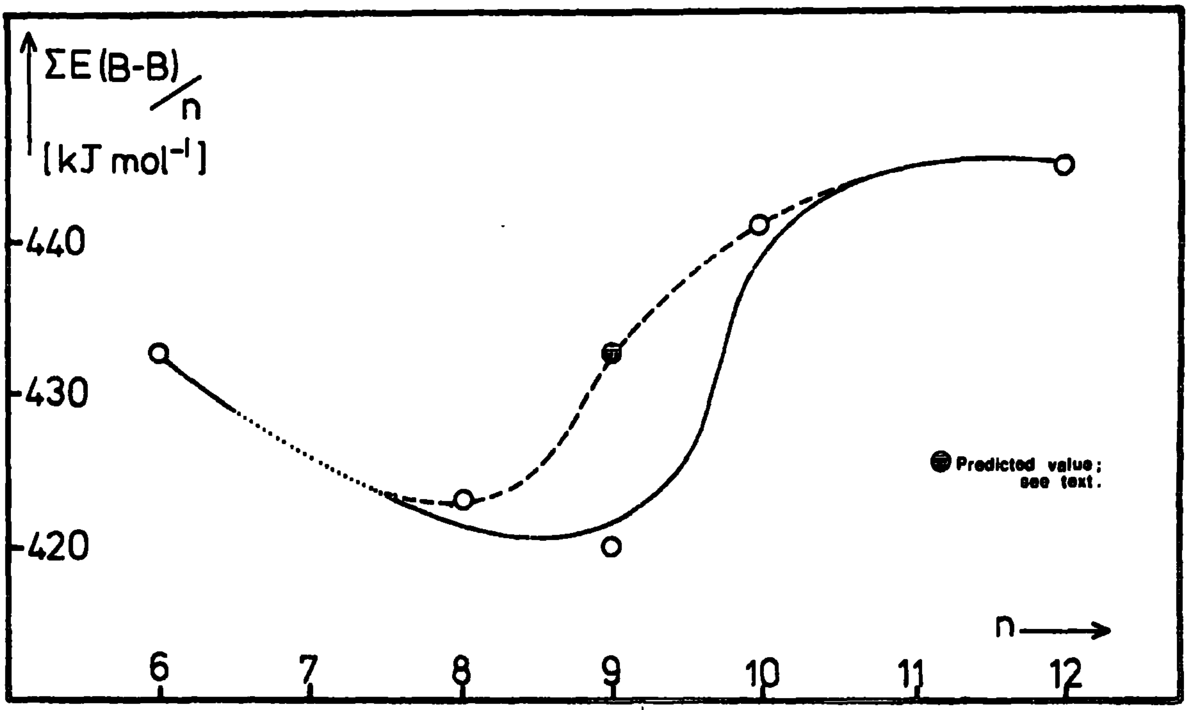
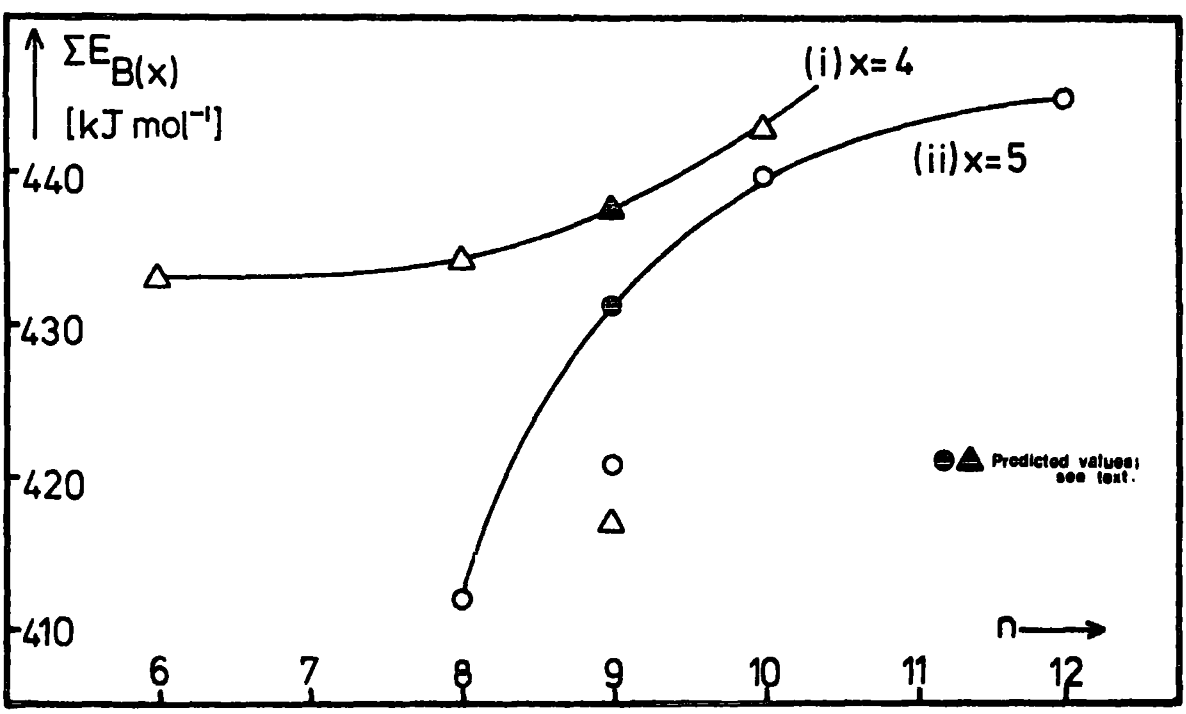


Figure 3.11 Average enthalpy per boron atom of coordination number x in $B_nH_n^{2-}$ cages.



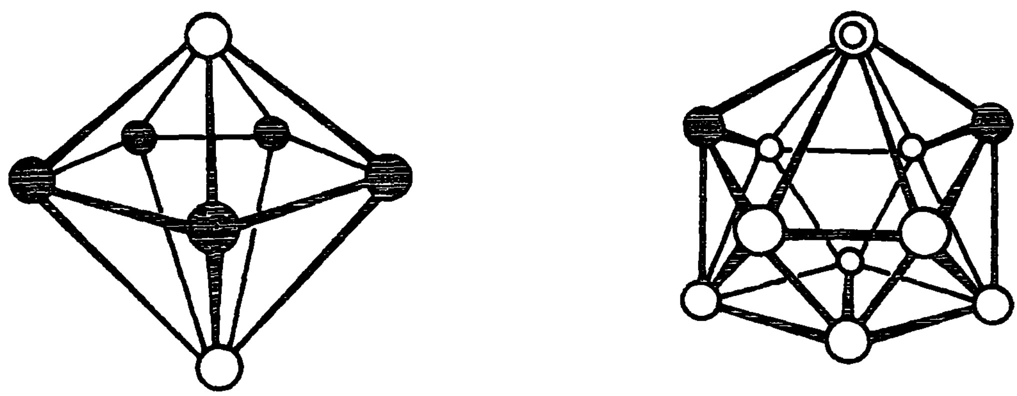
matic cage being distorted by crystal packing forces which cause lengthening (and hence weakening) of B-B bonds to two of the capping atoms. The revised enthalpy term of $E_{B(x=4)} \approx 438$ kJ mol^{-1} implies an enthalpy contribution of 219 kJ mol^{-1} for each bond to a capping atom. A revised length of $d(B_4—B_5) \approx$ 168-169pm is therefore proposed. This is consistent with the length of bond to the unique capping atom (Table 3.8) and suggests that a D_{3h} structure (rather than a distorted cage) is likely in solutions of $B_9H_9^{2-}$. For D_{3h} symmetry, the bonds within the central prism of the $B_9H_9^{2-}$ cage will be equivalent. Each 5-coordinate atom is attached to 2 capping atoms and 3 other central-prism atoms, (Figure 3.9c). From the revised enthalpy terms $E_{B(x=5)} \approx$ 431 kJ mol^{-1} and $E(B_4-B_5) \approx$ 219 kJ mol^{-1}, a revised value of $E(B_5-B_5) \approx$ 142 kJ mol^{-1} is suggested (equation 3.19). This implies a value of $d(B_5-B_5) \approx$ 188pm, which is in fact the average of the B_5-B_5 bond lengths listed in Table 3.8.

$$E_{B(x=5)} = \left\{ \frac{\frac{1}{2}\Sigma E(B_4-B_5) + \Sigma E(B_5-B_5)}{(\text{No. atoms with } x=5)} \right\} \quad (3.19)$$

Two further $B_nH_n^{2-}$ species are known: the heptahydroheptaborate(2-) ($B_7H_7^{2-}$) and the undecahydroundecaborate(2-) ($B_{11}H_{11}^{2-}$) anions. Although not characterised by X-ray crystallography, their structures are generally accepted to be the pentagonal bipyramid and octadecahedron respectively, (Figure 3.12).[173-175]

The $B_7H_7^{2-}$ cage contains two 5-coordinate and five 4-coordinate atoms. From the graphs in Figure 3.11 enthalpy terms of $E_{B(x=4)} \approx 433$ kJ mol^{-1} and $E_{B(x=5)} \ll 410$ kJ mol^{-1} are predicted. $B_7H_7^{2-}$ is the most highly reactive of all

Figure 3.12 Closo-$B_7H_7^{2-}$ and $B_{11}H_{11}^{2-}$ cages.



(a) (b)

● = 4-coordinate atom

○ = 5-coordinate atom

◎ = 6-coordinate atom

the known borane anions[174] and it is anticipated that the plot of $\Sigma E(B\text{-}B)/_n$ against n shown in Figure 3.10 will in fact have a minimum at n=7. This is indicated in Figure 3.13 where a minimum value of $\Sigma E(B\text{-}B)/_n \approx 420$ kJ mol^{-1} is suggested; i.e. the <u>average</u> enthalpy per boron atom in $B_7H_7^{2-}$ is ca. 420 kJ mol^{-1}. Hence $\Sigma E(B\text{-}B)_{n=7} \approx 2940$ kJ mol^{-1} giving a value of $E_{B(x=5)} \approx 388$ kJ mol^{-1}. Using equation 3.19 and an equivalent expression for x=4, average bond enthalpies in $B_7H_7^{2-}$ of $E(B_4\text{-}B_5) \approx 155$ kJ mol^{-1} and $E(B_4\text{-}B_4) \approx 278$ kJ mol^{-1} are suggested. These energies imply bond lengths of $d(B_4\text{-}B_5) \approx 184$ pm and $d(B_4\text{-}B_4) \approx 159$ pm, (from equation 3.12). These bond lengths are consistent with trends noted in the other anions, but all predicted enthalpies and bond lengths for $B_7H_7^{2-}$ must be regarded as <u>approximate</u> values.

The $B_{11}H_{11}^{2-}$ anion contains one 6-coordinate boron atom, (indicated as ◎ in Figure 3.12), and the cage is therefore unique among members of the series $B_nH_n^{2-} (6 < n < 12)$. It therefore seems inappropriate to attempt predictions of bond energy terms and bond lengths for this system.

Table 3.10 lists structural data for the anions $B_nH_n^{2-}$ (n=6, 7, 8, 9, 10 and 12) including predicted bond lengths for $B_7H_7^{2-}$ and revised data for $B_9H_9^{2-}$ which refer to a D_{3h} skeleton. Meaningful energy terms may be derived from these bond lengths using equation 3.12 and give an overall order of relative thermodynamic stabilities of

$$B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_6H_6^{2-} \approx B_9H_9^{2-} > B_8H_8^{2-} \gg B_7H_7^{2-}.$$

Figure 3.13 Average enthalpy per boron atom in $B_nH_n^{2-}$ cages ; (revised plot to include n=7).

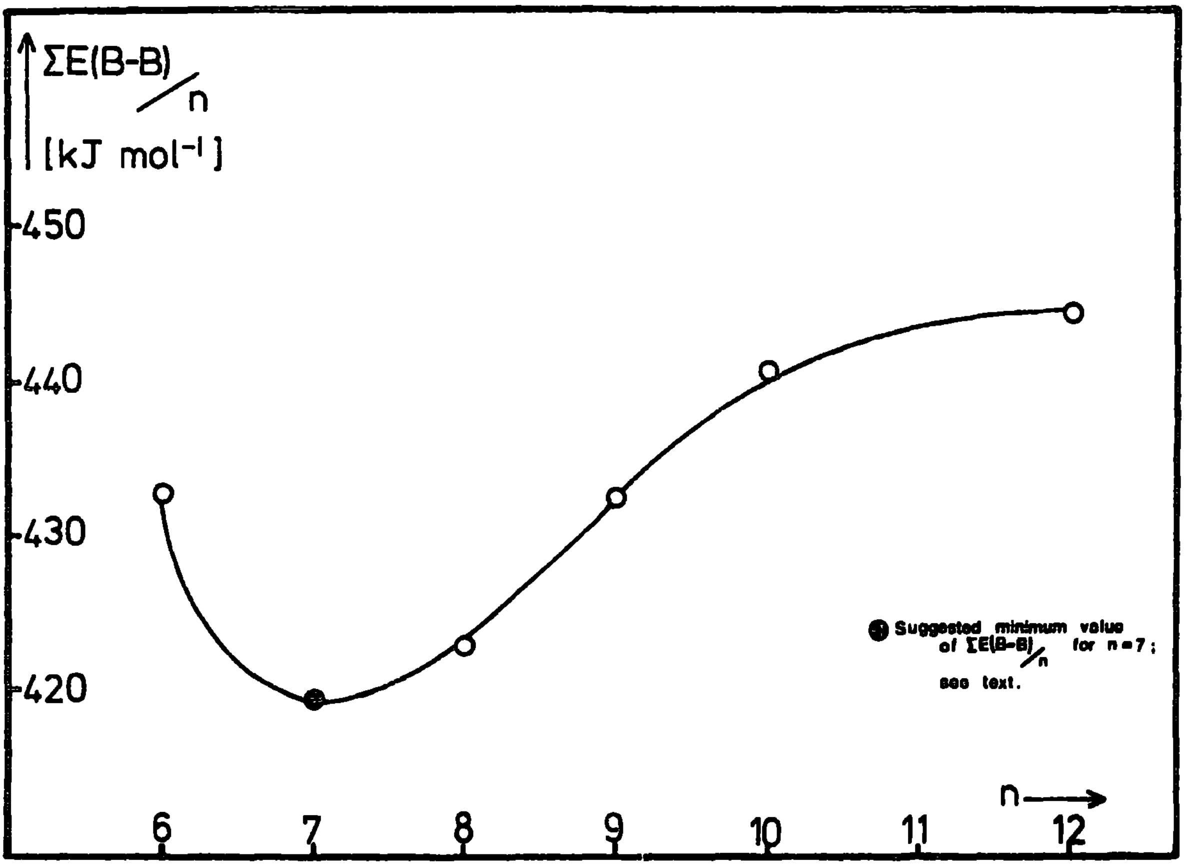


TABLE 3.10 Structural Data for $B_nH_n^{2-}$ Including Some Predicted Bond Lengths

Anion	Bond Type	Average d(B-B) pm	Number of Bonds
$B_6H_6^{2-}$	4-4	169	12
$B_7H_7^{2-}$	4-4	159*	5
	4-5	184*	10
$B_8H_8^{2-}$	4-4	156	2
	4-5	175	12
	5-5	193	4
$B_9H_9^{2-}$	4-5	169*	12
	5-5	188	9
$B_{10}H_{10}^{2-}$	4-5	168	8
	5-5	181	16
$B_{12}H_{12}^{2-}$	5-5	177.5	30

* Predicted or revised values;(see text).

3.5 Bond Orders and Electron Distribution in Borane Anions, $B_nH_n^{2-}$.

In this Chapter bond order is denoted by $\bar{n}$ instead of the usual n to avoid confusion with the use of n as the number of skeletal atoms.

Average bond orders in $B_nH_n^{2-}$ anions have previously been estimated from the even distribution of (n+1) skeletal electron pairs over (3n-6) polyhedral edge bonds,[169] although a second method has allowed for a change in bond order with coordination number. Assuming an equal electron distribution among the skeletal atoms, the edge bond order for a B-B link between atoms of coordination number x_1 and x_2 has been given by $(n+1)(x_1+x_2)/_{nx_1x_2}$. This method, however, underestimates the extent to which the various types of bond differ.[169]

The octahedral $B_6H_6^{2-}$ cage has 12 equivalent B-B bonds of length 169pm and estimated energy 217 kJ mol^{-1} (Table 3.8). It may be assumed that each edge bond will have a bond order, $\bar{n}$, of $(n+1)/_{12}$ = 0.583. Table 3.11 lists <u>average</u> bond energies calculated from <u>average</u> bond lengths (from Table 3.10) using equation 3.12. Using a fixed value of $\bar{n}$ = 0.583 for a bond of energy 217 kJ mol^{-1}, corresponding 'relative energies' are calculated for all other edge bonds, (column 5 in Table 3.11). Column 6 of the Table gives the sum of these relative energies, Σ(Rel.E.), for each anion. These values are compared with the number of skeletal bond pairs, (column 7), and are found to reproduce values of (n+1) for n=6, 7 and 8 thus suggesting a linear relationship between bond order and bond energy. However, Σ(Rel.E.) is greater than (n+1) for

TABLE 3.11 Relative Energies for Skeletal Bonds in $B_nH_n^{2-}$ Cages

Anion	Bond Type	Number of Bonds	Average E(B-B) kJ mol^{-1}	Relative Energies*	Σ(Rel.E.)	(n+1)
$B_6H_6^{2-}$	4-4	12	217	0.583†	6.996	7
$B_7H_7^{2-}$	4-4	5	278	0.747	7.895	8
	4-5	10	155	0.416		
$B_8H_8^{2-}$	4-4	2	298	0.801	9.026	9
	4-5	12	188	0.505		
	5-5	4	127	0.341		
$B_9H_9^{2-}$	4-5	12	219	0.588	10.494	10
	5-5	9	142	0.382		
$B_{10}H_{10}^{2-}$	4-5	8	222	0.596	11.856	11
	5-5	16	165	0.443		
$B_{12}H_{12}^{2-}$	5-5	30	178	0.478	14.340	13

* Relative Energy given by the ratio $\left[\frac{\text{Relative Energy}}{\text{E(B-B)}}\right] = \frac{0.583}{217}$

† Fixed value given by $(n+1)/_{12}$ (i.e. average bond order)

for n=9, 10 and 12. There are two possible explanations:

(a) The higher boranes make more effective use of their skeletal bonding electrons and hence values of Σ(Rel.E.) are anomolously high for $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.

(b) A linear bond energy-bond order relationship is NOT appropriate for the B-B polyhedral edge bonds.

From Figures 3.10 and 3.13 it is suggested that $B_9H_9^{2-}$ and $B_6H_6^{2-}$ have similar stabilities whereas the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ anions are considerably more stable. It is anticipated, therefore, that the $B_6H_6^{2-}$ and $B_9H_9^{2-}$ cages will utilise their bonding electrons to the same extent. Hence, whilst anomolous values of Σ(Rel.E.) for n=10 and 12 can be explained by (a), the high value of Σ(Rel.E.) for n=9 cannot be dismissed so easily. It is therefore concluded that (b) is a more probable explanation for the trend in Σ(Rel.E.) than is (a).

It is suggested that an empirical correlation of the type:

$$E(B\text{-}B) \propto [\bar{n}(B\text{-}B)]^m$$

might be applied to the polyhedral edge bonds in $B_nH_n^{2-}$ systems in place of the linear relationship which appears to be unsatisfactory. One fixed point, based on the octahedral $B_6H_6^{2-}$ cage, is already known: a bond of order 0.583 has an estimated energy of 217 kJ mol^{-1}. The icosahedral $B_{12}H_{12}^{2-}$ skeleton contains 24 bonds of length 178pm and 6 bonds of length 176pm. However, all bonds link 5-coordinate boron atoms and so are approximately equivalent, (average d(B-B) = 177.5pm). Each bond in $B_{12}H_{12}^{2-}$ therefore has an estimated average enthalpy contribution of 178 kJ mol^{-1}

and a bond order of $(n+1)/_{30} = 0.433$. Equation 3.20 is therefore suggested as relating B-B bond energy and bond order ($\bar{n}$).

$$E(B\text{-}B) = 309.2\,[\,\bar{n}(B\text{-}B)]^{0.66} \qquad (3.20)$$

Table 3.12 lists bond orders ($\bar{n}$) calculated using equation 3.20, $\Sigma\,\bar{n}(B\text{-}B)$, and the number of skeletal bonding pairs of electrons, (n+1). Overall, values of $\Sigma\,\bar{n}(B\text{-}B)$ correspond well to values of (n+1) although in $B_7H_7^{2-}$ and $B_8H_8^{2-}$ the bond orders seem to be slightly <u>under</u>estimated. The extent to which bond orders vary with bond type may well therefore be <u>over</u>estimated, (cf. bond orders obtained by MO treatments.[176,177]).

Bond orders from Table 3.12 can be used to estimate differences in electron distribution at 4- and 5-coordinate boron atoms. For a 4-coordinate atom (B_4) attached to 'a' 5-coordinate atoms (B_5) and to 'b' B_4-atoms, the electron distribution at B_4 (ρ_{B_4}) is given by equation 3.21. Equation 3.22 gives the electron distribution at a 5-coordinate atom (ρ_{B_5}); this atom is attached to 'c' B_4- and 'd' B_5-atoms.

$$\rho_{B_4} = \frac{1}{2}\{\, a\ \bar{n}(B_4\text{-}B_5) + b\ \bar{n}(B_4\text{-}B_4)\,\} \qquad (3.21)$$

$$\rho_{B_5} = \frac{1}{2}\{\, c\ \bar{n}(B_4\text{-}B_5) + d\ \bar{n}(B_5\text{-}B_5)\,\} \qquad (3.22)$$

The results are summarised in Table 3.13. In all systems containing both 4- and 5-coordinate boron atoms, the atom of lower coordinationnumber appears to be negatively charged relative to the remaining skeletal atoms. This supports previous results.[169,176,177] With the exception of $B_7H_7^{2-}$, both ρ_{B_4} and ρ_{B_5} increase with increasing nuclearity of cluster.

TABLE 3.12 Estimated Bond Orders in $B_nH_n^{2-}$ Anions

Anion	Bond Type	Number of Bonds	E(B-B) kJ mol^{-1}	$\bar{n}$(B-B)	Σ $\bar{n}$(B-B)	(n+1)
$B_6H_6^{2-}$	4-4	12	217	0.583*	6.996	7
$B_7H_7^{2-}$	4-4	5	278	0.851	7.765	8
	4-5	10	155	0.351		
$B_8H_8^{2-}$	4-4	2	298	0.946	8.584	9
	4-5	12	188	0.471		
	5-5	4	127	0.260		
$B_9H_9^{2-}$	4-5	12	219	0.593	9.888	10
	5-5	9	142	0.308		
$B_{10}H_{10}^{2-}$	4-5	8	222	0.605	11.016	11
	5-5	16	165	0.386		
$B_{12}H_{12}^{2-}$	5-5	30	178	0.433*	12.990	13

* Values of $\bar{n}$ calculated from $(n+1)/(3n-6)$

TABLE 3.13 Electron Distribution Around Skeletal Atoms in $B_nH_n^{2-}$ Cages

Anion	Bond Type	Estimated $\bar{n}$(B-B) (Table 3.12)	Estimated ρ_{B_4}	Estimated ρ_{B_5}
$B_6H_6^{2-}$	4-4	0.583	1.166	-
$B_7H_7^{2-}$	4-4	0.851	1.202	0.878
	4-5	0.351		
$B_8H_8^{2-}$	4-4	0.946	1.180	0.967
	4-5	0.471		
	5-5	0.260		
$B_9H_9^{2-}$	4-5	0.593	1.186	1.055
	5-5	0.308		
$B_{10}H_{10}^{2-}$	4-5	0.605	1.210	1.074
	5-5	0.386		
$B_{12}H_{12}^{2-}$	5-5	0.433	-	1.087

This suggests that ρ_{B_4} in $B_7H_7^{2-}$ has been overestimated and that the equatorial bonds in the pentagonal bipyramidal skeleton should be slightly longer (and hence the axial bonds slightly shorter) than originally predicted.

3.6 Conclusion

The empirical bond energy-bond length relationships:

$$E(B\text{-}B) = 1.766 \times 10^{11} [d(B\text{-}B)]^{-4.0}$$

and

$$E(B\text{-}H) = 4.476 \times 10^{11} [d(B\text{-}H)]^{-4.4}$$

can be applied to boron-boron and boron-hydrogen links in nido- and arachno-boranes, (B_nH_{n+4} and B_nH_{n+6}), and enthalpies of disruption may be estimated with a fairly high degree of accuracy for $4 \leqslant n \leqslant 10$. Using known structural data, disruption enthalpies for some higher boranes can be predicted. These values are in good agreement with approximate enthalpies predicted assuming $\Delta H_{disrupt.} \propto n$ for given x in B_nH_{n+x} species.

The close family relationship between closo-, nido-, arachno- and hypho-clusters makes it realistic to extend the applicability of the bond energy/length correlations to the borane anions $B_nH_n^{2-}$ ($6 \leqslant n \leqslant 12$). The trends in bond enthalpy terms which emerge support previous results with the exception of values for $B_9H_9^{2-}$. This anomoly is explained by the effects of crystal packing forces which distort the cage causing lengthening of several B-B links. Revised bond lengths and strengths are therefore proposed, and the final suggested sequence of thermodynamic stabilities is $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_6H_6^{2-} \approx B_9H_9^{2-} > B_8H_8^{2-}$. Predictions regarding B-B bond enthalpy contributions and bond lengths in $B_7H_7^{2-}$ are also made.

Assuming a bond energy-bond order correlation:

$$E(B\text{-}B) = 309.2[\,\bar{n}(B\text{-}B)]^{0.66}$$

estimates of polyhedral edge bond orders in $B_nH_n^{2-}$ cages are made and are used to calculate the possible electron distribution among the skeletal boron atoms. It is concluded that atoms of low coordination number have the greatest share of electronic charge and are therefore negatively charged with respect to atoms of higher coordination number. It may therefore be predicted that the capping atoms (i.e. 4-coordinate) will be the most susceptible to electrophilic attack.

CHAPTER FOUR

BOND ENTHALPY CONTRIBUTIONS IN TRANSITION METAL CARBONYL CLUSTER COMPOUNDS

4.1 Introduction

The gas phase disruption of a mononuclear metal carbonyl, $M(CO)_y$, involves the separation of y CO groups from the central metal atom, the heat of disruption for this process being given by equation 4.1.

$$M(CO)_y(g) \longrightarrow M(g) + yCO(g)$$

$$\Delta H_{disrupt.} = \Delta H^o_{f298}M(g) + y\Delta H^o_{f298}CO(g) - \Delta H^o_{f298}M(CO)_y(g) \quad (4.1)$$

$$D(M\text{-}CO) = \frac{1}{y}\Delta H_{disrupt.} \quad (4.2)$$

The metal-ligand mean bond dissociation energy, D(M-CO), (i.e. the mean energy required to remove a carbonyl ligand unchanged from the metal carbonyl), is given by equation 4.2. Many mononuclear metal carbonyls have been the subject of precise calorimetric measurements, and therefore values of D(M-CO) are readily determined.[178,179] For polynuclear metal carbonyls, microcalorimetric methods are generally used to measure standard enthalpies of formation.[5,6,178,180] $\Delta H_{disrupt.}$ comprises metal-metal, terminal carbonyl-metal and, perhaps, bridging carbonyl-metal bond enthalpy contributions. The question of allocation of differing amounts of energy to particular bonds therefore arises and has been the subject of several studies.[5,6,178,179,181,182]

In any estimation of individual bond energies in metal carbonyl clusters, one or more simplifying assumptions must be made to reduce the number of unknown variables. The most common is one of transferability of bond enthalpy terms from mononuclear metal carbonyls to their polynuclear counterparts in which the formal oxidation state of the metal remains unchanged.[178] For example, in the series of iron and cobalt carbonyls, equations 4.3 can be written combining E(M-M), $D(M\text{-}CO)_{term.}$ and $D(M\text{-}CO)_{br.}$. Solutions for each bond enthalpy term can be found assuming transferability of

$$\left.\begin{aligned} \Delta H_{disrupt.} Fe(CO)_5 &= 5D(Fe\text{-}CO)_{term.} \\ \Delta H_{disrupt.} Fe_2(CO)_9 &= E(Fe\text{-}Fe) + 6D(Fe\text{-}CO)_{term.} + 6D(Fe\text{-}CO)_{br.} \\ \Delta H_{disrupt.} Fe_3(CO)_{12} &= 3E(Fe\text{-}Fe) + 4D(Fe\text{-}CO)_{term.} + 10D(Fe\text{-}CO)_{br.} \\ &\text{(Similarly for } {}^{\cdot}Co(CO)_4,\ Co_2(CO)_8,\ Co_4(CO)_{12}). \end{aligned}\right\} \quad (4.3)$$

$D(M\text{-}CO)_{term.}$ and $D(M\text{-}CO)_{br.}$ between members of each series of compounds. From the results, the following simple relationships emerge:

$$E(M\text{-}M) \approx 0.68\ D(M\text{-}CO)_{term.} \qquad (4.4)$$

$$D(M\text{-}CO)_{br.} \approx 0.50\ D(M\text{-}CO)_{term.} \qquad (4.5)$$

Equations 4.4 and 4.5 are also assumed to be true for polynuclear carbonyls for which no mononuclear species exist, and individual bond enthalpy contributions are estimated, (Table 4.1).[178]

A second approach has been to use values of E(M-M) taken from the bulk metals themselves.[178] For a metal with known heat of sublimation, ΔH^{o}_{f298} M(g), and with coordination number, n, in the bulk state, the metal-metal bond enthalpy is:

$$E(M\text{-}M) = \frac{2}{n}\,\Delta H^{o}_{f298}\ M(g) \qquad (4.6)$$

Combining equations 4.4 and 4.6 gives:

TABLE 4.1 Standard Enthalpies of Formation and Bond Enthalpy Contributions for Metal Carbonyl Compounds.[178]

Compound	$\Delta H^{o}_{f298}(g)$ kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	E(M-M) kJ mol^{-1}	$D(M\text{-}CO)_{term.}$ kJ mol^{-1}	$D(M\text{-}CO)_{br}$ kJ mol^{-1}
$Cr(CO)_6$	- 908(2)	646		108	
$Mo(CO)_6$	- 916(2)	910		152	
$W(CO)_6$	- 885(3)	1069		178	
$\cdot Mn(CO)_5$	- 768(6)	496		99	
$Mn_2(CO)_{10}$	-1598(5)	1068	67	100	
$\cdot Re(CO)_5$	686(6)	908		182	
$Re_2(CO)_{10}$	-1559(21)	2029	128	187	
$Fe(CO)_5$	- 724(6)	585		117	
$Fe_2(CO)_9$	-1335(25)	1173	82	117	64
$Fe_3(CO)_{12}$	-1735(29)	1676	82	117	64
$Ru_3(CO)_{12}$	-1820(29)	2414	117	172	
$Os_3(CO)_{12}$	-1644(29)	2666	130	190	
$\cdot Co(CO)_4$	- 561(12)	544		136	
$Co_2(CO)_8$	-1172(10)	1160	83	136	68
$Co_4(CO)_{12}$	-1749(29)	2130	83	136	68
$Rh_4(CO)_{12}$	-1749(29)	2649	114	166	83
$Rh_6(CO)_{16}$	-2299(29)	3496	114	166	83
$Ir_4(CO)_{12}$	-1715(26)	3051	130	190	
$Ni(CO)_4$	- 600(4)	588		147	

$$D(M\text{-}CO)_{term.} \approx 0.9\ E(M\text{-}M) \quad \text{for } n = 8 \tag{4.7}$$

$$D(M\text{-}CO)_{br.} \approx 0.6\ E(M\text{-}M) \quad \text{for } n = 12 \tag{4.8}$$

Application of equations 4.7 and 4.8 to polynuclear carbonyls allows bond enthalpy contributions to be determined for systems for which a corresponding mononuclear species does not exist, (i.e. for M = Ru, Os, Rh, Ir). Values obtained in this way compare favourably with those in Table 4.1 for most polynuclear systems. The empirical relationships suggested by equations 4.7 and 4.8 are approximate, and can only provide an indication of the individual bond energies in metal carbonyl compounds.[178]

Metal-ligand bond dissociation energies in metal carbonyls have been estimated assuming that the standard enthalpy of formation per carbonyl ligand is constant, not only for a series of compounds $M_x(CO)_y$ where M = specified metal, but for different metals as well.[183] A value of -157kJ per CO is suggested whereas previously described methods[178] suggest a range of values from -135 to -160 kJ per CO. No estimate of E(M-M) is made as the disruption process considered is:

$$M_x(CO)_y\ (g) \longrightarrow M_x\ (g) + y\ CO(g)$$

The enthalpy of disruption is therefore given by equation 4.9, and rearrangement to equation 4.10 shows the suggested linear dependence of D(M-CO) on $\frac{1}{y}\ \Delta H^{o}_{f298}\ M_x(g)$. The linear relationship is established

$$\Delta H_{disrupt.} = \Delta H^{o}_{f298}M_x(g) + y\,\Delta H^{o}_{f298}CO(g) - \Delta H^{o}_{f298}M_x(CO)_y(g) \tag{4.9}$$

$$D(M\text{-}CO) = \frac{1}{y}\Delta H^{o}_{f298}M_x(g) + \Delta H^{o}_{f298}CO(g) - \frac{1}{y}\Delta H^{o}_{f298}M_x(CO)_y(g) \tag{4.10}$$

using experimentally determined values of D(M-CO)[184,185] for clusters of low nuclearity, and is used to estimate metal-ligand bond enthalpies for a wide range of carbonyl clusters of transition, lanthanide and actinide metals.

A fundamental problem underlies the treatments of thermochemical data which have been described so far; at some point in each calculation it has been assumed that a particular enthalpy contribution remains constant and may be transferred from one compound to another. No allowance is made for differences in bond energy which can be substantiated by variation in bond length. (It is assumed that metal-metal and metal-carbon bonds conform to the general concept that their bond energy will increase with decreasing bond length). In many of the carbonyl clusters considered, changes in bond length in going from one compound to another are small and may even lie within experimental error; (eg. d(M-M) in cobalt metal is 251(1)pm[186,187] ,in $Co_2(CO)_8$ is 252(1)pm[188], and in $Co_4(CO)_{12}$ is 249(1)pm[189,190]). Transferability of E(M-M) may be justified in such cases. However, iron and its carbonyls provide an example of a series of compounds in which transferability is not appropriate, (d(M-M) in iron metal is 248(1)pm,[186,187] in $Fe_2(CO)_9$ is 252(1)pm[191], and in $Fe_3(CO)_{12}$ are 256(1) and 268(1)pm[192]).

One attempt[193] has been made to rationalise the bond enthalpy contributions in $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ allowing for a change in the Rh-Rh bond length between the two clusters. Initially an expression equating the enthalpy of disruption with individual bond energies was established, (equations 4.11), and solved to give E(Rh-Rh) = 93 kJ mol^{-1}. Each equation was adapted to accommodate a slight weakening of the Rh-Rh bond with increasing length, (equations 4.12). The assumption

TABLE 4.2 Bond Enthalpy Contributions in $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.[193]

	d(M-M)	E(M-M) kJ mol^{-1}			D(M-CO) kJ mol^{-1}		
	pm	Ref.[6]	Equ.(4.12)	Equ.(4.13)	Ref.[6]	Equ.(4.12)	Equ.(4.13)
Rh metal	269[186]	93(1)[7]	93(1)[7]	93(1)[7]	184(8)[195]	184(8)[195]	184(8)*[195]
$Rh_4(CO)_{12}$	273[190]	114(8)	86(11)	91(11)	166(8)	178(8)	175(8)
$Rh_6(CO)_{16}$	278[194]	105(8)**	86(11)	89(11)	166(8)	178(8)	175(8)

* For CO adsorbed on film of Rh metal.

