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STEREOSELECTIVITY IN NUCLEOPHILIC ADDITION TO UNSATURATED LIGANDS BOUND TO MOLYBDENUM

ALLYLIC ALKYLATION OF CYCLOHEXANONE

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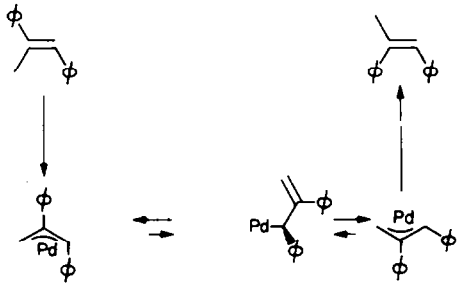
Abstract—The stereochemistry and regiochemistry of nucleophilic addition to olefinic, allylic, or diene moieties can be controlled in reactions of molybdenum complexes. The synthesis of a wide range of α-allylic cyclohexanones is feasible using (η^5-cyclopentadienyl)Mo(CO)(NO)(allyl) cations. The stereoselective preparation of (*RS,SR*)-2-(1-methyl-2-butenyl)cyclohexanone from the reaction of 1-pyrrolidino-1-cyclohexene with [CpMo(CO)(NO)(η^3-1,3-dimethylallyl)]BF_4 illustrates the methodology.

The extensive chemistry associated with allylpalladium complexes, such as that developed by Trost,[1] Backvall,[2] and Tsuji,[3] has already been shown to be valuable in natural product synthesis. The reactivity of olefins and dienes bound to cationic iron carbonyl systems has also been applied to synthetic advantage by Pearson,[4] Birch,[5] and Rosenblum.[6] We have developed reagents based on allyl and diene complexes of molybdenum which have substantial potential for analogous chemistry, and which may offer complementary or alternative approaches to those based on iron and palladium chemistry.

We had previously elucidated the detailed rearrangement mechanisms[7,8] and preferred configurations of substituted allyl palladium systems.[9] These studies showed that the *cis–trans* ratios of olefins derived from these complexes could be controlled and understood by consideration and manipulation of the π–σ–π equilibrium which readily occurs in the Pd-system. For example, this mode of equilibration was used in our development of a new approach for the conversion of *trans*-1,2-diphenylpropene to *cis*-1,2-diphenylpropene.[10]



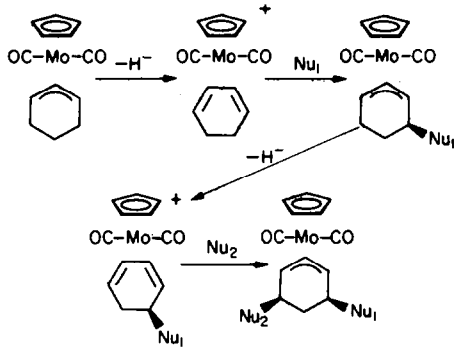
Although this π–σ–π rearrangement can be a problem if one wishes to retain stereochemistry about a double bond, an appreciation of the preferred geometries (*syn*[11] usually preferred) often allows one to account for product distributions in reactions of allylpalladium complexes. One should also note that π–σ–π process reverses the face of the olefin which is attached to the metal. This feature leads to racemization of chiral complexes if the substituents on one terminus of the allyl moiety are the same. The racemization is prevented if both termini are substituted[12] and this has been used in the design of asymmetric allyl alkylations by Bosnich.[13]

Backvall's studies also demonstrated that variations in conditions could yield attack either *trans* or *cis* to the metal[2] owing to the potential of binding the reagent or other ligands to the coordinately unsaturated Pd-ion. This potential for reversal of selectivity for attack on Pd-complexes, as well as the potential for stereochemical scrambling resulting from π–σ–π equilibration suggested that an alternative allyl system might prove to be of utility.

We chose to develop the (η^5-cyclopentadienyl)$Mo(CO)_2$(η^3-allyl) system because it was not prone toward rapid π–σ–π interconversions and since it was coordinatively saturated, should always undergo attack *trans* to the metal. It also offered the potential for combining some of the advantages of the $Fe(CO)_3$ systems exploited by Pearson and Birch with those of the Pd-systems. Generally these Mo-reagents are readily prepared, moderately air stable, and give reactions which proceed in high yield with high regio- and stereoselectivity. The (η^5-Cp)$Mo(CO)_2$ moiety can also be readily modified to allow resolution of diastereomers and procedures have been developed[14,15] for the production of chiral species in high optical purity.

