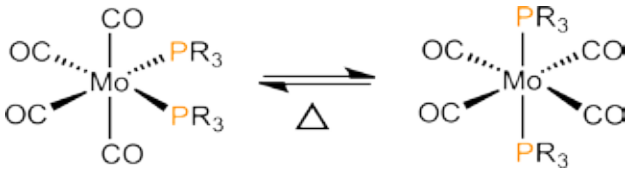
Monitoring the *cis-trans* isomerization of $Mo(CO)_4(PnBu_3)_2$ with $^{31}P\{^1H\}$ NMR Spectroscopy

Introduction

Organometallic chemistry is one of the most important areas in chemistry, owing largely to research involving the development and synthesis of new organometallic catalysts. Such catalysts have revolutionized the production of plastics,[1,2] synthesis of pharmaceuticals,[3] and production of synthetic fuels,[4] just to mention a few of the most common applications. Subsequently, laboratory experiments detailing the synthesis and mechanistic understanding of organometallic complexes is very important in inorganic undergraduate labs. In this application note, we detail how the $^1H/^{31}P$ NMReady-60PRO can make such a laboratory experience interesting, illustrative and appealing to undergrad students.

The process that we are going to study in this lab experiment is the *cis-trans* isomerization of $Mo(CO)_4(P^nBu_3)_2$ (scheme 1). The synthesis, characterization, and study of this compound was first reported in 1978[5] and the straightforward synthesis was extended to an undergraduate experiment in 2003.[6] However, only IR was used to study and characterize those complexes. In the first part of this application note we are going to focus only on the mechanism in the *cis-trans* isomerization.



Scheme 1. Thermal isomerization of *cis*-$Mo(CO)_4(PR_3)_2$

Pre-lab

In a pre-laboratory talk students can be guided to think about the experiment focusing specifically on the the isomerization process in particular.

- What's the most stable isomer? Why?
- How would you prepare the *cis* complex?
- Is the mechanism intra- or inter-molecular? How could you determine this?
- If the mechanism involves dissociation of one of the phosphines, how could you prove that?
- Which analytical technique best differentiates *cis*- and *trans*- isomers?

Procedure

1) Synthesis of *cis*-$Mo(CO)_4$(piperidine)$_2$

These complexes were prepared according to literature procedure.[5,6] $Mo(CO)_6$ (3.0 g, 11.36 mmol) and piperidine (7.5 mL) were refluxed in heptane (35 mL) for 4 h. The resulting yellow product was filtered hot, washed with heptane and dried under vacuum, yielding 4.1 g (10.9 mmol, 95%) of *cis*-$Mo(CO)_4$(piperidine)$_2$.

2) Synthesis of *cis*-$Mo(CO)_4(PR_3)_2$ (R = ^{n}Bu, Ph)

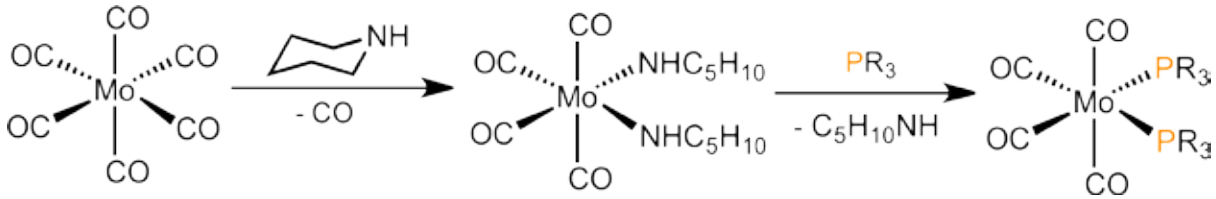
cis-$Mo(CO)_4$(piperidine)$_2$ (2.0 g, 5.31 mmol) and 2 mL of tributylphosphine were refluxed in dichloromethane (30 mL) for 15 minutes. Subsequently, the solution was filtered through celite and the filtrate was reduced in volume to afford a viscous oil. Cold methanol was added, the solution was cooled down below 0 °C and the white crystals formed were filtered in cold giving *cis*-$Mo(CO)_4(P^nBu_3)_2$ in 30% yield. The triphenylphosphine derivative was prepared in an identical manner as the described above affording *cis*-$Mo(CO)_4(PPh_3)_2$ in 45% yield.

