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CHIRALITY CHANGES IN REACTIONS OF ASYMMETRIC MOLYBDENUM COMPLEXES

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Summary

Optical rotatory dispersion and circular dichroism studies have allowed the determination of the changes in configuration at the molybdenum center upon displacement of carbonyl and iodide in neomenthylcyclopentadienyl—Mo(allyl)(NO)X systems Displacement of carbonyl by iodide occurs with retention of configuration Replacement of iodide with benzenesulfonate followed by replacement of the sulfonate with iodide occurs stereospecifically with net retention of configuration. In the case of cyclopentadienylMo(cyclooctenyl)(NO)I, the enantiomers were separated via a spontaneous resolution through crystallization of the complex in the space group $P2_12_12_1$ These studies have allowed the correlation not only of the absolute configuration at the metal center with CD studies, but also have established that a long wavelength optically active transition at approximately 400 nm can be correlated with *endo-exo* isomerism. Comparison of the rates of interconversion suggest that *endo* to *exo* isomerization occurs via a clockwise rotation of the allyl in the (*R*)-isomer. Crystallographic details· (—)-(*S*)-(NMCp)Mo(allyl)(NO)I crystallizes in the space group $P2_12_12_1$ with *a* 7 221(1), *b* 12.686(7), *c* 21.603(7) Å, $Z = 4$, $V = 1979(2)$ Å^3; $R_1 = 0.039$, $R_2 = 0.046$, (—)-(*S*)-(Cp)Mo(cyclooctenyl)(NO)I crystallizes in the space group $P2_12_12_1$ with *a* 8.466(1), *b* 10.449(2), *c* 16.372(2) Å, $Z = 4$, $V = 1448$ 3(6), $R_1 = 0$ 038. and $R_2 = 0$ 046

We have established that iodide displacement of carbonyl in [(η^5-neomenthylcyclopentadienyl)Mo(η^3-allyl)(NO)(CO)] cation occurs with retention of configuration at the metal center [1] (Fig 1). Within the currently accepted nomenclature rules [2] this conversion of (+)$_D$-[(NMCp)Mo(allyl)(NO)(CO)] ***

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** On sabbatical leave from Tel-Aviv University
*** NMCp = Neomenthylcyclopentadienyl

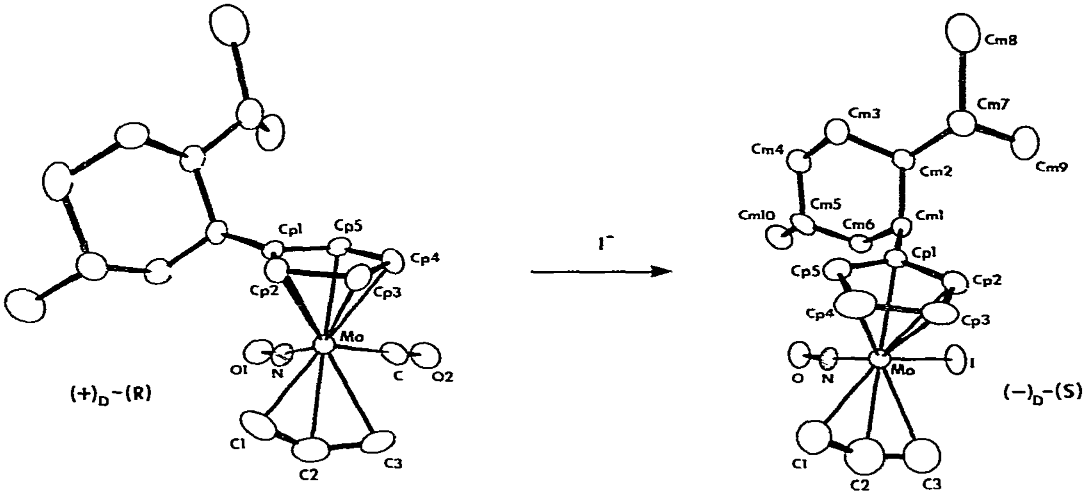
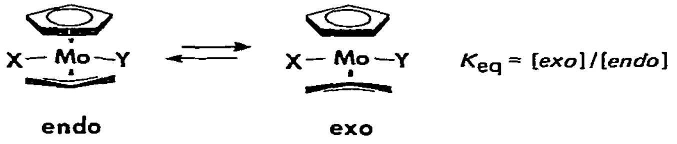


Fig. 1 Absolute configurations of $(+)_D$-*endo* [(NMCp)Mo(allyl)(NO)(CO)] and $(-)_D$-*endo*-[(NMCp)Mo(allyl)(NO)(I)]

ion to $(-)_D$-[(NMCp)Mo(allyl)(NO)(I)] occurs with conversion of the (R) isomer to the (S) isomer *, as well as rotational sign reversal. Nevertheless, the sense of the chirality ** at CpMo(allyl)(NO)X moiety is retained.

The chiroptical properties (see Figs. 2—7) of these complexes are complicated owing to conformational equilibria. Examination of the optical rotatory dispersion (ORD) spectrum of the (+)-cation shows a positive rotation throughout the visible spectrum and up to 300 nm in the UV (Fig. 2). This is partially the result of several overlapping, strongly optically active transitions having positive Cotton effects in the UV (290 and 320 nm). The (—)-iodide shows a negative rotation throughout most of the visible and near UV (Fig. 6) The iodide rapidly equilibrates ($t_{1/2}$ ~10 s) to a mixture of *endo* and *exo* isomers: whereas, the cation only equilibrates slowly ($t_{1/2}$ = 0.5 h). In the preparation of the cation,



K_{eq} = [*exo*]/[*endo*]

one obtains a kinetically-controlled non-equilibrium mixture of *endo-exo* isomers which is effectively pure *endo* The resolution of enantiomers is accomplished rapidly enough to prevent isomerization Thus, when the ORD or circular dichroism (CD) spectra are obtained shortly after dissolving the crystalline cation, one observes changing values until equilibrium is established.

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* The chirality can be described adequately by assuming the Cp, NO, allyl, and X are tetrahedrally arranged about the molybdenum atom *Endo-exo* isomerism of the allyl is considered separately

** By "sense of chirality" we mean that Cp, NO, and allyl maintain the same position relative to Mo and to each other but X is either CO or I

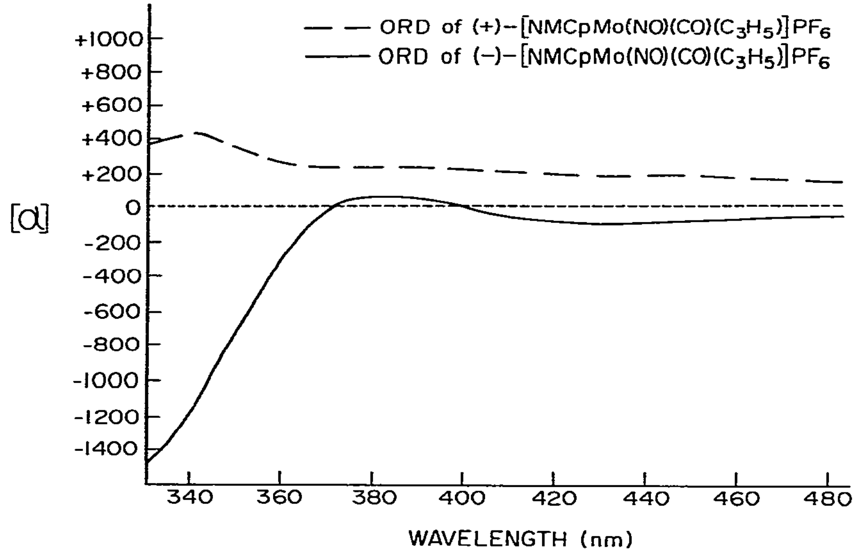

Fig 2 The ORD of (+)- and (—)-[(NMCp)Mo(allyl)(NO)(CO)]PF_6 (equilibrium mixture of conformers in acetone)

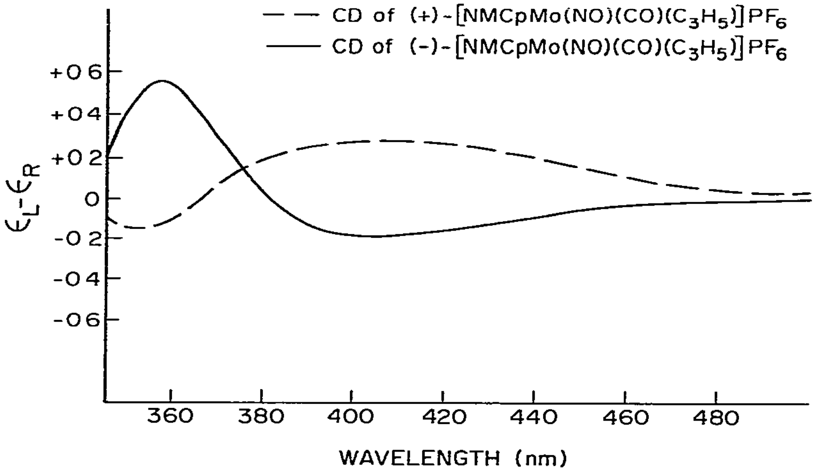

Fig 3 The CD of (+)- and (—)-[(NMCp)Mo(allyl)(NO)(CO)]PF_6 (equilibrium mixture of conformers in acetone)

The rapid equilibration of the iodide, however, allows an equilibrium ratio of *endo-exo* isomers to be established before the spectrum can be recorded Thus, one usually observes that the ORD and CD spectra of the cation initially vary with time, whereas, those of the iodide are constant *.

Examination of the CD spectrum of the allyl cation as a function of time clearly indicates that *endo-exo* isomerization reverses the sign of a band in the visible at ~410 nm (see Fig. 4). The sign of the rotation in the visible spectrum remains positive throughout the observed *endo-exo* interconversions. Hence,

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* The nature of the process responsible for the variations in ORD and CD spectra were not established unequivocally before this paper (see below).

