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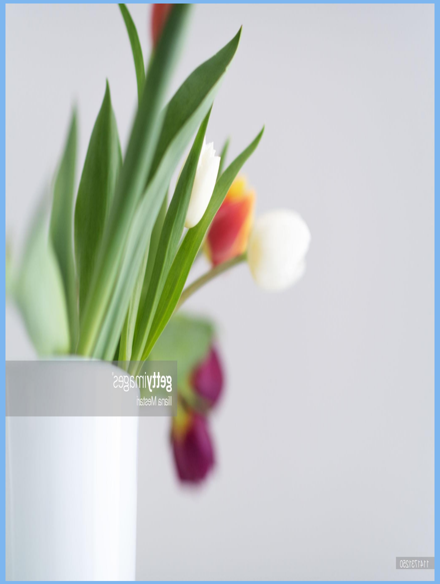

INORGANIC CHEMISTRY-I

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Scope of the present work

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- 18 -electron rule
- Isolopal concept and its usefulness
- Nitroysyl complxes
- Metallocene and arene complexes
- Application of organometallics

OBJECTIVES OF THE STUDY

- To unterstand the role of metal ions in biological process
- To learn the basic concept of alkyl metals.
- To learn the principle of cataiysis and reaction mechanism of organomatallics.

18-Electron Rule

- The 18-electron rule is a rule used primarily for predicting and rationalizing formulas for stable metal complexes, especially organometallic compounds.
- The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs.
- This means that the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding.
- When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period.
- The rule and its exceptions are similar to the application of the octet rule to main group elements.
- The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. The rule was first proposed by American chemist Irving Langmuir in 1921

18-electrons Rule Examples

Bulky ligands can preclude the approach of the full complement of ligands that would allow the metal to achieve the 18 electron configuration.

1. Ti(neopentyl)4 (8 e−)
2. Cp*2Ti(C2H4) (16e−)
3. V(CO)6 (17 e−)
4. Cp*Cr(CO)3 (17 e−)
5. Pt(PtBu3)2 (14 e−)
6. Co(norbornyl)4 (13 e−)
7. [FeCp2]+ (17 e−)

W(CO)3[P(C6H11)3]2 has 16 e−
Cp(PMe3)V(CHCMe3) (14 e−, diamagnetic)

High-spin complexes
CrCl3(THF)3 (15 e−)
[Mn(H2O)6]2+ (17 e−)
[Cu(H2O)6]2+ (21 e−

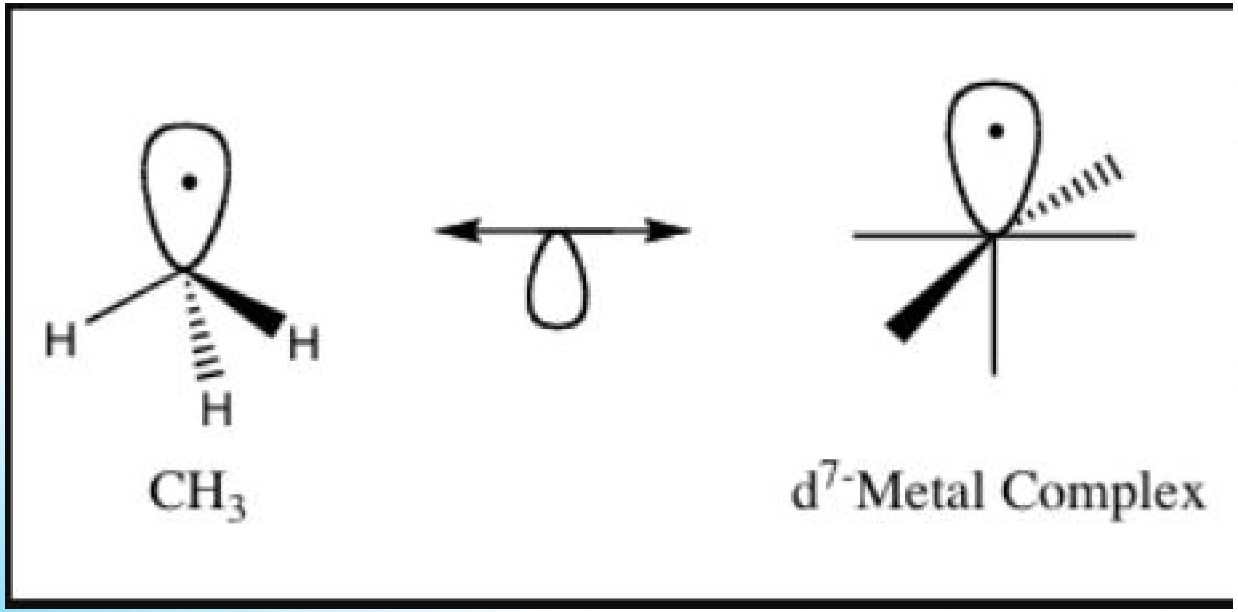
Isolopal concept and its usefulness

- The isolobal principle (more formally known as the isolobal analogy) is a strategy used in organometallic chemistry to relate the structure of organic and inorganic molecular fragments in order to predict bonding properties of organometallic compounds.