3) Isomerization

In a 1 dram vial, 60 mg $Mo(CO)_4(P^nBu_3)_2$ was dissolved in 0.4 mL of C_6H_5Cl and subsequently transferred to a 5 mm NMR tube. The $^{31}P\{^1H\}$ NMR spectrum at t_0 was acquired using 64 scans. After acquiring the spectrum at t_0 the sample was placed in an oil bath at a fixed temperature and subsequent spectra were acquired periodically until no further change was observed.

Discussion

The synthesis of the molybdenum complexes consists of two steps (scheme 2). The first step is the substitution of two CO ligands for two piperidine ligands, which requires approximately 5 hours for completion. The second step is rapid, requiring only a few minutes, results in the displacement of piperidine by the phosphine reagent. Therefore, depending on the number of sessions dedicated to the experiment, students can make all the complexes, start from the piperidine complex, or just do the isomerization study. All the reactions are straightforward and can be made in big scales.

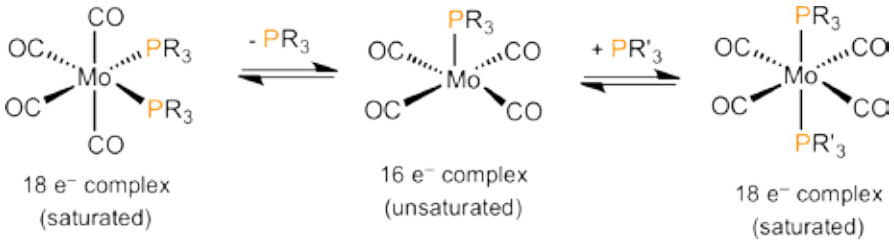


Scheme 2. General synthesis of *cis*-$Mo(CO)_4(PR_3)_2$

It is not possible to monitor the isomerization reaction using proton NMR spectroscopy because the resonances of the *cis* and *trans* complexes overlap significantly. Therefore, the best way to monitor these reactions is by ^{31}P NMR spectroscopy. ^{31}P chemical shifts range between +250 and -180 ppm and the resonances are very sharp, which minimizes signal overlap. Furthermore, we don't need to use deuterated solvents to dissolve the samples; the NMReady-60PRO can be easily configured to lock directly on the solvent's proton signal. For this particular experiment, we used chlorobenzene as the solvent and in order to get more accurate integrations we used inverse gated decoupling mode. In inverse gated the decoupling is 'on' only during the acquisition period, which minimizes NOE enhancements that effectively enhance the response factor of some resonances over others.

Probing the Reaction Mechanism

The isomerization reaction depicted in scheme 1 can proceed via two potential pathways, intramolecular or intermolecular. The intramolecular pathway proceeds via a simple 'rearrangement' of the ligands, no bonds are broken. The intermolecular pathway, on the other hand, involves two or more molecules. Because complexes of the type $Mo(CO)_4(PR_3)_2$ have 18 electrons one of the ligands has to dissociate first in order to create a free coordination site in the intermolecular pathway. Subsequently, another donor molecule can use that coordination site as shown in scheme 3.



Scheme 3. Intermolecular isomerization mechanism (dissociative process) R = ^{n}Bu, Ph

Because there is no ligand dissociation in the intramolecular pathway, addition of another donor ligand would not effect the isomerization; the new ligand would only be a spectator in the reaction. However, if the isomerization involves ligand dissociation we might be able to 'trap' the five-coordinate intermediate (16 e^-) species with excess phosphine. This can be quickly tested using a sigma donor ligand (e.g. another phosphine) in excess in the reaction mixture.

First, in order to determine the behavior of the complexes at high temperature, the isomerization of *cis*-$Mo(CO)_4(P^nBu_3)_2$ was performed at 85 °C. As you can see in figure 1, the isomerization is very clean and only *cis* and *trans* isomers are observed.

