# Analysis of conformational isomers of molybdenum allyl complexes using molybdenum-95 NMR spectroscopy

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# Analysis of Conformational Isomers of Molybdenum Allyl Complexes Using $^{95}$Mo NMR Spectroscopy

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A series of molybdenum allyl complexes of the general formula CpMo(X)(Y)(allyl), where X = Y = CO, X = $NO^+$ and Y = CO, and X = $NO^+$ and Y = $I^-$, has been examined by $^{95}$Mo NMR spectroscopy. These complexes exhibit resonances in the range −790 to −1850 ppm. For most $\pi$-allyl ligands, when X = Y = CO and X = CO and Y = $NO^+$, both exo and endo isomers can be observed with the exo isomer yielding resonances upfield of the endo isomer for a given allyl moiety. There is also a progressive downfield shift in the order $(CO)_2$, (NO)(CO), and (NO)(I). These results are discussed in terms of the use of $^{95}$Mo NMR in conformational analysis.

## Introduction

The use of $^{95}$Mo NMR in the examination of molybdenum complexes is an area of an increasing number of publications in recent years.[1-3] These studies indicate the potential to detect minor variations about the Mo center as a result of subtle electronic and steric effects. We wish to report the use of $^{95}$Mo NMR in the examination of a series of $\eta^3$-allyl $CpMo^{II}$ complexes of the general formula CpMo(X)(Y)($\pi$-allyl), where X = Y = CO, X = CO and Y = $NO^+$, and X = $I^-$ and Y = $NO^+$. Other CpMo complexes have been examined with their $^{95}$Mo chemical shifts falling between −350 and −2150 ppm,[2,3] a range sufficiently wide to enable one to detect minor differences at the molybdenum center. One group has reported the use of $^{95}$Mo NMR to detect diastereotopic Mo(II) complexes differing only in the configuration at the molybdenum center.[3]

The allyl moiety in the complexes examined in this study is capable of bonding to the metal center in either the endo conformation or exo conformation, as shown in Figure 1, depending upon the presence and positions of substituents on the allyl ligand. The conformational analysis of these complexes has been reported by using $^1$H NMR spectroscopy,[4,5] and we now report the correlation between $^{95}$Mo chemical shift and $\eta^3$-allyl conformation.

Table I. $^{95}$Mo NMR Chemical Shifts for Dicarbonyl $\eta^3$-Allyl Complexes

| compd | $\delta$ (acetone) | rel int | [exo]/[endo] by $^1$H NMR |
|---|---|---|---|
| allyl (**1a**) | −1658 | 1 (endo) | 4.27/1 (0 °C, $CDCl_3$)[a] |
| | −1832 | 4 (exo) | 3.48/1 (25 °C, $CDCl_3$)[a] |
| 1-Me (**2a**) | −1600 | 1 (endo) | |
| | −1789 | 7 (exo) | 7.0 (−19 °C, $CS_2$) |
| 1,1-$Me_2$ (**3a**) | −1688 | 1 (exo) | |
| 1,3-$Me_2$ (**4a**) | −1709 | 1 (endo) | |
| | −1752 | 4 (exo) | 17.5 (0 °C, $CDCl_3$)[a] |
| 2-Me (**5a**) | −1573 | 11 (endo) | |
| | −1752 | 1 (exo) | 0.11 (0 °C, $CDCl_3$) |
| 2-Cl (**6a**) | −1521 | 15 (endo) | |
| | −1709 | 1 (exo) | 0.14 (5 °C, $C_6D_6$) |
| 2-Br (**7a**) | −1540 | 12.5 (endo) | |
| | −1744 | 1 (exo) | 0.17 (0 °C, $CDCl_3$) |
| cyclohexenyl (**8a**) | −1824 | 100 (exo) | >100[b] |
| cycloheptenyl (**9a**) | −1718 | 100 (exo) | |
| cyclooctenyl (**10a**) | −1646 | 100 (exo) | >100[c] |
| 1,1,2-$Me_3$ (**11a**) | −1448 | 1 (endo) | |
| | −1657 | 20 (exo) | 14.1 (−5 °C, $CS_2$)[a] |

[a] Reference 4a. [b] Reference 4b. [c] Reference 7b.

