# Synthesis and Migratory-Insertion Reactivity of CpMo(CO)3(CH3): Small-Scale Organometallic Preparations Utilizing Modern Glove-Box Techniques

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**Abstract**

Experiments are described for the reliable small-scale glove-box preparation of CpMo(CO)3(CH3) and acetyl derivatives thereof through phosphine-induced migratory insertion. The robust syntheses introduce students to a variety of organometallic reaction mechanisms and glove-box techniques, and they are easily carried out during three laboratory meetings. Furthermore, the series of complexes offers several interesting case studies for symmetry analysis of IR and NMR spectra. Finally, we present preliminary findings regarding the use of these experiments to give students the opportunity to synthesize and crystallographically characterize previously unreported variants of the migratory insertion product containing assorted phosphine ligands.

**Introduction**

Preparation, characterization, and analysis of organometallic complexes have become indispensable tools for synthetic chemists, as demonstrated by three recent Nobel Prizes for work in the field of organometallic catalysis. Since such synthesis and analysis is routinely performed on small scales using modern glove-box techniques, we have set out to develop a robust set of laboratory experiments to expose advanced undergraduate students to a variety of organometallic reaction classes using these techniques. In this article, we present such a series of experiments based on cyclopentadienyl-supported molybdenum (CpMo) complexes.

An interesting series of syntheses based on the CpFe(CO)2 ("Fp") fragment has been developed at Caltech to introduce students to several organometallic reactions and the importance of symmetry considerations in the characterization of the resultant molecules.[1](#_ENREF_1) Intrigued by this series of laboratories, we implemented a similar set of experiments several years ago. However, students were continually frustrated by low yields, and we were eager to move away from the use of sodium/mercury amalgam required for reducing the Fp dimer. Winter has described a relative of the Fp experiment using the CpMo framework, but his procedures also call for the use of sodium/mercury amalgam as a reductant and sublimation of an important intermediate.[2](#_ENREF_3)

Herein, we report an adaptation of Winter's CpMo experiments to a series of reliable, small scale (50–200 mg) preparations using modern glove-box techniques. Following a related procedure from Gladysz and co-workers,[3](#_ENREF_4) we now use lithium triethylborohydride as a reductant, allowing students to avoid potentially toxic mercury waste. The experiments may be easily completed in a series of three laboratory meetings, and analysis of the reactants, intermediates, and final products provide useful case studies for the role of symmetry in determining important spectroscopic signatures for organometallic molecules. Finally, we introduce a recent modification to the laboratory that has allowed students to prepare several novel phosphine-supported molybdenum(II) acetyl complexes and publish their syntheses and crystallographic details in peer-reviewed journals.

The goals of this set of laboratory experiments are:

* To prepare Cp-supported Mo(II) methyl and acetyl complexes through a series of organometallic transformations
* To characterize the starting materials and products using IR and NMR spectroscopy
* To apply a knowledge of symmetry and group theory to interpretation of the IR and NMR spectra and propose likely geometries for each reactant or product
* To learn basic processes for performing small-scale preparations in an inert-atmosphere glove box

Starting with commercially available [CpMo(CO)3]2, phosphine-supported Mo(II) acetyl complexes of the general form *trans*-CpMo(PR3)(CO)2(COCH3) can be prepared in three steps (Scheme 1, see Synthetic Details for more information). Following a suggestion from a related procedure by Gladysz and co-workers,[3](#_ENREF_4) we utilize lithium triethylborohydride solution ("Super Hydride") to reduce [CpMo(CO)3]2 and break up the dimer into monomeric [CpMo(CO)3]– units. The reaction occurs quickly at ambient temperature, with concomitant evolution of hydrogen gas. Upon presenting students with a general scheme for the reaction, we have found it useful to pose the question of what the reductant is and what the byproduct of [CpMo(CO)3]– formation is. Presenting the question prior to beginning the synthesis allows students to predict that gas formation should be observed. The Mo(0) anion may be intercepted with methyl iodide, via an SN2-type oxidative addition, to form CpMo(CO)3(CH3), which is then isolated as a pure yellow solid in reasonable to good yields (typically 60–80%) following extraction into pentane and filtration through activated alumina.



