

JoVE: Science Education
Application of Group Theory to IR Spectroscopy
--Manuscript Draft--

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Overview:

Metal carbonyl complexes are used as metal precursors for the synthesis of organometallic complexes as well as catalysts. Infrared (IR) spectroscopy is one of the most utilized and informative characterization methods of CO containing compounds. Group theory, or the use of mathematics to describe the symmetry of a molecule, provides a method to predict the number of IR active C–O vibrational modes within a molecule. Experimentally observing the number of C–O stretches in the IR is a direct method to establish the geometry and structure of the metal carbonyl complex.

In this video, we will synthesize the molybdenum carbonyl complex $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$, which can exist in the *cis*- and *trans*-forms (**Figure 1**). We will use group theory and IR spectroscopy to determine which isomer is isolated.

Principles:

Selection Rules

Selection rules dictate the number of electronic transitions, from one quantum state to another, that are possible for a given molecule. IR spectroscopy probes vibrational transitions from the molecule's ground state, $\nu = 0$, to the first excited state, $\nu = 1$. The number of degrees of vibrational freedom (normal modes of vibration) for linear and non-linear molecules can be calculated using equations 1 and 2, respectively.

$$3N - 5 \quad (1)$$

$$3N - 6 \quad (2)$$

where N = the number of atoms in the molecule

For a normal mode of vibration to be IR active, the molecule's dipole must change. Therefore, any normal modes of vibration where a change in dipole does not occur are IR inactive. The number of active IR modes can be determined using group theory.

Group Theory

Chemists use group theory to understand the relationship between the symmetry and physical properties of a molecule. While the scope of group theory is too broad to rigorously cover in this video, we will provide the necessary tools needed to apply group theory to simple coordination complexes and show how it can be used to predict the number of IR active vibrational modes. To demonstrate, we will walk through the application of group theory to the molecule *cis*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$.

First, we need to determine the point group of the molecule. Point groups are used to describe the symmetry elements present in a given molecule. To determine the point group

of *cis*-Mo(CO)₄[P(OPh)₃]₂, we can use a flow chart called a symmetry tree, which asks a series of questions about the symmetry elements present in the molecule (**Figure 2**). Table 1 summarizes all of the symmetry elements included in the symmetry tree. Using the symmetry tree, and assuming that the ligands P(OPh)₃ are point ligands (ignoring the symmetry of those ligands), we find that *cis*-Mo(CO)₄[P(OPh)₃]₂ is in the point group *C*_{2v}.

Table 1. Symmetry elements used in point group determination		
Symmetry element	Symbol used	Example*
Identity	<i>E</i>	
Rotation axis (rotation by $\frac{360^\circ}{n}$)	<i>C</i> _n	
Horizontal mirror plane (reflection about xy plane)	<i>σ</i> _h	
Vertical mirror plane (reflection about xz or yz plane)	<i>σ</i> _v	
Diagonal mirror plane (reflection between xz and yz planes)	<i>σ</i> _d	

Inversion Center	i	
Improper rotation axis (rotation by $\frac{360^\circ}{n}$ followed by reflection perpendicular to rotation axis)	S_n	

* Examples are for an octahedral complex, where ligands 1 – 6 are equivalent. Upon performing the operation, the resulting molecule should be indistinguishable from its original configuration.

For the next step, we need to introduce character tables, which describe all of the symmetry present within a given point group. The character table for the point group C_{2v} is shown below.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The point group is indicated in the top left hand corner of the character table. To the right of the point group, all of the symmetry operations inherent to that point group are listed. The subsequent rows list all of the symmetry representations (irreducible representations, represented by Mulliken symbols, *ie.* A_1) contained in that point group, along with the symmetry of functions, which can tell us about the symmetry of atomic orbitals as well as linear movement along the x-, y-, and z-axis.

Using the character table for the point group C_{2v} , we generate a reducible representation (Γ_{red}) of the C–O stretching modes in the molecule $cis\text{-Mo(CO)}_4[\text{P(OPh)}_3]_2$ (**Figure 3**). The reducible representation, or the linear combination of irreducible representations, can be generated by applying each of the symmetry operations within the character table to the vibrations within molecule and recording the number of C–O vibrations that remain unchanged (in the same position in space). For example, upon applying the identity symmetry element to the C–O vibrations in $cis\text{-Mo(CO)}_4[\text{P(OPh)}_3]_2$, all four of the vibrational arrows remain in the same position. Therefore, the first value in our reducible representation is 4. If we continue this exercise, we generate the reducible representation shown below.

