6 The isolobal analogy

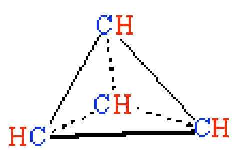
6.1 Introduction

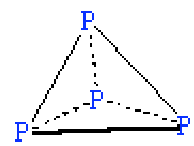
The outline of Wade's rule given above showed how quite different groups of atoms can give rise to similar shaped clusters. For example, the C-H group and the P atom have 5 electrons and can contribute 3 electrons to a cluster,

C-H has 4+1 electrons and uses 2 electrons for the C-H bond

P has 5 electrons and uses 2 electrons for a lone pair

Both fragments are 3 electrons short of making maximum use of their 4 valence orbitals (s and 3 ´ p) by achieving an octet. The clusters C_4H_4 or $(CH)_4$ (tetrahedrane) and P_4 have the same number of cluster electrons and therefore adopt the same shape:

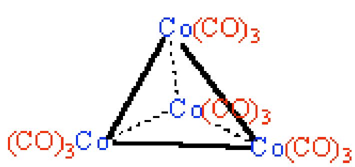




The organometallic fragment $Co(CO)_3$ has 15 electrons,

Co has 9 valence electrons and each CO donates 2e to the metal

The fragment is 3 electrons short of the stable electron count for an organometallic fragment of eighteen Eighteen electrons corresponds to making maximum use of the 9 valence orbitals of the transition metal (s + 3´ p and 5´ d). It can achieve 18 electrons by sharing 3 electrons to make 3 covalent bonds. The $Co(CO)_3$ fragment thus has the same requirements as the C-H unit and the P atom. The cluster $[Co(CO)_3]_4$ thus also has the same tetrahedral shape as that shown by C_4H_4 and P_4. It is also possible to swap the three fragments around:



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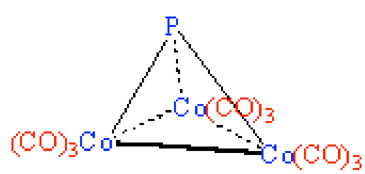
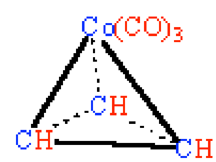


B



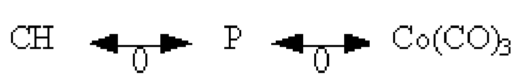
C

B and C are more conventionally thought of as (m ^{3}-P)[CoCO)$_3$]$_3$ and (h ^{3}-C_3H_3)$Co(CO)_3$ respectively but this hides the structural and electronic links between all these clusters.

The similarity between these fragments and between other groups of fragments has been investigated in detail by Roald Hoffmann. Fragments are deemed to be isolobal if

"the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar"

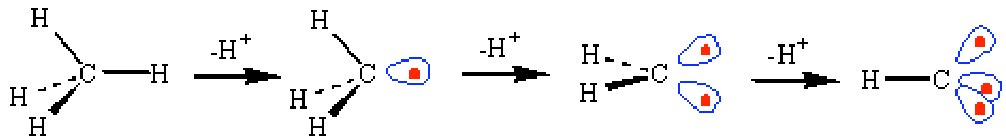
The isolobal relationship is symbolized by a double-headed arrow with a tear-drop,



The isolobal analogy relates the orbitals and bonding in inorganic, organometallic and cluster chemistry to that in organic and main group chemistry. The utility of the isolobal analogy is that one should be able to replace a (transition metal) MLn fragment in a molecule with the isolobal (main group) AHn fragment, and vice versa, to produce new molecules with very similar bonding.

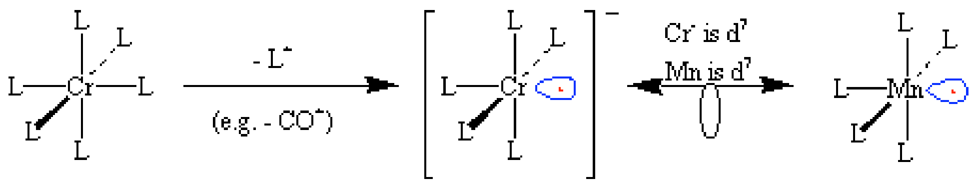
6.2 Generating isolobal fragments

Main group fragments can be generated by starting from methane, 1 (or any molecule obeying the octet rule). Homolytic cleavage of a C–H bond generates the methyl radical, 1 a,, which has one frontier orbital pointing towards the missing hydrogen with one electron in it. Homolytic cleavage of a second C–H gives methylene, 1b, which has too singly occupied hybrids pointing towards the two vacant hydrogen positions. Removal of a third hydrogen gives methine, 1c, with three singly occupied hybrids.



