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NUCLEOPHILIC ADDITION TO COORDINATED ALLYL LIGANDS. HETEROATOM NUCLEOPHILES WITH CATIONIC MOLYBDENUM COMPLEXES *

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Summary

The addition of the heteronuclear anions (methoxide, hydride, alkylnitronate and mercaptide) to a series of π-allylmolybdenum cations related to η^5-$C_5H_5Mo(CO)(NO)(\eta^3\text{-allyl})^+$ was examined. In each case, the adducts derived from nucleophilic attack at the terminus of the coordinated allylic group were isolated. Thiophenolate was found to add to the cyclooctenyl analogue to produce only one stereoisomer in high yields. The coordinated phenyl 3-cyclooctenyl sulfide was also converted stereospecifically to a single isomeric sulfoxide with *m*-chloroperbenzoic acid. Such a chiral oxidation of a sulfide to a sulfoxide is compared with the rather unselective sulfoxidation of the free phenyl 3-cyclooctenyl sulfide by the same reagent. The stereospecificity is analyzed in terms of steric features inherent of allyl sulfides coordinated to an optically active metal center.

Introduction

The functionalization of coordinated ligands can be achieved by nucleophilic addition [1], a strategy which is particularly applicable to an unsaturated allylic group activated by complexation [2]. In this regard the π-allylmolybdenum cations such as η^5-$C_5H_5Mo(CO)(NO)(\eta^3\text{-allyl})^+$ are of special interest owing to the remarkable stereoselectivity observed during the addition of carbon-centered nucleophiles [3–5]. The use of various heteronuclear anions (Nu^-) in nucleophilic additions and substitutions with the analogs of $CpMo(CO)(NO)(allyl)^+$ has been demonstrated with hydrides [4,6,7], methoxide [4,8], hydroxide [6,7], t-butylmercaptide [4] and dialkyldithiocarbamates [6,8]. In each case, the addition occurs at the

* Dedicated to Professor Lamberto Malatesta in recognition of his seminal contributions to organometallic chemistry.

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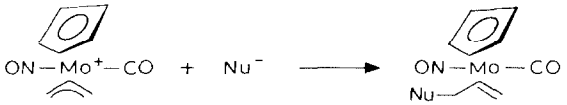
terminal allylic carbon centers in π-allyl and cyclooctenyl systems to afford isolable η^2-olefin complexes, i.e.



(1)

With inorganic iodide as the nucleophile, the attachment results in substitution at the metal center (with the loss of carbon monoxide) to afford a series of neutral iodomolybdenum complexes CpMo(NO)I(η^3-allyl) [9,10].

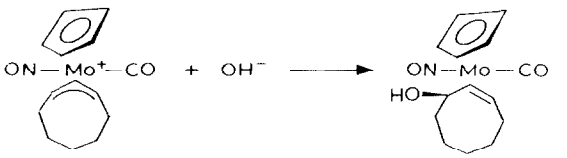
(2)

The observation of the iodide substitution with an optically active cation to proceed with an overall stereochemical retention at the metal center [10] can be accommodated by an initial nucleophilic attack at the coordinated CO ligand followed by a subsequent extrusion of carbon monoxide with retention of configuration [11], i.e.

(3)

Indeed this notion does raise the intriguing question of whether in addition and substitution there is a common intermediate, which undergoes subsequent Nu^- migration either (a) to the allylic carbon to afford the η^2-olefinic adduct, as in eq. 1, or (b) to the metal center with concomitant CO loss to effect substitution, as in eq. 2.

The existing X-ray crystallographic analysis of the olefin complex derived from the nucleophilic addition of hydroxide ion indicates that the attachment ultimately occurs on the allyl moiety with the regiochemistry and the stereochemistry suggestive of an addition to the terminal carbon which is *cis* to the coordinated NO and *anti* to the metal center, respectively, as illustrated by the example below [6].



(4)

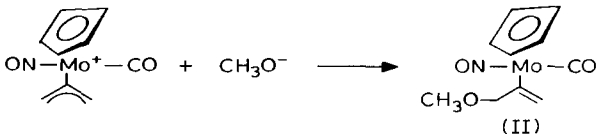
At this juncture however there is no indication of the generality of this regio- and stereochemical outcome. In other words, the possibility exists for the addition of certain nucleophiles (especially those with a selectivity intermediate between that of the soft I^- and the hard HO^-), to attack a site remote from the allylic terminus followed by internal transfer to the allyl ligand. Such a pathway would lead to a stereochemical result different from that in eq. 3, and it has been observed with π-allylpalladium complexes [12,13]. Previous studies have shown that many carbon-centered nucleophiles attack the π-allylmolybdenum cations at the allylic terminus *cis* to the coordinated NO and *anti* to the metal center as in eq. 4 [4,5,8,14]. In this study we explore the stereochemical course of nucleophilic addition of other heteronuclear anions to a series of π-allyl cations related to η^5-$C_5H_5Mo(CO)(NO)(\eta^3$-allyl)$^+$.

Results and discussion

Heteroatom nucleophiles of four distinct structural types were treated with a series of π-allylmolybdenum salts [I = (η^5-C_5H_5)Mo(CO)(NO)(η^3-allyl)$^+$ PF_6^-], in which the coordinated allyl ligand was either (a) allyl, (b) 2-methallyl or (c) cyclooctenyl.

Methoxide as a nucleophile

The reaction of the 2-methallyl complex Ib (η^5-C_5H_5)Mo(CO)(NO)(η^3-C_4H_7) with sodium methoxide in an acetonitrile/methanol mixture required ~ 22 h for completion. The methoxide adduct II was isolated in 16% yield and characterized as (η^5-C_5H_5)Mo(CO)(NO)(η^2-CH_2=$C(CH_3)CH_2OCH_3$) on the basis of its infrared and ^{1}H NMR spectra (eq. 5). Thus both the characteristic terminal CO and NO



(II) (5)

stretching bands were observed in the infrared spectrum of II (see Table 1.) The ^{1}H NMR spectrum exhibited cyclopentadienyl and methoxyl resonances as singlets with appropriate chemical shifts [4,8]. The allylic methylene protons appeared as a broad, unresolved singlet, which compared with the separate *syn* and *anti* resonances of the η^3-allyl ligand in the starting material Ib. We could find no evidence for the presence of either the substitution product η^5-$C_5H_5Mo(OCH_3)(NO)(\eta^3$-$C_4H_7)$ or the adduct to CO, i.e., η^5-$C_5H_5Mo(CO_2CH_3)(NO)(\eta^3$-$C_4H_7)$.

Borohydride as a nucleophile

The reduction of the π-allyl complex Ia with sodium borohydride proceeded readily at room temperature in a mixture of acetonitrile and methanol. The propene complex IIIa (η^5-C_5H_5)Mo(CO)(NO)(η^2-CH_2=$CHCH_3$) was isolated in 22% yield as previously reported [4,6,7]. No evidence for the formation of either the formyl complex (e.g., η^5-$C_5H_5Mo(CHO)(NO)(\eta^3$-$C_3H_5)$ or the metal hydride (η^5-$C_5H_5Mo(H)(NO)(\eta^3$-$C_3H_5)$ was found by their characteristic low field and high field resonances, respectively, in the ^{1}H NMR spectrum. Both CO and NO bands were apparent in the IR spectrum, and the methyl resonances resulting from the

TABLE 1

INFRARED STRETCHING FREQUENCIES OF CO AND NO LIGANDS IN SOME (η^5-C_5H_5)Mo(CO)(NO)(η^2-olefin) COMPLEXES [a]

Complex	ν(CO)	ν(NO)	Other
II	1960	1630	818
IIIa [b]	1975	1622	809
V	1966, 1907(sh)	1626, 1585(sh)	809
VI [c]	1971	1642	801
VII [c]	1977	1636	1051, 1018, 800

[a] Neat film, unless otherwise specified; ν in cm^{-1}. [b] KBr disc. [c] Cyclohexane solution.

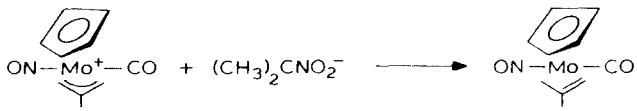
reduction of the allyl ligand were observed in both the ^{1}H and ^{13}C NMR spectra (see Tables 2 and 3).

(IIIa)

The borohydride reduction of the 2-methallyl analog gave essentially the same results, the η^2-isobutene complex IIIb (η^5-C_5H_5)Mo(CO)(NO)(η^2-CH_2=$C(CH_3)_2$) being isolated in 55% yield. Scrutiny of the ^{1}H NMR spectrum of the crude reaction mixture yielded no indication of the formation of either a formyl or a hydride complex.

Alkylnitronate as a nucleophile

The 2-methallyl cation Ib reacted readily with isopropylnitronate anion, which was generated in situ from 2-nitropropane and diethylamine is acetonitrile solutions. However, we could find no evidence for the formation of an alkylnitronate adduct. Upon work-up of the reaction mixture with methylene chloride, we isolated in 30% yield the hydride adduct IIIb which was identical with that found in the direct borohydride reduction of Ib (vide supra).