Commented [HK1]: I am a little rusty on group symmetry and point groups. What exactly does "E" stand for and what do the symmetry labels A_1 , A_2 , B_1 and B_2 mean? Should it be explained what 1 and -1 stands for or do you think students will understand this without an issue?

Commented [TP2]: I added "E" to table 1 above and a definition for Mulliken symbols. I do not want to go into explaining what 1 and -1 mean (I would have to go into a discussion of matrices which I believe is beyond the scope of this article). I have tried to provide enough information so that students can use character tables in this exercise. It is not necessary to understand how character tables are generated to be able to use them.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{red}	4	0	2	2

Next, we use the C_{2v} character table to find the linear combination of irreducible representations that generates Γ_{red} for the C–O vibrations within *cis*-Mo(CO)₄[P(OPh)₃]₂. Reduction of the reducible representation can be achieved using the reduction formula shown in equation 3.

$$n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r \quad (3)$$

where:

n_i = number of times the irreducible representation i occurs in the reducible representation

h = order of the group (total number of symmetry operations)

c = the class of operation

g_c = number of operations in the class

χ_i = character of the irreducible representation for the operations of the class

χ_r = character of the reducible representation for the operations of the class

Using equation 3 for each of the irreducible representations in the character table C_{2v} , we find that $\Gamma_{\text{red}} = 2A_1 + B_1 + B_2$. All three of the contributing irreducible representations, A_1 , B_1 , and B_2 , are IR active because they transform as either the x-, y-, or z-axis (see the symmetry of functions in the character table). Therefore, we predict that *cis*-Mo(CO)₄[P(OPh)₃]₂ will exhibit 4 C–O stretching modes in its IR spectrum.

To summarize, the following steps are needed in order to determine the number of IR active vibrational modes in a molecule:

1. Determine the point group of the molecule.
2. Generate a reducible representation of the C–O stretching vibrations within the molecule.
3. Reduce the reducible representation using equation 3.
4. Identify the number of translational irreducible representations present in the reduced representation from step 3.

If we follow these 4 steps with *trans*-Mo(CO)₄[P(OPh)₃]₂, we find that the molecule only possesses 1 active C–O vibrational mode.

Procedure:

1. Setup of the Schlenk Line (for a more detailed procedure, please review the “Schlenk Lines Transfer of Solvent” video in the *Essentials of Organic Chemistry* series). Schlenk line safety should be reviewed prior to conducting this experiment. Glassware should be inspected for star cracks before using. Care should be taken to ensure that O₂ is not condensed in the Schlenk line trap if using liquid N₂. At liquid N₂ temperature, O₂ condenses and is explosive in the presence of organic solvents. If it is suspected that O₂

has been condensed or a blue liquid is observed in the cold trap, *leave the trap cold under dynamic vacuum. Do **NOT** remove the liquid N₂ trap or turn off the vacuum pump.* Over time the liquid O₂ will sublime into the pump—it is only safe to remove the liquid N₂ trap once all of the O₂ has sublimed.

- 1.1. Close the pressure release valve.
- 1.2. Turn on the N₂ gas and the vacuum pump.
- 1.3. As the Schlenk line vacuum reaches its minimum pressure, prepare the cold trap with either liquid N₂ or dry ice/acetone.
- 1.4. Assemble the cold trap.
2. Synthesis of Mo(CO)₄[P(OPh)₃]₂ (**Figure 4**).¹ Use standard Schlenk line techniques for the synthesis of Mo(CO)₄[P(OPh)₃]₂ (see the “Synthesis of a Ti(III) Metallocene Using Schlenk line Technique” video). Metal carbonyl complexes are a source of free CO, which is highly toxic. Carbon monoxide poisoning occurs when CO binds to hemoglobin, resulting in significant reduction of oxygen supply to the body. Therefore it is extremely important to take appropriate safety measures when handling and working with metal carbonyl complexes. Reactions that generate free CO need to be conducted in a well-ventilated hood to prevent exposure to the toxic gas.
 - 2.1. Add 1.6 g (4.92 mmol) Mo(CO)₄(nbd) (nbd = 2,5-Norbornadiene) and 1.6 mL (9.84 mmol) triphenyl phosphite (P(OPh)₃) to a 100 mL Schlenk flask and prepare the Schlenk flask for the cannula transfer of solvent. *NOTE:* Mo(CO)₄(nbd) ((Bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0)) can be purchased from Sigma Aldrich or synthesized using literature methods.²
 - 2.2. Add 20 mL of degassed dichloromethane to the Schlenk flask *via* cannula transfer.
 - 2.3. Stir the reaction mixture for 4 h at room temperature under N₂.
 - 2.4. Remove the volatiles under vacuum and wash the resulting precipitate with cold hexanes (two washes each with 10 mL, -78°C). Filtration should be conducted under N₂ in a glove box.
 - 2.5. Dry the solid product under vacuum for 15 minutes.
 - 2.6. Measure the IR spectrum of the product in a solution of hexanes.

