flects both direct photodetachment into the continuum and indirect loss of an electron via the excited state, the agreement is excellent and suggests strongly that indeed $\pi \rightarrow \pi^*$ transitions cause the enhanced photodetachment probability in this region. The strong and the weak peaks are also in agreement with a PPP calculation[23] which predicts a degenerate intense $A_1'' \rightarrow E''$ transition well removed from the higher energy transitions and a forbidden $A_1'' \rightarrow A_2''$ transition about 100 nm to the red of the first one (D_{3h}).

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Stereospecificity in Reactions of Activated η^3-Allyl Complexes of Molybdenum

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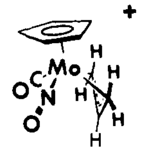
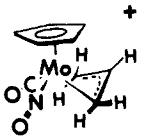
Abstract: Nucleophilic attacks on endo and exo η^3-allyl complexes, such as $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(1,3\text{-dimethylallyl})^+$ cation, are stereospecific. The structures of the olefinic derivatives formed by the addition of the nucleophile are consistent with nucleophilic attack trans to NO in the endo isomer and cis to NO in the exo isomer. The relative configuration of the newly formed chiral center implies that the attack occurs on the face of the allyl opposite to the metal and not directly at the metal center. The crystal structure determinations of two neutral olefin derivatives, $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_8H_{14}O)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_9H_{16}O)$, formed by addition of the enamine of isobutyraldehyde are reported. The olefinic bond tends to be aligned parallel to the molybdenum–carbonyl vector rather than parallel to the $\eta^5\text{-}C_5H_5$ plane. This orientational preference, which can readily be rationalized by back-bonding arguments, appears to have a profound effect on the selectivity of the reactions.

Introduction

Complexation of organic molecules to transition metal atoms leads to systematic variations in their reactivity and this forms the basis for an emerging branch of organic synthesis.[1] Nucleophilic addition to unsaturated ligands is of intense interest.[2] Recently we reported the preparation and rearrangement pathway of cationic $\eta^5\text{-}C_5H_5Mo(CO)(NO)$ (**1**).[3] These

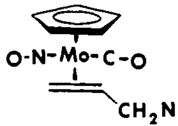


1n
ENDO

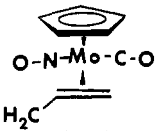


1x
EXO

allyl and homologated cations function as efficient electrophiles in addition sequences which may be used to synthetic advantage. For example, a wide range of inorganic and organic nucleophiles reacts cleanly with the conformational isomers **1n** and **1x** to provide stable η^2 olefin complexes of type **2** (eq 1). Olefin complexes of this type possess two chiral centers—one at the molybdenum atom and the other at the substituted olefin carbon atom, C(2). Thus, two diastereomeric complexes result in which the absolute configuration can be designated as shown for **2a** and **2b.**[4]



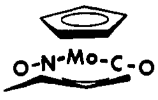
(R,R)
2a



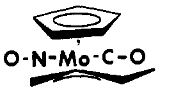
(R,S)
2b

$$\mathbf{1n}, \mathbf{1x} \rightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(CH_2{=}CHCH_2Nu)} \qquad (1)$$

We have now elucidated the stereochemistry of these nucleophilic addition reactions. Herein, we report the results of our studies of these additions to cationic methyl-substituted analogues of **1**, i.e., **3–5.** In each case we have observed addition to the allyl group with no competitive addition to cyclopentadienyl or carbonyl ligands.



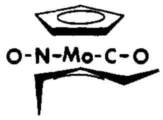
3a



3b

4a

4b



5

Experimental Section

Structural Analysis of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_8H_{14}O)$ (6a) and $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_9H_{16}O)$ (7). Collection and Reduction of Data. Crystals of **6a** were obtained by cooling hexane solutions to −20 °C overnight. A crystal of approximate dimensions 0.06 × 0.14 × 0.20 mm was sealed in a thin-walled glass capillary. After the crystal was mounted in a random orientation, 25 strong reflections were located and automatically centered on an Enraf-Nanius CAD-4 UK automatic diffractometer using the CAD-4 automatic search and center routines. Processing of this data led to the selection of a monoclinic unit cell. An examination of key reflections revealed the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, and thus identified the unique space group, $P2_1/c$. On this basis the crystal faces were identified as $\{001\}$, $\{011\}$, $\{01\bar{1}\}$, and $\{21\bar{1}\}$. Accurate cell parameters were subsequently obtained by the centering and least-squares refinement of 25 high angle ($2\theta > 40°$) reflections. Crystal data and data collection parameters are listed in Table I. Four standard reflections monitored approximately every 100 reflections showed only random ±3% fluctuations during the course of data collection. A total of 7191 reflections yielded 2279 conforming to the relation $F_o^2 > 2.0\sigma(F_o^2)$ after correction for Lorentz and polarization effects. The value of the p factor used in the determination of $\sigma(F_o^2)$ was 0.03. The linear absorption coefficient (Mo Kα) for **6a** is 8.331 cm^{-1}. No absorption correction was made.

Crystals of **7** were grown from hexane solutions cooled to −20 °C. A crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm was sealed in a thin-walled glass capillary and mounted in a random orientation on a CAD-4 diffractometer. Crystal analysis was performed as described above, and a monoclinic unit cell was selected. Inspection of key reflections revealed the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, and identified the space group as $P2_1/n$. Crystal data and data collection parameters are listed in Table I. A total of 3206 reflections were collected which, after Lorentz and polarization corrections, yielded 1382 for which $F_o^2 > 3.0\sigma(F_o^2)$. The linear absorption coefficient for **7** is 7.999 cm^{-1}, and no absorption correction was applied.

Table I. Experimental X-ray Diffraction Data for $(C_8H_{14}O)(\eta^5\text{-}C_5H_5)Mo(CO)(NO)$ and $(C_9H_{16}O)(\eta^5\text{-}C_5H_5)Mo(CO)(NO)$

	A. Crystal Data	
space group	$P2_1/c,[C_{2h}^5]$(No. 14)	$P2_1/n,[C_{2h}^5]$
temp, °C	+22 ± 2	+22 ± 2
cell parameters	$a = 6.410$ (1), $b = 18.126$ (5) $c = 26.987$ (9) Å $\beta = 96.65$ (2)° $V = 3114.4$ Å^3	6.557 (2), 17.782 (9) 14.062 (7) Å 96.61 (3)° 1628.7 Å^3
Z	8	4
ρ_{calcd}	1.47 g cm^{-3}	1.465 g cm^{-3}
μ	8.331 cm^{-1}	7.999
	B. Intensity Measurement Data	
radiation	Mo Kα	Mo Kα
monochromator	graphite	graphite
detector aperture	4 (vertical) × 2.5 mm (horizontal-increasing with 2θ angle)	
reflections measd	$+h, +k, \pm l$	$+h, +k, \pm l$
maximum 2θ, deg	53	50
scan type	coupled θ (crystal)-2θ (counter)	
θ scan speed (variable)	1.2°/min (minimum)	1.2°/min (minimum)
θ scan width	$A + B \tan\theta$ $A = 0.65$ $B = 0.35$	$A + B \tan\theta$ $A = 0.75$ $B = 0.35$
no. of data	7191	3206
no. of obsd data		
$F^2 > 3\sigma(F^2)$		1383
$F^2 > 2\sigma(F^2)$	2279	
p factor	0.03	0.02

