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## short report

### Hydrolysis Studies of *cis*-Disubstituted Tetracarbonylmolybdenum(0) Complexes with Binaphthol-based Chlorophosphite Ligands

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#### Abstract

Catalysts are used in industry to increase efficiency in large-scale production of chemical products. Hydroformylation reactions involve the conversion of alkenes to aldehydes through the addition of carbon monoxide. This process involves the use of a transition metal catalyst.

Asymmetric catalysts are of particular interest because they are used in the pharmaceutical industry to produce racemically pure products. Transition metal complexes with axially chiral (binaphthoxy-based) phosphite ligands are some of the best complexes for producing an enantiomeric excess in hydroformylation reactions of alkenes. Model

metal complexes containing these ligands are of interest in identifying possible structure-activity relationships.<sup>1-8</sup>

This report describes the characterization of *cis*-disubstituted tetracarbonylmolybdenum(0) complexes with binaphthol-based chlorophosphite ligands, which can be considered the parent for many of the complex ligands used in the catalysts. To determine the effect of altering the biaryl groups, the complex has been compared to the biphenol chlorophosphite analog.<sup>9</sup> The hydrolysis of *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub> is in some ways similar to the hydrolysis of the biphenol-based analog in that the observed product, when excess reagents are used, is the dianion and that an equilibrium exists between the

monoanion of the hydrolysis product and the dianion of the hydrolysis product. However, *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub> does not appear to be as reactive towards water, as no product is formed when stoichiometric ratios of reagents are added. Additionally, the equilibrium between monoanion and dianion may lie more towards the dianion for this complex.

## Introduction

Transition metal-catalyzed asymmetric synthesis is often used in industry to produce racemically pure products. This process is increasingly important, as the U.S. Food and Drug Administration requires that pharmaceuticals be racemically pure before they are approved. Many of the catalysts that perform asymmetric transformations well consist of phosphorus-based ligands containing binaphthol moieties. A common precursor of many of these ligands is phosphochloridite ester (**1**), shown in Figure 1. The coordination chemistry of the precursor and the reactions of the coordinated ligands have not been studied in detail.

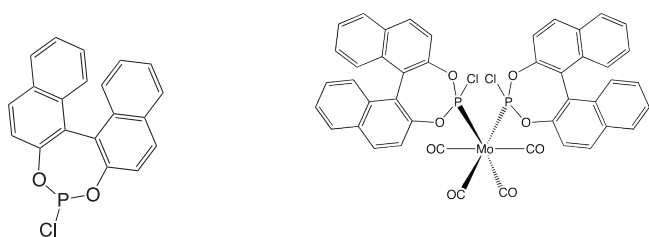


Figure 1. Chlorophosphite ligand (**1**) and its model complex, *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub>.

Although transition metal complexes in catalytic cycles cannot easily be characterized due to their transient natures and low concentrations, model complexes such as those discussed in this paper can give insight into the effects of changes in ligand environment on reactivity. Complexes of the type Mo(CO)<sub>6-n</sub>(P-donor ligand)<sub>n</sub> (n = 1, 2) are excellent model complexes for this type of characterization because the molybdenum(0) center is inert, allowing for the formation of stable products that can be studied by nuclear magnetic resonance (NMR) spectroscopy and X-ray crystallography. Additionally, the P-C coupling in the <sup>13</sup>C NMR resonances of the carbonyl ligands allows the coordination geometry of the molybdenum center to be determined.<sup>10</sup>

These model complexes may also have other applications. They could be used as sensors for mercury(II) in solution because the *cis*-*trans* isomerization reaction requires only catalytic amounts of mercury(II) chloride in order to proceed. Potentially interesting organometallic polymers could also be created using these compounds. The chloride groups on the chlorophosphite ligands are still reactive and could be displaced with nucleophiles to form polymer chains. These polymers could then undergo *cis*-*trans* isomerization in order to change the properties of the polymer or could potentially be cross-linked. These molecules are also interesting in

that they can serve as molecular gyroscopes when the tetracarbonylmolybdenum(0) center has a *trans* coordination geometry. The tetracarbonylmolybdenum(0) center can then freely rotate, while the P-donor ligands remain stationary.