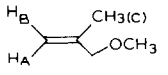
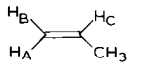
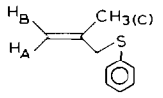
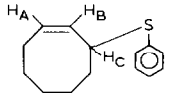
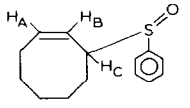
(IIIb)

In addition, the chloro substitution product (η^5-C_5H_5)Mo(Cl)(NO)(η^3-C_4H_7) (IV) was isolated as a red-orange solid in 11% yield. The IR spectrum of IV exhibited NO absorption at 1600 cm^{-1} but none for CO. Spin–spin coupling observed in the ^{1}H NMR spectrum was indicative of an intact η^3-allyl ligand, and separate resonances were observed for each *syn* and *anti* proton. The asymmetry of this complex was borne out in the ^{13}C NMR spectrum by a pair of separate triplets for each allylic terminus, and the chemical shift of the central carbon at δ 88.7 was characteristic of a predominant *endo* conformation at 25°C [15]. [Note also this preference for the *endo* conformer in the dicarbonyl precursor (η^5-C_5H_5)(Mo(CO)$_2$(η^3-C_4H_7).] Cyclopentadienyl resonances at δ 5.88 and 103.5 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, are at low field compared to the dicarbonyl complex (δ 5.20 and 90.4 resp.) [14,15], and they are indicative of the presence of an electronegative substituent attached to molybdenum. Indeed the mass spectrum of IV exhibited the parent ion *m/z* 283 and significant amounts of the fragments *m/z* 133 and 135 for (^{98}Mo–^{35}Cl) and (^{98}Mo–^{37}Cl) isotopes, respectively.

Thus the ultimate reactions of isopropylnitronate with the π-allyl cation Ib correspond to both (a) hydride transfer to a carbon terminus to produce the η^2-olefin complex III and (b) chloride displacement of CO to produce IV. The former represents an overall reduction of the cationic metal complex by the nitrocarbanion. As such, it is in marked contrast to the behavior of organic electrophiles which are known to react with nitrocarbanions by oxygen atom transfer [16,17]. Although it is certain that chlorine incorporation into IV occurred from a

TABLE 2

PROTON CHEMICAL SHIFTS (δ) IN [(η^5-C_5H_5)Mo(CO)(NO)(η^2-olefin) COMPLEXES [a]

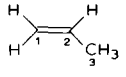
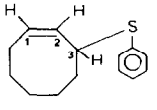
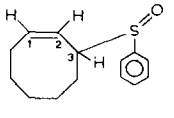
Complex	Olefin	Cp	H_A	H_B	H_C	Other
II		5.81 (s)	3.93 (br s)	3.87 (br s)	2.13 (br s)	3.71 (br s); 2.25 (br s)
IIIa		5.55 (s)	2.87 (br dd)		3.74 (m)	1.19 (d)
V		major 5.35 (s); minor 5.19 (s)	2.77 (br s)	2.23 (br s)	1.72 (br s)	7.23 (m) 3.38 (br s)
VI [b]		5.60 (s)	3.01 (m)		3.65 (m)	7.44 (m); 1.98–1.22 (br m)
VII [b]		5.71 (s)	3.05 (m)		3.63 (m)	7.74 (m); 2.73 (m); 1.97–1.55 (br m)

[a] δ in ppm relative to TMS; $CDCl_3$; 25°C. [b] 15°C.

reactive intermediate upon work-up with methylene chloride, we have been unable to identify the precursor responsible for this subsequent substitution reaction (see Experimental section). It is important to note however that the same competition for hydride addition and chlorine substitution to afford IIIb and IV, respectively, also obtains with the alkylnitronates derived from nitromethane, nitroethane, and 1-nitropropane.

TABLE 3

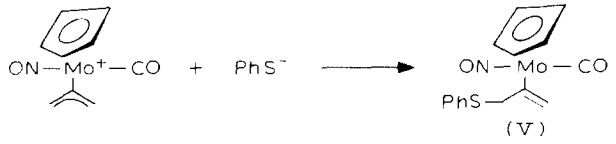
^{13}C CHEMICAL SHIFTS (δ) OF [(η^5-C_5H_5)Mo(CO)(NO)(η^2-olefin)] COMPLEXES [a]

Complex	Olefin	CO	Cp	C(1)	C(2)	C(3)	Other
IIIa		[c]	95.8	53.5	29.6	8.6	–
VI		249.5 (s)	96.3 (d)	[c]	[c]	62.7 (d)	132.8 (s); 131.1, 128.8, 126.9 (d); 52.7, 41.1, 32.8, 29.7 26.2 (t)
VII [b]		230.9 (s)	96.4 (d)	50.5 (br d)	66.1 (br d)	63.0 (d)	142.0 (s); 129.8, 128.7; 123.9 (d); 32.7, 31.3; 27.1, 26.6; 24.4 (t)

[a] δ in ppm relative to TMS. 25°C. [b] 0°C. [c] Not observed.

Mercaptide as a nucleophile

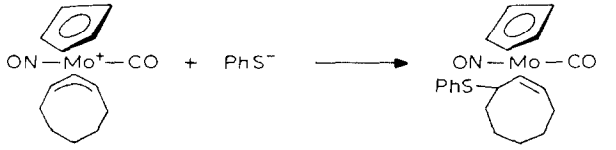
The π-allyl cation Ib reacted rapidly with thiophenolate anion which was generated in situ from thiophenol and triethylamine in acetonitrile solutions. The mercaptide adduct V η^5-$C_5H_5Mo(CO)(NO)(\eta^2$-$CH_2{=}C(CH_3)CH_2SPh)$ was isolated as a red-brown solid in 68% yield. This complex proved to be thermally unstable, and cleanly liberated 2-methallyl phenyl thioether upon slight heating. The mercaptide adduct V was produced as a mixture of two diastereomers, as indicated by the presence of a pair of minor absorptions appearing as shoulders on the major CO and NO stretching bands in the IR spectrum. The minor component also appeared in the ^{1}H NMR spectrum as a slightly shifted resonance of the Cp ligand as given in Table 2. A moderate selectivity was indicated by the diastereomeric ratio of ~4/1, evaluated by ^{1}H NMR integration and IR band intensities. The lack of complete stereospecificity in adduct formation is accountable if one considers both the rates of nucleophilic addition and the equilibrium population of *endo* and *exo* conformers of Ib [6,14].



(8)

(V)

In order to determine whether a chiral metal center would promote greater stereoselectivity, we examined the diastereomeric selectivity in the nucleophilic addition to a prochiral allylic ligand. Indeed the addition of thiophenolate to the cyclooctenyl complex Ic was rapid at −20°C to afford a single adduct VI.

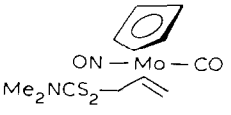


(9)

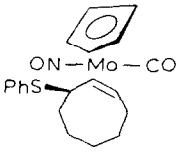
(VI)

This stereochemical outcome was readily apparent from the sharp single Cp resonance in both the ^{1}H and ^{13}C NMR spectra of VI, as well as the single resonance for the sulfur-bearing methine carbon in the ^{13}C NMR spectrum. The identity of the organic ligand was confirmed by comparison with an authentic sample of 3-cyclooctenyl phenyl thioether [18].

The high selectivity observed in mercaptide addition to the coordinated cyclooctenyl ligand in Ic mimics that previously observed with the carbon nucleophiles, deuteride and hydroxide, in which predominant nucleophilic attachment was shown to occur *cis* to the NO ligand (in the *exo* conformation of the cation) and the approach of the nucleophile is exclusively *anti* to the metal center [4,6,7,14]. We judge from the stereochemistry determined by X-ray crystallography for the adduct **A** derived from the addition of the dithiocarbamate ion to the π-allyl cation Ia [8], that the single isomer VI has the analogous structure **B** shown below.



(A)



(B)

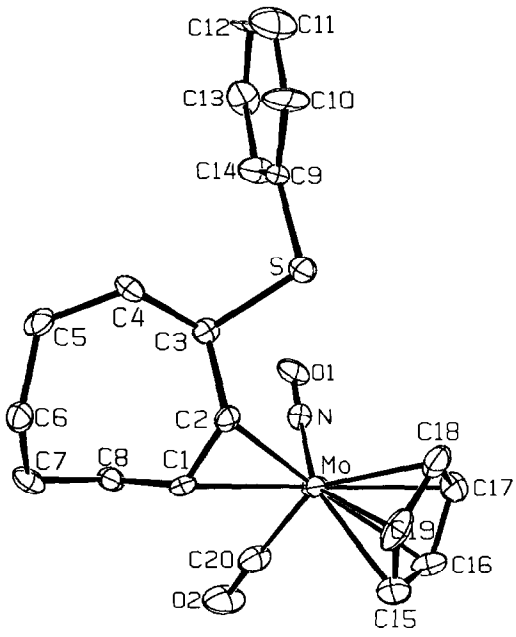


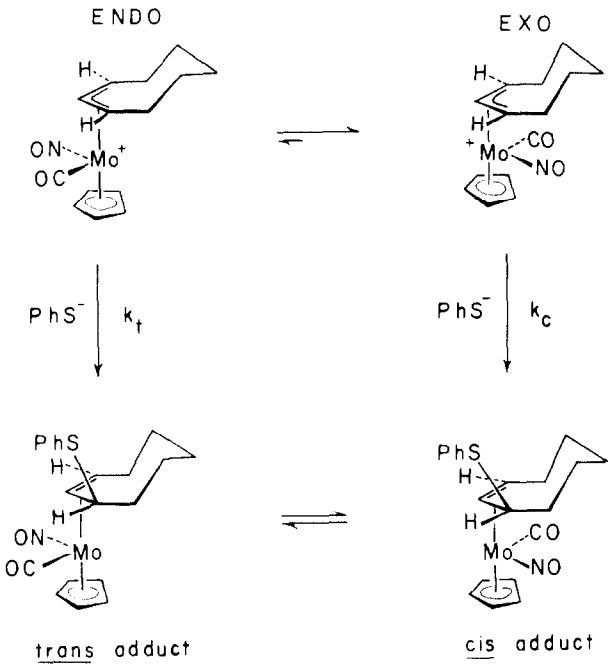
Fig. 1. ORTEP diagram of the phenyl 3-cyclooctenyl sulfide complex VI derived from the nucleophilic addition of thiophenolate to $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-cyclooctenyl})^+$. For clarity, the hydrogens are omitted.