Solution and Refinement of the Structure of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_8H_{14}O)$ (6a). The structure of **6a** was solved by the heavy-atom method. Assuming a reasonable density for **6a**, $\rho_{\text{calcd}} = 1.47$ g cm^{-3}, two independent molecules are required in the crystallographic asymmetric unit. A three-dimensional Patterson synthesis revealed the locations of the two molybdenum atoms. Full-matrix least-squares refinement using isotropic temperature factors produced the values of the residuals, $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = (\sum w_i(|F_o| - |F_c|)^2/\sum w_i F_o^2)^{1/2}$, of 0.254 and 0.355, respectively. The weights, w_i, were taken as $1/\sigma(F_o)^2$, and the function minimized in the refinement was $\sum w_i(|F_o| - |F_c|)^2$. Neutral atom scattering factors were calculated by the method of Cromer and Waber.[3] Anomalous dispersion effects were included for all nonhydrogen atoms.[4] A difference Fourier synthesis at this time revealed the positions of a cyclopentadienyl ring on Mo(1) and the carbonyl, nitrosyl groups and the olefinic carbons on each molybdenum atom. No attempt was made to distinguish the carbonyl carbons from the nitrosyl nitrogens at this stage. These atoms were refined as carbons. Refinement with isotropic temperature factors produced the residuals $R = 0.196$ and $R_w = 0.213$. Another difference Fourier revealed the remaining nonhydrogen atoms. At this time, the nitrogen atoms of the nitrosyl groups were identified owing to their shorter bond distances to the metal atom and small temperature factors. Subsequent refinement with anisotropic temperature factors for the metal atoms and isotropic factors for the remaining atoms produced the residuals $R = 0.066$ and $R_w = 0.082$. Refinement with anisotropic temperature factors for all atoms reduced the residuals to $R = 0.048$ and $R_w = 0.059$. A difference Fourier synthesis next revealed most of the hydrogen atoms in credible positions. However, idealized positions were calculated assuming fivefold symmetry for the cyclopentadienyl rings, tetrahedral symmetry for the alkyl substituents employing some located positions for the latter calculations, and bond distances of 0.95 Å.[5] In the final cycles contributions from the hydrogen atoms were added to the calculations,

Table II. Atomic Coordinates

atom	*x/a*	*y/b*	*z/c*
A. Crystalline (η^5-C_5H_5)Mo(CO)(NO)($C_8H_{14}O$)			
Mo(1)	0.16707 (11)	0.05373 (4)	0.14229 (3)
O(1)	0.5102 (10)	0.1672 (4)	0.1845 (3)
O(3)	0.4768 (9)	−0.0698 (3)	0.1460 (2)
O(5)	−0.3946 (11)	−0.0407 (5)	0.2816 (3)
N(1)	0.3535 (10)	−0.0198 (4)	0.1478 (2)
CP(11)	−0.0380 (18)	0.0159 (5)	0.0696 (4)
CP(12)	0.1041 (15)	0.0648 (7)	0.0565 (3)
CP(13)	0.0627 (18)	0.1307 (5)	0.0740 (4)
CP(14)	−0.1064 (16)	0.1228 (6)	0.0987 (4)
CP(15)	−0.1683 (12)	0.0525 (6)	0.0970 (3)
C(11)	0.0628 (16)	0.1446 (6)	0.2396 (4)
C(12)	0.1367 (13)	0.0721 (4)	0.2259 (3)
C(13)	−0.0017 (12)	0.0156 (4)	0.2074 (3)
C(14)	0.0352 (12)	−0.0630 (4)	0.2230 (3)
C(15)	−0.0512 (13)	−0.0818 (5)	0.2726 (3)
C(16)	−0.2854 (15)	−0.0819 (6)	0.2613 (4)
C(17)	0.0022 (20)	−0.1610 (6)	0.2861 (4)
C(18)	0.0278 (14)	−0.0334 (6)	0.3163 (3)
C(1)	0.3869 (14)	0.1257 (5)	0.1684 (3)
Mo(2)	0.66012 (11)	0.19971 (4)	0.40702 (3)
O(2)	0.9962 (9)	0.3245 (3)	0.4216 (3)
O(4)	0.9754 (9)	0.0810 (3)	0.4375 (2)
O(6)	0.072 (12)	0.1833 (4)	0.5634 (3)
N(2)	0.8500 (9)	0.1303 (4)	0.4282 (2)
CP(21)	0.3777 (15)	0.2440 (5)	0.3519 (4)
CP(22)	0.5431 (16)	0.2413 (6)	0.3271 (4)
CP(23)	0.5974 (15)	0.1724 (6)	0.3238 (3)
CP(24)	0.4612 (21)	0.1281 (5)	0.3462 (4)
CP(25)	0.3285 (14)	0.1758 (6)	0.3649 (3)
C(21)	0.5585 (14)	0.3372 (5)	0.4805 (3)
C(22)	0.6280 (13)	0.2578 (5)	0.4828 (3)
C(23)	0.4954 (11)	0.1976 (4)	0.4770 (3)
C(24)	0.5291 (12)	0.1274 (4)	0.5085 (3)
C(25)	0.4385 (12)	0.1291 (4)	0.5588 (3)
C(26)	0.2047 (14)	0.1345 (6)	0.5484 (3)
C(27)	0.4832 (15)	0.0543 (5)	0.5830 (3)
C(28)	0.5385 (14)	0.1920 (5)	0.5921 (3)
C(2)	0.8739 (13)	0.2783 (5)	0.4168 (3)
B. Crystalline (η^5-C_5H_5)Mo(CO)(NO)($C_9H_{16}O$)			
Mo	0.4150 (1)	0.17389 (4)	0.08645 (5)
O(1)	0.7274 (9)	0.0523 (3)	0.0920 (5)
O(2)	0.7431 (10)	0.2935 (4)	0.1650 (5)
O(3)	0.217 (2)	0.1166 (8)	0.4514 (9)
O(4)	0.196 (3)	−0.0739 (12)	0.4049 (14)
N	0.6037 (9)	0.1015 (4)	0.0959 (4)
CP(1)	0.087 (1)	0.1642 (6)	0.0003 (6)
CP(2)	0.130 (1)	0.2370 (6)	0.0087 (6)
CP(3)	0.286 (2)	0.2554 (5)	−0.0366 (7)
CP(4)	0.347 (1)	0.1921 (7)	−0.0764 (6)
CP(5)	0.222 (2)	0.1350 (5)	−0.0546 (7)
C(2)	0.621 (1)	0.2496 (5)	0.1364 (6)
C(11)	0.303 (1)	0.2665 (5)	0.2737 (6)
C(12)	0.388 (1)	0.1909 (4)	0.2482 (5)
C(13)	0.262 (1)	0.1311 (4)	0.3132 (5)
C(14)	0.304 (1)	0.0503 (4)	0.2458 (5)
C(15)	0.240 (1)	−0.0055 (5)	0.1664 (6)
C(16)	0.206 (1)	0.0337 (5)	0.3409 (6)
C(17)	0.312 (2)	0.0858 (6)	0.4167 (7)
C(18)	0.299 (2)	−0.0452 (6)	0.3774 (8)
C(19)	−0.030 (2)	0.0391 (6)	0.3291 (7)

but they were not refined. Refinement converged and yielded the final residuals $R = 0.041$ and $R_w = 0.041$. The largest value of the shift/error parameter on the final cycle was 0.35. The error in an observation of unit weight was 1.51. A final difference Fourier synthesis was featureless. The largest peaks were 0.34, 0.32, 0.31 e/Å,^{3} approximately the size of hydrogen atoms in the vicinity of the metal atoms. Lists of final fractional atomic coordinates and the thermal parameters are presented in Tables II and III. Bond distances and angles with errors derived from the inverse matrix of final cycle of refinement are listed in Tables IV and V. Least squares planes are listed in Table VI. Tables of observed and calculated structure factor amplitudes, intermolecular contacts, root-mean-square amplitudes of vibration, and a packing diagram are available (see paragraph at the end of the paper regarding microfilm material).

