UNIT III

# Organometallic Compounds II

## (Part II)

B.Sc. (H) Chemistry

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# Infrared Spectra for organometallic compounds

The carbonyl group in organometallic compounds are used to study by **Infrared spectroscopy**.

The position of the Infrared band can indicate the function of a ligand (e.g., terminal vs. bridging modes).

In the case of π –acceptor ligands, can describe the electronic environment of the metal.

The peak appear in the range between 2100-1700 cm-1

# Number of Infrared Bands

A molecular vibration is infrared active (i.e., excitation of the vibrational mode can be measured via an IR spectrum absorption) only if it results in a change in the dipole moment of the molecule

# Selected Vibrational Modes

It is often useful to consider a particular vibrational mode for a compound.

For example, useful information often can be obtained from the C-O stretching bands in infrared spectra of metal complexes containing CO (carbonyl) ligands.

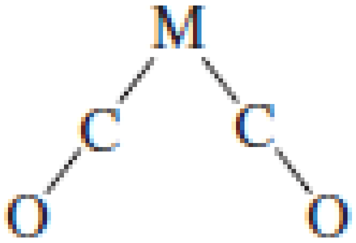
# Monocarbonyl Complexes

These complexes have a single C-O stretching mode and consequently show a single band in the IR.

# Dicarbonyl Complexes

Two geometries, linear and bent, must be considered:

**O – C – M – C – O**



Two CO ligands arranged linearly, Only an antisymmetric vibration of the ligands is IR active

Two CO ligands are oriented in a nonlinear fashion, both symmetric and antisymmetric vibrations result in changes in dipole moment, and both are IR active:

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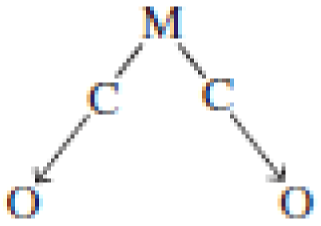
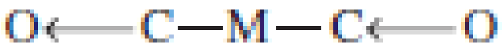
## Symmetric Stretch

No change in dipole moment:
IR inactive

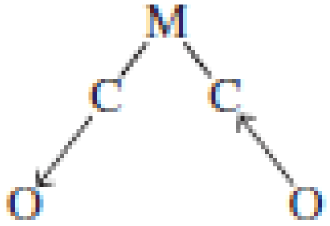


Change in dipole moment:
IR active

## Antisymmetric Stretch



Change in dipole moment:
IR active



Change in dipole moment:
IR active

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IR spectrum is a convenient tool for determining the structure of molecules with two CO ligands: a single band indicates linear orientation of the CO ligands, and two bands indicate nonlinear orientation.

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For molecules containing two CO ligands on the same metal atom, the relative intensities of the IR bands can be used to determine the approximate angle between the CO ligands, using the equation

$$\frac{I_{\text{symmetric}}}{I_{\text{antisymmetric}}} = cotan^2\left(\frac{\phi}{2}\right)$$

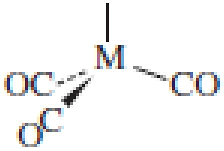
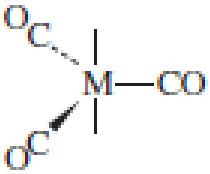
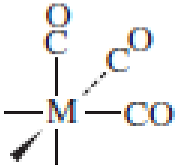
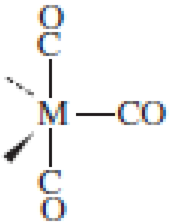
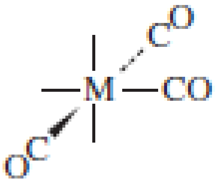
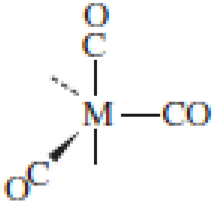
Where $\phi$ is the angle between ligands

# Complexes containing three or more carbonyls

- ✓The predictions for the Complexes containing three or more carbonyls are not quite so simple.
- ✓The exact number of carbonyl bands can be determined according to the symmetry approach. (not discussed here).
- ✓In carbonyl complexes, the number of C-O stretching bands cannot exceed the number of CO ligands.
- ✓The alternative is possible in some cases (more CO groups than IR bands), when vibrational modes are not IR active (do not cause a change in dipole moment).

For convenient reference, the numbers of bands expected for a variety of CO complexes are given in next slide.

# Carbonyl stretching bands

| | | Coordination Number | | |
|---|---|---|---|---|
| **Number of CO Ligands** | | **4** | **5** | **6** |
| 3 | |  |  |  |
| | IR bands: | 2 | 1 | 2 |
| | | |  |  |
| | IR bands: | | 3 | 3 |
| | | |  | |
| | IR bands: | | 3 | |

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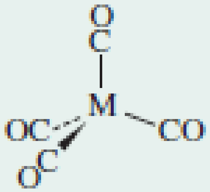
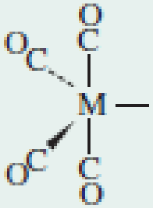
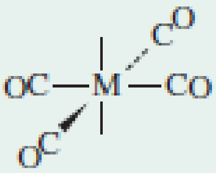
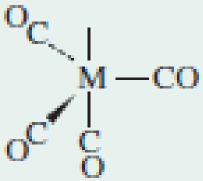
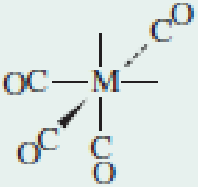
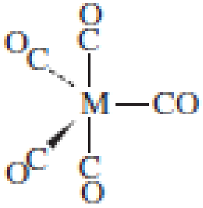
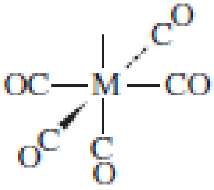
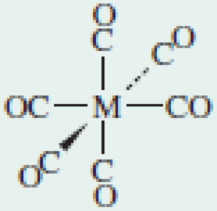
| 4 |  |  |  |
| IR bands: | 1 | 4 | 1 |
| | |  |  |
| IR bands: | | 3 | 4 |
| 5 | |  |  |
| IR bands: | | 2 | 3 |
| 6 | | |  |
| IR bands: | | | 1 |

# Positions of IR Bands

The position of the carbonyl stretching band always provides useful information.

In the case of the isoelectronic species $[Mn(CO)_6]^+$, $Cr(CO)_6$, and $[V(CO)_6]^-$, an increase in negative charge on the complex causes a significant reduction in the energy of the C-O band as a consequence of additional π back-bonding from the metal to the ligands.

The bonding mode is also reflected in the infrared spectrum, with energy decreasing in the order

**terminal CO > doubly bridging CO > triply bridging CO**

# Continue..

The position of the carbonyl bands provide important clues to the electronic environment of the metal.

The greater the electron density on the metal (and the greater the negative charge), the greater the back-bonding to CO, and the lower the energy of the carbonyl stretching vibrations.

The positions of infrared bands are also a function of other ligands present.

# References:

(1) Miessler, Fischer & Tarr Inorganic Chemistry

(2) Shriver & Atkins Inorganic Chemistry

# Thank You