In order to establish this point, we successfully grew a single crystal of the sulfide complex VI for X-ray crystallography. The ORTEP diagram in Fig. 1 indeed establishes the *anti* stereochemistry for the thiophenolate adduct **B**. It is interesting to note that the stable form in the crystal is to locate the sulfur atom in a pseudo-equatorial conformation as a result of a concomitant ring flip of the cyclooctenyl moiety. As a result, the nonbonded distance from the sulfur atom to the molybdenum center is 3.66 Å, which compares with 3.01 Å for the sum of the Van der Waal's radii of S and Mo.

Since the cyclooctenyl cation Ic is formed in the *endo* conformation [6], the production of the adduct **B** requires either *trans* addition (k_t) or a prior nucleophile-induced (*endo* → *exo*) interconversion followed by *cis* addition (k_c), as schematically presented below. Faller and coworkers favor the latter route [7]. The favored *cis* addition to the more stable *exo* conformer also accords with the theoretical calculations of Hoffman et al. [19].

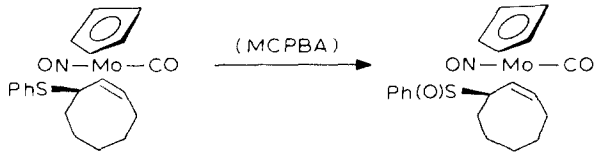
Stereospecific oxidation of coordinated sulfide ligands

Owing to the high stereoselectivity observed in the mercaptide addition, we also examined the possibility of employing the chiral metal center to effect high enantioselective conversion of the coordinated alkenyl phenyl sulfide to the corresponding sulfoxide. Treatment of the sulfide complex VI with *m*-chloroperbenzoic acid (MCPBA) indeed afforded a single isomer of $(\eta^5\text{-}C_5H_5)Mo(CO(NO)\text{-}(\eta^2\text{-}3\text{-}$cyclooctenyl phenyl sulfoxide) (VII). This new complex exhibited a strong band at 1051 cm^{-1} in the IR spectrum, characteristic of the sulfoxide stretching vibration [20], and the mass spectral analysis revealed the parent ion at m/z 455.



SCHEME 1

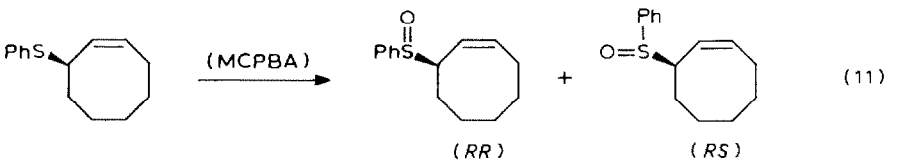
The formation of the sulfoxide complex VII as a single diastereomer was evident from the ^{1}H and ^{13}C NMR spectra which showed a pair of sharp single η^5-C_5H_5 resonances, and a single resonance for the sulfur-bearing methine group in the ^{13}C NMR spectrum. The temperature-independent NMR spectra over a 100° range from −50 to +55°C indicated the coordinated sulfoxide ligand to be rather firmly locked into a single conformation.



(10)

(VII)

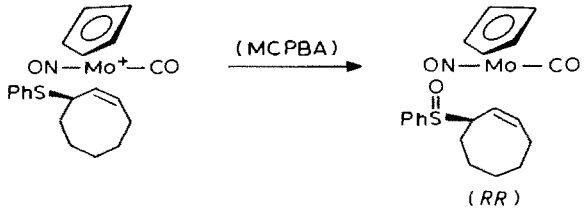
The coordinated sulfoxide is slowly liberated from the complex even at room temperature, and the free 3-cyclooctenyl phenyl sulfoxide was isolated in 95% yield as a sharp melting solid (m.p. 115–116°C). On the other hand, 3-cyclooctenyl phenyl sulfoxide obtained from the direct oxidation of 3-cyclooctenyl phenyl sulfide with *m*-chloroperbenzoic acid is an amorphous solid melting over a 5° range from 93.0 to 98.0°C. Inspection of the ^{1}H NMR spectrum of the latter clearly indicated it to consist of a 2/1 mixture of diastereoisomeric sulfoxides (see Experimental section). The sulfoxide diastereomers from *R*-3-cyclooctenyl phenyl sulfide are designated as *RR* (major) and *RS* (minor), as depicted in eq. 11.



(11)

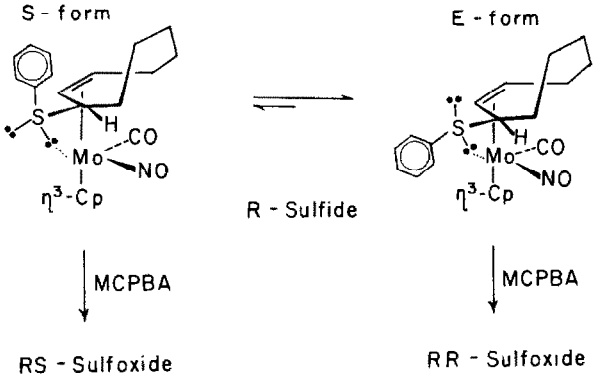
Thus in the free phenyl cyclooctenyl sulfide, the chirality at the methine center is insufficient to strongly differentiate the diastereotopic electron pairs on sulfur toward oxygen atom transfer from *m*-chloroperbenzoic acid.

The major isomer, as the racemate (*RR/SS*), was identical to that obtained from the sulfoxide complex VII as a single isomer. Thus the conversion of the sulfide complex VI to the sulfoxide complex VII in eq. 12 formally constitutes a stereospecific synthesis of sulfoxides from sulfides [21].



(12)

The stereoselective oxidation of the sulfur center in the sulfide complex VI could have occurred as a result of steric constraints imposed simply by complexation to the molybdenum center, especially since oxygen atom transfer from *m*-chloroperbenzoic acid is known to be strongly influenced by steric effects [22]. However, we believe that a more complete explanation invokes the exclusive diastereoselectivity to arise from the convergence of three types of chiral influences, viz., (a) the metal center, (b) the enantioface of the coordinated olefin and (c) the sulfur-bearing methine carbon. Proceeding from structure **B** (see Scheme 1) [23], we first envisage a ring flip of the cyclooctenyl moiety to allow the PhS substituent to adopt a pseudo-equatorial conformation (see Fig. 1). This conformation, presented in Scheme 2, allows juxtaposition of the sulfur and metal centers (indicated by the dotted line) sufficient to differentiate the two diastereotopic electron pairs on sulfur, which we have



SCHEME 2

designated as E (eclipsed) and S (staggered). If so, the preferential formation of the sulfoxide isomer *RR* (or *SS*) suggests E to be the more important conformer of VI in the oxygen atom transfer from *m*-chloroperbenzoic acid.

Various attempts to exploit the stereoselectivity inherent in the coordinated sulfoxide complex were unsuccessful (see Experimental section) [24].

Experimental section

Materials

Molybdenum hexacarbonyl (Aldrich Chemical Co.) and nitrosyl hexafluorophosphate (Alfa Products) were used as received. The series of π-allyl cations (η^5-C_5H_5)Mo(CO)(NO)(η^3-allyl)$^+$ (Ia, b and c) were prepared as the hexafluorophosphate salts from the dicarbonyl precursors by treatment in situ with nitrosyl hexafluorophosphate. The dicarbonyl precursors (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_3H_5) (IXa), (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_4H_7) (IXb) and (η^5-C_5H_5)Mo(CO)$_2$(η^3-C_8H_{13}) (IXc) was prepared by the method described by Hayter [25], and they have been previously characterized [10,15].

Acetonitrile (reagent grade) was refluxed over phosphorus pentoxide to remove water and then distilled. Tetrahydrofuran (reagent grade) was refluxed over sodium benzophenone under an argon atmosphere, distilled and stored under argon. It was redistilled from lithium aluminum hydride prior to use. Methylene chloride (reagent grade) was dried over Linde 4Å molecular sieve and saturated with argon prior to use. All reactions were carried out in Schlenk glassware with standard inert atmosphere techniques.

Instrumentation

Infrared spectra were recorded on either a Perkin–Elmer 337 or a Beckman IR-8 spectrophotometer, and only the principal bands are listed. ^{1}H NMR spectra were obtained at either 60, 100 or 300 MHz, using a Varian T-60, JEOL JNM-FX100 or Nicolet NT300 spectrometer, respectively. ^{13}C NMR measurements were obtained with the pulsed Fourier transform technique at 25.05 MHz using internal deuterium as a field frequency lock. Chemical shifts are reported in ppm relative to internal tetramethylsilane in the indicated solvent. [NMR measurements were routinely made at 25°C, unless otherwise specified.] Mass spectra were taken on an AEI MS-12 spectrometer at $\geqslant$ 60 eV. Only the most characteristic and/or the most intense fragment ions are tabulated. The parent ions of all the organomolybdenum compounds were taken to be those arising from ^{98}Mo in natural abundance of 23.78%.

Thin-layer chromatography (TLC) was performed using Eastman No. 6060 silica gel sheets with a fluorescent indicator. Developing solvents are as indicated, and visualization was achieved using a UV irradiation, or by spraying the plate with 50% v/v sulfuric acid in methanol. Column chromatography was carried out using gravity-flow columns packed with Fisher alumina (neutral or acid-washed, 80–200 mesh), florisil or Matheson, Coleman and Bell silica gel (100–200 mesh). The fractions were collected under argon. Flash chromatography [25] was performed on columns packed with either EM Reagents kieselgel 60 (200–400 mesh), or EM Reagents aluminum oxide 60 GF-254 (neutral, Type E), using argon pressure. Gasliquid chromatographic analysis was accomplished on a Varian Series 2800 instrument equipped with on-column injection capability and a flame ionization

detector with a 6′ × 1/4″ o.d. pyrex column packed with 6% OV-17 on Gas-Chrom Q (80–100 mesh) using a helium carrier flow of 30 ml min^{-1}.