** The value 105, ($^{11}/12$ of 114), is based on the bond enthalpy contribution per octahedron edge implicit in the method of refs. 6 and 178.

$$\left.\begin{aligned} \Delta H_{disrupt.}Rh_4(CO)_{12} &= 2648(29)\text{kJ mol}^{-1} \\ &= 6E(Rh\text{-}Rh) + 12D(Rh\text{-}CO) \\ \Delta H_{disrupt.}Rh_6(CO)_{16} &= 3874(29)\text{kJ mol}^{-1} \\ &= 12E(Rh\text{-}Rh) + 16D(Rh\text{-}CO) \end{aligned}\right\} \quad (4.11)$$

$$\left.\begin{aligned} Rh_4(CO)_{12} &: 2648(29)\text{kJ mol}^{-1} = 6(93-x) + 12D(Rh\text{-}CO) \\ Rh_6(CO)_{16} &: 3874(29)\text{kJ mol}^{-1} = 12(93-x) + 16D(Rh\text{-}CO) \end{aligned}\right\} \quad (4.12)$$

is made that $D(Rh\text{-}CO)_{br.} = 0.5\ D(Rh\text{-}CO)_{term.}$. The results are summarised in Table 4.2. An important feature of this treatment which contrasts with earlier methods is the bonding description of the octahedral metal cluster in $Rh_6(CO)_{16}$. Connor[6, 178] adheres to a classical 2-centre electron-pair bonding approach, considering there to be 11 metal-metal bonds resonating between 12 octahedral edges. Equations 4.12 and 4.13 assign an equal metal-metal bond energy term to each octahedral edge in $Rh_6(CO)_{16}$. An analogy is also drawn between the value of D(Rh - CO) in rhodium carbonyls and for CO adsorbed on a film of Rh metal.

It is clear that the methods of treating thermochemical data and assigning individual bond energies for metal carbonyl systems are far from satisfactory. This chapter is therefore devoted to the development of a new method of allocating possible bond enthalpy contributions in metal carbonyls.

4.2 Development of Method

It is now widely accepted[196-202] that analogies can be drawn between metal clusters and fragments of the bulk metal although a recent photoelectron spectroscopic study[203] has added a cautionary note to this concept. However, it appears justifiable to develop a method for treating thermochemical data based on the determination of the metal-metal bond strength in the bulk metal. By assuming a bond length-bond energy relationship of the type described previously (equation 4.13), a realistic metal-metal bond enthalpy term for the

$$E(X\text{-}Y) = A[d(X\text{-}Y)]^{-k} \qquad (4.13)$$

(A = constant)

metal carbonyl cluster may be suggested. A suitable equation is deduced in the following manner.

Metals generally adopt either face-centred cubic (f.c.c.), hexagonal closed packed (h.c.p.), or body-centred cubic (b.c.c.) structures. (A few metals, e.g. manganese, crystallise in a more complex form[187]). In a b.c.c. structure, each atom is surrounded by 8 nearest neighbours at a distance d, and by 6, slightly less strongly bound, neighbours at a distance 1.1547d. The third and fourth coordination spheres consist of 12 and 24 atoms at distances 1.6328d and 1.9149d from the central atom respectively. In a f.c.c. structure, each atom has 12 nearest neighbours at a distance d^1. The second and third coordination shells contain 6 and 16 atoms at distances $1.4142d^1$ and $1.7321d^1$ from the central atom respectively. For chromium, iron, titanium and hafnium, the metal structure changes with increasing temperature. If all metal-metal distances are corrected to room temperature, the ratio d^1/d is approximately

TABLE 4.3 Structures and Bond Lengths for Some Transition Metals

Metal	Temperature (^{o}C)	Structure	Nearest Neighbour distance (pm)[187,204]	Distance corrected* to room temp. (pm)	Ratio d^1/d
Chromium	20	b.c.c.	249.8	249.8	1.0172
	>1840	f.c.c.	261	254.1	
Iron	20	b.c.c.	248.23	248.23	1.0171
	916	f.c.c.	257.8	252.8	
Titanium	Room temp.	h.c.p.	289.56	289.56	1.0177
	882	b.c.c.	286.35	284.5	
Hafnium	Room temp.	h.c.p.	308.55	308.55	1.0179
	Room temp.	b.c.c.	303.1	303.1	

* Corrections made using coefficients of thermal linear expansion.[205-207]

constant (Table 4.3). (For alkali metals generally, $d^1/_d$ = 1.0180[208]). If the enthalpies of disruption for the b.c.c. and f.c.c. structures are written in terms of bond energy contributions depending on length, and the resulting expressions for $\Delta H_{disrupt.}$ are equated, a value of k, (from equation 4.13), for metal-metal bonds can be found, (equation 4.14). The heat of transition from b.c.c. to f.c.c. form is

$$\left.\begin{aligned} \Delta H_{disrupt.} &= 4Bd^{-k} + 3B(1.1547d)^{-k} + \ldots\ldots \\ &= 6B(d^1)^{-k} + \ldots\ldots \\ &(B = \text{constant}) \end{aligned}\right\} \quad (4.14)$$

small enough as to make negligible difference to the deduced value of k, (see p.119).

Equation 4.14 only takes into consideration the first coordination sphere for f.c.c. and the first and second spheres for b.c.c. structures. Additional terms in the series would involve interatomic interactions which are relatively weak and which can be justifiably ignored. This point is dealt with fully on p. 121.

Substitution of d^1 = 1.0172d into equation 4.14 gives k = 4.6; ratios of 1.0170 or 1.0175 would have resulted in values of k = 4.55 or 4.65 respectively. Hence for metal-metal bonds, the following equations are suggested:

$$E(M\text{-}M) = A[d(M\text{-}M)]^{-4.6} \quad (4.15)$$

or

$$\log E(M\text{-}M) = C - 4.6\log d(M\text{-}M) \quad (4.16)$$

(C and A are constants)

For a f.c.c. crystal of the bulk metal, $E(M\text{-}M) = \frac{1}{6}\Delta H_{disrupt.}$. For a b.c.c. structure, E(M-M) has conventionally been allocated as $^1/_4\ \Delta H_{disrupt.}$. However, if the 6 atoms in the second coordination shell are to be considered as having significant interaction with the central atom, expressions for $E(M\text{-}M)_{b.c.c.}$ can be deduced as follows:

E_1 = E(M-M) for 8 neighbours at distance d from central atom

E_2 = E(M-M) for 6 neighbours at distance 1.1547d from central atom

From equation (4.15):

$$\frac{E_1}{E_2} = \left[\frac{1.1547d}{d}\right]^{4.6} = 1.9380$$

Also:

$$\Delta H_{disrupt.} = 4E_1 + 3E_2$$

Hence:

$$E_1 = \frac{\Delta H_{disrupt.}}{5.55}$$

$$E_2 = \frac{\Delta H_{disrupt.}}{10.76}$$

Hence, for a series of transition metals which crystallise as either b.c.c. or close packed lattices, bond enthalpy contributions can be assigned and appropriate values of the constant A in equation 4.15 can be determined for specific metals, (Table 4.4).

Determination of k(M-M) = 4.6 from equation 4.14 depends on the equivalence of the enthalpies of disruption of b.c.c. and f.c.c. crystals. In reality, account should be taken of the heat of transition, $\Delta H_{trans.}$. For iron, $\Delta H_{trans.}$ (b.c.c. ⟶ f.c.c.) = 0.94 kJ mol^{-1} [8], which is negligible when compared with $\Delta H_{disrupt.}$ = 417.1 kJ mol^{-1} for the close packed lattice. The effect of including $\Delta H_{trans.}$ is shown below:

TABLE 4.4 Bond Energies in Bulk Metals; Application of $E(M\text{-}M) = A\ d(M\text{-}M)^{-4.6}$

Metal	Structure at room temp.	* $\Delta H_{disrupt.}$ [7,8,178] kJ mol^{-1}	†* E(M-M) kJ mol^{-1}	* d(M-M) pm	Calc. A x10^{13}
Fe	b.c.c.	417.1	75.2	248.2	0.780
Ru	c.p.	651.0	108.5	265.0	1.522
Os	c.p.	790.0	131.7	267.5	1.928
Co	c.p.	428.4	71.4	250.6	0.755
Rh	c.p.	557.3	92.9	269.0	1.396
Ir	c.p.	665.2	110.9	271.4	1.735
Re	c.p.	775.7	129.3	274.1	2.118
Cr	b.c.c.	397.5	71.6	249.8	0.766
Mo	b.c.c.	656.9	118.4	272.5	1.888
W	b.c.c.	853.5	153.8	274.1	2.519

† $E(M\text{-}M)_{c.p.} = \Delta H_{disrupt.}/6$; $E(M\text{-}M)_{b.c.c.} = \Delta H_{disrupt.}/5.55$

* Mean e.s.d. in $\Delta H_{disrupt.} \approx 5\text{-}10$ kJ mol^{-1} and in d(M-M) $\leqslant 1$ pm; mean e.s.d. in E(M-M) $\leqslant 1$ kJ mol^{-1}

$$\text{f.c.c. :}\quad \Delta H_{disrupt.} + \Delta H_{trans.} = 6B\ (1.0172d)^{-k}$$

$$\text{b.c.c. :}\quad \Delta H_{disrupt.} = 4Bd^{-k} + 3B(1.1547d)^{-k}$$

Substituting for $\Delta H_{disrupt.}$ and $\Delta H_{trans.}$ for iron gives $k = 4.7$. $\Delta H_{trans.}$ can therefore be ignored; this result is typical of metals in general.

Equation 4.14 is fundamental to the determination of k(M-M) and it is therefore important to justify the number of terms used in the expression. Equating enthalpies of disruption for the b.c.c. and f.c.c. crystals results in equation 4.17 of which equation 4.14 is an approximation.

$$\Delta H_{disrupt.}\ \text{b.c.c.} = \Delta H_{disrupt.}\ \text{f.c.c.}$$

$$\therefore\quad 4B(d)^{-k} + 3B(1.1547d)^{-k} + 6B(1.6328d)^{-k} + 12B(1.9149d)^{-k}\ldots = 6B(d^1)^{-k} + 3B(1.4142d^1)^{-k} + 8B(1.7321d^1)^{-k}\ldots \quad (4.17)$$

$$(B = \text{constant};\ d^1 = 1.0172d)$$

The effect of including an increasing number of energy contributions is summarised in Table 4.5.

TABLE 4.5 Effect of Number of Coordination Shells considered on the value of k(M-M).

Number of terms in equation (4.17)		Total number of atoms surrounding central atom.		Resultant k(M-M)
b.c.c.	f.c.c.	b.c.c.	f.c.c.	
2	1	14	12	4.6
3	2	26	18	4.9
4	3	50	34	5.0

Having established an appropriate bond length-strength relationship for each transition metal, metal-metal bond enthalpy terms for a variety of metal carbonyls, $M_x(CO)_y$, may be proposed. Values of D(M-CO) can then be estimated from:

$$D(M\text{-}CO) = \frac{1}{y} \Delta H_{disrupt.} - \Sigma E(M\text{-}M)$$

It is assumed that $D(M\text{-}CO)_{br.} = 0.5\ D(M\text{-}CO)_{term.}$; this is supported by the fluxional nature of most metal carbonyl systems.[184,209-211] Individual bond energies so obtained are summarised in Table 4.6 along with previously determined[178] values for comparison.

Several important features emerge from the data. Firstly, the metal-metal bonds in the clusters are generally weaker than previous treatments have suggested; consequently the metal-ligand bonds are slightly stronger. These conclusions support one previous set of results.[193] Secondly, the degree of metal-metal bonding, expressed as a percentage of $\Delta H_{disrupt.}$, appears to be about 6% for dinuclear clusters, 10% for tri-nuclear clusters, 20% for tetranuclear clusters and 25% for hexanuclear clusters. Thirdly, a slight, but significant, increase in D(M-CO) is noted with increasing nuclearity of the metal cluster, i.e. as the number of carbonyl ligands per metal decreases. This feature has previously been noted,[215,216] and also emerges from spectroscopic studies, particularly from matrix isolation work.[218,223-226] Infra-red carbonyl stretching frequencies (ν_{CO}) are a qualitative,[217] (if not a quantitative), measurement of the C-O bond enthalpy. An increase in ν_{CO} along the series $M(CO)_x$ $x = 1 \longrightarrow n$ therefore reflects the increasing carbon-oxygen bond strength. Figure 4.1 shows how $d\pi$ - orbitals on the metal combine with $p\pi$ - orbitals on carbon. The $d\pi$ - $1p\pi$ overlap is completely bonding, whereas $d\pi$ - $2p\pi$ is bonding in the M-C region but antibonding in the C-O region.[218] The decreased transfer

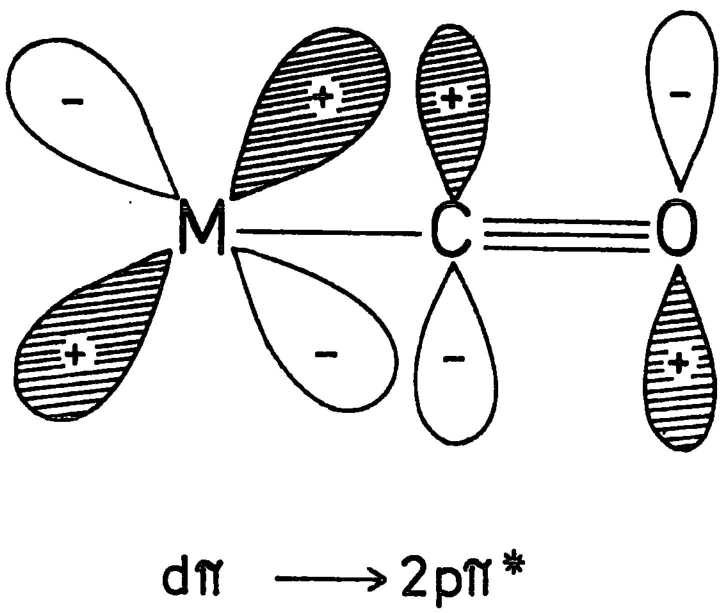
TABLE 4.6 Bond Lengths and Bond Energies in Metals and Metal Carbonyls.

	$\Delta H_{disrupt.}$ kJ mol^{-1}	d(M-M)† pm	E(M-M) kJ mol^{-1} Ref.178	E(M-M) kJ mol^{-1} This work†	D(M-CO) kJ mol^{-1} Ref. 178	D(M-CO) kJ mol^{-1} This work††	%(M-M)* Ref.178	%(M-M)* This work
Fe**	417(4) [8]	248 [186]	104	75	-	-	-	-
$Fe(CO)_5$	585(8) [178]	-	-	-	117	117	0	0
$Fe_2(CO)_9$	1173(25) [178]	252 [191]	82	70	121	123	7	6
$Fe_3(CO)_{12}$	1676(29) [178]	256 [192]	82	65	121	126	14	10
		268	82	52				
Ru	651(8) [178]	265 [186]	109	109	-	-	-	-
$Ru_3(CO)_{12}$	2414(29) [178]	285 [212]	117	78	172	182	15	10
Os	790(8) [178]	268 [186]	132	132	-	-	-	-
$Os_3(CO)_{12}$	2690(29) [5]	288 [213]	130	94	190	201	15	11
Co	428(2) [8]	251 [186]	71	71	-	-	-	-
$Co_2(CO)_8$	1160(12) [178]	252 [188]	83	70	136	136	7	6
$Co_4(CO)_{12}$	2121(29) [5,180]	249 [189,190]	83	74	136	140	24	21
Rh	557(4) [7]	269 [186]	93	93	-	-	-	-
$Rh_4(CO)_{12}$	2648(29) [178]	273 [189,190]	114	86	166	178	26	20
$Rh_6(CO)_{16}$	3874(29) [6]	278 [194]	114	80	166	182	32	25
Ir	665(8) [7]	271 [186]	111	111	-	-	-	-
$Ir_4(CO)_{12}$	3051(29) [178]	269 [214]	130	115	190	197	26	23

† e.s.d. < 1 pm   † mean e.s.d. ≈ 2 kJ mol^{-1} †† mean e.s.d. ≈ 3 kJ mol^{-1}

*%(M-M) = 100 $\Sigma E(M\text{-}M) / \Delta H_{disrupt.}$ **b.c.c. metal; $E(M\text{-}M) = \Delta H_{disrupt.} / 5.55$

Figure 4.1 Formation of a metal → carbon π-bond in metal carbonyl complexes.



of electrons from the metal d-orbitals to empty carbon 2pπ* orbitals which accompanies an increase in coordination number therefore has the effect of weakening the M-C bond and strengthening the C-O bond. This feature is illustrated in Tables 4.7 and 4.8 for several series of metal carbonyl species. For some compounds, (e.g. each of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$), more than one carbonyl stretching band is infra-red active. However, the general trend of increasing ν_{CO} , (and therefore E(C-O)), with decreasing nuclearity of cluster is apparent.

TABLE 4.7 Carbonyl Infra-Red Stretching Frequencies for Some Related Metal Carbonyl Systems.

Species	Environment	ν_{CO} (cm^{-1})	Ref.
CO	Free gas	2143	216,219
$Fe(CO)_5$	KBr disc	2115, 2033, 2003, 1980	220
$Fe_2(CO)_9$	Nujol mull	2082, 2026, 1845, 1833, 1825	221
$Fe_3(CO)_{12}$*	Hexane	2046, 2023, 2013, 1867, 1835	222
	Ar Matrix	2110, 2056, 2051, 2036, 2032, 2021, 2013, 2003, 1871, 1867, 1833	223
$Ni(CO)_4$	Matrix	2052	218
$Ni(CO)_3$		2017	
$Ni(CO)_2$		1967	
Ni(CO)		1996	
$Ta(CO)_6$	Matrix	1967	218
$Ta(CO)_5$		1953	
$Ta(CO)_4$		1943	
$Ta(CO)_3$		1916	
$Ta(CO)_2$		1897, 1891	
Ta(CO)		1831, 1819	
$V(CO)_6$	Ar Matrix	1976, 1970	224
$V(CO)_5$		1952, 1943	
$V(CO)_4$		1893	
$V(CO)_3$		1920	

*Ar matrix spectrum probably resembles that of solid, cf. solution spectrum.

TABLE 4.8 Carbonyl Infra-Red Stretching Frequencies for Some Lanthanide Carbonyl Species[225,226]

(Values of ν_{CO} in cm^{-1})

Species	M = Pr	M = Nd	M = Eu	M = Gd	M = Ho	M = Yb
$M(CO)_6$	1989	1990	2000	1986	1982	2008
$M(CO)_5$	1965	1965	1974	1967	1961	1995
$M(CO)_4$	1940	1940	1968	1945	1929	1986
$M(CO)_3$	1885	1891	-	1901	1902	1976
$M(CO)_2$	1858	1861	1873	1864	1859	1966
M(CO)	1835	1840	-	1841	1830	1958

In the $Ni(CO)_n$ and $V(CO)_n$ series (Table 4.7), discrepancies from the general ν_{CO} trend are noted, namely in $Ni(CO)_2$ and $V(CO)_4$. This underlines the fact that CO stretching frequencies can only be used as an indication of expected trends in bond strengths. A comparison of CO force constants (f_{CO}) is really necessary but these cannot be derived accurately from the few observed frequencies which are available. However, the Cotton-Kraihanzel method [227] may be used to give approximate values of f_{CO} and when applied to $Ni(CO)_n$ [218] gives a series of force constants in line with the anticipated trend in bond strengths. One possible explanation for the anomalous value of ν_{CO} in $V(CO)_4$ is that some bands are obscured due to band overlap or missed because of their low intensities. [224] In general though, trends in infra-red stretching frequencies are indicative of trends in CO bond strengths, but values of ν_{CO} must be used with caution.

4.3 Prediction of Heats of Formation from Structural Data

It has been established that possible metal-metal bond energies can be suggested using the relationship:

$$E(M\text{-}M) = A[d(M\text{-}M)]^{-4.6}$$

and that when appropriate values of E(M-M), (estimated from structural data), are used in conjunction with experimentally determined enthalpies of disruption of metal carbonyl compounds, meaningful estimates of D(M-CO) can be obtained. An important application of this treatment is the prediction of previously undetermined heats of formation of metal carbonyls from known structural parameters. Recently, several new neutral osmium carbonyl clusters, ($Os_4(CO)_{13}$, $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$), have been prepared. [228,229] The metal clusters of $Os_5(CO)_{16}$, $Os_6(CO)_{18}$ and $Os_7(CO)_{21}$ have been structurally characterised;[230-232] (the metal-carbon and carbon-oxygen distances are known much less accurately than the metal-metal bond lengths). Metal-metal bond enthalpies can therefore be estimated using equation 4.18, (see Table 4.4).

$$E(Os\text{-}Os) = 1.928 \times 10^{13} [\, d(Os\text{-}Os)]^{-4.6} \qquad (4.18)$$

The metal-ligand mean bond dissociation energy, D(Os-CO), is estimated by allowing what appears to be a realistic increase (based on 201 kJ mol^{-1} in $Os_3(CO)_{12}$, see Table 4.6) as the cluster nuclearity increases. Structural data and estimated values of E(Os-Os) and D(Os-CO) are summarised in Table 4.9, along with calculated standard enthalpies of disruption and formation which are quoted to the nearest 10kJ. (The method of calculation does not justify a more accurate assessment of these enthalpies). (ΔH^{o}_{f298} Os(g) and CO(g) are taken as 789.9 kJ mol^{-1}[7,178] and 110.5 kJ mol^{-1}[70]). The mono-nuclear species, $Os(CO)_5$, is included in Table 4.9 for comparison. The value of D(Os-CO) = 205.4 kJ mol^{-1} was estimated using electron impact measurements and assuming a trigonal bipyramidal structure consistent with that of $Fe(CO)_5$.[185] A correction for the high electron impact appearance potentials, (inherent in mass spectroscopic bond energy determinations), is included. By comparison with the trend of D(Os-CO) for $Os_x(CO)_y$ with $x \geq 3$, a value of 205.4 kJ mol^{-1} still appears to be marginally high.

TABLE 4.9 Bond Enthalpy Contributions and Estimated Standard Enthalpies of Formation for Some Binary Osmium Carbonyls.

Species	d(M-M)[†] pm	No. M-M bonds	E(M-M)[†] kJ mol^{-1}	D(M-CO)[*] kJ mol^{-1}	$\Delta H_{disrupt.}$ kJ mol^{-1}	ΔH^{o}_{f298} kJ mol^{-1}
$Os(CO)_5$	-	-	-	205.4[185]	1027	-790.8[185]
$Os_3(CO)_{12}$	288[213]	3	94	201	2690(29)[5]	-1644(29)
$Os_5(CO)_{16}$	275[230]	5	116	205	4240(50)	-2050(50)
	288	4	94			
$Os_6(CO)_{18}$	273[231]	1	120	208	5035(60)	-2280(60)
	278	3	110			
	280	5	107			
	283	3	102			
$Os_7(CO)_{21}$	282[232]	6	103	209	5870(70)	-2660(70)
	285	5	98			
	288	4	94			

† e.s.d. < 1 pm † Mean e.s.d. ≈ 2 kJ mol^{-1} * Mean e.s.d. ≈ 3 kJ mol^{-1}

4.4 Reorganisation Energies and Site Preferences of Carbonyl Ligands

The metal-ligand bond enthalpy D(M-CO) is the mean energy required to remove a carbonyl ligand, (whether in a terminal or bridging position), from the metal carbonyl cluster, and is the difference between the metal-carbon bond energy, $\Delta E(M\text{-}C)$, and the reorganisation energy $\Delta E(C\text{-}O)$, of the coordinated CO group on being released to form free carbon monoxide. The separate enthalpies can be determined if the appropriate structural parameters, (i.e. d(M-C) and d(C-O)), are known with great enough precision. Whereas metal-metal bond lengths can be measured accurately using X-ray diffraction techniques, precise location of the carbonyl groups is considerably more difficult. In many cases, d(M ---- O) can be determined with a fair degree of accuracy. A value of d(C-O) may then be assumed in order to obtain an estimate of d(M-C); e.g. in a recent structural study of $Ir_4(CO)_{12}$,[214] d(C-O) is assumed to be 114 pm.

The interatomic distances in $Fe_2(CO)_9$ have been determined by Cotton [191] and are shown in Figure 4.2. The molecule contains three bridging carbonyl ligands, d(C-O) = 117.6(5) pm, and six terminal ligands, d(C-O) = 115.6(4) pm. The bond in free carbon monoxide is, (as would be expected from infra-red spectroscopic data), shorter (d(C-O) = 112.8(1) pm [89]) and therefore stronger than in the complex. The bond energy of carbon monoxide is 1070(2) kJ mol^{-1}.[8] It has previously (p. 29) been suggested that the energies and lengths of carbon-oxygen bonds, irrespective of their formal bond orders, are related according to equation 4.19. The energy of any carbon-

$$E(C\text{-}O) = (1.955 \times 10^{13})[d(C\text{-}O)]^{-5.0} \qquad (4.19)$$

oxygen bond of known length can now be determined. It follows from equation 4.19 that in $Fe_2(CO)_9$, $E(C\text{-}O)_{term.}$ = 947(16)kJ mol^{-1} and $E(C\text{-}O)_{br.}$ = 869(20)kJ mol^{-1}. The reorganisation energies are therefore $\Delta E(C\text{-}O)_{term.}$ = 123(16)kJ mol^{-1} and $\Delta E(C\text{-}O)_{br.}$ = 201(20)kJ mol^{-1}.

The total energy assignable to the metal-carbon bonds in $Fe_2(CO)_9$ is given by:

$$\Sigma E(M\text{-}C) = \Delta H_{disrupt.} + \Sigma\Delta E(C\text{-}O) - E(M\text{-}M)$$

E(M-M) has been calculated to be 70kJ (Table 4.6) and $\Delta H_{disrupt.}$ = 1173(25)kJ mol^{-1},[178] thus giving $\Sigma E(M\text{-}C)$ = 2444(110)kJ mol^{-1}. Hence:

$$6E(M\text{-}C)_{term.} + 6E(M\text{-}C)_{br.} = 2444(110)\text{kJ mol}^{-1} \qquad (4.20)$$

Since there is no way of establishing with certainty a relationship between the length and strength of metal-carbon bonds, it is assumed that a correlation of the type $E = Ad^{-k}$ is realistic. For carbon-carbon bonds, k = 3.2[37] and for metal-metal bonds, k = 4.6. Hence it seems reasonable that for metal-carbon bonds, $k \approx 4$, i.e. $E(M\text{-}C) = A[d(M\text{-}C)]^{-4}$. Equation 4.21 applies this relationship to the specific case of $Fe_2(CO)_9$. Combining equations 4.20 and 4.21 gives the

$$\frac{E(Fe\text{-}C)_{term.}}{E(Fe\text{-}C)_{br.}} = \left[\frac{d(Fe\text{-}C)_{br.}}{d(Fe\text{-}C)_{term.}}\right]^4 = \left[\frac{201.6}{183.8}\right]^4 = 1.4474 \qquad (4.21)$$

individual energies $E(Fe\text{-}C)_{term.}$ and $E(Fe\text{-}C)_{br.}$ = 241(10) and 166(8)kJ mol^{-1} respectively. The implications of these values of E(Fe-C) with respect to removal of carbonyl ligands are:

$$D(Fe\text{-}CO)_{term.} = E(Fe\text{-}C)_{term.} - \Delta E(C\text{-}O)_{term.} = 118(25)\text{kJ mol}^{-1}$$

$$D(Fe\text{-}CO)_{br.} = 2E(Fe\text{-}C)_{br.} - \Delta E(C\text{-}O)_{br.} = 131(25)\text{kJ mol}^{-1}$$

The results are summarised in Table 4.10. There appears to

Figure 4.2 Structure of $Fe_2(CO)_9$.

[Distances in pm.]

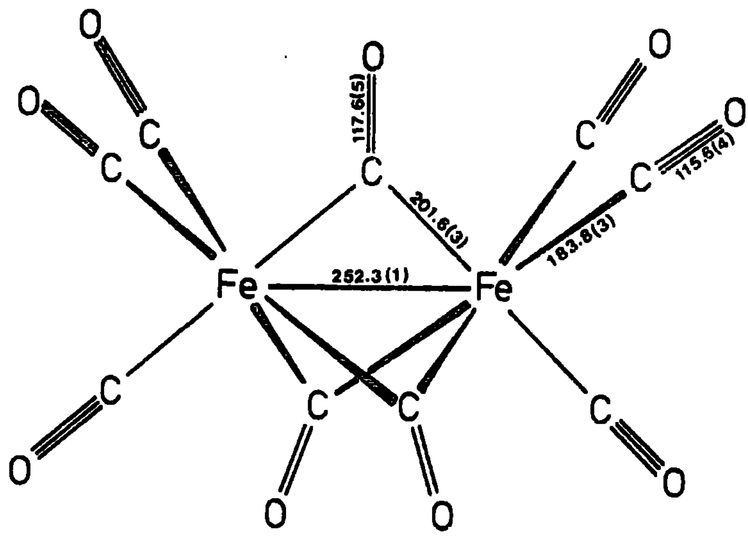
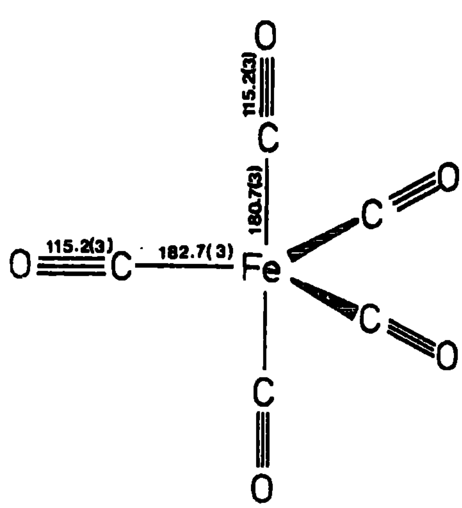


Figure 4.3 Structure of $Fe(CO)_5$.

[Distances in pm.]



be a slight preference for the bridging ligand-site over the terminal site, but the errors in the calculated bond enthalpies, (which arise from quite substantial errors in the interatomic distances), make it unrealistic to discuss site preference in quantitative terms.

Analogies are often drawn between metal carbonyl clusters and carbon monoxide adsorbed on metal surfaces.[197,200] The type of coordination adopted by adsorbed carbon monoxide on iron metal might provide evidence for site preference in iron carbonyls. This aspect is discussed further in Section 4.5.

If the bond enthalpy contributions estimated for $Fe_2(CO)_9$ are realistic, compatible results should be obtained if the same treatment is applied to $Fe(CO)_5$, the structure of which is also known accurately;[235] Figure 4.3. The carbon-oxygen bond lengths are 115.2(3)pm for both axial and equatorial ligands; (a slight difference between $d(C\text{-}O)_{axial}$ and $d(C\text{-}O)_{equatorial}$ would have been expected to correspond to the different values of $d(Fe\text{-}C)_{axial}$ and $d(Fe\text{-}C)_{equatorial}$). Application of equation (4.19) gives $E(C\text{-}O) = 963(12)\text{kJ mol}^{-1}$, and hence $\Delta E(C\text{-}O) = 107(12)\text{kJ mol}^{-1}$. The enthalpy of disruption of $Fe(CO)_5$ is $585(8)\text{kJ mol}^{-1}$[178] and therefore:

$$\Sigma E(Fe\text{-}C) = 585 + \Sigma\Delta E(C\text{-}O) = 1120(60)\text{kJ mol}^{-1} \qquad (4.22)$$

Assuming $E(Fe\text{-}C) = A[d(Fe\text{-}C)]^{-4}$, the following relationship between axial and equatorial metal-carbon bond enthalpies can be written:

$$\frac{E(Fe\text{-}C)_{axial}}{E(Fe\text{-}C)_{equ.}} = \left[\frac{d(Fe\text{-}C)_{equ.}}{d(Fe\text{-}C)_{axial}}\right]^4 = \left[\frac{182.7}{180.7}\right]^4 = 1.045 \qquad (4.23)$$

Combining equations 4.22 and 4.23 gives $E(Fe\text{-}C)_{axial} = 230(10)\text{kJ mol}^{-1}$ and $E(Fe\text{-}C)_{equ.} = 220(10)\text{kJ mol}^{-1}$. The mean be a slight preference for the bridging ligand-site over the terminal site, but the errors in the calculated bond enthalpies, (which arise from quite substantial errors in the interatomic distances), make it unrealistic to discuss site preference in quantitative terms.

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$$\Sigma E(Fe\text{-}C) = 585 + \Sigma\Delta E(C\text{-}O) = 1120(60)\text{kJ mol}^{-1} \qquad (4.22)$$

Assuming $E(Fe\text{-}C) = A[d(Fe\text{-}C)]^{-4}$, the following relationship between axial and equatorial metal-carbon bond enthalpies can be written:

$$\frac{E(Fe\text{-}C)_{axial}}{E(Fe\text{-}C)_{equ.}} = \left[\frac{d(Fe\text{-}C)_{equ.}}{d(Fe\text{-}C)_{axial}}\right]^4 = \left[\frac{182.7}{180.7}\right]^4 = 1.045 \qquad (4.23)$$

Combining equations 4.22 and 4.23 gives $E(Fe\text{-}C)_{axial} = 230(10)\text{kJ mol}^{-1}$ and $E(Fe\text{-}C)_{equ.} = 220(10)\text{kJ mol}^{-1}$. The mean

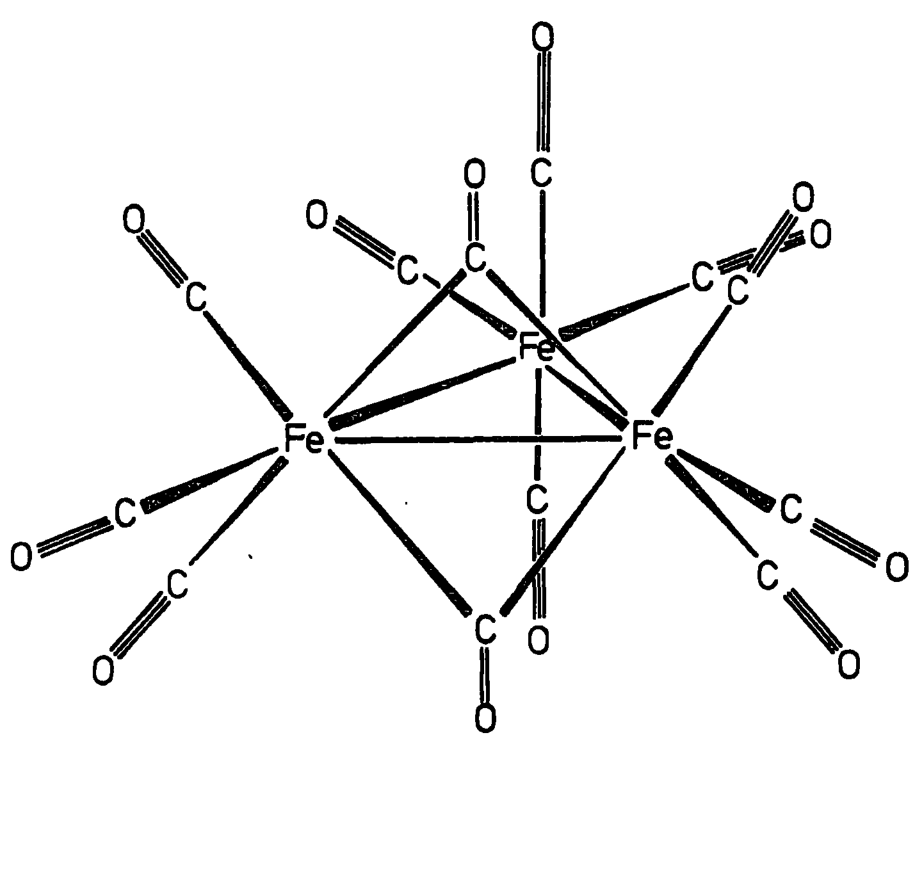
TABLE 4.10 Individual Bond Enthalpy Contributions in $Fe_2(CO)_9$ and $Fe(CO)_5$

Compound	Bond	d pm	E(C-O) kJ mol^{-1}	ΔE(C-O) kJ mol^{-1}	E(Fe-C) kJ mol^{-1}	D(Fe-CO) kJ mol^{-1}
$Fe(CO)_5$	$C-O_{axial}$, $C-O_{equ.}$	115.2(3)	963(12)	107(12)	-	-
	$Fe-C_{axial}$	180.7(3)	-	-	230(10)	123(16)
	$Fe-C_{equ.}$	182.7(3)	-	-	220(10)	113(16)
$Fe_2(CO)_9$	$C-O_{term.}$	115.6(4)	947(16)	123(16)	-	-
	$C-O_{br.}$	117.6(5)	869(20)	201(20)	-	-
	$Fe-C_{term.}$	183.8(3)	-	-	241(10)	118(25)
	$Fe-C_{br.}$	201.6(3)	-	-	166(8)	131(25)

dissociation energies of the metal-ligand bonds are therefore $D(Fe\text{-}CO)_{axial}$ = 123(16)kJ mol^{-1} and $D(Fe\text{-}CO)_{equ.}$ = 113(16)kJ mol^{-1}, (Table 4.10).