- Roald Hoffmann described molecular fragments as isolobal "if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar – not identical, but similar.

- One can predict the bonding and reactivity of a lesser-known species from that of a better-known species if the two molecular fragments have similar frontier orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

- Isolobal compounds are analogues to isoelectronic compounds that share the same number of valence electrons and structure.
- A graphic representation of isolobal structures, with the isolobal pairs connected through a double-headed arrow with half an orbital below, is found in Figure 1



Nitrosyl Complexes

- Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation, NO+.
- The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes.
- The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding. The compounds Co(NO)(CO)3 and Ni(CO)4 illustrate the analogy between NO+ and CO.
- In an electron-counting sense, two linear NO ligands are equivalent to three CO groups. This trend is illustrated by the isoelectronic pair Fe(CO)2(NO)2 and [Ni(CO)4].[2] These complexes are isoelectronic and, incidentally, both obey the 18-electron rule.
- The formal description of nitric oxide as NO+ does not match certain measureable and calculated properties. In an alternative description, nitric oxide serves as a 3-electron donor, and the metal-nitrogen interaction is a triple bond.

Linear vs bent nitrosyl ligands

- The M-N-O unit in nitrosyl complexes is usually linear, or no more than 15° from linear. In some complexes, however, especially when back-bonding is less important, the M-N-O angle can strongly deviate from 180° .
- Linear and bent NO ligands can be distinguished using infrared spectroscopy. Linear M-N-O groups absorb in the range 1650–1900 cm−1, whereas bent nitrosyls absorb in the range 1525–1690 cm−1.
- The differing vibrational frequencies reflect the differing N-O bond orders for linear (triple bond) and bent NO (double bond).
- The bent NO ligand is sometimes described as the anion, NO−. Prototypes for such compounds are the organic nitroso compounds, such as nitrosobenzene. A complex with a bent NO ligand is trans-[Co(en)2(NO)Cl]+.

Bridging nitrosyl ligands

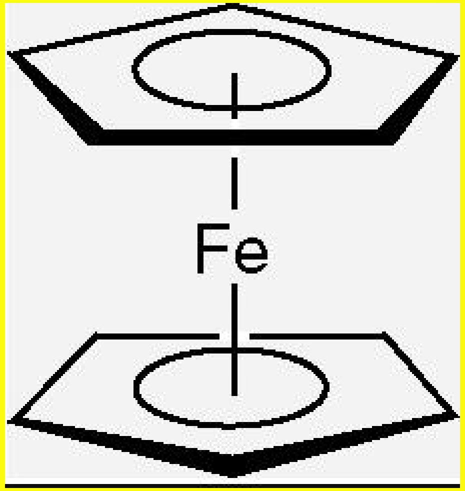
- Nitric oxide can also serve as a bridging ligand. In the compound [Mn3(η5C5H5)3 (μ2-NO)3 (μ3-NO)], three NO groups bridge two metal centres and one NO group bridge to all three.

Metallocenes

- Metallocenes are known with most metals (discovery of ferrocene in 1951 and report of its sandwich structure in 1952), and have applications in organic, polymer and medicinal chemistry.

- With the MCp2 structure, they are sandwich complexes in which the two Cp rings are parallel (ferrocene).
- The sandwich MCp2 structure is very robust with NVE = 18 (Fe, Ru, Os). The neutral metallocenes of the 1st-row with 15 to 20 e− (V, Cr, Mn, Fe, Co, Ni) correspond to the filling of the 5d orbitals split in three MO levels (e1g: bonding, double; a1g: non-bonding, simple, e*1g; antibonding, double) under the influence of the pseudo-octahedral field of the two Cp ligands.
- The metallocenes are all the more fragile as their NVE is further from 18, but they are stabilized by the Cp* (η5-C5Me5) ligand.

- Ferrocene is a diamagnetic (low spin) orange, crystalline solid stable up to 400° C, covalent (nil dipole moment), soluble in hydrocarbons, with free rotation about the Fe-Cp ring axis.
- It readily oxidizes to blue ferrocenium [FeCp2]+, (most often synthesized as the PF6 − salt), a useful single-electron mild oxidant. Ferrocene is a superaromatic, starting point of many syntheses, for instance of Friedel-Crafts type.
- The α-ferrocenylcarbonium ions FcCR2 + (Fc = ferrocenyl) are stabilized by conjugation with Fe.