Reaction of [(η^3-C_5H_5)Mo(NO)(CO)(η^3-2-methallyl)]PF_6 with sodium methoxide

A solution of 0.384 g (1.40 mmol) of (cyclopentadienyldicarbonyl(η^3-2-methallyl)molybdenum (IXb) in 5 ml degassed acetonitrile was stirred at 0°C under an argon atmosphere. Conversion of IXb to Ib was accomplished by the addition of a solution of 0.25 g (1.43 mmol) nitrosyl hexafluorophosphate in acetonitrile, and stirring the resultant mixture at 0°C for 30 min. Thereafter 2 ml of a saturated solution of anhydrous sodium carbonate in methanol (pH ~ 9) was added via syringe, and the reaction mixture allowed to warm to room temperature. Stirring at this temperature for a period of 22 h while monitoring the reaction by TLC (SiO_2, CH_2Cl_2) finally revealed a fast-moving yellow spot which stained deep blue upon spraying with an acidic methanol solution ($R_f = 0.48$). Most of the solvent was removed in vacuo, and the residue taken up in tetrahydrofuran. This solution was filtered rapidly through a bed of acid-washed alumina (act. II), and the solvent removed in vacuo to yield 0.28 g of a red-orange, amorphous solid. The crude product was purified by preparative TLC on silica gel (CH_2Cl_2 eluent) to afford 69.1 mg (16.1%) [(η^5-C_5H_5)Mo(NO)(CO)(η^2-2-methallyl methyl ether)] (II) as a yellow-orange, air sensitive semi-solid. IR (neat): 3090w, 2950m, 1960s, 1630s, 818s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.81 (br s, 5H), 3.93 (v br s, 1H), 3.87 (v br s, 1H), 3.71 (br s, 3H), 2.25 (v br s, 2H), 2.13 (br s, 3H).

Reaction of [(η^5-C_5H_5)Mo(NO)(CO)(η^3-allyl)]PF_6, with sodium borohydride

A solution of 0.536 g (2.06 mmol) of (cyclopentadienyl)dicarbonyl(η^3-allyl)molybdenum (IXa) in 3 ml degassed acetonitrile was stirred at 0°C under an argon atmosphere. An aliquot (4.10 ml) of a 0.516 *M* nitrosyl hexafluorophosphate solution in acetonitrile was added via syringe. [This solution was prepared by dissolving the appropriate amount of $NOPF_6$ (weighed quickly, minimizing exposure to the atmosphere) in 10 ml degassed acetonitrile. This standard solution may be stored for several weeks at 0°C under argon in all-glass containers, and aliquots withdrawn as needed against a counter-current of argon.] The resultant yellow-orange solution was stirred at 0°C for 30 min (i.e., until all gas evolution had ceased). Then a cold solution (~ 0°C) of 50 mg sodium borohydride in 10 ml methanol was added, and the resulting mixture stirred at room temperature for 1 h. Most of the solvent was removed in vacuo, and the residue filtered quickly through a bed of acid-washed alumina (act. IV) with the aid of chloroform. The chloroform solution, analyzed by both TLC (SiO_2, CH_2Cl_2) and ^{1}H NMR spectroscopy indicated the presence of one major organomolybdenum compound ($R_f = 0.75$, δ 5.55 ppm). Removal of solvent afforded 121 mg (22.3% yield) of [(η^5-C_5H_5)Mo(NO)(CO)(η^2-propene)] (IIIa) as a bright yellow, air-sensitive solid. [*Note*: No high field signals, characteristic of metal hydrides, were observed in the ^{1}H NMR spectrum. Similarly, low field resonances, characteristic of metal formyls were also absent.] IR (KBr pellet): 3090w, 2970m, 1975s, 1622s, 809s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.55 (s, 5H), 3.74 (br m, 1H), 2.87 (br dd, *J* 11.7, 7.1 Hz, 2H), 1.19(d, *J* 5.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 95.8(d), 53.5(t), 29.6(d), 8.6(q), CO omitted.

Reaction of [(η^5-C_5H_5)Mo(NO)(CO)(η^3-2-methallyl)]PF_6, with sodium borohydride

A solution of 0.397 g (1.45 mmol) of (cyclopentadienyl)dicarbonyl(η^3-2-methallyl)molybdenum (IXb) in 3 ml degassed acetonitrile was stirred at 0°C under an argon atmosphere. An aliquot (2.55 ml) of 0.572 *M* nitrosyl hexafluorophosphate solution in acetonitrile (prepared as described above) was added with the aid of a hypodermic syringe. The resultant yellow-orange solution was stirred at 0°C for 30 min until all gas evolution had ceased. Then a cold solution of 50 mg sodium borohydride in 10 ml methanol was added, and the resulting mixture stirred at room temperature for 1 h. Most of the solvent was removed in vacuo, and the residue was filtered quickly through a bed of acid-washed alumina (act. IV) with the aid of chloroform. The chloroform solution, analyzed by both TLC (SiO_2, CH_2Cl_2) and ^{1}H NMR spectroscopy, indicated the presence of one major organomolybdenum compound (R_f = 0.72, δ 5.50 ppm). Removal of solvent afforded 220 mg (54.8%) of [(η^5-C_5H_5)Mo(NO)(CO)(η^2-isobutene) (IIIb) as a bright yellow, air-sensitive solid. [*Note*: No high field signals, characteristic of metal hydrides were observed by ^{1}H NMR spectroscopy. Similarly, low field resonances, characteristic of metal formyls were also absent.] IR (KBr pellet): 3130w, 2980m, 1952s, 1603s, 798s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.50(s, 5H), 2.34 (s, 1H), 2.29 (s, 1H), 1.83 (s, 3H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 235.6(s), 95.9(d), 79.7 (s), 38.9(t), 30.2(q), 28.7(q); MS (rel. Int.): *m/z* 27(5), 28(100), 39(25), 41(51), 55(15), 56(25), 66(10), 161(6), 163(7), 165(5), 193(12), 215(5), 217(4), 249(6), 277(5). The ^{1}H and ^{13}C NMR spectra of IIIb were unaffected by increasing the temperature from −52 to +62°C. Complex IIIb proved to be identical to the major product obtained upon admixture of a nitronate anion (vide infra).

Reaction of [(η^5-C_5H_5)Mo(NO)(CO)(η^3-2-methallyl)]PF_6, with diethylammonium isopropylnitronate

A solution of 0.748 g (2.73 mmol) of (cyclopentadienyl)dicarbonyl(η^3-2-methallyl)molybdenum (IXb) in 3 ml degassed acetonitrile was stirred at 0°C under argon. Conversion to Ib was accomplished by the addition of 5.5 ml of a 0.495 *M* nitrosyl hexafluorophosphate solution in acetonitrile, and stirring the resultant solution at 0°C for 30 min. A 1.96 *M* diethylammonium isopropylnitronate solution was prepared by mixing equimolar amounts of diethylamine and 2-nitropropane in the appropriate volume of acetonitrile. A 2 ml aliquot (3.82 mmol) of this solution was then added to the solution of Ib maintained at 0°C. The resultant mixture was stirred at 0°C for 2 h, then at room temperature for an additional 1 h. Most of the solvent was removed in vacuo. The residue was taken up in methylene chloride which was then filtered quickly through a bed of acid-washed alumina (act. IV). Removal of solvent afforded 1.0 g of a red-orange, semi-solid. ^{1}H NMR analysis of the crude product indicated the presence of two organomolybdenum compounds (δ 5.88, 5.50). Fractionation of this sample on an acid-washed alumina column (act. II), using a 4/1 mixture of hexane and dichloromethane as the eluent, followed by solvent removal, afforded 230 mg (30.4%) of a bright yellow, air-sensitive solid, homogeneous by TLC (SiO_2, CH_2Cl_2, R_f 0.72). This product proved to be identical in all respects (i.e., IR, ^{1}H NMR, ^{13}C NMR, MS) to complex IIIb (vide supra). Subsequent elution of the alumina column with methylene chloride afforded a second, orange-colored band. Evaporation of solvent from this second fraction afforded 82 mg of a red-orange, amorphous solid, characterized as [(η^5-

C_5H_5)(MoCl(NO)(η^3-C_4H_7)] (IV) (10.6%). IR (KBr pellet): 3060w, 1600s, 799s cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.88 (s, 5H), 4.48 (br s, 1H), 3.90 (br d, J 5.2 Hz, 1H), 2.66 (dd, J 4.2, 2.2 Hz, 1H), 2.37(br d, J 2.2 Hz, 1H), 2.14(s, 3H); ^{13}C NMR ($CDCl_3$): δ 103.5(d), 88.7(s), 70.7(t), 48.7(t), 21.8(q), CO omitted; MS (rel. int.): m/z 27(48), 28(73), 29(36), 30(29), 39(75), 41(34), 43(25), 55(54), 57(22), 133(26), 135(23), 136(21), 170(26), 172(30), 208(100), 212(67), 214(68), 216(77), 218(75), 253(68), 283(49). [*Note*: No high field signals, characteristic of metal hydrides were observed in the ^1H NMR spectrum of the crude product. Similarly, low field signals, characteristic of metal formyls were also absent.]