From the summarised results in Table 4.10, it is noted that the terminal iron-carbon bond in $Fe_2(CO)_9$ is longer, but appears stronger than such bonds in $Fe(CO)_5$. In view of the errors incurred in bond length determinations, (particularly in d(C-O)), such discrepancies cannot be regarded as being significant. However it can be proposed that for d(Fe-C) = 181-184pm, an energy of E(Fe-C) = 220-240kJ mol^{-1} is possibly realistic.

Figure 4.4 Structure of $Fe_3(CO)_{12}$.



Inclusion of $Fe_3(CO)_{12}$ (Figure 4.4) in these calculations is not feasible since the measured values of d(C-O),[192] (d$(C\text{-}O)_{term.}$ range 107-121(5)pm and $d(C\text{-}O)_{br.}$ = 112(5) and 114(2)pm), are clearly of low precision. (Some of the carbon-oxygen bonds appear to be shorter, and therefore stronger, than in free carbon monoxide itself). Values of d(Fe-C) are also subject to a fairly high degree of error, ($d(Fe\text{-}C)_{term.}$ = 182(2)pm, $d(Fe\text{-}C)_{br.}$ = 205(2)pm). It is however plausible to suggest that in $Fe_3(CO)_{12}$ $d(C\text{-}O)_{term.} \approx$ 116pm and $d(C\text{-}O)_{br.}$ ≈118pm by comparison with $Fe(CO)_5$ and $Fe_2(CO)_9$. Hence $E(C\text{-}O)_{term.} \approx 930kJ\ mol^{-1}$ and $E(C\text{-}O)_{br.} \approx 855kJ\ mol^{-1}$ (equation 4.19), giving $\Delta E(C\text{-}O)_{term.} = 140kJ\ mol^{-1}$ and $\Delta E(C\text{-}O)_{br.} = 215kJ\ mol^{-1}$. Again by comparison with $Fe(CO)_5$ and $Fe_2(CO)_9$, and allowing for a slight increase in the metal-ligand bond enthalpy term with increased cluster nuclearity, it is suggested that $d(Fe\text{-}C)_{term.} \approx$ 182pm and $d(Fe\text{-}C)_{br.} \approx$ 200pm in $Fe_3(CO)_{12}$. The enthalpy of disruption of $Fe_3(CO)_{12}$ = 1676(29)kJ mol^{-1}[178] and $\Sigma E(Fe\text{-}Fe) = 169kJ\ mol^{-1}$ (Table 4.6). Equations 4.24 and 4.25 can therefore be written. These give the results that

$$10E(Fe\text{-}C)_{term.} + 4E(Fe\text{-}C)_{br.} = \Delta H_{disrupt.} + \Sigma E(C\text{-}O) - \Sigma E(Fe\text{-}Fe)$$

$$= 3337kJ\ mol^{-1} \qquad (4.24)$$

$$\frac{E(Fe\text{-}C)_{term.}}{E(Fe\text{-}C)_{br.}} = \left[\frac{d(Fe\text{-}C)_{br.}}{d(Fe\text{-}C)_{term.}}\right]^4 = \left[\frac{200}{182}\right]^4 = 1.458 \qquad (4.25)$$

$E(Fe\text{-}C)_{term.}$ and $E(Fe\text{-}C)_{br.} \approx$ 260 and 180kJ mol^{-1} respectively, and thus $D(Fe\text{-}CO)_{term.}$ and $D(Fe\text{-}CO)_{br.} \approx$ 120 and 145kJ mol^{-1}. A preference for the bridging site is again apparent. A reassessment of the individual bond enthalpy contributions in all three iron carbonyls will be possible when more accurate crystallographic data are available.

4.5 Analogies Between Metal Carbonyls and CO Adsorbed on Metal Surfaces

A metal carbonyl cluster may be regarded as a model for carbon monoxide adsorbed on a metal surface.[197,200,236] Photoelectron spectroscopic studies have provided evidence for similarities between the two systems and recently the photoelectron spectra of $W(CO)_6$ and $Ru_3(CO)_{12}$ have been compared with spectra of CO adsorbed on tungsten and ruthenium surfaces respectively.[236] It appears that multimetal carbonyl clusters compare favourably with surface systems. However, caution is needed when applying such analogies because

(a) photoelectron spectroscopy measures the excitation spectrum of an ionic system and it does not necessarily follow that ground state properties will be the same, and

(b) comparison of a surface system with a metal carbonyl cluster limits the bonding description to a triply bridging carbonyl group; (interaction of a CO molecule with e.g. 4 surface metal atoms cannot be paralleled in cluster bonding).

Comparisons between the initial heats of chemisorption and estimated values of D(M-CO) for $M_x(CO)_y$ have previously been made.[178,193,197,237] These values are summarised in Table 4.11 along with results from this work. A close correlation exists between $\Delta H_{adsorption}$ and D(M-CO) and in some cases, (e.g. $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$), use of a bond length-bond energy relationship greatly enhances agreement between the two quantities.

Adsorbed carbon monoxide has been studied structurally using infra-red spectroscopy. It is generally accepted that

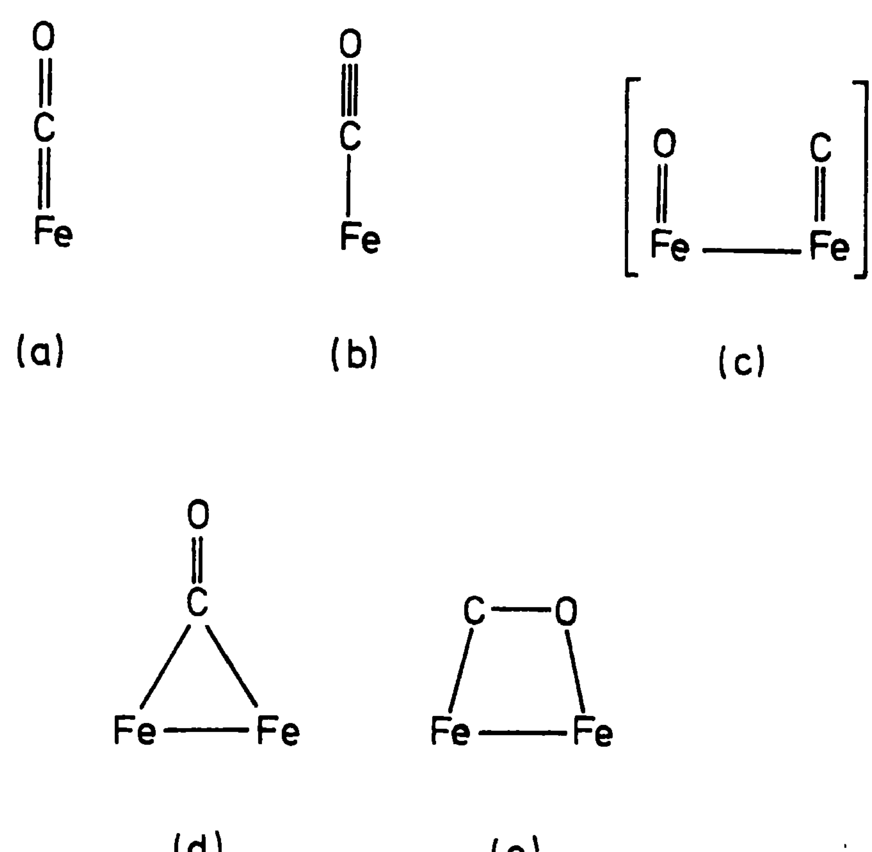
TABLE 4.11 Comparison Between Initial Heats of Adsorption of CO on Transition Metal Surfaces at 273K and Calculated Values of D(M-CO) in Metal Carbonyl Compounds.

Metal	Initial $\Delta H_{adsorption}$ kJ mol^{-1} 178,193,197,237	D(M-CO)* kJ mol^{-1} (Ref.178)	D(M-CO)* kJ mol^{-1} (this work)
Fe	146	117	117-126
Ru	-	172	182
Os	-	190	201
Co	192	136	136-140
Rh	176-184	166	178-182
Ir	209	190	197
Cr	<Mo	108	108
Mo	159-326	152	152
W	209-335	178	178
Ni	176	147	147

* Values of D(M-CO) taken to cover range of x and y in $M_x(CO)_y$ for each metal, (Table 4.6). For M = Cr, Mo, W and Ni D(M-CO) in $M(CO)_y = \frac{1}{y} \Delta H_{disrupt.}$ as in ref.178

IR bands between 2140 and 1950 cm^{-1} are representative of linearly bound CO, and that bands with $\nu_{CO} < 1950$ cm^{-1} indicate either bridging CO groups or linear CO groups whose IR stretching frequency has been lowered as a result of e.g. high electron density on the metal itself.[217] CO adsorbed on Fe surfaces has been studied spectroscopically.[238-241] Five modes of surface bonding are possible, (Figure 4.5),

Figure 4.5 Possible modes of bonding for CO adsorbed on Fe metal.[238]



although structure (c) can be eliminated on the grounds that strong IR absorptions appear at 1950 cm^{-1} (ν_{CO}) and 580 cm^{-1} (δ_{CO}). The experimental value of ν_{CO} lies ambiguously between the regions usually associated with either terminal or bridging groups, but from force constant and group theory data it is tentatively suggested[238] that CO is terminally bound on the iron surface with a C-O bond order of 2 to 3. Later work[239-241] supports these suggestions although X-ray and ultra-violet He$^{(1)}$ photoelectron spectroscopic studies[242] indicate that the Fe-CO interactions are more complex than might be expected from analogy with simple metal carbonyls. It is therefore difficult to draw any meaningful conclusions regarding site preference of carbon monoxide adsorbed on an iron surface for comparison with iron carbonyl compounds.

Larger metal clusters are expected to be closer approximations to surface systems than are dinuclear or trinuclear species such as $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. It is anticipated that the mode of bonding of CO adsorbed on rhodium metal will be related to that found in $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, Figure 4.6. Accurate carbon-oxygen bond distances are not available for these compounds and it is not possible to predict the relative stabilities of terminal and bridging ligand sites. However, CO adsorbed on alumina-supported rhodium metal has been studied by infra-red spectroscopy.[243] Absorptions are recorded at ca. 2000 cm^{-1}, (corresponding to linearly bound CO, Figure 4.7a), at 2100 and 2030 cm^{-1}, corresponding to an $Rh(CO)_2$ grouping, Figure 4.7b), and a broad band between 1850 and 1900 cm^{-1}, (corresponding to a mixture of bridging CO groups, Figures 4.7c and 4.7d). The

Figure 4.6 Structures of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.

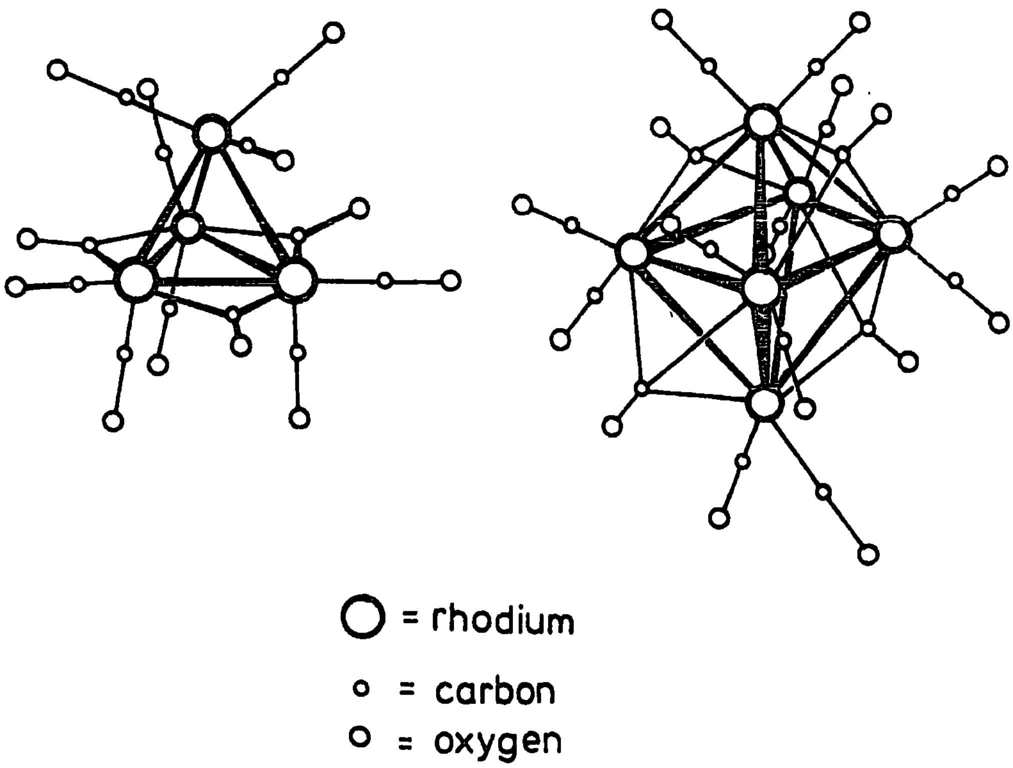
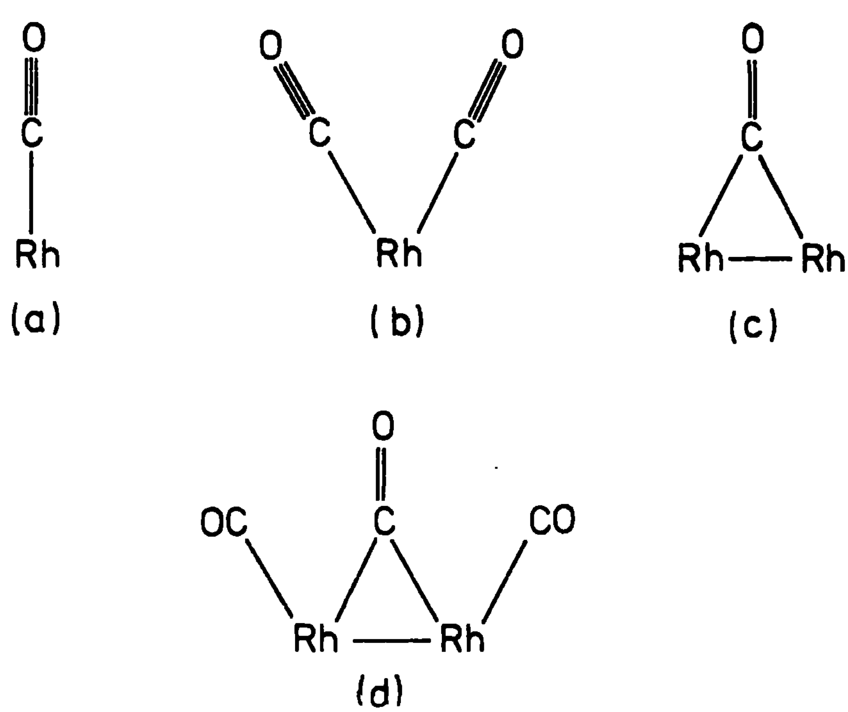


Figure 4.7 Modes of bonding for CO adsorbed on Rh metal.[243]



relative thermal stabilities of the adsorbed CO molecules are $Rh_2(CO) > Rh(CO) > Rh(CO)_2$. This supports the suggestion that bridging environments may be thermodynamically preferred to terminal sites.

4.6 Conclusion

The close relationship which exists between small metal fragments and the bulk metal allows the latter to be used as a model for metal clusters. Use of the bond length-bond energy relationship:

$$E(M\text{-}M) = A[d(M\text{-}M)]^{-4.6}$$

allows metal-metal bond enthalpies which are consistent with changes in structural data to be estimated for series of transition metal carbonyl compounds. By combining values of E(M-M) with experimentally determined enthalpies of disruption, estimates of D(M-CO), (the metal-ligand mean bond dissociation energy), can be obtained.

The treatment can be further developed to gain insight into the preference of a particular ligand for bridging or terminal sites. It is tentatively concluded that for $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ there is little difference between the binding energies of a carbonyl group to a terminal or bridging site, although slight preference for the bridging position is indicated. Attempts have been made to compare these results with those obtained from spectroscopic investigations of carbon monoxide adsorbed on metal surfaces. It is difficult to rationalise the literature data available for the Fe-CO system in terms of similarity to the cluster bonding in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. This is probably a consequence of comparing a dinuclear or trinuclear metal carbonyl, (which cannot realistically be classified as 'cluster' compounds), with a surface system. Such analogies do however appear to be more appropriate for larger clusters (e.g. $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$) where studies of CO adsorbed on a rhodium surface indicate a bridging site to be preferred over a terminal one.

It is anticipated that this work be extended when more precise crystallographic data are available. At present accurately determined C-O bond lengths in metal carbonyl systems are lacking.

CHAPTER FIVE

BOND ENTHALPIES OF METAL-METAL MULTIPLE BONDS

5.1 Introduction

In 1844, the first compound to contain a metal-metal quadruple bond, the chromium acetate complex, $Cr_2(O_2CMe)_4 \cdot 2H_2O$, was prepared.[244] However, it was over a century later that the existence of multiple metal-metal bonds was in fact recognised.[49,245] Over the past fifteen years a large number of complexes involving double, triple and quadruple M-M bonds have been characterised, although of these it is the bonds of orders 3 and 4 which have aroused the most interest.

Compounds which contain multiple M-M bonds typically involve the Group VIa and VIIa transition metals, and to a lesser extent the metals of Group Va and possibly Group VIII. Some examples are listed in Table 5.1 and are illustrated in Figure 5.1. Values of d(M-M) are given in the Table along with the Pauling values for the corresponding 'maximum valence' single bond distances;[246] (these lengths are appropriate for transition metals having a covalence of 9, i.e. 9 hybrid-spd orbitals). (Comprehensive surveys of compounds containing triple or quadruple metal-metal bonds can be found in several excellent reviews).[275-279]

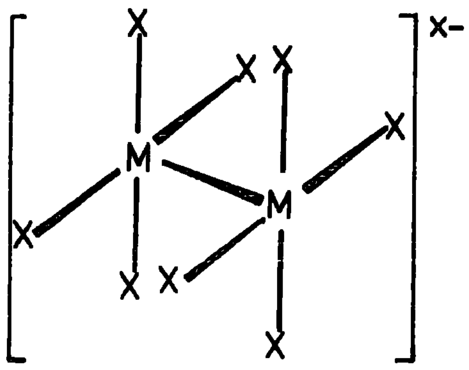
The degree of interaction in these very short metal-metal bonds has been the subject of much discussion. Indeed, *ab initio* MO calculations based on photoelectron spectroscopic results[280] have been reported showing that there is in fact <u>no</u> net M-M bonding in $Cr_2(O_2CMe)_4 \cdot 2H_2O$ despite its short M-M distance and its diamagnetism.[281] However it has been argued that the lengthening of the Cr-Cr bond in going from anhydrous

TABLE 5.1 Structural Data for Some Systems Involving Metal-Metal Multiple Bonds

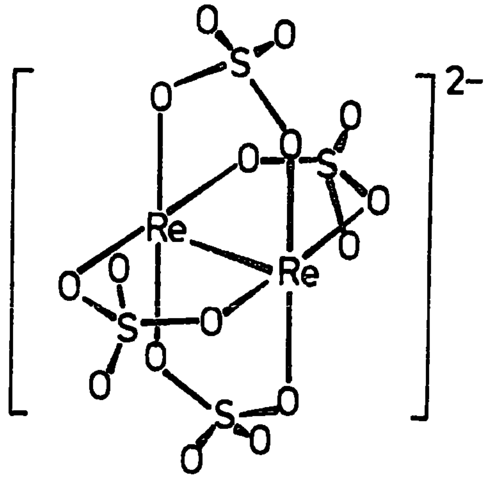
Compound	Figure	Ref.	d(M-M) pm	Pauling's Single Bond Distance[246] pm
$K_2Re_2Cl_8 \cdot 2H_2O$	5.1a	247	224.1(7)	271
$Cs_2Re_2Br_8$	5.1a	248	222.8(4)	271
$Na_2Re_2(SO_4)_4 8H_2O$	5.1b	249	221.4(1)	271
$Re_2(piv)_2Cl_4$	5.1c	250	220.9(2)	271
$Tc_2(piv)_4Cl_2$	5.1d	251	219.2(2)	276
$K_3Tc_2Cl_8.nH_2O$	5.1a	252	211.7(2)	276
$Cr_2(O_2CMe)_4.2H_2O$	5.1d	253,254	236.2(1)	252
$Cr_2(O_2CMe)_4$(anhyd.)	5.1d	255	228.8(2)	252
$Li_4Cr_2Me_8 \cdot 4THF$	5.1e	256	198.0(5)	252
$Cr_2(PhNNNPh)_4$	5.1f	257	185.8(1)	252
$Cr_2(TMP)_4$	5.1g	258	184.9(2)	252
$Cr_2(DMP)_4$	5.1h	259	184.7(1)	252
$Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2.6Et_2O$	5.1i	260	183.0(4)	252
$Mo_2(NMe_2)_6$	5.1j	261,262	221.4(2)*	278
$K_4Mo_2Cl_8 \cdot 2H_2O$	5.1a	263	213.9(4)	278
$Mo_2(O_2CPh)_4$.2 Diglyme	5.1d	264	210.0(1)	278
$Mo_2(O_2CMe)_4$	5.1d	265	209.34(8)	278
$Mo_2(O_2CH)_4$	5.1d	266	209.1(2)	278
$Mo_2(PhNNNPh)_4$	5.1f	257	208.3(2)	278
$Mo_2(DMP)_4$	5.1h	260	206.4(1)	278
$Cs_3W_2Cl_9$	5.1k	267	240.9(a)	280
$W_2(C_8H_8)_3$	5.Il	268	237.5(1)	280
$W_2(NMe_2)_6$	5.1j	269,270	229.4(1)	280
$Li_4W_2Me_8.4Et_2O$	5.1e	271,272	226.4(1)	280
$V_2(DMP)_4$	5.1h	273	220.0(2)	-
$Rh_2(O_2CMe)_4.2py$	5.1d	274	239.94(5)	272
$Rh_2(O_2CMe)_4 \cdot 2H_2O$	5.1d	253,254	238.55(5)	272

*Mean of d(M-M) for 2 crystallographic independent molecules

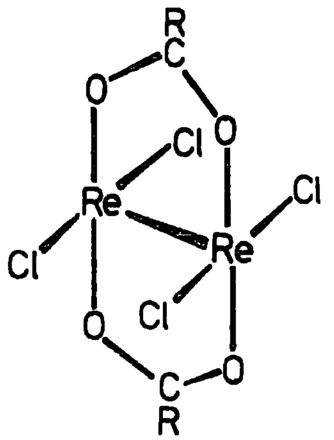
Figure 5.1 Structures of systems involving multiple metal-metal bonds.



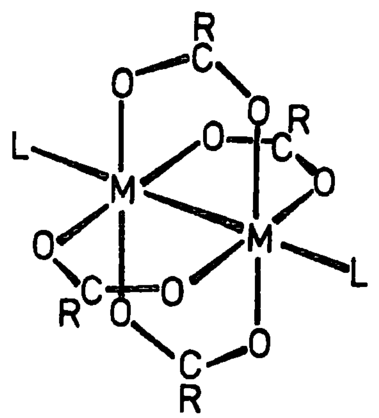
(a) M=Re ; X=Cl, Br ; x=2
M=Tc ; X=Cl ; x=3
M=Mo ; X=Cl ; x=4



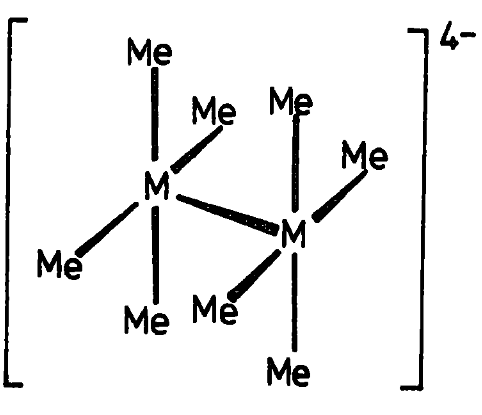
(b)



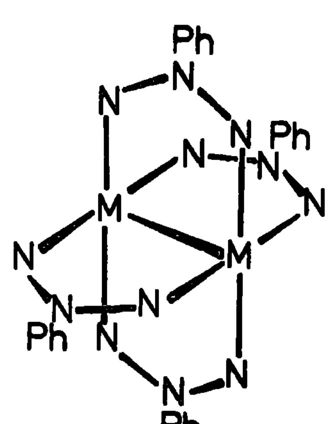
(c) R = $C(CH_3)_3$; [RCO_2 = piv.]



(d) M = Tc, Cr, Mo, or Rh
R = H, Me, CMe_3, or Ph
L = H_2O, diglyme, py, Cl, or no L

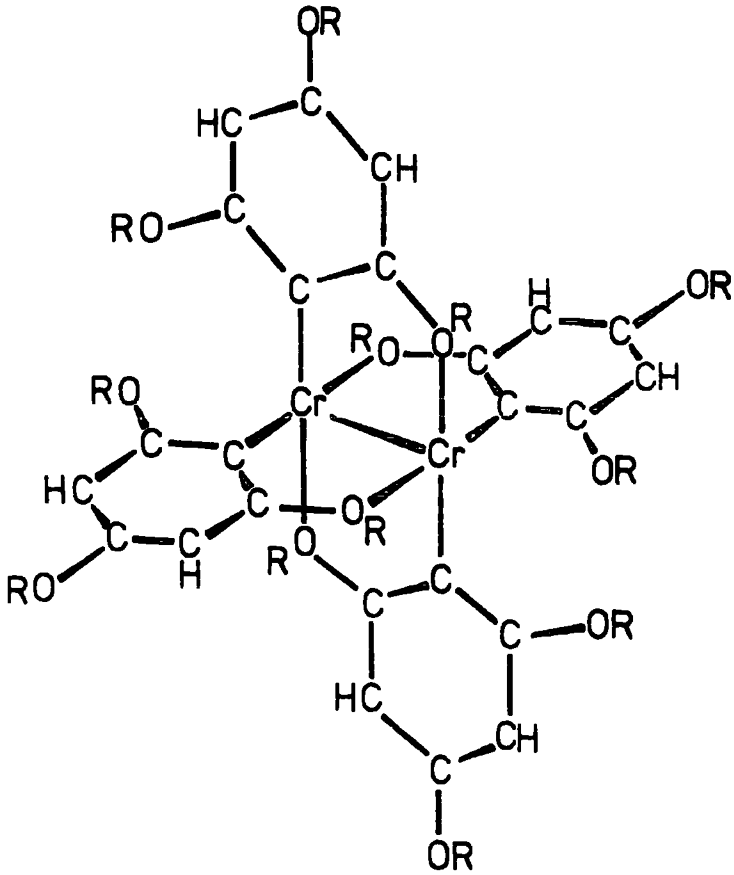


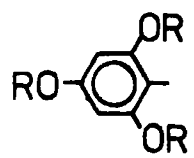
(e) M=Cr; W

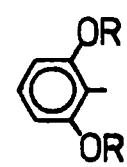


(f) M= Cr ; Mo

Figure 5.1 (contd.)



(g) R = Me ;  = TMP

(h) R = Me ; M = V, Cr, Mo ;  = DMP

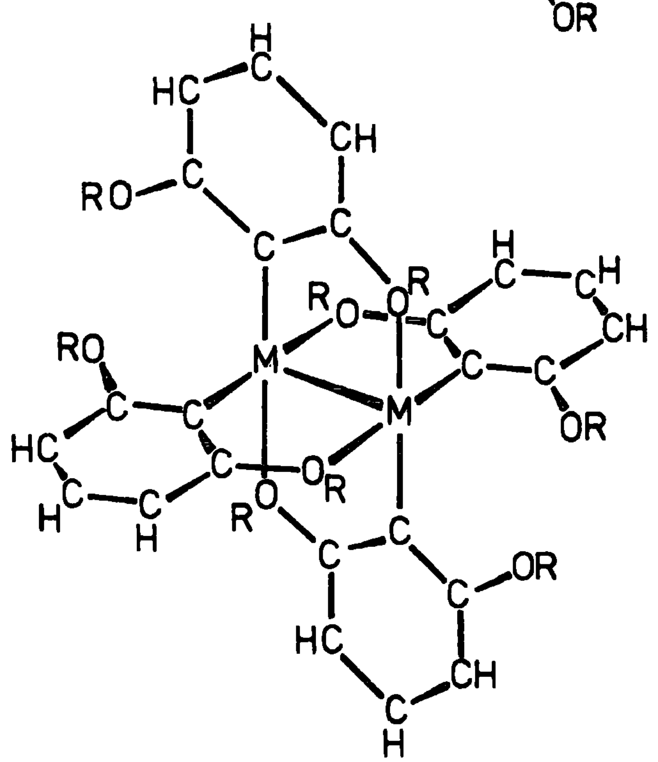
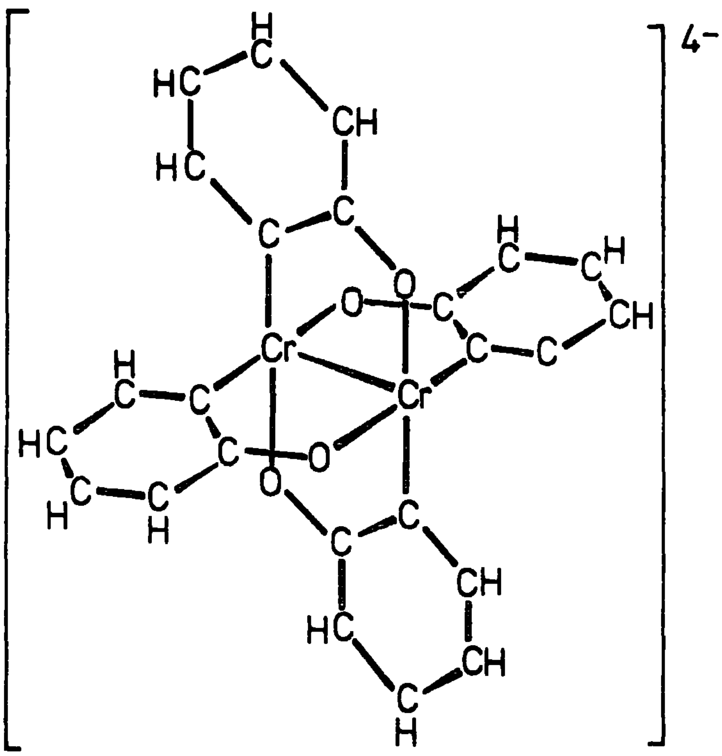
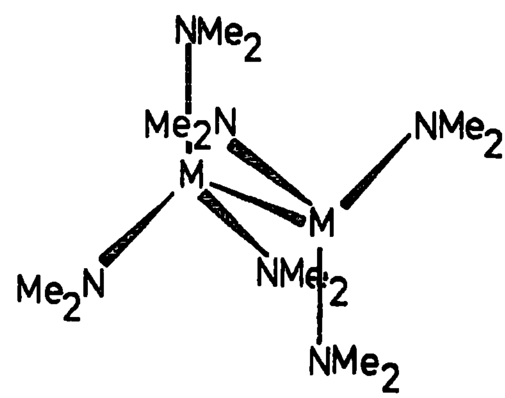


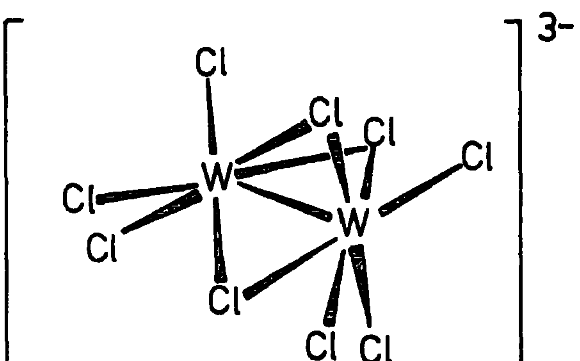
Figure 5.1 (contd.)



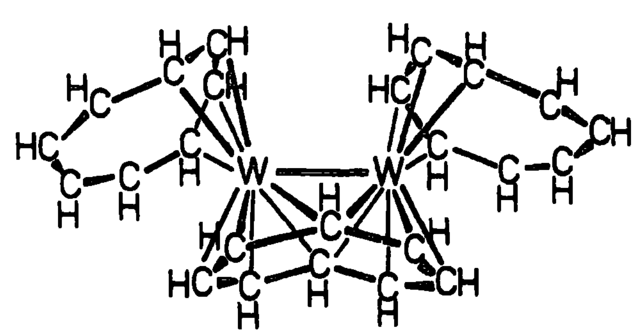
(i)



(j) M = Mo; W



(k)



(l)

$Cr_2(O_2CMe)_4$ to $Cr_2(O_2CMe)_4 \cdot 2H_2O$ s caused by the competition of the additional axial ligands for σ-electrons which are otherwise available for M-M bonding.[255,282] The concept of triple, quadruple and even, perhaps, pentuple[283] bonds in transition metal complexes is, however, now becoming accepted.

A quadruple bond consists of a σ-component (d_z2-d_z2 overlap), two equivalent π-components (d_{xz}-d_{xz} and d_{yz}-d_{yz} overlap), and a δ-component (d_{xy}-d_{xy} overlap), the z-axis being defined to coincide with the M-M link, (Figure 5.2). The basic requirementfor maximum δ-bonding is an eclipsed configuration. The triple metal-metal bond comprises σ- and 2 π-components. The $Mo_2(SO_4)_4{}^{3-}$ ion is reported to have intermediate character, i.e. a bond order of 3.5.[284,285]

Several transition metal diatomic molecules have also been predicted to have bond orders $\geq$ 4;[286-289] the synthesis of these species by matrix isolation techniques has only recently been achieved.

Whilst systems containing triple or quadruple metal-metal bonds have attracted a great deal of attention structurally, few conclusive results regarding their thermochemistry have been obtained. The diatomic, M_2, molecules are the simplest multiply bonded species and their dissociation energies have been estimated by spectroscopic techniques. Table 5.2 lists dissociation enthalpies (D_o) for some gaseous M_2 molecules and gives bond lengths and proposed bond orders where available. The enthalpy data, although sparse, gives an indication of the strength of these metal-metal bonds. A comparison with bond strengths in the bulk metal or suggested bond strengths in metal carbonyl systems (Chapter Four) lends support to the possible multiple bond character of the M_2 molecules.

Figure 5.2 σ-, π-, and δ-components of metal-metal quadruple bond.