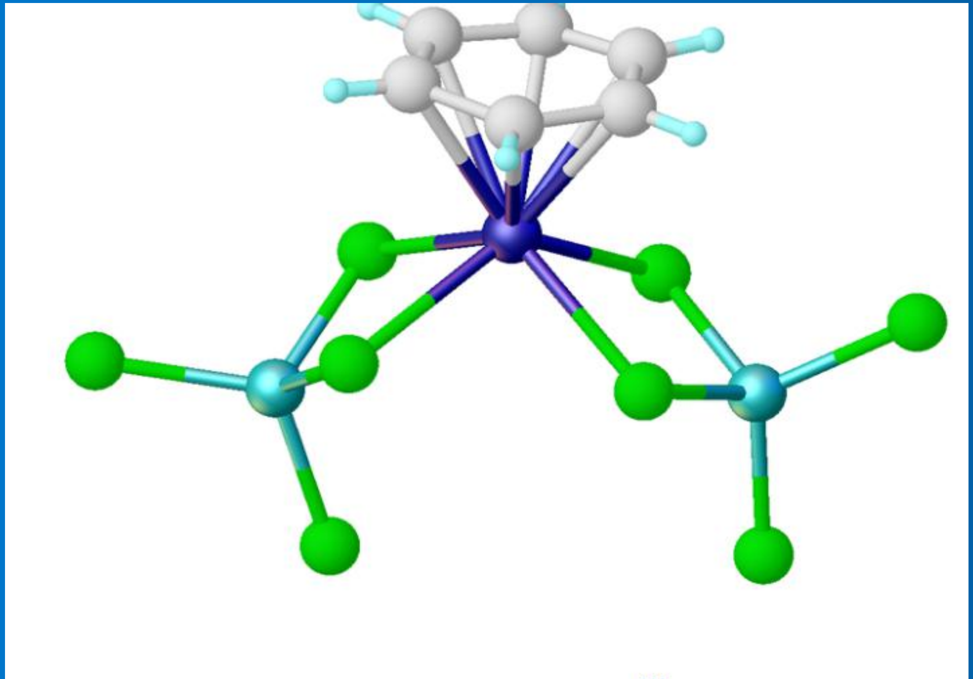
Arene complexes

- Metal arene complexes are organometallic compounds of the formula (C6R6)xMLy. Common classes of are of the type (C6R6)ML3 and (C6R6)2M. These compounds are reagents in inorganic and organic synthesis. The principles that describe arene complexes extend to related organic ligands such as many heterocycles (e.g. thiophene) and polycyclic aromatic compounds (e.g. naphthalene).

Fischer–Hafner synthesis

- Also known as reductive Friedel–Crafts reaction, the Fischer–Hafner synthesis entails treatment of metal chlorides with arenes in the presence of aluminium trichloride and aluminium metal.
- The method was demonstrated in the 1950s with the synthesis of bis(benzene)chromium by Walter Hafner and his advisor E. O. Fischer.

- The method has been extended to other metals, e.g. [Ru(C6Me6)2]2+. In this reaction, the AlCl3 serves to remove chloride from the metal precursor, and the Al metal functions as the reductant.The Fischer-Hafner synthesis is limited to arenes lacking sensitive functional groups.



, illustrative intermediate in Fischer-Hafner syntheses.[2]

Direct synthesis of Arene complexes

By metal vapor synthesis, metal atoms co-condensed with arenes react to give complexes of the type M(arene)2. $Cr(C_6H_6)_2$ can be produced by this method.

- $Cr(CO)_6$ reacts directly with benzene and other arenes to give the piano stool complexes $Cr(C_6R_6)(CO)_3$.[4] The carbonyls of Mo and W behave comparably. The method works particularly well with electron-rich arenes (e.g., anisole, mesitylene).
- The reaction has been extended to the synthesis of $[Mn(C_6R_6)(CO)_3]^+$:

$$BrMn(CO)_5 + Ag^+ + C_6R_6 \rightarrow [Mn(C_6R_6)(CO)_3]^+ + AgBr + 2\ CO$$

Fluxional molecules

- Fluxional molecules are molecules that undergo dynamics such that some or all of their atoms interchange between symmetry-equivalent positions.

- Because virtually all molecules are fluxional in some respects, e.g. bond rotations in most organic compounds, the term fluxional depends on the context and the method used to assess the dynamics.

- Often, a molecule is considered fluxional if its spectroscopic signature exhibits line-broadening (beyond that dictated by the Heisenberg uncertainty principle) due to chemical exchange. In some cases, where the rates are slow, fluxionality is not detected spectroscopically, but by isotopic labeling. Where such movement does not occur, the molecule may be described as a semi-rigid molecule.

NMR spectroscopy

Temperature dependent changes in the NMR spectra result from dynamics associated with the fluxional molecules when those dynamics proceed at rates comparable to the frequency differences observed by NMR.

The experiment is called DNMR and typically involves recording spectra at various temperatures. In the ideal case, low temperature spectra can be assigned to the "slow exchange limit", whereas spectra recorded at higher temperatures correspond to molecules at "fast exchange limit".

Typically, high temperature spectra are simpler than those recorded at low temperatures, since at high temperatures, equivalent sites are averaged out. Prior to the advent of DNMR, kinetics of reactions were measured on nonequilibrium mixtures, monitoring the approach to equilibrium.

Many molecular processes exhibit fluxionality that can be probed on the NMR time scale.[15] Beyond the examples highlighted below, other classic examples include the Cope rearrangement in bullvalene and the chair inversion in cyclohexane.

For processes that are too slow for traditional DNMR analysis, the technique spin saturation transfer (SST) is applicable. This magnetization transfer technique provides rate information, provided that the rates exceed 1/T1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