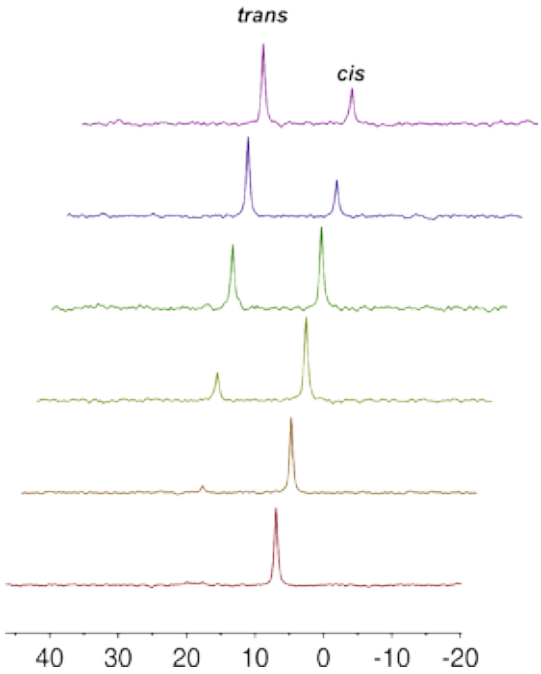


Figure 1. Stacked $^{31}P\{^{1}H\}$ NMR spectrum of $Mo(CO)_4(P^nBu_3)_2$ isomerization at 85 °C

In order to understand the reaction mechanism, the isomerization reaction at 85 °C was repeated, but free PPh_3 (10-fold excess) was added to the NMR tube before the sample was heated. If the reaction goes through a Mo–P bond breaking, $16e^-$ intermediate, as depicted in scheme 3 a new complex (or several complexes) should be observed in the NMR spectrum. In figure 2 we can see that initially (bottom spectrum) there are only *cis*-$Mo(CO)_4(P^nBu_3)_2$ complex and excess PPh_3 present. As the sample is placed in an oil bath at 85 °C only formation of *trans*-$Mo(CO)_4(P^nBu_3)_2$ is observed and no additional peaks appear in the reaction mixture after 60 minutes. This suggests that the reaction is intramolecular and there is no Mo–P bond breaking in the isomerization.