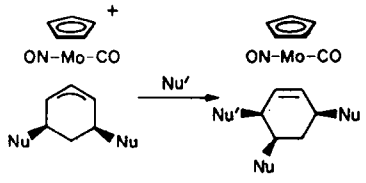
All of the reactions in our Mo-system are stoichiometric rather than catalytic. This however can be an advantage when the directing influences can be multiplied in several sequential additions to the same substrate.

One generally expects that nucleophilic attack will occur most readily on cationic species and that a neutral species, such as a (η^5-Cp)$Mo(CO)_2$(η^3-allyl) will be relatively unreactive. On the other hand, a neutral or anionic species should readily undergo hydride abstraction. Thus, one can anticipate the utilization of several sequential hydride abstraction and nucleophilic addition steps in a procedure which would eventually attach several groups selectively to one side of an organic ligand. We have demonstrated this approach in the addition of two methyl substituents to a cyclohexenyl system.[16]

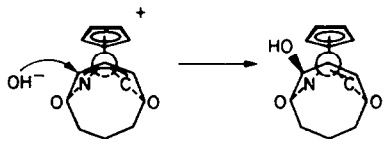


A wide range of nucleophiles can be used in these reactions,[17] e.g. CN^-, OH^-, $R_2NCS_2^-$, but relatively soft C—C bond-forming nucleophiles, such as malonates and enamines are likely to be the most useful synthetically. We have also effected intramolecular cyclizations by these procedures.[16] This approach has been extended by Pearson[18] for stereocontrolled lactone syntheses and the production of intermediates which might be useful in macrolide antibiotic syntheses.

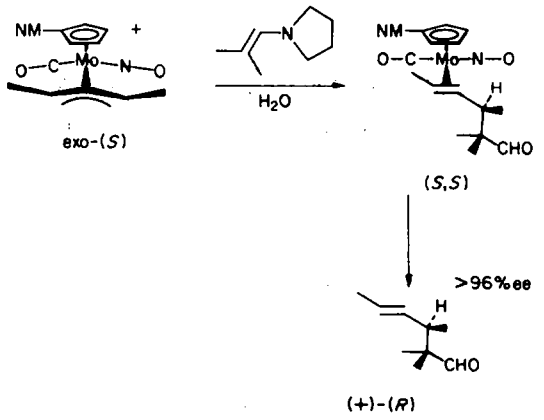
These reactions with the η^4-diene cation complexes yield neutral η^3-allyl complexes, from which the allyl fragment must be liberated. There are a number of methods for accomplishing this which will be discussed subsequently; however, a method which allows the introduction of a third nucleophile is particularly interesting. This involves activating the complex to nucleophilic attack by replacing a carbonyl group by NO^+. This introduces a positive charge and allows attack on the three carbon η^3-allyl to yield a neutral olefin complex, from which the olefin can be released by oxidation of the metal.



The nitrosyl ligand not only provides a positive charge on the complex which promotes nucleophilic attack, but provides a directing influence which directs regioselective attack *cis* to the nitrosyl. The resulting stereochemistry was confirmed in the formation of the η^2-cycloocten-3-ol complex from the reaction of water with $[CpMo(CO)(NO)(\eta^3\text{-cyclooctenyl})]^+$ cation.[19]

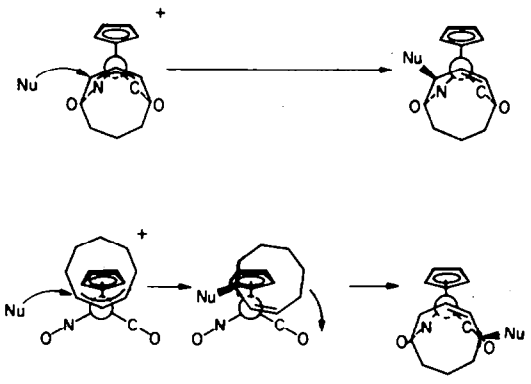


Since the metal center is chiral at this stage (Cp, CO, NO, and η^3-allyl substituents), introduction of a neomenthyl group onto the cyclopentadienyl ligand allows relatively straightforward separation of diastereomers and ultimately a route to the preparation of chiral allylically substituted olefins in high enantiomeric purity.[14,15]



