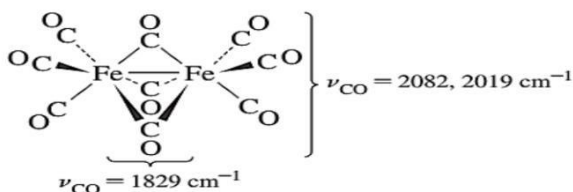


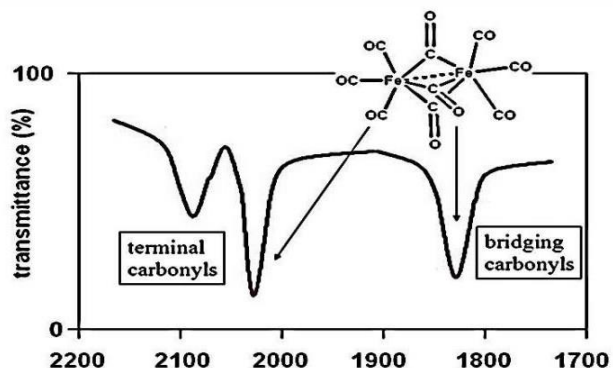
Bridging Modes of CO:

Many cases are known in which CO forms bridges between two or more metals. Many bridging modes are known (Given below)

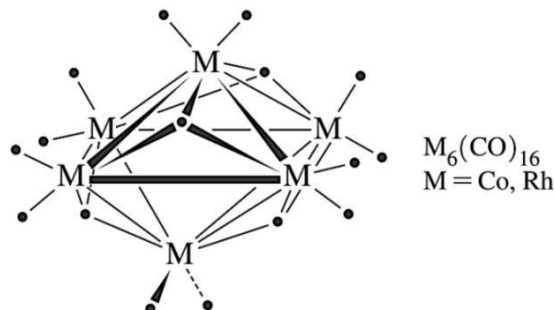
| Type of CO | Approximate Range for $\nu(\text{CO})$ in Neutral Complexes (cm^{-1}) |
|--|--|
| Free CO | 2143 |
| Terminal $\text{M}-\text{CO}$ | 1850–2120 |
| Symmetric ^a $\mu_2-\text{CO}$ | 1700–1860 |
| Symmetric ^a $\mu_3-\text{CO}$ | 1600–1700 |



IR spectrum and bridging versus terminal carbonyls in $[\text{Fe}_2(\text{CO})_9]$



The bridging mode is strongly correlated with the position of the C-O stretching band. In cases in which CO bridges two metal atoms, both metals can contribute electron density into π^* orbitals of CO to weaken the C-O bond and lower the energy of the stretch. Consequently, the C-O stretch for doubly bridging CO is at a much lower energy than for terminal COs. An example is shown in Figure above. Interaction of three metal atoms with a triply bridging (as shown in figure below) CO further weakens the C-O bond; the infrared band for the C-O stretch is still lower than in the doubly bridging case.



Ordinarily, terminal and bridging carbonyl ligands can be considered 2 electron donors, with the donated electrons shared by the metal atoms in the bridging cases. For example, in the complex below, the bridging CO is a 2-electron donor overall, with a single electron donated to each metal. The electron count for each Re atom according to covalent method.

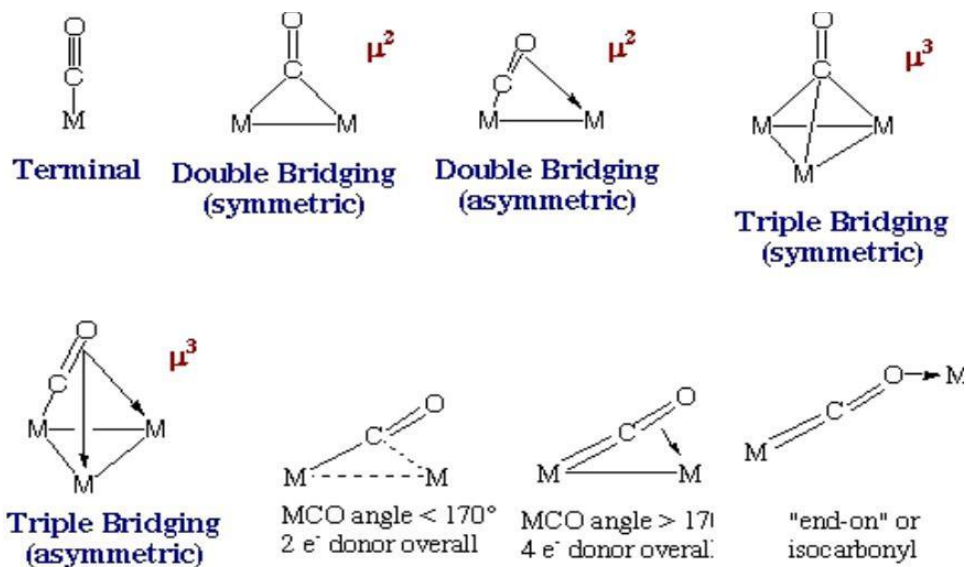


Figure: Bridging modes of CO

**There are three points of interest with respect to metal carbonyls:-

1. CO is not ordinarily considered a very strong Lewis base, and yet it forms strong bonds to the metals in these compounds.