**Scheme 1.** General synthetic scheme for preparation of Mo(II) methyl and acetyl complexes.

The final acetyl complex, resulting from phosphine-induced migratory insertion of a carbonyl ligand into the Mo–CH3 bond, may be prepared using a number of different tertiary or secondary phosphines. We originally introduced the procedure using triphenylphosphine, but have since incorporated methyldiphenylphosphine, benzyldiphenylphosphine, tri-2-furylphosphine, and dicyclohexylphosphine. Thus far, we have encountered only two limitations with the preparation. First, bulky phosphines such as tri-*o*-tolylphosphine do not react due to steric encumbrance.[4](#_ENREF_5) Additionally, secondary phosphines have been observed to reduce the Mo(II) methyl complex to Mo(CO)x(HPR2)y species when used in excess and allowed to react for long periods of time. In the Supporting Information, we present syntheses and spectral data for triphenyl- and methyldiphenylphosphine derivatives, though we are constantly incorporating a number of other tertiary phosphines into the laboratory.

The phosphine-induced migratory-insertion reaction is also interesting due to the role of solvent. The reaction is best performed in acetonitrile, though we suspect other strongly coordinating solvents would also work well. When our students have performed the reaction in diethyl ether, a much poorer donor than acetonitrile, the reaction proceeded exceptionally slowly (ca. 50% conversion over the period of one week as opposed to full conversion in less than one day in acetonitrile). This can be explained by the equilibrium that likely precedes phosphine association (Scheme 2). As with related reactions, migratory insertion of a ligand leaves a vacant coordination site.[5](#_ENREF_6) Although the uninserted methyl species is thermodynamically favored, the equilibrium can be shifted by solvent coordination. The solvated migratory insertion product may react with a phosphine ligand, trapping the acetyl complex. In the absence of a strongly coordinating solvent, the concentration of Mo(II) acetyl is exceptionally low, so the reaction proceeds slowly.



**Scheme 2.** Coordinating solvents favor migratory insertion by raising the concentration of the acetyl intermediate available for trapping by phosphine.

**Hazards**

Care should be taken to avoid exposure to all chemicals used in this laboratory, and performing the syntheses in the glove box should minimize student exposure. The tetrahydrofuran, acetonitrile, and pentane solvents utilized are flammable and harmful. Special care should be taken with iodomethane, which is toxic and volatile, to avoid contamination of the glove box and exposure of researchers during removal from the glove box. As a result, we recommend that waste containing iodomethane be kept separate and sealed prior to removal from the glove box, then immediately transferred to a fume hood for disposal. Lithium triethylborohydride solution is extremely reactive with moisture and should be handled only in an inert atmosphere and quenched with 2-propanol/toluene if necessary. Triethylborane, which is formed as a byproduct of the lithium triethylborohydride reduction, is flammable, corrosive, toxic, and volatile. It is removed under vacuum during workup of CpMo(CO)3(CH3), so it is recommended that the solvent trap be immediately moved to a fume hood once syntheses are complete. Students and instructors should consult the MSDS for each chemical prior to laboratory work, and waste should be collected and disposed according to safety regulations.

**Equipment suggestions for small-scale glove-box manipulations**

The preparations reported in this article have been optimized for small-scale preparations in an inert-atmosphere glove box, and our syntheses are routinely performed in 20-mL disposable scintillation vials. Our glove box is equipped with a −35°C freezer, purge valve, and vacuum inlet for performing filtrations and removing solvent. We frequently use the freezer for storage of organometallic complexes such as CpMo(CO)3(CH3) in order to minimize the rate of decomposition, but it is not necessary for the procedure reported herein. Use of vacuum in the glove box is an important tool in this set of preparations, and most glove boxes can easily be retrofitted to provide a vacuum inlet connected to an external pump and solvent trap if one is not available.