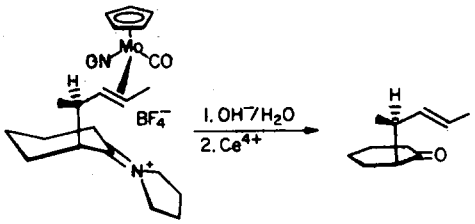
Selectivity

The addition of the nucleophile occurs *cis* to the nitrosyl ligand and on the face of the η^3-allyl group opposite to the metal (the β-face). The stereochemical consequences of this addition are influenced strongly by the thermodynamically preferred conformation of the allyl group relative to the NO and Cp ligands. *Under most reaction conditions a single isomer is preferred and a single diastereomeric product is obtained.* One should note, however, that the kinetic product from the addition of NO^+ is usually not the thermodynamically stable product. Under controlled conditions one can force the reaction to occur with the kinetic product and a different stereochemistry will result.[19]



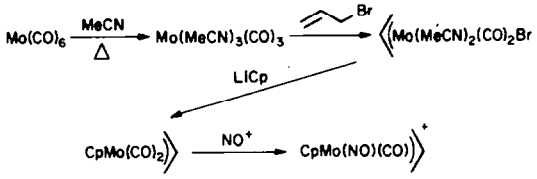
Generally, the reaction conditions catalyze the conversion of the $CpMo(NO)(CO)(\eta^3\text{-allyl})$ cation to the stable isomer, particularly with acyclic allyls. The rate of this catalytic interconversion is usually more rapid than the rate of nucleophilic addition, and hence, these interconversions are not generally of significance with regard to routine use of these reagents for synthesis.

The potential for stereoselectivity is illustrated in the reaction of pyrrolidine enamine of cyclohexanone with the $[CpMo(NO)(CO)(\eta^3\text{-1,3-dimethylallyl})]^+ BF_4^-$. In this case the regioselectivity is ~100% on the β-face of the allyl and *cis* to the NO. There is a stereoselection of 5:1 for the prochiral α-positions of the 1-pyrrolidino-1-cyclohexanone. The major isomer crystallizes readily as the pure complex of the (*RS,SR*)-allylically substituted iminium salt, which can be hydrolyzed and then readily decomplexed by oxidation with ceric ion.[20]



Routes to the $[CpMo(NO)(CO)(\eta^3\text{-}allyl)]^+$ *reagents*

Method 1. The most efficient route to these complexes allows the preparation of quantities of up to 50 g in an afternoon. Molybdenum carbonyl is refluxed in acetonitrile to yield $(CH_3CN)_3Mo(CO)_3$. Addition of an allyl bromide produces an immediate reaction giving $(\eta^3\text{-allyl})Mo(CO)(CH_3CN)_2Br$, which when treated with LiCp yields relatively air-stable yellow or orange crystals of $CpMo(CO)_2(\eta^3\text{-allyl})$. Treatment of the dicarbonyl complex with nitrosyl hexafluorophosphate or tetrafluoroborate yields the desired reagent.



Method 2. An approach which we recently developed and which is given in detail in the experimental section uses an allylic acetate in place of the allylic bromide of Method 1. This reaction requires an overnight reflux of the acetate with $(MeCN)_3Mo(CO)_3$ owing to the decreased reactivity of the acetate.

Method 3. Treatment of $CpMo(CO)_2(NO)$ with an allyl halide and silver hexafluorophosphate yields the reagent.[21]

Method 4. Abstraction of hydride from $CpMo(CO)(NO)(\eta^2\text{-olefin})$ with trityl hexafluorophosphate also yields the desired product.

Method 5. Protonation of $CpMo(CO)(NO)(\eta^2\text{-diene})$ complexes provides one of mildest routes to these reagents.[17,19]

Methods 3–5 require $CpMo(CO)_2(NO)$, which is available in quantity (~20 g) through Inorganic Synthesis preparations using Diazald.[22,23] Smaller quantities can easily be prepared by a photochemical reaction from $[CpMo(CO)_3]_2$ and NO gas.[24]

Decomplexation of product olefins

Oxidation of the product complexes is usually the best approach for removing the olefin. The choice of oxidizing conditions depends on the sensitivity of the olefinic product to the conditions.

Method 1. Air oxidation of the product in chloroform solution is one of the mildest methods and generally produces insoluble molybdenum-containing residues which can be removed by passage of the solution through a filter of alumina, silica, Celite, or glass fibers. This method is slow and may require a day or more for the compound to decompose completely.