The model complex, *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub> (Figure 1), has previously been synthesized and reported by our group.<sup>10</sup> Racemic 1'-1-bi-2-naphthol was used in the synthesis of the chlorophosphite ligand (**1**), and both diastereomers of the model complex were obtained. These were separated by fractional crystallization, and X-ray crystal structures of the two diastereomeric products were obtained. The crystal structures showed intramolecular pi-pi interactions for both diastereomers with stronger interactions seen in the *cis*-RR/SS diastereomer. The *cis*-RS diastereomer shows intermolecular pi-pi stacking. Images of the crystal structures for both diastereomers are shown in Figure 2.<sup>10</sup>

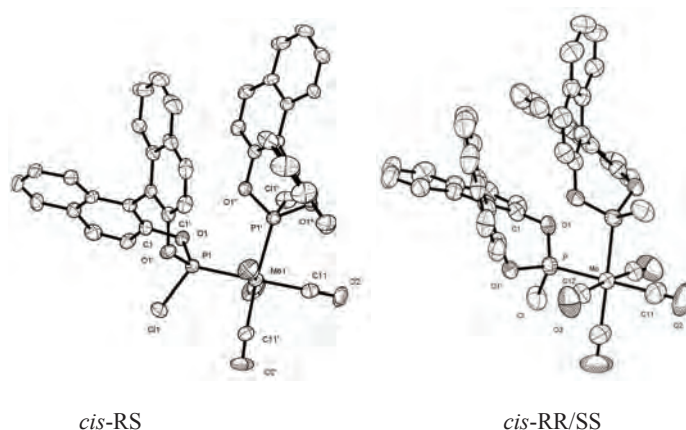


Figure 2. Crystal Structures of both the RS and the RR/SS diastereomers of *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub> previously reported.<sup>10</sup>

In this paper we report further characterization of both diastereomers of this complex through comparison of the hydrolysis of these complexes to those of their previously reported biphenoxy analogs using <sup>31</sup>P NMR spectroscopy.<sup>9</sup>

## Materials and Methods

All reactions were performed under nitrogen. Triethylamine and tetrahydrofuran were dried by distillation from Na/benzophenone. Glassware was flame dried or dried in an oven before use. The starting material, *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub>, was synthesized using methods previously described in the literature.<sup>10</sup> Hydrolysis reactions were followed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy on a Bruker DRX400 spectrometer using chloroform as the deuterated solvent. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were calibrated using an external 85 % phosphoric acid reference.

A solution containing 0.0311 g (0.0342 mmol) of *cis*-Mo(CO)<sub>4</sub>(**1**)<sub>2</sub> in 0.055 mL of tetrahydrofuran, triethylamine (13.0 μL, 0.0932 mmol), deionized water (1.0 μL, 0.056 mmol) and 0.1 mL of chloroform-*d* was added to an NMR

tube. The NMR tube was sealed with Teflon tape and a cap, and the hydrolysis reaction was monitored using  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The  $^{31}\text{P}$  NMR resonances of the two diastereomers of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$  were observed at 193.64 ppm and 192.78 ppm. When little reaction was observed after 5 h and 5 min, an additional 13.0  $\mu\text{L}$  (0.0932 mmol) of triethylamine and 1.0  $\mu\text{L}$  (0.056 mmol) of water were added. Because the reaction continued to go slowly, 26.0  $\mu\text{L}$  (0.186 mmol) of triethylamine and 2.0  $\mu\text{L}$  (0.11 mmol) of water were added after 24 h and 6 min. After 48 h and 7 min, the  $^{31}\text{P}$  NMR resonances of the two diastereomers of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$  could no longer be observed, and two new  $^{31}\text{P}$  NMR resonances were observed at 166.93 ppm and 166.73 ppm. The volatile components in the NMR tube were removed by blowing a stream of nitrogen through the tube. Next, chloroform and tetrahydrofuran were added to dissolve the solid residue, and then 0.50 mL of a  $6.84 \times 10^{-5}$  M aqueous acetic acid solution was added. The solvent was then removed once more using a stream of nitrogen. Solvent was added again, and new resonances appeared at 176.58 ppm and 176.00 ppm. Throughout the reaction, a blue precipitate formed. This precipitate was suspected to be an oxidized molybdenum compound. At different times throughout the reaction, no peaks were observed on the NMR spectra. We speculate that, when mixtures of species were present in solution, exchange occurred.