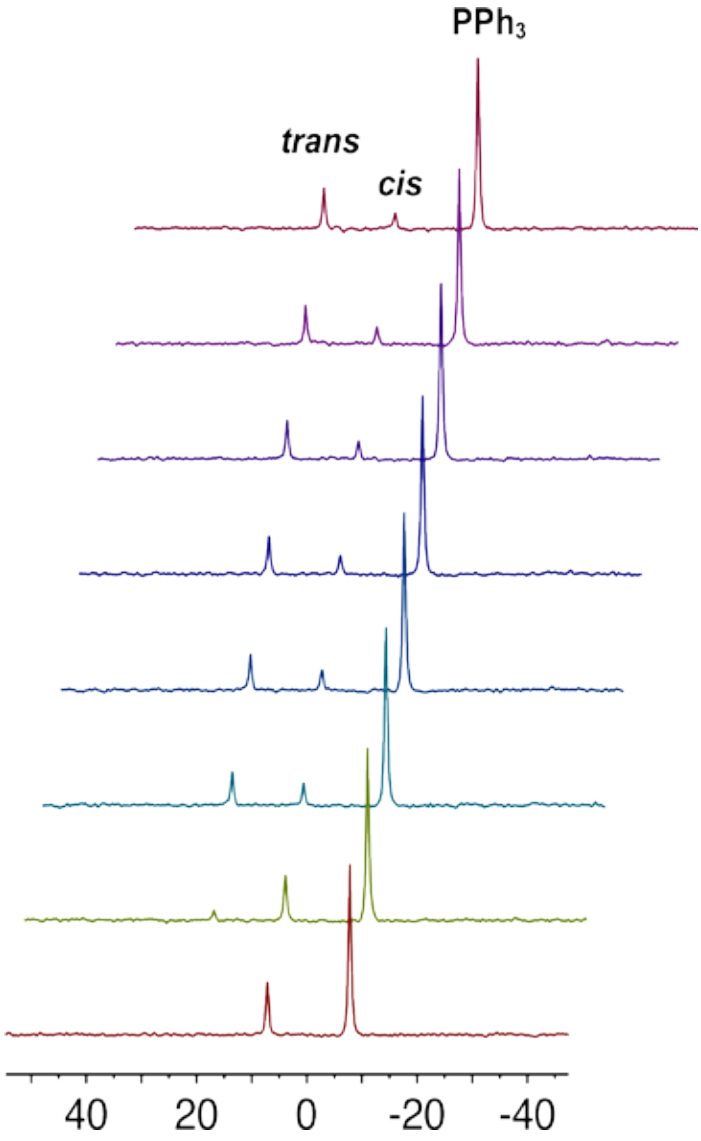


Figure 2. Stacked $^{31}P\{^1H\}$ NMR spectrum of *cis*-$Mo(CO)_4(P^nBu_3)_2$ isomerization at 85 °C in the presence of PPh_3

Interestingly, however, for Mo carbonyl complexes with weaker phosphine donors, *cis*-$Mo(CO)_4(PPh_3)_2$, are reported to occur by the dissociative mechanism as depicted in scheme 3.[5] In a similar experiment, free P^nBu_3 was added to a solution of *cis*-$Mo(CO)_4(PPh_3)_2$ in C_6H_5Cl.

In figure 3 we can see that initially only *cis* complex is present (bottom spectrum). As the reaction progresses the *cis*-$Mo(CO)_4(PPh_3)_2$ complex slowly disappears and several new compounds form in the reaction mixture. Keep in mind that based on the ^{31}P spectra none of the new species corresponds to *trans*-$Mo(CO)_4(PPh_3)_2$ (it should appear around 50 ppm). This indicates that the isomerization indeed follows a dissociative mechanism… we have successfully 'trapped' the 5-coordinate intermediate!

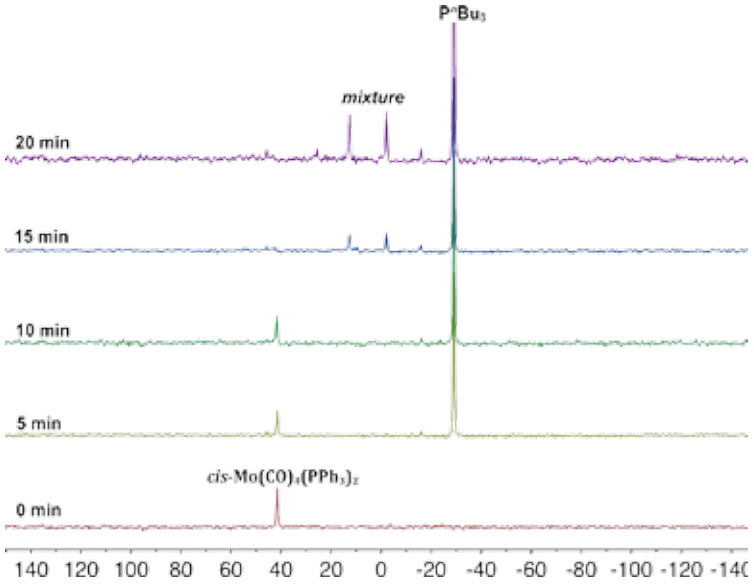
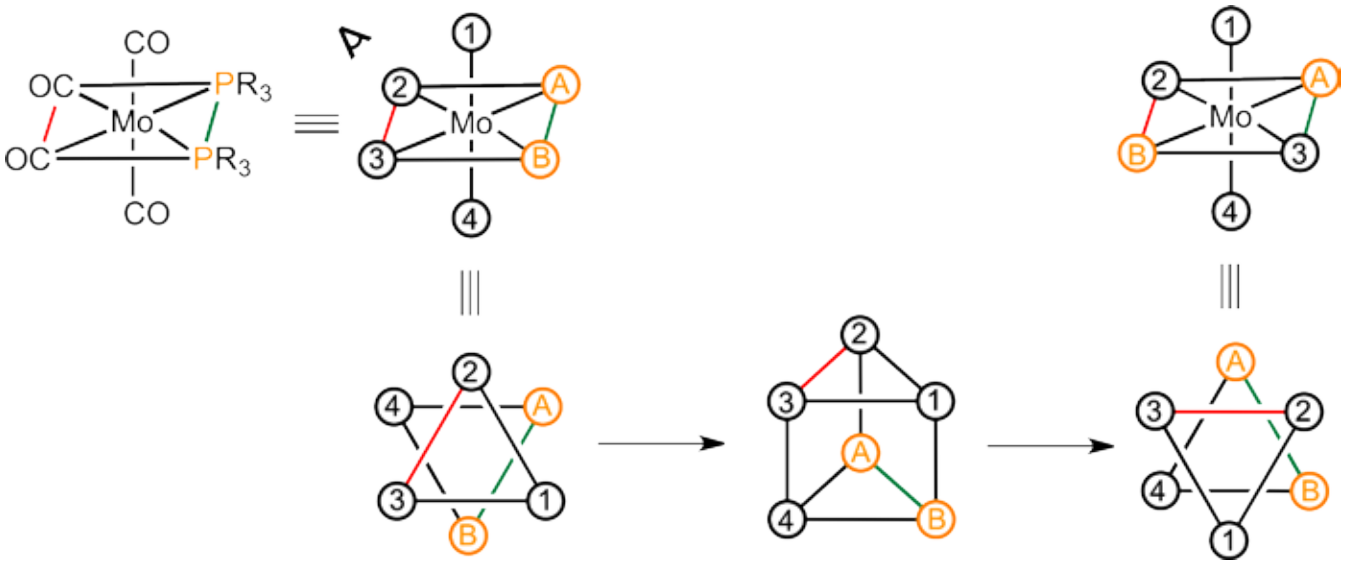