Solution and Refinement of the Structure of (η^5-C_5H_5)Mo(CO)-(NO)(η^2-$C_9H_{16}O$) (7). The structure of **7** was also solved by the heavy-atom method. Assuming a reasonable density for **7**, $\rho_{calcd} = 1.465$, $Z = 4$, one molecule is required in the crystallographic asymmetric unit. A three-dimensional Patterson function revealed the location of the molybdenum atom. Refinement with an isotropic temperature factor produced the residuals $R = 0.236$ and $R_w = 0.335$. The weighting scheme, function minimized, scattering factor values, and anomalous dispersion corrections were as described above. A difference Fourier synthesis next revealed the positions of all remaining nonhydrogen atoms except the aldehyde oxygen. Refinement with isotropic temperature factors reduced the residuals to $R = 0.083$ and $R_w = 0.099$. The subsequent difference Fourier synthesis revealed two moderately small peaks at the terminus of the long allyl chain. One peak was ~50% larger than the second. Each peak was ~1.0 Å from a carbon atom and suggested that the aldehyde function was disordered between two positions. The carbon atoms attached to these oxygens showed no signs of disorder. Refinement was continued using an anisotropic temperature factor for the molybdenum atom and isotropic factors for all remaining nonhydrogen atoms. The nitrosyl group was identified and a 50:50 disorder model for the aldehyde oxygens was included. The residuals were reduced to $R = 0.065$ and $R_w = 0.073$. One of the aldehyde oxygens displayed a large temperature factor (i.e., 11.5), and was subsequently reduced to a 0.4 occupancy while the other was increased to 0.6. A difference Fourier synthesis next revealed most of the hydrogen atoms. However, idealized positions were calculated (vide supra). For the final cycles all nonhydrogen atoms except the aldehyde oxygens were refined with anisotropic temperature factors. Hydrogen atoms were included in the calculations but were not refined. The final values of the residuals were $R = 0.043$ and $R_w = 0.041$. The largest value of the shift/error parameters in the final cycle was 0.03. The error in an observation of unit weight was 1.83. The largest peaks in a final difference Fourier synthesis were 0.57 and 0.50 e/Å^3, about the size of hydrogen atoms, and were in the vicinity of the disordered aldehyde group. No attempt was made to include the aldehyde hydrogen atoms in the structure factor calculation. Structural data are presented in Tables I–V.

Preparation and Characterization of Compounds. The cationic carbonyl nitrosyl complexes were prepared by addition of $NOPF_6$ to acetonitrile or acetone solutions of the appropriate (η^5-C_5H_5)-$Mo(CO)_2$(allyl).[3] This procedure yields the endo cation (**3a**) of the allyl and crotyl species, whereas it produces a mixture of endo and exo isomers of the *syn,syn*-dimethylallyl species (**4a** and **4b**). The exo cation of *syn,anti*-dimethylallyl is formed directly by this procedure and yields stereospecifically the configuration with the NO ligand cis to the anti methyl group.[6] The *exo*-crotyl cation with the NO ligand trans to the methyl (**3b**) can be prepared by addition of crotyl halide to (η^5-C_5H_5)$MO(CO)_2NO$ in the presence of $AgPF_6$;[9] however, we have found it more convenient to prepare this derivative via abstraction of a proton from the *endo*-crotyl compound to produce the η^2-butadiene derivative and reprotonation with HPF_6.[8]

Compound **6a** was prepared in 75% yield by addition of 1-pyrrolidino-2-methylpropene (0.15 mL, 1.0 mmol) to the *exo*-crotyl cation (**3b**) (0.30 g, 0.75 mmol) dissolved in acetonitrile (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. Hydrolysis with water and extraction with methylene chloride provided the crude aldehyde derivative. Chromatography on silica gel (25 g) and elution with methylene chloride provided the product which was crystallized from pentane at 0 °C and melted at 105 °C.

Compound **7** was obtained in 70% yield via an analogous procedure starting with a mixture of *endo*- and *exo*-dimethylallyl cations (**4a** and **4b**). The product was obtained as long yellow needles melting at 109–110 °C. Carbonyl bands were observed in cyclohexane solution

