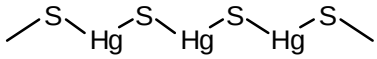
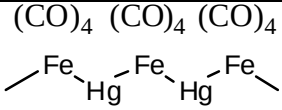
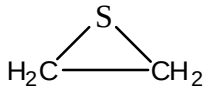
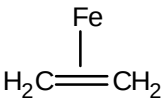
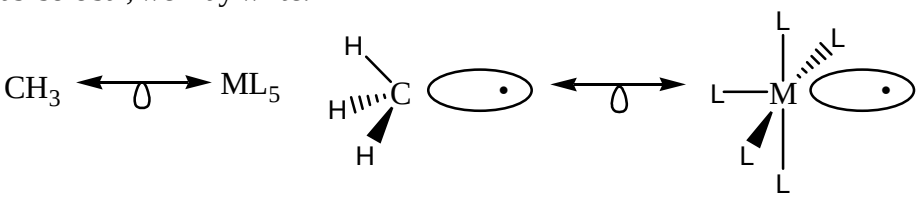
Table: Parallels between Sulfur and $Fe(CO)_4$.

Characteristic	Examples	Examples
Ion of 2-charge	S^{2-}	$[Fe(CO)_4]^{2-}$
Neutral compound	S_8	$Fe_2(CO)_9.[Fe(CO)_4]_3$
Hydride	H_2S: pK_1 = 7.24; pK_2=14.92; Ph_3PS	$H_2Fe(CO)_4$: pK_1 = 4.44; pK_2=14, $Ph_3PFe(CO)_4$
Polymeric mercury compound		
Compound with ethylene	 (ethylene sulfide)	 (π-complex)

The Isolobal Analogy:

Hoffmann defined molecular fragments to be isolobal, if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electron in them are similar–not identical, but similar.

The parent compounds have filled valence shell electron configurations, an octet for CH_4 and 18-electrons for ML_6[$Cr(CO)_6$)] is an example of such an ML_6 compound]. Methane may be considered to use sp^3 hybrid orbitals in bonding, with 8-electrons occupying bonding pairs formed from interactions between the hybrids and 1s orbital on hydrogen. The metal in ML_6, by similar reasoning, uses d^2sp^3 hydrids in bonding to the ligands, with 12 electrons occupying bonding orbitals and 6 essentially non-bonding electrons occupying d_{xy}, d_{xz} and d_{yz} orbitals. Molecular fragments containing fewer ligands than the parent polyhedra can now be described. For the purpose of the analogy, these fragments will be assumed to preserve the geometry of the remaining ligands. In the 7-electron fragment CH_3, three of the sp^3 orbitals of carbon are involved in σ bonding with the hydrogens. The fourth hybrid is singly occupied and at higher energy than the σ-bonding pairs of CH_3. This situation is similar to the 17-electron fragment $Mn(CO)_5$. The σ interactions between the ligands and Mn in this fragment may be considered to involve five of the metals d^2sp^3 hybrid orbitals. The sixth hybrid is singly occupied and at higher than the five σ-bonding orbitals. As above figure shows, each of these fragments has single electron in a hybrid orbital at the vacant site of the parent polyhedron. These orbitals are sufficiently similar to meet Hoffmann's isolobal definition. Using Hoffmann's symbol $\longleftrightarrow$ to designate groups as isolobal, we may write.



	Organic	Inorganic	Organometallic example	Vertices Missing from parent polyhedron	Electrons short of filled shell
Parent	CH_4	ML_6	$Cr(CO)_6$	0	0
Fragments	CH_3	ML_5	$Mn(CO)_5$	1	1
	CH_2	ML_4	$Fe(CO)_4$	2	2
	CH	ML_3	$Co(CO)_3$	3	3

The isolobal species $Ir(CO)_3$, $Co(CO)_3$, CR and P may also be combined in several different ways $Ir(CO)_3$, a 15-electron fragment, forms $[Ir(CO)_3]$, which has T_d symmetry. The isoelectronic complex $Co_4(CO)_{12}$ has a nearly tetrahedral array of cobalt atoms, but has three bridging carbonyls and hence C_3 symmetry. Compounds are also known that have a central tetrahedral structure, with one or more $Co(CO)_3$ fragments [which are isolobal and isoelectronic with $Ir(CO)_3$] replaced by the isolobal CR fragment. This is similar to the replacement of phosphorus atoms in the P_4 tetrahedron by $Co(CO)_3$, fragments: P may also be described as isolobal with CR.

Extensions of the Analogy:

1. The isolobal definition may be extended to isoelctronic fragments having the same coordination number. For example,

$$\underset{(17-\text{electron fragment})}{Mn(CO)_5} \longleftrightarrow \underset{(7-\text{electron fragment})}{CH_3}, \begin{matrix} Re(CO)_5 \\ [Fe(CO)_5]^+ \\ [Cr(CO)_5]^- \\ (17-\text{electron fragment}) \end{matrix} \longleftrightarrow \underset{(7-\text{electron fragment})}{CH_3}$$

2. Gain or loss electrons from two isolobal fragments yields isolobal fragments. For examples

$$\underset{(17-\text{electron fragment})}{Mn(CO)_5} \longleftrightarrow \underset{(7-\text{electron fragment})}{CH_3}, \begin{matrix} Cr(CO)_5 \\ Mo(CO)_5 \\ W(CO)_5 \\ (16-\text{electron fragment}) \end{matrix} \longleftrightarrow$$

$$\underset{(6-\text{electron fragment})}{CH_2}, \begin{matrix} Fe(CO)_5 \\ Ru(CO)_5 \\ Os(CO)_5 \\ (18-\text{electron fragments}) \end{matrix} \longleftrightarrow \underset{(8-\text{electron fragment})}{CH_3^-}$$

Note that all the examples show above are one ligand of the parent complex. $Fe(CO)_5$ is isolobal with CH_3^-, for example, because both have filled electron shells and both are one vertex short of the parent polyhedron. By contrast, $Fe(CO)_5$ and CH_4 are not isolobal. Both have filled electron shells (18 and 8 electrons, respectively), but CH_4 has all vertices of the tetrahedron occupied, whereas $Fe(CO)_5$ has an empty vertex in the octahedron.

3. Other 2-electron donors are treated similarly to CO:

$$Mn(CO)_5 \longleftrightarrow Mn(PR_3)_5 \longleftrightarrow [MnCl_5]^{5-} \longleftrightarrow Mn(NCR)_5 \longleftrightarrow CH_3$$

4. $\eta^5 - C_5H_5$ and $\eta^6 - C_6H_6$ are considered to occupy three coordinates sites and to be 6-electron donors.

$$\begin{cases} (\eta^5 - C_5H_5)Fe(CO)_2 \\ (\eta^6 - C_6H_6)Mn(CO)_2 \end{cases} \longleftrightarrow [Fe(CO)_5]^+ \longleftrightarrow Mn(CO)_5 \ (17-\text{electron fragments})$$

$$\begin{matrix} (\eta^5 - C_5H_5)Mn(CO)_2 \\ (\eta^6 - C_6H_6)Cr(CO)_2 \end{matrix} \longleftrightarrow [Mn(CO)_5]^+ \longleftrightarrow Cr(CO)_5 \ (16-\text{electron fragments})$$