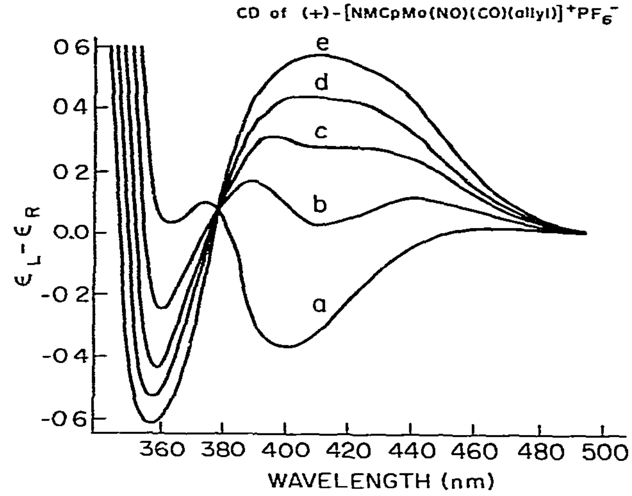

Fig 4 The CD of (+)$_D$-[(NMCp)Mo(allyl)(NO)(CO)]PF$_6$ as a function of time (min) after dissolving the *endo* isomer in acetone a 9, b 20 c 29 d 36 e 45 Ambient spectrometer temperature ~20°C

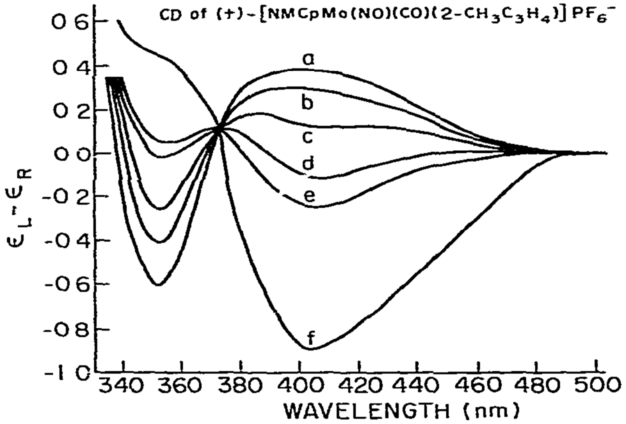

Fig 5. CD of (+)$_D$-[(NMCp)Mo(methallyl)(NO)(CO)]PF$_6$ as a function of time (min) after dissolving a mixture rich in the *exo* isomer (*exo/endo* ~2) in acetone a, 10 b, 20, c, 610, d, 1420; e, 1850; f ∞ Ambient spectrometer temperature 30°C

it is convenient to empirically characterize configurations at the metal by the sign of the rotation at the sodium D line. Nevertheless, one must recognize that significant changes in the rotational strength at ~400 nm may be masked be other features

As indicated by a crystal structure determination [1], the cation can be crystallized as the *endo* isomer. This complex slowly isomerizes to an equili-

TABLE 1

SOLVENT EFFECTS ON THE CD SPECTRUM OF (—)$_D$-NMCpMo(allyl)(NO)I

Solvent	K_{eq}	$\Delta\epsilon$ (420)	$\Delta\epsilon$ (λ_{max})
Chloroform	0.11	—0.682	—0.682 (420)
Cyclohexane	0.16	—0.537	—0.580 (430)

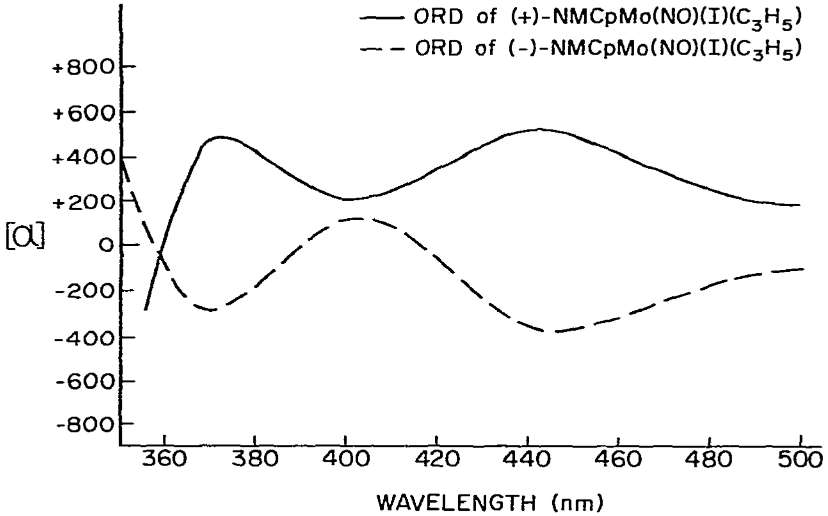

Fig 6 ORD of $(+)_D$- and $(—)_D$-[(NMCp)Mo(allyl)(NO)I] in chloroform *endo* predominates (90%)

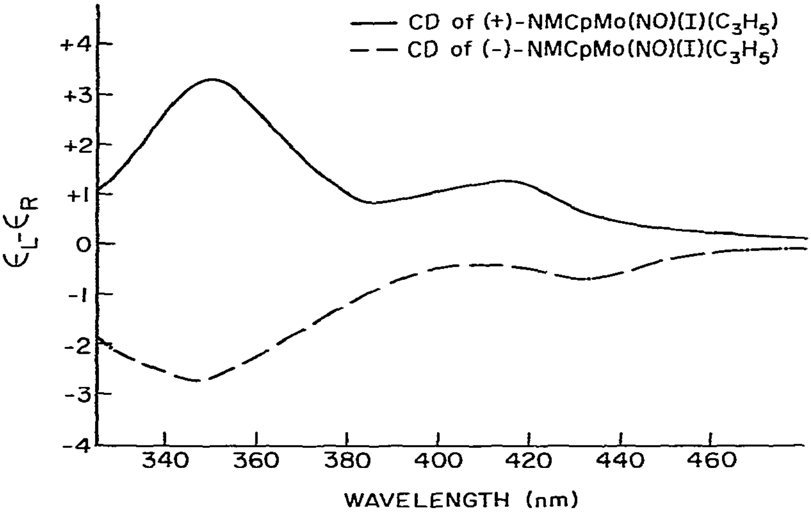

Fig 7 CD of $(+)_D$- and $(—)_D$-[(NMCp)Mo(allyl)(NO)I] in chloroform *endo* predominates (90%)

brium mixture which predominates in the *exo* isomer (K_{eq} = 3.8 in acetone by NMR). Furthermore, the NMR spectrum indicates that no racemization of either isomer occurs in this process *.

The (—)-iodide shows two negative CD bands (Fig 7) in the visible and near UV at 421 and 351 nm in chloroform for which the *endo* isomer predominates. (K_{eq} = 0 11 by NMR) Since the *endo-exo* equilibrium is readily perturbed by the polarity of the solvent, significant variations in the CD spectrum can be observed upon changes in solvent. (See Table 1) These changes are consistent with a similar reversal in sign in the long wavelength region.

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* It remains to be proven that this does not occur with inversion at the metal in the CpMo(allyl)(NO)(CO) center Studies reported later in this paper suggest that this interconversion occurs via rotation of allyl, hence, the configuration at molybdenum should be retained

The origin of the CD and ORD changes in the cations

X-ray structures [1] of the two key complexes, (+)$_D$-*endo*-[(NMCp)Mo(allyl)(NO)(CO)]PF_6 and (—)$_D$-*endo*-[(NMCp)Mo(allyl)(NO)I] provide the basis for establishing the relationship of the CD spectra to the absolute configuration at the metal center. The absolute configuration at the metal center was determined by reference to the chiral centers in the neomenthyl group, which are known with virtual certainty through chemical methods [3,4]. In order to demonstrate unequivocally the absolute configuration of the neomenthyl moiety, Friedl pairs were recollected for the iodide and the structure refined using both $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ The presence of both iodide and molybdenum produce large anomalous dispersion effects and both R-factor tests and comparisons of reflections with large anomalous dispersion effects confirmed the absolute configurations of the neomenthyl centers and the metal center [5,6,7]. This confirms the absolute configurations of the centers in the neomenthyl group, and thus secures the absolute configuration at the metal center in the (+)$_D$-*endo*-[(NMCp)Mo(allyl)(NO)(CO)] cation.

With the absolute configurations of the metal centers in hand, the correlations with CD spectra would be straightforward, if it were not for the facility of *endo-exo* isomerism. Thus, spectra are usually observed on equilibrium populations of *endo* and *exo* isomers, rather than the pure isomer found in the crystal. Although the configuration at the metal center might be expected to dominate the CD transitions, at least in the visible and near UV [8,9], the *endo-exo* conformational isomerism apparently gives rise to large effects.

In order to demonstrate that the changes in CD arising from variations in solvent in the iodide, or the changes occurring with time upon dissolving the cation, were associated with *endo-exo* isomerism, we investigated the effects of substituents on the allyl group. We had shown previously that the free energy associated with the *endo-exo* equilibrium can be varied as much as 5 kcal/mole by steric interaction of the central allyl substituent with the cyclopentadienyl ring in the CpMo(allyl)$(CO)_2$ analogs [10] [*]. Thus, substitution at the central position greatly enhances the stability of the *endo* isomer, whereas, *anti*-substitution favors the *exo* isomer.

In order to explore these variations we examined the effect of a 2-methyl substituent in the (+)$_D$-[(NMCp)Mo(methallyl)(NO)(CO)] cation. We have generally found that the kinetic cationic product has the opposite stability to the thermodynamically preferred product. Thus, the *endo*-CpMo(allyl)(NO)(CO) cation is isolated from the reaction mixture upon treatment of CpMo(allyl)$(CO)_2$ with $NOPF_6$, even though the *exo* isomer is more stable thermodynamically [12] In contrast, the *exo*-CpMo(methallyl)(NO)(CO) cation is isolated initially and converts to an isomeric mixture rich in the *endo* isomer Thus, we anticipated that the (+)$_D$-[(NMCp)Mo(methallyl)(NO)(CO)] cation would initially be isolated as the *exo* isomer and convert in solution to an isomeric mixture high in *endo* over a comparable time period to that found in the Cp analog.

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[*] The interaction of the ring with the central substituent in the *exo* isomer in the nitrosyl compounds is reduced owing to the tilting of the allyl induced by the electronic asymmetry of the system [11]

The CD spectra of $(+)_D$-*endo*-[(NMCp)Mo(allyl)(NO)(CO)] as a function of time after dissolution is shown in Fig. 4 Note how $\Delta\epsilon$ at 405 nm increases from −0 397 after 8 67 min to +0 560 after 45.33 min The methallyl cation $(+)_D$-[(NMCp)Mo(methallyl)(NO)(CO)]$^+$ shows a reversal of this behavior, initially having a $\Delta\epsilon$ at 403 nm of +0 382 at 20 min and −0 239 after 1850 min The slower interconversion for the methallyl process is consistent with the analogous behavior for *endo-exo* interconversion in the cyclopentadienyl complexes

In order to demonstrate the effect further, we attempted to prepare a complex with two *anti* substituents, i e., the (NMCp)Mo(η^3-cyclooctenyl)(NO)(CO)$^+$ cation. Crystals suitable for X-ray analysis of this complex have eluded us so far The model cyclopentadienyl compound, however, has shown the typical behavior of forming the unstable cation kinetically and conversion to the thermodynamically stable *exo*-[(NMCp)Mo(cyclooctenyl)(NO)(CO)] species on standing. Based on NMR evidence this species is nearly exclusively the *exo* isomer at equilibrium ($K_{eq} > 100$)

The similarity in rates of formation as determined by NMR (which are less accurate) to those observed in the changes of the ORD and CD provide very strong evidence that the changes observed in the spectra of the cations arise from *endo-exo* isomerism (see Table 2). The observation that the rate of *endo-exo* interconversion for the cyclooctenyl and the allyl derivative are nearly the same suggests that the mechanism for interconversion is the same, i.e., via rotation of the allyl (vida infra).

