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Controlling the regiochemistry of nucleophilic attack on unsymmetrical allyl complexes

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Abstract

The NO and CO ligands in a $[CpMo(NO)(CO)(\eta^3\text{-allyl})]^+$ complex exert differential electronic effects on the allyl moiety and control the regiochemistry of nucleophilic attack. These directing influences are sufficiently strong that they overcome the normal directing influences of substituents of the allyl moiety. An essential task, therefore, is arranging for the appropriate terminus of the allyl to have the relationship to the nitrosyl group that will result in attack at the desired location. Replacement of a single CO ligand in a neutral monosubstituted allyl complex of $CpMo(CO)_2$ with NO^+ yields a product for which addition occurs at the unsubstituted end of the allyl. Hence, an *E*-olefin with no newly created chiral centers is formed upon nucleophilic attack. A new synthetic strategy has been developed which allows us to build a chiral center in the allylic position of a terminal olefin. Sequential addition of two nucleophiles to a $CpMo(NO)(CO)(allyl)^+$ cation creates these chiral centers, which were not accessible by addition of NO^+ to the dicarbonyl. Addition of nucleophiles to homochiral (Neomenthylcyclopentadienyl)Mo(NO)(CO)(phenylallyl)$^+$ complexes yields chiral olefins in high enantiomeric purity.

The cationic phenylallyl complexes prepared by different routes were identified by single crystal X-ray diffraction determinations. *endo-cis-syn*-$[CpMo(NO)(CO)(\eta^3\text{-}CH(Ph)CHCH_2)]BF_4$ crystallizes in the monoclinic space group $P2_1/n$ with a 8.226(2), b 12.273(2), c 16.051(2) Å, β 100.02(2)°, V 1595.7(9) Å^3, $Z = 4$. *exo-cis-syn*-$[CpMo(NO)(CO)(\eta^3\text{-}CH(Ph)CHCH_2)]BF_4$ crystallizes in the monoclinic space group $P2_1/c$ with a 10.706(3), b 14.700(4), c 10.491(3) Å, β 96.48(2)°, V 1640.5 Å^3, $Z = 4$.

Introduction

The NO and CO ligands in the $[Cp(Mo)(NO)(CO)(\eta^3\text{-}C_3H_5)]^+$ ion exert differential electronic effects on the allyl moiety and control the regiochemistry of

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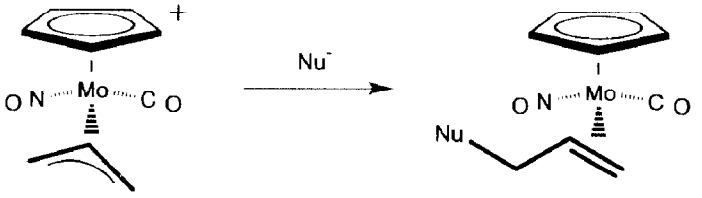
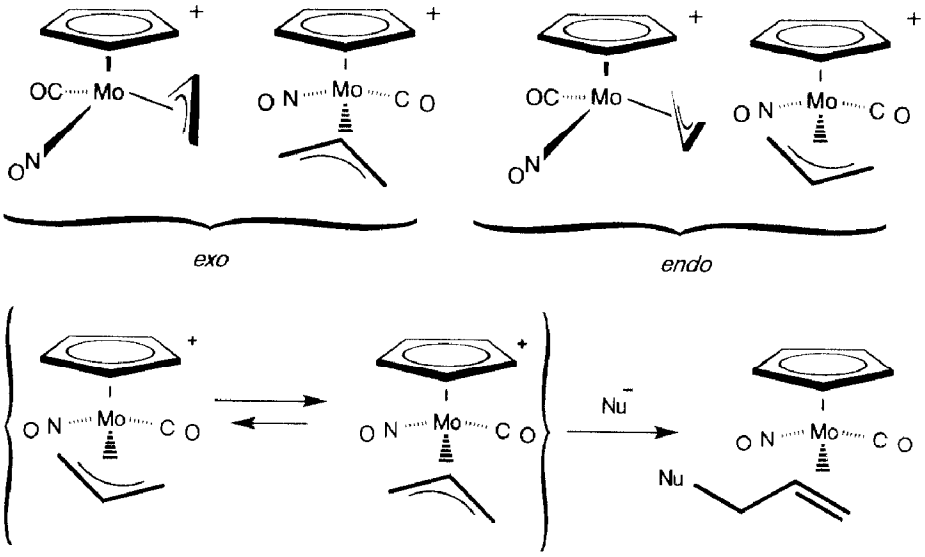
nucleophilic attack. This attack has been shown to occur *cis* to nitrosyl in a number of complexes [1]. These directing influences are sufficiently strong that they overcome the normal effects of substituents of the allyl moiety. For example, in the unsymmetrical $[CpMo(NO)(CO)(methyl\text{-}C_3H_3\text{-}isopropyl)]^+$ complex, addition is forced to the side of the more bulky isopropyl-substituted terminus of the allyl in the isomer with the NO placed properly [2].



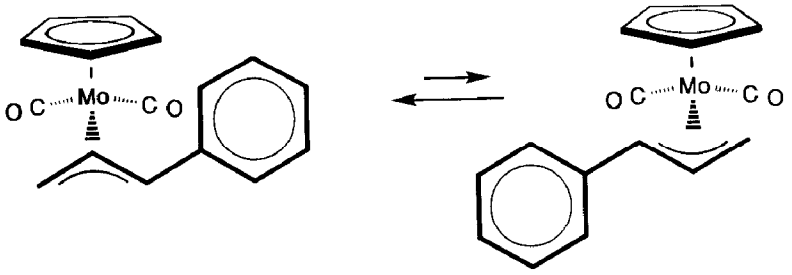
There is also the potential for *exo-endo* isomerism which can further complicate the analysis of intermediates, even though it usually does not affect the stereochemistry of the products. The *exo* isomer has the central carbon atom of the allyl proximal to the Cp ring. Two views are shown in the structural drawing. As several aspects of stereochemistry of the allyl will be important, we generally will depict the structures using the convention that the plane of the olefin or allyl is in the plane of the paper with the metal behind the plane. For nitrosylcarbonyl complexes of this type the usual mode of interconversion of *endo* and *exo* isomers is via rotation of the allyl group. Although the interconversion rates of the isomers are usually relatively slow ($t_{1/2} > 0.5$ h), under the reaction conditions the rates are enhanced [1,3]. The products which are obtained are those that would arise from nucleophilic addition *cis* to the nitrosyl in the *exo* isomer and from attack on the face opposite to the metal.



