number of 2-centre-2-electron B–B bonds, and x is the number of BH_2-units. The formula of the borane is given by B_pH_{p+q}.

$$s + x = q \qquad s + t = p \qquad t + y = p - q/2 \qquad \text{Eqn 4.2}$$

An exercise in *styx* rules exemplified by B_5H_9:

1. Consider a particular borane and define p and q:
   For B_5H_9: $p = 5$ $q = 4$.
2. Choose integral values of s between the limits $0 \le s \le p$:
   For B_5H_9: $0 \le s \le 5$.
3. Solve Eqn 4.2 for each value of s:

For $s = 0$,	$x = 4$	$t = 5$	$y = -2$
For $s = 1$,	$x = 3$	$t = 4$	$y = -1$
For $s = 2$,	$x = 2$	$t = 3$	$y = 0$
For $s = 3$,	$x = 1$	$t = 2$	$y = 1$
For $s = 4$,	$x = 0$	$t = 1$	$y = 2$
For $s = 5$,	$x = -1$	$t = 0$	$y = 3$

4. Discard solutions from (3.) which include negative values of x, t, or y as these are not real; (see the definitions of *styx* which require positive values):
   For B_5H_9, only three solutions remain:
   styx = (2302) or (3211) or (4120)
5. Interpret the real solutions of *styx* in terms of structural diagrams:
   The possible structures deduced for B_5H_9 are shown in Fig. 4.22. For example, the result *styx* = (2302) means that there are two 3-centre-2-electron B–H–B interactions, three 3-centre-2-electron B–B–B interactions, no 2-centre-2-electron B–B bonds, and two BH_2-units. Although it is difficult to choose between the predicted forms, in hindsight, the experimentally determined structure implies that (4120) is preferred.

B_6H_{12}
$6B_2 + 6_2$
$6 + 2 \times 6$
$= 18/2 = 9$
B_nH_{n+6}

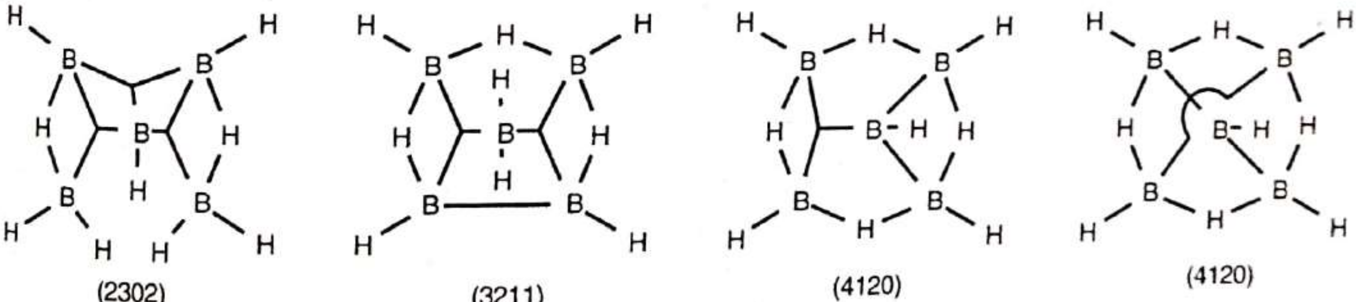
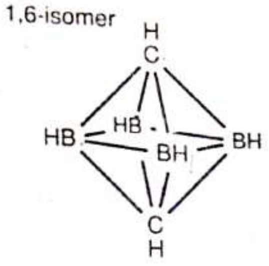


Fig. 4.22 Structures for B_5H_9 deduced by use of *styx* rules. Note that *styx* = (4120) leads to two valence structures.

consistent with a 6-vertex units.
the octahedron, and $C_2B_4H_6$ will be a 6-vertex parent deltahedron, i.e. will be a *closo*-cluster.

Two isomers are possible, either 1,2-$C_2B_4H_6$ or 1,6-$C_2B_4H_6$.