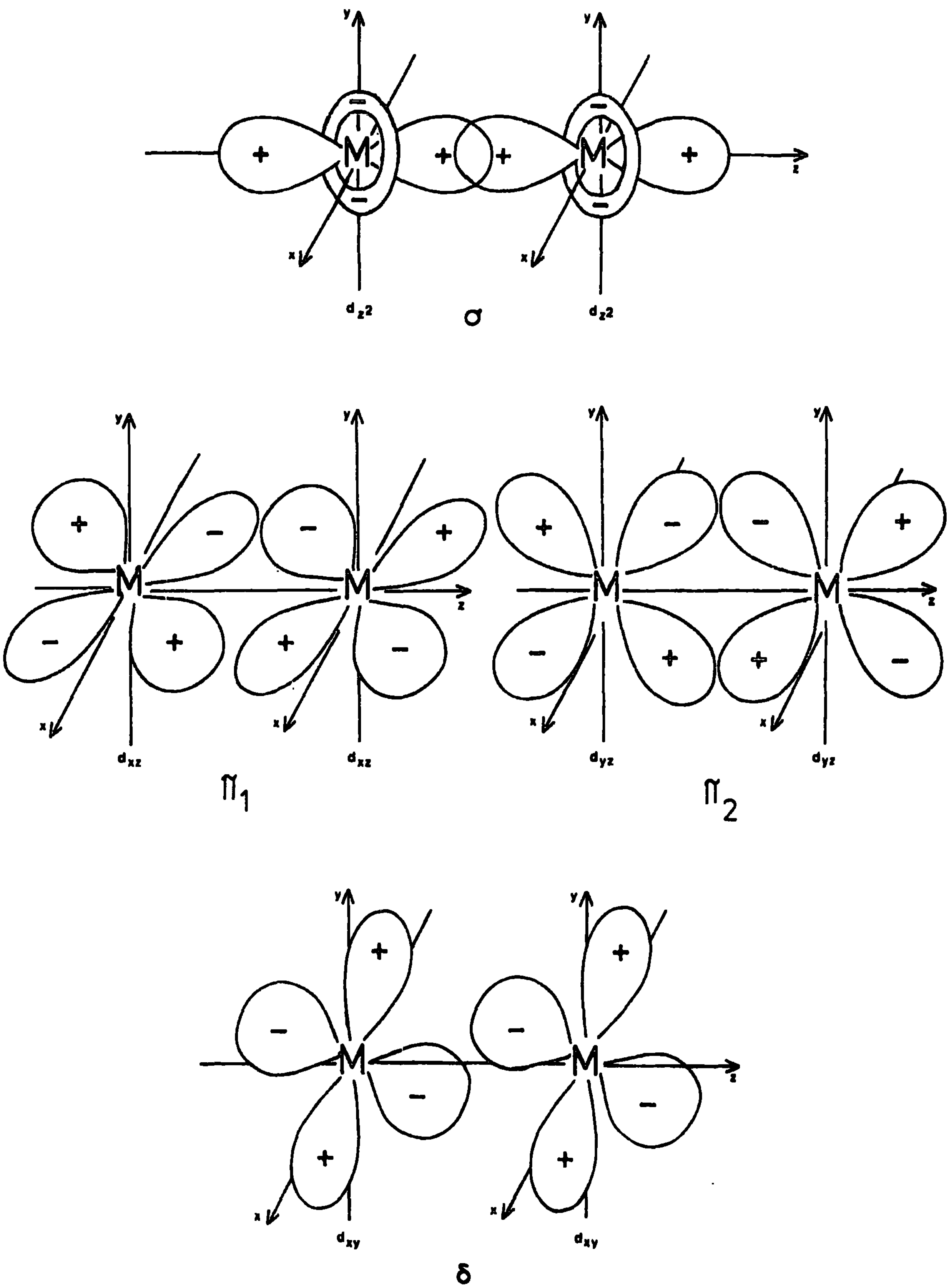


TABLE 5.2 Thermochemical and Structural Data for Some Diatomic, M_2, Molecules

Diatomic (gaseous)	D_o(M-M) † kJ mol^{-1}	d(M-M) pm	Suggested n(M-M)	Ref.
V_2	240-295	232	-	290
	241			289
Cr_2	154	-	-	288
	151(30)			289
	184			1
Mo_2	328	210*	> 4	287,288
	406(20)		6	289
Rh_2	271(1)	-	-	291
	274(25)			292

* Calculated value

† Errors given where available

Attempts have been made to estimate the metal-metal bond enthalpy contributions in the metal halide ions $Mo_2Cl_8^{4-}$ and $Re_2X_8^{2-}$ (X = Cl or Br), (Figure 5.1a). A semiquantitative indication of the strengths of the metal-metal bonds in these anions has been given from force constant data. Force constants of 3.0-4.5 mdyn $Å^{-1}$ for these Re-Re and Mo-Mo bonds were estimated, compared to values of ca. 1.0 mdyn $Å^{-1}$ for the corresponding single bonds. Hence, strong metal-metal bonds of order 3 to 4 were proposed for the $M_2X_8^{x-}$ anions. Strong σ- and π-components and a weaker δ-component were suggested.[293] A total energy of E(Re■Re) = 1530 kJ mol^{-1} has been suggested from MO calculations for the bond in $Re_2Cl_8^{2-}$; estimated component energies were $E_\sigma \approx 360$, $\Sigma E_\pi \approx 960$, and $E_\delta \approx 210$ kJ mol^{-1}.[294] However, the photochemical cleavage of $Re_2Cl_8^{2-}$ gives results indicating that the upper limit for the rhenium-rhenium bond enthalpy is ca. 540 kJ mol^{-1}.[295] Application of the Birge-Sponer extrapolation using electronic spectral data (Chapter One, Section 1.1) has provided estimates of E(Re⊟Re) and E(Mo⊟Mo) of ca. 480-540 and 460-670 kJ mol^{-1} respectively in $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$ and $Mo_2Cl_8^{4-}$.[296] However, bond dissociation energies measured by this method are typically ca. 20% too high and allowance for this has been made in a recent paper.[297] Values of E(Re⊟Re) and E(Mo⊟Mo) are both reduced to ca. 500 kJ mol^{-1}. Finally, molecular orbital calculations for $Mo_2Cl_8^{4-}$ suggest a value of E(Mo⊟Mo) ≈ 1245 kJ mol^{-1} with component energies $E_\sigma \approx 250$, $\Sigma E_\pi \approx 780$ and $E_\delta \approx 215$ kJ mol^{-1} [298]; the latter value shows a striking agreement with the previous value of $E_\delta(Re_2Cl_8^{2-}) \approx 210$ kJ mol^{-1}.[294] The overall picture for quadruple metal-metal bond energies estimated either by spectroscopic methods or *ab initio* MO calculations therefore appears far from satisfactory with values for E(M⊟M) ranging from 480 to 1530 kJ mol^{-1} for M = Re and from 460 to 1245 kJ mol^{-1} for M = Mo.

Actual thermochemical investigations of compounds containing multiple metal-metal bonds are confined mainly to the hexa(dimethylamino)-tungsten and -molybdenum derivatives, although the standard enthalpy of formation of <u>crystalline</u> tetraacetatodimolybdenum(II), $Mo_2(O_2CMe)_4$, has been determined as -1977(9) kJ mol^{-1} and a molybdenum-molybdenum bond enthalpy of ca. 500 kJ mol^{-1} suggested.[299] Values of $\Delta H^o_{f298}Mo_2(NMe_2)_6(g) = 128.2$ kJ mol^{-1} and $\Delta H^o_{f298}W_2(NMe_2)_6(g) = 132.5$ kJ mol^{-1} have recently been measured.[300] In order to calculate metal-metal bond enthalpy terms in these compounds, it is assumed that values of D(M — NMe_2) are transferable from the mononuclear species $Mo(NMe_2)_4$ and $W(NMe_2)_6$. However, because of the differences in oxidation state of the metal in going from mononuclear to dinuclear species and since D(M-NMe_2) varies with oxidation state, the estimated values of M-M bond energies are subject to a large degree of uncertainty: E(Mo≡Mo) = 592(196) kJ mol^{-1} and E(W≡W) = 775(218) kJ mol^{-1}.[300]

In Chapter Four, metal-metal bond enthalpy contributions in some binary transition metal carbonyl systems were estimated using the empirical relationship:

$$E(M\text{-}M) = A[d(M\text{-}M)]^{-4.6} \qquad (5.1)$$

Since most of the compounds containing multiple metal-metal bonds have been structurally characterised by X-ray crystallography, it seems logical to use the accurately determined metal-metal bond lengths as a basis for suggesting a self-consistent set of bond energy terms using equation 5.1. Such a possibility is explored in this Chapter.

5.2 Bond Length-Based Enthalpies for Multiple Metal-Metal Bonds

In Chapter Four the strength and corresponding length of a bond in the bulk metal were used as the basis for estimating bond enthalpy contributions in metal carbonyls using equation 5.1; (for the derivation of this equation, see Section 4.2). In a close packed metal lattice, the bonds are essentially half-bonds and in the carbonyls $M_x(CO)_y$, the metal-metal links are again relatively weak and of low bond order. The extrapolation of empirical correlations from bonds of order 1 to 3 appears to be realistic for a range of main group systems, (see Chapter Two). It therefore seems feasible to attempt an extrapolation of equation 5.1 over a range of metal-metal bonds of formal bond orders $\frac{1}{2}$ to 4.

Values of the constant, A, in equation 5.1 are first calculated for each metal involved in multiple bonding, (i.e. V, Cr, Mo, W, Re, Tc, Rh), using the length and strength of the M-M bond in the metals themselves, (Table 5.3). Using these values, bond energy contributions for metal-metal multiple bonds may be determined for a variety of complexes which have been structurally characterised. Table 5.4 lists a range of examples and compares the proposed values of E(M-M) with previous estimates. Besides triple and quadruple bonds, Table 5.4 also includes two metal-metal links which are formally double bonds. In all cases the suggested values of the multiple metal-metal bond strengths are considerably lower than previous methods have implied.

The major differences between systems containing multiple metal-metal bonds (excluding diatomic molecules) and metal carbonyl species are:

(a) The systems containing multiple bonds are more complex.
(b) In some cases the coordination number of the multiply bonded metal is greater than in the metal carbonyl compounds.
(c) The metal atoms involved in multiple bonding are not in zero oxidation state.
(d) Many systems containing triple or quadruple bonds are ionic.

It is perhaps not surprising therefore that direct application of equation 5.1 to multiple metal-metal bonds does not seem to be appropriate.

TABLE 5.3 Thermochemical and Structural Data For Some Bulk Metals

Metal	Structure	$\Delta H_{disrupt.}$ [3,178*] kJ mol^{-1}	E(M-M)[*†] kJ mol^{-1}	d(M-M)[187*] pm	Calc.A x 10^{13}
V	b.c.c.	514.6	92.7	261.8	1.230
Cr	b.c.c.[**]	397.5	71.6	249.8	0.766
Mo	b.c.c.	656.9	118.4	272.5	1.888
W	b.c.c.	853.5	153.8	274.1	2.519
Re	c.p.	775.7	129.3	274.1	2.118
Tc	c.p.	695.0	115.8	268.0	1.711
Rh	c.p.	557.3	92.9	269.0	1.396

* Mean e.s.d. in $\Delta H_{disrupt.}$ $\approx$5-10 kJ mol^{-1}, therefore mean e.s.d. in E(M-M) $\leqslant$1 kJ mol^{-1}; mean e.s.d. in d(M-M) $\leqslant$1 pm

† $E(M\text{-}M)_{c.p.} = \Delta H_{disrupt.}/6$; $E(M\text{-}M)_{b.c.c.} = \Delta H_{disrupt.}/5.55$

** Chromium is body centred cubic below 1840°C.

Compound	Proposed Multiplicity (n) of M-M Bond	d(M-M)† pm	E(M-M)* kJ mol^{-1}	Previous Estimates of E(M-M) (kJ mol^{-1}) and Method**
$(\eta^5\text{-}C_5H_5)(OC)_3V\text{-}V(CO)_2(\eta^5\text{-}C_5H_5)$	1<n<3	246.2(2)[301,302]	123.0	-
$V_2(DMP)_4$	3	220.0(2)	206.4	-
$Cr_2(O_2CMe)_4.2H_2O$	4	236.2(1)	92.6	-
$Cr_2(O_2CMe)_4$.(anhyd.)	4	228.8(2)	107.3	-
$Cr_2Me_8{}^{4-}$ in $Li_4Cr_2Me_8.4THF$	4	198.0(5)	208.7	-
$Cr_2(TMP)_4$	4	184.9(2)	286.0	-
$Cr_2(DMP)_4$	4	184.7(1)	287.4	-
$Mo_2(NMe_2)_6$	3	221.4(2)	307.7	592(196) ; T[300]
$Mo_2Cl_8{}^{4-}$ in $K_4Mo_2Cl_8.2H_2O$	4	213.9(4)	360.6	460-670 ; B[296] (ca.500 for $Mo_2Br_8{}^{4-}$) ; B[297]
$Mo_2(O_2CMe)_4$	4	209.34(8)	398.2	-
$Mo_2(PhNNNPh)_4$	4	208.3(2)	407.4	-
$Mo_2(DMP)_4$	4	206.4(1)	424.9	-
$Cs_3W_2Cl_9$	3	240.9(2)	278.5	648.5 ; MO [267,304]
$W_2(C_8H_8)_3$	3	237.5(1)	297.3	-

Compound	Proposed Multiplicity (n) of M-M Bond	d(M-M)† pm	E(M-M)* $kJ\ mol^{-1}$	Previous Estimates of E(M-M) ($kJ\ mol^{-1}$) and Method**
$W_2(NMe_2)_6$	3	229.4(1)	348.7	775(218) ; T [300]
$W_2Me_8^{4-}$ in $Li_4W_2Me_8 \cdot 4Et_2O$	4	226.4(1)	370.5	-
Re_3Cl_9	2	246(1)[303]	212.6	357 ; T [305] 427 ; MO[305]
$Re_2Cl_8^{2-}$ in $K_2Re_2Cl_8 \cdot 2H_2O$	4	224.1(7)	326.5	1530 ; MO[294] <540 ; P[295] 480-540 ; B[296]
$Re_2(piv)_2Cl_2$	4	220.9(2)	348.8	-
$Tc_2(piv)_4Cl_2$	4	219.2(2)	292.0	-
$K_3Tc_2Cl_8 \cdot nH_2O$	4	211.7(2)	342.7	-
$Rh_2(O_2CMe)_4 \cdot 2H_2O$	4	238.55(5)	161.4	-

† Structural references are only given for compounds not included in Table 5.1.

*Mean e.s.d. in E(M-M) ≤1 $kJ\ mol^{-1}$

**Method of measurement:
T = Thermochemical ; transferability of M-ligand enthalpies from mononuclear to polynuclear derivatives
MO = Molecular orbital calculations
B = Birge-Sponer extrapolation using electronic spectroscopic data
P = Photochemical cleavage of M-M bond

5.3 Conclusion

An empirical bond enthalpy-bond length relationship which uses as a basis the bonds in the bulk metal itself does not seem appropriate when applied to triple and quadruple metal-metal bonds in complexes of the type $M_2X_8^{x-}$ (x=2 or 4), $M_2X_9^{3-}$ (X = halogen), or M_2L_4 (L = bidentate ligand). The enthalpies suggested by such an approach appear to be greatly underestimated when compared to literature data. It is therefore concluded that the proposed multiple metal-metal bond energies be used only as an indication of lower limiting values. Upper limiting values are given by dissociation energies obtained from spectroscopic methods and MO calculations, (see Table 5.4).

CHAPTER SIX

SKELETAL ELECTRON COUNTING IN CLUSTERS: CLASSIFICATION OF SOME MAIN GROUP, TRANSITION METAL AND HYDROCARBON SYSTEMS

6.1 Introduction: Rules for Skeletal Electron Counting

The close structural relationship between boranes, carboranes and some transition metal structures was noted at the beginning of this decade.[75-78] Previously, the structures of the boranes and carboranes had been characterised as icosahedral fragments, (pentaborane-9 (B_5H_9) being the only exception).[129] Bonding within the borane skeletons was described in terms of 2- and 3-centre electron pair links,[129] (see Chapter Three). However, the structural characterisation of the series of $B_nH_n^{2-}$ anions ($6 \leq n \leq 12$) showed that the structures of other known boranes and carboranes could be rationalised in terms of the closo-triangular-faced polyhedra listed in Table 6.1 and illustrated in Figure 6.1.[76] This qualitative idea was developed to give a set of simple electron counting rules which enabled clusters to be classified according to the number of skeletal bonding pairs of electrons which they possessed.[75,77,78]

The concepts involved in skeletal electron counting schemes are explained in detail in several review articles.[79-82] Using molecular orbital treatments,[129,306] the closo-polyhedra shown in Figure 6.1 can be shown to be appropriate structural units for n skeletal atoms contributing (n+1) skeletal bonding pairs of electrons. The four main classes of cluster species are the closo-, nido-, arachno- and hypho-structures. These are defined as:

TABLE 6.1 Closo-Polyhedra with n vertices

n	Polyhedron	Figure
[5	Trigonal bipyramid	6.1a] *
6	Octahedron	6.1b
7	Pentagonal bipyramid	6.1c
8	Dodecahedron	6.1d
9	Tricapped trigonal prism	6.1e
10	Bicapped Archimedean antiprism	6.1f
11	Octadecahedron	6.1g
12	Icosahedron	6.1h

* Closo-polyhedron for n=5 is included for completeness although $B_5H_5^{2-}$ has not been isolated.

closo: a complete polyhedron of n atoms which contribute (n+1) skeletal bonding pairs of electrons.

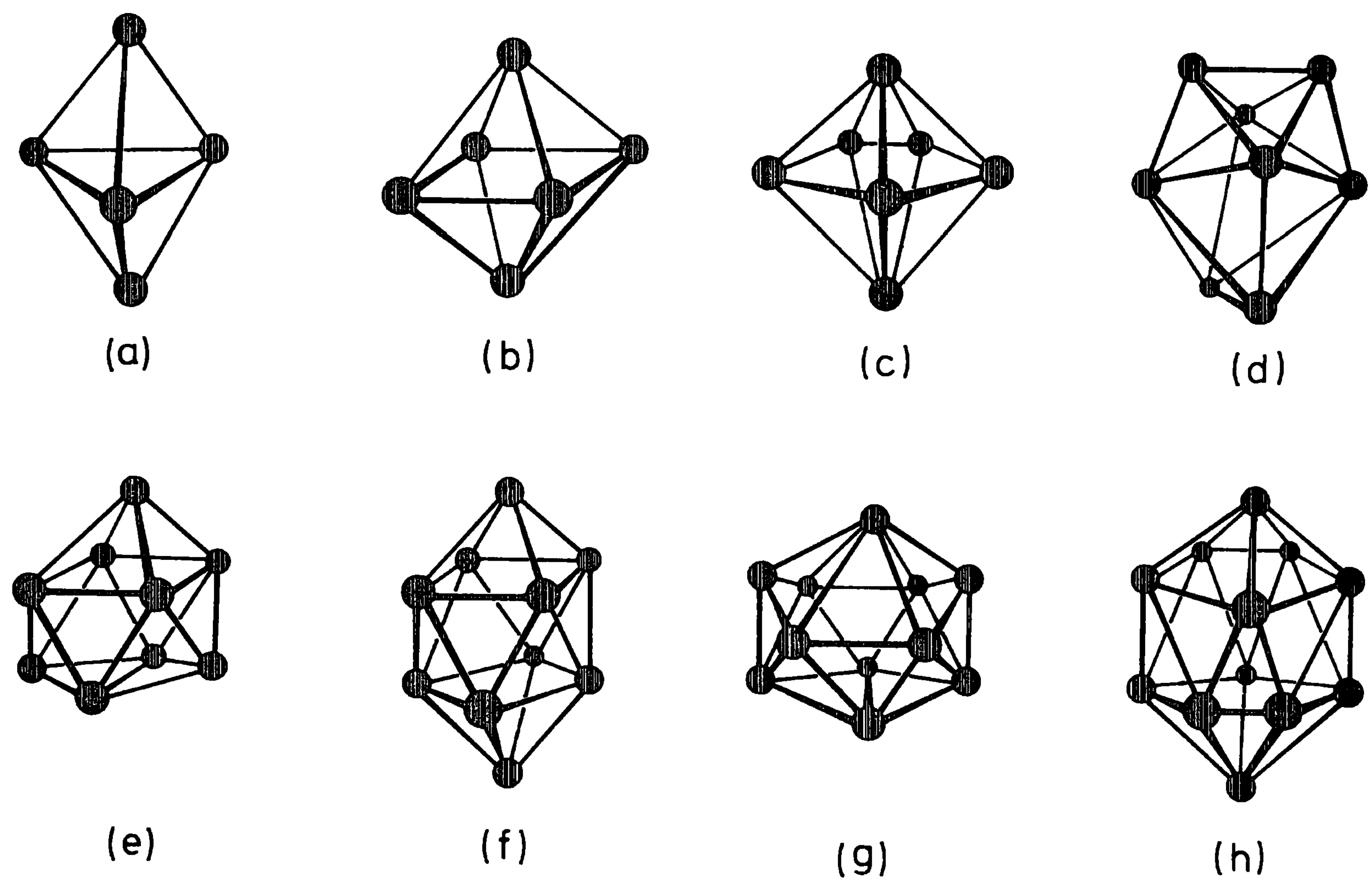
nido: n atoms defining a polyhedron with one vacant site and having (n+2) skeletal bonding pairs.

arachno: n atoms defining a polyhedron with 2 vacant sites and contributing (n+3) skeletal electron pairs.

hypho: n atoms defining a polyhedron with 3 vacant sites and having (n+4) skeletal bonding pairs of electrons.

In addition to providing a rationale for the structures of borane, carborane and some transition metal clusters, the skeletal electron counting method gives an indication of .

Figure 6.1 Closo-polyhedra with n vertices: $5 \leq n \leq 12$

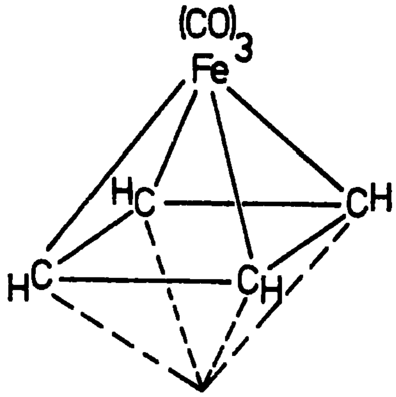


possible new synthetic routes; (e.g. oxidative removal of 2 electrons from a nido-species should produce a closo-species).[307]

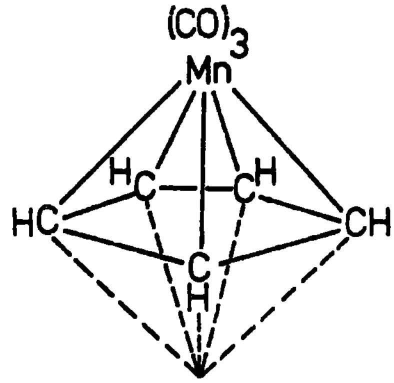
A number of transition metal π-hydrocarbon systems and cyclic hydrocarbon systems have now been classified according to the number of skeletal pairs of electrons which they possess. For instance π-cyclobutadiene-iron-tricarbonyl, $(\pi\text{-}C_4H_4)Fe(CO)_3$, cyclopentadienyl-manganese-tricarbonyl, $(\pi\text{-}C_5H_5)Mn(CO)_3$, benzene chromium tricarbonyl, $(\pi\text{-}C_6H_6)Cr(CO)_3$ and π-cycloheptatrienyl-vanadium-tricarbonyl, $(\pi\text{-}C_7H_7)V(CO)_3$ are all nido-species based on the octahedron and the pentagonal, hexagonal and heptagonal bipyramids respectively, (Figure 6.2); (the hexagonal and heptagonal bipyramids are accepted as alternative 8- and 9-cornered polyhedra which are sometimes adopted in preference to the usual dodecahedron and tricapped trigonal prism).[308] The cyclic hydrocarbons $C_4H_4^{2-}$, $C_5H_5^-$, C_6H_6 and $C_7H_7^+$ are all arachno-species based on the octahedron and the pentagonal, hexagonal, and heptagonal bipyramids, (Figure 6.3).[79,309] The non-classical carbocations, $C_5H_5^+$ and $C_6Me_6^{2+}$ are nido-species based on the octahedron and pentagonal bipyramid, (Figure 6.4).[76,80-82]

The aim of this Chapter is to indicate the wide application of skeletal electron counting schemes, firstly by outlining new ideas for the classification of small cyclic hydrocarbons and secondly by surveying structural patterns in main group, transition metal, metal π-hydrocarbon and cyclic hydrocarbon systems. To facilitate this, Tables 6.2 and 6.3 list numbers of electron pairs provided by some common main group and transition metal skeletal units. (These Tables are based on ones found in references 79, 80 and 307).

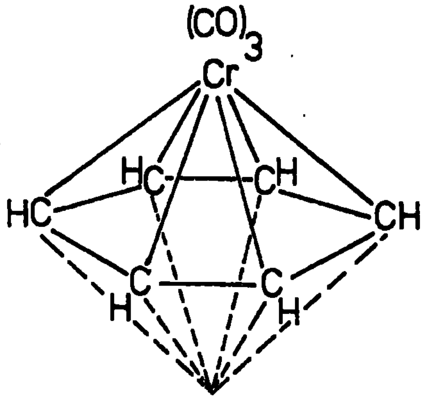
Figure 6.2 Some metal π-hydrocarbon systems as nido-clusters.



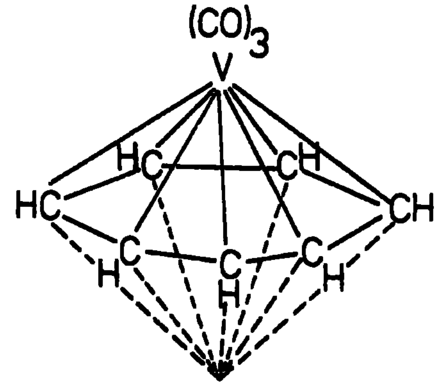
(π-C_4H_4)Fe$(CO)_3$



(π-C_5H_5)Mn$(CO)_3$

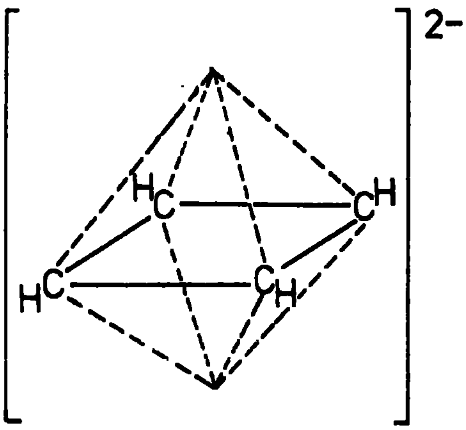


(π-C_6H_6)Cr$(CO)_3$

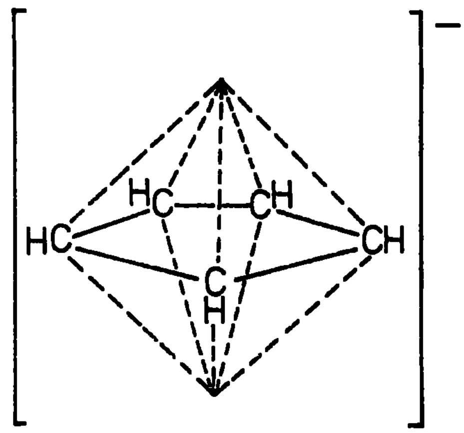


(π-C_7H_7)V$(CO)_3$

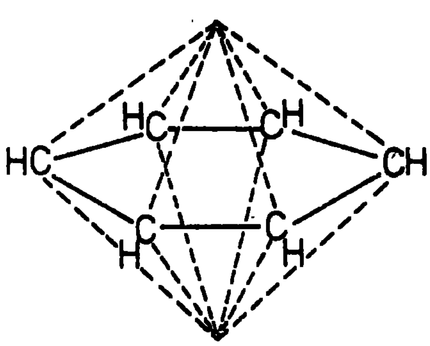
Figure 6.3 Some cyclic hydrocarbons as arachno-clusters.



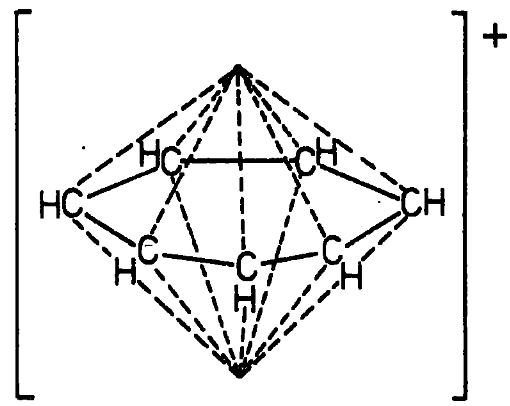
$C_4H_4^{2-}$



$C_5H_5^-$

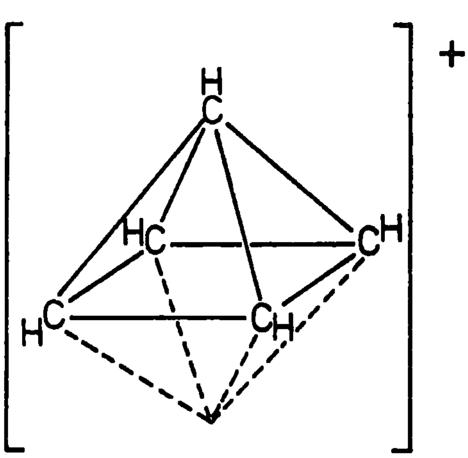


C_6H_6

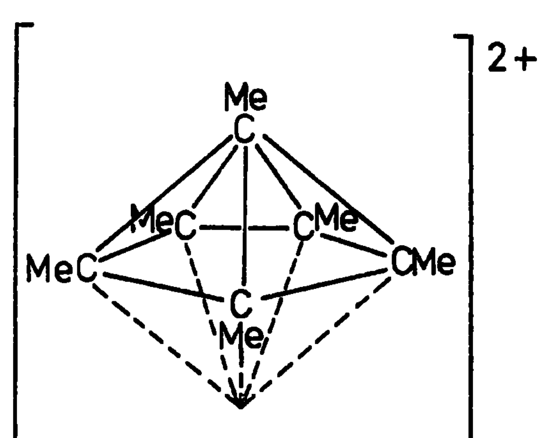


$C_7H_7^+$

Figure 6.4 Some non-classical carbocations as nido-clusters.



$C_5H_5^+$



$C_6Me_6^{2+}$

TABLE 6.2 Number of Skeletal Bonding Electrons (v+x-2) Provided by Some Main Group Cluster Units; (v = valence shell electrons of main group element, E; x = electrons donated by ligand).

v	Main Group Element (E)	Skeletal Cluster Unit: E (x=0)	EH; ER* (x=1)	EH_2; EL (x=2)
1	Li, Na	[-1]†	0	1
2	Be, Mg, Zn, Cd, Hg	0	1	2
3	B, Al, Ga, In, Tl	1	2	3
4	C, Si, Ge, Sn, Pb	2	3	4
5	N, P, As, Sb, Bi	3	4	5
6	O, S, Se, Te	4	5	6
7	F, Cl, Br, I	5	[6]†	[7]†

* R = alkyl or σ-bonded aryl group

† Cluster unit rarely found

TABLE 6.3 Number of Skeletal Bonding Electrons (v+x-12) Provided by Some Common Transition Metal Cluster Units; (v = valence shell electrons of metal, M; x = electrons provided by ligand).

v	Transition Metal (M)	Skeletal Cluster Unit				
		M(CO) $M(PPh_3)$ (x=2)	$M(CO)_2$ $M(PPh_3)_2$ (x=4)	$M(\eta^5\text{-}Cp)$ (x=5)	$M(CO)_3$ $M(PPh_3)_3$ (x=6)	$M(CO)_4$ $M(PPh_3)_4$ (x=8)
6	Cr, Mo, W	[-4]†	[-2]†	-1	0	2
7	Mn, Tc, Re	[-3]†	-1	0	1	3
8	Fe, Ru, Os	-2	0	1	2	4
9	Co, Rh, Ir	-1	1	2	3	5
10	Ni, Pd, Pt	0	2	3	4	6

† Cluster unit rarely found

6.2 Cyclic Hydrocarbons as Cluster Species: Two New Cluster Types

The manner in which the structures of some hydrocarbon systems resemble borane, carborane and some transition metal π-hydrocarbon species has already been noted in the previous Section: the electron rich aromatic ring systems $C_4H_4^{2-}$, $C_5H_5^-$, C_6H_6, $C_7H_7^+$ and $C_8H_8^{2+}$ may be classed as arachno-cluster species,[79,309] and the carbocations $C_5H_5^+$ and $C_6Me_6^{2+}$, (the pyramidal structures of which have been proposed from theoretical investigations and n.m.r. spectroscopic data[310-318]), may be considered as nido-species structurally analogous to B_5H_9 and B_6H_{10}.[80, 81, 319, 320] Further to these, benzvalene (and hence the recently trapped isomer, isobenzvalene[321]) are 9 electron pair systems, the structures of which are derived from the dodecahedron with 2 vacant sites,[80] (Figure 6.6f). Cyclopropane (C_3H_6) and the cyclopropylcation ($C_3H_7^+$) are arachno-species based on the trigonal bipyramid,[81] (Figure 6.6a). Despite the recognition of these few hydrocarbons as members of the structural groups to which boranes and carboranes belong, it is by no means appreciated that many other cyclic hydrocarbons adopt structures clearly related to triangular-faced polyhedral skeletons.

There is a wide range of small cyclic hydrocarbons containing between 3 and 7 skeletal carbon atoms. Each CH or CR unit is capable of providing 3 skeletal electrons, each CH_2 or CR_2 unit 4 skeletal electrons, and each CH_3 unit 5 electrons, (see Table 6.2). Extra electrons are provided by any additional H atoms or overall negative charges. Hence, bicyclo[1.1.0]butane,[324] C_4H_6, (Figure 6.6c) comprises 2 CH_2 and 2 CH units and is thus a 7 electron pair system analogous to B_4H_{10}. It adopts a 'butterfly' configuration which is derived from the octahedron. A variety of cyclic hydrocarbons is surveyed in Tables 6.4 to 6.7. The number of skeletal atoms (n), the number of skeletal bonding pairs of electrons (s), and the parent polyhedron for each system are listed. The same hydrocarbons are illustrated in Figures 6.5 - 6.8. Some systems have already been mentioned; many are classified as cluster species for the first time.