With an unsymmetrically substituted allyl, there is a practical problem of synthesizing a pure isomer with the nitrosyl in the desired position. We report here an effective strategy for synthesizing the required isomers and effecting an asymmetric synthesis. We have chosen the phenylsubstituted allyl (i.e., cinnamyl) complexes to demonstrate the approach.

Results

The synthesis of moderately air sensitive orange crystals of $CpMo(CO)_2(\eta^3$-$CH(Ph)CHCH_2)$ was readily accomplished by reaction of cinnamyl chloride with $Mo(CO)_3(CH_3CN)_3$ and LiCp. As expected, the ^1H NMR of this complex was broad at room temperature. Cooling the sample to $-70\,^\circ C$ gave a spectrum containing two Cp signals and two sharp sets of allylic resonances in a ratio of 8.5/1. Examination of the IR spectrum (C_6H_{12}) showed two sets of carbonyl absorptions: a weaker set at 1968 and 1901 cm^{-1} and a stronger set at 1956 and 1883 cm^{-1}. The greater intensity of the low frequency set indicates that the predominant isomer of $CpMo(CO)_2(\eta^3$-$CH(Ph)CHCH_2)$ has the *exo* conformation [4].



Treatment of the dicarbonyl with NO^+ gave a single isomer of the nitrosyl-carbonyl cation, **1**, which was identified as the *endo-cis* isomer by single crystal X-ray diffraction (see Fig. 1). The electronic asymmetry produced by the CpMo(NO)(CO) moiety tilts the allyl so that it tends to align with the Mo–(CO) direction and this is reflected in the drawings that are used throughout our discussion.

In contrast to the relatively rapid *exo-endo* equilibration observed for other cationic π-allyl complexes, isomerization of the cinnamyl cation was extremely slow. After 46 h in solution, an NMR sample in acetone-d_6 showed relative amounts of *endo-cis*-**1** to be 72%, and of two additional isomers of 19 and 9%. This ratio does not represent an equilibrium mixture, but sample decomposition prevented further

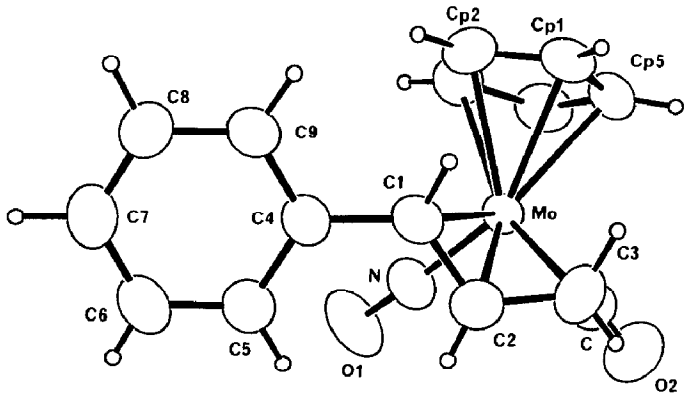
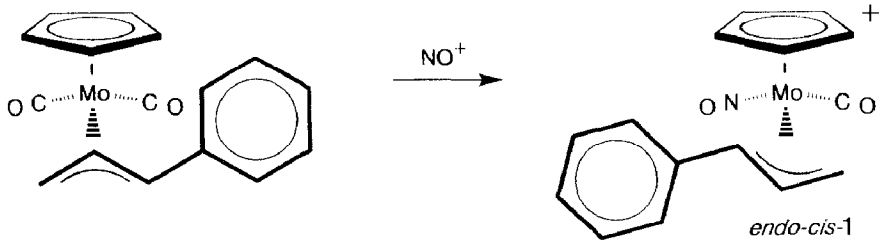


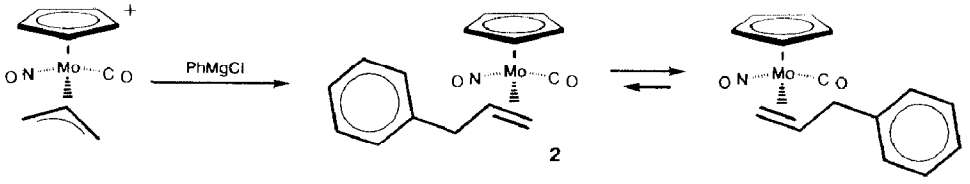
Fig. 1. ORTEP drawing of the *endo-cis*-[CpMo(NO)(CO)(phenylallyl)]$^+$ cation showing 50% probability ellipsoids for non-hydrogen atoms. Hydrogen atoms are shown at refined positions, but with smaller thermal parameters.

monitoring of the reaction. In view of the demonstrated effectiveness of iodide catalysis in promoting *exo-endo* equilibration in cation complexes such as [CpMo(NO)(CO)(η^3-cyclooctenyl)]$^+$ [1a], we attempted a similar catalysis with the *endo-cis* isomer **1**. Within 15 min catalysis by iodide in acetone produced no isomers of **1**, but a 3/2 mixture of CpMo(NO)(I)(cinnamyl) isomers. It was thus apparent that our normal methods of preparing these cations would only provide the *endo-cis* isomer. Based on our previous results for acyclic symmetrical allyls, addition to the unsubstituted terminus would be expected. If we were to expect chiral olefin products from attack on the phenyl substituted terminus of the allyl, we believed that the *exo-cis* isomer would be required. Therefore, a new strategy was needed to prepare *exo-cis*-**1**, and once prepared, it indeed showed the expected regiochemistry in its reactions.



A route to the exo-cis-cinnamyl complex.

Since attack occurs *cis* to nitrosyl in symmetrical allyl complexes, we took the approach of constructing the cinnamyl ligand on the metal starting with the simple unsubstituted allyl complex, [CpMo(NO)(CO)(η^3-allyl)]$^+$. Addition of phenyl magnesium bromide gave the 3-phenylpropene complex **2** in 70% yield. The ^{1}H NMR spectrum is broad at room temperature owing to rotational equilibration of the olefin conformers. At $-30\,^\circ$C two Cp resonances at δ 5.34 and 5.49 are observed in a ratio of 5/2 which average to the broad Cp resonance at δ 5.38 observed at room temperature. Thus only enantiomers of one diastereomer are formed, but two conformations exist in solution. Based on the expected attack *cis* to NO in the *exo*-(η^3-C_3H_5) cation, the product should be a racemic mixture of conformers of (*RS,SR*)-**2** (only the *R* configuration at the metal is shown).