The solvent variations in $\Delta\epsilon$ found for the iodides are explicable in terms of solvent effects on the equilibrium constant between *endo* and *exo* isomers. As suggested by the cyclopentadienyl analogs (Table 2) the rates of interconversion are expected to be very rapid for the iodides; hence, equilibrium conditions are established immediately In an effort to determine the spectrum of an isomer with an essentially pure *exo* conformation, we examined the cyclooctenyl iodide. Since we were having difficulty isolating appropriate crystals of the

TABLE 2

HALF-LIVES OF *endo-exo* INTERCONVERSION

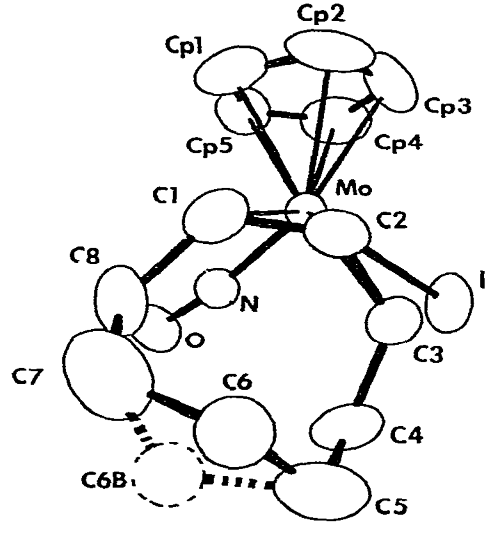
All cation interconversion rates were measured in acetone Faster rates (~ X 4) were observed for cations in acetonitrile Optical rotations were measured in a thermostated cell held at 25 0°C (and are significantly more accurate than those obtained by NMR)

Ligand	X	Allyl	$t_{1/2}$ (25°C)	K_{eq}	Method
NMCp	CO	allyl	28 min		[α]
NMCp	CO	allyl	26 min	3 8	NMR
Cp	CO	allyl	63 min	5 2	NMR
NMCp	CO	methallyl	5700 min	0 22	NMR
Cp	CO	methallyl	4900 min	0 21	NMR
Cp	CO	cyclooctenyl	35 min	100 [a]	NMR
Cp	I	allyl	11 sec [b]	0 29	NMR
Cp	I	methallyl	50 sec [b]	0 16	NMR
Cp	I	cyclooctenyl		100 [c]	NMR

[a] A value of 99 9% *exo* was obtained from extrapolation of rate data obtained over 2 h. [b] Rates at 25°C for the iodides were estimated from $\Delta G^{\star}$ obtained by line broadening rate determinations in toluene-d_8 at 80°C [c] No *endo* isomer could be observed by NMR.

NMCp derivative, we set about verifying the *exo* structure of the cyclooctenyl derivative of the Cp complex by X-ray crystallography *. Upon observing the unit cell size and the systematic absences, we tentatively surmised that the space group was $P2_12_12_1$. This was rather unusual since this non-centric space group would require only molecules of a single absolute configuration in a given crystal We tested this hypothesis of a spontaneous resolution by dissolving individual single crystals and observing the rotations in a polarimeter Positive and negative rotations were observed depending on the crystal Completion of the structure and comparison of Friedl pair intensities, indicated that the absolute configuration of the particular enantiomorphic crystal which was chosen had the (*S*) absolute configuration at the metal (See Fig 8). After completion of X-ray data collection and measurement of the crystal dimensions for the absorption correction, the crystal was removed from the capillary, dissolved in chloroform, and its rotation measured. The rotation for the solution (121 μg in 6 ml) was —0.002° at 589 nm and +0 023° at 436 nm

Hand-separation of a set of crystals showing left and right rotations respectively were combined to provide samples for good signal to noise in CD and ORD experiments. These spectra are shown in Fig. 9 and 10. Correlation of the observed rotation with the ORD indicates that the X-ray structure determination was performed on the $(-)_D$-*exo*-[(Cp)Mo(cyclooctenyl)(NO)I]. Certain features in the ORD and CD curves of this complex would be expected to coincide with those of (NMCp)Mo(allyl)(NO)I, Fig. 6 and 7. There appears to be some correlation between rotational signs of particular bands and absolute configuration in the series. They are tentative, but may prove to be useful.



(—)-(S)

Fig. 8. The structure of $(-)_D$-*exo*-[(Cp)Mo(cyclooctenyl)(NO)I]

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* No X-ray structures of an *exo*-allyl had yet been determined for a CpMo(allyl)(NO)X system

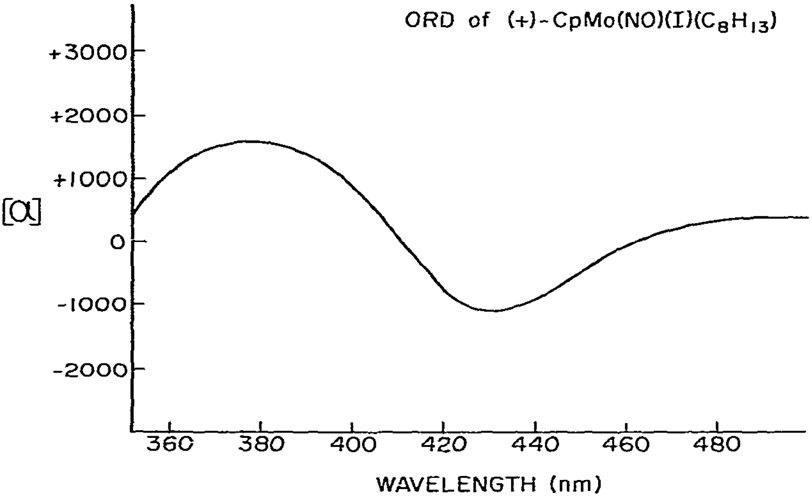

Fig 9 The ORD of $(+)_D$-*exo* [(Cp)Mo(cyclooctenyl)(NO)I] in chloroform

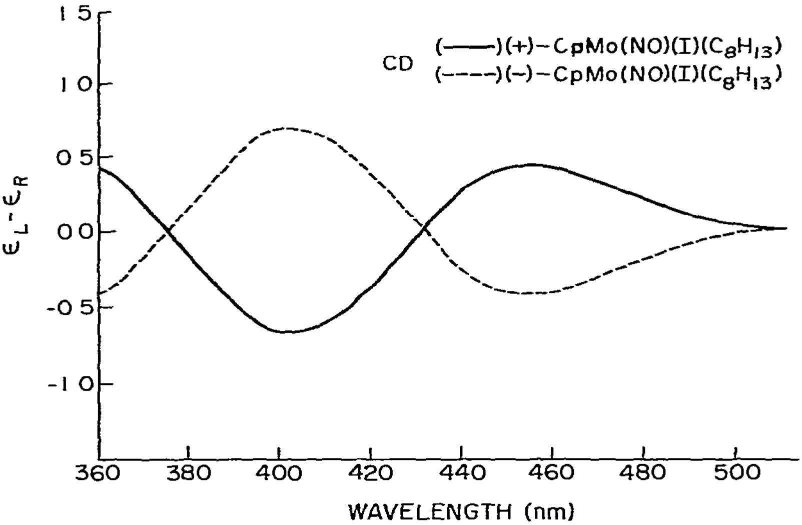

Fig 10 The CD of $(+)_D$- and $(-)_D$-*exo* [(Cp)Mo(cyclooctenyl)(NO)I] in chloroform

Correlations of configuration with CD spectra

The inversion of a long wavelength CD transition (~402 nm) from negative to positive in the allyl cation on standing (Fig. 4) occurs concomitantly with *endo* to *exo* interconversion. The inversion of this transition in $(+)_D$-[(NMCp)-Mo(methallyl)(NO)(CO)] occurs with a change from positive to negative (Fig. 5). This suggests that the sign of this transition is determined by both the absolute configuration at the metal center and the orientation of the allyl group, i.e., *endo* or *exo* *. Further, since the sign of rotation of the Na D line

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* The chirality at the metal is assumed to be retained during the rearrangement

is not reversed, it is dominated by the rotational strength of other transitions The shape of the long wavelength feature in the CD spectrum of the (+)$_D$-isomer suggests that there are at least two bands at wavelengths over 400 nm· one at ~400 nm which reverses sign from negative to positive on conversion from *endo* to *exo* and another at ~435 nm which remains positive Given these correlations, one might anticipate that similar ones might obtain in the iodides.

Since the *endo-exo* interconversions in the iodides are rapid, one can only observe the spectra of equilibrium mixtures of *endo* and *exo* Nevertheless, solvent effects can modify K_{eq} and the results in Table 1 support the generality of inversion of a long wavelength transition on conversion from *endo* to *exo*

Although similar electronic transitions in the visible and near UV might be anticipated for the cyclooctenyl and allyl iodides, one must consider the effect of opposite preferred conformations. The NMR of the cyclooctenyl complex indicates no presence of any *endo* (99% *exo*). Thus, the curves in Fig. 9 and 10 are essentially of the pure *exo* complex Since in chloroform the *endo* isomer predominates (90% endo) in (—)$_D$-[(NMCp)Mo(allyl)(NO)I], the spectra in Fig 6 and 7 are effectively those of the *endo* isomer. In (—)$_D$=[(NMCp)Mo(methallyl)-(NO)I] the CD curve (Fig. 11) implies the (*S*) configuration and represents nearly pure *endo* (>99%).