Table 6.4 and Figure 6.5 list nido-cluster species. The only new member of this series is tetrahedrane. The ^{t}butyl-derivative ($^{t}Bu_4C_4$) has recently been synthesised and its tetrahedral structure is supported by spectroscopic data.[322]

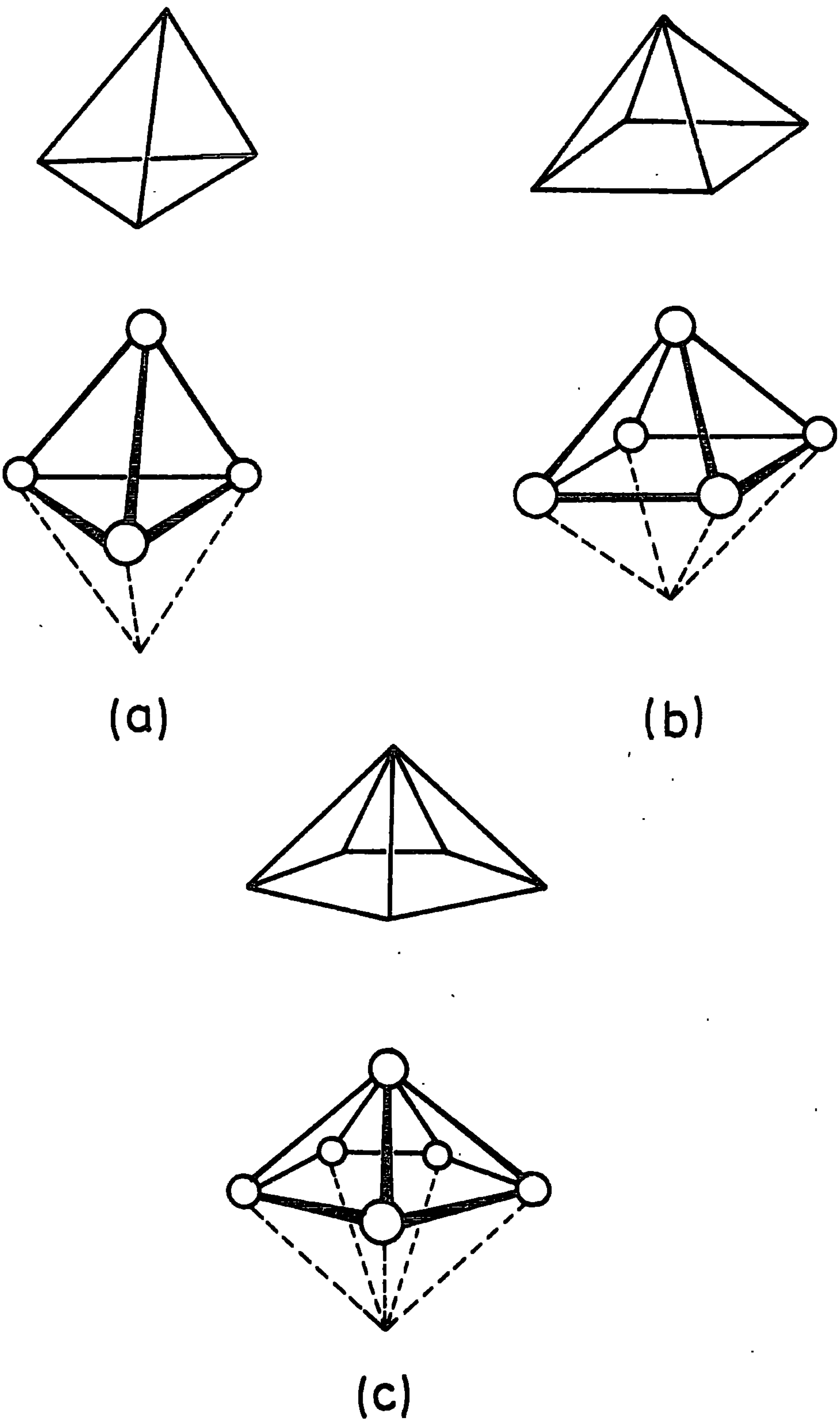
Table 6.5 and Figure 6.6 give arachno-cluster systems. New members of this series are bicyclo[1.1.0]butane[324], and the hexamethylbicyclo[2.1.1]hexenyl cation.[315,319] The structure of this non-classical carbocation has been proposed on the basis of ^{1}H and ^{13}C n.m.r. spectroscopic data, and it has been concluded that the apical atom (C_6 in Figure 6.6g) will be positively charged relative to the remaining carbon atoms. If an analogy is drawn between the closo-borane anion $B_8H_8^{2-}$ and the arachno-carbocation $C_6Me_6H^+$, it is predicted that atom C_6, (which occupies a high coordination site on the dodecahedral skeleton), does indeed have a lesser share of the electron distribution than do atoms occupying sites of low coordination number, (Chapter Three, Section 3.5).

Tables 6.6 and Figure 6.7 list hypho-cluster species, none of which has previously been recognised as having a structure relatable to a closo-polyhedral skeleton. The puckered rings of cyclopentene[334] and bicyclo[2.1.0]pentane[335,336] are clearly defined in the skeleton of the dodecahedron, (Figures 6.7c and 6.7d). Perhaps the most striking result

TABLE 6.4 Cyclic Hydrocarbons as Nido-Species; (see Figure 6.5)

Species	Formula	n	s	Parent Polyhedron	Figure
Tetrahedrane [322]	C_4H_4	4	6	Trigonal bipyramid	6.5a
Cyclopentadienyl cation [310-314]	$C_5H_5^+$	5	7	Octahedron	6.5b
Hexamethylbenzene dication [315-318]	$C_6Me_6^{2+}$	6	8	Pentagonal bipyramid	6.5c

Figure 6.5 Cyclic hydrocarbons as nido-species.

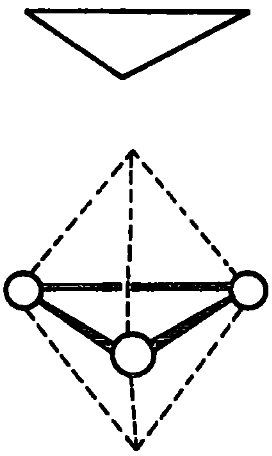


(a) (b) (c)

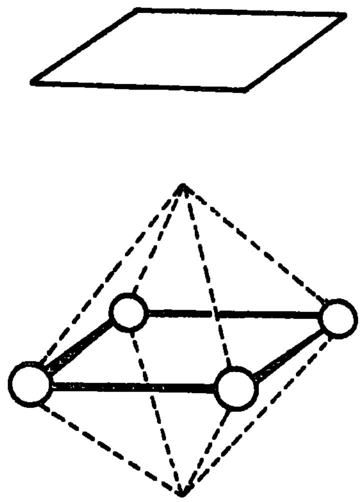
TABLE 6.5 Cyclic Hydrocarbons as Arachno-Species; (see Figure 6.6)

Species	Formula	n	s	Parent Polyhedron	Figure
Cyclopropane	C_3H_6	3	6	Trigonal bipyramid	6.6a
Cyclopropyl cation [323]	$C_3H_7^+$	3	6	Trigonal bipyramid	6.6a
Cyclobutadiene dianion	$C_4H_4^{2-}$	4	7	Octahedron	6.6b
Bicyclo[1.1.0]butane [324]	C_4H_6	4	7	Octahedron	6.6c
Cyclopentadienyl anion	$C_5H_5^-$	5	8	Pentagonal bipyramid	6.6d
Benzene	C_6H_6	6	9	Hexagonal bipyramid	6.6e
Benzvalene, Isobenzvalene [321]	C_6H_6	6	9	Dodecahedron	6.6f
Hexamethylbicyclo[2.1.1]hexenyl cation [315,319]	$C_6Me_6H^+$	6	9	Dodecahedron	6.6g
Cycloheptatrienyl cation	$C_7H_7^+$	7	10	Heptagonal bipyramid	6.6h
Cyclooctatetraenyl dication	$C_8H_8^{2+}$	8	11	Octagonal bipyramid	6.6i

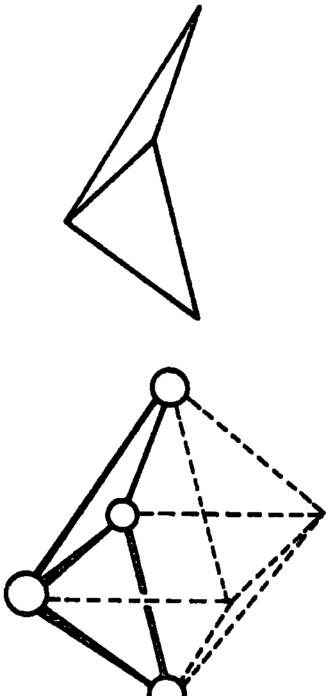
Figure 6.6 Cyclic hydrocarbons as arachno-species.



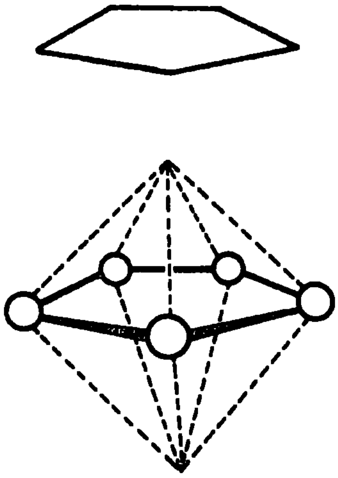
(a)



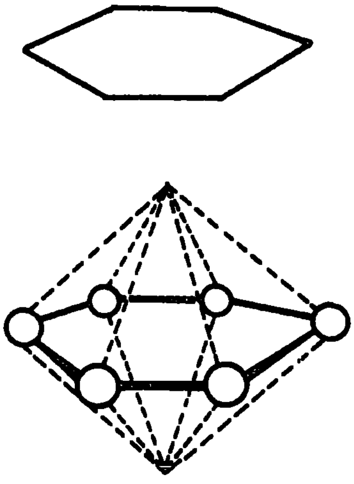
(b)



(c)

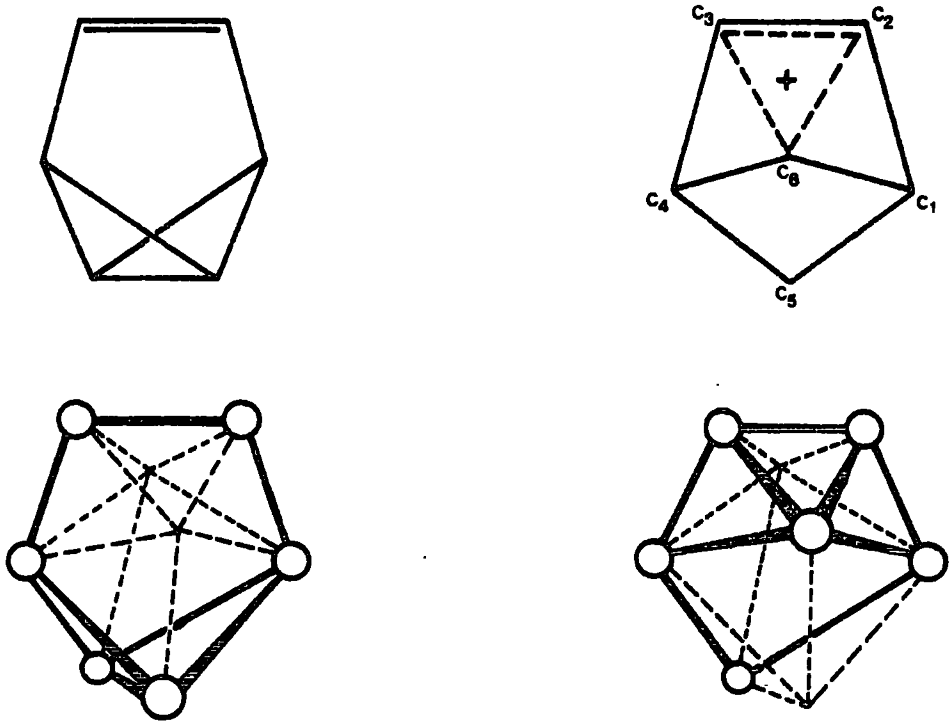


(d)

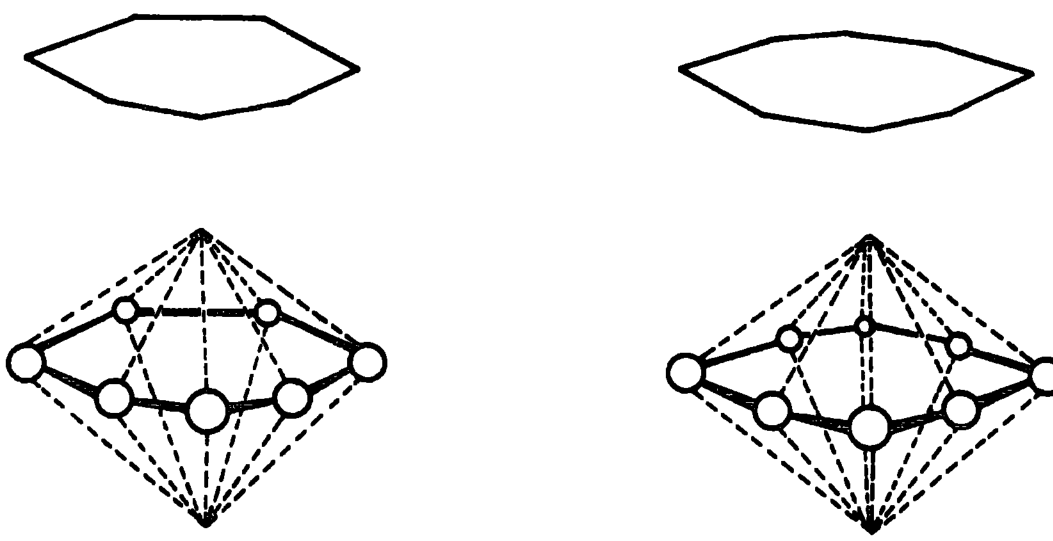


(e)

Figure 6.6 (contd.)



(f) (g)

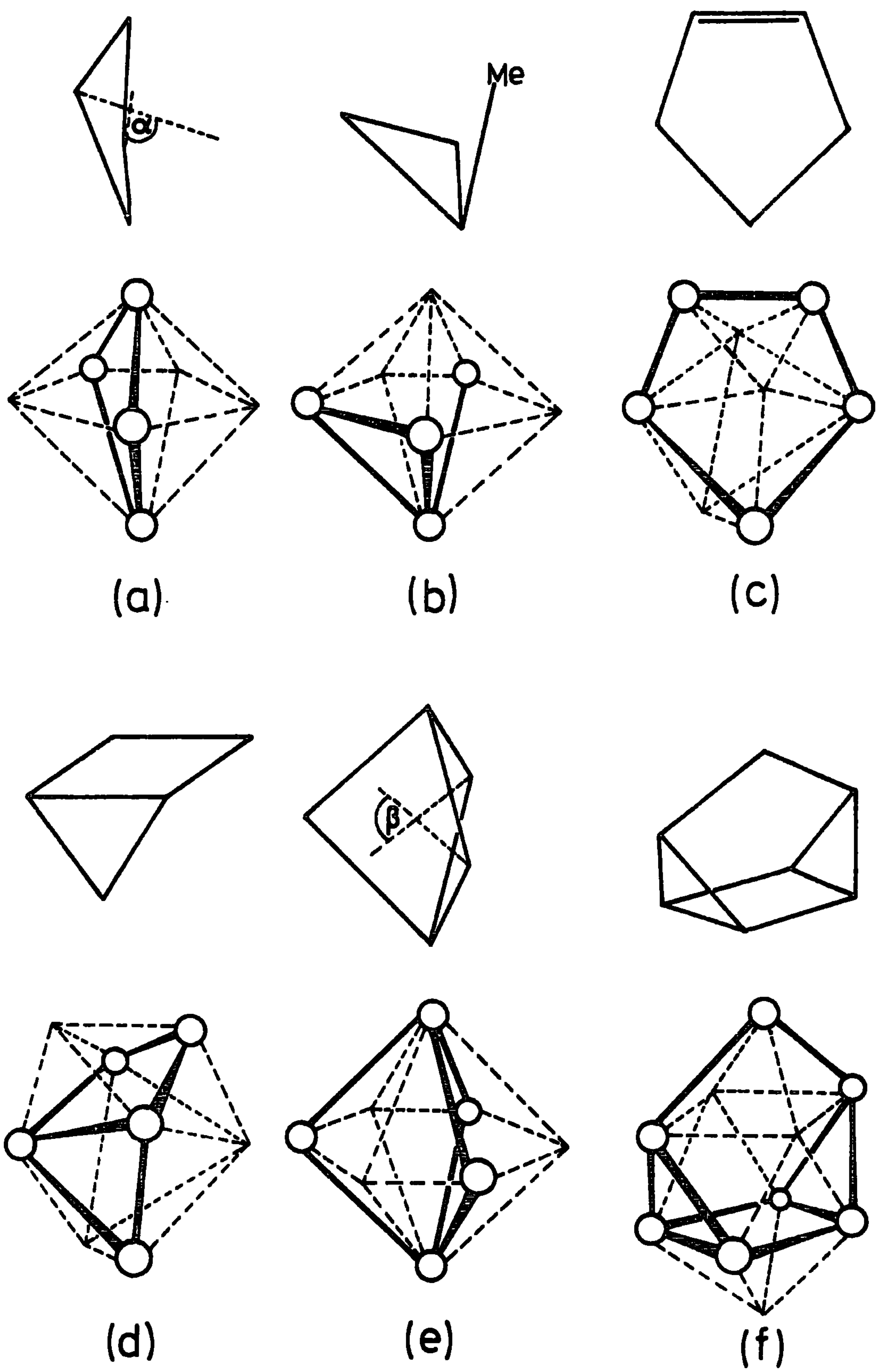


(h) (i)

TABLE 6.6 Cyclic Hydrocarbons as Hypho-Species; (see Figure 6.7)

Species	Formula	n	s	Parent Polyhedron	Figure
Cyclobutane [325-332]	C_4H_8	4	8	Pentagonal bipyramid	6.7a
Methyl-cyclopropane [333]	C_4H_8	4	8	Pentagonal bipyramid	6.7b
Cyclopentene [334]	C_5H_8	5	9	Dodecahedron	6.7c
Bicyclo[2.1.0]pentane [335,336]	C_5H_8	5	9	Dodecahedron	6.7d
Bicyclo[1.1.1]pentane [337,338]	C_5H_8	5	9	Hexagonal bipyramid	6.7e
Tetracyclo[3.2.0.0^{2,7}0^{4,6}]heptane [339] (Quadricyclane)	C_7H_8	7	11	Bicapped Archimedean Antiprism	6.7f

Figure 6.7 Cyclic hydrocarbons as hypho-species.



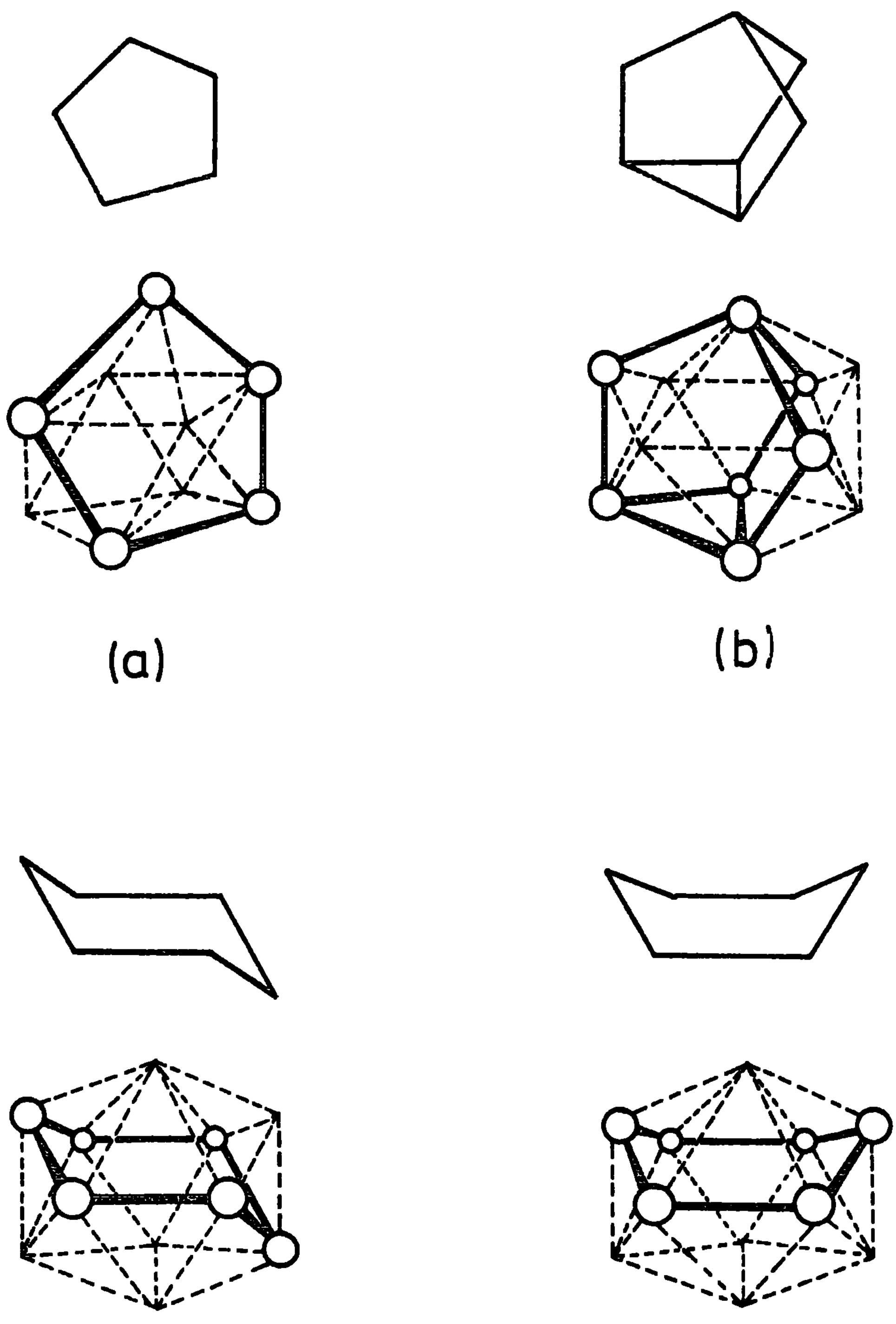
(a) (b) (c)

(d) (e) (f)

TABLE 6.7 Cyclic Hydrocarbons Derived from Closo-Polyhedra with More Than 3 Sites Vacant; (see Figure 6.8)

Species	Formula	n	s	Parent Polyhedron	Figure
Cyclopentane [340-342]	C_5H_{10}	5	10	Tricapped trigonal prism	6.8a
Tricyclo[2.2.1.$0^{2.6}$]heptane [343] (nortricyclene)	C_7H_{10}	7	12	Octadecahedron	6.8b
Cyclohexane: chair conformer	C_6H_{12}	6	12	Octadecahedron	6.8c
Cyclohexane: boat conformer	C_6H_{12}	6	12	Octadecahedron	6.8d

Figure 6.8 Cyclic hydrocarbons derived from closo-polyhedra with more than 3 sites vacant.



which emerges from this series is the excellent agreement between predicted and experimentally determined values of the dihedral angles in cyclobutane, (angle α in Figure 6.7a) and bicyclo[1.1.1]pentane, (angle β in Figure 6.7e). The folded ring of cyclobutane is constrained by the D_{5h} symmetry of the pentagonal bipyramid leading to a dihedral angle (α) of 36°, (cf. a literature value of ca. 35° [326-332]). It is predicted that bicyclo[1.1.1]pentane has a geometry imposed by the D_{6h} symmetry of the hexagonal bipyramid. This produces a dihedral angle (β) of 120° in perfect agreement with the measured value.[337]

Table 6.7 and Figure 6.8 list several cyclic hydrocarbon systems, the structures of which are derived from triangular-faced polyhedra with either 4 or 5 vacant skeletal sites. The puckered ring structure of cyclopentane may be derived from the 9-vertex tricapped trigonal prism, (Figure 6.8a). Both the boat and chair conformers of cyclohexane are clearly defined in the 11-vertex octadecahedron (Figures 6.8c and 6.8d), a feature which has previously been noted.[80] The complex ring system of nortricyclene can also be rationalised in terms of its relationship to the octadecahedron (Figure 6.8b) and is analogous to several main group species, e.g. Sb_7^{3-}, P_7^{3-}, Se_3As_4 (see Section 6.3).

The survey of cyclic hydrocarbons given in this Section is <u>not</u> comprehensive and it is anticipated that many more systems may have structures which are closely related to those of boranes and carboranes. It should be noted that skeletal electron counting cannot be used to rationalise the structures of <u>all</u> cyclic hydrocarbon systems, although several structures which at first appear to be unrelated to the appropriate triangular-faced parent polyhedron are worthy of further consideration.

For example, cubane (C_8H_8), as its name implies, has a cubic skeleton.[344] The 8 CH units provide 12 skeletal bonding pairs of electrons and a hypho-species based on the 11-vertex octadecahedron might therefore be predicted. This appears not to be the case. However, removal of the 6- and two 5-coordinate skeletal sites leaves a framework of atoms which easily rearrange (via the cleavage of 2 bonds and formation of 2 new bonds) to give the cubane structure containing 12 localised 2-centre C-C edge bonds. This feature is further noted in main group and transition metal chemistry (Section 6.3) and is illustrated in Figure 6.16.

It may be concluded therefore that the potential use of skeletal electron counting methods in hydrocarbon chemistry has been greatly underestimated and that in fact a large number of cyclic systems have structures which bear a close family relationship to boranes and carboranes. It is further suggested that two new cluster types be defined as follows:

<u>fisco</u>: n atoms defining a polyhedron with 4 sites vacant and having (n+5) pairs of skeletal bonding electrons.

<u>reticulo</u>: n atoms defining a polyhedron with 5 sites vacant and contributing (n+6) skeleton electron pairs.

(The suggested names 'fisco' and 'reticulo' are derived from the Latin for a 'basket' and a 'small net' respectively).

6.3 Cluster Patterns in Main Group, Transition Metal, Metal π-Hydrocarbon and Cyclic Hydrocarbon Systems

The number of cluster species which have been synthesised and structurally characterised over the last ten or twenty years is vast. No one review has yet brought together main group, transition metal, metal π-hydrocarbon and cyclic hydrocarbon systems as all possessing structures related to polyhedral skeletons. The primary aim of this Section is therefore to survey the large number of clusters now known in an attempt to show to what extent the same structural patterns hold for the different compounds. The survey is not exhaustive, its objective being to exemplify each class of cluster for a given polyhedron rather than to classify all cluster species. (For instance there are numerous tetrahedral cluster compounds which have not been included in this Chapter; an excellent review of tetranuclear species can be found in reference 345. Further reviews of cluster structures may be found in references 80, 81, 346 and 347).

The data are arranged in tabular form according to the numbers of skeletal electron pairs (s) and parent polyhedra, (Tables 6.8 to 6.16). Each Table is followed by a corresponding Figure illustrating the structural types which may be derived from a particular polyhedron, (Figures 6.9 to 6.17). Points of interest arising from each Table are discussed in separate sub-sections.

6.3.1 Systems with 6 Skeletal Bonding Pairs of Electrons

For systems contributing 6 skeletal electron pairs, there exists an additional category of structure: the capped-closo cluster, i.e. a capped trigonal bipyramid. Here, the 6 skeletal bond pairs hold together 6 skeletal atoms. The capping metal atom uses its 3 vacant orbitals to bond to the 3 metal atoms of a triangular polyhedral face without modifying the bonding MO's in the rest of the cluster.[80] $Os_6(CO)_{18}$ exemplifies this particular cluster type.

Nido-species with 6 skeletal bond pairs are tetrahedral in shape. A wide variety of such structures is found in transition metal compounds and only a few have been selected to represent this group in Table 6.8. Similarly, triangular clusters of metal atoms are common. It is interesting that both equilateral and isosceles triangles can be accommodated in the trigonal bipyramidal framework, (Figures 6.9d and 6.9e).

TABLE 6.8 Systems with s=6 Based on the Trigonal Bipyramid; (Figure 6.9)

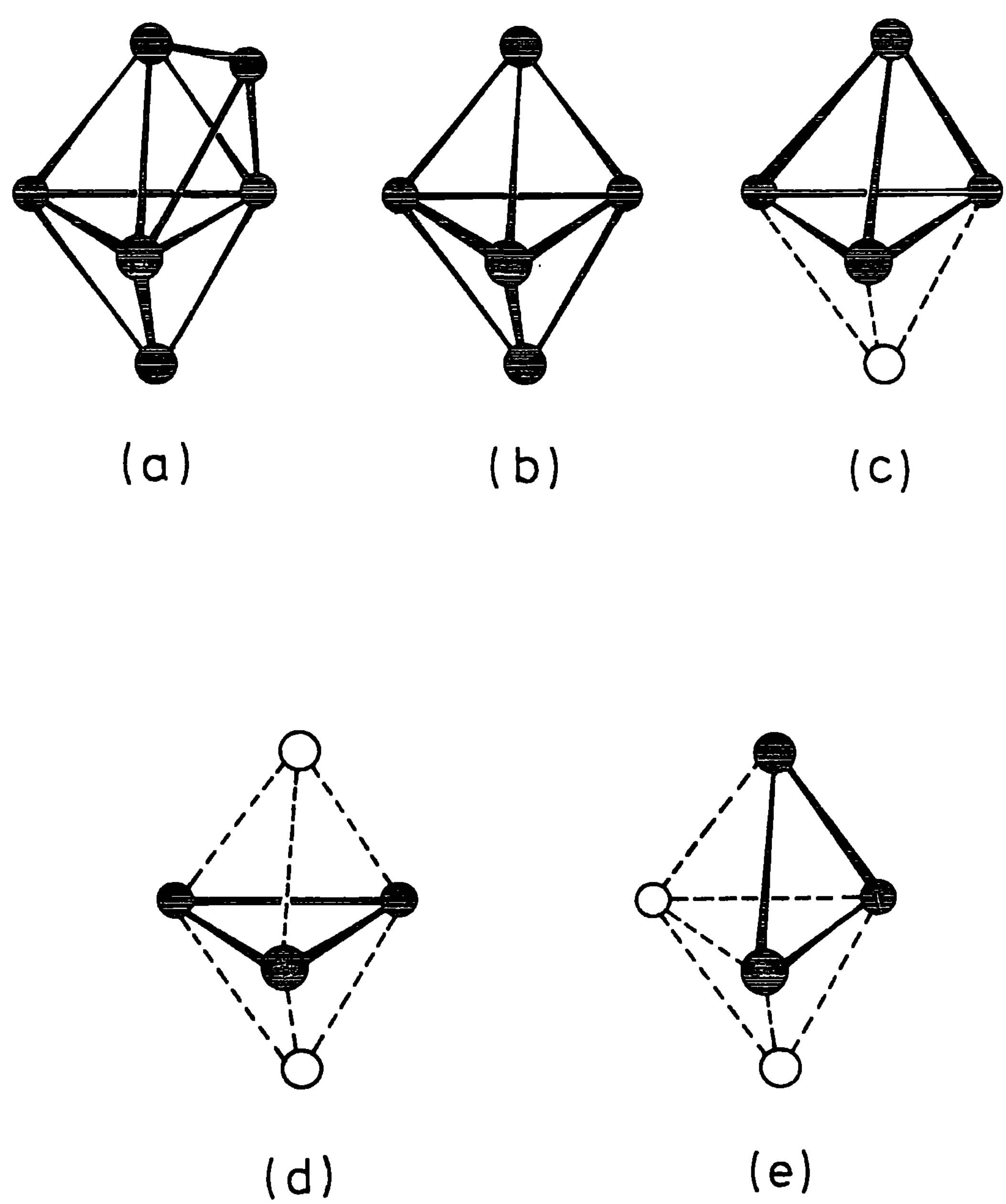
Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
6	Capped-closo	6.9a	$Os_6(CO)_{18}$	231
5	Closo	6.9b	$Os_5(CO)_{16}$	230
			$HOs_5(CO)_{15}^-$	348,349
			$Fe_3(CO)_9(RC{\equiv}CR)$	350
			Bi_5^{3+}	351
			Sn_5^{2-}; Pb_5^{2-}	352,353
			$B_5H_5^-$	351
			$C_2B_3H_5$	354
* 4	Nido	6.9c	$H_4Ru_4(CO)_{12}$	355
			$Rh_4(CO)_{12}$	189,190
			$H_2Ir_4(CO)_{10}^{2-}$	356
			$H_6Re_4(CO)_{12}^{2-}$	357
			$H_2Os_4(CO)_{12}^{2-}$	358
			$H_2Os_3(CO)_9S$	359
			$Co_3(CO)_9CR$	360
			$H_3CoOs(CO)_{12}$	361
			$Co(CO)_3C_3Ph_3$	362
			$[(\pi\text{-}C_5H_5)W(CO)_2]_2(HC{\equiv}CH)$	363
			$(\pi\text{-}C_5H_5)Rh_2Fe_2(CO)_8$	364,365
			$Fe_2(CO)_6B_2H_6$	366
			$^tBu_4C_4$	322
			P_4	-

TABLE 6.8 (Continued)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
* 3	Arachno	6.9d	$Ru_3(CO)_{12}$	212
			$Os_3(CO)_{12}$	213
			$[(\pi\text{-}C_5H_5)Rh(CO)]_3$	367
			C_3H_6	81
			$C_3H_7^+$	81,323
3	Arachno	6.9e	$Fe_3(CO)_{12}$	192
			$H_2Os_3(CO)_{10}$	368,369
			$H_2Re_3(CO)_{12}^-$	370
			$B_3H_8^-$	371

* A few typical examples have been selected from the wide range of tetra- and trinuclear cluster species with s=6 which are known.

Figure 6.9 Systems with s=6 based on the trigonal bipyramid.



6.3.2 Systems with 7 Skeletal Bonding Pairs of Electrons

As was the case for s=6, capped-closo structures are also found for some systems with s=7, i.e. 7 pairs of skeletal electrons hold together 7 atoms in a capped-octahedral arrangement, (e.g. $Os_7(CO)_{21}$, $Rh_7(CO)_{16}^{3-}$ and $Rh_7(CO)_{16}I^{2-}$).

Numerous closo-octahedral clusters have been characterised. Examples in Table 6.9 include transition metal, main group, and organometallic compounds. A second closo-species with s=7 is noted: the capped-square based pyramid. Although of lower symmetry than the octahedron, the capped-pyramid is found to be the preferred structure for $H_2Os_6(CO)_{18}$ and $Os_6(CO)_{16}(CPh)_2$.

Over the past few years several square planar Group VI cations have been synthesised and characterised. The structures of S_4^{2+}, Se_4^{2+}, Te_4^{2+} and $[Te_4Se_{4-n}]^{2+}$ (n=1→3) can be rationalised on the basis of these cations being 7 electron pair arachno-species. For completeness, the Group VI anions S_3^{2-}, Se_3^{2-} and Te_3^{2-} may be included in Table 6.9 as hypho-species, the non-linear structures of which may be derived from the octahedron.