In neutral CpMo(NO)(CO)(olefin) complexes the hydrogen atoms allylic to the η^2-double bond (and *cis* to nitrosyl) are electron rich and subject to abstraction by trityl ion [5]. This abstraction yields a single isomer of **1** after treating **2** with trityl tetrafluoroborate. This isomer was identified as *exo-cis-syn*-[CpMo(NO)(CO)(η^3-CH(Ph)CHCH$_2$)]BF_4 by single crystal X-ray diffraction analysis (Fig. 2). Considering that *exo-endo*, *cis-trans*, and *syn-anti* isomerism can yield eight possible isomers, the formation of one isomer demonstrates the impressive selectivity of this particular reaction. The analogous hydride abstraction from CpMo(NO)(CO)(η^2-*trans*-β-methylstyrene) yielded a mixture of cationic η^3-allyl complexes, among

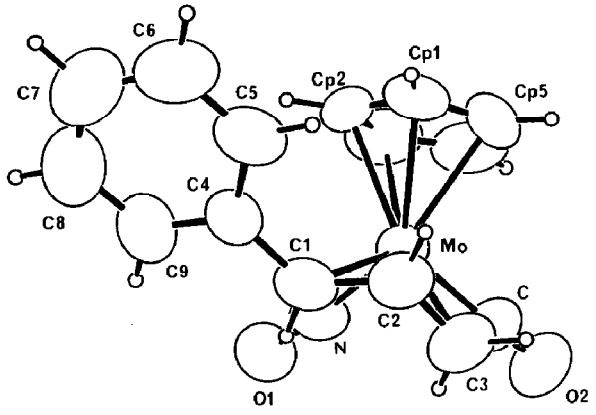
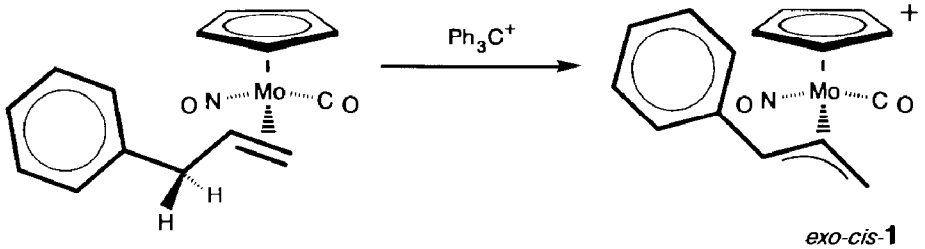


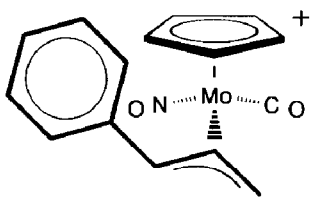
Fig. 2. An ORTEP drawing of *exo-cis-syn*-[CpMo(CO)(NO)(phenylallyl)]$^+$ cation showing 50% probability ellipsoids. Hydrogen atoms are shown in calculated positions.

which the *endo-cis* form **1**, predominated by a factor of three. Clearly, the route using the 3-phenylpropene complex was superior.

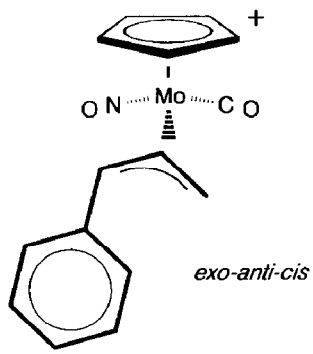


exo-cis-**1**

The NMR of *exo-cis*-**1** in acetone-d_6 showed sharp resonances indicative of maintaining the *exo-cis-syn* configuration in solution and demonstrating that this isomer shows no tendency to convert to other isomers even upon standing for one day at room temperature, or one week at 0 °C. Thus, **1** differs from unsubstituted allyls or cyclic allyls where there is relatively facile *endo-exo* interconversion.



exo-syn-cis

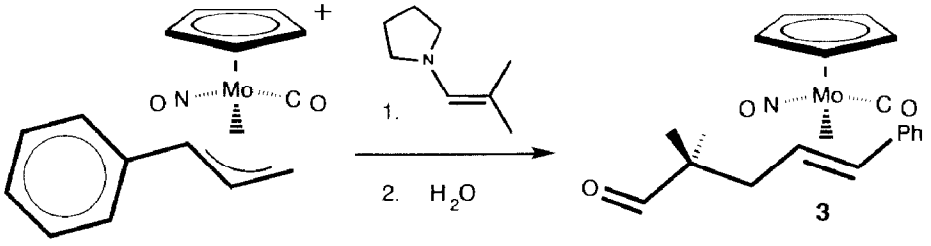


exo-anti-cis

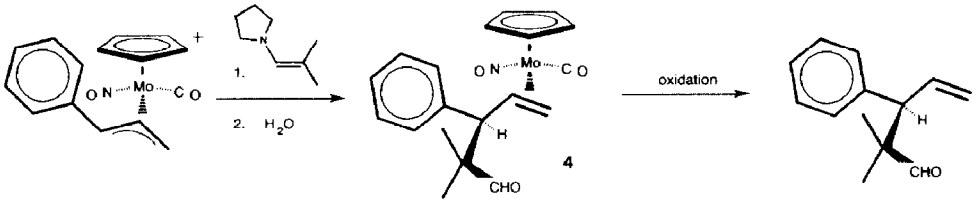
Nucleophilic additions to endo-1 and exo-1

Reaction of *endo-cis* isomer **1** with 1-pyrrolidino-2-methylpropene followed by hydrolysis of the iminium intermediate gave the product expected for addition to the unsubstituted terminus of the allyl, CpMo(CO)(NO)(η^2-(*E*)-2,2-dimethyl-5-phenyl-4-pentenal) **3**. The room temperature ^{1}H NMR spectrum of this complex

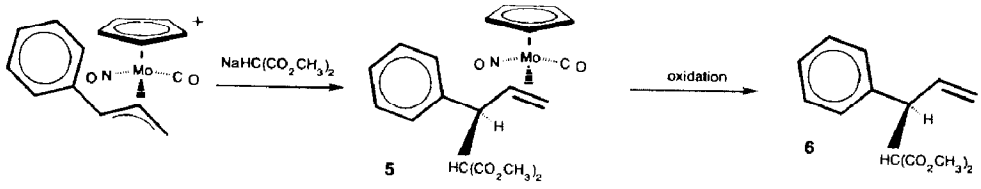
showed two broad sets of signals attributable to interconversion of the two conformers of the η^2-olefin. At low temperature ($-40\,^\circ$C) there were two sharp sets of signals present in a ratio of 72/28. Warming to $70\,^\circ$C resulted in the appearance of some free olefin, as well as a new set of resonances consistent with the formation of an additional (diastereomeric) isomer (14% of total isomers present). The olefin showed the characteristic couplings of a *trans*-olefin rather than a terminal vinyl group.