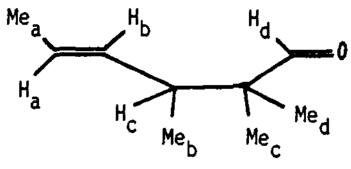


Table III. Thermal Parameters

atom	β(1,1)[b,c]	β(2,2)	β(3,3)	β(1,2)	β(1,3)	β(1,4) (β(2,3))
A. Crystalline (η^5-C_5H_5)Mo(CO)(NO)($C_8H_{14}O$)[a]						
Mo(1)	0.2673 (19)	0.0366 (3)	0.0151 (2)	−0.0034 (15)	0.0041 (8)	0.0079 (4)
Mo(2)	0.2295 (17)	0.0361 (3)	0.0146 (1)	0.0013 (15)	0.0134 (7)	−0.0014 (4)
O(1)	0.461 (22)	0.072 (3)	0.036 (2)	−0.185 (14)	−0.039 (10)	0.010 (4)
O(2)	0.324 (19)	0.054 (3)	0.053 (2)	−0.086 (13)	0.056 (10)	−0.004 (4)
O(3)	0.420 (20)	0.058 (3)	0.030 (1)	0.116 (13)	0.025 (9)	0.010 (2)
O(4)	0.360 (18)	0.054 (3)	0.028 (1)	0.086 (12)	0.009 (8)	0.003 (3)
O(5)	0.432 (25)	0.162 (6)	0.036 (2)	−0.036 (22)	−0.023 (11)	0.015 (6)
O(6)	0.529 (26)	0.098 (4)	0.048 (2)	0.120 (18)	0.059 (12)	0.000 (5)
N(1)	0.319 (21)	0.042 (3)	0.019 (1)	0.043 (14)	0.019 (9)	0.012 (3)
N(2)	0.257 (19)	0.049 (3)	0.015 (1)	0.008 (13)	0.000 (8)	−0.008 (3)
C(1)	0.385 (29)	0.049 (4)	0.023 (2)	−0.026 (2)	0.001 (12)	0.010 (5)
C(2)	0.275 (25)	0.045 (4)	0.027 (2)	0.029 (17)	0.030 (11)	−0.003 (4)
C(11)	0.513 (38)	0.058 (5)	0.031 (2)	0.040 (24)	0.023 (16)	−0.001 (6)
C(12)	0.410 (28)	0.031 (3)	0.017 (1)	−0.055 (16)	0.032 (11)	0.002 (4)
C(13)	0.302 (24)	0.028 (3)	0.014 (1)	−0.003 (15)	0.003 (10)	0.004 (3)
C(14)	0.276 (24)	0.039 (3)	0.019 (1)	0.036 (16)	0.029 (10)	0.021 (4)
C(15)	0.354 (29)	0.044 (4)	0.019 (2)	−0.041 (17)	0.010 (11)	0.019 (4)
C(16)	0.427 (33)	0.084 (6)	0.030 (2)	−0.009 (24)	0.084 (14)	0.017 (6)
C(17)	0.830 (50)	0.066 (5)	0.040 (3)	0.029 (29)	0.118 (19)	(0.044 (6))
C(18)	0.444 (31)	0.101 (6)	0.013 (1)	−0.207 (22)	−0.053 (11)	(0.018 (5))
C(21)	0.461 (32)	0.036 (3)	0.025 (2)	0.008 (19)	0.047 (13)	(−0.012 (5))
C(22)	0.381 (29)	0.043 (3)	0.015 (1)	−0.019 (18)	0.007 (11)	(−0.009 (4))
C(23)	0.275 (23)	0.038 (3)	0.015 (1)	−0.026 (16)	0.027 (9)	(−0.007 (4))
C(24)	0.279 (24)	0.033 (3)	0.015 (1)	0.013 (15)	0.012 (9)	(0.002 (4))
C(25)	0.289 (24)	0.035 (3)	0.014 (1)	0.003 (16)	0.022 (9)	(−0.003 (3))
C(26)	0.355 (29)	0.078 (5)	0.021 (2)	0.079 (22)	0.058 (12)	(−0.010 (5))
C(27)	0.548 (34)	0.051 (4)	0.017 (2)	0.064 (22)	0.048 (12)	(0.007 (5))
C(28)	0.417 (30)	0.064 (4)	0.020 (2)	−0.134 (20)	0.015 (12)	(−0.015 (5))
CP(11)	0.843 (47)	0.044 (4)	0.021 (2)	−0.079 (24)	−0.134 (15)	(0.003 (5))
CP(12)	0.405 (33)	0.112 (7)	0.017 (2)	0.020 (27)	−0.024 (12)	(0.014 (6))
CP(13)	0.877 (37)	0.064 (4)	0.030 (2)	−0.310 (22)	−0.131 (16)	(0.058 (5))
CP(14)	0.675 (42)	0.068 (5)	0.020 (2)	0.180 (23)	−0.060 (15)	(0.008 (5))
CP(15)	0.326 (27)	0.126 (6)	0.016 (2)	−0.169 (24)	−0.013 (11)	(0.046 (5))
CP(21)	0.483 (35)	0.054 (4)	0.029 (2)	0.156 (20)	−0.109 (14)	(−0.017 (5))
CP(22)	0.487 (36)	0.091 (5)	0.025 (2)	−0.164 (23)	−0.023 (14)	(0.046 (5))
CP(23)	0.0477 (3)	0.117 (6)	0.017 (2)	0.308 (2)	0.003 (12)	(−0.033 (5))
CP(24)	1.248 (59)	0.021 (3)	0.026 (2)	−0.112 (24)	−0.175 (18)	(−0.001 (4))
CP(25)	0.406 (29)	0.117 (6)	0.011 (1)	−0.246 (21)	−0.005 (11)	(−0.005 (5))
B. Crystalline (η^5-C_5H_5)Mo(CO)(NO)($C_9H_{16}O$)						
Mo	0.168 (1)	0.0282 (2)	0.0468 (3)	0.002 (2)	0.015 (1)	(−0.0004 (9))
O(1)	0.320 (20)	0.054 (3)	0.105 (5)	0.100 (10)	0.040 (20)	(−0.012 (6))
O(2)	0.360 (20)	0.074 (3)	0.122 (6)	−0.170 (10)	0.040 (20)	(−0.033 (7))
N	0.200 (20)	0.038 (3)	0.052 (4)	0.010 (10)	0.050 (10)	(−0.012 (6))
CP(1)	0.250 (20)	0.093 (5)	0.074 (6)	−0.160 (20)	−0.110 (20)	(0.103 (10))
CP(2)	0.400 (30)	0.077 (5)	0.060 (6)	0.190 (20)	−0.010 (20)	(0.001 (10))
CP(3)	0.720 (40)	0.041 (4)	0.090 (7)	−0.150 (20)	−0.210 (30)	(0.069 (9))
CP(4)	0.260 (30)	0.132 (8)	0.050 (5)	0.050 (30)	0.050 (20)	(−0.006 (12))
CP(5)	0.590 (40)	0.042 (4)	0.085 (7)	0.060 (20)	−0.220 (30)	(−0.038 (9))
C(2)	0.290 (30)	0.041 (4)	0.057 (5)	0.010 (20)	0.030 (20)	(0.010 (8))
C(11)	0.360 (30)	0.036 (3)	0.077 (6)	−0.000 (20)	0.060 (20)	(−0.025 (8))
C(12)	0.240 (20)	0.024 (3)	0.044 (4)	−0.000 (20)	0.060 (20)	(−0.003 (6))
C(13)	0.170 (20)	0.029 (3)	0.043 (5)	0.000 (10)	0.030 (20)	(0.010 (6))
C(14)	0.220 (20)	0.030 (30)	0.050 (5)	−0.030 (10)	−0.010 (20)	(0.007 (7))
C(15)	0.440 (30)	0.030 (3)	0.067 (6)	−0.020 (20)	−0.010 (20)	(0.010 (8))
C(16)	0.350 (30)	0.041 (3)	0.046 (5)	−0.080 (20)	0.000 (20)	(0.006 (8))
C(19)	0.480 (30)	0.094 (5)	0.062 (6)	−0.240 (20)	−0.030 (20)	(0.070 (9))
O(3)	10.6 (4)[d]					
O(4)	10.0 (5)[d]					
C(17)	8.8 (3)[d]					
C(18)	7.6 (3)[d]					

[a] All hydrogen atoms were assigned isotropic temperatures of 5.0. This value was not refined. [b] The form of the expression for the anisotropic temperature factors is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c] Anisotropic temperature factors multiplied by 10.0. [d] Isotropic temperature factors.

in the IR at 1973 and 1643 cm^{-1} and a very weak nitrosyl band appeared at 1725 cm^{-1}. The 270-MHz ^{1}H NMR spectrum of 7 at 20 °C in $CDCl_3$ exhibited resonances at (downfield from Me_4Si) 9.45 (s, H_d), 3.01 (dq, H_a), 2.93 (dd, H_b), 1.52 (dq, H_c), 1.36 (d, Me_2), 1.10, 1.05 (s, $Me_{c,d}$), and 5.51 ppm (s, Cp). Coupling constants clearly demonstrated the trans arrangement of the substituents: $J(H_a\text{-}H_b) = 11.7$, $J(H_b\text{-}H_c) = 9.2$, $J(H_a\text{-}Me_a) = 6.0$, $J(H_b\text{-}Me_a) = 0.1$, and $J(H_b\text{-}Me_b) = 0.1$ Hz. This averaged spectrum is sharp at room temperature but lowering the temperature to −70 °C produces broadening and eventual resolution into two complex overlapping