## Results and Discussion

**Dicarbonyl Complexes.** The $^{95}$Mo NMR spectra of most of the dicarbonyl complexes examined in this study contain two resonances which are assigned to the endo and exo conformations of the allyl moiety (Figure 1). These spectral results are summarized in Table I. The range in observed shifts is −1521 to −1833 ppm with respect to the $Na_2MoO_4$ ($\delta$ 0) reference, with line widths of 40–65 Hz. The relative concentrations for exo and endo conformations of many of these dicarbonyl complexes have previously been determined by $^1$H NMR spectroscopy, and so we can assign the $^{95}$Mo resonances on the basis of their relative intensities. Where both isomers are present, the resonances are all well resolved with the smallest peak separation being 43 ppm for complex **4a**. On the basis of these assignments, we see that for all the complexes examined where both the exo and endo isomers are observed, the resonance for the exo species is always upfield of the corresponding endo resonance. In addition, there appears

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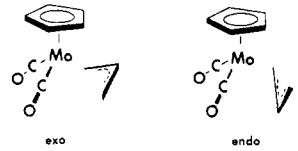


**Figure 1.** Endo and exo isomers.

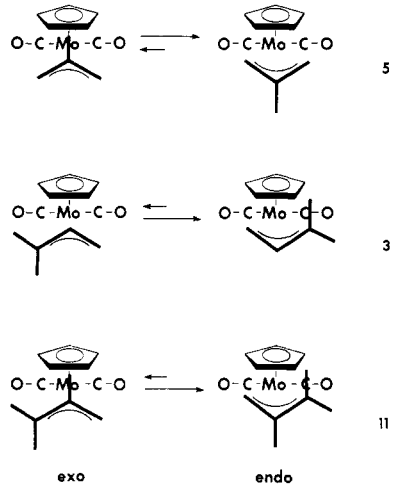


**Figure 2.** Steric interactions in methyl-substituted allyls.

to be a general trend that the exo complexes exhibit resonances upfield of ca. −1700 ppm while the chemical shifts of the endo isomers appear downfield of this position. The cyclooctenyl (**10a**) and 1,1-dimethylallyl (**3a**) complexes, known to exist predominantly in the exo conformation,[4] yield resonances at −1646 and −1688 ppm, respectively, slightly downfield of the −1700 ppm value, and are thus exceptions to this trend. The cyclohexenyl (**8a**) and cycloheptenyl (**9a**) complexes yield single resonances at −1824 and −1718 ppm, respectively, consistent with their exo conformational assignment.[4] Also, the endo isomer of the 1,3-dimethylallyl complex **4a** gives rise to a peak at −1709 ppm, but its exo isomer does appear upfield of this position, at −1752 ppm. Thus it appears that one should be able to reliably assign conformations based upon the molybdenum center being more shielded in the exo conformation of the allyl moiety than for the endo conformation.[4,7] The trimethylallyl complex **11b** also yields a resonance assignable to the exo isomer which appears at −1659 ppm, but the endo conformation gives rise to a peak well downfield of this value (−1448 ppm). There are two steric interactions to consider for this complex: (1) the 2-methyl group and (2) the *anti*-1-methyl group, both of which interact with the cyclopentadienyl ring (see Figure 2). For complex **3a**, the 1,1-dimethylallyl complex, the *anti*-1-methyl group forces the equilibrium to favor the exo conformation. For a 2-methyl substituent, the endo isomer is favored on steric grounds. For complex **11a** it appears that the *anti*-1-methyl group's steric requirement has the greatest influence on the observed conformation.