## Results and Discussion

It was anticipated that the hydrolysis of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$  might be similar to that of the biphenoxy analog of the complex  $\text{cis-Mo}(\text{CO})_4(2,2'\text{-C}_{12}\text{H}_8\text{O}_2\text{PCL})_2$ .<sup>9</sup> The reaction scheme presented in Figure 3 is therefore a comparison to that obtained for the analog. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in Figure 4 show that, when excess triethylamine and water were added to the  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$ , the  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances for the two diastereomers of this complex at 193.64 ppm and 192.78 ppm completely disappear, and a new set of narrow  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances are observed significantly upfield at 166.93 ppm and 166.73 ppm. To gain insight into the nature of this product, one equivalent of acetic acid was added to the solution. This addition caused the narrow  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances at 166.93 ppm and 166.73 ppm to disappear and a new set of broad resonances at 176.58 ppm and 176.00 ppm to appear. This behavior is consistent with the narrow upfield resonances belonging to the dianion of the hydrolysis product (complex B, shown in Figure 3) and the broad, downfield resonances resulting from an exchange between the dianion and monoanion (complex C, shown in Figure 3) of the hydrolysis product. The effect of the addition of excess reagents can also be compared to results from a previous paper describing the hydrolysis reaction of  $\text{cis-Mo}(\text{CO})_4(\text{Ph}_2\text{PCL})_2$ .<sup>11</sup> The hydrolysis of this complex in the presence of excess triethylamine and water resulted in the formation of only the monoanion. Comparing the three analogs, it is not unexpected that the binaphthol

analog being investigated would react more similarly to the biphenoxy compound. The differences in these reactivities likely relate to the ability of the intramolecular hydrogen bond in the monoanion to be broken to form the dianion from the monoanion. With the biphenoxy and binaphthoxy compounds, it would be expected that this process would be easier, as these are more electron-withdrawing ligands.

For the equilibrium between the monoanion and the dianion, shown in Figure 3, both the biphenoxy and the binaphthoxy analogs resulted in the formation of monoanion when a stoichiometric amount of acetic acid was added to the dianion complex. After this addition, the  $^{31}\text{P}$  NMR spectrum for the previously reported biphenoxy analog showed a sharp peak indicating the formation of only the monoanion. In contrast, after the addition of the acetic acid, the  $^{31}\text{P}$  NMR spectrum of the binaphthoxy analog showed a broad peak consistent with the exchange between dianion and the monoanion. This observation would suggest that it is harder to re-protonate the dianion of the binaphthoxy complex than it is to re-protonate the dianion of the biphenoxy complex and that the equilibrium between the monoanion and the dianion may lie toward the monoanion to a greater degree for the biphenoxy analog than it does for the binaphthoxy analog. An attempt was made to form the monoanion directly from the reaction of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$  with a stoichiometric amount of water and triethylamine, but no reaction was observed. This behavior is quite different from that of the biphenoxy analog, for which this reaction yielded the corresponding monoanion.

Increasing the temperature of the reaction in order to sharpen the peaks was considered; however, this reaction was not attempted, as it has been previously shown that the hydrolysis products can decompose upon heating. Additionally, for the biphenoxy analogs, it was observed that the equilibrium could be pushed by adding excess triethylamine to the monoanion.<sup>9</sup> This reaction has not yet been attempted for the  $\text{Mo}(\text{CO})_4(\mathbf{1})_2$  complex.

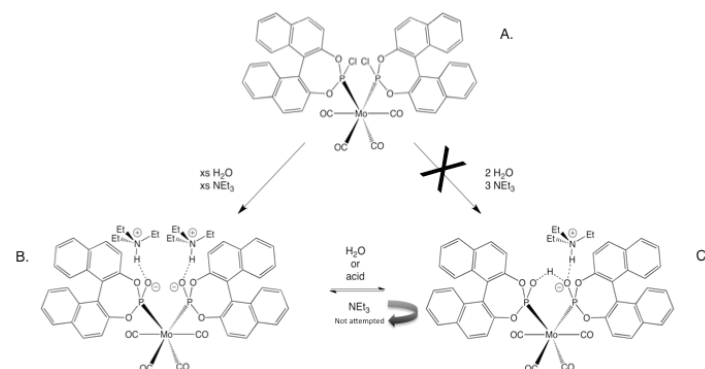


Figure 3. Hydrolysis of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$ , A, to yield either the dianion of the hydrolysis product, B, or the monoanion product of the hydrolysis product, C.