Reaction of *exo-cis* isomer **1** with 1-pyrrolidino-2-methylpropene followed by hydrolysis gave a single product, **4**, in 75% yield. The rotational barrier for the olefin in **4** is relatively low and the ^{1}H NMR signals were only slightly broad at room temperature. A single Cp resonance at δ 5.09 and a single aldehyde resonance at δ 9.60 indicated that only one diastereomer had been formed. The characteristic vinyl pattern of the coordinated olefin ($\delta(H_a)$2.19 (dd, 10.0, 3.5 Hz); $\delta(H_s)$2.35 (dd, 9.5, 3.5 Hz); $\delta(H_c)$3.41 (ddd, 12.0, 10.4, 9.5 Hz)) indicated that substitution had occurred at the substituted terminus of the allyl. Air oxidation of **4** gave a 95% yield of the olefin, which was identified as 2,2-dimethyl-3-phenylpent-4-enal by comparison of its IR, NMR, and m.p. of its 2,4-dinitrophenylhydrazone with literature values [6].



Since it appeared that the *exo-cis* isomer of **1** would provide chiral olefins, another nucleophile, sodiodimethylmalonate, was used to test the generality of the selectivity. This nucleophile also gave a 75% yield of a single isomer of **5**, which could be air-oxidized to yield racemic dimethyl 3-phenyl-1-butene-4,4-dicarboxylate (**6**) as the only olefin product (90% yield).



This highly selective addition to the substituted terminus of the allyl suggested that the use of a homochiral analog of *exo-cis*-**1** would allow the formation of an enantiomerically enriched sample of **6**. (+)-(Neomenthylcyclopentadienyl)-

Mo(NO)(CO)(η^3-allyl]PF_6 can be conveniently prepared [1b,7] and provides a source of an enantiomerically pure (*R*)-CpMo(NO)(CO)(allyl) stereogenic center. Addition of phenyl Grignard followed by abstraction of hydride provides enantiomerically pure [*exo-cis*-NMCpMo(NO)(CO)(η^3-CH(Ph)$CHCH_2$)]$^+$ (**7**). Treatment of **7** with malonate followed by oxidation yields (+)-**5** in 97% ee, as determined by chiral lanthanide shift reagent studies.

Discussion

The differential electronic effects responsible for the selectivity exhibited in these complexes are also manifested in several aspects of the structures of *endo*-**1** and *exo*-**1**. As evident in Fig. 1 and 2, the η^3-allyl moieties in both the *endo* and *exo* isomers tend to align with the Mo–CO vector as opposed to the Mo–NO vector. We have observed this preferential alignment effect in other Mo(NO)(CO) complexes [8] and it appears to be a general phenomenon associated with ligands of substantially different π-acceptor strengths. The extent of the alignment is indicated by the displacement of the carbonyl carbon atom from the C(1)–Mo–C(3) plane of 0.85 Å in *exo*-**1** and 0.81 Å in *endo*-**1**. This contrasts with the displacement of the nitrosyl nitrogen atom from the C(1)–Mo–C(3) plane of 1.67 Å in *exo*-**1** and 1.63 Å in *endo*-**1**. Although more elaborate measures of alignment might be devised and calculated, another simply calculated alignment indicator is the dihedral angle between the C(1)–Mo–C(3) plane and the [midpoint C(1)–C(3)]–Mo–C plane of 25° in *exo*-**1** and 24° in *endo*-**1**. The comparable dihedral angle between the C(1)–Mo–C(3) plane and the [midpoint C(1)–C(3)]–Mo–N plane of 67° in *exo*-**1** and 68° in *endo*-**1**.

The alignment of olefin π^*, methylene *p*, and even dihydrogen σ^* also follows this trend of alignment with the weaker π-bonding ligands [8,9]. Consideration of similar orbital interactions also allow rationalization of the alignment of η^2-O_2 and η^2-S_2O in CpMo oxo complexes [10]. This preferential alignment is attributable to the increased backbonding available in the frontier *d* orbital interacting with the CO [8] (see Fig. 3). As NO is a better π acceptor than CO, the fragment MO containing the *d* orbital interacting with NO effectively has a weaker backbonding capability owing to a lowering of its energy relative to the important orbital of the appropriate symmetry on the allyl. Alternatively, one can consider that the relative

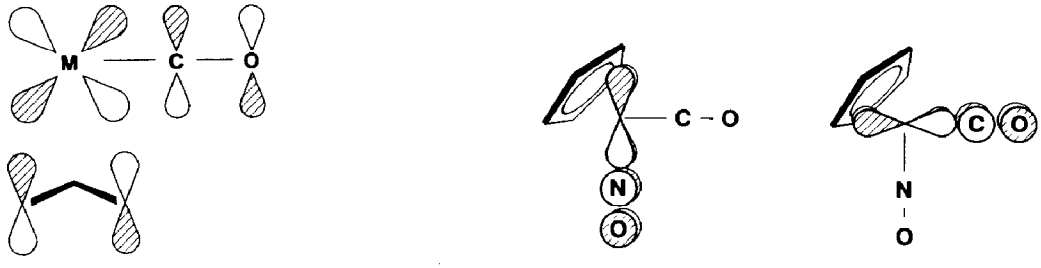


Fig. 3. Basis orbitals for interaction of an M–CO fragment with a nonbonding allyl orbital. The orbitals shown are the metal d_{xz} and the p_z orbitals on the ligands.

Fig. 4. The d_{xz} and d_{yz} orbitals which interact with π^* orbitals on CO and NO and with orbitals on ligands aligned with the M–C (*x*-axis) or M–N (*y*-axis).