Method 2. High pressure CO will rapidly remove the olefin and recover the $CpMo(CO)_2(NO)$, but is often inconvenient in labs not equipped with autoclaves.

Method 3. Strong base will generally cause near immediate decomposition and yield free olefin (if the olefin can withstand the treatment).

Method 4. Ceric ion oxidation can be tolerated by most systems and is probably the most generally useful method. Buffering with acetate appears to improve the yields.[18]

The allylic moiety can be removed from $[CpMo(CO)(NO)(allyl)]^+$ cations and the $CpMo(CO)_2(allyl)$ complexes which result from addition of nucleophiles, but a group must be added or removed as these complexes can be viewed as containing stabilized allyl cations or anions.

Thus for the $[CpMo(CO)(NO)(allyl)]^+$ cation, hydride can be added to produce the olefin complex or a proton can be removed by base (a hindered amine) to yield a diene complex.[17,19] The olefins can then be removed by methods above.

Protonation of $CpMo(CO)_2(allyl)$ complexes with trifluoroacetic acid also yields the olefin. Furthermore, Pearson has developed a relatively mild iodolactonization procedure which may be useful in some cases.[18]

DISCUSSION

Improvements in selectivity in the preparation of α-allylic cyclohexanones has been explored and methodology recently developed which utilizes Pd-catalyzed enol stannane[25] addition to allyl acetates or enolate addition to allylammonium[26] salts. The addition of 1-pyrrolidino-1-cyclohexene to the $CpMo(NO)(CO)(\eta^3\text{-}1,3\text{-dimethylallyl})$ cation provides a moderately stereoselective route to (*RS,SR*) - 2 - (1 - methyl - 2 - butenyl) - cyclohexanone. The *E* isomer is obtained exclusively and the pure (*RS,SR*) isomer can be obtained by demetallation of the recrystallized olefin complex.

Although we have not yet carried out the reaction, our ability to prepare the (+)-2,2,3-trimethylhex-4-enal in over 96% ee[14] via attack of 1-pyrrolidino-2-methylpropene on $[(neomenthylcyclopentadienyl)Mo(NO)(CO)(\eta^3\text{ - }1,3\text{ - dimethylallyl})]^+$ suggests that reaction with the enamine of cyclohexanone would yield the pure (*RS*) - 2 - (1 - methyl - 2 - butenyl) - cyclohexanone.

The thrust of this report has been directed towards the control of multiple sites of stereochemistry. The use of this technique also may be of value in the addition of less substituted allyls. Reactions with $[CpMo(NO)(CO)(\eta^3\text{-crotyl})]$ yield exclusively the 2-[(*E*)-2-butenyl]cyclohexanone upon decomplexation of the olefin. We anticipate that extensions of these systems may provide useful alternatives to the currently available methods of achieving allylic alkylations with control of selectivity.

EXPERIMENTAL

General synthetic procedures. All operations involving the handling of organometallic complexes in soln were carried out under an atmosphere of N_2 using standard inert atmosphere techniques. All solvents were dried before use. THF was distilled from sodium benzophenone ketyl under N_2 before each use. CH_2Cl_2 and acetonitrile were distilled from CaH_2 before use. All reactions should be carried out in an efficient hood since CO is evolved during some reactions.

Molybdenum carbonyl can be purchased from several suppliers of inorganic and organometallic reagents or direct from American Metal Climax in bulk. Molybdenum carbonyl is crystalline white solid which can generally be used without

further purification. Sublimation is generally used to separate the pure material from any blue residues.

Cyclopentadienyl lithium can be purchased as a dry powder from Alfa Products and used as received for small scale preparations. Large scale preparations might use CpLi or CpNa obtained from cyclopentadiene monomer in THF from BuLi or NaH. $[CpMo(CO)_3]_2$ can be purchased from Alfa Products and Strem Chemicals. Neomenthylcyclopentadiene is prepared by the method of Cesarotti *et al.*[27] with the exception that greatly improved yields are obtained if the reflux period with NaCp is increased to 10 hr.