The (—)$_D$ isomers of the allyl and cyclooctenyl complexes have the same absolute configurations at the metal. If a correlation similar to that in the cation were to hold, the sign of $\Delta\epsilon$ at 402 nm would be reversed presumably owing to the conformational difference The CD spectra of the iodides appear to be dominated by three optically active transitions at ~360, ~400 nm, and another variable position band between 420 and 450 nm. Thus, whereas the signs of $\Delta\epsilon$ for all three of these bands are negative in (—)$_D$-*endo*-[(NMCp)Mo(allyl)-

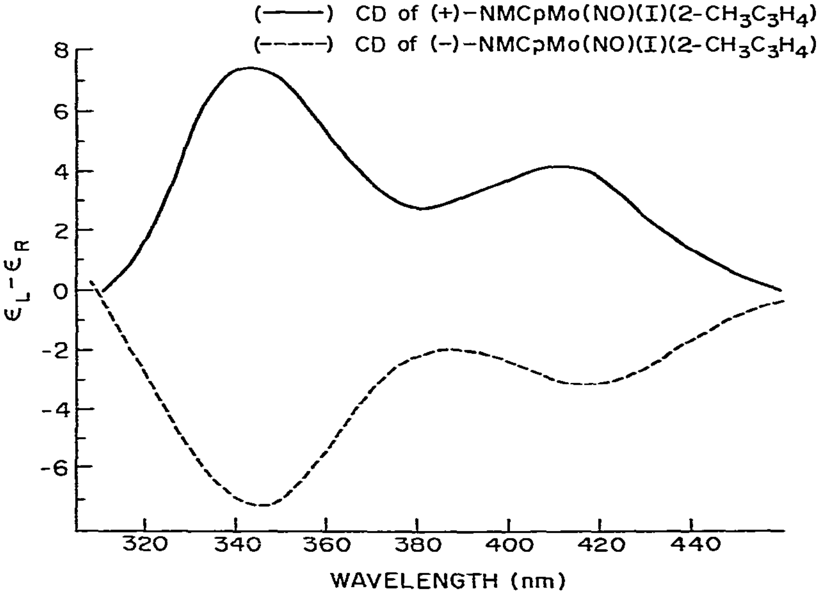


Fig 11 The CD of (+)$_D$- and (—)$_D$-*exo*-[(NMCp)Mo(NO)(I)(2-MeC$_3$H$_4$)] in chloroform.

(NO)I], they alternate from negative to positive to negative in (—)$_D$-*exo*-[CpMo(cyclooctenyl)(NO)I]

Although these correlations appear to allow rationalization of the results presented here, the limited number of compounds suggests prudence in their application In particular, substituent effects might seriously influence the chiroptical properties Thus, the substituents on the terminal allyl carbons may influence the spectra as with olefin and allyl palladium and platinum complexes [13,14]

Mechanism of *endo-exo* interconversion

In relatively fast reactions where spin saturation transfer experiments can be carried out using NMR methods [15,16] we were able to demonstrate that *endo-exo* interconversion occurred preferentially by π—σ interconversion in the iodides [17]. Rotation of the allyl was not ruled out on a much longer time scale, but is at least 6 kcal/mol higher These processes are illustrated in Fig 12.

The cyclooctenyl complex represents a particularly interesting species in this regard because the geometric constraints of the ring prevent the π—σ—π rearrange-

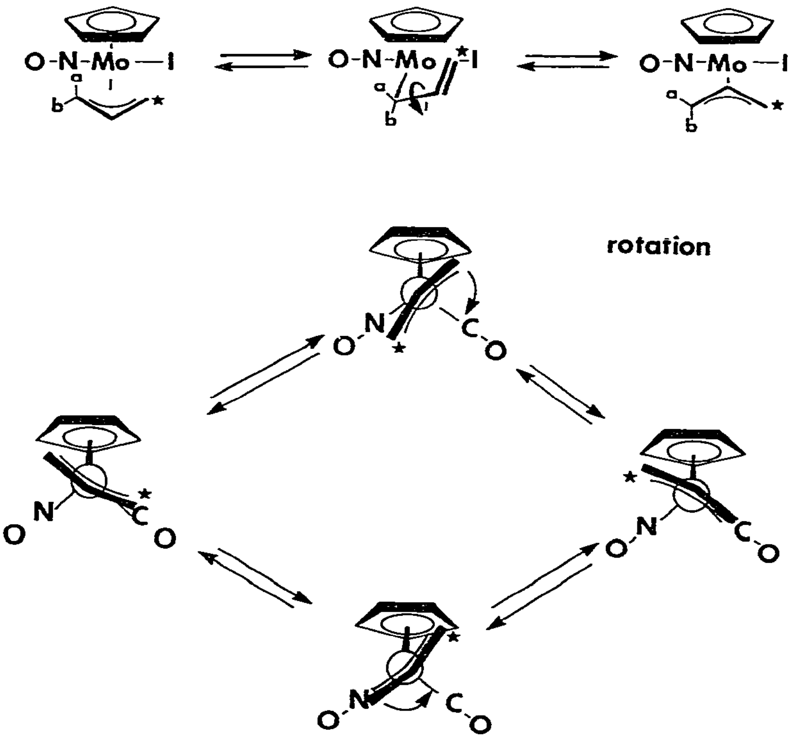
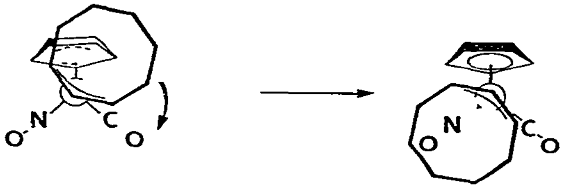


Fig 12 A comparison of interchanges resulting from σ—π—σ and rotational interconversion of *endo* and *exo* isomers

ment from effecting an *endo-exo* interconversion*. Thus, the most reasonable path for both the iodide and carbonyl complex with a cyclooctenyl ligand is via rotation. Generally, however, rotation appears to be preferred in the carbonyl-nitrosyl cations and π—σ—π rearrangement is preferred in the nitrosyl iodides, as has also been suggested by examining interconversions in deuterium-labeled allyls [17].

The examination of the rates of interconversion can also provide some insight into the path of the rotation. For the (R)-configuration shown in Fig. 8, there are two routes by which *endo* to *exo* interconversion can occur. Thus, the upper path involves a clockwise rotation which would require a close approach of the central substituent to the Cp ring, whereas, the lower path involves a counterclockwise rotation, which would involve a close approach of the terminal substituents to the Cp ring.

Since the barrier for rotation of the cyclooctenyl complex and the allyl complex are nearly the same, it follows that they are interconverting via the same path. The slower interconversion of the methallyl complex suggests an alternative path or greater steric hindrance along the same path. These observations are consistent with the rotation via the upper or clockwise path for *endo* to *exo* interconversion in the (R) enantiomer.



Retention of configuration in substitution reactions

The determinations of the absolute configurations of the $(+)_D$-[(NMCp)-Mo(allyl)(NO)(CO)] cation and $(-)_D$-[(NMCp)Mo(allyl)(NO)I] provide proof that displacement of CO by iodide occurs with retention of configuration. An attractive mechanism which explains the retention of configuration in this

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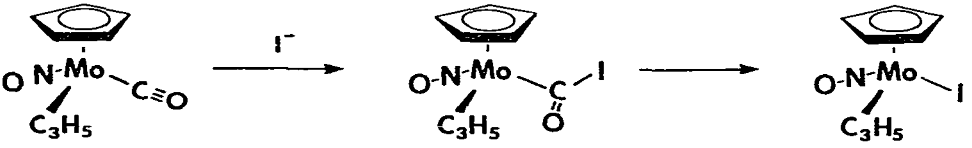
[*] The π—σ—π rearrangement occurs with retention of configuration of the termini of the allyl relative to the NO group [17]. That is, if a given terminus starts *trans* to NO it ends *trans* to NO after the rearrangement. Although this process is occurring rapidly in the $(-)_D$-[(NMCp)Mo(allyl)(NO)I] it does not lead to epimerization at the metal center. The rotations observed for the iodides are stable in solution for days. The rotation only degrades by 10% after one week in solution. The cyclooctenyl derivative might form a σ intermediate but it would return to the same configuration since the ring prevents *syn-anti* interchange.

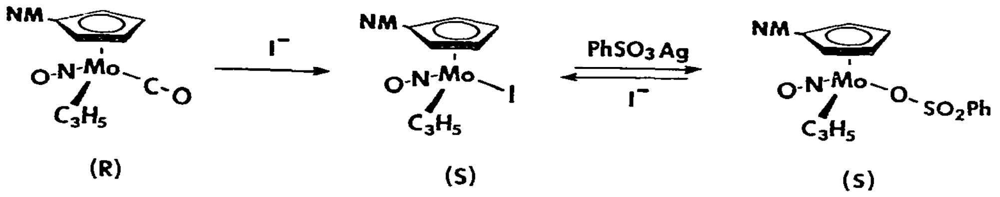
second order reaction involves attack on the carbonyl by iodide followed by migration to the metal and elimination of CO



Other halides or pseudohalides might be expected to displace CO with retention, as well. Azide produces an NCO complex via an organometallic analog of the Curtius rearrangement [18], whereas NCO attacks the allyl as well as displacing CO. A discussion of these reactions will be published separately.

The halide can be displaced stereospecifically by benzenesulfonate to produce $(-)_D$-[(NMCp)Mo(allyl)(NO)($PhSO_3$)] which on treatment with iodide returns the $(-)_D$-[(NMCp)Mo(allyl)(NO)I] with ~99% stereoselectivity. The similarity of the CD curves for the benzene sulfonate and the iodide complexes suggest that they have the same configuration Thus, although the overall retention in the cycle might occur with double inversion, we favor the interpretation that silver benzenesulfonate displacement occurs with retention. Scheme 1 sum-

SCHEME 1



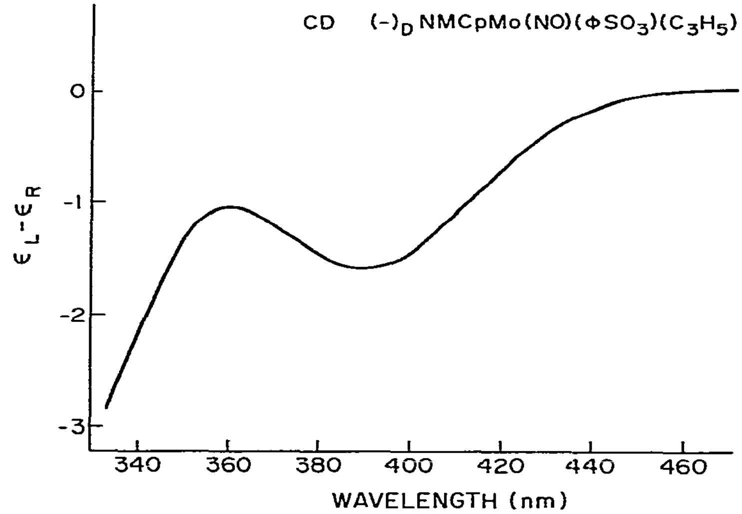


Fig 13 The CD of $(-)_D$-[(NMCp)Mo(allyl)(NO)($C_6H_5SO_3$)] in chloroform

marizes these interconversions (N B the absolute configuration of the sulfonate has not been proven)

Experimental

General procedures. All operations involving the handling of organometallic complexes in solution were carried out using standard inert atmosphere techniques under an atmosphere of nitrogen. THF was distilled from sodium benzophenone ketyl before use Other solvents were deoxygenated with a stream of dry nitrogen and stored over molecular sieves Neomenthylcyclopentadiene (NMCpH) [3] and (allyl)Mo(CO)$_2$(CH$_3$CN)$_2$Cl [19] were prepared by literature methods Other reagents were used as received from commercial sources The silica used for most chromatographic separations was Mallinckrodt SilicAR CC-7

PMR spectra were obtained with a Bruker HX-270 spectrometer operating at 270 MHz and chemical shifts are reported as ppm downfield from TMS. ORD and CD measurements were obtained with a Cary 60 spectropolarimeter with a CD attachment Accurate rotations were measured with a Perkin—Elmer 241 polarimeter with a thermostated cell Sample concentrations were measured by weighing the complex on a microbalance (± 1 μg) and weighing the solvent and converting to g/cm^3 using the density of the solvent Concentrations reported with specific rotations are in units of g/100 cm^3. Infrared spectra were obtained with a Nicolet 7199 FT IR with 0.5 cm^{-1} resolution. Melting points were determined on samples in sealed evacuated capillaries and are uncorrected.