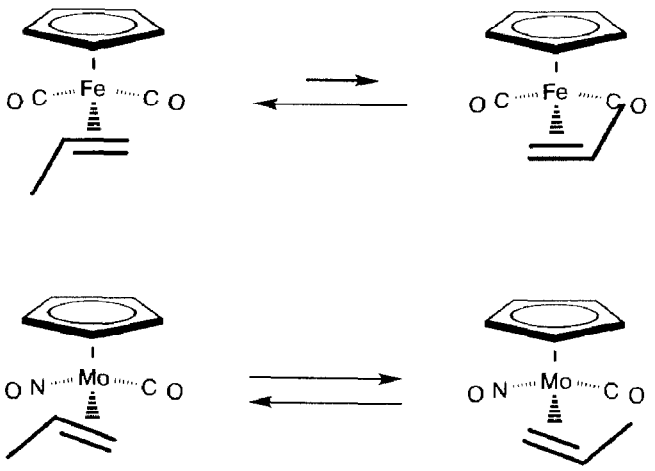


Fig. 5. The influence of olefin alignment on stability of *endo* and *exo* conformers.

contributions of metal *d*, XO π^*, and allyl nonbonding orbitals to the MO and consequently their population depends on the relative placement of the CO and NO orbital energies. Thus looking down the *z* axis, the allyl orbitals interact better with d_{xz} owing to the weaker acceptor π^* of CO than with d_{yz} which interacts with the better acceptor π^* of the NO (see Fig. 4).

The preferential alignment along the M–C≡O also has an important effect on the relative stability of substituted *endo* and *exo* olefin and allyl isomers owing to variations in interactions with the Cp ring. For example, $[CpFe(CO)_2(propylene)]^+$ exists nearly completely in the *exo* conformation [11]; whereas CpMo(NO)(CO)-(propylene) exists as mixture of nearly equal populations of *exo* and *endo* isomers [8]. Since the stable orientation of the olefin is parallel to the Cp ring in the dicarbonyl complex, steric interactions of the methyl group with the Cp ring destabilizes the *endo* isomer. With the (*R*,*S*)-nitrosylcarbonyl complex, the methyl group does not undergo a severe steric interaction with the ring in either isomer (see Fig. 5).

The stability of the *endo-cis* allyl isomer of **1** is expected since the phenyl group is oriented away from the Cp ring. The greater relative stability of *exo-cis*-**1** might not

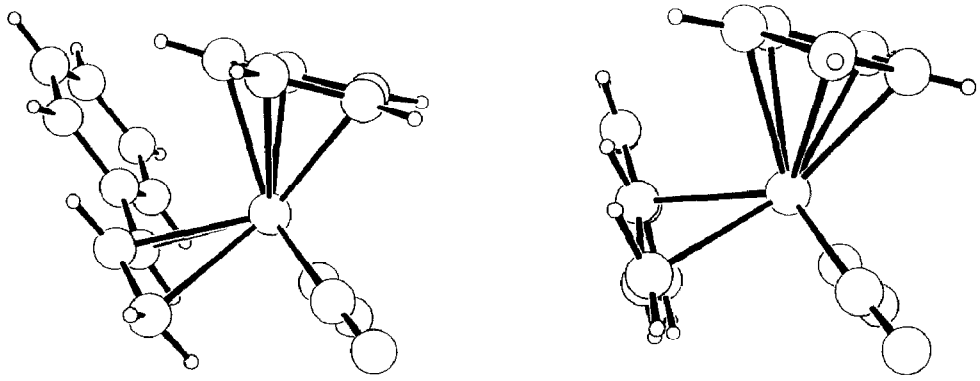


Fig. 6. Side views comparing the orientation of the allyl plane in *exo* and *endo* allyl isomers.

be anticipated, however, owing to the orientation of the phenyl group up toward the Cp ring. Since the phenyl is effectively in the plane of the allyl (dihedral angle 6°) and the plane of an *exo*-allyl is more nearly parallel to the Cp plane, the phenyl-Cp steric interaction is consequently not great. This important difference in the orientation of the plane of the allyl relative to the Cp ring can be appreciated in side views of *endo* and *exo* allyl isomers (see Fig. 6).

The dihedral angle between the Cp plane and the allyl plane is 38° for the *exo-cis* isomer of **1**, but is 74° for the *endo-cis* isomer. Alternatively one might note that the allyl plane is more nearly parallel to the N–Mo–C plane in the *exo* isomer (8° for *exo*-**1**, but 34° for *endo*-**1**).

Experimental

X-ray crystallographic analyses

Data collection parameters for the *endo-cis*-**1**, and *exo-cis*-**1** are given in Table 1. The methods used follow those we have published elsewhere [10] and only features specific to these structures are given here. From the systematic absences of $0k0$, $k = 2n + 1$; and $h0l$, $h + l = 2n + 1$, the space group was determined to be $P2_1/n$ for *endo-cis*-**1**. From the systematic absences of $0k0$, $k = 2n + 1$; and $h0l$, $l = 2n + 1$, the space group was determined to be $P2_1/c$ for *exo-cis*-**1**. The structures were solved using the Patterson heavy-atom method, which revealed the position of the molybdenum atom. The coordinates of the remaining non-hydrogen atoms were located in subsequent difference Fourier synthesis. These hydrogen atoms, with isotropic thermal parameters fixed at 5 $Å^3$, were included in full-matrix least-squares refinement for *endo-cis*-**1**. Neutral atom scattering factors were calculated by standard procedures [12a]. Anomalous dispersion corrections were applied to all atoms [12b,13].

An numerical absorption correction was applied for *exo*-**1**. Calculations were performed on a VAX-station 2000 computer using SDP-Plus Software developed by Enraf–Nonius and B.A. Frenz & Associates. Positional parameters, bond distances and bond angles are given in Tables 2, 3, and 4. Tables of calculated hydrogen positions and structure factor tables can be obtained from the authors.