1,6-isomer

The isolobal principle

It is possible to convert a borane into a carbaborane cluster by replacing a $\{BH^-\}$ by a $\{CH\}$-unit because both fragments possess the same frontier orbital properties. The two sets of MOs have the same symmetry characteristics, are of approximately the same energy, and contain the same number of electrons available for cluster bonding. The $\{BH^-\}$ and $\{CH\}$ fragments are said to be *isolobal*. The principle can be extended to include a range of atoms and molecular fragments all of which exhibit similar frontier orbitals. Series of isolobal *p*-block fragments are as follows:

$\{BH^-\} \equiv \{BR^-\} \equiv \{CH\} \equiv \{CR\} \equiv \{NR^+\}$ where R is a one electron donor e.g. alkyl, aryl, halogen atom

$\{BR\} \equiv \{AlR\} \equiv \{GaR\} \equiv \{GeR^+\} \equiv \{SR^{3+}\}$ where R is a one electron donor e.g. alkyl, aryl, halogen atom

$\{BH\} \equiv \{Tl^-\} \equiv \{Sn\} \equiv \{Pb\} \equiv \{N^+\} \equiv \{S^{2+}\}$ where each bare atom carries an *exo*-lone pair of electrons

The isolobal principle is not restricted to *p*-block elements. Certain transition metal fragments are isolobal with a $\{BH\}$-fragment and one of these is the conical (C_{3v} symmetry) $\{M(CO)_3\}$-unit where M is a group 8 metal (Fe, Ru, or Os). The frontier MOs of the $\{M(CO)_3\}$ unit are drawn in Fig. 4.24. The same diagram is appropriate for C_{3v} $\{M'(CO)_3{}^+\}$-units (M' = Co, Rh, or Ir), or C_{3v} $\{M''(CO)_3{}^-\}$-units (M'' = Mn or Re) units.

The similarities in orbital properties between a $\{BH\}$- and C_{3v} $\{M(CO)_3\}$-fragment (M = group 8 metal) allows a $\{BH\}$-unit in a borane cluster to be replaced by an $\{M(CO)_3\}$-unit. This leads to a series of *metallaborane* clusters. When applying *PSEPT* to a metallaborane compound containing an $\{M(CO)_3\}$-unit (M = group 8 metal), the unit is treated as a source of two valence electrons. Moving to the left or right of group 8 in the periodic table

The orientation of the ligands attached to the metal atom affects the number and symmetries of the frontier MOs. An $\{M(CO)_3\}$-unit is isolobal with a $\{BH\}$-fragment if the three carbonyl ligands define a cone so that the fragment has C_{3v} symmetry.

decreases or increases, respectively, the number of electrons provided by a transition metal tricarbonyl unit. Since different *exo*-ligands donate different numbers of electrons to the metal atom, the number of valence electrons provided by a transition metal fragment for cluster bonding can also be adjusted by altering the nature of the ligands attached to the metal as indicated in Eqn 4.3.