Table IV. Bonded Intramolecular Distances

atoms	distance, Å	atoms	distance, Å
A. $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$			
Mo(1)-N(1)	1.785 (7)	Mo(2)-N(2)	1.797 (8)
Mo(1)-C(1)	1.988 (10)	Mo(1)-C(2)	1.973 (9)
Mo(1)-C(12)	2.311 (7)	Mo(2-C(22)	2.330 (7)
Mo(1)-C(13)	2.275 (7)	Mo(2)-C(23)	2.269 (6)
Mo(1)-CP(11)	2.334 (9)	Mo(2)-CP(21)	2.347 (8)
Mo(1)-CP(12)	2.314 (10)	Mo(1)-CP(22)	2.325 (10)
Mo(1)-CP(13)	2.347 (10)	Mo(2)-CP(23)	2.290 (10)
Mo(1)-CP(14)	2.356 (9)	Mo(2)-CP(24)	2.351 (10)
Mo(1)-CP(15)	2.347 (9)	Mo(2)-CP(25)	2.332 (9)
N(1)-O(3)	1.206 (6)	N(2)-O(4)	1.208 (7)
C(1)-O(1)	1.139 (8)	C(1)-O(2)	1.144 (8)
CP(11)-CP(12)	1.335 (4)	CP(21)-CP(22)	1.320 (4)
CP(11)-CP(15)	1.347 (5)	CP(21)-CP(25)	1.332 (4)
CP(12)-CP(13)	1.320 (5)	CP(22)-CP(23)	1.303 (5)
CP(13)-CP(14)	1.345 (6)	CP(23)-CP(24)	1.376 (15)
CP(14)-CP(15)	1.340 (5)	CP(24)-CP(25)	1.352 (16)
C(11)-C(12)	1.460 (10)	C(21)-C(22)	1.506 (10)
C(12)-C(13)	1.407 (9)	C(22)-C(23)	1.381 (9)
C(13)-C(14)	1.497 (9)	C(23)-C(24)	1.532 (9)
C(14)-C(15)	1.546 (9)	C(24)-C(25)	1.536 (9)
C(15)-C(16)	1.497 (12)	C(25)-C(26)	1.496 (10)
C(15)-C(17)	1.505 (11)	C(25)-C(27)	1.518 (9)
C(15)-C(18)	1.508 (11)	C(25)-C(28)	1.544 (9)
C(16)-O(5)	1.199 (11)	C(26)-O(6)	1.182 (9)
B. $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_9H_{16}O)$			
Mo-N	1.780 (6)	CP(3)-CP(4)	1.338 (12)
Mo-C(2)	1.975 (8)	CP(4)-CP(5)	1.360 (12)
Mo-C(12)	2.314 (6)	CP(5)-CP(1)	1.343 (12)
Mo-C(13)	2.269 (6)	C(11)-C(12)	1.514 (8)
Mo-CP(1)	2.350 (7)	C(12)-C(13)	1.402 (7)
Mo-CP(2)	2.341 (8)	C(13)-C(14)	1.525 (8)
Mo-CP(3)	2.343 (8)	C(14)-C(15)	1.516 (8)
Mo-CP(4)	2.311 (8)	C(14)-C(16)	1.576 (9)
Mo-CP(5)	2.336 (8)	C(16)-C(17)	1.517 (10)
N-O(1)	1.199 (6)	C(16)-C(18)	1.591 (10)
C(2)-O(2)	1.157 (8)	C(16)-C(19)	1.541 (10)
CP(1)-CP(2)	1.326 (13)	C(17)-O(3)	0.996 (12)
CP(2)-CP(3)	1.306 (12)	C(18)-O(4)	0.964 (17)

patterns. The details of the olefin rotation processes which lead to averaging will be discussed elsewhere.

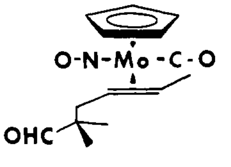
Compound **8** was obtained in a similar manner from **5.** The distinctive features were the appearance of doubling of the IR bands and the breadth of the NMR resonances at room temperature. The two rotational conformers give rise to separate bands in the IR producing bands at 1982, 1972, 1730, 1720, and 1644 cm^{-1}. The averaging of the resonances of the rotational conformers is incomplete at room temperature and leads to broad resonances (20 °C downfield from Me_4Si) at 9.99 (s, H_d), 3.13 (br d, H_2), 2.49 (br d, H_b), 1.69 (br d, H_c), 1.38 (br d, Me_a), 0.79 (br d, Me_b), 1.14, 1.04 (s, $Me_{c,d}$), and 5.49 (s, Cp). The breadth of the resonances arises from a slightly higher barrier to olefin rotation in **8** than in **7**, as well as a more nearly equal population ratio of conformers. These spectra will be discussed in detail elsewhere.

The propene complex **2b** (Nu = H) was prepared by dissolving 3.07 g of the allyl salt, $[\eta^5\text{-}C_5H_5Mo(CO)(NO)(allyl)]PF_6$ (*endo*-**1**) in 125 mL of freshly distilled THF chilled to −78 °C and addition of an equimolar amount of $NaBH_3CN$ (0.48 g). After warming to room temperature and stirring for 4 h, the solvent was removed under vacuum. Chromatography of the residue on alumina with hexane-methylene chloride mixtures gave a yellow band from which the solvent was evaporated by vacuum. The residue was crystallized from petroleum ether at −20 °C giving 1.45 g of yellow needles (73%).

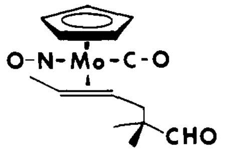
The olefins may be liberated from their complexes in nearly quantitative yield by heating the complex in chloroform above 60 °C for several hours. Both complexes **7** and **8** gave the identical olefin which was characterized by its NMR spectrum as the trans isomer. The 270-MHz ^1H NMR spectrum in $CDCl_3$ gave resonances at (downfield from Me_4Si) 9.39 (s, H_d), 5.47 (m, H_2), 5.31 (m, H_b), 2.32 (m, H_c), 1.65 (dd, Me_2), 0.93 (dd, Me_b), and 0.98 (s, $Me_{c,d}$). The following coupling constants were confirmed by double resonance studies: $J(H_a\text{-}H_b)$ = 13.7, $J(H_b\text{-}H_c)$ = 7.6, $J(H_a\text{-}Me_a)$ = 5.8, $J(H_b\text{-}Me_2)$ = 0.1, and $J(H_b\text{-}Me_b)$ = 1.4 Hz. The variations in coupling constants to the methyl groups compared with those in the complexed olefin presumably arise from variations in preferred conformations about the single bonds.

Results

Product Stereochemistry. The reactions of either cation **3a** or **3b** or mixtures of them with the enamine of isobutyraldehyde produced upon hydrolysis a single product which analyzed as $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$. The 270-MHz ^1H NMR spectrum at 50 °C showed a pattern[10] which indicated that attack had occurred on the unsubstituted end of the allyl group. The *gem*-dimethyl groups were nonequivalent as expected for diastereotopic groups. Lowering the temperature produced broadening and at −70 °C two superimposed $C_8H_{14}O$ were resolved. A process expected to give these dynamic NMR spectra is the interconversion of two conformations of the olefin by rotation about the metal-olefin bond. These data are consistent with the presence of either of the diastereomers **6a** or **6b**; however, an X-ray crystallographic analysis (see below) unequivocally established the correct configuration as **6a.** The dynamic NMR process would involve conversion of the conformer with the methyl group endo to the cyclopentadienyl ring to that with an *exo*-methyl group; however, this process would not allow interconversion of diastereomers **6a** and **6b.**



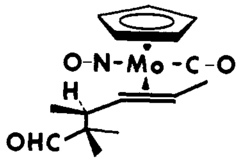
6a



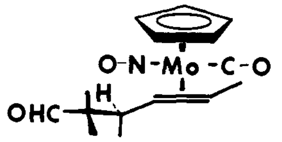
6b

A mixture of disubstituted cations, **4**, reacted with the enamine and gave upon hydrolysis a single stereomer $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_9H_{14}O)$ (**7**). The detailed molecular structure of **7** was also determined by X-ray crystallographic analysis and is described below.

The mechanistic importance of the chiralities of the asymmetric centers in **7** is substantiated by NMR evidence for the stereochemistry of the products of enamine reactions with the *syn-anti*-dimethyl complex, **5**. In this case a single diastereomeric olefin product, **8**, was formed. The NMR spectrum of the free olefin obtained by the thermal decomposition of **8** was found to be identical with the spectrum of the free olefin obtained by the thermal decomposition of **7**. However, when the olefin was complexed in **8**, it was bound in such a way as to be isomeric with **7**. Complexes **7** and **8** can be diastereomeric by virtue of an opposite configuration displayed at the allyl carbon which has undergone nucleophilic attack. This configuration was apparently determined by the direction of attack of the nucleophile. The attack must occur trans to the metal (as indicated by the relative configuration at C(14) in **7**, Figure 1). Thus the configuration at this carbon was determined by the configuration of the allyl substituent (syn or anti), and the free ligands produced upon dissociation of **7** and **8** are enantiomers. The diastereomers **7** and **8** are stable and we find no evidence of interconversion between them.