Syntheses

Preparation of $CpMo(CO)_2(\eta^3\text{-}CH(\phi)CHCH_2)$. Molybdenum hexacarbonyl (8.0 g, 30.2 mmol) was dissolved in 120 ml dry acetonitrile and the reaction refluxed 4 h to give a deep yellow solution of $Mo(CO)_3(CH_3CN)_3$. Cinnamyl chloride (6.9 g, 45 mmol) was added to the hot solution, causing vigorous gas evolution accompanied by an immediate color change to dark red. The reaction was allowed to cool to room temperature and left to stir overnight. After this time, there was a significant amount of orange precipitate apparent in a pale orange solution. Solvent volume was reduced to 30 ml and 125 ml of 4/1 anhydrous ether/pentane added. The light colored supernatant was removed via syringe and the remaining solid vacuum dried. Lithium cyclopentadienide, freshly prepared from cyclopentadiene (3.0 ml, 36 mmol) and n-butyllithium (1.35 *M*, 22.4 ml, 30.2 mmol) was added at 0°C to a THF solution of the redissolved molybdenum complex. This reaction was allowed to stir for 18 h before solvent was removed under vacuum to give the crude dicarbonyl complex as a dark brown oil. This oil was extracted with multiple small portions of

Table 1

Crystallographic data for X-ray diffraction studies of *endo-cis-* and *exo-cis-*[η^5-(C_5H_5)Mo(NO)(CO)-($C_6H_5C_3H_4$)]BF_4

(A) Crystal parameters at 23 ± 2°		
Formula	$Mo_1F_4O_2N_1C_{15}B_1H_{14}$	
	*endo-cis-***1**	*exo-cis-***1**
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.226(2)	10.706(3)
b, Å	12.273(2)	14.700(4)
c, Å	16.051(2)	10.491(3)
β, °	100.02(2)	96.48(2)
V, Å^3	1595.7(9)	1640.5(15)
FW	423.02	423.02
ρ_{calcd}, g/cm^3	1.761 ($Z = 4$)	1.699 ($Z = 4$)
(B) Intensity measurements		
Diffractometer	Enraf–Nonius CAD4	
Monochrometer	graphite	
Radiation	Mo-K_α (0.71073 Å)	
Reflections measured	$+h, +k, \pm l$	$\pm h, -k, +l$
Maximum 2θ	50	50
No. refl. measured	3153	3196
(C) Structure solution and refinement		
Data used, $F^2 > 3\sigma(F^2)$	2445	1318
Parameters refined	273	217
Abs. coeff. (cm^{-1})	8.501	8.204
Crystal dimensions	0.25 × 0.34 × 0.31	0.54 × 0.25 × 0.07
Abs. correction	not applied	numerical 82.20 to 94.65% on I
p factor	0.02	0.02
Final residuals R_1, R_2	0.025, 0.030	0.043, 0.044
Esd of unit weight	1.81	2.15
Convergence, largest shift/error	0.00	0.00

ether and the combined extracts filtered through a 10 cm × 5 cm column of deactivated alumina to give a clear deep gold solution. Ether was removed under reduced pressure, the resulting gold solid extracted with pentane, and the extracts chromatographed on a 30 cm × 2 cm column of alumina. The orange eluant was reduced in volume under a flow of nitrogen and stored at −30 °C giving $CpMo(CO)_2(\eta^3\text{-}CH(\phi)CHCH_2)$ as air sensitive orange crystals (4.492 g, 13.44 mmol, 42% yield, m.p. 88–99 °C dec). IR (C_6H_{12}): ν(C≡O) 1968w, 1956s, 1901w, 1883s cm^{-1}. ^{1}H NMR (toluene-d_8, −70 °C, 500 MHz): major isomer, δ 4.27 (s, Cp), 4.03 (ddd, J 10.3, 10.3, 7.3 Hz, H_c), 2.33 (d, J 7.3 Hz, H_s), 1.98 (d, J 10.3 Hz, $H_{a'}$), 0.89 (d, J 10.3 Hz, H_a), minor isomer, δ 4.36 (s, Cp), 3.95 (ddd, J 11.5, 10.0, 6.5 Hz, H_c), 3.01 (d, J 11.5 Hz, $H_{a'}$); 2.54 (d, J 6.5 Hz, H_s), 1.39 (d, J 10.0 Hz, H_a); for both isomers: δ 7.28–6.86 (ϕ); isomer ratio 8.5/1. Anal. Found: C, 57.64; H, 4.24. $C_{16}H_{14}O_2Mo$ calcd.: C, 57.50; H, 4.22%.

*Preparation of endo-cis-[CpMo(CO)(NO)(η^3-CH(Ph)CHCH$_2$)]BF$_4$ (endo-cis-***1***).* A solution of $CpMo(CO)_2(\eta^3\text{-}CH(\phi)CHCH_2)$ (2.500 g, 7.48 mmol) in 75 ml dry acetonitrile was cooled to 0 °C and $NOBF_4$ (0.874 g, 7.48 mmol) was added in

Table 2a

Positional and thermal parameters for *endo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

Atom	x/a	y/b	z/c	B_{eqv}
Mo	0.31986(3)	0.17042(2)	0.14086(1)	2.766(4)
F(1)	0.5515(3)	−0.1354(2)	0.1181(1)	5.88(5)
F(2)	0.7769(3)	−0.0772(2)	0.2064(1)	6.22(5)
F(3)	0.6160(3)	−0.2064(2)	0.2493(1)	6.40(5)
F(4)	0.7715(3)	−0.2445(2)	0.1509(1)	7.11(6)
O(1)	0.2962(3)	0.3316(2)	0.2764(1)	6.30(6)
O(2)	0.4979(3)	0.0239(2)	0.2925(1)	6.38(6)
N	0.3130(3)	0.2700(2)	0.2228(1)	3.97(5)
C	0.4400(4)	0.0739(3)	0.2370(2)	4.25(7)
Cp(1)	0.1916(4)	0.0803(3)	0.0159(2)	3.78(6)
Cp(2)	0.0996(4)	0.1746(3)	0.0263(2)	4.11(7)
Cp(3)	0.0351(4)	0.1627(3)	0.1013(2)	4.35(7)
Cp(4)	0.0899(4)	0.0622(3)	0.1368(2)	4.23(7)
Cp(5)	0.1859(4)	0.0108(2)	0.0838(2)	3.88(6)
C(1)	0.4215(3)	0.3069(2)	0.0554(2)	3.30(6)
C(2)	0.5527(3)	0.2624(2)	0.1112(2)	3.71(6)
C(3)	0.5862(4)	0.1519(3)	0.1089(2)	4.40(7)
C(4)	0.3646(3)	0.4200(2)	0.0576(2)	3.18(6)
C(5)	0.4242(4)	0.4924(3)	0.1231(2)	3.95(7)
C(6)	0.3728(4)	0.5990(3)	0.1203(2)	4.32(7)
C(7)	0.2583(4)	0.6355(3)	0.0534(2)	4.58(7)
C(8)	0.1980(4)	0.5664(3)	−0.0112(2)	4.84(8)
C(9)	0.2508(4)	0.4592(2)	−0.0093(2)	3.92(7)
B	0.6794(5)	−0.1663(3)	0.1818(2)	4.06(8)

several portions to the initially clear orange solution. There was immediate gas evolution, and the solution lightened to a gold color. The reaction was kept at 0 °C for 20 min, and then allowed to warm to room temperature. Slow addition of the