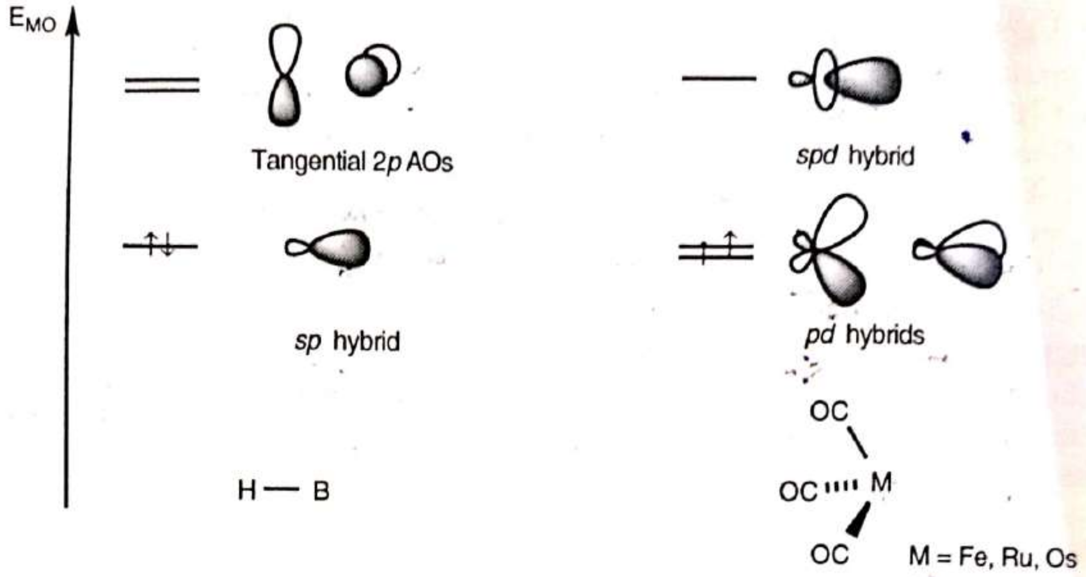


Fig. 4.24 Comparison of the three frontier MOs of {BH}- and C_{3v} {M(CO)$_3$}-fragments (M = group 8 metal). The fragments are isolobal because the number, symmetries, and approximate energies of the orbitals are equal, and each set contains the same number of electrons. The *order* of the MOs does not influence the bonding capability of the fragment.

If x = number of valence electrons provided by a transition metal fragment for cluster bonding, then:

$$x = v + n - 12 \qquad \textbf{Eqn 4.3}$$

where v = number of ve of the metal atom and n = number of electrons donated by the ligands.

CO is a two electron donor ligand.

PR_3 is a two electron donor ligand.

An η^n-C_nH_n ring is an n π-electron donor ligand.

NO may be a one or three electron donor ligand.

Application of Eqn 4.3 shows that the cluster unit {Os(CO)$_3$} provides 2 ve since $x = (8 + 6 - 12)$. Similarly, {Co(PPh$_3$)$_2$} provides 1 ve since $x = (9 + 4 - 12)$, {Ni(η^5-C_5H_5)} provides 3 ve since $x = (10 + 5 - 12)$, and {Rh(PPh$_3$)(CO)$_2$} provides 3 ve since $x = (9 + 6 - 12)$.

The isolobal principle combined with *PSEPT* suggests that it should be possible to systematically replace {BH}-units in a borane cluster by, for example, {Ru(CO)$_3$}-units. Thus, starting from B_5H_9, a series of metallaboranes including $B_4H_8Ru(CO)_3$, $B_3H_7Ru_2(CO)_6$, and $B_2H_6Ru_3(CO)_9$ can be postulated. References detailing metallaboranes are listed in the further reading list (Section 1.4).

The bridging hydride interaction, whether it involves two boron atoms, two metal atoms, or one boron and one metal atom, is best described in terms of a three-center, two-electron bond (see Chapter 11).

Parallels with Nonmetal Chemistry: Isolobal Fragments

Many of the reactions of metal carbonyl complexes parallel closely those of certain nonmetal elements and compounds. For example, the $Mn(CO)_5$ fragment has 17 valence electrons, one short of the total necessary to fulfill the 18-electron rule. It is analogous to the chlorine atom and the methyl free radical, each with seven valence electrons, one short of a noble gas configuration. The compounds and reactions of the pentacarbonyl fragment may thus be related to similar ones for chlorine or the methyl group. All three are formally free radicals and much of their chemistry derives from pairing the odd electron: The manganese carbonyl normally exists as a dimer, $Mn_2(CO)_{10}$ (cf. Cl_2, C_2H_6), but it may be reduced to the anion, $[Mn(CO)_5]^-$ (cf. Cl^-, CH_3^- in CH_3MgX), which is the conjugate base of an acid, $HMn(CO)_5$ (cf. HCl, CH_4); furthermore, it will combine with other species having a single unpaired electron, for example, $R^\cdot$ and $I^\cdot$, to form neutral molecules, $RMn(CO)_5$ (cf. RCl, RCH_3) and $Mn(CO)_5I$ (cf. ICl, CH_3I). The three fragments may be considered as *electronically equivalent groups*[35] or as *isolobal fragments*.[36] The concept is an outgrowth of equating the Lewis octet rule of organic and main-group chemistry with the 18-electron rule of transition metal organometallic chemistry.[37] Of course one should not push these ideas too far. For example, pentacarbonylhydridomanganese is a much weaker acid than is HCl, and methane is normally not considered to be an acid at all. The isolobal formalism is more concerned with structural predictions based on electronic similarities than with topics like polarity.