**IR and NMR analysis of reactants and products**

The series of complexes presented in this set of experiments provides a useful introduction for students to the use of symmetry and group-theory arguments in the interpretation of spectral data. We generally begin by having students analyze the carbonyl region of the infrared spectrum of the dimeric [CpMo(CO)3]2 starting material (Figure 1). There are three obvious CO stretches, all at >1900 cm–1 in dichloromethane solution, indicating that there are no bridging carbonyl ligands. The fact that there are only three CO stretches for six carbonyl ligands implies a high degree of symmetry, and students ultimately conclude that the complex is likely centrosymmetric but does not contain a 3-fold rotational axis. The proposed structure corresponds with the reported single-crystal X-ray structure of the dimer,[6](#_ENREF_7) which has *C*2*h* symmetry. Other likely isomers with *C*2*v* or *C*2 symmetry would exhibit 5 or 6 IR-active CO stretching modes, respectively.[7](#_ENREF_8),[8](#_ENREF_9)

Assuming that it adopts a four-legged piano-stool geometry, similar to related Cp-supported molybdenum complexes, CpMo(CO)3(CH3) is expected to have two equivalent carbonyl ligands. This geometry is supported by 13C NMR spectroscopy, which exhibits two Mo–CO resonances (δ 240.0 and 226.9 ppm in CDCl3). Group theory predicts three IR-active stretches (2A' + A'') for the *Cs* structure, but only two bands are observed (Figure 1). The lower-energy band is broadened and slightly split, consistent with overlapping A' and A'' modes.[9](#_ENREF_10) When analyzing the data for CpMo(CO)3(CH3), students are confronted with seemingly contradictory spectral data and must conclude that they are unable to resolve all of the IR-active modes that are predicted by group theory.



**Figure 1.** Infrared spectrum of CpMo(CO)3(CH3) in CH2Cl2 shows overlapping A' and A'' CO stretching modes.

The structure of the migratory-insertion product, *trans*-CpMo(PR3)(CO)2(COCH3), may also be elucidated by NMR. Two isomers, in which the CO ligands are *cis* and *trans*, can be envisioned. Although both should exhibit IR-active symmetric and asymmetric stretching modes, the *trans* product should have only one M–CO resonance by 13C NMR, whereas the *cis* product would have two. The 13C resonances for the carbonyl and acetyl carbons are also doublets due to two-bond coupling to 31P. In most cases, students are able to assign all resonances in the 1H, 13C, and 31P NMR spectra, frequently utilizing the primary literature and reference spectra collected for the free phosphines. Interpretation of spectra for *trans*-CpMo(PR3)(CO)2(COCH3) products also provides the opportunity for discussion about the variation of C–P coupling constants for aryl phosphines between free and bound phosphines.[10](#_ENREF_11)

**Additional Studies**

As mentioned above, we have presented students with the option of making novel Mo(II) acetyl complexes by utilizing a variety of tertiary (and in some cases secondary) phosphines to induce migratory insertion of the Mo(II) methyl complex. Although bulky phosphines such as tri-*o*-tolylphosphine do not react and secondary phosphines such as diphenyl- and dicyclohexylphosphine have been observed to reduce the Mo(II) complex, possibly through loss of Cp–CH3, several other phosphines have been utilized successfully. This approach provides several advantages. First, students are able to prepare previously unreported complexes and gain experience interpreting relatively simple NMR and IR spectra for them. Second, when students are able to crystallize the final product, we have been able to include them in peer-reviewed publication of the single-crystal X-ray structures in crystallographic journals.[11](#_ENREF_12) Performing this suite of related reactions would be exceptionally difficult without a glove box, as many of the products are soluble in acetonitrile and cannot be isolated by the simple filtration described by Winter.[2](#_ENREF_3)

Though we have not explored reactivity of the Mo(II) acetyl products, prior literature suggests that there should be readily identifiable trends in decarbonylation reactivity of the acetyl complexes based on the bulkiness and electron-richness of the phosphine ligands.[4](#_ENREF_5),[12](#_ENREF_14)

**Conclusions**

We have presented a reliable synthesis for obtaining a range of phosphine-supported CpMo(II) acetyl complexes that introduces students to small-scale glove-box manipulations involving several fundamental organometallic transformations: chemical reduction, oxidative addition, and migratory insertion. The procedures may be completed during three laboratory periods, and the products are well-suited for analysis by infrared and multinuclear NMR spectroscopy. Additionally, the final step of the synthesis is readily adaptable using a variety of commercially available phosphines to allow students to prepare and characterize previously unreported complexes.

**References**

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