Reactions of Ib with other nitronates

(A) Nitromethide. A solution of 0.495 g (1.81 mmol) IXb was converted at 0°C to Ib as before, and treated with a 3 ml aliquot of a 0.72 *M* diethylammonium nitromethide solution (prepared by mixing equimolar amounts of diethylamine and nitromethane in the appropriate volume of acetonitrile). The reaction mixture was stirred at 0°C for 1 h, then at room temperature for an additional 2 h. Filtration of the concentrated mixture through Florisil, followed by removal of solvent in vacuo afforded 0.84 g of a red-brown semi-solid. The crude product was fractionated through an acid-washed alumina column with chloroform as the eluent to yield 0.103 g of a mixture of IIIb, (26.4% by ^1H NMR analysis, δ 5.50) and IV, (14.9% by ^1H NMR analysis, δ 5.88), and an unidentified remainder of polar material (TLC: SiO_2, CH_2Cl_2, $R_f < 0.10$).

(B) Ethylnitronate. A solution of 0.521 g (1.90 mmol) IXb in acetonitrile was converted to Ib as before, and treated with a 2.5 ml aliquot of a 0.87 *M* diethylammonium ethylnitronate solution (prepared by mixing equimolar amounts of diethylamine and nitroethane in the appropriate volume of acetonitrile). The reaction mixture was stirred at 0°C for 30 min, then at room temperature for an additional 2 h. Concentration and work-up afforded 0.172 g of a mixture of IIIb, (24.5% by ^1H NMR analysis, δ 5.50) and IV, (15.5% by ^1H NMR analysis δ 5.88). Chromatography on neutral alumina (act. II), using a hexane methylene chloride (4/1) mixture as eluent, yielded 62.6 mg of pure IIIb (11.9%), which exhibited a proton NMR spectrum identical to that of IIIb which was obtained from isopropylnitronate (vide supra).

(C) n-Propylnitronate. A solution of 0.495 g (1.81 mmol) IXb in acetonitrile was converted to Ib, and treated with a 2.5 ml aliquot of a 0.90 *M* diethylammonium n-propylnitronate solutin (prepared by mixing equimolar amounts of diethylamine and 1-nitropropane in the appropriate volume of acetonitrile). The reaction mixture was stirred at 0°C for 30 min, then at room temperature for an additional 2 h. Concentration and work-up afforded 0.170 g of a mixture of IIIb, (26.0% by ^1H NMR analysis, δ 5.50) and IV, (14.0% by ^1H NMR analysis, δ 5.88). Chromatography on neutral alumina (act. II), using 4/1 mixture of hexane and methylene chloride as eluent, afforded 66.4 mg of pure IIIb (13.3%), which exhibited an identical ^1H NMR spectrum compared with that of IIIb obtained from isopropylnitronate (vide supra).

(D) Isopropylnitronate (deuteration conditions). A solution of 0.407 g (1.49 mmol) IXb in acetonitrile-d_3 was converted to Ib as before, and treated with a 0.75 ml aliquot of a 2.2 *M* *N,N*-dideuterio-diethylammonium isopropylnitronate solution (prepared by mixing 0.5 ml *N*-deuterio-diethylamine and 0.5 ml 2-deuterio-2-

nitropropane in a total volume of 2.00 ml of acetonitrile-d_3). [2-Deuterio-2-nitropropane was prepared by shaking 2-nitropropane repeatedly with solutions of diethylamine in D_2O, followed by distillation. It was assayed to be > 90% deuterated by ^1H NMR analysis. *N*-deuterio-diethylamine was prepared by the slow addition of n-butyllithium (in hexane) to a neat solution of diethylamine, followed by quenching in D_2O and distillation. It was assayed to be > 98% deuterated by ^1H NMR analysis.] The reaction mixture was stirred at 0°C for 2 h, and warmed to room temperature while simultaneously removing the solvent in vacuo. The residue was exhausted with methylene chloride and the solution filtered quickly through a bed of acid-washed alumina (act. II). Removal of solvent afforded 0.311 g of a mixture of IIIb, (66% by ^1H NMR analysis, δ 5.50) and IV, (34% by ^1H NMR analysis, δ 5.88). Flash chromatography of the crude product on silica gel (using a 1/1 mixture of hexane and dichloromethane as the eluent), yielded 96 mg of pure IIIb (23.3%). This sample exhibited a ^1H NMR spectrum and a mass spectrum identical with those of IIIb synthesized using non-deuterated reagents, indicative of little or no deuterium incorporation.

Control experiments

(A) A solution of 0.65 g (2.39 mmol) IXb in acetonitrile was converted to the cation Ib as described previously, and divided into two portions. Through one portion was bubbled a slow flow of carbon monoxide while cooling to −20°C, followed by the addition of a solution of diethylammonium isopropylnitronate via syringe. The reaction mixture was warmed to 0°C, and stirred 1 h with continuous bubbling of CO. Thereafter, the solvent was removed in vacuo, methylene chloride added, and the solution filtered quickly through acid-washed alumina (act. II). Removal of solvent afforded a dark brown semi-solid. ^1H NMR analysis of the crude product revealed a very broad Cp resonance at − 5.40 ppm, however, no sharp signals attributable to either IIIb or IV were observed.

(B) The remainder of the original solution of Ib in acetonitrile was transferred to an NMR tube, sealed with a septum cap under argon, and 0.10 ml diethylamine was added via syringe. Immediate darkening was observed. ^1H NMR analysis indicated the presence of a board Cp resonance at − 5.40 ppm, but no signal due to IIIb was observed. Subsequent addition of 2-nitropropane led to no IIIb at 0°C. After prolonged agitation at room temperature (− 1 h), followed by filtration through acid-washed alumina (act. II) with the aid of methylene chloride and solvent removal, the ^1H NMR analysis indicated the presence of both IIIb (δ 5.50) and IV (δ 5.88) in the crude product (− 1/1 by NMR integration).

(C) A similar experiment with "inverse addition" of 2-nitropropane followed by diethylamine addition to a solution of Ib, monitored by TLC (SiO_2, CH_2Cl_2), afforded IIIb only after introduction of the amine. Work-up in methylene chloride afforded both IIIb and IV (δ 5.50, 5.88, resp. by ^1H NMR analysis).

Reaction of [(η^5-C_5H_5)Mo(NO)(CO)(η^3-2-methallyl)]PF_6 with triethylammonium thiophenolate

A solution of 0.397 g (1.45 mmol) of (cyclopentadienyl)dicarbonyl(η^3-2-methallyl)molybdenum (IXb) in 3 ml degassed acetonitrile was stirred at 0°C under argon. Conversion to Ib was accomplished by the addition of 2.55 ml of a 0.572 *M* nitrosyl hexafluorophosphate solution in acetonitrile and stirring the resultant

mixture at 0°C for 30 min. A solution of 7.25 *M* triethylammonium thiophenolate was prepared by mixing 7.98 g (72.5 mmol) thiophenol dissolved in 5 ml acetonitrile with 5 ml triethylamine. A 0.2 ml aliquot (1.45 mmol) of this solution was added to the solution containing Ib. The resultant mixture was stirred at 0°C for 2 h. Thereafter, the solvent was removed in vacuo, the residue triturated with chloroform, and the chloroform solution filtered quickly through a bed of Florisil. The filtrate was washed with cold (− 5°C) 0.1 *N* aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and the solvent removed in vacuo to afford 0.382 g (68.4%) of [(η^5-C_5H_5)Mo(NO)(CO)(η^2-2-methallylphenylthioether)] (V) as a red-brown, amorphous solid. TLC analysis (SiO_2, hexane/CH_2Cl_2, 1/1) showed a single component (R_f 0.66). ^{1}H NMR and IR analysis, however, indicated the presence of two η^2-olefin complexes (δ 5.35, 5.19; ν(CO) 1966, 1907 cm^{-1}; ν(NO) 1626, 1585 cm^{-1}), in a ratio of 4/1, respectively. IR (neat): 3100w, 3050w, 2940m, 1966s, sh. 1907, 1626s, sh. 1585, 809s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.23 (br m, 5H), 5.35, 5.19(s, 5H), 3.38(br s, 2H), 2.77(br s, 1H), 2.23(br s, 1H), 1.72(br s, 3H). After 2.5 h at 60°C, the δ 5.35 resonance had completely disappeared, and signals arising from free thioether (vide infra) had appeared (δ 4.77(m), 3.47(s), 1.82(s)). To confirm this analysis, an authentic sample of 2-methallyl-phenyl-thioether was prepared as follows: 10.74 g (119 mmol) of 2-methyl-3-chloropropene was stirred in anhydrous ether at room temperature. To this solution was added 20 ml of a 1/1 v/v mixture of triethylamine and thiophenol, and the resultant mixture stirred at room temperature 4 h. The ethereal solution was washed quickly with cold (− 5°C) 0.1 *N* aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and the volatiles removed in vacuo. Kugelrohr distillation afforded 12.7 g (65.9%) of 2-methallyl-phenylthioether, distilling at an air bath temperature of 84–86°C at 1.5 mmHg. IR (neat): 3075w, 2970s, 2940s, 2922w, 1650m, 1595m, 1233m, 1092m, 895m, 736m, 692m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.21(br m, 5H), 4.77(m, 2H), 3.47(br s, 2H), 1.82(s, 3H); ^{13}C NMR ($CDCl_3$): 140.3(s), 136.3(s), 129.5(d), 128.3(d), 125.7(d), 113.6(t), 41.4(t), 20.8(q).