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2. The metals are always in a low oxidation state, most often formally in an oxidation state of Zero, but also in low positive & negative oxidation states.

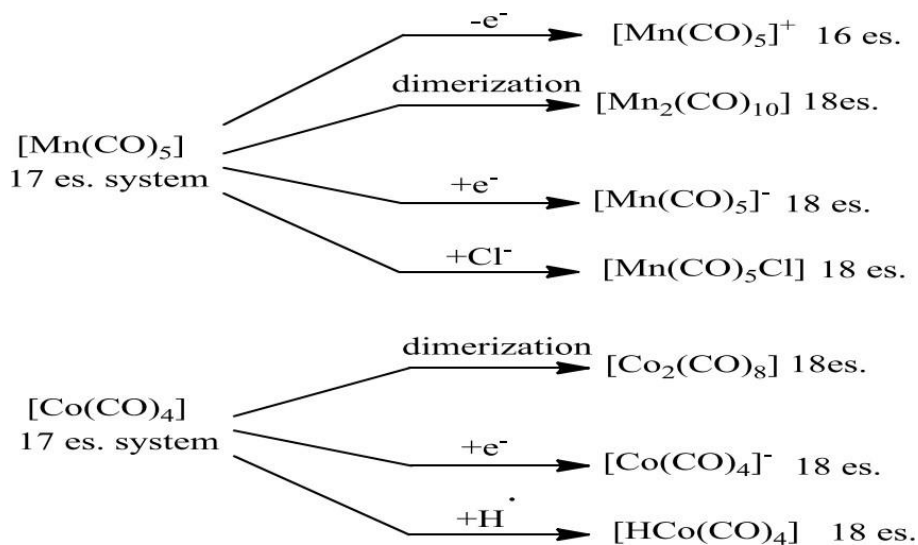
3. The 18-electrons rule is obeyed with remarkable frequency.

**Metals with odd atomic number can't satisfy the 18-es. By simple addition of CO ligand, since the resultant moiety will have an odd number of electrons. In such case there are several options open to these metals by which the 18-es. Rule can be satisfied:-

* The addition of an electron by reducing agent to form an anion such as $[\text{V}(\text{CO})_6]^-$.

* The electron deficient moiety can bond covalently with an atom or group that also has single unpaired electron available, example:- hydrogen or chlorine : $\text{HM}(\text{CO})_n$ or $\text{M}(\text{CO})_n\text{Cl}$.

* If neither species are available with which to react, two moieties each with an odd atom can dimerize with resultant pairing of the odd electrons, examples



* Binary carbonyls, containing only metal atoms and CO, are numerous. Most of these complexes obey the 18-electron rule.

* One other binary carbonyl does not obey the rule, the 17-electron $\text{V}(\text{CO})_6$. This

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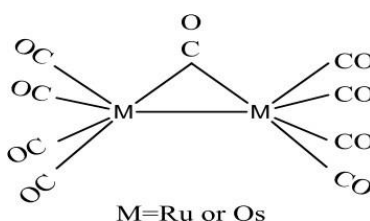
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complex is one of a few cases in which strong π -acceptor ligands do not afford an 18-electron configuration. In $V(CO)_6$, the vanadium is apparently too small to permit a seventh coordination site; hence, no metal-metal bonded dimer, which would give an 18 electron configuration, is possible. However, $V(CO)_6$ is easily reduced to $[V(CO)_6]^-$, an 18-electron complex

* An interesting feature of the structures of binary carbonyl complexes is that the tendency of CO to bridge transition metals decreases going down the periodic table. For example, in $Fe_2(CO)_9$ there are three bridging carbonyls; but in $Ru_2(CO)_9$ and $Os_2(CO)_9$, there is a single bridging CO. A possible explanation is that the orbitals of bridging CO are less able to interact effectively with transition-metal atoms as the size of the metals increases, along with the metal-metal bond lengths.