TABLE 6.9 Systems with s=7 Based on the Octahedron; (Figure 6.10)

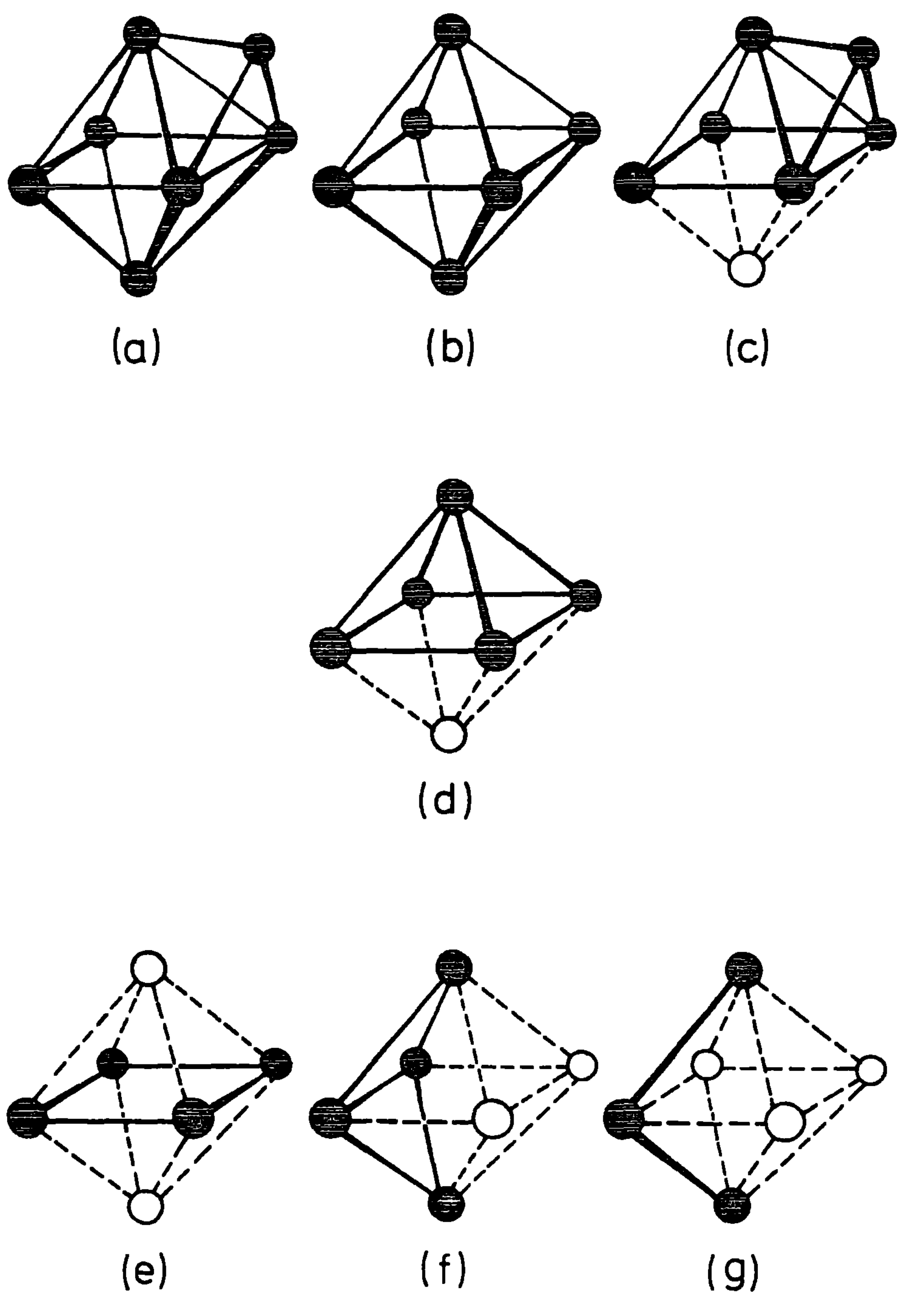
Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
7	Capped-closo	6.10a	$Os_7(CO)_{21}$	232
			$Rh_7(CO)_{16}^{3-}$	372
			$Rh_7(CO)_{16}I^{2-}$	373
* 6	Closo(i)	6.10b	$Rh_6(CO)_{16}$	194
			$[Rh_6(CO)_{15}]_2^{2-}$	374
			$Co_6(CO)_{15}^{2-}$	375
			$Co_6(CO)_{14}^{4-}$	376
			$H_2Ru_6(CO)_{18}$	377
			$HRu_6(CO)_{18}^{-}$	378
			$Ru_6(CO)_{17}C$	379
			$Ru_4(CO)_{12}(PhC{\equiv}CPh)$	380
			$Os_6(CO)_{18}^{2-}$;$HOs_6(CO)_{18}^{-}$	381
			$Co_4(CO)_{10}(EtC{\equiv}CEt)$	382
			$Fe_6(CO)_{16}C^{2-}$	383,384
			$Ni_6(CO)_{12}^{2-}$	385
			$Ir_4(CO)_{15}(C_8H_{12})_2(C_8H_{10})$	386
			$B_6H_6^{2-}$	164
			$B_4C_2H_6$	354,387,388
			B_5CH_7	388-390
6	Closo(ii)	6.10c	$H_2Os_6(CO)_{18}$	381
			$Os_6(CO)_{16}(CPh)_2$	391
5	Nido	6.10d	$Fe_5(CO)_{15}C$	392
			$Ru_5(CO)_{15}C$;$Os_5(CO)_{15}C$	393
			$Os_3(CO)_{10}(RC{\equiv}CR)$	394
			$H_2Os_3(CO)_9(RC{\equiv}CR)$	395
			B_5H_9	148

TABLE 6.9 (Continued)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
5 (contd.)	Nido	6.10d	B_5H_8Me	396
			$B_4H_8Fe(CO)_3$	397,398
			$B_4H_8Co(\pi-C_5H_5)$	399
			$B_3C_2H_7$	400
			$B_3C_2H_5Fe(CO)_3$	398
			$C_5H_5^+$	310-314
4	Arachno (i)	6.10e	S_4^{2+}	401
			Se_4^{2+}	402
			Te_4^{2+}	402,403
			$[Te_4Se_{4-n}]^{2+}$ (n=1→3)	404,405
			Bi_4^{2-}	406
			S_2N_2	407-409
			$C_4H_4^{2-}$	–
4	Arachno (ii)	6.10f	$H_3Os_4(CO)_{12}I$	410
			B_4H_{10}	143-147
			C_4H_6(i.e.bicyclo[1.1.0]butane)	324
3	Hypho	6.10g	S_3^{2-}; Se_3^{2-}; Te_3^{2-}	411

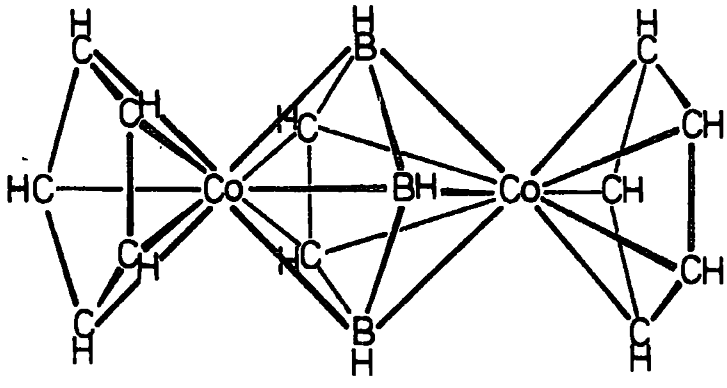
* A few examples only selected from the wide range of octahedral clusters which are known.

Figure 6.10 Systems with s=7 based on the octahedron.



6.3.3 Systems with 8 Skeletal Bonding Pairs of Electrons

The closo-pentagonal bipyramid and its derivatives seem not to be well represented amongst transition metal compounds, although main group species with s=8 are common. In metalloboranes the group of triple-decker sandwich compounds presents interesting examples of closo-species. An example is illustrated below. The two apical (π-C_5H_5)Co groups each contribute a single skeletal electron, the remaining 7 skeletal bonding pairs being provided by the $B_3C_2H_5$ ligand.



$B_3C_2H_5[Co(\pi\text{-}C_5H_5)]_2$

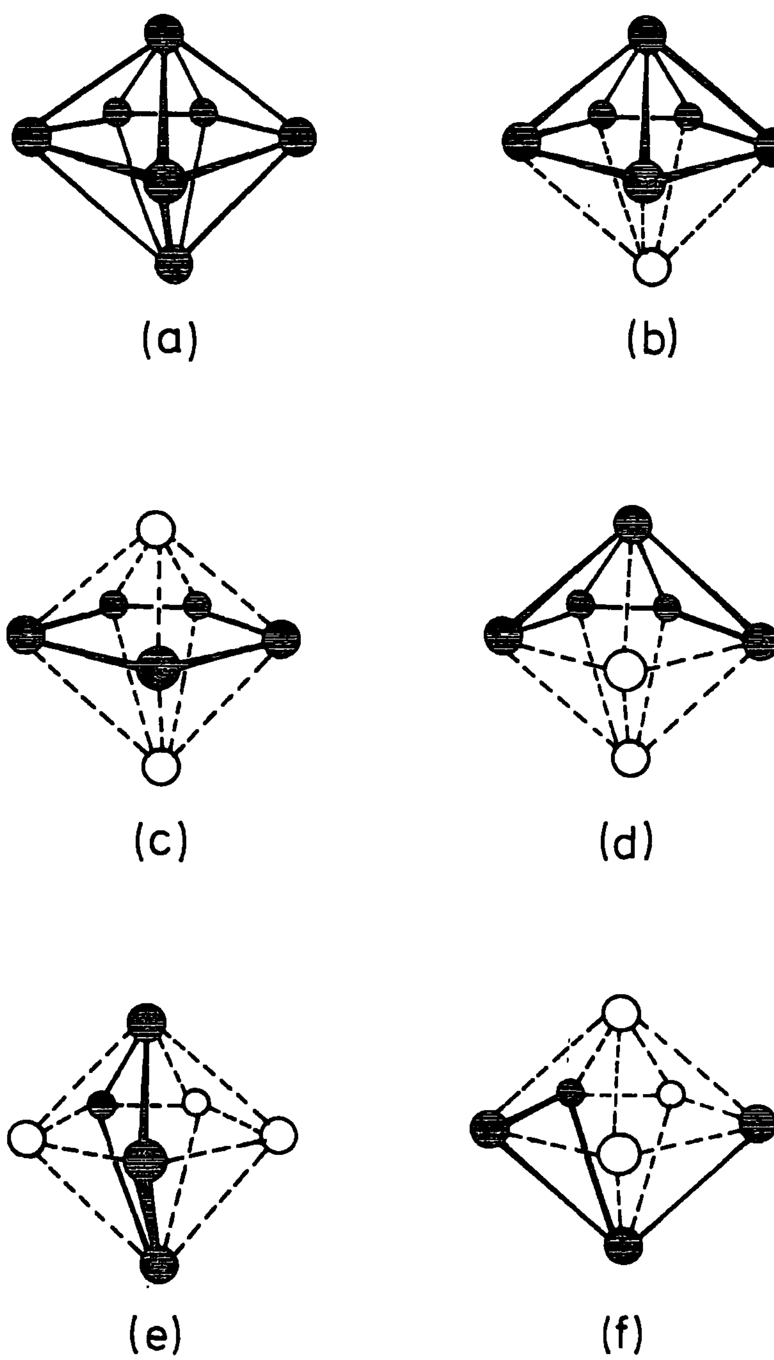
Two arachno-species are found with s=8; (i) a planar 5-membered ring represented by $C_5H_5^-$ and several sulphur-nitrogen ring systems and (ii) a structure based on the pentagonal bipyramid with one apical and one equatorial site vacant, e.g. B_5H_{11}.

Cyclobutane and methyl-cyclopropane as hypho-clusters have already been discussed, (Section 6.2). Analogous species are found in $P_4(CF_3)_4$ and $H_4Re_4(CO)_{15}^{2-}$ respectively. As with cyclobutane, the measured dihedral angle in $P_4(CF_3)_4$ is close to the predicted value of 36^o.

TABLE 6.10 Systems with s=8 Based on the Pentagonal Bipyramid; (Figure 6.11)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
7	Closo	6.11a	$B_7H_7^{2-}$	173
			$B_5C_2H_7$	412
			$B_4C_2H_6GaMe$	413
			$B_4C_2H_6ML_x$ (ML_x=$Ni(PPh_3)_2$; $Fe(CO)_3$; $Co(\pi-C_5H_5)$)	414
			$B_3C_2H_5[Co(\pi-C_5H_5)]_2$	414
			Various triple-decker sandwich compounds	423,424
6	Nido	6.11b	B_6H_{10}	150,151
			$B_5H_9Fe(CO)_3$	398,415
			B_5CH_9	416
			B_4CH_8	416.417
			$B_3C_3H_7$	418
			$B_3C_2H_7Fe(CO)_3$	398,400,419
			$B_2C_4H_6$	420
			$(BI)C_5Me_5^+$	421
			$(\pi-C_5H_5)Mn(CO)_3$	422
			$C_6Me_6^{2+}$	315-318
5	Arachno (i)	6.11c	$C_5H_5^-$	-
			$R_2C_2N_2S$	425-427
			$Ph_2C_2N_2Se$	426
			$RCN_2S_2^+$	428
5	Arachno (ii)	6.11d	$Fe(CO)_3(H_2C=CHCH=CH_2)$	429
			B_5H_{11}	138,139,144,149
4	Hypho(i)	6.11e	C_4H_8(i.e.cyclobutane)	325-332
			$P_4(CF_3)_4$	430
4	Hypho(ii)	6.11f	C_3H_5Me	333
			$H_4Re_4(CO)_{15}^{2-}$	431-432

Figure 6.11 Systems with s=8 based on the pentagonal bipyramid.



6.3.4 Systems with 9 Skeletal Bonding Pairs of Electrons

Two basic closo-polyhedra are found for systems contributing 9 skeletal bonding pairs of electrons, (Figures 6.12a and 6.13a), although of these the dodecahedron is more common. This is expected as preference for low coordination sites is usually shown; (the dodecahedron possesses four 4- and four 5-coordination sites whilst the hexagonal bipyramid contains two 6- and six 4-coordination sites).

Table 6.11, lists clusters with structures derived from the dodecahedron. A second 'closo'-species is noted; $Co_8(CO)_{18}C^{2-}$ adopts a distorted square antiprismatic structure, (Figure 6.12b). Comparison of Figures 6.12a and 6.12b shows there to be little difference between the two cages; the central carbido atom causes distortion away from an idealised antiprismatic structure thus producing a skeleton not unlike that of the dodecahedron itself. The dodecahedral cage (D_{2d} symmetry) is adopted by the $B_8H_8^{2-}$ anion in the crystal lattice. However, in solution, the polyhedral skeleton may undergo rearrangement to either the square antiprism (D_{4d} symmetry) or the square-faced bicapped trigonal prism (C_{2v} symmetry). The energy barriers between structures are strikingly low.[175, 488, 489]

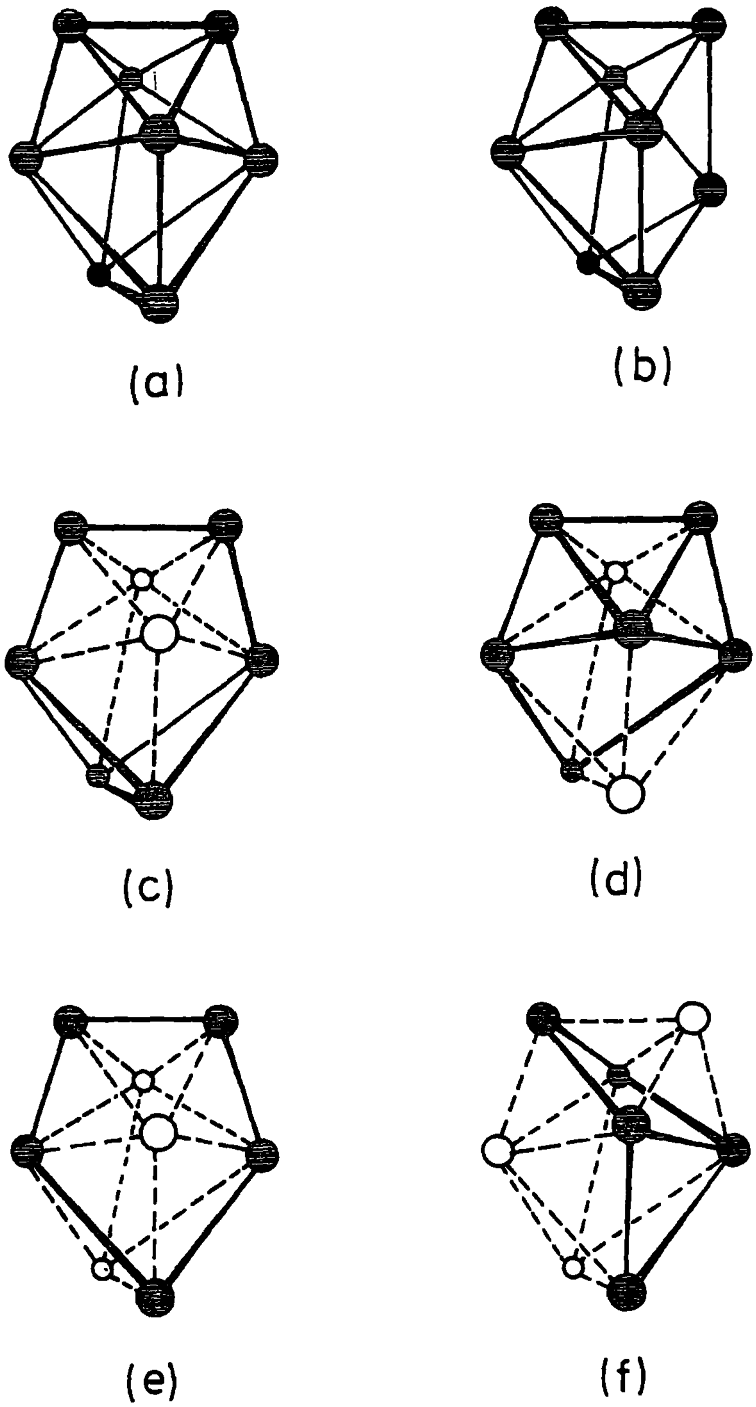
The two possible hypho-species have been noted in Section 6.2. The puckered ring of cyclopentane is again seen in the sulphur-nitrogen cation $S_3N_2Cl^+$ in which the unique sulphur atom is bent out of the ring plane. A very recent addition to this group of clusters is the first fully characterised ferracyclopent-2-en-5-one in which the ketone group is out-of-plane.

TABLE 6.11 Systems with s=9 Based on the Dodecahedron; (Figure 6.12)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
8	Closo (i)	6.12a	$Fe_4(CO)_{11}(RC{\equiv}CR)_2$ $B_8H_8^{2-}$	433 165
8	* Closo (ii)	6.12b	$Co_8(CO)_{18}C^{2-}$	434,435
6	Arachno (i)	6.12c	C_6H_6 (i.e. benzvalene and isobenzvalene)	321
6	Arachno (ii)	6.12d	$C_6Me_6H^+$	315,319
5	Hypho(i)	6.12e	C_5H_8 (i.e. cyclopentene) $(PhMe_2P)(OC)_3\overline{FeCOCH_2C(CO_2Me)=C}(OMe)$ $S_3N_2Cl^+$	334 436 437
5	Hypho (ii)	6.12f	C_5H_8 (i.e.bicyclo[2.1.0]pentane)	335,336

* See Sub-section 6.3.4

Figure 6.12 Systems with s=9 based on the dodecahedron.

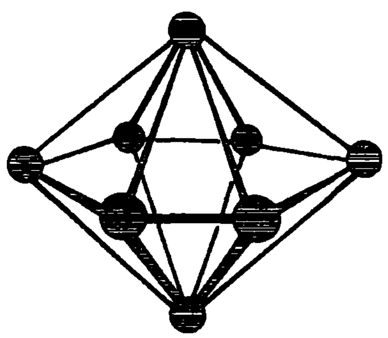


(a) (b) (c) (d) (e) (f)

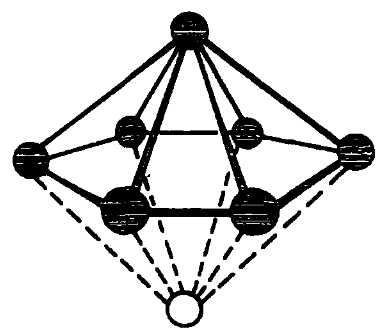
TABLE 6.12 Systems with s=9 Based on the Hexagonal Bipyramid; (Figure 6.13)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
8	Closo	6.13a	-	-
7	Nido	6.13b	$(\pi\text{-}C_6H_6)Cr(CO)_3$	438,439
6	Arachno	6.13c	C_6H_6	-

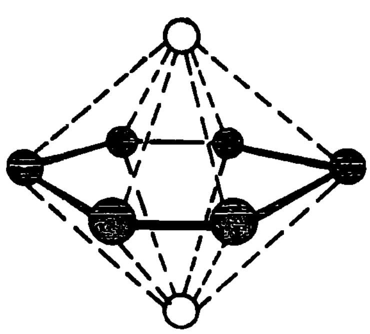
Figure 6.13 Systems with s=9 based on the hexagonal bipyramid.



(a)



(b)



(c)

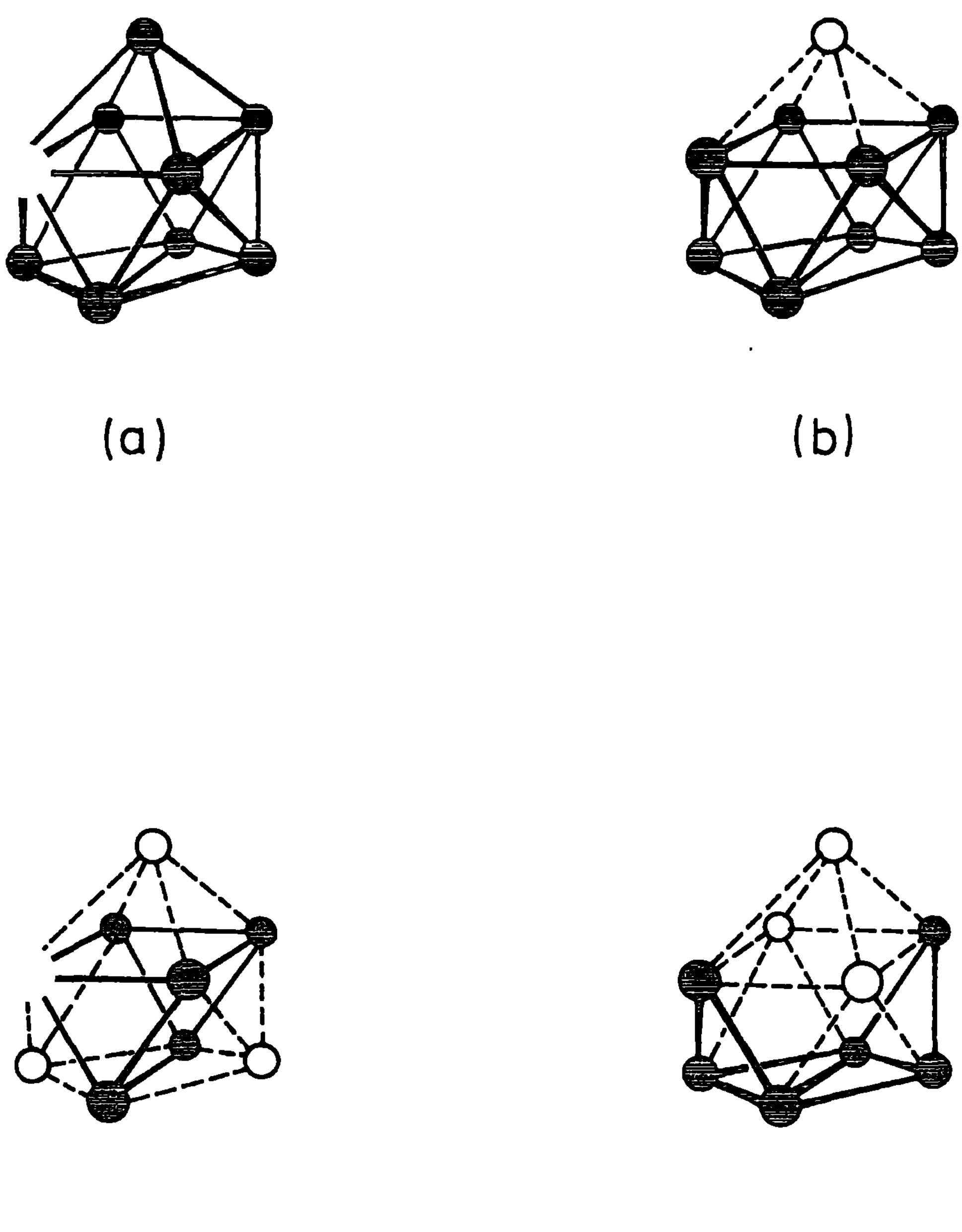
6.3.5 Systems with 10 Skeletal Bonding Pairs of Electrons

The tricapped trigonal prism and its derivatives produce several interesting examples of cluster compounds, in particular the hypho-species. The hexanuclear tellurium cation, Te_6^{4+}, has a prismatic structure which is easily rationalised in terms of its 10 electron pairs. (The cation Te_6^{6+} is also predicted to have a prismatic structure[447] which, on the basis of its 9 skeletal bond pairs, can be rationalised in terms of localised 2-centre edge bonding).

TABLE 6.13 Systems with s=10 Based on the Tricapped Trigonal Prism; (Figure 6.14)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
9	Closo	6.14a	Ge_9^{2-}	440
			$B_9H_9^{2-}$	166
			$B_7H_7C_2R_2$ (R=Me;H)	441,442
			$B_6C_2H_8Co(\pi\text{-}C_5H_5)$	443,444
			$B_5C_2H_7[Co(\pi\text{-}C_5H_5)]_2$	414,445
8	Nido	6.14b	B_8H_{12}	157,158
			$B_6C_2H_{10}$	446
6	Hypho(i)	6.14c	Te_6^{4+}	447
6	Hypho(ii)	6.14d	$Co_6(CO)_{16}P^-$	448

Figure 6.14 Systems with s=10 based on the tricapped trigonal prism.



6.3.6 Systems with 11 Skeletal Bonding Pairs of Electrons

Table 6.14 lists species which contribute 11 skeletal pairs of electrons. Besides the group of closo-borane and carborane compounds, a new antimony/tin cluster anion ($SbSn_9^-$) has been produced which is predicted[451] to have the bicapped Archimedean antiprismatic structure. A series of related anions, $[Pb_xSn_{9-x}]^{4-}$ ($x=0\rightarrow9$) has been formed using Na/Sn/Pb alloys dissolved in ethylenediamine. These are predicted to have an 'open'[451] nido-skeletal structure.

The Bi_9^{5+} cation occurs in two slightly different forms. In $Bi_{12}Cl_{14}$, the Bi_9^{5+} cation forms a slightly distorted trigonal prism with three capping atoms. In the crystal lattice, this distortion (caused by the surrounding chlorine atoms[453]) is sufficient for the cage to be misinterpreted as a monocapped Archimedean antiprism. In $Bi_{10}(HfCl_6)_3$, the Bi_9^{5+} unit is approximately regular.[454]

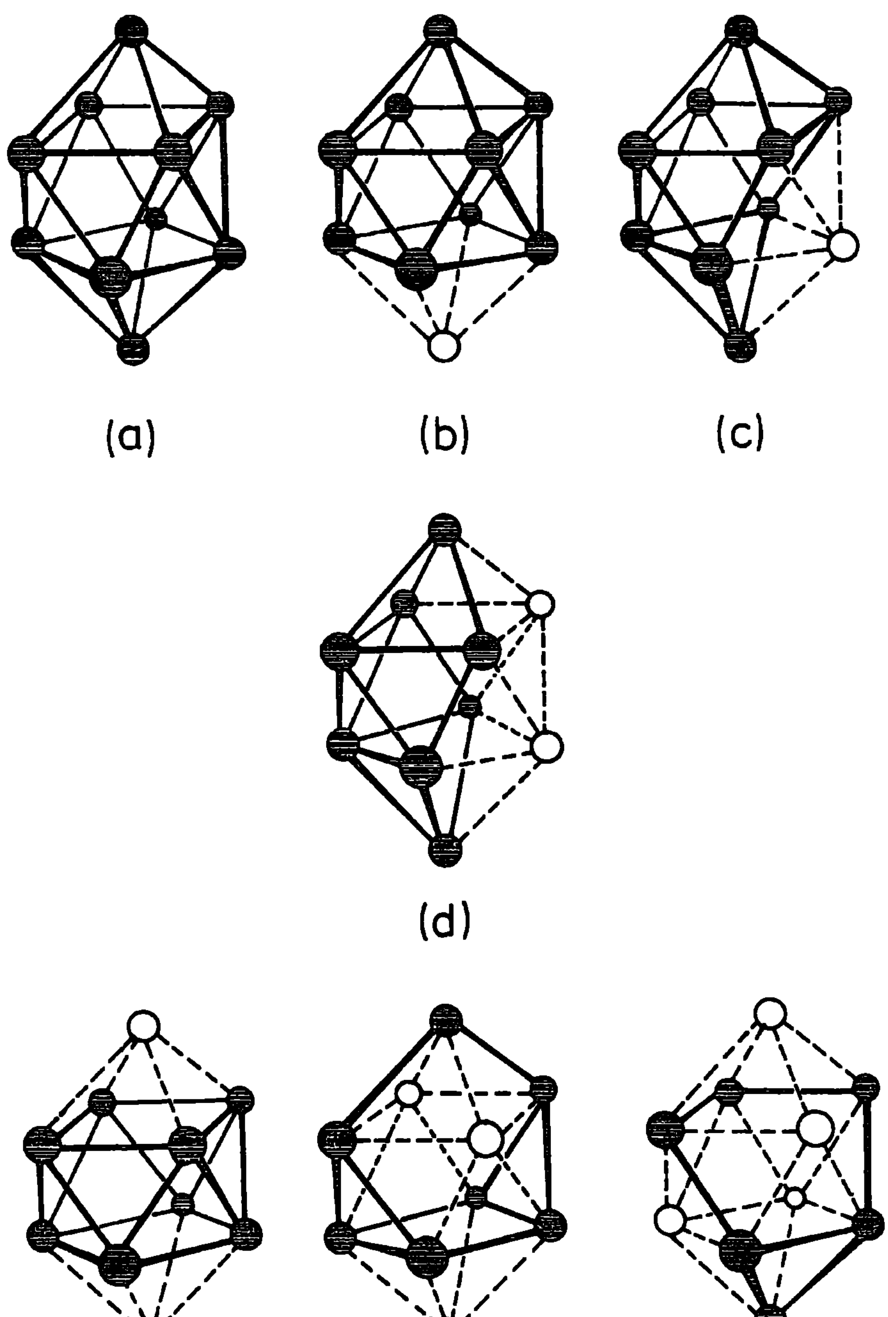
The fisco-clusters Te_6^{2+}, $Te_3Se_3^{2+}$ and $Te_2Se_4^{2+}$ each have a distorted 'chair' configuration, readily rationalised in terms of the 11 skeletal bonding pairs of electrons.

TABLE 6.14 Systems with s=11 Based on the Bicapped Archimedean Antiprism; (Figure 6.15)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
10	Closo	6.15a	$B_{10}H_{10}^{2-}$	167
			2,2'-$[1\text{-}B_9H_8S]_2$	449
			$B_8H_8C_2Me_2$	450
			$B_5C_2H_7[Co(\pi\text{-}C_5H_5)]_3$	414
		*	$SbSn_9^-$	451
9	Nido(i)	6.15b	$Rh_9(CO)_{21}P^{2-}$	452
		*	Bi_9^{5+}	453,454
			Sn_9^{4-}	455
			Ge_9^{4-}	440
			$[Pb_xSn_{(9-x)}]^{4-}$ (x=0→9)	451
9	Nido(ii)	6.15c	$B_7H_9C_2Me_2$	456
8	Arachno (i)	6.15d	B_8H_{14}	457
8	Arachno (ii)	6.15e	Bi_8^{2+}	351
7	Hypho	6.15f	C_7H_8 (i.e. quadricyclane)	339
6	Fisco	6.15g	Te_6^{2+}	447,458
			$Te_3Se_3^{2+}$; $Te_2Se_4^{2+}$	458

* see Subsection 6.3.6

Figure 6.15 Systems with s=11 based on the bicapped Archimedean antiprism.



(a) (b) (c)

(d)

(e) (f) (g)

6.3.7 Systems with 12 Skeletal Bonding Pairs of Electrons

The large number of clusters with structures derivable from the octadecahedron is quite surprising. The closo-, nido-, and arachno-boranes and carboranes listed in Table 6.15 are well documented. The structure of the recently synthesised $SbSn_9^{3-}$ anion[451] is also predicted to be derived from the 11-vertex polyhedron.

The formation of a 'hypho'-species with 12-skeletal bond pairs is illustrated in Figure 6.16d. The cubane structure has previously been described in Section 6.2, and Table 6.15 includes C_8H_8 with main group and transition metal examples of the 8-centre 12-electron pair systems which rearrange from the possible hypho-structure to the preferred cubic framework involving localised bonding.

A remarkably large group of compounds containing 7 skeletal atoms and having 12 pairs of bonding electrons exists. Several of these species have previously been noted as having structures related to the octadecahedron.[490] However this group of fisco-species appears to be more extensive than originally suggested.

Finally two classes of reticulo-cluster are apparent. The 'chair' and 'boat' conformers of cyclohexane have previously been mentioned, (Section 6.2). The boat-form is seen again in S_6, Te_6 and $S_3N_3Cl_3$.

TABLE 6.15 Systems with s=12 Based on the Octadecahedron; (Figure 6.16)

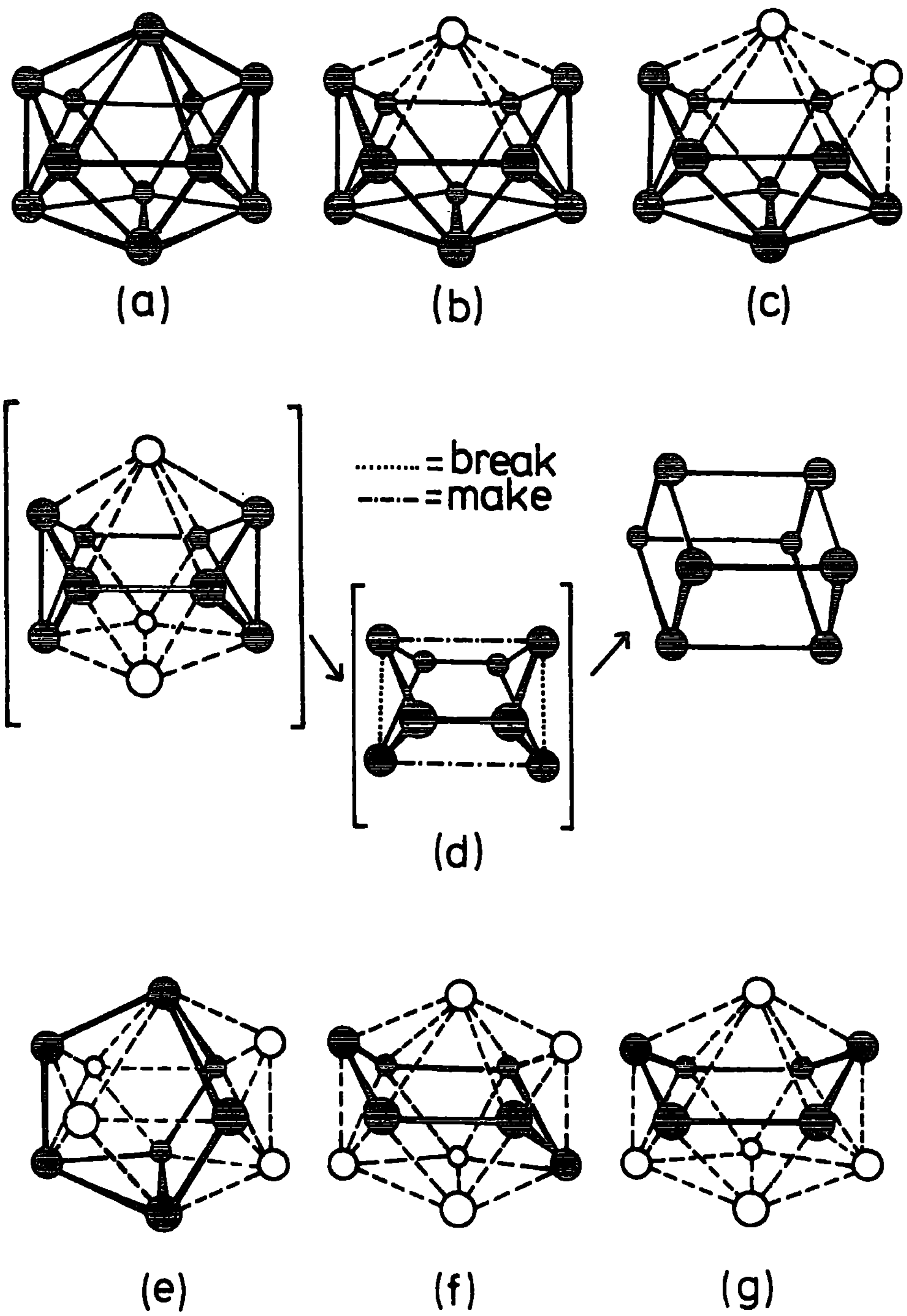
Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
11	Closo	6.16a	$B_{11}H_{11}^{2-}$	173-175
			$B_9H_9C_2Me_2$	459
			$B_8C_2H_{10}Co(\pi\text{-}C_5H_5)$	444,445
10	Nido	6.16b	$B_{10}H_{14}$	152,153
			$[B_{10}H_{13}]_2$	460,461
			$B_{10}H_{12}^{2-}$	462
			$B_7C_2H_{11}Co(\pi\text{-}C_5H_5)$	463
		*	$SbSn_9^{3-}$	451
9	Arachno	6.16c	B_9H_{15}	159
			$B_9H_{14}^-$	464
			$B_7H_{11}C_2Me_2$	465
8	*(Hypho)	6.16d	$Ni_8(CO)_8(PPh)_6$	466
			$(PhAlNPh)_4$	467,468
			$(MeZnOMe)_4$	469
			C_8H_8	344
7	Fisco	6.16e	P_7^{3-}	470,471
			As_7^{3-}	472
			Sb_7^{3-}	473
			P_4S_3	474
			$P_3S_4^+$	475
			$P_3Se_3P{=}Se$	476
			As_4Se_3	477
			C_7H_{10} (i.e. nortricyclene)	343
6	Reticulo (1)	6.16f	C_6H_{12}(boat conformer)	–

TABLE 6.15 (continued)

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
6	Reticulo (ii)	6.16g	C_6H_{12} (chair conformer)	-
			S_6	478
			$S_3N_3Cl_3$	479
			Te_6	447

* See Subsection 6.3.7

Figure 6.16 Systems with s=12 based on the octadecahedron.