Reaction of [(η^5-C_5H_5)Mo(NO)(CO)(η^3-cyclooctenyl)]PF_6 with triethylammonium thiophenolate

A solution of 0.289 g (0.882 mmol) of (cyclopentadienyl)dicarbonyl(η^3-cyclooctenyl)molybdenum (IXc) in 3 ml degassed acetonitrile was stirred at −20°C. Conversion to Ic was accomplished by the addition of 1.05 ml of a 0.875 *M* nitrosyl hexafluorophosphate solution in acetonitrile (prepared as described above), and stirring at −20°C for 30 min. A mixture of 1.08 g thiophenol and 1.10 g triethylamine diluted to a total volume of 10 ml with acetonitrile was prepared, and a 1 ml aliquot (corresponding to 0.98 mmol triethylammonium thiophenate) of this solution was added to the organomolybdenum mixture with the aid of a hypodermic syringe. The resultant reaction mixture was stirred at −20°C for a period of 30 min. Thereafter, the solvent was removed in vacuo, the residue triturated with methylene chloride, and the solution percolated quickly through a bed of Florisil. Removal of the solvent in vacuo, and "flash" chromatography on silica gel using a 3/2 mixture of hexane and methylene chloride as the eluent, followed by evaporation of solvent afforded 0.238 g (61.5%) of [(η^5-C_5H_5)Mo(CO)(NO)(η^2-cyclooctenyl-3-phenyl-thioether)] (VI) as a yellow-orange, air-sensitive semi-solid, homogeneous by TLC analysis (SiO_2, hexane/dichloromethane (1/1), R_f 0.64). IR (C_6H_{12}): 3060w, 1971s,

1642s, 801s cm^{-1}; mass spectrum (EI), *m/e* (rel. int.): 439(2), 411(2), 330(0.8), 301(4), 272(3), 270(3), 269(2), 219(7), 218(48), 110(15), 109(40), 108(23), 79(8), 77(9), 67(25), 65(18), 50(20), 41(20), 40(15), 39(100), 29(20), 28(4), 27(31); ^1H NMR ($CDCl_3$): δ 7.44(br m, 5H), 5.60(s, 5H), 3.65(br m, 1H), 3.01 (br m, 2H), 1.98–1.22(br m, 10H); ^{13}C NMR ($CDCl_3$): δ 249.5(s), 132.8(s), 131.1(d), 128.8(d), 126.9(d), 96.3(d), 62.7(d), 52.7(t), 41.1(t), 32.8(t), 29.7(t), 26.2(t), (olefinic carbons too broad to be observed). When the complex VI was heated above 55°C, it resulted in decomposition with liberation of the allylic thioether. This was evident from the disappearance of the cyclopentadienyl resonance, concomitant with the appearance of new signals due to the free thioether (vide infra) by ^1H NMR spectroscopy. An authentic sample of cyclooctenyl-3-phenyl thioether was prepared as follows: 5.00 g of 3-bromo-cyclooctene (45.5 mmol) was stirred in anhydrous ether at room temperature. A mixture of 6.0 g thiophenol and 6.2 g triethylamine was added dropwise with constant stirring, and the resultant mixture was stirred at room temperature for 12 h. Thereafter the reaction mixture was washed with 0.1 *N* aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and the volatiles removed in vacuo. Kugelrohr distillation of the residual oil afforded 6.85 g (69.1%) of the pure thioether. ^1H NMR ($CDCl_3$): δ 7.20(br m, 5H), 5.57(m, 2H), 4.10(m, 1H), 2.37–1.04(v br m, 10H); ^{13}C NMR ($CDCl_3$): δ 136.2(s), 133.0(d), 130.2(d), 129.6(d), 128.3(d), 125.6(d), 43.3(d), 35.5(t), 29.1(t), 26.5(t), 26.2(t), 25.5(t). Pyrolysis of the thioether complex VI, in the injection part of a gas chromatograph yielded a single band with a retention time identical to that of the authentic thioether (21.0 min, temp. program: init. temp. 100°C for 5 min, then 8°C min^{-1} to a final temp. of 250°C).

Reaction of [(η^5-C_5H_5)Mo(CO)(NO)(η^2-cyclooctenyl-3-phenylthioether)] with m-chloroperbenzoic acid

A mixture of 0.238 g (0.542 mmol) of (η^5-C_5H_5)molybdenum(carbonyl)-(nitrosyl)(η^2-cyclooctenyl-3-phenylthioether) (VI) 10 ml methylene chloride, and 1.0 g anhydrous potassium carbonate was stirred at −70°C under an argon atmosphere. A solution of 69 mg (0.40 mmol) *m*-chloroperbenzoic acid in 5.0 ml methylene chloride was prepared, and transferred to the organomolybdenum solution. The resultant solution was stirred for 1 h while slowly warming it to −20°C, then it was percolated quickly through a bed of basic alumina (act. II). The solvent was then removed in vacuo to afford 0.218 g of a yellow-orange, amorphous solid. Flash chromatography of the crude product on silica gel (using a 1/1 mixture of hexane and methylene chloride as the eluent and an argon head pressure) revealed two bands. The faster moving band, after evaporation of solvent, yielded 0.117 g VI (49.2% recovered starting material). The slower moving band, after evaporation of solvent, afforded 86.2 mg (68.6%, based on recovered VI) of [(η^5-C_5H_5)Mo(CO)(NO)(η^2-cyclooctenyl-3-phenylsulfoxide)] (VII) as a bright yellow, air sensitive, microcrystalline solid. IR (C_6H_{12}): 3040w, 3020w, 2920m, 1977s, 1636s, 1051m, 1018m, 800s cm^{-1}; mass spectrum (EI), *m/e* (rel. int.): 455(2), 427(6), 411(1), 320(3), 288(4), 218(7), 163(3), 126(51), 110(26), 109(50), 108(25), 93(16), 91(13), 79(40), 78(25), 77(30), 67(100), 66(24), 65(25), 55(40), 53(20), 51(27), 41(55), 39(50), 29(14), 28(25), 27(26); ^1H NMR ($CDCl_3$, 15°C): δ 7.47(br m, 5H), 5.71(s, 5H), 3.63(v br dd; d upon irrad. ~ 1.76 ppm, *J* 7.7 Hz, 1H), 3.05(v br d, *J* 9.7 Hz; v br s upon irrad. ~ 1.76 ppm, 2H), 2.73(v br d, *J* 11Hz; v br s upon irrad. ~ 1.76

ppm, 2H), 1.97–1.55(v br m, 8H); ^{13}C NMR ($CDCl_3$, 0°C): δ 230.9(s), 142.0(s), 129.8(d), 128.7(d), 123.9(d), 96.4(d), 66.1(br d), 63.0(d), 50.5 (br d), 32.7(t), 31.3(t), 27.1(t), 26.6(t), 24.4(t). Neither the ^1H NMR spectrum nor the ^{13}C NMR spectrum of VII was greatly affected upon changing the NMR probe temperature from -50 to $+55$°C (i.e., no coalescence of further splitting of signals was observed).

To the sulfoxide complex VII dissolved in methylene chloride, a slow stream of air was passed until the yellow solution darkened to red-orange ($\sim$ 15 min). The methylene chloride solution was washed with aq. $NaHCO_3$ 3 times, and dried over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo afforded a colorless micro-crystalline solid: m.p. 109–111°C (without recrystallization). ^1H NMR ($CDCl_3$): δ 7.55–7.40(m, 5H), 5.90–5.70(m, 1H), 5.55–5.30(dd, J 9.1, 8.8 Hz, 1H), 3.80–3.60(ddd, J 12.0, 9.1, 4.5 Hz, 1H), 2.15–1.75(m, 3H), 1.75–1.40(m, 5H), 1.40–1.10(m, 2H).

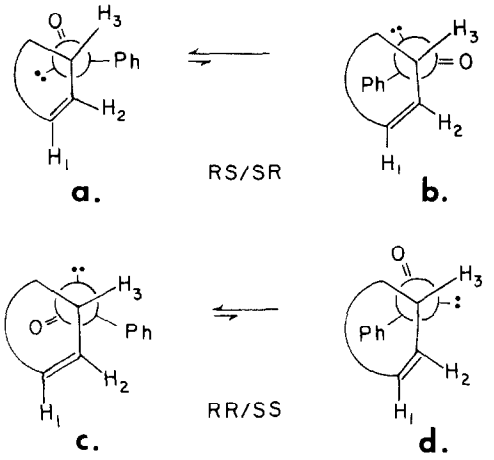
Oxidation of phenyl 3-cyclooctenyl sulfide with m-chloroperbenzoic acid

An authentic sample of phenyl 3-cyclooctenyl sulfoxide was prepared by the method of Johnson [20] as follows: A solution of 155 mg (0.90 mmol) *m*-chloroperbenzoic acid in 15 ml methylene chloride was added dropwise, with stirring, to a solution of 246 mg (1.00 mmol) phenyl 3-cyclooctenyl sulfide in 10 ml methylene chloride (maintained at 0°C). The solution was stirred at 0°C for 12 h, and filtered. The filtrate was then washed three times with 25 ml portions of aqueous $NaHCO_3$, dried over $MgSO_4$, and the solvent removed in vacuo to afford 300 mg of a yellow, amorphous solid. The crude product was purified by flash chromatography on silica gel with a 1/1 mixture of hexane and methylene chloride, and the solvent removed in vacuo to afford 205 mg (78.2% yield) of a diastereomeric mixture of cyclooctenyl-3-phenylsulfoxides as a white, amorphous powder (m.p. 93.0–98.0°C). IR (KBr pellet): 3030w, 2970m, 2945m, 1575m, 1052s, 1044s; ^1H NMR ($CDCl_3$, 22°C, 300 MHz): δ 7.68–7.60(m) for the minor isomer and 7.54–7.45(m) for the major isomer with 5H total; δ 5.90–5.72(br m) with 1H total; δ 5.68–5.57(dd, J 12.3, 9.3 Hz) for H_2 of the minor isomer and 5.51–5.40(dd, J 9.0, 9.0 Hz) for H_2 of the major isomer with 1H total; δ 3.76–3.63(ddd, J 12.0, 9.0, 4.5 Hz) for H_3 of the major isomer and 3.63–3.53(ddd, J 12.3, 8.6, 3.6 Hz) for H_3 of the minor isomer with 1H total; 2.15–1.80(br m) with 3H total; 1.70–1.50(br m) with 5H total, 1.50–1.25(br m) with 2H total.