Representative Results:

IR spectrum will be provided on the day of filming.

Solution IR in saturated hydrocarbon (cm⁻¹): 2049 (s), 1965 (vs), 1948 (vs), 1941* (sh).³

Commented [HK3]: Will an IR spectrum be provided on the day of filming? Would it be possible to have an IR of the cis and trans product to compare and validate the calculated C-O vibrational modes?

Commented [PTM4R3]: Yes, an IR will be provided the day of. If we wanted to do a comparison, wouldn't we have to show the synthesis of the other compound? We could just do a literature comparison here instead.

Commented [HK5]: If a literature IR is available, then I think it is a great idea to use this.

*The resonance at 1941 cm^{-1} can only be seen under high-resolution conditions. Therefore, only 3 of the 4 resonances may be observed under certain conditions.

Summary:

In this video, we learned how to use group theory to predict the number of IR active vibrational modes in a molecule. We synthesized the molecule $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$ and used IR to determine which isomer was isolated. We observed that the product had three C–O vibrations in its IR spectrum, which is consistent with the *cis*-isomer.

Applications:

Group theory is a powerful tool that is used by chemists to not only predict IR active vibrational modes, but also vibrational, rotational, and other low-frequency modes observed in Raman spectroscopy. Additionally, group theory is implemented in molecular orbital (MO) theory, which is the most widely used model to describe bonding within transition metal complexes. MO diagrams, used by organic and inorganic chemists, can predict and explain a molecule's observed reactivity.

1st, 2nd, and 3rd row metal carbonyl complexes are used widely in inorganic synthesis as metal precursors for more complex organometallic compounds. Some of the most common types of reactions with metal carbonyl complexes include CO ligand substitution, redox at the metal center, and nucleophilic attack at the CO unit. Metal carbonyl complexes themselves are widely used in catalysis. For example, hydroformylation, the industrial production of aldehydes from alkenes, is catalyzed by the metal carbonyl complex $\text{HCo}(\text{CO})_3$ (Figure 5).

Legend:

Figure 1. The *cis*- and *trans*-isomers of $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$.

Figure 2. Symmetry tree used for point group determination.

Figure 3. CO vibrational stretches in *cis*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$.

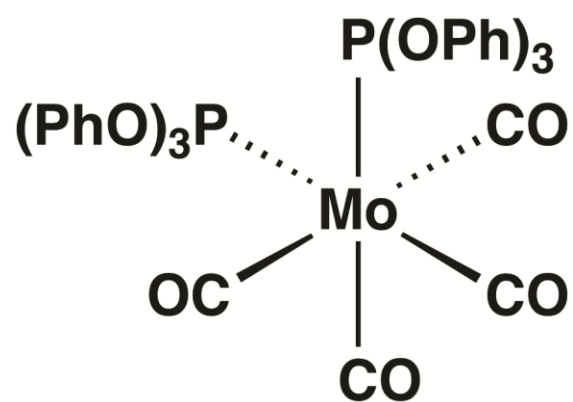
Figure 4. Synthesis of $\text{Mo}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$.

Figure 5. Hydroformylation by the metal carbonyl complex $\text{HCo}(\text{CO})_3$.