Kinetic measurements give the best fit for the first order approach to equilibrium in $A \overset{k_f}{\to} B; B \overset{k_r}{\to} A$ Half-lives are given as 0 693/($k_f + k_r$)

Preparation of NMCpMo(CO)$_2$(allyl) Neomenthylcyclopentadiene $[\alpha]_D$ +42 0° (*c* 3 53, CHCl$_3$) was prepared according to Cesarotti, Kagan et al. [3], who reported $[\alpha]_D$ +33.0° (*c* 3.1, CHCl$_3$). It was converted to the lithium derivative and treated with (η^3-C$_3$H$_5$)Mo(CO)$_2$(CH$_3$CN)$_2$Cl according to the general procedure described by Cesarotti, Kagan et al. for TiCl$_4$ [3] After the reaction mixture was stirred for 4 h, the solvent was removed and the residue washed well with ether The combined ether washings were concentrated and the yellow complex chromatographed on alumina with petroleum ether. In a typical reaction of 2 or 3 g of NMCpH yields of ~65% based on NMCpH were obtained. Crystallization from hexane gave yellow needles melting at 66—68°C $[\alpha]_D^{20}$ +44.9° (*c* 0.247, hexane). Carbonyl bands were observed in the IR at 1962 7, 1894.3 (*endo*), 1953.9 and 1878 3 (*exo*) cm^{-1} (cyclohexane). At −40°C proton resonances (δ, ppm) were observed in CDCl$_3$ for the *exo* conformer at 5 39, 5.22, 5.13, and 5.04 (m, 4 CpH of NMCp); 4.05 (m, H$_c$), 2.79 (d, 6 6 Hz, H$_s$), 0.88 (d, 10.5 Hz, H$_a$), 0.884, 0.883, 0.676 (d, ~6 Hz, 3 Me of NMCp); and for the *endo* conformer at 6.51, 6.50, 6.33, 5.35 (m, 4 CpH of NMCp); 3.62 (m, H$_c$); 2 72 (d, 6.2 Hz, H$_s$); 0.74 (d, 6 Hz, Me of NMCp), H$_a$ and two Me of NMCp obscured; K_{eq} = 4 0. Assignments were based on comparisons with analogous cyclopentadienyl compounds [10]. Anal. Found. C, 61.0, H, 7.47. C$_{20}$H$_{28}$O$_2$Mo calcd.. C, 60.6, H, 7.07%.

Preparation of [NMCpMo(NO)(CO)(allyl)]PF$_6$. The dicarbonyl, NMCpMo-(CO)$_2$(allyl), (1 584 g, 4.0 mmol) was suspended in acetonitrile (15 ml) at 0°C.

Nitrosonium hexafluorophosphate (0.70 g, 4.0 mmol) was added in portions. After 5 min at 0°C the mixture was poured into cold ether (200 ml) and the crude product filtered and washed with cold ether. This crude product $[\alpha]_D$ +60 5° (*c* 0 236, acetone), was isolated in 74% yield (1.60 g). After two rapid crystallizations from acetone/ether the sample showed an $[\alpha]_D$ +117° immediately after dissolving The NMR spectrum of this sample in contrast to the crude material showed no signals which could be assigned to the other diastereomer. This material melted at 187—190°C with decomposition and showed single carbonyl and nitrosyl bands in the IR at 2091.1 and 1722.6 cm^{-1} in acetonitrile The structure in the solid was verified by a single crystal X-ray determination

The NMR varied with time but initially showed resonances (δ) in acetone-d_6 corresponding to the *endo* isomer at 6 86, 6 63, 6 45 and 6.09 (m, 4 CpH of NMCp), 5 45 (m, H_c), 5 20 (dd, H_s, J_{cs} 7 4, $J_{ss'}$ 3 1 Hz), 4 90 (dd, H_s , J_{cs} 7 4, J_{ss} 3 1 Hz); 3 64 (d, H_a, J_{ca} 13.6); 3 30 (d, H_a , J_{ca} 12.4 Hz), 0 98, 0.92, 0.78 (d, ~6 Hz, 3 Me in NMCp).

On standing the resonances of the *exo* isomer appeared at 7 00, 6 32, 6 15, and 6.06 (m, 4 CpH of NMCp), 5 73 (m, H_c); 5 11 (ddd, H_s, J_{cs} 7.4, J_{ss} 3 7, J_{sa} 1 Hz); 4 37 (ddd, $H_{s'}$, $J_{cs'}$ 7.4, $J_{ss'}$ 3 7, $J_{a's}$ 1 Hz), 3 45 (dd, H_a, J_{ca} 13 6, J_{sa} 1 Hz), 3.85 (dd, $H_{a'}$, $J_{ca'}$ 12.4, $J_{s'a'}$ 1 Hz), 1 02, 0 90, 0 81 (d, ~6 Hz, 3 Me in NMCp).

The optical rotation of the product was found to be time dependent. At room temperature the following changes (*c* 0 215 acetone) were observed

ν	α (*t* 0)	α (*t* 120 min)	$[\alpha]$ (*t* 120 min)
589	0 251	0 364	+170
578	0 263	0 388	+181
546	0 297	0 475	+222
436	0 319	1 136	+531

Polarimetric kinetics measurements were carried out over 6 h at 20 0°C and indicated $[\alpha]^{20}_{436}$ (*t* ∞) +596° and $[\alpha]^{20}_{546}$ (*t* ∞) +242 The half-times for approach to equilibrium were 52 min at 20°C and 20 min at 30°C

(—)$_D$-[(NMCp)Mo(allyl)(NO)(CO)]PF$_6$. The diastereomeric ratio in the initial preparation of the cations, as determined by NMR was (+)/(—) = 1 44. Several crystallizations of the mother liquors from the isolation of the (+)-cation gave a pale yellow solid $[\alpha]_D$ —45.9°; $[\alpha]_{436}$ —288°, which had a nearly mirror image CD spectrum to that of the equilibrated (+)-cation. Both the ORD and CD curves were time independent, which suggested that *endo-exo* equilibrium had been established during the purification The resonances of the major isomer (*exo*) in acetone-d_6 appeared at 6.26, 6 06, 5 90, 5 78 (m, 4 CpH of NMCp), 5.28 (m, H_c); 4.98 (dd, H_s, J_{cs} 7.6, $J_{ss'}$ 3.2), 4.84 (dd, H_s, J_{cs} 7 6, $J_{ss'}$ 3 2), 3.40 (d, H_a, J_{ca} 14 Hz) 2.96 (d, $H_{a'}$, $J_{ca'}$ 14 Hz); 0 99, 0 97, 0 81 (d, ~6 Hz, 3 Me of NMCp). Some clearly resolved characteristic resonances of the minor isomer (*endo* ~15%) were 6.43, 6.22, 5.99, 5.72 (m, 4 CpH of NMCp), 3.31 (d, 14 Hz, H_a); 2.98 (d, 14 Hz, H_a)

Preparation of NMCpMo(CO)$_2$(2-CH$_3$C$_3$H$_4$). Following the same procedure as in the preparation of the allyl, except for the use of methallyl chloride in the preparation of the molybdenum acetonitrile complex. An orange oil was obtained in greater than 60% yield This complex showed carbonyl bands in cyclohexane at 1956 6 and 1866 9 cm^{-1} and had $[\alpha]_D$ +42 0°.

Preparation of $(+)_D$-exo-[(NMCp)Mo(methallyl)(NO)(CO)]PF$_6$ Following the procedure for the allyl complex, the diastereomerically pure complex was obtained as yellow crystals (~40% yield) The initial rotation was $[\alpha]_D^{22}$ +113° which changed very slowly with time. (t 0) +113°, (t 1445 min) +97.4° The yellow crystals melt with decomposition at 121°C and show carbonyl and nitrosyl absorptions at 2104.5 and 1715.7 cm^{-1} in acetonitrile. Anal Found 43 19, 5 40 $C_{20}H_{30}O_2MoNPF_6$ calcd · C. 43 10; H, 5 43%

The ^{1}H NMR in acetone-d_6 of the sample immediately upon dissolving (*exo* isomer) exhibits resonances (δ, ppm) at 6 99, 6 36, 6 11, 5.62 (m, 4 CpH of NMCp), 5 06 (d, H_s, $J_{ss'}$ 3 7 Hz), 4.95 (d, $H_{s'}$, $J_{ss'}$ 3.7 Hz), 3.67 (s, H_a); 3 10 (s, H_a); 2 13 (s, Me of methallyl) 1 01, 0 90, 0.77 (d, 6 Hz, 3 Me in NMCp)

Additional resonances appear on standing characteristic of the *endo* isomer. 6.96, 6.60, 6 27, 6.18 (m, 4 CpH of NMCp), 5.00 (d, H_s, J_{ss} 4 6), 4.24 (d, H_s , J_{ss} 4.6 Hz), 3.77 (s, H_a); 4 10 (s, H_a), 2.09 (Me in methallyl), 1.04, 0 86, 0.77 (d, 3 Me in NMCp)