1 **1a** **1b** **1c**

The transition metal fragments are generated in an analogous way. For example, from the starting point of CrL_6, 2, where L is a two electron donor such as CO, (or any molecule obeying the eighteen electron rule such as 3), the fragments 2a, 2b and 2c are generated by successive *homolytic* cleavage of M–L bonds on one octahedral face. As L is a two-electron donor, homolytic cleavage of CrL_6 gives CrL_5^- and L^+. To remove the charge, the metal is then replaced by Mn (the element one to the right in the 3d series):

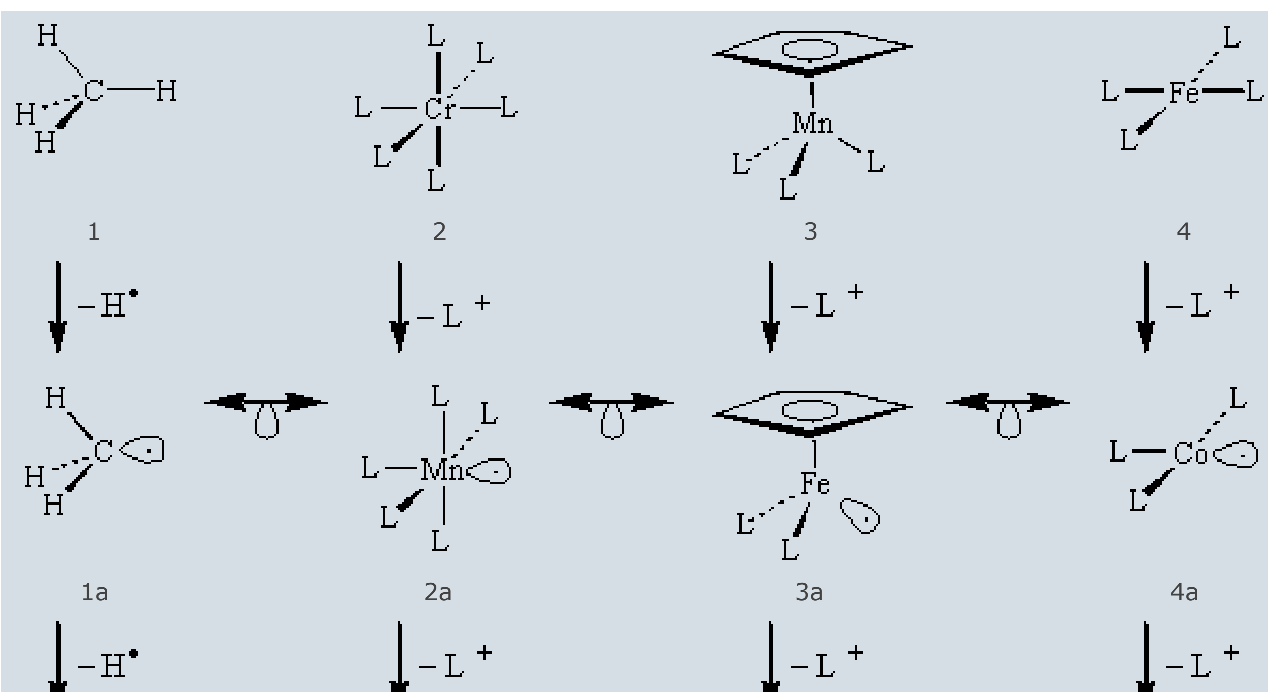


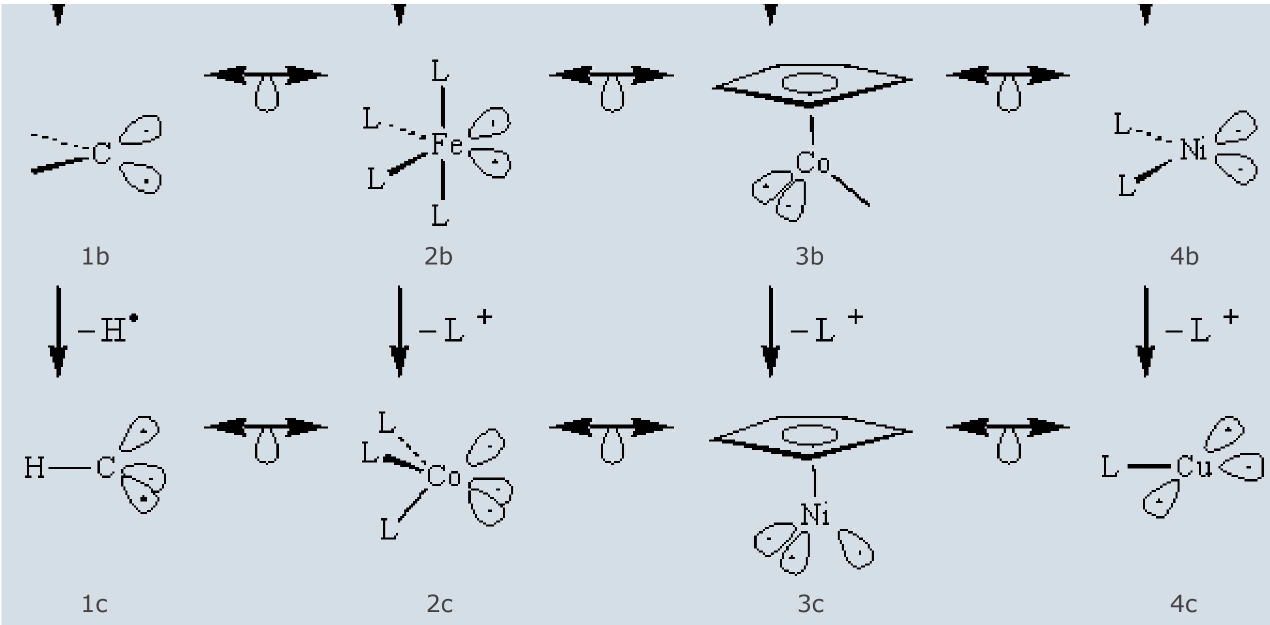
2 **2a**

6.3 Isolobal scheme

The isolobal scheme generated by this approach is shown below.

8–electron	18-electron		16-electron





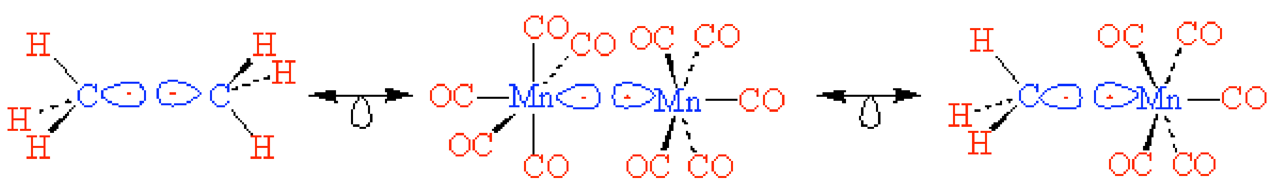
As long as the electron count is maintained or consistent changes are made, the metal or main group element can be substituted. Thus,

CH_3	Me_3Sn	$Mn(CO)_5$	$Fe(PPh3)_5{}^+$	$Mo(CO)_5{}^-$
CH_3+	BH_3	$Mn(CO)_5{}^+$	$Cr(CO)_5$	$Rh(PPh_3)^{3+}$