Compound $(CH_3CN)_3Mo(CO)_3$. A 200 ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and N_2 inlet and bubbler at the top of the condenser was charged with 2.64 g (10 mmol) of $Mo(CO)_6$ and 80 ml of acetonitrile. The resulting suspension was heated gently to boiling and then heated under *vigorous* reflux for 3 hr. The progress of the reaction could be monitored by turning off the N_2 flow momentarily and watching the CO evolution through the bubbler. This pale yellow soln of the trisacetonitrile adduct was used immediately in subsequent reactions.

The preparation of $CpMo(CO)_2(\eta^3$-1,3-*dimethylallyl*$)$ *using* 1-*methyl*-2-*butenyl acetate*. The most efficient syntheses of $(\eta^3$-allyl$)Mo(CO)_2(MeCN)_2X$ complexes result from addition of allyl halides to $(MeCN)_3Mo(CO)_3$, as described in detail elsewhere.[14,19,28] The procedure for the acetate represents an alternative if the halides are not readily available, but may require up to a 12 hr reflux period compared to the nearly immediate reaction with allyl bromides.

The 1-methyl-2-butenyl acetate (1.30 g, 10 mmol) was added to the acetonitrile soln of $(MeCN)_3Mo(CO)_3$ and heated at reflux for 12 hr. The clear orange soln was cooled to room temp and 0.72 g (10 mmol) of LiCp powder was added to the soln under a counter current of N_2. The soln turned yellow and a fine light brown ppt formed as the mixture was stirred for 1 hr. After standing for 10 min a clear yellow–orange soln was decanted from the ppt and the solvent was removed on a rotary flash evaporator. The residue was taken up in ether and filtered through a 2×6 cm column of Celite. The yellow eluants were collected in a flask fitted with an N_2 inlet. The solvent was removed on a rotary flash evaporator to yield the product, $CpMo(CO)_2(\eta^3$-1,3-dimethylallyl$)$, as yellow crystals.

This product should be pure enough for subsequent reactions if it is yellow. It could be purified further by chromatography on a 2.5×12 cm column of deactivated alumina with 1:1 petroleum ether/CH_2Cl_2. Elution of a yellow band, solvent removal and recrystallization from pentane yields the pure complex (2.1 g, 72%), which shows identical physical properties to those previously reported.[14,28] A convenient identifying property is the presence of carbonyl bands for the complex at 1947, 1874 (*exo*); 1886 (*endo*) cm^{-1} in cyclohexane.

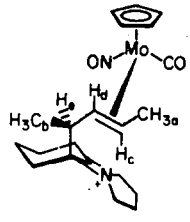
If the allyl acetate has not reacted completely before the addition of LiCp, the $CpMo(CO)_3^-$ ion will be produced, which eventually decomposes by oxidation of itself or its hydride into the red dimer $[CpMo(CO)_3]_2$. This material is easily identified as a slow moving red band in chromatography with petroleum ether–methylene chloride mixtures.

One should note that the $CpMo(CO)_2$(allyl) complexes are a rapidly equilibrating mixture of *endo* and *exo* conformers[28] and that the room temp NMR spectra will be broad. As solids they are relatively air stable and may be weighed and manipulated in air for brief periods. The allyl, crotyl, cyclohexenyl, cycloheptenyl, and cyclooctenyl complexes are particularly robust; whereas, the 1,3-dimethylallyl is relatively sensitive. The complexes are stable at 0° in the dark for years. Slight decomposition from exposure to air leads to dark blue decomposition products. Fortunately, chromatography will often yield over 90% pure material from an apparently hopelessly decomposed sample.

The preparation of $[CpMo(NO)(CO)(\eta^3$-1,3-*dimethylallyl*$)]BF_4$. A 100 ml, 3-neck flask equipped with a magnetic stirrer and N_2 inlet was charged with 1.00 g (0.33 mmol) of $CpMo(CO)_2(\eta^3$-1,3-dimethylallyl) in 10 ml of acetonitrile and to this soln at 0° was added 0.38 g (0.32 mmol) $NOBF_4$. The resulting yellow–orange soln was stirred for 5 min and quickly added to 100 ml of ether at 0°, which gave an immediate pale yellow ppt of the cation in quantitative yield upon decantation of the solvent.

These nitrosyl molybdenum salts can generally be recrystallized from acetone–ether or acetonitrile–ether to yield larger yellow crystals, but recrystallization must be performed quickly to prevent isomerization. The kinetic product obtained in the initial precipitation of the η^3-1,3-dimethylallyl complex was identical to that previously described and identified as the *endo*-isomer.[14] Under subsequent reaction conditions or upon standing in soln for several hr it converts to the *exo*-isomer. Since the interconversion rates of these isomers are slow, they can readily be monitored by NMR.