Preparation of $(-)_D$-[(NMCp)Mo(allyl)(NO)I] Sodium iodide (50.0 mg, 0 331 mmol) was dissolved in acetone (6 ml) at room temperature. $(+)_D$-*endo*-[(NMCp)Mo(allyl)(NO)(CO)], $[\alpha]_D$ +117°, (180 mg, 0 331 mmol) was added to the NaI solution. Gas evolution was observed initially and the red solution was allowed to stir at room temperature for seven minutes and then evaporated to dryness The residue was extracted with methylene chloride and the complex was chromatographed with toluene on silica A single dark red band was eluted and collected. There was no apparent fractionation or decomposition and the product gave a single spot on tlc $[\alpha]_D$ − 144° (c 0.329, acetone). The product was crystallized twice from methylene chloride/hexane to yield 154 mg (94%) of red crystals, m.p. 155–156°C, IR ν(NO) 1674 1 cm^{-1}, $[\alpha]_D^{25}$ −144° (c 0.14, chloroform). The assumed structure was verified by a single crystal X-ray determination

The ^{1}H NMR gave allyl resonances (δ, ppm) in chloroform for the *endo* isomer (90%) at 6 10, 6 03, 5 75, 5.52 (m, 4 CpH of NMCp); 5 44 (m, H_c); 4.73 (dd, H_s, J_{cs} 7.7, J_{ss} 3.72); 3.93 (d, H_a, J_{cs} 13.7), 3 23 (dd, $H_{s'}$, $J_{cs'}$ 6.2, $J_{ss'}$ 3.72), 2 49 (d, H_a , J_{ca} 11 2), 1 03, 0.93, 0 80 (d, 3 Me of NMCp). Some well-resolved resonances for the *exo* isomer were. 5 00 (m, H_c, 4.87 (m ,H_s), 4.03 (d, H_a), 3.49 (m, H_s), 2 64 (d, $H_{a'}$)

The product collected from the mother liquors of the crystallizations had $[\alpha]_D$ −136° (c 0.287, acetone). Neither the crude nor the crystallized sample exhibited NMR signals assignable to a second diastereomer

Isolation of $(+)_D$-[NMCpMo(allyl)(NO)(I)] Using partially resolved NMCpMo(allyl)(NO)(CO) obtained from the mother liquors remaining from the resolution of $(+)_D$-[(NMCp)Mo(allyl)(NO)(CO)], reaction with NaI as above produced a mixture of $(+)_D$- and $(-)_D$-[(NMCp)Mo(allyl)(NO)I]. Fractional crystallization from 1/1 pentane-dichloromethane led to crystallization of the (−)-isomer leaving the (+)-isomer in solution. Recrystallization of the (+)-isomer from pentane gave red needles melting at 102–104°C. This complex showed a nitrosyl band at 1670.2 cm^{-1} in the IR (cyclohexane) and had $[\alpha]_D$ +90°. The NMR showed resonances for the major isomer (*endo*) in $CDCl_3$ at 6.06, 5.97, 5 75, 5.60 (m, 4H of Cp in NMCp), 5.39 (m, H$_c$), 4 72 (m, H$_s$), 3 90 (m, H$_a$), 3.18 (m, H$_s$), 2 29 (m, H$_a$), 0 99, 0 88, 0 78 (d, 3 Me of NMCp)

Preparation of (—)$_D$-[(NMCp)Mo(methallyl)(NO)I] Following the same procedure as for the allyl complex red crystals were obtained in over 80% yield, m.p. 107—109°C, $[\alpha]_D^{17}$ — 153°, IR ν(NO) 1658.2 (cyclohexane). The ^{1}H NMR showed resonances (δ, ppm) in CDCl$_3$ at (*endo*) 6 03, 5 97, 5.72, 5 47 (m, 4 CpH in NMCp); 4.52 (d, H$_s$, J_{ss} 4 4); 3.19 (s, H$_a$), 2 97 (dd, J_{ss} 4 4, $J_{s\,a}$ 2.2 H$_s$); 2.32 (d, $J_{s\,a}$ 2 2, H$_a$). 1 97 (s, Me of methallyl), 0 99, 0 91, 0 77 (d, 3 Me of NMCp)

The *exo* isomer (~20%) produced well resolved resonances at: 5 91, 5 91, 5.70, 5.60 (m, 4 H of Cp in NMCp); 4 22 (m, H$_s$); 3 02 (dd, J_{ss} 4 0, $J_{s\,a}$ 1 8, H$_{s'}$), 1.95 (s, Me of methallyl), 0.98, 0.88, 0.77 (d, 6 Hz, 3 Me in NMCp)

Optical stability of the iodides. Endo-exo equilibrium is established rapidly at room temperature in the iodides, hence, variations of [α] with time are not observed. No loss of rotation was observed within 2 h in the absence of free iodide An acetone solution of the NMCpMo(allyl)(NO)I complex (0 0058 *M*) and sodium iodide (0 042 *M*) lost approximately 7% of its original rotation value after standing for two hours at room temperature

Preparation of (—)$_D$-(NMCp)Mo(allyl)(NO)(OSO$_2$C$_6$H$_5$) and reaction with sodium iodide Silver benzenesulfonate (88 mg, 0 33 mmol) was added to a solution of (—)$_D$-[(NMCp)Mo(allyl)(NO)I] (150 mg. 0 30 mmol) in methylene chloride (5 ml) The reaction mixture was kept at 0°C until the disappearance of the starting material (TLC, silica, benzene) The residue was removed by centrifugation and the yellow solution was evaporated to yield a yellow oil, IR ν(NO) 1630 cm^{-1} (chloroform), $[\alpha]_D$ —38° (*c* 0 067, acetone)

The product above was treated with a stoichiometric quantity of sodium iodide in acetone at 0° for 45 min and warmed to room temperature at which time all of the starting material had reacted (TLC). The solid residue was removed by centrifugation and the red solution evaporated to dryness The red solid was chromatographed on silica with benzene A single red band was eluted which yielded red crystals on evaporation. The TLC properties and the NMR spectra were identical to those of the starting iodide complex No other signals were observed in the NMR assignable to the other diastereomer indicating that the pure diastereomer had been obtained, $[\alpha]_D$ —145° (*c* 0 194, acetone)

Preparation of (η^5-C$_5$H$_5$)Mo(CO)$_2$(η^3-C$_8$H$_{13}$). The cyclic allyl bromide was prepared by combining 20 ml (0.16 mol) of cyclooctene and 27 g (0.15 mol) of recrystallized *N*-bromosuccinamide with 0 25 g of benzoyl peroxide in CCl$_4$. After filtration of the succinamide, which floats to the surface of the solvent as the reaction proceeds, and evaporation of the CCl$_4$, the crude allyl bromide was heated with 22.6 g (75 mmol) of Mo(CO)$_3$(CH$_3$CN)$_3$ in acetonitrile at 80°C for 2 h. Evaporation of the solvent gave 31 g (78%) of the (C$_8$H$_{13}$)Mo(CO)$_2$(CH$_3$CN)$_2$Br complex. The solid was dissolved in THF and cooled to —78°C and then 0 058 mol of LiC$_5$H$_5$ in THF was added slowly The mixture was allowed to warm to room temperature with stirring overnight The THF was evaporated and the carbonyl complex extracted from the residue by Soxhlet extraction with petroleum ether. A yield of 11 3 g of the cyclopentadienyloctenyl complex melting at 117—118° (dec) was obtained, which corresponds to a 60% yield based on LiCp or 47% yield based on $Mo(CO)_6$. The complex showed only two carbonyl bands in the IR indicating the presence of only the *exo* isomer (1954 and 1878 cm^{-1}, cyclohexane). The ^1H NMR spectrum at 25°C in $CDCl_3$ gave resonances (δ, ppm) at 5 23 (s, Cp), 4 15 (t, 8.1 Hz, H_c), 3.74 (ddd, 8 2, 8.1, 8 5 Hz, H_s), 2 30, 2.18, 1 46, 1 20 (m, methylenes)

The assumed structure was verified by a single crystal X-ray determination.

Preparation of $[(Cp)Mo(C_8H_{13})(NO)(CO)]BF_4$ The nitrosyl cation was obtained by combining 1 0 g (3 3 mmol) of $(Cp)Mo(C_8H_{13})(CO)_2$ with 8 ml of acetonitrile at 0°C with 0 36 g (3 0 mmol) of $NOBF_4$. The reaction mixture was stirred for 2 min and then poured into dry ethyl ether which was agitated with a stream of nitrogen gas. A flocculent yellow-brown precipitate was separated by centrifugation and washed three times with ether. Drying under vacuum gave 1 14 g (84% yield) of the desired salt Carbonyl and nitrosyl bands were observed in the IR at 2084 and 1712 cm^{-1} (methylene chloride) Anal Found: C, 40 61, H, 4 27. $C_{14}H_{18}MoNO_2BF_4$ calcd C, 40 51; H, 4 37%

After *exo-endo* equilibration the 25°C ^1H NMR exhibited resonances corresponding to a single isomer (*exo*) in acetone· 6 32 (s, Cp); 4 99 (t, 8.3 Hz, H_c), 6.44 (dddd, 8.3, 9.2, 9 2, 2.4 Hz, H_s), 5.91 (dddd, Hz, 8.3, 9.2, 9.2, 2.4 H_s); 2 84—1.50 (m, methylenes). *Endo* 6.42 (s, Cp); 5.57 (t, 8.7 Hz, H_c), 6.39 (dt, 8.7, 8 7 Hz, H_s), 5.92 (dt, 8.7, 9.0 Hz, H_s); 2.84—1.50 (m, methylenes).

Preparation of (Cp)Mo(cyclooctenyl)(NO)I. This complex was prepared following the procedure above for the allyl iodide. Chromatography on alumina with methylene chloride, however, produced the product in lower yield (55%) as a thick red oil Crystallization was effected by evaporating the residual methylene chloride under vacuum, adding pentane, and then adding sufficient acetone to bring the oil into solution. Storing the pentane/acetone solution at 10°C for 24 h produced large well-formed red-orange crystals melting at 106—108°C. The structure was verified by a single crystal X-ray determination

A single nitrosyl band was observed in the IR at 1630 cm^{-1} (methylene chloride). The ^1H NMR at 25°C in $CDCl_3$ exhibited resonances (δ) at: 5.78 (s, Cp); 6 26 (ddd, 8,8, 8 8, 8.4 Hz, H_s), 4.79 (t, 8.8 Hz, H_c); 4.38 (ddd, 8.8, 10.4, 8.8 Hz, $H_{s'}$), 2.59, 2.13, 1.59 (m, methylenes). Only resonances for the *exo* isomer were observed.