**Nitrosyl Carbonyl Cations.** The nitrosyl complexes examined herein are all prepared by the addition of $NO^+$ to the dicarbonyl complexes as shown in eq 1. Their $^{95}Mo$ NMR spectra are summarized in Table II. One observes that the nitrosyl cations yield resonances downfield of their dicarbonyl analogues, in the range −1326 to −1576 ppm,

$$CpMo(CO)_2(allyl) + NOPF_6 \rightarrow [CpMo(NO)(CO)(allyl)]PF_6 + CO \quad (1)$$

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**Table II. NMR Parameters for CpMo(NO)(CO)(allyl) Cations**

| subst | compd | δ | initial ratio | final ratio |
|---|---|---|---|---|
| H | **1b** | −1530 | 10 | 1 |
| | | −1576 | 1 | 2 |
| 1-Me | **2b** | −1480 | 20 | |
| | | −1511 | 1 | |
| | | −1521 | 1 | |
| 1,3-$Me_2$ | **4b** | −1402 | 1 | |
| | | −1472 | 3.3 | |
| 2-Me | **5b** | −1488 | 1 | 3 |
| | | −1494 | 6 | 1 |
| 2-Cl | **6b** | −1426 | 2 | 3 |
| | | −1433 | 1 | 1 |
| 2-Br | **7b** | −1434 | 2 | 3.5 |
| | | −1442 | 1 | 1 |
| cyclohexenyl | **8b** | −1494 | 100 | 100 |
| cycloheptenyl | **9b** | −1378 | 1 | 0 |
| | | −1475 | 8 | 100 |
| cyclooctenyl | **10b** | −1390 | 5 | 1 |
| | | −1444 | 1 | 1 |
| 1,1,2-$Me_3$ | **11b** | −1326 | 1 | 2.4 |
| | | −1347 | 2.3 | 4.4 |
| | | −1373 | 11.3 | 1 |
| | | −1407 | 6.5 | 1 |

indicating that a deshielding of the molybdenum center occurs upon replacement of a CO ligand with $NO^+$. This observation can be rationalized by the increased ability of the nitrosyl ligand for π-back-bonding compared to the carbonyl group,[6] thus removing electron density from the Mo center and thereby causing the observed downfield shift in $^{95}Mo$ resonances. The increased asymmetry at the molybdenum results in increased line widths (110–160 Hz) owing to more efficient quadrupolar relaxation.

From $^1H$ NMR studies of the carbonyl displacement reaction (eq 1), it has been demonstrated that one obtains a kinetically controlled, nonequilibrium mixture of endo and exo isomers which gradually proceeds toward thermodynamic equilibrium.[5] For example, if the exo isomer for a given allyl dicarbonyl complex is the stable isomer, then the initially formed nitrosyl cation complex is the endo isomer and, with time, equilibration takes place converting this endo isomer to the more stable exo isomer until the thermodynamic equilibrium is reached. Unlike the dicarbonyl complexes, this exo = endo isomerization is often much slower ($t_{1/2}$ > 15 min) and thus one is able to follow it by normal spectroscopic techniques such as $^1H$ NMR. The equilibration is also known, in many instances, to be accelerated by the addition of a catalytic amount of NaI.[7] Thus, in all cases where this equilibration is sufficiently slow, it can be examined by $^{95}Mo$ NMR.

The chemical shifts and relative intensities observed for the initially formed nitrosyl cation complexes are given in Table II. In most cases, when the carbonyl nitrosyl complexes are first formed, the products yield $^{95}Mo$ NMR spectra with a reversal of intensity between the upfield and downfield chemical shifts as compared to their dicarbonyl analogues. This is consistent again with the assignment of the upfield resonances to the exo isomers. For example, in the case of the 2-methylallyl dicarbonyl complex, **5a**, the endo isomer is favored and an exo/endo isomer ratio of 1:11 is observed. When the nitrosyl cation complex **5b** is formed, the $^{95}Mo$ spectrum shows the upfield resonance, assigned to the exo isomer, to be the major resonance by 6:1. Upon the addition of a catalytic amount of NaI, this ratio changes to 1:3 with the downfield resonance being predominant: i.e., the endo isomer becomes the major isomer. These observations are consistent with previous $^1H$ NMR studies.[5]

The exo conformation for the 2-chloro and 2-bromo complexes **6b** and **7b**, respectively, appears to be somewhat