7



8

Table V. Pertinent Intramolecular Bond Angles

atoms	angle, deg	atoms	angle, deg
A. $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$			
N(1)-Mo(1)-C(1)	91.2 (3)	N(2)-Mo(2)-C(2)	91.6 (3)
N(1)-Mo(1)-C(12)	99.0 (3)	N(2)-Mo(2)-C(22)	99.4 (3)
N(1)-Mo(1)-C(13)	94.7 (3)	N(2)-Mo(2)-C(23)	95.0 (3)
C(1)-Mo(1)-C(12)	72.3 (3)	C(2)-Mo(1)-C(22)	71.8 (3)
C(1)-Mo(1)-C(13)	107.8 (3)	C(2)-Mo(1)-C(23)	106.5 (3)
C(12)-Mo(1)-C(13)	35.7 (2)	C(22)-Mo(1)-C(23)	34.9 (2)
Mo(1)-C(12)-C(11)	116.3 (6)	Mo(2)-C(22)-C(21)	116.9 (5)
Mo(1)-C(12)-C(13)	70.8 (4)	Mo(2)-C(22)-C(23)	70.0 (4)
Mo(1)-C(13)-C(12)	73.5 (4)	Mo(2)-C(23)-C(22)	74.9 (4)
Mo(1)-C(13)-C(14)	115.6 (5)	Mo(2)-C(23)-C(24)	115.3 (5)
C(11)-C(12)-C(13)	122.3 (7)	C(21)-C(22)-C(23)	125.1 (7)
C(12)-C(13)-C(14)	121.3 (6)	C(22)-C(23)-C(24)	123.3 (6)
C(13)-C(14)-C(15)	113.1 (6)	C(23)-C(24)-C(25)	115.4 (6)
C(14)-C(15)-C(16)	105.9 (7)	C(24)-C(25)-C(26)	108.1 (6)
C(15)-C(15)-C(17)	109.5 (8)	C(24)-C(25)-C(27)	106.9 (6)
C(14)-C(15)-C(18)	115.3 (7)	C(24)-C(25)-C(28)	110.8 (6)
C(16)-C(15)-C(17)	103.0 (8)	C(26)-C(25)-C(27)	105.8 (7)
C(16)-C(15)-C(18)	113.5 (8)	C(26)-C(25)-C(28)	113.6 (7)
C(17)-C(15)-C(18)	109.0 (8)	C(27)-C(25)-C(28)	111.3 (6)
C(15)-C(16)-O(5)	122.1 (12)	C(25)-C(26)-O(6)	122.9 (10)
CP(12)-CP(11)-CP(15)	107.4 (11)	CP(22)-CP(21)-CP(25)	109.1 (1.2)
CP(11)-CP(12)-CP(13)	110.3 (1.3)	CP(21)-CP(22)-CP(23)	107.9 (1.2)
CP(12)-CP(13)-CP(14)	106.0 (1.2)	CP(22)-CP(23)-CP(24)	110.0 (1.2)
CP(13)-CP(14)-CP(15)	109.7 (1.2)	CP(23)-CP(24)-CP(25)	104.4 (1.0)
CP(14)-CP(15)-CP(11)	106.5 (1.1)	CP(24)-CP(25)-CP(21)	108.4 (1.1)
Mo(1)-C(1)-O(1)	178.2 (8)	Mo(2)-C(2)-O(2)	178.7 (8)
Mo(1)-N(1)-O(3)	172.9 (6)	Mo(2)-N(2)-O(4)	173.3 (6)
B. $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_9H_{16}O)$			
N-Mo-C(2)	91.5 (3)	C(14)-C(16)-C(17)	106.6 (6)
N-Mo-C(12)	99.0 (2)	C(14)-C(16)-C(18)	105.1 (7)
N-Mo-C(13)	94.0 (2)	C(14)-C(16)-C(19)	113.5 (6)
C(2)-Mo-C(12)	72.1 (3)	C(16)-C(17)-O(3)	114.8 (12)
C(2)-Mo-C(13)	107.4 (3)	C(16)-C(18)-O(4)	109.7 (15)
C(12)-Mo-C(13)	35.6 (2)	C(17)-C(16)-C(18)	100.6 (6)
Mo-C(12)-C(11)	114.9 (4)	C(17)-C(16)-C(19)	114.3 (7)
Mo-C(12)-C(13)	70.4 (3)	C(18)-C(16)-C(19)	115.6 (7)
Mo-C(13)-C(12)	73.9 (4)	CP(1)-CP(2)-CP(3)	111.7 (9)
Mo-C(13)-C(14)	118.0 (4)	CP(2)-CP(3)-CP(4)	106.4 (9)
C(11)-C(12)-C(13)	122.4 (6)	CP(3)-CP(4)-CP(5)	108.4 (9)
C(12)-C(13)-C(14)	122.0 (5)	CP(4)-CP(5)-CP(1)	107.1 (9)
C(13)-C(14)-C(15)	111.7 (5)	CP(5)-CP(1)-CP(2)	106.4 (8)
C(13)-C(14)-C(16)	110.7 (5)	Mo-C(2)-O(2)	179.4 (7)
C(15)-C(14)-C(16)	113.5 (5)	Mo-N-O(1)	173.4 (5)

There are two pathways available for interconversion of diastereomers of structure **2**. These involve either CO-NO ligand interchange, which results in racemization at the metal center, or a dissociative process involving ligand loss and recombination on the enantiotopic face. Evidence relating to the configurational integrity of the molybdenum center in diastereomeric olefin complexes was obtained from the following observations. All complexes of type **2** examined to date exhibit irreversible decomposition upon heating in chloroform solution to liberate free olefin. In the instance of diastereomer formation as indicated in eq 4, we did not observe line broadening that would be indicative of exchange phenomena up to the decomposition temperature (~70 °C). Therefore, we do not believe that complexes such as **2** engage in facile racemization. Hence, resolved complexes should prove useful reagents in asymmetric syntheses.

Description of Structures. The molecular structures of **6a** and **7** are shown in Figure 1. Both compounds contain regular η^2-olefinic ligands. Compound **6a** contains two independent molecules in the asymmetric crystal unit. The molybdenum-olefinic carbon distances are quite normal being Mo(1)-C(12) = 2.311 (7), Mo(1)-C(13) = 2.275 (7), Mo(2)-C(22) = 2.330 (7), Mo(2)-C(23) = 2.269 (6) Å in **6a** and Mo-C(12) = 2.314 (6) and Mo-C (13) = 2.269 (6) Å in **7**.

In each case the bonding is slightly skewed such that the carbon atom bearing the methyl substituent is slightly further from the metal atom. The olefinic carbon-carbon bond distances for **6a** are C(12)-C(13) = 1.407 (9) and C(22)-C(23) = 1.381 (9) Å and for **7** C(12)-C(13) = 1.402 (7) Å. Increases in the carbon-carbon internuclear separations for coordinated olefins are well known and understood. The alkyl substituents are trans to one another and are folded away from the site of coordination. A measure of this fold can be obtained from a consideration of the dihedral angle between the atomic planes formed by the adjacent carbon of the alkyl substituent and the two olefinic carbons. These angles are 39.8 and 40.1° for **6a** and 41.0° for **7**.