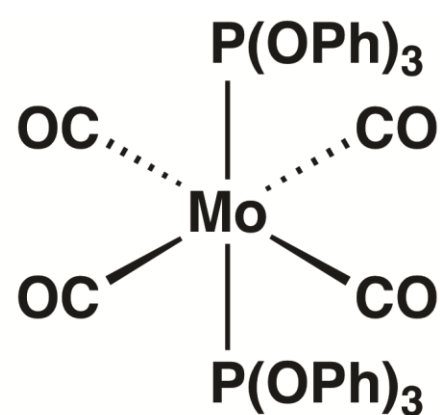
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- ¹ Fukumoto, K.; Nakazawa, H. Geometrical isomerization of *fac/mer*- $\text{Mo}(\text{CO})_3(\text{phosphite})_3$ and *cis/trans*- $\text{Mo}(\text{CO})_4(\text{phosphite})_2$ catalyzed by $\text{Me}_3\text{SiOSO}_2\text{CF}_3$. *Organomet. Chem.* **2008**, 693, 1968-1974.
- ² Darensbourg, M. Y.; Magdalena, P.; Houliston, S. A.; Kidwell, K. P.; Spencer, D.; Chojnacki, S. S.; Reibenspies, J. H. Stereochemical nonrigidity in heterobimetallic complexes containing the bent metallocene-thiolate fragment. *Inorg. Chem.* **1992**, 31, 1487-1493.

³ Darensbourg, M. Y.; Darensbourg, D. J. Infrared Determination of Stereochemistry in Metal Complexes. *J. Chem. Ed.* **1970**, *47*, 33-35.



cis-



trans-

Figure 1. The cis- and trans-isomers of $\text{Mo(CO)}_4[\text{P(OPh)}_3]_2$.