6.3.8 Systems with 13 Skeletal Bonding Pairs of Electrons

The usual closo-polyhedron envisaged for s=13 is the icosahedron. However, $H_3Rh_{13}(CO)_{24}^{2-}$ adopts a structure resembling a hexagonal close-packed lattice; 12 Rh atoms are skeletal and one is sited at the centre of symmetry of the Rh_{12} cage. (Figure 6.17d shows the Rh_{12} skeleton). Of the remaining clusters with 13 skeletal pairs of electrons, carboranes and metallocarboranes are the predominant species. All are either closo-, nido-, or arachno-systems with structures derived from the icosahedron.

TABLE 6.16 Systems with s=13 Based on

(i) the Icosahedron; (Figure 6.17(i))

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
12	Closo	6.17a	$B_{12}H_{12}^{2-}$	168
			$B_{10}C_2H_{12}$	480
			$B_7C_2H_9[Co(\pi\text{-}C_5H_5)]_3$	445
			Various metallo-carboranes $XC_2B_9H_{11}$	346
11	Nido	6.17b	$B_{11}H_{13}^{2-}$	481
			$B_{10}CH_{11}^{3-}$	482
			$B_9C_2H_{12}^{-}$	483
			$B_9H_{11}SPt(PEt_3)_2$	484
10	Arachno	6.17c	$B_{10}H_{14}^{2-}$	485
			$B_9H_{11}(NEt_3)S$	486

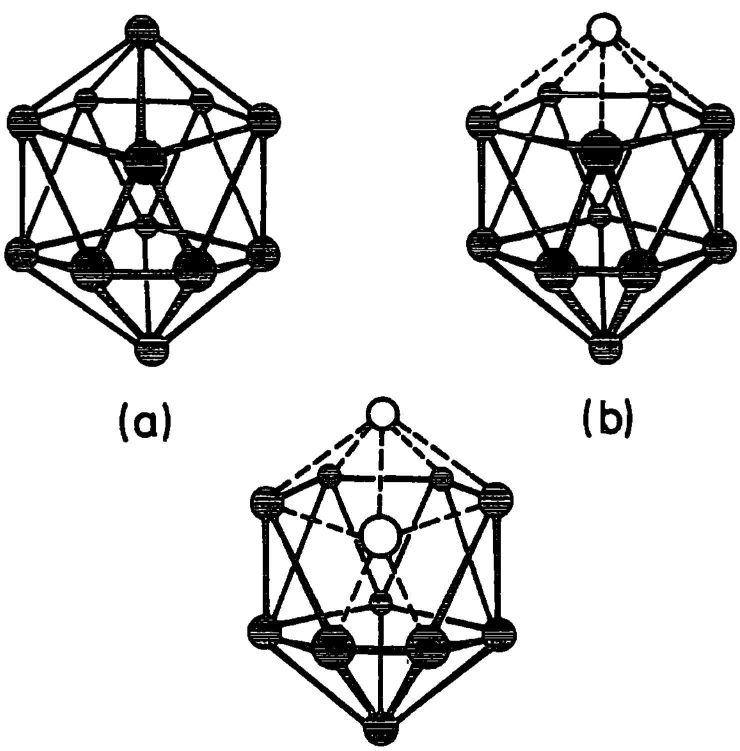
(ii) an 'Hexagonal Close-Packed' Unit*; (Figure 6.17(ii))

Number of Skeletal Atoms	Cluster Type	Figure	Examples	Structural Reference
12	Closo	6.17d	$H_3Rh_{12}(CO)_{24}Rh^{2-}$	487

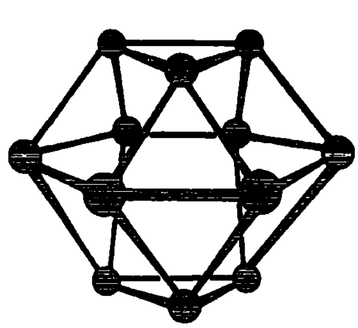
* See Sub-Section 6.3.8

Figure 6.17 Systems with s=13 based on

[i] the icosahedron.



[ii] "hexagonal close-packed" unit.



(d)

6.4 Conclusion

The data presented in Section 6.3 indicates that, without a doubt, the use of skeletal electron counting for classifying cluster species has been underestimated in the past. One of the most striking features is perhaps the ability to rationalise the bonding in such species as the Te_6^{x+} (x=0,2,4,6) clusters. The structures of all 3 cations are readily derived from the appropriate closo-polyhedra and that of Te_6 is rationalised in terms of localised bonding. This particular group of cluster species cannot all be rationalised in terms of any other one bonding picture.

CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The main aim of the work described in this thesis has been to suggest new ways in which self-consistent sets of bond energy contributions might be estimated for bonds in cluster species and related systems.

The exploration of empirical bond energy-bond length and bond energy-bond order correlations in simple main group systems, (particularly in boron containing compounds), provided encouragement for the application of such relationships to more complex systems.

The basis for determining metal-metal bond energies in metal carbonyl clusters has been to use the lengths and strengths of the bonds in the bulk metals themselves. Although it was indicated in Chapter Four that some doubt had been cast on the feasibility of analogies between bulk metal fragments and metal clusters, it is extremely encouraging to find that the results of very recent molecular orbital calculations do in fact support such analogies.[491] It would therefore appear that an extension of this work is justified. An important application would be to metal π-hydrocarbon complexes. Estimations of metal-carbon bond enthalpies in such systems could be of great value in understanding the energetics of metal surface catalysis reactions.

The limitations of the bond energy-bond length correlations were noted in attempts to estimate the enthalpies of multiple metal-metal bonds. It appears that the environments in which multiple M-M bonds occur are not sufficiently like those in the bulk metals to allow direct analogies to be drawn between the two systems.

The last part of this thesis has been devoted to a study of the applications of skeletal electron counting methods. It has been shown that accurate qualitative structural predictions can be made in clusters containing both transition metal and main group elements, and that previously, the potential of such electron counting schemes had been greatly underestimated. The data summarised in Chapter Six brings the application of skeletal electron counting up to date. However, as the synthesis and characterisation of new metal and main group cluster species are now frequent occurrences, the future updating of the information provided in this thesis will be of prime importance. It is anticipated that in addition to the two new cluster types reported in this work (i.e. fisco- and reticulo-species), further cluster groups will be recognised in future years, particularly if closo-polyhedra with 13 or more vertices are considered as parent polyhedral skeletons.

APPENDIX ONE

TREATMENT OF ERRORS

1. In Calculations

For a function, $f(x,y,....)$, the error, δ_f, in $f(x,y,....)$ is given by:

$$\delta_f = \sqrt{(\frac{\partial f}{\partial x})^2 \cdot (\delta x)^2 + (\frac{\partial f}{\partial y})^2 (\delta y)^2 + \ldots\ldots}$$

Hence for a function:

$$y = n_A (A \pm \delta_A) \pm n_B(B \pm \delta_B) \pm \ldots\ldots\ldots\ldots$$

the error in y, (δ_y) is:

$$\delta_y = \sqrt{n_A^2 \delta_A^2 + n_B^2 \delta_B^2 + \ldots\ldots\ldots}$$

For a function $f = (^x/_y)^k$, the error in the function, δ_f, is given by:

$$\delta_f = \sqrt{k^2 x^{2(k-1)} y^{-2k} (\delta x)^2 + k^2 x^{2k} y^{-2(k+1)} (\delta y)^2 \ldots\ldots}$$

2. In Graphical Representations

In general, a graphical correlation is given by a least squares fit to a set of n points. This minimizes the sum, S, of the squares of deviations of points from the line:

$$\text{For} \quad y_i = a + bx_i \qquad \begin{pmatrix} a = \text{intercept} \\ b = \text{slope} \end{pmatrix}$$

$$S = \Sigma (y_i - a - bx_i)^2$$

$$\therefore \quad \frac{\partial S}{\partial a} = -2 \Sigma (y_i - a - bx_i)^2 = 0$$

$$\text{and} \quad \frac{\partial S}{\partial b} = -2 \Sigma x_i (y_i - a - bx_i)^2 = 0$$

For n points:

$$\Sigma y_i = na + b\,\Sigma x_i \qquad \text{(i)}$$

$$\Sigma x_i y_i = a\,\Sigma x_i + b\,\Sigma x_i^2 \qquad \text{(ii)}$$

The 'best' slope is given by:

$$b = \frac{n\,\Sigma x_i y_i - \Sigma x_i\,\Sigma y_i}{n\,\Sigma x_i^2 - (\Sigma x_i)^2} \qquad \text{(iii)}$$

The 'best' intercept is obtained by substitution of b from (iii) into (i).

The correlation coefficient, r, (which is $\pm$ 1.0 for a perfect linear correlation between x and y) is given by:

$$r = \left\{ \frac{n\,\Sigma x_i y_i - \Sigma x_i\,\Sigma y_i}{\left(\left[n\,\Sigma x_i^2 - (\Sigma x_i)^2\right]\left[n\,\Sigma y_i^2 - (\Sigma y_i)^2\right]\right)^{1/2}} \right\}$$

In this thesis values of $r \geq 0.99999$ or $r \leq -0.99999$ are approximated to $\pm$ 1.00 respectively.

APPENDIX TWO

ABBREVIATIONS

The following abbreviations for substituents and ligands have been used in the text:

Bu	butyl
Cp	π-cyclopentadienyl
diglyme	diethyleneglycoldimethyl ether
DMP	2,6-dimethoxyphenyl
Et	ethyl
Me	methyl
Ph	phenyl
piv	pivalato ($(CH_3)_3CCO_2$)
Pr	propyl
py	pyridine
THF	tetrahydrofuran
TMP	2,4,6-trimethoxyphenyl

APPENDIX THREE

The Board of Studies in Chemistry requires that each postgraduate research thesis should contain an appendix listing all research colloquia, seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period when research for the thesis was carried out.

Research Colloquia, Seminars and Lectures Arranged by the Department of Chemistry between October 1976 and September 1979 (* indicates lectures attended)

*20 October 1976

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur"

*10 November 1976

Dr. J.S. Ogden (University of Southampton), "The Characterisation of High Temperature Species by Matrix Isolation"

*17 November 1976

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids"

24 November 1976

Dr. M.I. Page, (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions"

*8 December 1976

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals"

26 January 1977

Dr. A. Davis (E.R.D.R.), "The Weathering of Polymeric Materials"

2 February 1977

Dr. M. Falk, (N.R.C. Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases"

*9 February 1977

Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions"

*23 February 1977

Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines"

*25 February 1977

Professor H.T. Dieck (Frankfurt University), "Diazadienes - New Powerful Low-Valent Metal Ligands"

2 March 1977

Dr. F. Hibbert (Birkbeck College, University of London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids"

4 March 1977

Dr. G. Brink (Rhodes University, South Africa), "Dielectric Studies of Hydrogen Bonding in Alcohols"

*9 March 1977

Dr. I.O. Sutherland (University of Sheffield), "The Stevans' Rearrangement: Orbital Symmetry and Radical Pairs"

*18 March 1977

Professor H. Bock (Frankfurt University), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist"

30 March 1977

Dr. J.R. MacCallum (University of St. Andrews), "Photooxidation of Polymers"

*20 April 1977

Dr. D.M.J. Lilley (Research Division, G.D. Searle), "Tails of Chromatin Structure - Progress Towards a Working Model"

*27 April 1977

Dr. M.P. Stevens (University of Hartford), "Photocycloaddition Polymerisation"

4 May 1977

Dr. G.C. Tabisz (University of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases"

11 May 1977

Dr. R.E. Banks (U.M.I.S.T.), "The Reactions of Hexafluoropropene with Heterocyclic N-Oxides"

*18 May 1977

Dr. J. Atwood (University of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates"

25 May 1977

Professor M.M. Kreevoy (University of Minnesota), "The Dynamics of Proton Transfer in Solution"

*1 June 1977

Dr. J. McCleverty (University of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten"

*6 July 1977

Professor J. Passmore (University of New Brunswick, Canada), "Adducts Between Group V Pentahalides and a Postscript on S_7I^+"

27 September 1977

Dr. T.J. Broxton (La Trobe University, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents"

*19 October 1977

Dr. B. Heyn (University of Jena, D.D.R.), "σ-Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts"

*27 October 1977

Professor R.A. Filler (Illinois Institute of Technology), "Reactions of Organic Compounds with Xenon Fluorides"

*2 November 1977

Dr. N. Boden (University of Leeds), "N.M.R. Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-$\frac{1}{2}$ Pairs"

9 November 1977

Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids"

*14 December 1977

Dr. R.O. Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry"

25 January 1978

Dr. G. Richards (University of Oxford), "Quantum Pharmacology"

*1 February 1978

Professor K.J. Irvin (Queens University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring-Opening Polymerisation of Cycloalkenes"

*3 February 1978

Dr. A. Hartog (Free University, Amsterdam), "Some Surprising Recent Developments in Organo-Magnesium Chemistry"

*22 February 1978

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere"

1 March 1978

Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions"

*3 March 1978

Dr. G. van Koten (University of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds"

15 March 1978

Professor G. Scott (University of Aston), "Fashioning Plastics to Match the Environment"

*22 March 1978

Professor H. Vahrenkamp (University of Freiburg), "Metal-Metal Bonds in Organometallic Complexes"

*19 April 1978

Dr. M. Barber (U.M.I.S.T.), "Secondary Ion Mass Spectra of Surfaces Adsorbed Species"

*15 May 1978

Dr. M.I. Bruce (University of Adelaide), "New Reactions of Ruthenium Compounds with Alkynes"

16 May 1978

Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals"

18 May 1978

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science"

*22 May 1978

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds"

*24/25 May 1978

Professor P. von R. Schleyer (University of Erlangen, Nürnberg),

(i) "Planar Tetra-Coordinate Methanes, Perpendicular Ethylenes and Planar Allenes"

(ii) "Aromaticity in Three Dimensions"

(iii) "Non-Classical Carbocations"

21 June 1978

Dr. S.K. Tyrlik (Academy of Sciences, Warsaw), "Dimethylglyoxime-Cobalt Complexes - Catalytic Black Boxes"

23 June 1978

Professor W.B. Person (University of Florida), "Diode Laser Spectroscopy at 16 μm"

*27 June 1978

Professor R.B. King (University of Georgia, Athens, Georgia, U.S.A.), "The Use of Carbonyl Anions in the Synthesis of Organometallic Compounds"

30 June 1978

Professor G. Mateescu (Cape Western Reserve University), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion Pairs: Facts, Plans and Dreams"

*15 September 1978

Professor W. Siebert (University of Marburg, West Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry"

*22 September 1978

Professor T. Fehlner (University of Notre Dame, U.S.A.), "Ferraboranes: Syntheses and Photochemistry"

12 December 1978

Professor C.J.M. Stirling (University of Bangor), "Parting is Such Sweet Sorrow - the Leaving Group in Organic Reactions"

14 February 1979

Professor B. Dunnell (University of British Columbia), "The Application of N.M.R. to the Study of Motions in Molecules"

*16 February 1979

Dr. J. Tomkinson (Institute Laue-Langevin, Grenoble), "Studies of Adsorbed Species"

*14 March 1979

Dr. J.C. Walton (University of St. Andrews), "Pentadienyl Radicals"

*28 March 1979

Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices"

5 April 1979

Dr. S. Larsson (University of Uppsala), "Some Aspects of Photoionisation Phenomena in Inorganic Systems"

25 April 1979

Dr. C.R. Patrick (University of Birmingham), "Chlorofluorocarbons and Stratospheric Ozone: An Appraisal of the Environmental Problem"

1 May 1979

Dr. G. Wyman (European Research Office, U.S. Army), "Excited State Chemistry in Indigoid Dyes"

*2 May 1979

Dr. J.D. Hobson (University of Birmingham), "Nitrogen-centred Reactive Intermediates"

*8 May 1979

Professor A. Schmidpeter (Institute of Inorganic Chemistry, University of Munich), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus"

9 May 1979

Dr. A.J. Kirby (University of Cambridge), "Structure and Reactivity in Intramolecular and Enzymic Catalysis"

*9 May 1979

Professor G. Maier (Lahn-Giessen), "Tetra-tert-butyltetrahedrane"

10 May 1979

Professor G. Allen, F.R.S. (Science Research Council), "Neutron Scattering Studies of Polymers"

*16 May 1979

Dr. J.F. Nixon (University of Sussex), "Spectroscopic Studies on Phosphines and their Coordination Complexes"

*23 May 1979

Dr. B. Wakefield (University of Salford), "Electron Transfer in Reactions of Metals and Organometallic Compounds with Polychloropyridine Derivatives"

*13 June 1979

Dr. G. Heath, (University of Edinburgh), "Putting electrochemistry into mothballs - (Redox processes of metal porphyrins and phthalocynanines)".

14 June 1979

Professor I. Ugi (University of Munich), "Synthetic Uses of Super Nucleophiles"

*20 June 1979

Professor J.D. Corbett (Iowa State University, Ames, Iowa, U.S.A.), "Zintl Ions: Synthesis and Structure of Homo-polyatomic Anions of the Post-Transition Elements"

27 June 1979

Dr. H. Fuess (University of Frankfurt), "Study of Electron Distribution in Crystalline Solids by X-ray and Neutron Diffraction"

REFERENCES

1. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, 3rd. edn., Chapman and Hall, London (1968)

2. G. Herzberg, Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules, 2nd. edn., D. van Nostrand, Toronto (1950)

3. H. A. Skinner, Advances in Organometallic Chem., 2, 49 (1964)

4. J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London (1970)

5. J. A. Connor, H. A. Skinner and Y. Virmani, Faraday Symposium Chem. Soc., 8, 18 (1973)

6. D. L. S. Brown, J. A. Connor and H. A. Skinner, J. C. S. Faraday I, 71, 699 (1975)

7. G. Pilcher, Internat. Review of Science, Thermochem. and Thermodynamics, Phys.Chem. Series 2, ed. H. A. Skinner, 10, Butterworths, London (1975)

8. J. Chao *et al.*, JANAF Thermochemical Tables, (Dow Chemical Company, Midland, Michigan), U.S. Dept. of Commerce, Nat. Bureau of Standards, Institute for Applied Technology (1965); addenda (1967; 1968)

9. L. V. Gurvich, G. V. Karachievtziev, V. N. Kondratiev, Yu. A. Lebedev, V. A. Medvedev, V. K. Potapov and Yu. S. Hodiev, Dissociation Energies of Chemical Bonds, Ionisation Potentials and Electron Affinities, Nauka, Moscow (1974)

10. J. A. Kerr, Chem.Rev., 66, 465 (1966)

11. T. L. Cottrell, The Strengths of Chemical Bonds, Butterworths, London (1954)

12. E. U. Condon and G. H. Shortley, Theory of Atomic Spectra, Cambridge University Press (1935)

13. J. Hinze and H. H. Jaffé, J. Amer.Chem.Soc., 84, 540 (1962)

14. G. Pilcher and H. A. Skinner, J. Inorg. Nucl. Chem., 24, 937 (1962)

15. P. W. Atkins, Molecular Quantum Mechanics, Part III, Vol.II, p.302, Clarendon Press, Oxford (1970)

16. F. A. Cotton and J. R. Leto, J.Chem.Phys., 30, 993 (1959)

17. D. J. G. Ives, Chemical Thermodynamics, p.49-52, Macdonald, London (1971)

18. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd. edn., p.123, Wiley Interscience, New York (1972)

19. C. H. D. Clark, Nature, 143, 800 (1939)

20. J. L. Kavanau, J.Chem.Phys., 12, 467 (1944)

21. J. L. Kavanau, J.Chem.Phys., 15, 77 (1947)

22. R. T. Lagemann, J.Chem.Phys., 14, 743 (1946)

23. H. A. Skinner, Trans. Faraday Soc., 41, 645 (1945)

24. W. Gordy, J.Chem.Phys., 15, 305 (1947)

25. H. J. Bernstein, J.Chem.Phys., 15, 284 (1947)

26. G. Glockler, J.Chem.Phys., 16, 842 (1948)

27. G. Glockler, J.Chem.Phys., 21, 1242 (1953)

28. H. O. Jenkins, J.Amer.Chem.Soc., 77, 3168 (1955)

29. G. Glockler, J.Phys.Chem., 61, 31 (1957)

30. J. C. Earl, Tetrahedron, 9, 65 (1960)

31. M. Gosselin, J.Chim.Phys.Physiocochim.Biol., 65, 1090 (1968)

32. A. Julg, J.Chim.Phys.Physicochim.Biol., 65, 541 (1968)

33. G. Haefelinger, Chem.Ber., 103 2902; 2922; 2941 (1970)

34. V. G. Dashevskii, Zh.Strukt.Khim., 11, 489 (1970)

35. Z. Szabo and T.I. Konkoly, Magy.Kem.Foly., 80, 317 (1974)

36. Z. G. Szabo and T.I. Konkoly, Acta Chim.Acad.Sci. Hung., 86, 127 (1975)

37. J. B. Holbrook, Ph.D.Thesis, University of London, Birkbeck College (1975)

38. G. Glockler, Trans.Faraday Soc., 59, 1080 (1963)

39. L. Maijs, Latv.P.S.R.Zinat.Akad.Vestis Kim.Ser., p.505 (1967); C.A. 68, 43341h (1968)

40. J. P. Fackler and D. Coucouvanis, Inorg.Chem., 7, 181 (1968)

41. R. S. Roy, Proc.Phys.Soc., London, At.Mol.Phys., (2), 1, 445 (1968)

42. P. A. Koz'min, Dokl.Akad.Nauk. S.S.S.R., 206, 1384 (1972)

43. V. S. Mastryukov, Zh.Strukt.Khim., 13, 576 (1972)

44. I. D. Brown and R. D. Shannon, Acta Cryst., 29A, 266 (1973)

45. I. D. Brown, Chem.Soc.Rev., 7, 359 (1978)

46. K. Waltersson, Acta Cryst., 34A, 901 (1978)

47. M. P. Bhutra, S.P. Tandon and P. P. Vaishnava, Z. Naturforsch.(A), 30, 21 (1975)

48. D. C. McKean, Chem.Soc.Rev., 7, 399 (1978)

49. F. A. Cotton, Inorg.Chem., 4, 334 (1965)

50. F. A. Cotton and R. M. Wing, Inorg.Chem., 4, 314 (1965)

51. L. Pauling, The Nature of the Chemical Bond, 3rd. edn., p.91, Cornell University Press (1960)

52. T. L. Allen, J.Chem.Phys., 27, 810 (1957)

53. J. Stals, Rev. Pure and Applied Chem., 20, 1 (1970)

54. M. G. Brown, Trans. Faraday Soc., 55, 694 (1959)

55. M. J. S. Dewar and A. N. Schmeising, Tetrahedron, 5, 166 (1959)

56. R. Alden, J. Kraut and T. G. Traylor, J.Phys.Chem., 71, 2379 (1967)

57. F. E. Morris and W. J. Orville-Thomas, J.Mol.Spectrosc., 6, 572 (1961)

58. A. Julg and O. Julg, Theor.Chim.Acta, 22, 353 (1971)

59. A. G. Robiette, Molecular Structure by Diffraction Methods, Vol.1, p.160-197, Specialist Periodical Reports, Chem.Soc. (1973)

60. C. C. Costain, J.Chem.Phys., 29, 864 (1958)

61. K. Kuchitsu, T. Fukuyama and Y. Morino, J.Mol.Struct. 1, 463 (1968)

62. L. S. Bartell, K. Kuchitsu and R. J. de Neui, J.Chem. Phys., 35, 1211 (1961)

63. R. L. Hilderbrandt and J. D. Wieser, J.Chem.Phys., 55, 4648(1971); 56, 1143 (1972)

64. D. R. Lide and M. Jen, J.Chem.Phys., 38, 1504 (1963)

65. T. A. Halgren, R.J. Anderson, D. S. Jones and W. N. Lipscomb, Chem.Phys.Letters, 8, 547 (1971)

66. W. N. Lipscomb, Trans.Amer.Crystallogr.Ass., 8, 79 (1972)

67. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd. edn., p.102, Wiley Interscience, New York (1972)

68. A. Finch and P. J. Gardner, Progress in Boron Chemistry, 3, p.177-210, ed. R. J. Brotherton and H. Steinberg, Pergamon Press, Oxford (1970)

69. CODATA Task Group, J.Chem.Thermodynamics, 10, 903 (1978)

70. D. D. Wagman *et al.*, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, (U.S.), Tech.Note 270-3, Washington D.C. (1968)

71. M. F. Guest, J. B. Pedley and M. Horn, J.Chem.Thermodynamics, 1, 345 (1969)

72. R. W. Mar and R. G. Bedford, High Temp.Sci., 8, 365 (1976)

73. J. B. Pedley *et al.*, CATCH Tables (Nitrogen Compounds), University of Sussex (1972)

74. J. B. Pedley *et al.*, CATCH Tables (Halogen Compounds), University of Sussex (1972)

75. K. Wade, J.C.S. Chem.Comm., p.792 (1971)

76. R. E. Williams, Inorg.Chem., 10, 210 (1971)

77. D. M. P. Mingos, Nature Phys.Sci., 236, 99 (1972)

78. R. W. Rudolph and W. R. Pretzer, Inorg.Chem., 11, 1974 (1972)

79. K. Wade, Chem. in Britain, 11, 177 (1975)

80. K. Wade, Adv.Inorg.Chem.Radiochem., 18, 1 (1976)

81. R. E. Williams, Adv.Inorg.Chem.Radiochem., 18, 67 (1976)

82. R. W. Rudolph, Accounts Chem.Res., 9, 446 (1976)

83. S. Geller, Phys. and Chem. Solids, 10, 340 (1959)

84. A. Finch, P. J. Gardner and G. B. Watts, Chem.Comm., p. 1054 (1967)

85. A. Finch, P.J. Gardner, E. J. Pearn and G. B. Watts, Trans.Faraday Soc., 63, 1880 (1967)

86. A. Finch, P. J. Gardner, N. Hill and K. S. Hussain, J.C.S. Dalton, p.2543 (1973)

87. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., p.113, Wiley Interscience, New York (1972)

88. R. C. Weast (ed.), C.R.C. Handbook of Chemistry and Physics, 58th ed., C.R.C. Press, Cleveland (1977)

89. P. R. Bunter, J.Mol.Spectrosc., 39, 90 (1971)

90. J. B. Pedley *et al.*, CATCH Tables, University of Sussex (1977)

91. D. M. Golden and S. W. Benson, Chem.Rev., 69, 125 (1969)

92. L. Batt, K. Christie, R. T. Milne and A. J. Summers, Int.J.Chem.Kinetics, 6, 877 (1974)

93. H. E. O'Neal and S. W. Benson, Free Radicals, ed. J. K. Kochi, p.275, Wiley, New York (1973)

94. W. A. Chupka and C. Lifshitz, J.Chem.Phys., 48, 1109 (1968)

95. G. Herzberg and J. W. C. Johns, Astrophys.J., 158, 399 (1969)

96. A. H. Clark and G. A. Anderson, Chem.Comm., p.1082 (1969)

97. R. S. Pease, Acta Cryst., 5, 356 (1952)

98. W. Harshbarger, G. Lee, R. F. Porter and S. H. Bauer, Inorg.Chem., 8, 1683 (1969)

99. M. A. Viswamitra and S. N. Vaidya, Z.Kristallogr., 121, 472 (1965)

100. K. Anzenhofer, Mol.Phys., 11, 495 (1966)

101. K. P. Coffin and S. H. Bauer, J.Phys.Chem., 59, 193 (1955)

102. C. H. Chang, R. F. Porter and S. H. Bauer, Inorg.Chem., 8, 1677 (1969)

103. L. Pauling, Proc.Natl.Acad.Sci. U.S.A., 56, 1646 (1966)

104. L. Pauling, The Nature of the Chemical Bond, 3rd ed., Ch.7, Cornell University Press (1960)

105. R. H. Wentoff, J.Chem.Phys., 26, 956 (1957)

106. P. J. Schapiro, Dissert.Abst., 22, 2607 (1962)

107. H. Hess, Acta Cryst., 25B, 2338 (1969)

108. H. Hess, Z.Kristallogr., 118, 361 (1963)

109. P. S. Bryan and R. L. Kuczkowski, Inorg.Chem., 10, 200 (1971)

110. A. E. Douglas and G. Herzberg, Can.J.Research, 18A, 179 (1940)

111. D. R. Armstrong and P. G. Perkins, J.C.S.(A), p.1044 (1969)

112. P. G. Perkins and J. J. Stewart, Inorg.Chim.Acta, 4, 40 (1970)

113. P. O. Schissel and W. S. Williams, Bull.Amer.Phys.Soc., 4, 139 (1959)

114. L. H. Dreger, V. V. Dadape and J. L. Margrave, J.Phys.Chem., 66, 1557 (1962)

115. R. C. Schoonmaker, A. Buhl and J. Lemley, J.Phys.Chem., 69, 3455 (1965)

116. E. L. Muetterties, The Chemistry of Boron and its Compounds, p.482, Wiley, New York (1967)

117. R. S. Mulliken, Chem.Rev., 41, 207 (1947)

118. T. D. Coyle, S. L. Stafford and F. G. A. Stone, J.C.S. p.3103 (1961)

119. K. Ohkubo, H. Shimada and M. Okada, Bull.Chem.Soc. Japan, 44, 2025 (1971)

120. M. F. Guest, I. H. Hillier and V. R. Saunders, J.Organometal. Chem., 44, 59 (1972)

121. C. D. Good and D. M. Ritter, J.Amer.Chem.Soc., 84, 1162 (1962)

122. G. A. Chamberlain and E. Whittle, Trans.Faraday Soc., 67, 2077 (1971)

123. H. A. Skinner and N. B. Smith, J.C.S., p.2324 (1954)

124. O. T. Beachley and B. Washburn, Inorg.Chem., 15, 725 (1976)

125. F. B. Clippard and L. S. Bartell, Inorg.Chem., 9, 2439 (1970)

126. F. C. Gunderloy and C. E. Erickson, Inorg.Chem., 1, 349 (1962)

127. J. C. Baldwin, M. F. Lappert, J. B. Pedley, P.N.K. Riley and R. D. Sedgwick, Inorg.Nucl.Chem.Letters, 1, 57 (1965)

128. M. F. Lappert, M. R. Litzow, J. B. Pedley, P.N.K. Riley, T. R. Spalding and J. A. Treverton, J.C.S.(A), p.2320 (1970)

129. W. N. Lipscomb, Boron Hydrides, Benjamin, New York (1963)

130. E. J. Prosen, Symposium on Hydrides, Spring 1955, Amer.Chem.Soc.Meeting (Abst.No.68, Division of Phys. and Inorg. Chem.).