Crystallographic analyses All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromatized Mo-K_α radiation. Space groups were determined from the systematic absences $h00$, $0k0$, and $00l = 2n + 1$, which were observed in the data collection for both structures

All calculations were performed on a Digital Equipment PDP 11/45 computer using the Enraf-Nonius SDP program library. Both structures were solved by the heavy-atom method. Anomalous dispersion corrections [20a] were added to the neutral-atom scattering factors [20b] for all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function $\Sigma w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pF_o^2)^2]^{1/2}/Lp$. Crystallographic data parameters are listed in Table 3. Other results are compiled in Tables 4—9.

Structure analysis of $(-)_D$*-exo-[(Cp)Mo(cyclooctenyl)(NO)I].* A specimen

TABLE 3

EXPERIMENTAL X-RAY DIFFRACTION DATA FOR (—)-NMCpMo(η^3-C_3H_5)(NO)I AND CpMo(η^3-C_8H_{13})(NO)I

	(η^3-C_3H_5)	(η^3-C_8H_{13})
(A) Crystal parameters		
Space group	$p2_12_12_1$ (D_2^4)(No 19)	
Temperature (°C)	22	
a (Å)	7 221(1)	8 466(1)
b (Å)	12 686(7)	10 449(2)
c (Å)	21 603(7)	16 372(2)
V (Å^3)	1979(2)	1448 3(6)
Z	4	4
Mol wt	566 36	427 14
ρ_{calcd} (g/cm^3)	1 901	1 959
(B) Measurement of intensity data		
Radiation	Mo-K_α	
Monochrometer	graphite	
Detector aperture (mm)		
horizontal A + B tan θ	$A = 3$ 0	
	$B = 1$ 0	
vertical	4 0	
Reflections measured	(+h +k +l and —h —k —l)	
Maximum 2θ	54°	60°
Scan type	moving crystal-stationary counter	
ω scan width	0 85	
Background	1/4 additional scan at each end of scan	
ω scan rate (deg/min) max min	10 1 8	10 1 3
Number of reflections measured	4 012	3 820
Number of reflections $F^2 > 3\sigma(F^2)$	3 659	3 717
(C) Treatment of data		
Abs coeff (μ cm^{-1})	22 490	30 298
Grid	10 × 10 × 8	10 × 10 × 8
Transmission coeff max min	0 769 0 543	0 523 0 317
p factor	0 03	0 03
Final residuals R_1 R_2	0 039 0 046	0 038 0 046
Esd of unit weight	1 901	2 156

TABLE 4

RATIOS OF THE LARGEST BIJVOET DIFFERENCES FOR CpMo(η^3-C_8H_{13})(NO)I

$F(hkl)/F(\bar{h}\bar{k}\bar{l})$

h	k	l	Calculated (R)	Calculated (S)	Observed
2	2	7	0 84	1 19	1 17
1	1	12	0 84	1 19	1 17
1	7	1	0 85	1 18	1 16
1	3	8	0 86	1 16	1 11
1	2	6	0 88	1 13	1 13
1	3	12	0 89	1.12	1 10
8	2	5	1 11	0 90	0 92
8	3	7	1 13	0 88	0 88
4	1	9	1 19	0 84	0 88
4	2	7	1 21	0 82	0 89
1	1	2	1 26	0 80	0 86
4	1	1	1 28	0 78	0 82
5	2	6	1 36	0 73	0 75
5	2	2	1.54	0 63	0 62

TABLE 5

RATIOS OF THE LARGEST BIJVOET DIFFERENCES FOR (—)-NMCpMo(η^3-C_3H_5)(NO)I

$F(hkl)/F(\bar{h}\bar{k}\bar{l})$

h	k	l	Calculated (R)	Calculated (S)	Observed
3	5	1	0 64	1 58	1 49
1	7	2	0 79	1 27	1 28
3	5	3	0 80	1 25	1 08
4	3	2	0 88	1 14	1 18
3	7	3	0 88	1 14	1 15
4	3	10	0 88	1 14	1 14
1	10	6	0 89	1 12	1 13
4	2	14	0 90	1 12	1 11
2	11	2	1 12	0 89	0 99
3	6	7	1 14	0 88	0 87
2	5	1	1 15	0 87	0 89
1	8	4	1 15	0 87	0 84
3	3	3	1 15	0 87	0 87
4	2	4	1 16	0 86	0 85
1	1	4	1 21	0 83	0 82

of approximate dimensions 0 31 × 0 32 × 0 37 mm was selected for X-ray diffraction work and mounted in a thin-walled glass capillary. A preliminary unit cell was determined from 25 randomly selected reflections An orthorhombic crystal type was indicated and a preliminary set of reflections were collected to identify the space group. The systematic extinctions ($h00$, $0k0$, and $00l = 2n + 1$ absent) indicated the space group $P2_12_12_1$. This is a non-centric space group and suggested that a spontaneous resolution had produced crystals, each of which contained only one enantiomer. Dissolving single crystals and measuring the rotations with a polarimeter confirmed this expectation Using twelve high-angle reflections and their Friedl equivalents (hkl and $\bar{h}\bar{k}\bar{l}$)a new orientation matrix and unit cell parameters were obtained The intensities of each reflection and its Friedl equivalents were measured sequentially to reduce

TABLE 6

POSITIONAL PARAMETERS FOR (—)-CpMo(η^3-C_8H_{13})(NO)I

I	0 16735(4)	−0 46002(5)	−0 37214(2)
Mo	−0 16366(4)	−0 49056(3)	−0 36845(2)
O	−0 1818(4)	−0 4368(4)	−0 1903(2)
N	−0 1685(4)	−0 4506(3)	−0 2629(2)
Cp(1)	−0 3520(8)	−0 6498(5)	−0 3894(5)
Cp(2)	−0 2846(8)	−0 6273(6)	−0 4663(3)
Cp(3)	−0 1327(10)	−0 6626(5)	−0 4636(3)
Cp(4)	−0 0948(9)	−0 7066(5)	−0 3844(4)
Cp(5)	−0 2356(9)	−0 7024(5)	−0 3406(3)
C(1)	−0 3846(6)	−0 3538(5)	−0 3853(3)
C(2)	−0 2670(6)	−0 3225(5)	−0 4410(3)
C(3)	−0 1234(6)	−0 2659(4)	−0 4211(3)
C(4)	−0 0964(7)	−0.1697(5)	−0 3541(3)
C(5)	−0 1940(10)	−0 0457(5)	−0 3694(3)
C(6)	−0 3670(9)	−0 0570(8)	−0 3864(4)
C(7)	−0 4728(8)	−0 1337(6)	−0 3335(4)
C(8)	−0 4289(7)	−0.2728(6)	−0 3118(4)
C(6B)	−0 3795(31)	−0 0390(25)	−0 3338(16)

TABLE 7

ATOMIC COORDINATES FOR (−)-NMCpMo(η^3-C_3H_5)(NO)I

Atom	x/a	y/b	z/c
Mo	0.10017(7)	0.04971(4)	0.27634(2)
I	−0.24344(6)	−0.05223(4)	0.29082(2)
O	0.2850(7)	−0.1564(3)	0.2601(2)
N	0.2083(6)	−0.0746(4)	0.2637(2)
Cp(1)	0.1262(8)	0.0669(4)	0.3839(2)
Cp(2)	−0.0066(9)	0.1436(4)	0.3641(2)
Cp(3)	0.0787(10)	0.2190(4)	0.3258(2)
Cp(4)	0.2670(11)	0.1894(4)	0.3209(3)
Cp(5)	0.2960(8)	0.0971(5)	0.3562(2)
Cm(1)	0.0835(8)	−0.0177(4)	0.4336(2)
Cm(2)	0.1425(8)	0.0180(4)	0.4983(2)
Cm(3)	0.3528(9)	0.0155(5)	0.5050(3)
Cm(4)	0.4283(10)	−0.0957(5)	0.4902(3)
Cm(5)	0.3704(10)	−0.1383(4)	0.4269(3)
Cm(6)	0.1618(9)	−0.1275(4)	0.4191(3)
Cm(7)	0.0529(9)	0.1223(4)	0.5197(2)
Cm(8)	−0.1574(11)	0.1124(6)	0.5258(3)
Cm(9)	0.1316(12)	0.1632(5)	0.5808(3)
Cm(10)	0.4328(12)	−0.2509(5)	0.4191(3)
C(1)	0.268(1)	0.1132(6)	0.1927(4)
C(2)	0.090(2)	0.0726(8)	0.1710(5)
C(3)	−0.064(1)	0.1008(7)	0.1833(5)

errors from X-ray source fluctuations. Three reflections were selected as intensity standards and measured every 4000 sec throughout the data collection. No significant variations in the intensities of the standards were observed. The crystal faces were identified as $0\bar{1}\bar{2}$, 0.12, $0\bar{1}\bar{2}$, $01\bar{2}$, $10\bar{1}$, $\bar{1}02$, and $\bar{2}0\bar{1}$. The crystal was mounted such that the normal to the 100 plane was oriented 8.1° from the diffractometer ϕ axis. The remainder of the data collection parameters are given in Table 3.

In the initial stages of refinement only the $+h+k+l$ reflections were used. A three-dimensional Patterson map was used to obtain the coordinates of the Mo and I atoms. These coordinates were refined to yield an R factor of 18.4%. A structure factor calculation using these coordinates and a difference Fourier map revealed the location of the remaining non-hydrogen atoms. These coordinates were then refined by a least-squares process using the full data set which was corrected for absorption effects. With anisotropic temperature factors for the Mo and I and isotropic temperature factors for the remaining atoms, agreement factors R_1 5.4% and R_2 7.0% were obtained for the configuration designated (R).

The absolute configuration was investigated at this point. The signs of all of the atomic coordinates were reversed, which corresponds to converting the molecule to its mirror image, and the least-squares refinement repeated. This yielded an R_1 5.2% and R_2 6.6%, indicating that the inverted structure, i.e., (S) was the correct one. This difference, according to Hamilton's R factor significance test, indicates that the probability of the new configuration being the correct one is over 99.5%.