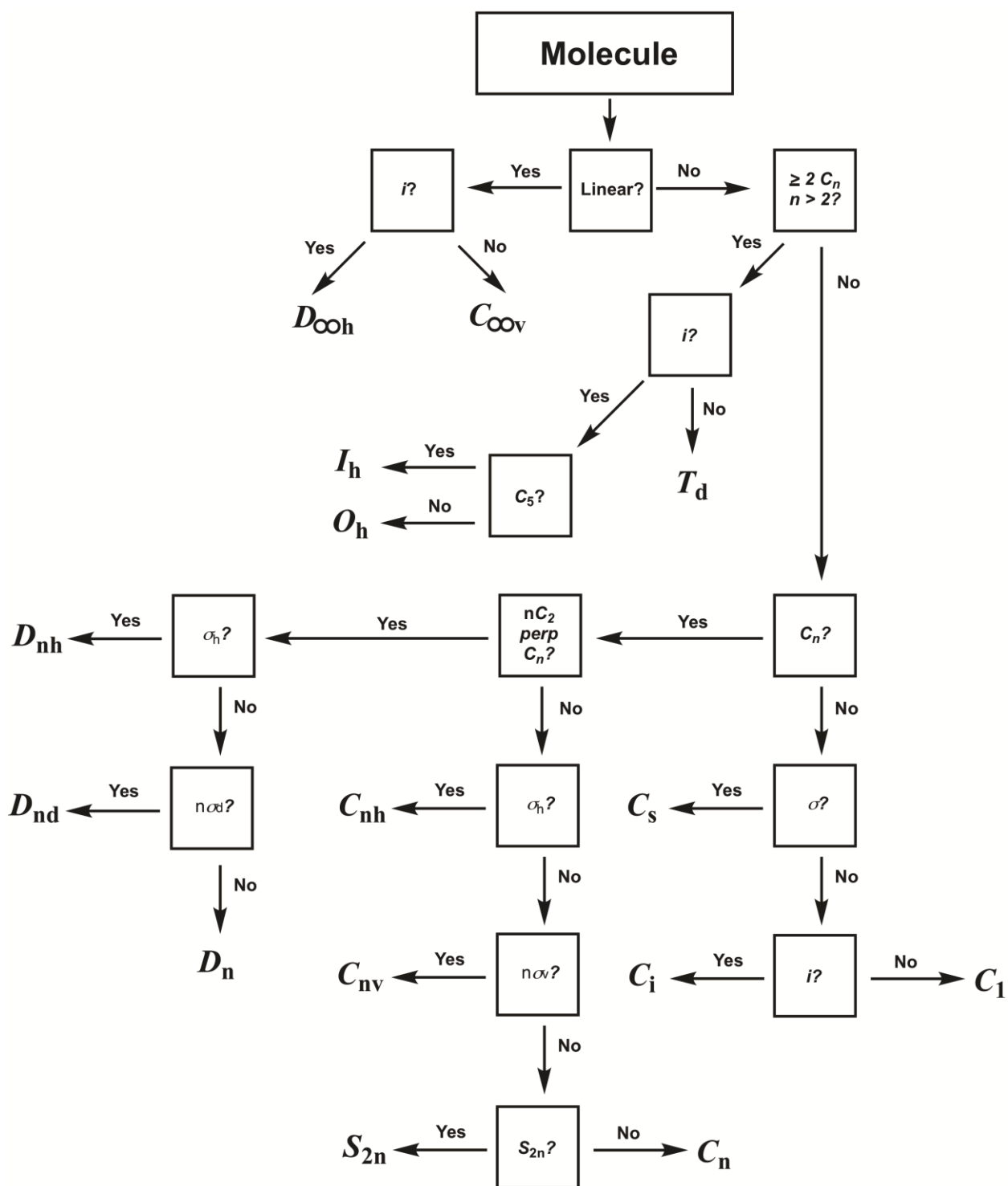


Figure 2. Symmetry tree used for point group determination.

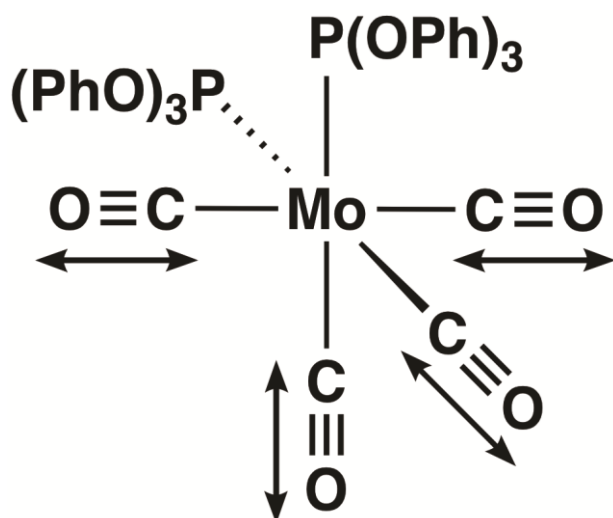


Figure 3. CO vibrational stretches in *cis*-Mo(CO)₄[P(OPh)₃]₂.

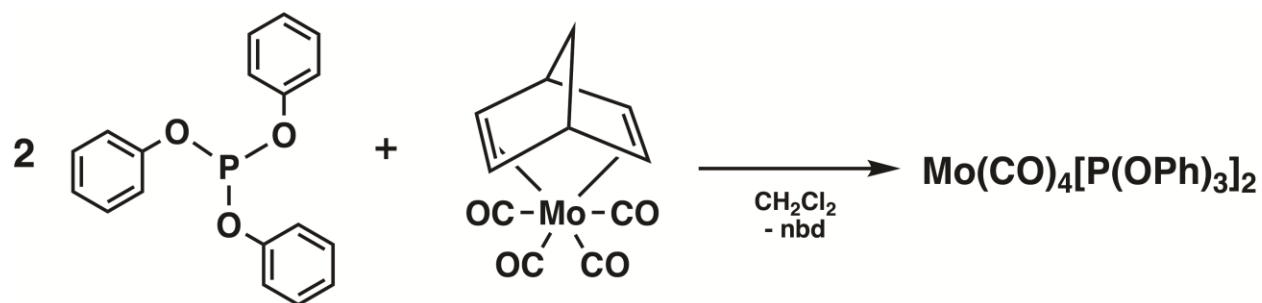


Figure 4. Synthesis of Mo(CO)₄[P(OPh)₃]₂.

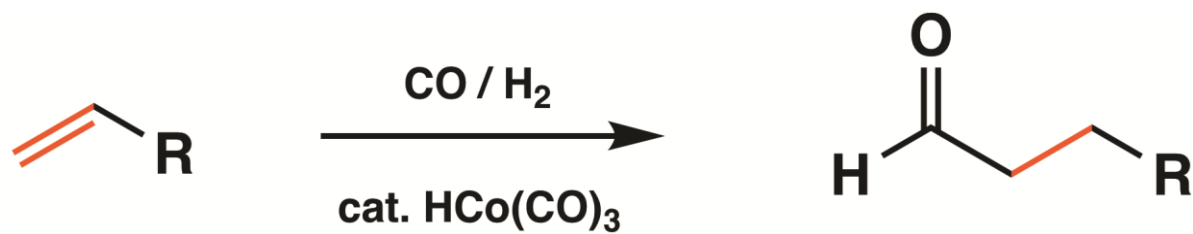


Figure 5. Hydroformylation by the metal carbonyl complex HCo(CO)₃.