The mixture of diastereomers (after purification by column chromatography on alumina) was dissolved in a minimum amount of methylene chloride, and twice the volume of n-hexane was added. Slow evaporation of the solvent afforded 2 distinct types of crystals which could be separated by hand. The major constituent consisted of long needles: m.p. 115–116°C. The minor constituent appeared as small prisms: m.p. 72–75°C. ^1H NMR (major constituent): identical with that obtained from the sulfoxide complex (vide supra). ^1H NMR (minor component): enriched in the minor isomer (55/45), as clearly judged by the intensity ratio of the unresolved multiplet due to the vinylic protons H_1 for both isomers plus H_2 for the minor isomer centered at δ 5.8(m, 1.55H) and the characteristic doublet splittings (dd, J 9.1, 8.8 Hz, 0.45H) of H_2 for the major isomer (vide supra) in the 90 MHz spectrum

Phenyl 3-cyclooctenyl sulfoxide liberated from complex VII exhibited a ^1H NMR spectrum which was the same as that of the major stereoisomer formed in the oxidation of free phenyl 3-cyclooctenyl sulfide (vide supra). Assignment of structures

for these two diastereomers was made by considering their Newman projections as follows.



a. b. c. d.

The sulfoxide oxygen in the (*RS/SR*) pair is flanked by H_3 in both of the predominant rotamers (**a** and **b**), while in the (*RR/SS*) sulfoxides, O approaches H_3 only in rotamer **d**. This effect is predicted to result in an upfield shift for H_3 in the (*RS/SR*) stereoisomer [27]. The minor isomer in the mixture under consideration possesses an upfield shifted signal for H_3 (δ 3.58 vs. δ 3.68 in the major isomer). Furthermore, the aromatic protons in 1-phenylethyl aryl sulfoxides have been observed to occur upfield in the (*RR/SS*) configurations relative to the (*RS/SR*) configurations [27a]. This effect is also observed for the major isomer in the mixture under consideration. These factors thus lead to the assignment of the (*RR/SS*) configuration to the major isomer formed in the standard organic oxidation of phenyl 3-cyclooctenyl sulfide.

Consequently, this same relative stereochemistry is present in the complexed sulfoxide VII. Further verification of these assignments are in progress.

Attempted desulfurization of VII

A solution of 80 mg VII in 3 ml anhydrous methanol was stirred at room temperature under an argon atmosphere. Thereafter, 0.30 ml trimethyl phosphite was added, and the reaction mixture stirred at room temperature for a period of 16 h. The solution was then poured into 50 ml water, and partitioned with methylene chloride. Subsequent drying of the combined extracts over anhydrous sodium sulfate, and evaporation of solvent afforded 59 mg crude VII, apparently unchanged judging by IR, ^{1}H NMR, and ^{13}C NMR analysis.

Attempted alkylation of VII

A solution of 59 mg VII in 3 ml tetrahydrofuran was stirred at -70°C under an argon atmosphere. Thereafter, 0.10 ml of a 1.6 *M* n-butyllithium solution in hexane was added, and the mixture stirred at -70°C for 30 min. Then, 1 ml methyl iodide was added, and the resultant mixture was stirred while allowing it to warm to room temperature; the solution was stirred for an additional 4 h, and poured into 50 ml water. It was partitioned with methylene chloride. Subsequent drying of the com-

bined extracts over anhydrous sodium sulfate, and evaporation of solvent afforded VII, largely unchanged judging by IR and ^{1}H NMR analysis.

In a second attempt, a solution of 59 mg VII in 3 ml tetrahydrofuran and 1 ml hexamethylphosphoramide was stirred at −70°C under an argon atmosphere. Addition of n-butyllithium and methyl iodide, followed by aqueous work-up was described above, afforded a dark brown, amorphous solid. Analysis of this material by TLC (SiO_2, hexane/ethyl acetate, 4/1) indicated the complete absence of fast-moving ($R_f > 0.10$) organomolybdenum compounds (although several unidentified organic compounds were evident).

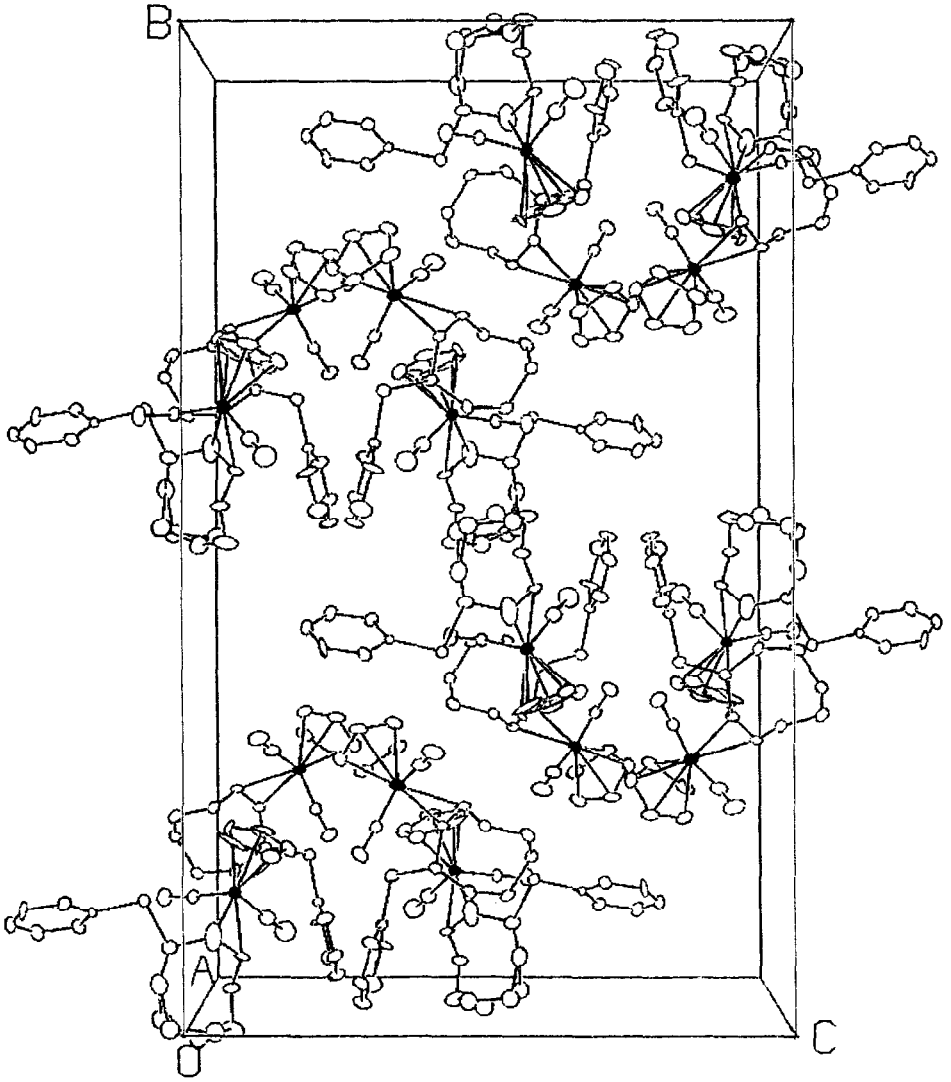


Fig. 2. ORTEP packing diagram for (η^5-C_5H_5)Mo(CO)(NO)(η^2-$C_8H_{13}SC_6H_5$) (VI) showing two independent molecules comprising the asymmetric unit.

Crystal structure of the phenyl 3-cyclooctenyl sulfide complex VI

Single crystals of (η^5-C_5H_5)Mo(CO)(NO)(η^2-phenyl 3-cyclooctenyl sulfide) suitable for X-ray crystallographic analysis were obtained by the slow evaporation of a solution consisting of a 3/1 mixture of hexane and methylene chloride at −20°C. A small yellow-orange plate of approximate dimensions $0.5 \times 0.5 \times 0.2$ mm was mounted on an Enraf–Nonius CAD-4 automatic diffractometer equipped with a Mo-K_α target tube. The final cell constants, as well as other information pertinent to data collection and refinement are listed in Table 1.

The Laue symmetry was determined to the *mmm* and from the systematic absences noted, the space group was unambiguously shown to be *Pbca*. Intensity standards showed no decay over the course of the data collection, and no absorption correction was made owing to the low value of the absorption coefficient.