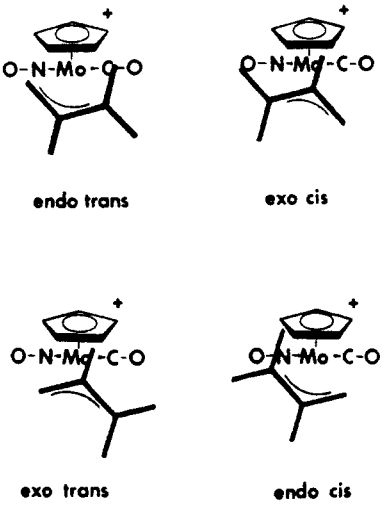


**Figure 3.** Isomers of CpMo(NO)(CO)(1,1,2-trimethylallyl) cation.

less stable than was observed for the 2-methyl complex. Isomerization occurred more quickly and had proceeded to a significant extent by the time their $^{95}$Mo NMR spectra were recorded. With time, the amount of endo isomer present for these complexes increased slightly more until thermodynamic equilibrium was reached (see Table II).

Within the cyclic allyl series, the cyclohexenyl complex **8b** isomerizes to the thermodynamically stable product by the time the $^{95}$Mo NMR spectrum is recorded, and thus, only the exo conformation is observed. The cycloheptenyl cation isomerizes more slowly, and so the endo conformer was observed in the $^{95}$Mo spectrum but its isomerization to the more stable exo conformation had already proceeded to a significant extent (exo/endo = 8:1). Addition of a trace amount of NaI accelerated and quickly completed the conversion to form essentially all exo isomer. The cyclooctenyl complex converts from the initially formed endo isomer to the exo isomer even more slowly than the $C_7$-allyl complex and an exo/endo ratio of 1:5 was observed. This species then slowly converted to the more stable exo isomer, and after ca. 30 min a 1:1 mixture of endo and exo isomers was seen by $^{95}$Mo NMR.

In the spectrum of the trimethylallyl complex **11b**, we observe four resonances at −1326, −1349, −1373, and −1406 ppm. There are four possible isomers for this complex as shown in Figure 3. The initial spectrum shows the two upfield resonances to be the predominant peaks. After the addition of a trace of NaI and allowing the equilibration to proceed, a different spectrum was obtained in which the downfield resonances had increased in intensity at the expense of the upfield resonances. Consideration of relative intensities suggests that the isomer which yields the $\delta$ −1373 resonance converts to the isomer giving rise to the one at $\delta$ −1349. Similarly, the resonance at $\delta$ −1326 increases at the expense of that at $\delta$ −1406. According to the relative positions of these resonances, the initially formed complexes are tentatively assigned to the cis and trans isomers of the exo conformation. This suggests that the endo isomer resonances are the ones which increase with time. Further assignment of these resonances to cis and trans isomers would be tenuous at best and was, therefore, not attempted.

For the 2-methyl complexes **5a** and **5b**, the interaction of the Cp ligand with the 2-methyl group causes the exo = endo equilibrium to lie in favor of the endo conformation.[4a,5a] In the case of the 1,1-dimethyl complexes **3a** and **3b**, the *anti*-methyl group ($Me_a$) on the allyl ligand forces the equilibrium in favor of the exo conformation (see Figure 2).[4b,5b] For the 1,1,2-trimethyl complexes there are methyl groups at both the 2-position and the 1-anti-position of the allyl ligand. Our $^{95}$Mo NMR correlations suggest that the endo conformation is the stable conformation in the nitrosyl complex, and so it appears that the steric interactions of the 2-methyl group control the stereochemistry of the complex. One should note that the allyl moiety in the isomers of the CpMo(NO)(X)(allyl) complexes are oriented differently[7] (see Figure 3) than in the dicarbonyl complexes owing to the different electronic effects of the NO and X groups. Thus, the relative importance of steric effects would be expected to differ significantly from those observed in the dicarbonyl case. We would predict that the tilting of the allyl would reduce the steric interaction between the *anti*-methyl group and the Cp ring in the trans endo isomer.[8]