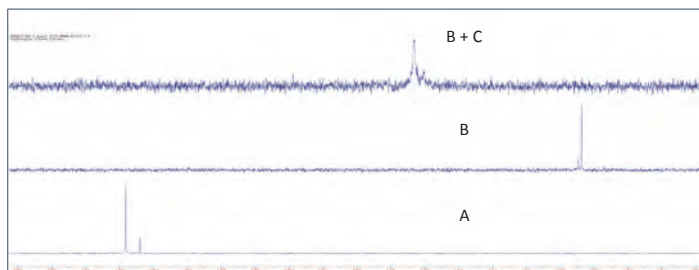


Figure 4.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $\text{cis-Mo}(\text{CO})_4(\mathbf{1})_2$ , A bottom, its dianion hydrolysis product, B center, and an exchanging mixture of the monoanion hydrolysis product, C, and the dianion hydrolysis product, B + C top.

## Conclusion

As expected, the hydrolysis reactions of  $\text{cis-RS}$  and  $\text{RR/SS}$  exhibit some similarities to those of the biphenoxy analogs in that the addition of excess triethylamine and water results in the formation of the dianion product. This product appears to be in equilibrium with the monoanion, as adding stoichiometric amounts of acid can push the equilibrium towards the monoanion. The results differed from those observed for the biphenoxy analog of the compound in that the formation of the monoanion directly from stoichiometric ratios of the reagents was not observed. It is likely that  $\text{Mo}(\text{CO})_4(\mathbf{1})_2$  is less reactive towards hydrolysis.<sup>12</sup> Additionally, the equilibrium between the monoanion and the dianion products of hydrolysis may lie more towards the dianion for the binaphthoxy analog than it does for the biphenoxy analog.

## References

1. Darensbourg, D., & Graves, A. Correction. Steric contributions to the solution dynamics involving phosphorus ligand dissociation in substituted derivatives of molybdenum hexacarbonyl. *Inorg. Chem.* 18, 2336–2336 (1979).
2. Diéguez, M., Pàmies, O., Ruiz, A., Castellón, S., & Claver, C. Chiral diphosphites derived from d-glucose: New ligands for the asymmetric catalytic hydroformylation of vinyl arenes. *Chemistry - A European Journal.* 7, 3086–3094 (2001).
3. Cserépi-Szűcs, S., Tóth, I., Párkányi, L., & Bakos, J. Asymmetric hydroformylation of styrene using rhodium and platinum complexes of diphosphites containing chiral chelate backbones and chiral 1,3,2-dioxaphosphorinane moieties. *Tetrahedron: Asymmetry.* 9, 3135–3142 (1998).
4. Buisman, G. J. H., et al. Chiral cooperativity in diastereomeric diphosphite ligands: Effects on the rhodium-catalyzed enantioselective hydroformylation of styrene. *Organometallics.* 16, 2929–2939 (1997).
5. Nozaki, K. et al. Highly enantioselective hydroformylation of olefins catalyzed by rhodium(I) complexes of new chiral phosphine–phosphite ligands. *J. Am. Chem. Soc.* 119, 4413–4423 (1997).
6. Deerenberg, S., Kamer, P. C. J., & van Leeuwen, P. W. N. M. New chiral phosphine–phosphite ligands in the enantioselective rhodium-catalyzed hydroformylation of styrene. *Organometallics.* 19, 2065–2072 (2000).
7. Cobley, C. J. et al. Synthesis and application of a new bisphosphite ligand collection for asymmetric hydroformylation of allyl cyanide. *J. Org. Chem.* 69, 4031–4040 (2004).
8. Kadyrov, R., Heller, D., & Selke, R. New carbohydrate bisphosphites as chiral ligands. *Tetrahedron: Asymmetry.* 9, 329–340 (1998).
9. Byrd, H., Harden, J. D., Butler, J. M., Jablonsky, M. J., & Gray, G. M. Unusual hydrolysis reactions of  $\text{cis-bis}((2,2'\text{-biphenylene})\text{phosphochloridite ester})\text{tetracarbonylmolybdenum}(0)$ . *Organometallics.* 23, 3239–3245 (2004).
10. Hastings, S. D., Owens, S. B., Jr., & Gray, G. M. Synthesis, characterization, and coordination of chiral 1,1'-bi-2-naphthenephosphorochloridite ester with molybdenum. (2013).
11. Gray, G. M., & Kraihanzel, C. S. Reactions of coordinated ligands. *Journal of Organometallic Chemistry.* 146, 23–37 (1978).