TABLE 8

BOND DISTANCES (Å) FOR (—)-(Neomenthyl C_5H_4)Mo(η^3-C_3H_5)(NO)I AND (η^5-C_5H_5)Mo($\eta^3$$C_8H_{13}$)(NO)I

	NMCp—allyl	Cp—cyclooctenyl
Mo—Cp(1)	2.341(3)	2.330(4)
Mo—Cp(2)	2.369(4)	2.349(4)
Mo—Cp(3)	2.404(4)	2.393(4)
Mo—Cp(4)	2.349(5)	2.346(4)
Mo—Cp(5)	2.310(4)	2.340(4)
Mo—C(1)	2.320(6) [a]	2.370(3)
Mo—C(2)	2.295(8) [a]	2.294(3)
Mo—C(3)	2.424(8) [a]	2.523(3)
Mo—I	2.814(1)	2.821(1)
Mo—N	1.781(4)	1.778(2)
N—O	1.179(4)	1.202(3)
Cp(1)—Cp(2)	1.432(6)	1.403(7)
Cp(2)—Cp(3)	1.408(6)	1.338(7)
Cp(3)—Cp(4)	1.415(8)	1.413(8)
Cp(4)—Cp(5)	1.413(6)	1.391(7)
Cp(5)—Cp(1)	1.417(6)	1.382(8)
C(1)—C(2)	1.461(10) [a]	1.388(5)
C(2)—C(3)	1.202(10) [a]	1.391(5)
C(3)—C(4)		1.505(5)
C(4)—C(5)		1.557(6)
C(5)—C(6)		1.495(8) [a]
C(6)—C(7)		1.481(8) [a]
C(7)—C(8)		1.542(6)
C(8)—C(1)		1.518(6)
Cp(1)—Cm(1)	1.548(5)	
Cm(1)—Cm(2)	1.530(6)	
Cm(2)—Cm(3)	1.526(6)	
Cm(3)—Cm(4)	1.546(6)	
Cm(4)—Cm(5)	1.528(7)	
Cm(5)—Cm(6)	1.522(7)	
Cm(6)—Cm(1)	1.535(6)	
Cm(2)—Cm(7)	1.543(6)	
Cm(7)—Cm(8)	1.530(8)	
Cm(7)—Cm(9)	1.527(7)	
Cm(5)—Cm(10)	1.507(7)	

[a] Owing to the disorder, the reported standard deviations may underestimate the error

At this point the ratios of the F_{calc} for the Friedl pairs were computed and twenty-six were found to differ by more than 10%. The intensities of these reflections were measured again using 600 sec scan times to increase the accuracy of the measurements. The setting angles were determined using twelve high-angle reflections and their Friedl equivalents. The coordinates obtained using the (R) and (S) structures should be the best representation of the structure for the crystallographic enantiomorph which was studied. Using the (R) coordinates and the 52 observations and refining only the scale factor, agreement factors of R_1 15.8% and R_2 19.2% were obtained. The "correct" (S) structure gave values of R_1 10.3% and R_2 12.7%. This large variation gave us

TABLE 9

BOND ANGLES (deg) FOR (—)-(Neomenthyl-C_5H_4)Mo(η^3-C_3H_5)(NO)I AND (η^5-C_5H_5)Mo($\eta^3$$C_8H_{13}$)(NO)I

	NMCp—allyl	Cp—cyclooctenyl
N—Mo—C(1)	87.7(2)	87.3(1)
N—Mo—C(2)	88.5(2)	96.7(1)
N—Mo—C(3)	109.0(2)	108.3(1)
N—Mo—I	89.8(1)	91.0(1)
M—N—O	174.8(3)	172.2(3)
C(1)—C(2)—C(3)	129.9(8) [a]	125.0(3)
C(2)—C(3)—C(4)		125.9(3)
C(3)—C(4)—C(5)		111.0(3)
C(4)—C(5)—C(6)		119.0(4) [a]
C(5)—C(6)—C(7)		121.8(5) [a]
C(6)—C(7)—C(8)		120.0(4) [a]
C(7)—C(8)—C(1)		113.7(4)
C(8)—C(1)—C(2)		124.5(3)
Cp(1)—Mo—Cp(2)	35.4(1)	34.7(2)
Cp(2)—Mo—Cp(3)	34.3(2)	32.6(2)
Cp(3)—Mo—Cp(4)	34.6(2)	34.7(2)
Cp(4)—Mo—Cp(5)	35.3(2)	34.6(2)
Cp(5)—Mo—Cp(1)	35.5(2)	34.4(2)
Cp(5)—Cp(1)—Cp(2)	105.7(4)	107.1(5)
Cp(1)—Cp(2)—Cp(3)	110.2(4)	108.4(5)
Cp(2)—Cp(3)—Cp(4)	106.5(4)	109.8(5)
Cp(3)—Cp(4)—Cp(5)	108.8(4)	105.5(5)
Cp(4)—Cp(5)—Cp(1)	108.9(4)	109.1(4)
Cp(1)—Cm(1)—Cm(2)	111.9(3)	
Cm(6)—Cm(1)—Cm(2)	110.7(4)	
Cm(1)—Cm(2)—Cm(3)	110.9(3)	
Cm(2)—Cm(3)—Cm(4)	110.5(4)	
Cm(3)—Cm(4)—Cm(5)	114.2(4)	
Cm(4)—Cm(5)—Cm(6)	109.8(4)	
Cm(4)—Cm(5)—Cm(10)	110.7(5)	
Cm(5)—Cm(6)—Cm(1)	102.5(3)	
Cm(2)—Cm(7)—Cm(8)	111.8(4)	
Cm(2)—Cm(7)—Cm(9)	113.3(4)	
C(4)—C(5)—C(6B)		118.4(8)
C(5)—C(6B)—C(7)		123(1)
C(6B)—C(7)—C(8)		126(1)

[a] Owing to the disorder, the reported standard deviations may underestimate the error

greater confidence that the (*S*) structure was more correct than the 0.004 difference in R_2 with the full data set *.

A difference Fourier map gave the position of most of the hydrogen atoms but also indicated that the end of the cyclooctenyl ring was disordered. Somewhat larger isotropic thermal parameters for C(4), C(5), and C(6) also suggested the disorder. A difference map using all of the atomic coordinates except C(5) gave electron density at the positions of C(5) and C(5A) in a ratio of approximately 4/1.

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* With a large data set virtually any improvement in R_1 or R_2 will indicate significance at better than the 99.5% level. Thus for the full data set the ratio of the R factors $R(R_1) = 1.04$ and $R(R_2) = 1.06$. The criterion for 99.5% significance is R greater than $R_{1,3715,0.005} = 1.001$. For the limited set of 52 reflections $R(R_1) = 1.53$, and $R(R_2) = 1.51$ with $R_{1,51,0.005} = 1.08$. In either case the significance is well beyond the 99.5% level.

The least-squares refinement was continued for the (S) configuration with all non-hydrogen atoms anisotropic except C(5A) and C(5), which were kept isotropic and refined with occupancies of 0.2 and 0.8 respectively. Hydrogen atom positions were calculated for all carbon atoms except C(5A) Those for C(4), C(5), and C(6) were included with occupancies of 0.8. Hydrogen atoms were included in the structure factor calculations, but were not refined. This resulted in the final agreement factors of R_1 3 8% and R_2 4 6% *. Inversion of the coordinates and refinement to test the (R) configuration gave R_1 4 1% and R_2 5 2% *

Using the final atomic coordinates obtained by refinement of the (R) and (S) structures and refining only the scale factor the (R) configuration gave R_1 14.4% and R_2 16.2%, whereas, the (S) configuration gave R_1 5.8% and R_2 6.9% for the 26 accurately determined Friedl pairs having a high anomalous dispersion contribution

A final confirmation that the (S) configuration was the correct one arises from comparison of the ratios of the largest Bijvoet differences (see Table 4) The ratios of the observed and calculated values of $F(hkl)$ and $F(\overline{hkl})$ are consistently in the proper direction for all Friedl pairs with large anomalous dispersion corrections.

Determination of sign of rotation of (S)-[(Cp)Mo(cyclooctenyl)(NO)I] Examination of a number of crystals did not indicate a striking difference between enantiomorphic crystals Thus, it was necessary to determine the sign of the rotation of the enantiomer in the crystal used in the X-ray crystal structure determination Since this was such a crucial measurement, the mass of the crystal was estimated from its density (as determined by the unit cell size) and the microscopic dimensions required for the absorption correction. This calculation indicated that the crystal has a mass of 121 μg. The capillary was broken and the crystal dissolved in 6 0 cm^3 of chloroform. The following rotations were observed. α_D −0 002° α_{436} +0.023°, α_{365} −0.022°. This corresponds to $[\alpha]_D$ −100°; $[\alpha]_{436}$ +1100°; $[\alpha]_{365}$ −1100°. Specific rotation of greater accuracy were determined below, but the negative rotation at the Na D line is sufficiently precise to give the correct sign. Examination of the ORD curve of partially resolved samples (see below) show that the sign of the rotation is negative at 589, 578, 546, and 365 nm, but is positive at 436 nm.

Isolution of pure (+)- and (—)-enantiomers of (Cp)Mo(cyclooctenyl)(NO)I] Quantities on the order of 10 mg of pure material could be separated in an hour by dissolving one crystal at a time; observing the rotation of the solution; and combining all solutions with the same rotational sign.

Structure analysis of (—)$_D$-endo[(NMCp)Mo(allyl)(NO)I] Since this structure contains a neomenthyl group, which has three centers of known absolute configuration, an anomalous dispersion X-ray study is not required to establish the absolute configuration at the metal center We have published a preliminary report of this structure [1]. Nevertheless, to establish credibility in our methodology and to anticipate the magnitude of anomalous dispersion effects in com-

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* Both final refinements were carried out until the shift/error parameter for all atoms was 0 00 (four cycles) The Hamilton tests again showed the (S) configuration to be correct at well beyond the 99 5% confidence level $R(R_1) = 1$ 08, $R(R_2) = 1$ 13 and $R_{1,3715,0\,005} = 1.001$.

plexes with no established chiral reference points, we recollected the data and the Friedl equivalents for this complex. A crystal 0 32 × 0 15 × 0 16 mm was selected and mounted in a thin-walled glass capillary. The crystal faces were identified as $0\bar{1}2$, $01\bar{2}$, $0\bar{1}\bar{2}$, 012, $\bar{2}11$, and 211 The crystal was mounted with the normal to the 100 plane coincident (0.0°) with the diffractometer ϕ axis. The structure has been determined previously using only $+h+k+l$ data Following the method described for the cyclooctenyl complex, Friedl pairs were collected and the data reduced and corrected for absorption No significant differences in bond lengths or angles were observed in the use of the larger data set.

The final agreement factors for the (*S*) configuration after refinement were R_1 0.039% and R_2 0.046%, whereas for the (*R*) configuration after refinement R_1 0.042% and R_2 0.051% were obtained. The agreement with the ratios of the largest Bijvoet differences also confirms the configuration of the neomenthyl group and the chirality at the metal (see Table 5)

Supplementary material

Tables of thermal parameters, and observed and calculated structure factors are available *.

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