The olefin is tilted with respect to the remainder of molecule such that the direction along the carbon-carbon bond is nearly colinear with the direction of the metal-carbon to carbonyl bond. The small angles between the planes defined by the metal atom and the olefinic carbons and the metal, one olefinic carbon, and the carbonyl atom tend to reveal this relationship (cf. Table VI). The alkyl chains showed no unusual distortions;

Table VI. Various Weighted Least-Squares Planes

A. (η^5-C_5H_5)Mo(CO)(NO)($C_8H_{14}O$)

a. Distances from Planes

plane no.	atoms	distance from plane, Å
1	Mo(1)	0.000
	C(12)	0.000
	C(1)	0.000
2	CP(11)	0.006 (10)
	CP(12)	−0.002 (9)
	CP(13)	−0.004 (10)
	CP(14)	0.007 (10)
	CP(15)	−0.007 (10)
	Mo(1)[a]	−2.044 (1)
3	Mo(1)	0.000
	C(12)	0.000
	C(13)	0.000
	C(11)[a]	1.163 (10)
	C(14)[a]	−1.199 (8)
4	C(11)	0.000
	C(12)	0.000
	C(13)	0.000
	C(14)	−0.820 (8)
5	C(12)	0.000
	C(13)	0.000
	C(14)	0.000
	C(11)[a]	−0.790 (10)
6	Mo(2)	0.000
	C(22)	0.000
	C(2)	0.000
7	CP(21)	0.008 (10)
	CP(22)	0.001 (10)
	CP(23)	−0.010 (9)
	CP(24)	0.018 (11)
	CP(25)	−0.014 (8)
	Mo(2)[a]	−2.031 (1)
8	Mo(2)	0.000
	C(22)	0.000
	C(23)	0.000
	C(21)[a]	1.161 (9)
	C(24)[a]	−1.198 (8)
9	C(21)	0.000
	C(22)	0.000
	C(23)	0.000
	C(24)[a]	−0.825 (7)
10	C(22)	0.000
	C(23)	0.000
	C(24)	0.000
	C(21)[a]	−0.794 (9)

b. Selected Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1-2	48.7	6-7	48.9
1-3	6.1	6-8	6.1
1-4	68.6	6-9	68.5
1-5	71.8	6-10	71.6
2-3	46.4	7-8	46.6
2-4	40.3	7-9	40.8
2-5	73.2	7-10	73.6
3-4	70.5	8-9	70.5
3-5	69.7	8-10	69.4
4-5	39.8	9-10	40.1

c. Equations of the Planes Are of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.6147	0.7524	−0.2366	−0.5545
2	−0.5108	0.1973	−0.8368	−1.2752
3	−0.6928	0.6794	−0.2417	−0.6939
4	0.1599	0.3225	−0.9330	−5.2009
5	0.6299	−0.1409	−0.7638	−4.7016
6	−0.5995	0.6496	−0.4676	−4.5240
7	−0.5103	−0.0756	−0.8567	−9.0988
8	−0.6788	0.5809	−0.4492	−4.8070
9	0.1687	0.0100	−0.9856	−12.2838
10	0.6315	−0.3871	−0.6718	−8.9142

B. (η^5-C_5H_5)Mo(CO)(NO)($C_9H_{16}O$)

a. Distances from Planes

plane no.	atoms	distance from plane, Å
1	CP(1)	−0.005 (8)
	CP(2)	0.003 (9)
	CP(3)	0.001 (10)
	CP(4)	−0.005 (9)
	CP(5)	0.006 (10)
	Mo[a]	−2.042 (1)
2	Mo	0.000
	C(12)	0.000
	C(2)	0.000
3	Mo	0.000
	C(12)	0.000
	C(13)	0.000
	C(11)[a]	1.218
	C(14)[a]	−1.187
4	C(11)	0.000
	C(12)	0.000
	C(13)	0.000
	C(14)[a]	−0.849 (8)
5	C(12)	0.000
	C(13)	0.000
	C(14)	0.000
	C(11)[a]	−0.839 (9)

b. Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1-2	47.9	2-4	70.1
1-3	45.3	2-5	69.2
1-4	41.6	3-4	72.4
1-5	76.3	3-5	66.6
2-3	7.1	4-5	41.0

c. Equations of the Planes Are of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.5343	0.1915	−0.8233	0.2550
2	−0.6486	0.7274	−0.2238	0.3038
3	−0.7348	0.6386	−0.2285	−0.1991
4	0.1547	0.3177	−0.9355	−1.8324
5	0.6551	−0.1338	−0.7436	−1.6278

[a] These atoms were not used in the calculation of the plane.

however, crystallographic disorder was observed in the location of the aldehyde group in **7**. The nature of this disorder is shown in Figure 1.

The molybdenum-carbon (cyclopentadienyl and carbonyl) distances are typical of the distances reported for a host of molybdenum complexes containing these ligands.[11-21] The molybdenum-nitrogen distances X, Mo(1)-N(1) = 1.785 (7) and Mo(2)-N(2) = 1.797 (7) Å, and Y, Mo-N = 1780 (6) Å, are very similar to the molybdenum-nitrogen distances 1.75-1.801 Å reported for other nitrosyl complexes. In each molecule of **6a** as well as that of **7**, the Mo-N distance is ~0.18 Å shorter than the Mo-C (carbonyl) distance. A similar observation was made for the complex (η^5-C_5H_5)Mo(NO)(CO)(η^2-$C_3H_5S_2CN(CH_3)_2$).[9]

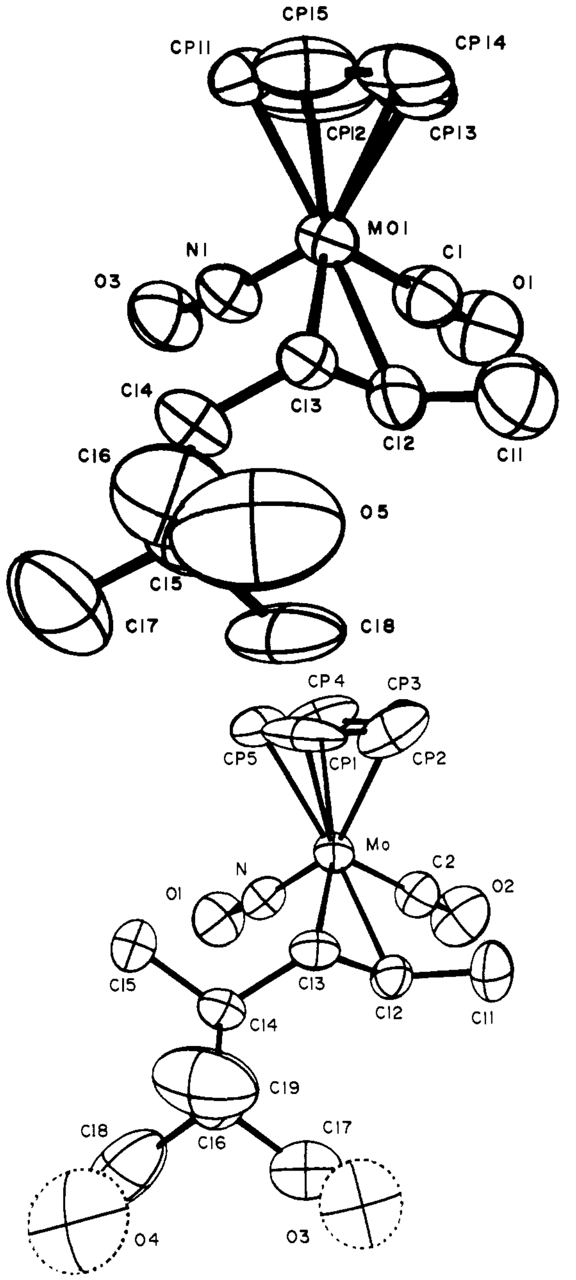
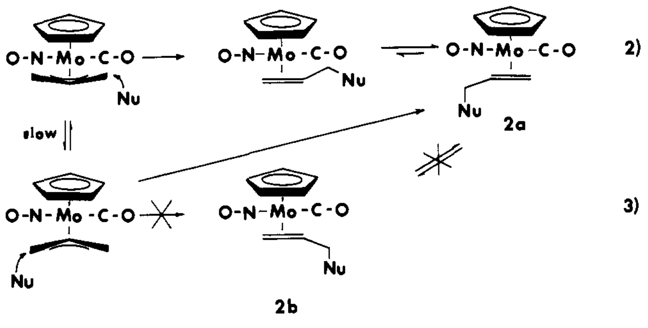


Figure 1. The structure found in crystals of **6a** (top) and **7** (bottom). The dotted lines for O(3) and O(4) in **7** indicate positions of a disordered carbonyl oxygen atom in the carboxaldehyde.