131. S. R. Gunn and L. G. Green, J.Phys.Chem., 65, 2173 (1961)

132. K. Wade, Electron Deficient Compounds, p.62-64, Nelson, London (1971)

133. S. H. Bauer, J.Amer.Chem.Soc., 80, 294 (1958)

134. G. Will and K. H. Kossobutzki, Z.Kristallogr., 142, 383 (1976)

135. G. Will and K. H. Kossobutzki, J. Less-Common Metals, 47, 33 (1976)

136. R. F. Gould (ed.), Borax to Boranes, (Adv.Chem.Series), Amer.Chem.Soc., Washington D.C. (1961)

137. B. F. Decker and J. S. Kasper, Acta Cryst., 12, 503 (1959)

138. E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens and W. N. Lipscomb, J.Amer.Chem.Soc., 92, 3837 (1970)

139. E. Switkes, W. N. Lipscomb and M. D. Newton, J.Amer.Chem. Soc., 92, 3847 (1970)

140. L. D. Brown and W. N. Lipscomb, Inorg.Chem., 16, 2989 (1977)

141. J. D. Dill, P. von R. Schleyer and J. A. Pople, J.Amer.Chem.Soc., 97, 3402 (1975)

142. M. J. S. Dewar and M. L. McKee, J.Amer.Chem.Soc., 99, 5231 (1977)

143. M. E. Jones, K. Hedberg and V. Schomaker, J.Amer. Chem.Soc., 75, 4116 (1953)

144. E. B. Moore, R. E. Dickerson and W. N. Lipscomb, J.Chem.Phys., 27, 209 (1957)

145. C. E. Nordman and W. N. Lipscomb, J.Chem.Phys., 21, 1856 (1953)

146. C. E. Nordman and W. N. Lipscomb, J.Amer.Chem.Soc., 75, 4116 (1953)

147. G. S. Pawley, Acta Cryst., 20, 631 (1966)

148. H. J. Hrostowski and R. J. Myers, J.Chem.Phys., 22, 262 (1954)

149. L. Lavine and W. N. Lipscomb, J.Chem.Phys., 22, 614 (1954)

150. F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert and W. N. Lipscomb, J.Chem.Phys., 28, 56 (1958)

151. I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens and W. N. Lipscomb, Inorg.Chem., 10, 171 (1971)

152. A. Tippe and W. C. Hamilton, Inorg.Chem., 8, 464 (1969)

153. V. S. Mastryukov, O. V. Dorofeeva and L. V. Vilkov, Zhur.Strukt.Khim, 29, 801 (1975)

154. L. S. Bartell and B. L. Carroll, J.Chem.Phys., 42, 1135 (1965)

155. K. Kuchitsu, J.Chem.Phys., 49, 4457 (1968)

156. B. Callmer, Acta Cryst., 33B, 1951 (1977)

157. R. E. Enrione, F. P. Boer and W. N. Lipscomb, J.Amer.Chem.Soc., 86, 1451 (1964)

158. R. E. Enrione, F. P. Boer and W. N. Lipscomb, Inorg.Chem., 3, 1659 (1964)

159. R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, J.Chem.Phys., 27, 200 (1957)

160. J. C. Huffman, D. C. Moody, J. W. Raithke and R. Schaeffer, J.C.S.Chem.Comm., p.308 (1973)

161. J. C. Huffman, D. C. Moody and R. Schaeffer, Inorg.Chem., 15, 227 (1976)

162. P. G. Simpson and W. N. Lipscomb, J.Chem.Phys., 39, 26 (1963)

163. P. G. Simpson, K. Folting, R. D. Dobrott and W.N. Lipscomb, J.Chem.Phys., 39, 2339 (1963)

164. R. Schaeffer, Q. Johnson and G. S. Smith, Inorg.Chem., 4, 917 (1965)

165. L. J. Guggenberger, Inorg.Chem., 8, 2771 (1969)

166. L. J. Guggenberger, Inorg.Chem., 7, 2260 (1968)

167. J. T. Gill and S. J. Lippard, Inorg.Chem., 14, 751 (1975)

168. J. A. Wunderlich and W. N. Lipscomb, J.Amer.Chem.Soc., 82, 4427 (1960)

169. K. Wade, Inorg.Nucl.Chem.Letters, 8, 823 (1972)

170. R. L. Middaugh, Boron Hydride Chemistry, (ed.E.L.Muetterties), Ch.8, Academic Press, New York (1975)

171. E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth and H. C. Miller, Inorg.Chem., 3, 444 (1964)

172. J. Aihara, J.Amer.Chem.Soc., 100, 3339 (1978)

173. F. Klanberg and E. L. Muetterties, Inorg.Chem., 5, 1955 (1966)

174. F. Klanberg, D. R. Eaton, L. J. Guggenberger and E. L. Muetterties, Inorg.Chem., 6, 1271 (1967)

175. E. L. Muetterties, E. L. Hoel, C. G. Salentine and M. F. Hawthorne, Inorg.Chem., 14, 950 (1975)

176. D. R. Armstrong, P. G. Perkins and J. J. P. Stewart, J.C.S. Dalton, p.627 (1973)

177. D. A. Dixon, D. A. Kleier, T. A. Halgren, J. H. Hall and W. N. Lipscomb, 99, 6226 (1977)

178. J. A. Connor, Topics in Current Chem., 71, 71 (1977)

179. F. A. Cotton, A. K. Fischer and G. Wilkinson, J.Amer. Chem.Soc., 78, 5168(1956); 81, 800 (1959)

180. D. L. S. Brown, J. A. Connor, H. A. Skinner, C. P. Demain, M. L. Leung, J. A. Martinho-Simeos and M.T. Zafaroni, J.Organometal. Chem., 142, 321 (1977)

181. G. Battison, G. Sbrignadello, G. Bor and J. A. Connor, J.Organometal. Chem., 131, 445 (1977)

182. J. A. Connor, J.Organometal. Chem., 94, 195 (1975)

183. R. G. Behrens, J. Less-Common Metals, 58, 47 (1978)

184. B. F. G. Johnson and J. Lewis, Pure Applied Chem., 44, 43 (1975)

185. R. G. Behrens, J. Less-Common Metals, 56, 55 (1977)

186. L. E. Sutton (ed.), Tables of Interatomic Distances, Supplementary Volume, Chem.Soc.Spec.Publn.No.18 (1965)

187. J. Donohue, The Structures of the Elements, Wiley, New York (1974)

188. G. G. Sumner, H. P. Klug and L. E. Alexander, Acta Cryst., 17, 732 (1964)

189. F. A. Cotton, F. H. Carré and B. A. Frenz, Inorg.Chem., 15, 380 (1976)

190. C. H. Wei, G. R. Wilkes and L. F. Dahl, J.Amer.Chem. Soc., 89, 4792 (1967)

191. F. A. Cotton and J. M. Troup, J.C.S. Dalton, p.800 (1974)

192. F. A. Cotton and J. M. Troup, J.Amer.Chem.Soc., 96, 4155 (1974)

193. K. Wade, Inorg.Nucl.Chem.Letters, 14, 71 (1978)

194. E. R. Corey, L. F. Dahl and W. Beck, J.Amer.Chem.Soc., 85, 1202 (1963)

195. D. Brennan and F. H. Hayes, Phil.Trans.Roy.Soc., 258A, 347 (1965)

196. J. M. Basset and R. Ugo, Aspects of Homogenous Catalysis, 3, 137 (1976)

197. E. L. Muetterties, Bull.Soc.Chim.Belges, 84, 959 (1975)

198. P. Chini, G. Longoni and V. G. Albano, Adv.Organometal. Chem., 14, 285 (1976)

199. J. W. Lauher, J.Amer.Chem.Soc., 100, 5305 (1978)

200. H. Conrad, G. Ertl, H. Knözinger, J. Küppers and E. E. Latta, Chem.Phys.Letters, 42, 115 (1976)

201. H. Vahrenkamp, Angew.Chem.Int.Edn., 17, 379 (1978)

202. K. A. Gingerich, S. K. Gupta and R. M. Atkins, Inorg.Chem., 17, 3211 (1978)

203. J. C. Green, E. A. Sneddon and D. M. P. Mingos, J.C.S.Chem.Comm. p.94 (1979)

204. J. D. H. Donnay and H. M. Ondik (eds.), Crystal Data, 2, 3rd edn., U.S. Dept. of Commerce, Nat.Bureau of Standards, Joint Committee on Powder Diffraction Standards, Washington D.C. (1973)

205. J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson (eds.), Comprehensive Inorganic Chemistry, 3, Pergamon Press, Oxford (1973)

206. C. J. Smithells (ed.), Metals Reference Book, 5th ed., Butterworths, London (1976)

207. C. A. Hampel (ed.), Rare Metals Handbook, 2nd edn., Reinhold, London (1961)

208. J. B. Holbrook, F. M. Khaled and B. C. Smith, J.C.S. Dalton, p.1631 (1968)

209. B. F. G. Johnson, J.C.S.Chem.Comm. p.211 (1976)

210. J. Evans, Adv.in Organometal. Chem., 16, 319 (1977)

211. B. F. G. Johnson, J.C.S.Chem.Comm.,p.703 (1976)

212. M. R. Churchill, F. J. Hollander and J. P. Hutchinson, Inorg.Chem., 16, 2655 (1977)

213. M. R. Churchill and D. G. DeBoer, Inorg.Chem., 16, 878 (1977)

214. M. R. Churchill and J. P. Hutchinson, Inorg.Chem., 17, 3528 (1978)

215. D. V. Korol'Kov, Zh.Strukt.Khim., 15, 1012 (1974)

216. D. W. Smith, J.C.S. Dalton, p.834 (1976)

217. L. H. Little, Chemisorption and Reactions on Metallic Films, 1, ed. J. R. Anderson, Academic Press, London (1971)

218. R. L. Decock, Inorg.Chem., 10, 1205 (1971)

219. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York (1963)

220. R. Cataliotti, A. Faffani and L. Marchetti, Inorg.Chem., 10, 1594 (1971)

221. K. Farmery, M. Kilner, R. Greatex and N. Greenwood, J.C.S.Chem.Comm., p.593 (1968)

222. J. Knight and M. J. Mays, J.C.S.Chem.Comm., p.1006 (1970)

223. M. Poliakoff and J. J. Turner, J.C.S.Chem.Comm., p.1008 (1970)

224. L. Hanlan, H. Huber and G. A. Ozin, Inorg.Chem., 15, 2592 (1976)

225. J. L. Slater, T. C. DeVore and V. Calder, Inorg.Chem., 12, 1918 (1973)

226. J. L. Slater, T. C. DeVore and V. Calder, Inorg.Chem., 13, 1808 (1974)

227. F. A. Cotton and C. S. Kraihanzel, J.Amer.Chem.Soc., 84, 4432 (1962)

228. B. F. G. Johnson, C. Eady and J. Lewis, J.Organometal Chem., 37, C39 (1972)

229. C. R. Eady, B. F. G. Johnson and J. Lewis, J.C.S. Dalton, p.2606 (1975)

230. B. F. G. Johnson, C. R. Eady, J. Lewis, B.E. Reichert and G. M. Sheldrick, J.C.S.Chem.Comm., p.271 (1976)

231. R. Mason, K. M. Thomas and D. M. P. Mingos, J.Amer.Chem. Soc., 95, 3802 (1973)

232. C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock and K. M. Thomas, J.C.S.Chem.Soc., p.385 (1977)

233. F. Calderazzo and P. L'Eplattenier, Inorg.Chem., 6, 1220 (1967)

234. D. K. Huggins, N. Flitcroft and H. D. Kaesz, Inorg.Chem., 4, 166 (1965)

235. B. Beagley and D. G. Schmidling, J.Mol.Struct., 22, 466 (1974)

236. E. W. Plummer, W. R. Salaneck and J. S. Miller, Phys.Rev.B, 18, 1673 (1978)

237. D. O. Hayward, Chemisorption and Reactions on Metallic Films, 1, ed. J. R. Anderson, Academic Press, London (1971)

238. G. Blyholder, J.Chem.Phys., 36, 2036 (1962)

239. G. Blyholder and L. D. Neff, J.Phys.Chem., 66, 1464 (1962)

240. G. Blyholder, J.Chem.Phys., 44, 3134 (1966)

241. G. Blyholder and M. Tanaka, J.Phys.Chem., 76, 3180 (1972)

242. K. Kishi and M. W. Roberts, J.C.S. Faraday I, 71, 1715 (1975)

243. H. C. Yao and W. G. Rothschild, J.Chem.Phys., 68, 4774 (1978)

244. E. Peligot, Compt. Rend., 19, 609 (1844)

245. F. A. Cotton, Science, 145, 1305 (1964)

246. L. Pauling, Proc.Natl.Acad.Sci. U.S.A., 72, 3799 (1975)

247. F. A. Cotton and C.B. Harris, Inorg.Chem., 4, 330 (1965)

248. F. A. Cotton, B. G. DeBoer and M. Jeremic, Inorg.Chem., 9, 2143 (1970)

249. F. A. Cotton, B. A. Frenz and L. W. Shive, Inorg.Chem., 14, 649 (1975)

250. F. A. Cotton, L. D. Gage and C. E. Rice, Inorg.Chem., 18, 1138 (1979)

251. F. A. Cotton and L. D. Gage, Nouv.J.Chim., 1, 441 (1977)

252. F. A. Cotton and L. W. Shive, Inorg.Chem., 14, 2032 (1975)

253. F. A. Cotton, B. G. DeBoer, M. D. Laprade, J. R. Pipal and D. A. Ucko, J.Amer.Chem.Soc., 92, 2926 (1970)

254. F. A. Cotton, B. G. DeBoer, M. D. Laprade, J. R. Pipal and D. A. Ucko, Acta Cryst., 27B, 1664 (1971)

255. F. A. Cotton, C. E. Rice and G. W. Rice, J.Amer.Chem.Soc., 99, 4704 (1977)

256. J. Krausse, G. Marx and G. Schödl, J.Organometal.Chem., 21, 159 (1970)

257. F. A. Cotton, G. W. Rice and J. C. Sekutowski, Inorg.Chem., 18, 1143 (1979)

258. F. A. Cotton and M. Millar, Inorg.Chim.Acta, 25, L105 (1977)

259. F. A. Cotton, S. Koch and M. Millar, J.Amer.Chem.Soc., 99, 7372 (1977)

260. F. A. Cotton and S. Koch, Inorg.Chem., 17, 2021 (1978)

261. F. A. Cotton, B. A. Frenz, L. Shive and M. Chisholm, J.C.S.Chem.Comm., p.480 (1974)

262. F. A. Cotton, M. H. Chisholm, B. A. Frenz, W. W. Reichert, L. W. Shive and B. R. Stults, J.Amer.Chem.Soc., 98, 4469 (1976)

263. F. A. Cotton, C. L. Angell, B. A. Frenz and T. R. Webb, J.C.S.Chem.Comm., p.399 (1973)

264. F. A. Cotton, D. M. Collins and C. A. Murillo, Inorg.Chem., 15, 2950 (1976)

265. F. A. Cotton, Z. C. Mester and T. R. Webb, Acta Cryst., 30B, 2768 (1974)

266. F. A. Cotton, J. G. Norman, B. R. Stults and T. R. Webb, J.Coord.Chem., 5, 217 (1976)

267. D. V. Korol'kov and V. N. Pak, Zh.Strukt.Khim., 11, 734 (1970)

268. F. A. Cotton and S. A. Koch, J.Amer.Chem.Soc., 99, 7371 (1977)

269. F. A. Cotton, B. R. Stults, J. M. Troup, M. H. Chisholm and M. Extine, J.Amer.Chem.Soc., 97, 1242 (1975)

270. F. A. Cotton, M. H. Chisholm, M. Extine and B. R. Stults, J.Amer.Chem.Soc., 98, 4477 (1976)

271. F. A. Cotton, D. M. Collins, S. Koch, M. Millar and C. A. Murillo, J.Amer.Chem.Soc., 99, 1259 (1977)

272. F. A. Cotton, D. M. Collins, S. Koch, M. Millar and C. A. Murillo, Inorg.Chem., 17, 2017 (1978)

273. F. A. Cotton and M. Millar, J.Amer.Chem.Soc., 99, 7886 (1977)

274. Y. B. Koh and G. G. Christoph, Inorg.Chem., 17, 2593 (1978)

275. F. A. Cotton, Accounts Chem.Res., 2, 240 (1969)

276. F. A. Cotton, Chem.Soc.Rev., 4, 27 (1975)

277. F. A. Cotton, Accounts Chem.Res., 11, 225 (1978)

278. W. C. Trogler and H. B. Gray, Accounts Chem.Res., 11, 232 (1978)

279. M. H. Chisholm and F. A. Cotton, Accounts Chem.Res., 11, 356 (1978)

280. C. D. Garner, I. H. Hillier, M. F. Guest, J. C. Green and A. W. Coleman, Chem.Phys.Letters, 41, 91 (1976)

281. B. N. Figgis and R. L. Martin, J.Chem.Soc., p.3837 (1956)

282. F. A. Cotton and G. G. Stanley, Inorg.Chem., 16, 2668 (1977)

283. A. Dedieu, T. A. Albright and R. Hoffman, J.Amer.Chem. Soc., 101, 3141 (1979)

284. F. A. Cotton, B. A. Frenz and T. R. Webb, J.Amer.Chem. Soc., 95, 4431 (1973)

285. A. Bino and F. A. Cotton, Inorg.Chem., 17, 1159 (1978)

286. G. A. Ozin and W. Klotzbücher, Inorg.Chem., 16, 984 (1977)

287. H. B. Gray, J. G. Norman, H. J. Kolari and W. C. Trogler, Inorg.Chem., 16, 987 (1977)

288. G. A. Ozin, W. Klotzbücher, J. G. Norman and H. J. Kolari, Inorg.Chem., 16, 2871 (1977)

289. K. A. Gingerich, S. K. Gupta and R. M. Atkins, Inorg.Chem., 17, 3211 (1978)

290. W. F. Cooper, G. A. Clarke and C. R. Hare, J.Phys.Chem., 76, 2268 (1972)

291. V. Piacente, G. Balducci and G. Bardi, J.Less-Common Metals, 37, 123 (1974)

292. K. A. Gingerich and D. L. Cocke, J.C.S.Chem.Comm., p.536 (1972)

293. W. K. Bratton, F. A. Cotton, M. DeBeau and R. A. Walton, J.Coord.Chem., 1, 121 (1971)

294. F. A. Cotton and C. B. Harris, Inorg.Chem., 6, 924 (1967)

295. G. L. Geoffroy, H. B. Gray and G. S. Hammond, J.Amer. Chem.Soc., 96, 5565 (1974)

296. W. C. Trogler, C. D. Cowman, H. B. Gray and F. A. Cotton, J.Amer.Chem.Soc., 99, 2993 (1977)

297. R. J. H. Clark and N. R. D'Urso, J.Amer.Chem.Soc., 100, 3088 (1978)

298. R. Kh. Zacheslavskaya and D. V. Korol'kov, Teor.Éksp. Khim., 9, 21 (Eng.Trans.p.14) (1973)

299. H. A. Skinner, J.Chem.Thermodynamics, 10, 309 (1978)

300. J. A. Connor, G. Pilcher, H. A. Skinner, M. H. Chisholm and F. A. Cotton, J.Amer.Chem.Soc., 100 7738 (1978)

301. F. A. Cotton, B. A. Frenz and L. Kruczynski, J.Amer. Chem.Soc., 95, 951 (1973)

302. F. A. Cotton, L. Kruczynski and B. A. Frenz, J.Organometal. Chem., 160, 93 (1978)

303. F. A. Cotton and J. T. Mague, Inorg.Chem., 3, 1402 (1964)

304. D. V. Korol'kov and Kh.Missner, Teor.Éksp.Khim., 9, 336 (1973)

305. D. V. Korol'kov , Kh. Missner and K. V. Ovchinnikov, Zh.Strukt.Khim., 14, 717 (1973)

306. H. C. Longuet-Higgins, Quart.Rev.Chem.Soc., 11, 121 (1957)

307. K. Wade, Inorg.Nucl.Chem.Letters, 8, 559 (1972)

308. K. Wade, Inorg.Nucl.Chem.Letters, 8, 563 (1972)

309. K. Wade, Nature Phys.Sci., 240, 71 (1972)

310. W.-D. Stohrer and R. Hoffman, J.Amer.Chem.Soc., 94, 1661 (1972)

311. S. Masamune, M. Sakai, H. Ona and A. J. Jones, J.Amer.Chem.Soc., 94, 8956 (1972)

312. H. Hart and M. Kuzuya, J.Amer.Chem.Soc., 94, 8960 (1972)

313. W. J. Hehre and P.v.R. Schleyer, J.Amer.Chem.Soc., 95, 5837 (1973)

314. H. Hart and R. Willer, Tetrahedron Letters, p.4189 (1978)

315. H. Hogeveen and P. W. Kwant, J.Amer.Chem.Soc., 95, 7315 (1973)

316. H. Hogeveen and P. W. Kwant, Tetrahedron Letters, p.1665 (1973)

317. H. T. Jonkman and W. C. Nieuwpoort, Tetrahedron Letters, p.1671 (1973)

318. H. Hogeveen, P. W. Kwant, J. Postma and P. T. van Duynen, Tetrahedron Letters, p.4351 (1974)

319. H. Hogeveen and P. W. Kwant, Accounts Chem.Res., 8, 413 (1975)

320. M. J. S. Dewar and R. C. Haddon, J.Amer.Chem.Soc., 95, 5836 (1973)

321. U. Szeimies-Seebach, J. Harnisch, G. Szeimies, M. van Meerssche, G. Germain and J.-P. Declerq, Angew.Chem.Int.Ed., 17, 848 (1978)

322. G. Maier, S. Pfriem, U. Schäfer and R. Matusch, Angew.Chem.Int.Ed., 17, 520 (1978)

323. G. A. Olah and P.v.R. Schleyer (eds.), Carbonium Ions, 5, Ch.38, Wiley, New York (1976)

324. K. W. Cox and M. D. Harmony, J.Chem.Phys., 50, 1976 (1969)

325. J. D. Dunitz and V. Schomaker, J.Chem.Phys., 20, 1703 (1952)

326. A. Almenningen, O. Bastiansen and P. N. Skancke, Acta Chem.Scand., 15, 711 (1961)

327. D. A. Dows and N. Rich, J.Chem.Phys., 47, 333 (1967)

328. T. Ueda and T. Schimanouchi, J.Chem.Phys., 49, 470 (1968)

329. J. M. R. Stone and I. M. Mills, Mol.Phys., 18, 631 (1970)

330. S. Meiboom and L. Snyder, J.Chem.Phys., 52, 3857 (1970)

331. F. A. Miller and R. J. Capwell, Spec.Acta, 27A, 947 (1971)

332. E. Castellucci, M. G. Migliorini and P. Manzelli, Acta Cryst., 27A, 432 (1972)

333. R. G. Ford and R. A. Beaudet, J.Chem.Phys., 48, 4671 (1968)

334. M. I. Davis and T. W. Muecke, J.Phys.Chem., 74, 1104 (1970)

335. R. K. Bohn and Y-H. Tai, J.Amer.Chem.Soc., 92, 6447 (1970)

336. R. D. Suenram and M. D. Harmony, J.Chem.Phys., 56, 3837 (1972)

337. J. F. Chiang and S. H. Bauer, J.Amer.Chem.Soc., 92, 1614 (1970)

338. A. Almenningen, B. Anderson and B. A. Nyhus, Acta Chem.Scand., 25, 1217 (1971)

339. K. Mizuno, T. Fukuyama and K. Kuchitsu, Chem.Letters, p.249 (1972)

340. J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, J.Amer.Chem.Soc., 69, 2483 (1947)

341. W. J. Adams, H. J. Geise and L. S. Bartell, J.Amer. Chem.Soc., 92, 5013 (1970)

342. J. L. Nelson, C. C. Cobb and A. A. Frost, J.Chem.Phys., 60, 712 (1974)

343. R. K. Bohn, K. Mizuno, T. Fukuyama and K. Kuchitsu, Bull.Chem.Soc.Japan, 46, 1395 (1973)

344. P. E. Eaton and T. V. Cole, J.Amer.Chem.Soc., 86, 3157 (1964)

345. P. Chini and B. T. Heaton, Topics in Current Chemistry, 71, 1 (1977)

346. K. P. Callahan and M. F. Hawthorne, Adv.Organometal. Chem. 14, 145 (1976)

347. P. Chini, G. Longoni and V. G. Albano, Adv.Organometal. Chem., 14, 285 (1976)

348. J. J. Guy and G. M. Sheldrick, Acta Cryst., 34B, 1722 (1978)

349. B. F. G. Johnson, C. R. Eady, J. J. Guy, J. Lewis, G. M. Sheldrick and M. C. Malatesta, J.C.S. Chem. Comm. p.807 (1976)

350. J. F. Blount, L. F. Dahl, C. Hoogzand and W. Hübel, J.Amer.Chem.Soc., 88, 292 (1966)

351. J. D. Corbett, Inorg.Chem., 7, 198 (1968)

352. J. D. Corbett and P. A. Edwards, J.C.S.Chem.Comm., 984 (1975)

353. J. D. Corbett and P. A. Edwards, Inorg.Chem.,16, 903 (1977)

354. E. A. McNeill, K. L. Gallaher, F. R. Scholer and S. H. Bauer, Inorg.Chem., 12, 2108 (1973)

355. R. D. Wilson, S. M. Wu, R. A. Love and R. Bau, Inorg. Chem., 17, 1271 (1978)

356. V. G. Albano, G. Ciani, M. Manassero, F. Canziani, G. Giordano, S. Martinengo and P. Chini, J. Organometal. Chem., 150, C17 (1978)

357. M. R. Churchill, H. D. Kaesz, B. Fontal, R. Bau and S. W. Kirtley, J.Amer.Chem.Soc., 91, 1021 (1969)

358. B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick and G. Süss, J.Organometal.Chem., 162, 179 (1978)

359. B. F. G. Johnson, J. Lewis, D. Pippard, P. R. Raithby, G. M. Sheldrick and K. D. Rouse, J.C.S.Dalton, p.616 (1979)

360. B. R. Penfold and B. H. Robinson, Accounts Chem.Res., 6, 73 (1973)

361. B. F. G. Johnson, S. Bhaduri, J. Lewis, P. R. Raithby and D. J. Watson, J.C.S.Chem.Comm., p.343 (1978)

362. T. Chiang, R. C. Kerber, S. D. Kimball and J. W. Lauher, Inorg.Chem., 18, 1687 (1979)

363. D. S. Ginley, C. R. Bock, M. S. Wrighton, B. Fischer, D. L. Tipton and R. Bau, J.Organometal.Chem., 157 41 (1978)

364. M. R. Churchill and M. V. Veidis, J.Chem.Soc. (D), p.529 (1970)

365. M. R. Churchill and M. V. Veidis, J.Chem.Soc.(A), p.2170 (1971)

366. E. L. Anderson and T. P. Fehlner, J.Amer.Chem.Soc., 100, 4606 (1978)

367. O. S. Mills and E. F. Paulus, Chem.Comm., p.815 (1966)

368. A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick and K. D. Rouse, J.C.S.Chem.Comm., p.723 (1978)

369. M. R. Churchill, F. J. Hollander and J. P. Hutchinson, Inorg.Chem., 16, 2697 (1977)

370. M. R. Churchill, P. M. Bird, H. D. Kaesz, R. Bau and B. Fontal, J.Amer.Chem.Soc., 90, 7135 (1968)

371. C. R. Peters and C. E. Nordman, J.Amer.Chem.Soc., 82, 5758 (1960)

372. V. G. Albano, P. L. Bellon and G. F. Ciani, Chem.Comm., p.1024 (1969)

373. V. G. Albano, G. Ciani, S. Martinengo, P. Chini and G. Giordano, J.Organometal.Chem., 88, 381 (1975)

374. V. G. Albano and P. L. Bellon, J.Organometal.Chem., 19, 405 (1969)

375. V. G. Albano, P. Chini and V. Scatturin, J.Organometal. Chem., 15, 423 (1968)

376. V. G. Albano, P. L. Bellon, P. Chini and V. Scatturin, J.Organometal.Chem., 16, 461 (1969)

377. M. R. Churchill and J. Wormald, J.Amer.Chem.Soc., 93, 5670 (1971)

378. B. F. G. Johnson, C. R. Eady, J. Lewis, P. Machin, C. M. Malatesta and M. McPartlin, J.C.S.Chem.Comm., p.945 (1976)

379. A. Sirigu, M. Bianchi and E. Benedetti, Chem.Comm., p.596 (1969)

380. B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Schorpp and G. M. Sheldrick, J.C.S.Dalton, p.1417 (1977)

381. M. McPartlin, C. R. Eady, B. F. G. Johnson and J. Lewis, J.C.S.Chem.Comm. p.883 (1976)

382. L. F. Dahl and D. L. Smith, J.Amer.Chem.Soc., 84, 2450 (1962)

383. M. R. Churchill, J. Wormald, J. Knight and M. J. Mays, J.Amer.Chem.Soc., 93, 3073 (1971)

384. M. R. Churchill and J. Wormald, J.C.S.Dalton, p.2410 (1974)

385. L. F. Dahl, J. C. Calabresse, A. Cavalieri, P. Chini, G. Longoni and S. Martinengo, J.Amer.Chem.Soc., 96, 2616 (1974)

386. G. F. Stuntz, J. R. Shapley and C. G. Pierpont, Inorg. Chem., 17, 2596 (1978)

387. R. A. Beaudet and R. L. Poynter, J.Chem.Phys., 53, 1899 (1970)

388. E. A. McNeill and F. R. Scholar, Inorg.Chem., 14, 1081 (1975)

389. G. L. McKnown, B. P. Don, R. A. Beaudet, P. J. Vergamini and L. H. Jones, J.C.S.Chem.Comm. p.765 (1974)

390. G. L. McKnown, B. P. Don, R. A. Beaudet, P. J. Vergamini and L. H. Jones, J.Amer.Chem.Soc., 98, 6909 (1976)

391. J. M. Fernandez, B. F. G. Johnson, J. Lewis and P. R. Raithby, Acta Cryst., 34B, 3086 (1978)

392. E. H. Braye, L. F. Dahl, W. Hübel and D. L. Wampler, J.Amer.Chem.Soc., 84, 4633 (1962)

393. B. F. G. Johnson, C. R. Eady, J. Lewis and T. Matheson, J.Organometal.Chem., 57, C82 (1973)

394. C. G. Pierpont, Inorg.Chem., 16, 636 (1977)

395. A. J. Deeming, J.Organometal.Chem., 150, 123 (1978)

396. E. A. Cohen and R. A. Beaudet, J.Chem.Phys., 48, 1220 (1968)

397. N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison and S. S. Wreford, J.C.S.Chem.Comm. p.718 (1974)

398. J. A. Ulman, E. L. Anderson and T. P. Fehlner, J.Amer. Chem.Soc., 100, 456 (1978)

399. L. G. Sneddon and D. Voet, J.C.S.Chem.Comm. p.118 (1976)

400. D. A. Franz, V. R. Miller and R. N. Grimes, J.Amer.Chem. Soc., 94, 412 (1972)

401. R. J. Gillespie, J. Passmore, P. K. Ummat and O. C. Vaidya, Inorg.Chem., 10, 1327 (1971)

402. D. J. Prince, J. D. Corbett and B. Garbisch, Inorg.Chem., 9, 2731 (1970)

403. T. W. Couch, D. A. Lokken and J. D. Corbett, Inorg.Chem., 11, 357 (1972)

404. C. R. Lassigne and E. J. Wells, J.C.S.Chem.Comm., p.956 (1978)

405. G. J. Schrobilgen, R. C. Burns and P. Granger, J.C.S.Chem.Comm., p.957 (1978)

406. A. Cisar and J. D. Corbett, Inorg.Chem., 16, 2482 (1977)

407. C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito and H. J. Heeger, J.Amer.Chem.Soc., 97, 6358 (1975)

408. M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran and J. Kleppinger, J.Amer.Chem.Soc., 98, 3844 (1976)

409. P. R. Adkins and A. G. Turner, J.Amer.Chem.Soc., 100, 1383 (1978)

410. B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong and M. McPartlin, J.C.S. Dalton, p.673 (1978)

411. A. Cisar and J. D. Corbett, Inorg.Chem., 16, 632 (1977)

412. E. A. McNeill and F. R. Scholer, J.Mol.Struct., 27, 151 (1975)

413. R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan and P. T. Greene, J.Amer.Chem.Soc., 94, 1865 (1972)

414. V. R. Miller, L. G. Sneddon, D. C. Beer and R. N. Grimes, J.Amer.Chem.Soc., 96, 3090 (1974)

415. S. G. Shore, J. D. Ragaini, R. L. Smith, C. E. Cottrell and T. P. Fehlner, Inorg.Chem., 18, 670 (1979)

416. T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart and R. E. Williams, J.Amer.Chem.Soc., 88, 2061 (1966)

417. F. P. Boer, W. E. Streib and W. N. Lipscomb, Inorg.Chem., 3, 1667 (1964)

418. C. L. Bramlett and R. N. Grimes, J.Amer.Chem.Soc., 88, 4269 (1966)

419. R. N. Grimes, J.Amer.Chem.Soc., 93, 261 (1971)

420. J. P. Pasinski and R. A. Beaudet, J.C.S.Chem.Comm., p.928 (1973)

421. P. Jutzi and A. Seufert, Angew,Chem.Int.Ed., 16, 330 (1977)

422. A. F. Berndt and R. E. Marsh, Acta Cryst., 16, 118 (1963)

423. W. Siebert, J. Edwin and M. Bochmann, Angew.Chem.Int.Ed., 17, 868 (1978)

424. R. N. Grimes, Accounts Chem.Res., 11, 420 (1978)

425. S. V. Dobyns and L. Pierce, J.Amer.Chem.Soc., 85, 3553 (1963)

426. M. Mellini and S. Merlino, Acta Cryst., 32B, 1074 (1976)

427. F. A. Momany and R. A. Bonham, J.Amer.Chem.Soc., 86, 162 (1964)

428. O. Andreasen, A. C. Hazell and R. A. Hazell, Acta Cryst., 33B, 1109 (1977)

429. O. S. Mills and G. Robinson, Proc.Chem.Soc., p.421 (1960)

430. G. J. Palenik and J. Donohue, Acta Cryst., 15, 564 (1962)

431. V. G. Albano, G. Ciani, M. Freni and P. Romiti, J.Organometal.Chem., 96, 259 (1975)

432. V. G. Albano, G. Ciani and A. Immirzi, J.Organometal, Chem., 121, 237 (1976)

433. E. Sappa, A. Tiripicchio and M. Tiripicchio-Camellini, J.C.S.Dalton, p.419 (1978)

434. V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton and S. Martinengo, J.Amer.Chem.Soc., 98, 5027 (1976)

435. V. G. Albano, P. Chini, G. Ciani, S. Martinengo and M. Sansoni, J.C.S.Dalton, p.463 (1978)

436. T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, K. Nakatsu, K. Kinoshita and Y. Miyagawa, J.C.S.Chem.Comm. p.579 (1979)

437. A. Zalkin, T. E. Hopkins and D. H. Templeton, Inorg.Chem., 5, 1767 (1966)

438. B. Rees and P. Coppens, J.Organometal.Chem., 42, C102 (1972)

439. B. Rees and P. Coppens, Acta Cryst., 29B, 2516 (1973)

440. C. H. E. Belin, J. D. Corbett and A. Cisar, J.Amer.Chem. Soc., 99, 7163 (1977)

441. K-K. Lau and R. A. Beaudet, Inorg.Chem., 15, 1059 (1976)

442. T. F. Koetzle, F. E. Scarbrough and W. N. Lipscomb, Inorg.Chem., 7, 1076 (1968)

443. W. J. Evans, G. B. Dunks and M. F. Hawthorne, J.Amer. Chem.Soc., 95, 4565 (1973)

444. D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan and M. F. Hawthorne, J.Amer.Chem.Soc., 96, 3085 (1974)

445. W. J. Evans and M. F. Hawthorne, Inorg.Chem., 13, 869 (1974)

446. A. J. Gotcher, J. F. Ditter and R. E. Williams, J.Amer. Chem.Soc., 95, 7514 (1973)

447. R. J. Gillespie, W. Luk and D. R. Slim, J.C.S.Chem.Comm., p.791 (1976)

448. P. Chini, G. Ciani, S. Martinengo, A. Sironi, L. Longhetti and B. T. Heaton, J.C.S.Chem.Comm., p.188 (1979)

449. W. R. Pretzer, T. K. Hilty and R. W. Rudolph, Inorg.Chem., 14, 2459 (1975)

450. T. F. Koetzle and W. N. Lipscomb, Inorg.Chem., 9, 2279 (1970)

451. R. W. Rudolph, W. L. Wilson, F. Parker, R. C. Taylor and D. C. Young, J.Amer.Chem.Soc., 100, 4629 (1978)

452. J. L. Vidal, W. E. Walker, R. L. Pruett and R. C. Schoening, Inorg.Chem., 18, 129 (1979)

453. A. Hershaft and J. D. Corbett, Inorg.Chem., 2, 979 (1963)

454. R. M. Friedman and J. D. Corbett, Inorg.Chem., 12 1134 (1973)

455. J. D. Corbett and P. A. Edwards, J.Amer.Chem.Soc., 99, 3313 (1977)

456. R. R. Rietz and R. Schaeffer, J.Amer.Chem.Soc., 93, 1263 (1971)

457. D. C. Moody and R. Schaeffer, Inorg.Chem., 15, 233 (1976)

458. R. J. Gillespie, M. Luk, E. Maharajh and D. R. Slim, Inorg.Chem., 16, 892 (1977)

459. C. Tsai and W. E. Streib, J.Amer.Chem.Soc., 88, 4513 (1966)

460. S. K. Boocock, N. N. Greenwood, J. D. Kennedy and D. Taylorson, J.C.S.Chem.Comm. p.16 (1979)

461. N. N. Greenwood, J. D. Kennedy, W. S. McDonald, J. Staves and D. Taylorson, J.C.S.Chem.Comm. p.17 (1979)

462. L. J. Guggenberger, J.Amer.Chem.Soc., 94, 114 (1972)

463. K. P. Callahan, F. Y. Lo, C. E. Strouse, A. L. Sims and M. F. Hawthorne, Inorg.Chem., 13, 2842 (1974)

464. N. N. Greenwood, H. J. Gysling and J. A. McGinnety, J.C.S.Chem.Comm., p.505 (1970)

465. D. Voet and W. N. Lipscomb, Inorg.Chem., 6, 113 (1967)

466. L. D. Lower and L. F. Dahl, J.Amer.Chem.Soc., 98, 5046 (1976)

467. J. Idris Jones and W. S. McDonald, Proc.Chem.Soc., p.366 (1962)

468. T. R. R. McDonald and W. S. McDonald, Proc.Chem.Soc., p.382 (1963)

469. H. M. M. Shearer and C. B. Spencer, Chem.Comm., p.194 (1966)

470. W. Dahlmann and H. G. von Schnering, Naturwissen., 59, 420 (1972)

471. W. Dahlmann and H. G. von Schnering, Naturwissen., 60, 429 (1973)

472. W. Schmettow and H. G. von Schnering, Angew.Chem. Int.Ed., 16, 857 (1977)

473. D. G. Adolphson, J. D. Corbett and D. J. Merryman, J.Amer.Chem.Soc., 98, 7234 (1976)

474. Y. C. Leung, J. Waser, S. van Houten, A. Vos, G. A. Wiegers and F. H. Wiebenga, Acta Cryst., 10, 574 (1957)

475. G. L. Penney and G. M. Sheldrick, J.Chem.Soc.(A), p.243 (1971)

476. Y. Monteil and H. Vincent, Z.Anorg.Allg.Chem., 416, 181 (1975)

477. T. J. Bastow and H. J. Whitfield, J.C.S. Dalton, p.959 (1977)

478. B. Meyer, Adv.Inorg.Chem.Radiochem., 18, 287 (1976)

479. G. A. Wiegers and A. Vos, Acta Cryst., 20, 192 (1966)

480. R. K. Bohn and M. D. Bohn, Inorg.Chem., 10, 350 (1971)

481. C. J. Fritchie,(Jr.), Inorg.Chem., 6, 1199 (1967)

482. W. H. Knoth, J.Amer.Chem.Soc., 89, 3342 (1967)

483. R. A. Wiesboeck and M. F. Hawthorne, J.Amer.Chem.Soc., 86, 1642 (1964)

484. A. R. Kane, L. J. Guggenberger and E. L. Muetterties, J.Amer.Chem.Soc., 92, 2571 (1970)

485. D. S. Kendall and W. N. Lipscomb, Inorg.Chem., 12, 546 (1973)

486. T. K. Hilty and R. W. Rudolph, Inorg.Chem., 18, 1106 (1979)

487. V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo and M. Anker, J.C.S.Chem.Comm., p.859 (1975)

488. E. L. Muetterties, R. J. Wiersema and M. F. Hawthorne, J.Amer.Chem.Soc., 95, 7520 (1973)

489. E. L. Muetterties, Tetrahedron, 30, 1595 (1974)

490. R. H. Cragg, J. D. Smith and G. E. Toogood, Chem.Soc. Annual Reports (A), 74, 143 (1977)

491. J. Lauher, J.Amer.Chem.Soc., 101, 2604 (1979)