For the dicarbonyl complexes there appears to be a large chemical shift difference between the exo and endo isomers (at least 43 ppm for the complexes studied here). However, the nitrosyl cations, although still showing the trend of the endo isomer of a given allyl ligand exhibiting the further downfield resonance compared to its exo isomer, exhibit less of a difference in chemical shifts between the exo and endo isomers. As shown in Table II, the 2-substituted allyls (2-Br, 2-Cl, and 2-Me) all exhibit differences in chemical shifts of less than 10 ppm (8, 7, and 6 ppm, respectively). In addition, for the nitrosyl cations, there are no separate characteristic shift regions for exo complexes and endo complexes, as was observed for the dicarbonyl complexes.

**Nitrosyl Iodide Complexes.** The preparation of these complexes is shown in eq 2. The iodide complexes in this

$$[CpMo(CO)(NO)(allyl)]PF_6 + NaI \rightarrow CpMo(NO)(I)allyl + CO + NaPF_6 \quad (2)$$

study were prepared in situ by the addition of 1 equiv of an acetone solution of NaI directly to the NMR samples of the corresponding nitrosyl carbonyl species. The $^{95}$Mo resonances for the iodide species are typically much broader than the dicarbonyl or carbonyl nitrosyl complexes (line widths in the range 170–280 Hz) and for some complexes could not be readily observed. The chemical shifts for these complexes are further downfield than the corresponding nitrosyl cations, and thus in replacing a carbonyl ligand by an iodide, the molybdenum center becomes further deshielded. Much less is known concerning the stereochemistry of the nitrosyl iodide complexes as compared to their dicarbonyl and carbonyl nitrosyl analogues, and so it is more difficult to make conformational assignments. By $^1$H NMR, it has been determined that for the allyl and 2-methylallyl nitrosyl iodide complexes, **1c** and **5c**, the endo isomer is more stable with exo/endo ratios of 1:3.5 and 1:6.3, respectively.[8] Since we observe only single resonances for these complexes in the $^{95}$Mo NMR spectra, several explanations are possible. First, the resonances that are observed are broad and the minor isomer may not be observed owing to low concentrations or because of the fairly low signal/noise ratio observed for all of the nitrosyl iodide complexes. A second less likely explanation is that both isomers appear at the same chemical shift.

The allyl complex **1c** has been shown by X-ray crystallography to exist as the endo isomer in the solid, and thus, the resonance at −1093 ppm is assigned to the endo isomer of **1c**. The cyclooctenyl complex **10c** has also been examined by $^1$H NMR and X ray crystallography and was found to exist in the exo conformation.[7b] Therefore, we

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Table III. $^{95}$Mo NMR Spectral Results for Nitrosyl Iodide Complexes

| allyl | compd | δ | |
|---|---|---|---|
| allyl | 1c | −1093 | (endo) |
| 1-Me | 2c | −974 | (endo) |
| 2-Me | 5c | −1042 | (endo) |
| 2-Cl | 6c | −1021 | (endo) |
| 2-Br | 7c | −1028 | (endo) |
| cyclohexenyl | 8c | −895 | (exo) |
| cycloheptenyl | 9c | −878 | (exo) |
| cyclooctenyl | 10c | −884 | (exo) |
| 1,1,2-Me$_3$ | 11c | −795 | (exo) |
| | | −791 | (exo) |

assign the $^{95}$Mo resonance observed at −884 ppm for complex **10c** to its exo conformation. It is also most likely that the cyclohexenyl and cycloheptenyl complexes exist mainly in the exo conformation, and so the $^{95}$Mo resonances at −895 and −878 ppm for these complexes are also assigned to the exo conformation.

It is apparent from these complexes that the general trend of the exo isomers exhibiting resonances upfield of the endo isomers is no longer followed. In fact, the trend seems to be reversed, i.e., exo isomers being downfield of the endo isomers which leads to the assignments shown in Table III.