Discussion

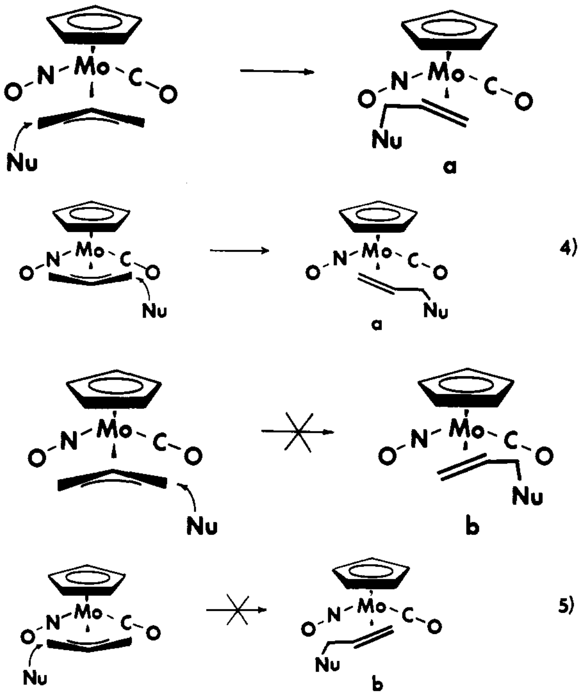
We have demonstrated that the reactions of either conformer **1a** or **1b** invariably produce a single diastereomer. This indicates a marked selectivity for one of the two nonequivalent ends of the allyl ligand. For example, for the situations of Nu: = $H^-(NaBH_3CN)$, S^tBu, and $C(CH_3)_2CHO$ (from pyrrolidine enamine of isobutyraldehyde) both conformers independently or admixed provide the same diastereomer, as indicated by IR and ^1H NMR (270 MHz) spectroscopy. These results may be attributed to the following selectivity in the reactions of the conformers.



The identity of the diastereomer as **2a** was established by an X-ray crystallographic analysis of the product, Nu = dithiocarbamate.[4] Unfortunately, from this preliminary report it was not possible to establish the allyl conformation of the starting material (**1a** or **1b**) and the potential regiospecificity and stereospecificity occurring in these reactions were not noted. However, the structural aspects of the complexes reported herein firmly establish these relationships.

The temperature-dependent NMR spectra of these olefin complexes indicate that there is a barrier to interconversion of the exo to endo conformers of ~15 kcal/mol (see Figure 2).[25] We will make the crude assumption that the maximum in the energy profile lies at 90° to the preferred orientation shown in the crystal. With this assumption we would expect that a transition state which involved formation of an incipient olefin aligned in the orientation found in the crystal (a) could be nearly 15 kcal/mol lower in energy than one perpendicular to it (b), eq 4-5. Thus, *attack cis to NO in the exo conformer and trans to NO in the endo conformer produces an olefin in the most stable orientation* (eq 4), whereas the reverse attacks produce an olefin in an unstable orientation (eq 5).

The reactivity of the *syn,syn*-1,3-dimethylallyl cation (**3**), which exists as a 2:1 kinetic mixture of exo and endo isomers, is very similar to that of **1**. This reaction produces a single isomer in good yield (73%). The conformation has been confirmed by the structural analysis of **7** which shows that the enamine has attacked the allyl group from the side opposite to the metal atom and only at the carbon atom cis to the nitrosyl ligand. This is again in accord with the expectations of reaction 4.



Addition reactions to unsymmetrically substituted substrates could occur with either regiochemistry as shown in eq 6 and 7. We find that this reaction also produces only a single yellow crystalline compound in good yield, which is now assigned **6a** on the basis of our crystallographic results. This is consistent with attack at site 1 which again produces olefin products in the most stable conformation. Thus the stereo-

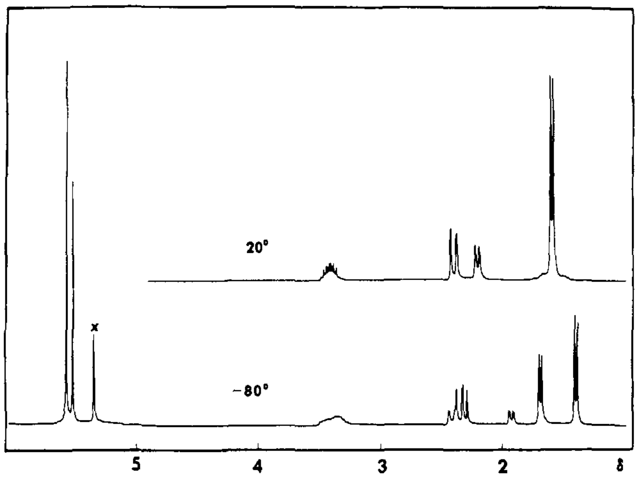
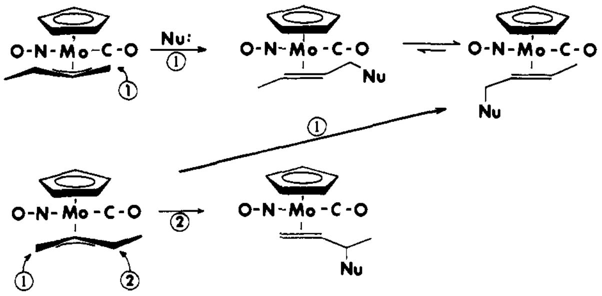


Figure 2. The 270-MHz ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(propene)PF_6$. The endo and exo olefin rotamers are observed in the low-temperature spectrum in a ratio of 1:1.7.



6)

7)

chemical consequences of eq 2 and 6 have all been confirmed by X-ray structural analyses.

Conclusions

The result of both structural characterizations confirms a stereospecific nucleophilic attack cis to the NO ligand in the exo conformers and trans to NO in the endo isomers.

Attack on the allyl ligand must occur trans to the metal atom. This is established by the configuration at C(14) in **7**, Figure 1. This point is important in terms of providing the ability to induce asymmetry at this center in an optically active molybdenum cation.

Finally, we believe that attack occurs at the coordinated η^3-allyl ligand at the point determined by the position of lowest electron density, as well as that producing the olefin in the most favorable orientation. This control of regiochemistry is exerted by an electronic effect arising from the different effective electronegativities of the CO and NO ligands. The CO and NO ligands tend to polarize the electronic distribution at the metal center and indirectly that in the coordinated allyl, and the coordinated olefin product.[22] Presumably, the allyl is distorted with one C-C bond becoming more single bond in character and the other more double bond in character, thus enhancing the probability of attack at a particular terminus. Furthermore, the differing demands of CO and NO in π-back-bonding control the orientation of the olefin in the products, which in turn determines transition-state stabilities. Thus, stereoselective reactions are to be expected and now the directions can be readily rationalized and predicted.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Tables 7A and 7B), hydrogen atom coordinates for $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_9H_{16}O)$ (Table 8), root-mean-square amplitudes of thermal vibration (Tables 9A and 9B), and intermolecular distances (Tables 10A and 10B), and stereoscopic views of unit cells (Figures 4 and 5) of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_9H_{16}O)$ and an ORTEP diagram of molecule 2 in the asymmetric unit of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(C_8H_{14}O)$ (Figure 3) (36 pages). Ordering information is given on any current masthead page.

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