Table 2b

Positional and thermal parameters for refined H atoms in *endo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)(C_6H_5-C_3H_4)]BF_4

Atom	x/a	y/b	z/c	B_{iso}
Hp(1) [a]	0.256(3)	0.066(2)	−0.028(2)	4.9(7)
Hp(2)	0.084(3)	0.236(2)	−0.002(2)	4.6(7)
Hp(3)	−0.029(3)	0.213(2)	0.123(2)	4.7(7)
Hp(4)	0.062(3)	0.040(2)	0.180(2)	5.2(8)
Hp(5)	0.238(3)	−0.057(2)	0.089(2)	4.5(7)
H(1)	0.392(3)	0.271(2)	0.003(1)	2.7(5)
H(2)	0.600(3)	0.302(2)	0.152(2)	4.2(7)
H(3s)	0.661(3)	0.123(2)	0.144(2)	3.7(6)
H(3a)	0.553(4)	0.110(3)	0.052(2)	5.2(7)
H(5)	0.504(3)	0.467(2)	0.166(2)	4.5(7)
H(6)	0.413(4)	0.640(2)	0.160(2)	4.4(7)
H(7)	0.221(4)	0.712(3)	0.055(2)	6.3(8)
H(8)	0.119(4)	0.591(3)	−0.062(2)	6.6(9)
H(9)	0.215(3)	0.410(2)	−0.055(2)	4.1(6)

[a] Hp(n) = H atoms attached to C atoms of the cyclopentadienyl ring.

Table 2c

Positional and thermal parameters for *exo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

Atom	*x/a*	*y/b*	*z/c*	B_{eqv}
Mo	0.20627(7)	−0.06581(6)	0.22157(7)	4.51(1)
F(1)	0.2963(8)	−0.3803(5)	0.1674(6)	12.3(2)
F(2)	0.1803(6)	−0.3574(5)	0.3181(7)	13.4(3)
F(3)	0.3776(6)	−0.3772(5)	0.3624(6)	11.6(2)
F(4)	0.2661(8)	−0.4928(5)	0.2953(7)	14.3(3)
O(1)	0.1150(6)	0.0629(4)	0.0129(6)	7.8(2)
O(2)	0.0775(6)	−0.2280(4)	0.0568(6)	7.9(2)
N	0.1437(6)	0.0116(5)	0.0949(6)	5.4(2)
C	0.1207(8)	−0.1701(6)	0.1172(8)	6.0(3)
Cp(1)	0.3820(8)	−0.0708(7)	0.3751(8)	6.0(2)
Cp(2)	0.4052(8)	−0.0101(7)	0.280(1)	7.8(3)
Cp(3)	0.4095(9)	−0.0605(8)	0.1712(9)	8.3(3)
Cp(4)	0.3822(9)	−0.1497(7)	0.1949(9)	7.8(3)
Cp(5)	0.3676(9)	−0.1561(6)	0.326(1)	7.4(3)
C(1)	0.1035(7)	0.0491(6)	0.3438(7)	5.1(2)
C(2)	0.0927(8)	−0.0396(6)	0.3877(8)	5.7(2)
C(3)	0.0245(8)	−0.1052(7)	0.3146(8)	6.4(3)
C(4)	0.1811(7)	0.1220(6)	0.4028(8)	4.7(2)
C(5)	0.2500(8)	0.1133(6)	0.5256(8)	6.1(2)
C(6)	0.3224(9)	0.1843(7)	0.5756(9)	8.0(3)
C(7)	0.3274(9)	0.2650(7)	0.510(1)	8.4(3)
C(8)	0.261(1)	0.2751(7)	0.391(1)	8.1(3)
C(9)	0.1882(9)	0.2034(6)	0.3426(8)	6.4(3)
B	0.279(1)	−0.4028(8)	0.284(1)	6.7(3)

crude product solution to anhydrous ether gave an immediate lemon yellow precipitate of [CpMo(CO)(NO)(η^3-CH(ϕ)CHCH$_2$)]BF_4 (*endo-cis*-**1**) (2.743 g, 6.48 mmol, 87% yield) as > 99% of a single isomer. A sample of this material was recrystallized from acetonitrile/ether and identified by single crystal X-ray diffraction analysis as the *endo-cis* isomer.

*Preparation of endo-cis-[CpMo(CO)(NO)(η^3-CH(Ph)CHCH$_2$)]PF_6 (endo-cis-**1**).* An analogous preparation using $NOPF_6$ gave the hexafluorophosphate salt in 81% yield. IR (CH_2Cl_2): ν(C≡O) 2086, ν(N=O) 1719 cm^{-1}. ^{1}H NMR (acetone-d_6, 30 °C, 500 MHz) δ 7.67–7.43 (Ph), 6.40 (s, Cp), 6.34 (ddd, *J* 13.5, 12.5, 7.0 Hz, H_c), 5.80 (br d, *J* 12.5 Hz, $H_{a'}$), 5.03 (ddd, *J* 7.0, 1.8, 1.0 Hz, H_s), 3.25 (ddd, *J* 13.5, 1.8, 1.1 Hz, H_a). Anal. Found: C, 37.49; H, 2.98-$C_{15}H_{14}NO_2MoPF_6$ calcd: C, 37.44; H, 2.93%.