## Conclusion

We have shown that for the dicarbonyl complexes and the carbonyl nitrosyl cations the exo isomers of a given allyl ligand yield resonances upfield of their corresponding endo isomers. In addition, for the dicarbonyl complexes the exo conformations of nearly all the allyl ligands examined yield resonances upfield of the endo complexes as a whole.

In conclusion, we can see that the use of $^{95}$Mo NMR may prove to be a valuable tool in the stereochemical analyses of closely related complexes.

## Experimental Section

**Complexes.** The molybdenum dicarbonyl complexes CpMo(CO)$_2$(allyl) and nitrosyl carbonyl cations [CpMo(CO)(NO)(allyl)]PF$_6$ were prepared by published methods.[4,5] The nitrosyl iodide complexes[7] CpMo(NO)(I)(allyl) were prepared by adding 0.2 M solutions of NaI in acetone directly to the NMR samples of the corresponding nitrosyl cations and were not isolated.

**Physical Measurements.** The $^{95}$Mo NMR spectra were obtained on a Bruker WM500 spectrometer using a multinuclear probe and operating at 32.59 MHz with a deuterium lock. The spectrometer was calibrated by using an external standard of 2 M $Na_2MoO_4$ in $D_2O$. Complex concentrations ranged from 0.1 to 0.5 M in acetone-$d_6$ or 1:1 $(CH_3)_2CO/(CD_3)_2CO$. Spectra of acceptable signal to noise could be obtained in 15 min. The shifts relative to $Na_2MoO_4$ were obtained indirectly by measuring the shifts relative to the lock on $(CD_3)_2CO$. The shifts were corrected for the field shift in locking on $D_2O$ by subtracting 2.5 ppm. All measurements were conducted at 303 K.

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# Synthesis and Characterization of $[Co_4(CO)_{11}C(O)Me]^-$. The X-ray Crystal Structure of Tetraphenylphosphonium Tris(μ-carbonyl)octacarbonylacetyl-*tetrahedro*-tetracobaltate(1−)

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The alkylidyne complex $Co_3(CO)_9COC(O)Me$ decomposes in THF to produce $[Co(CO)_4]^-$, $Co_4(CO)_{12}$, and an unidentified intermediate which reacts with $[Co(CO)_4]^-$ to produce $[Co_4(CO)_{11}C(O)Me]^-$ (I). Complex I is also produced by the reaction of $Co_4(CO)_{12}$ with MeLi and has been characterized by IR and NMR spectroscopy and by a single-crystal X-ray diffraction study, as a tetraphenylphosphonium salt. The salt crystallizes in the monoclinic space group $P2_1/c$, with $a$ = 12.026 (1) Å, $b$ = 23.835 (3) Å, $c$ = 12.788 (2) Å, $\beta$ = 90.492 (9)°, and $Z$ = 4. The structure has been solved from 4949 reflections with $I > 3\sigma(I)$ and refined by least-squares calculations to $R$ = 3.7%. The structure of the anion is derived from that of $Co_4(CO)_{12}$, with a mean cobalt–cobalt distance of 2.512 (3) Å. Three of the carbonyl groups are edge bridging, defining a basal triangle, while the remaining eight are terminal. The acetyl ligand is terminally bound in an axial position on the basal triangle, with a cobalt–carbon distance of 1.953 (4) Å.

## Introduction

Recently in this laboratory several anionic ketenylidene cluster complexes have been synthesized via reductive cleavage of $\mu_3$-C–O bonds. For example, reduction of the anions $[M_3(CO)_{10}COC(O)Me]^-$ (M = Fe, Ru, or Os) with $Na/Ph_2CO$ affords the dianions $[M_3(CO)_9CCO]^{2-}$, containing face-capping ketenylidene ligands.[1,2] These complexes possess a rich and varied chemistry,[2-4] one aspect of which is metal fragment substitution reactions to form new mixed-metal ketenylidene complexes. For example, reaction of $[PPN]_2[Fe_3(CO)_9CCO]$ with $Co_2(CO)_8$ affords $[PPN][CoFe_2(CO)_9CCO]$, a monoanionic ketenylidene complex containing cobalt.[5] For many years the homo-

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