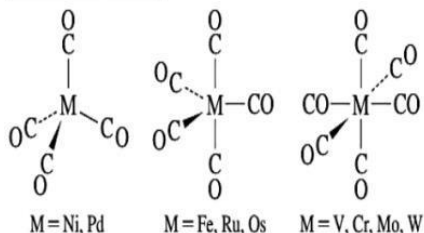


Exercise:- Verify the 18-electron rule for following binary carbonyls—

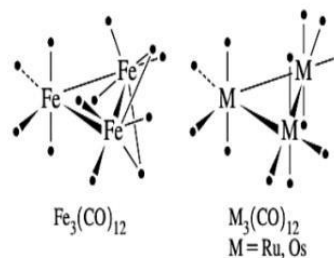
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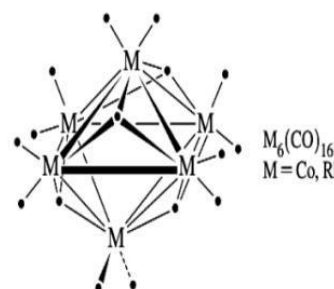
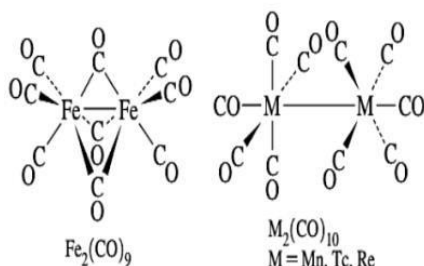
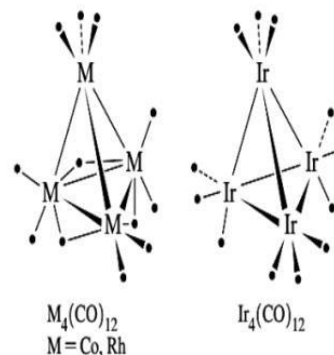
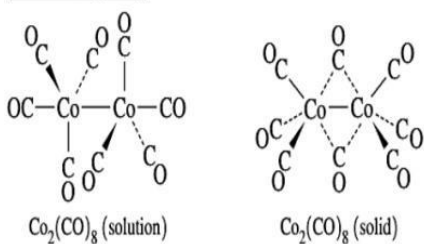
Mononuclear [M(CO)_x]



Polynuclear (CO represented by • for clarity)



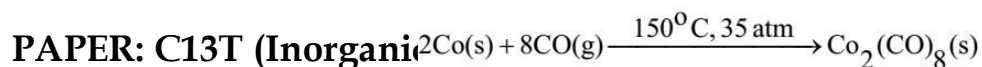
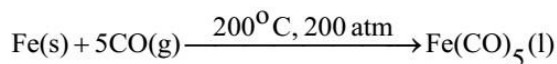
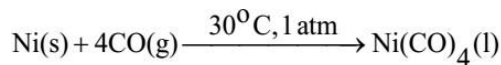
Binuclear [M₂(CO)_x]



Preparation of Metal Carbonyls:

1. Direct Combination:

Only Ni(CO)₄ and Fe(CO)₅ and Co₂(CO)₈ are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure



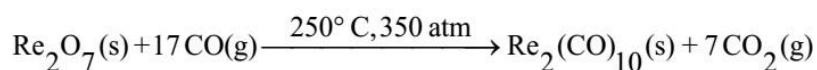
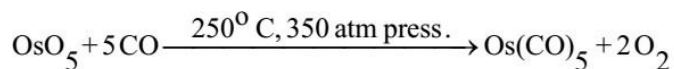


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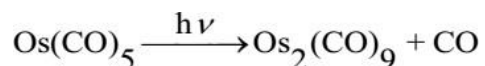
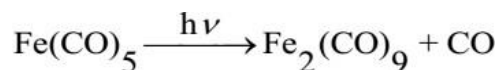
Typical examples are shown in the following Eq. :

2. **Reductive carbonylation:** Many metallic carbonyls are obtained when metal salts like are treated with carbon monoxide in presence of suitable reducing agent like Mg, Ag, Cu, Na, H₂, AlLiH₄ etc .

Sometimes CO acts as a carbonylating and reducing agent



Preparation of Dinuclear carbonyls obtained from mononuclear carbonyls by irradiated with ultra-violet light



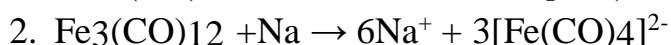
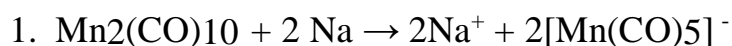
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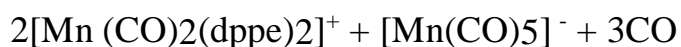


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Carbonylate ions: Numerous anionic carbonyl complexes are called carbonylate ions. They are often electronically and structurally related to neutral carbonyl complexes. A common method of preparing carbonylate ions is reduction of neutral carbonyl complexes. e.g.;



Not all reactions leading to carbonylate ions require strong reducing agents. Some involve reduction of metal by CO already present in the metal carbonyls or disproportionation of the complex. Often a Lewis base will effect disproportionation of a complex.



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