The structure was solved by MULTAN [28], which revealed the positions of the molybdenum and sulfur atoms in the two independent molecules comprising the asymmetric unit, as shown in the ORTEP packing diagram of the unit cell in Fig. 2. The remaining non-hydrogen atoms were located during the difference Fourier syntheses. The two molecules were found to possess the same basic geometry. However, one of them had a partial disorder of the cyclooctene ring at C(5)/C(6). This disorder was accounted for by refining two separate semi-rigid groups having 50% populations at this site. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideally calculated positions. The hydrogens associated with the disorder were given 50% populations, and all hydrogens were assigned isotropic thermal parameters based on the thermal motion of the associated carbons. In the final cycles of full-matrix least-squares,

(*Continued on p. 53*)

TABLE 4

SUMMARY OF THE CRYSTAL DATA, INTENSITY COLLECTION, AND STRUCTURE REFINEMENT

Space group	*Pbca*, orthorhombic
Cell constants	*a* 11.914(2) Å
	b 33.166(12) Å
	c 19.804(4) Å
	V 7825 Å^3
Molecular formula	$MoSO_2NC_{20}H_{23}$
Formula weight	437.4
Formula units per cell	$Z = 16$
Density	ρ 1.49 g cm^{-3}
Absorption coefficient	μ 7.68 cm^{-1}
Radiation (Mo-K_α)	λ 0.71073 Å
Collection range	$4° \leqslant 2\theta \leqslant 35°$
Scan width	$\Delta\theta = (0.85 + 0.35 \tan\theta)°$
Maximum scan time	150 s
Scan speed range	0.5 to 5.0° min^{-1}
Total data collected	2834
Independent data, $I > 3\sigma(I)$	1735
Total variables	433
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.040
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.040
Weights	$w = \sigma(F)^{-2}$

TABLE 5

POSITIONAL AND THERMAL PARAMETERS FOR η^5-$C_5H_5Mo(CO)(NO)(\eta^2$-$C_8H_{13}SC_6H_5)$ (VI)

Atom	x	y	z	B (Å^2) [a]
Mo	0.41114(9)	0.12298(3)	0.06400(5)	3.16(3)
S	0.2166(3)	0.1229(1)	−0.0793(2)	4.22(9)
O(1)	0.5292(7)	0.1118(3)	−0.0666(4)	6.3(3)
O(2)	0.5908(8)	0.0715(3)	0.1412(5)	9.4(3)
N	0.4809(8)	0.1146(3)	−0.0132(4)	3.8(3)
C(1)	0.327(1)	0.0599(3)	0.0779(6)	3.6(3)
C(2)	0.2619(9)	0.0828(3)	0.0345(6)	9.8(3)
C(3)	0.245(1)	0.0735(3)	−0.0394(5)	5.4(3)
C(4)	0.1478(9)	0.0418(4)	−0.0504(6)	6.0(4)
C(5)	0.225	0.002	−0.052	8*
C(5A)	0.173	−0.004	−0.035	8*
C(6)	0.223	−0.016	0.012	8*
C(6A)	0.193	−0.009	0.040	8*
C(7)	0.318(1)	−0.0136(4)	0.0624(8)	9.6(5)
C(8)	0.392(1)	0.0239(3)	0.0569(6)	4.9(4)
C(9)	0.214(1)	0.1104(3)	−0.1665(5)	2.8(3)
C(10)	0.303(1)	0.0913(3)	−0.1981(6)	3.8(3)
C(11)	0.298(1)	0.0853(4)	−0.2671(6)	5.1(4)
C(12)	0.210(1)	0.0981(4)	−0.3038(6)	4.8(4)
C(13)	0.124(1)	0.1171(4)	−0.2737(5)	5.4(4)
C(14)	0.124(1)	0.1235(4)	−0.2053(6)	4.5(3)
C(15)	0.461(1)	0.1844(4)	0.1080(8)	6.9(4)
C(16)	0.396(1)	0.1917(4)	0.0539(6)	8.6(5)
C(17)	0.294(1)	0.1802(4)	0.0650(8)	10.4(5)
C(18)	0.291(1)	0.1648(4)	0.1312(7)	7.5(4)
C(19)	0.397(1)	0.1683(4)	0.1553(6)	6.2(4)
C(20)	0.523(1)	0.0897(4)	0.1135(7)	5.7(4)
Mo′	0.6691(1)	0.76330(3)	0.65603(6)	3.51(3)
S′	0.5201(3)	0.86238(9)	0.6687(2)	3.67(9)
O(2′)	0.8808(7)	0.7230(3)	0.5927(5)	7.2(3)
O(1′)	0.8098(7)	0.8287(2)	0.7162(4)	5.1(2)
N′	0.7545(8)	0.8026(3)	0.6901(4)	3.3(2)
C(1′)	0.666(1)	0.7843(3)	0.5433(5)	3.2(3)
C(2′)	0.5886(9)	0.8067(3)	0.5800(5)	3.1(3)
C(3′)	0.6048(9)	0.8509(3)	0.5934(5)	3.0(3)
C(4′)	0.5638(9)	0.8774(3)	0.5340(5)	3.4(3)
C(5′)	0.634(1)	0.8777(4)	0.4695(6)	4.1(3)
C(6′)	0.635(1)	0.8376(4)	0.4285(6)	4.2(3)
C(7′)	0.737(1)	0.8115(4)	0.4355(6)	4.0(3)
C(8′)	0.766(1)	0.8008(3)	0.5078(6)	3.4(3)
C(9′)	0.551(1)	0.9134(3)	0.6862(5)	3.2(3)
C(10′)	0.461(1)	0.9390(4)	0.6879(7)	6.2(4)
C(11′)	0.477(1)	0.9791(4)	0.7064(8)	7.7(5)
C(12′)	0.580(1)	0.9931(3)	0.7205(7)	6.3(4)
C(13′)	0.667(1)	0.9677(4)	0.7193(6)	5.6(4)
C(14′)	0.652(1)	0.9276(4)	0.7024(6)	5.0(4)
C(15′)	0.574(1)	0.7011(4)	0.6634(7)	6.5(4)
C(16′)	0.635(1)	0.7063(4)	0.7232(7)	6.5(4)
C(17′)	0.587(1)	0.7393(4)	0.7552(7)	5.9(4)
C(18′)	0.502(1)	0.7540(4)	0.7183(7)	6.3(4)
C(19′)	0.493(1)	0.7293(4)	0.6592(7)	5.9(4)
C(20′)	0.802(1)	0.7384(4)	0.6146(6)	5.1(4)
H(1)	0.3352	0.0683	0.1251	5*
H(2)	0.2213	0.1055	0.0527	5*

TABLE 5 (continued)

Atom	x	y	z	B (Å^2) [a]
H(3)	0.3202	0.0577	−0.0615	5*
H(4A)	0.1025	0.0469	−0.0942	8*
H(4B)	0.0924	0.0417	−0.0083	8*
H(4C)	0.1193	0.0445	−0.0996	8*
H(4D)	0.0837	0.0508	−0.0163	8*
H(5A)	0.3087	0.0108	−0.0645	8*
H(5B)	0.1956	−0.0173	−0.0898	8*
H(5C)	0.2465	−0.0140	−0.0620	8*
H(5D)	0.1062	−0.0230	−0.0500	8*
H(6A)	0.2063	−0.0471	0.0039	8*
H(6B)	0.1538	−0.0035	0.0383	8*
H(6C)	0.1484	−0.0336	0.0572	8*
H(6D)	0.1642	0.0176	0.0627	8*
H(7A)	0.3704	−0.0399	0.0511	8*
H(7B)	0.2886	−0.0155	0.1095	8*
H(7C)	0.3542	−0.0370	0.0289	8*
H(7D)	0.3221	−0.0241	0.1105	8*
H(8A)	0.4143	0.0249	0.0035	5*
H(8B)	0.4634	0.0169	0.0837	5*
H(10)	0.3651	0.0828	−0.1717	5*
H(11)	0.3564	0.0716	−0.2887	5*
H(12)	0.2069	0.0942	−0.3514	5*
H(13)	0.0635	0.1273	−0.3008	5*
H(14)	0.0585	0.1347	−0.1840	5*
H(15)	0.5380	0.1904	0.1132	5*
H(16)	0.4264	0.2045	0.0137	5*
H(17)	0.2312	0.1795	0.0344	5*
H(18)	0.2282	0.1525	0.1525	5*
H(19)	0.4173	0.1601	0.2002	5*
H(1′)	0.6567	0.7559	0.5415	5*
H(2′)	0.5224	0.7935	0.5949	5*
H(3′)	0.6892	0.8577	0.6009	5*
H(4A′)	0.5623	0.9075	0.5528	5*
H(4B′)	0.4828	0.8683	0.5228	5*
H(5A′)	0.7185	0.8825	0.4838	5*
H(5B′)	0.6057	0.9007	0.4394	5*
H(6A′)	0.6238	0.8468	0.3766	5*
H(6B′)	0.5630	0.8213	0.4424	5*
H(7A′)	0.8060	0.8273	0.4126	5*
H(7B′)	0.7237	0.7851	0.4059	5*
H(8A′)	0.7970	0.8258	0.5316	5*
H(8B′)	0.8298	0.7779	0.5055	5*
H(10′)	0.3898	0.9296	0.6765	5*
H(11′)	0.4155	0.9966	0.7070	5*
H(12′)	0.5930	1.0203	0.7333	5*
H(13′)	0.7411	0.9766	0.7304	5*
H(14′)	0.7145	0.9094	0.7015	5*
H(15′)	0.5856	0.6806	0.6314	5*
H(16′)	0.6970	0.6909	0.7386	5*
H(17′)	0.6102	0.7486	0.7980	5*
H(18′)	0.4588	0.7781	0.7276	5*
H(19′)	0.4343	0.7322	0.6241	5*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

none of the hydrogen parameters were varied and the semi-rigid groups were also fixed. After all shift/e.s.d. ratios were less then 0.1, convergence was reached at the agreement factors listed in Table 4. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than 0.90 e/Å^3, which was in the vicinity of the disordered bridge. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs, with the exception of the determination of the disordered bridge models which were achieved through use of the SHELX-76 series of programs of G. Sheldrick (Cambridge). The final atomic positional and thermal parameters for (η^5-C_5H_5)Mo(CO)(NO)(η^2-cyclooctenyl-3-phenyl thioether) (VI) are given in Table 5. Lists of structure factors may be obtained from the authors.

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