The reaction of $[CpMo(NO)(CO)(\eta^3$-1,3-*dimethylallyl*$)]BF_4$ *with* 1-*pyrrolidino*-1-*cyclohexene*. The nitrosyl cation (1.125 g, 3 mmol) was partially dissolved in 50 ml of 1:2 MeCN/THF. The suspension was cooled to 0° and 0.48 ml (3.0 mmol) of 1-pyrrolidino-cyclohexene was added. The remaining solid quickly dissolved and the resulting gold soln was stirred for 0.5 hr at 0°. Solvent was removed and the crude product was redissolved in CH_2Cl_2 and loaded onto a 25×1 cm silica gel column (Mallinckrodt 200–425 mesh, Type 60 Å Special) prepared with the same solvent. Elution with CH_2Cl_2 removed a small amount of hydrolyzed material. Subsequent elution with a 1:1 mixture of $MeCN/CH_2Cl_2$ carried the desired iminium salt through the column. Solvent was removed under reduced pressure and the deep gold solid which remained was redissolved in a minimum amount of MeCN. This solution was added to a large volume of ether (~100 ml) which led to immediate formation of fine lemon yellow crystals. These were filtered in a Schlenk apparatus and vacuum dried to give 0.775 g (1.47 mmol, 49%) of the product as a mixture (~5:1) of isomers [IR, CH_2Cl_2, 1981 (CO); 1631 (NO) cm^{-1}]. Slow crystallization from acetonitrile/ether at 0° allowed the separation of the pure major isomer. This isomer was identified by X-ray diffraction analysis and gave the same NMR spectrum as that identified in the mixture described below as the major isomer.



The NMR spectra of this complex, as well as many olefin complexes of this type can be confusing owing not only to the mixture of isomers, but also the presence of two rotamers of the olefin relative to the Mo—CO direction. The rate of rotation is sufficiently fast at room temp that *most* resonances are averaged; however, some are still broad and are not observed. Other resonances were also obscurred by overlap. Resonances are observed in the ^{1}H-NMR (CD_3CN, 25°, 500 MHz) at: (major) δ 3.21 (dd, H_e, 11.5, 10.5 Hz), 3.07 (H_c, dq, 11.5, 6.6 Hz), 1.36 (d, Me, 6.6 Hz), 1.23 (d, Me, 6.6 Hz); (minor) 1.48 (d, Me, 6.8 Hz), 1.11 (d, Me, 6.7 Hz). Neither vinyl proton was observed for the minor isomer; nor was H_e observed for either isomer. The resonances for some protons overlap: δ 5.67 (s, Cp); 4.16–3.96 (m, CH_2N); 2.27–2.05 (m, CH_2); 1.90–1.50 (m, CH_2).

Hydrolysis of the coordinated iminium salt. The mixture of isomers of the $[CpMo(CO)(NO)(C_5H_9C_6H_9{=}NC_4H_8)]BF_4$ (0.526 g, 1 mmol) salt was dissolved in a mixture of 15 ml of MeCN and 4 ml of distilled water. One ml of 0.1 M KOH was added to this gold soln and the resulting solution was stirred for 2 hr at room temp. There was no change in color during the

hydrolysis and at the end of the 2 hr period the apparent pH was 10. One ml of 0.1 M HCl was added to neutralize the mixture. The soln volume was reduced under vacuum and the resulting aqueous soln extracted with four 10 ml portions of CH_2Cl_2. The gold CH_2Cl_2 extracts were then extracted with three 10 ml portions of water and the organic layer dried over $MgSO_4$. The CH_2Cl_2 soln was decanted from the drying agent and filtered through Celite. The crude product was chromatographed on a 25 × 1 cm column of silica gel with CH_2Cl_2. Evaporation of the solvent from the gold band which was eluted from the column gave 0.349 g (0.91 mmol, 91%) of the coordinated 2-(1-methyl-2-butenyl)-cyclohexanone product as a mixture of isomers (~5:1): IR (C_6H_{12}) 1976, 1967 (CO); 1652, 1642 (NO); 1714 (C=O) cm^{-1}.