CH_3-	NH_3	$Mn(CO)_5{}^-$	$Fe(CO)_5$	$Rh(CO)_5{}^+$

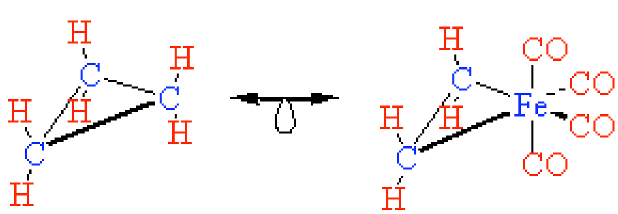
It should be noted that the main use of the isolobal analogy is in generating alternative fragments *in molecules*. The geometry of the fragment *in a molecule* not as an isolated species is important. Thus, CH_3 and BH_3 are considered as pyramidal (not planar) species and $Cr(CO)_5$ is considered as a square-based pyramid (not trigonal bipyramid).

6.4 Applications

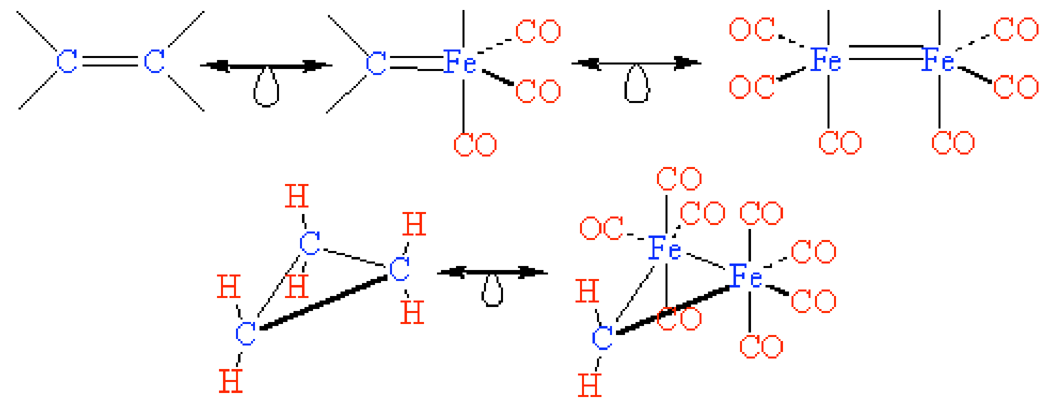
The isolobal analogy between CH_3 and d^7 MnL_5 implies similar bonding in the following compounds:



The isolobal relationship of CH_2, with $Fe(CO)_4$ generates the compounds illustrated below. The transition metal molecule has been drawn as a metallocyclopropane. A more common description is to consider it as an ethene complexes, (h2–C_2H_4)$Fe(CO)_4$. The isolobal relationship shows that cyclopropane itself can be consider as (h2–C_2H_4)CH_2.



Other known compounds generated using this relationship include:



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