Isolobal fragments have relationships that go beyond simple electron counting. The calculated electron density of the MnH_5 fragment (isolobal with $Mn(CO)_5$, but simpler for calculations) may be compared with that of the methyl radical, CH_3 (Fig. 18.11).

Table 18.5 lists a number of examples of transition metal fragments that are isolobal with main-group fragments. Metal fragments with 16 electrons will behave as Group VIA (16) elements. Thus $Fe(CO)_4$ may form $H_2Fe(CO)_4$ (cf. H_2S) and $[Fe(CO)_4]^{2-}$ (cf. S^{2-}). Fifteen-electron fragments such as $Ir(CO)_3$ are isolobal

Table 18.5 Some isobal transition metal and main group fragments

CH_4	CH_3	CH_2	CH	C
$Ni(CO)_4$	$Mn(CO)_5$	$Fe(CO)_4$	$Co(CO)_3$	$Fe(CO)_3$
$Fe(CO)_5$	$Co(CO)_4$	$Cr(CO)_5$	$Mn(CO)_4$	$Cr(CO)_4$
$Cr(CO)_6$	$Fe(CO)_2Cp$	$Ni(CO)_3$	$Cr(CO)_2Cp$	$Ni(CO)_2$
CH_3^-	H	Co(CO)Cp	NiCp	CoCp
	CH_2^-	S	P	CH^+
		CH^-	CH_2^+	
		CH_3^+		

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[35] Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, 97, 5631–5633. Ellis, J. E. *J. Chem. Educ.* 1976, *53*, 2–6

[36] Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1982**, 27, 711–724.

[37] The isolobal concept, like most of Sherlock Holmes's explanations, seems obvious in hindsight, but it was first proposed in its present form by Halpern. It has since been elaborated by Dahl, Mingos, Wade, and Ellis, and extensively developed by Hoffmann. (See p 42 of Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding (Berlin)* 1987, *68*, 29–87.) It was Hoffmann's theoretical work in this area, much of which is beyond the scope of this book, that formed the basis for his Nobel laureate address (see Footnote 36).