As observed with the iminium salt, olefin rotation prevents the observation of some resonances at room temp. Resonances which are observed in the ^{1}H-NMR ($CDCl_3$, 25°, 500 MHz) appear at: (major) δ 3.22 (dd, H_d, 12.2, 10.0 Hz), 3.04 (dq, H_c, 12.2, 6.3 Hz), 1.38 (d, Me_a, 6.3 Hz), 1.25 (d, Me_b, 7.0 Hz); (minor) δ 3.12 (dd, H_d, 11.8, 10.0 Hz), 1.43 (d, Me, 6.3 Hz), 1.20 (d, Me, 6.8 Hz). Neither H_a nor H_c is observed in the minor isomer and H_e is not observed in the major isomer. Resonances which overlap in both isomers appear at: δ 5.53 (s, Cp), 2.46–2.23 (m, $CHCOCH_2$), 2.06–1.56 (m, CH_2).

Decomplexation of 2-(1-*methylbut*-2-*enyl*)*cyclohexanone.* The olefin complex (200 mg, 0.54 mmol) and 1 g of NaOAc (hydrated) were dissolved in acetone and 100 mg portions of $(NH_4)_2Ce(NO_3)_6$ were added until CO evolution ceased. Addition of water, extraction with ether and separation on preparatory TLC (silica gel) plates gave a 43% yield of 2-(1-methylbut-2-enyl)cyclohexanone as a mixture of isomers: IR (CH_2Cl_2) 1706 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$, 23°, 200 MHz), most resonances of both isomers overlap, d 5.58–5.18 (m, H_c, H_d), 2.74–2.54, 2.46–2.18, 2.06–1.46 (m, methylenes); (major), δ 1.62 (m, Me_a, J_{ac} = 5.8 Hz), 0.97 (d, Me_b, 6.9 Hz); (minor), δ 0.95 (d, Me_b, 6.7 Hz), Me_a obscured.

Analogous reactions to yield 2-(2-*butenyl*)*cyclohexanone.* The reaction of $CpMo(CO)_2(\eta^3$-crotyl) with NO^+ selectively yields the *endo–cis* isomer of the $[CpMo(NO)(CO)(\eta^3$-crotyl)$]^+$ cation. This complex rearranges in the reaction and adds to the least substituted terminus in 100% regioselectivity. The coordinated 2-(2-butenyl)cyclohexanone shows complex NMR spectra as a result of olefin rotamers and the diastereomers produced from the chirality at the coordinated olefin: (^{1}H-NMR, $CDCl_3$, −35°, 250 MHz), δ 5.29, 5.28, 5.26, 5.24 (s, Cp); 3.30–3.16, 3.12–2.82 (m, vinyl); 2.54–1.05 (broad m, Me, CH_2); IR (C_6H_{12}) 1979, 1946 (CO); 1645 (NO); 1714 (C=O).

Decomplexation gave 2-(2-butenyl)cyclohexanone in approximately 50% yield: IR (C_6H_{12}) 1718 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 25°, 500 MHz): δ 5.54–5.35 (m, vinyl); 2.37–1.0 (m, methylenes); 1.47 (m, Me, 5.5 Hz).

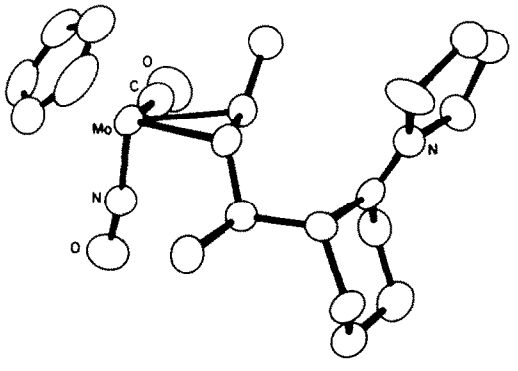


Fig. 1. An ORTEP diagram showing 50% probability ellipsoids of the major product of the reaction of $[CpMo(NO)(CO)(\eta^3$-1,3-dimethylallyl$]^+$ with $C_4H_8NC_6H_9$.

Crystallographic analysis. The salt, $Mo_1F_4O_2N_2C_{21}B_1H_{31}$, crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell of dimensions a = 9.807(3) Å, b = 10.837 Å, c = 11.717(4) Å, α = 97.56(2)°, β = 102.23(3)°, γ = 103.18°. For 2376 reflections and 280 parameters the structure refined to R_1 = 0.040 and R_2 = 0.041. The details of the structure will be published elsewhere.

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