Figure 3. Stacked $^{31}P\{^1H\}$ NMR spectrum of *cis*-$Mo(CO)_4(PPh_3)_2$ isomerization at 95 °C in the presence of P^nBu_3

For students it is fairly easy to understand the mechanism for the intermolecular isomerization, somehow it just makes sense. However, it is considerably more difficult to visualize how the intramolecular isomerization takes place. There are several possibilities for this to happen.[7,8] Here we will discuss the Bailar twist. The Bailar twist proceeds by twisting the complex about its C_3 symmetry axis as shown in scheme 4. The University of Liverpool has an excellent 3D view of the Bailar twist.[9]



Scheme 4. Intramolecular isomerization mechanism (Bailar twist)

Conclusion

In this part of the experiment we have studied the *cis-trans* isomerization of a series of Mo carbonyl complexes and found that the mechanism is dependent on the strength of the phosphine donor. For the strong trialkylphosphine donors in $Mo(CO)_4(P^nBu_3)_2$, the results revealed that the process was intramolecular and does not involve dissociation of one of the phosphines. Interestingly, for the weaker triarylphosphine donors in $Mo(CO)_4(PPh_3)_2$, is mechanism is intermolecular and requires dissociation of a triphenyl phosphine in the first step.

References

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Questions/Discussion

1) Is this governed by steric or electronic factors? What is the cone angle of triphenylphosphine *vs.* tributylphosphine? What are the relative pK_a's?

2) Can you draw the bonding MO for the *cis* organometallic complex?

3) What is the relative effect of PPh_3 vs. P^nBu_3 on the CO molecular orbitals?

4) Can you verify the relative bonding strengths of PPh_3 vs. P^nBu_3 spectroscopically? Explain.

5) What governs the ratio of *cis* to *trans* isomers? Will the reaction reach 100% conversion to the *trans*?

6) What mechanism would you expect PMe_3 to isomerize by? Why?

7) Is this isomerization under thermodynamic or kinetic control?

8) What would happen if you do the same experiment starting from the *trans* isomer?

9) Can you propose another method to determine if the mechanism is intra- or intermolecular?

10) Why does one of the phosphine dissociate and not one of the carbonyl ligands? What bond is stronger?

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