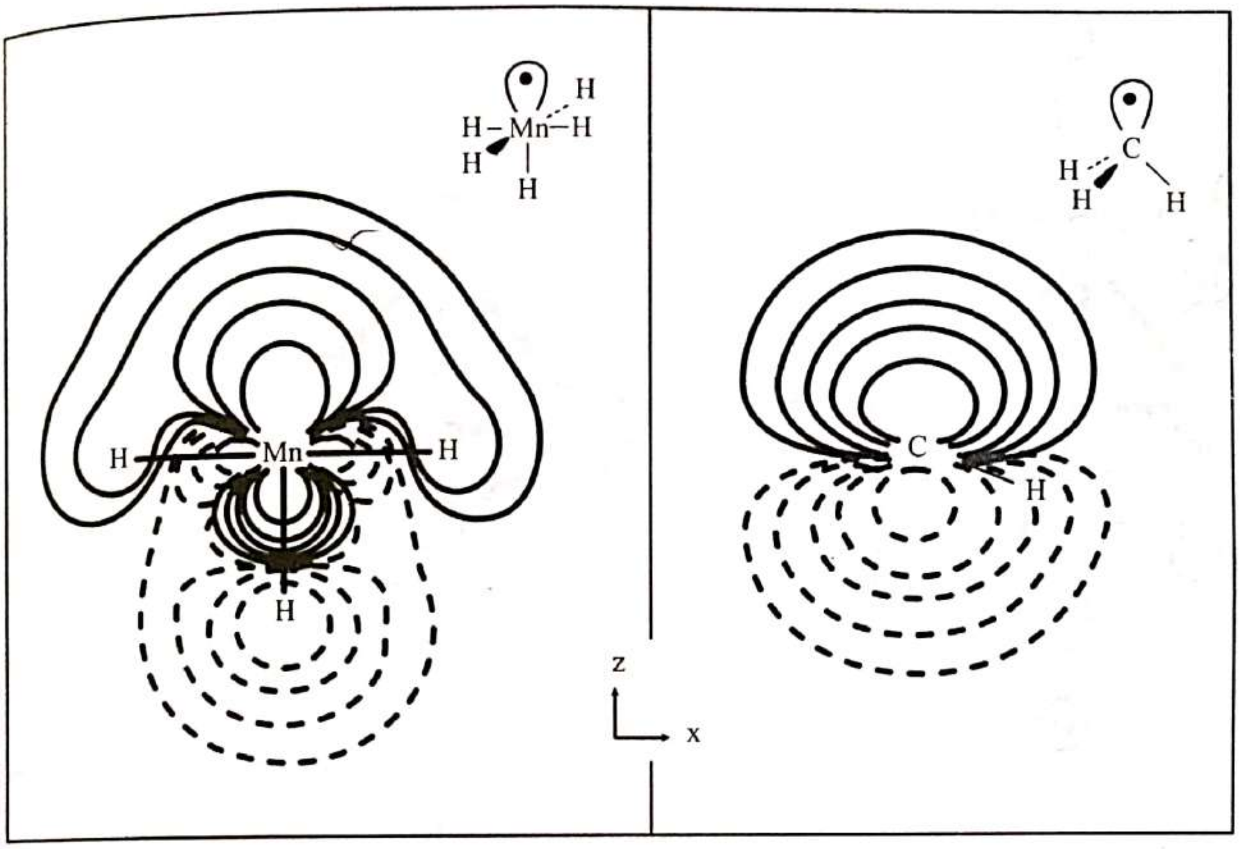

Fig. 18.11 Calculated contour diagrams for the isolobal a_1 orbitals of $[MnH_5]^-$ (left) and (CH_3) (right). The contours are plotted in a plane passing through manganese and three hydrogen atoms and through carbon and one hydrogen. [From Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1982,** *21*, 711–724. Reproduced with permission.]

with CH and with Group VA (15) elements, such as phosphorus. Each of these is three electrons short of a closed shell and each has three directed orbitals which form a triangular face. Hence the complex $Ir_4(CO)_{12}$ is isostructural with the P_4 molecule (Fig. 18.12) as well as with tetrahedrane, $(CH)_4$.

Earlier in this chapter, the polynuclear carbonyl complex $Os_4(CO)_{16}$ was referred to as an analogue of cyclobutane. It should now be clear that the connection between the two compounds goes beyond the fact that both possess a four-membered ring. The building blocks of the two structures, CH_2 and $Os(CO)_4$, are isolobal fragments. In fact the isostructural series has been extended to include $Os_2(CO)_8(CH_2)_2$, which has two $Os(CO)_4$ and two CH_2 fragments in the ring, and $Os(CO)_4(CH_2)_3$, with a ring consisting of one $Os(CO)_4$ and three CH_2 units.[38] Our earlier comparison of the bridging hydrides of boron and transition metals also could have been couched in terms of isolobality. The Lewis acids, BH_3 and $Cr(CO)_5$, are isolobal fragments, as are BH_4 and $[HCr(CO)_5]^-$.

Less obvious than the above examples are isolobal relationships that exist between fragments which appear to have different numbers of frontier orbitals. The addition or subtraction of H^+ to an organic fragment does not change the number of electrons in its frontier orbitals. As a consequence, CH_2, CH_3^+, and CH^- are isolobal fragments. This result is less surprising if you consider that there are a variety of ways in which the carbon atom may be hybridized. It is worth noting that *if two fragments are both isolobal with a third, they are isolobal with each other as well.*