*Preparation of CpMo(NO)(CO)(η^2-(E)-2,2-dimethyl-5-phenyl-4-pentenal) (**3**).* A suspension of [CpMo(CO)(NO)(η^3-CH(Ph)CHCH$_2$)]BF_4 (0.423 g, 1.0 mmol) in 30 ml dry THF was cooled to 0 °C and 1-pyrrolidino-2-methylpropene (0.141 g, 1.1 mmol) added. Within 10 min, all residual solid in the reaction mixture has dissolved to give a gold solution. After an additional 20 min at low temperature, distilled H_2O (0.05 ml, excess) was added, the reaction stirred an additional 15 min, and solvent removed under reduced pressure to give the crude product as a brown-gold oily solid. This material was redissolved in CH_2Cl_2 and filtered through an 8 cm × 2 cm pad of silica gel. Solvent was removed from the gold eluant under a flow of nitrogen, and the residual gold solid crystallized at −30 °C from CH_2Cl_2/pentane

Table 3a

Bond distances (Å) for *endo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

Mo–Cp(1)	2.372(2)	Cp(1)–Cp(2)	1.410(4)
Mo–Cp(2)	2.346(2)	Cp(1)–Cp(5)	1.391(3)
Mo–Cp(3)	2.320(2)	Cp(1)–Hp(1) [a]	0.98(2)
Mo–Cp(4)	2.303(2)	Cp(2)–Cp(3)	1.404(4)
Mo–Cp(5)	2.353(2)	Cp(2)–Hp(2)	0.88(3)
Mo–N	1.804(2)	Cp(3)–Cp(4)	1.401(4)
Mo–C	2.057(3)	Cp(3)–Hp(3)	0.92(3)
Mo–C(1)	2.404(2)	Cp(4)–Cp(5)	1.406(4)
Mo–C(2)	2.342(2)	Cp(4)–Hp(4)	0.82(3)
Mo–C(3)	2.346(3)	Cp(5)–Hp(5)	0.93(2)
N–O(1)	1.171(2)	C(1)–C(2)	1.389(3)
C–O(2)	1.118(3)	C(1)–C(4)	1.467(3)
		C(1)–H(1)	0.94(2)
B–F(1)	1.386(3)	C(2)–C(3)	1.386(3)
B–F(2)	1.372(3)	C(2)–H(2)	0.85(3)
B–F(3)	1.373(3)	C(3)–H(3s)	0.84(2)
B–F(4)	1.368(3)	C(3)–H(3a)	1.04(3)
		C(4)–C(5)	1.399(3)
		C(4)–C(9)	1.382(3)
		C(5)–C(6)	1.374(4)
		C(5)–H(5)	0.92(2)
		C(6)–C(7)	1.375(4)
		C(6)–H(6)	0.84(3)
		C(7)–C(8)	1.364(4)
		C(7)–H(7)	0.99(3)
		C(8)–C(9)	1.385(3)
		C(8)–H(8)	0.99(3)
		C(9)–H(9)	0.95(2)

[a] See footnote Table 2b.

to give 0.198 g (0.50 mmol, 50% yield) of product as orange crystals. A ^{1}H NMR spectrum of the crystalline product (toluene-d_8, 25 °C, 500 MHz) showed broad resonances. Cooling the sample to −40 °C gave two sharp sets of signals; warming

Table 3b

Bond distances (Å) for *exo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

Mo–Cp(1)	2.336(8)	C(5)–C(6)	1.37(1)
Mo–Cp(2)	2.300(9)	C(6)–C(7)	1.38(1)
Mo–Cp(3)	2.297(9)	C(7)–C(8)	1.37(1)
Mo–Cp(4)	2.295(9)	C(8)–C(9)	1.37(1)
Mo–Cp(5)	2.350(9)	Cp(1)–Cp(2)	1.38(1)
Mo–C(1)	2.455(8)	Cp(1)–Cp(5)	1.36(1)
Mo–C(2)	2.268(9)	Cp(2)–Cp(3)	1.37(1)
Mo–C(3)	2.346(9)	Cp(3)–Cp(4)	1.37(2)
Mo–N	1.818(7)	Cp(4)–Cp(5)	1.41(1)
Mo–C	2.041(9)	N–O(1)	1.160(9)
C(1)–C(2)	1.39(1)	C–O(2)	1.13(1)
C(1)–C(4)	1.45(1)	B–F(1)	1.30(1)
C(2)–C(3)	1.39(1)	B–F(2)	1.33(1)
C(4)–C(5)	1.42(1)	B–F(3)	1.32(1)
C(4)–C(9)	1.36(1)	B–F(4)	1.34(1)

the sample to 70 °C gave coalescence of nearly all signals of the original pair of isomers as well as the appearance of a new set of resonances consistent with an additional isomer. The ratio of original isomers to new isomer was 6.3/1, with a small amount of free olefin evident in the spectrum. IR (C_6H_{12}): ν(C=O) 1981, ν(N=O) 1650, ν(C=O) 1728 cm^{-1}. ^1H NMR (toluene-d_8, −40 °C, 500 MHz): major isomer, δ 9.26 (s, H_f), 4.64 (s, Cp), 3.70–3.53 (m, H_a, $H_{a'}$), 2.80 (dd, J 14.5, 2.0 Hz, methylene), 1.37 (dd, J 14.5, 10.0 Hz, methylene), 0.87 (s, CH_3), 0.74 (s, CH_3). minor isomer, δ 9.18 (s, H_f), 4.65 (s, Cp), 2.43 (dd, J 13.5, 2.0 Hz, methylene), 0.84 (s, CH_3), 0.79 (s, CH_3), 0.41 (dd, J 13.5, 11.8 Hz, methylene), (H_a and $H_{a'}$ were obscured); for both isomers δ 7.30–6.77 (Ph); isomer ratio 1.6/1. ^1H NMR (toluene-d_8, 70 °C, 500 MHz): (new isomer) δ 9.31 (s, H_f), δ 7.17–6.63 (Ph), 4.65 (s, Cp), 3.98 (d, J 12.8 Hz, $H_{a'}$), 3.41 (ddd, J 12.8, 11.8, 2.5 Hz, H_a), 2.83 (dd, J 15.0 2.5 Hz, methylene), 0.90 (s, CH_3), 0.80 (s, CH_3), (the second methylene resonance was obscured).

Table 4a

Bond angles (°) for *endo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

N–Mo–C	85.12(9)	C(2)–C(1)–C(4)	124.9(2)
N–Mo–C(1)	90.12(8)	C(2)–C(1)–H(1)	116(1)
N–Mo–C(2)	87.25(9)	C(4)–C(1)–H(1)	115(1)
N–Mo–C(3)	112.0(1)	C(1)–C(2)–C(3)	120.2(3)
C–Mo–C(1)	131.27(9)	C(1)–C(2)–H(2)	118(2)
C–Mo–C(2)	97.28(9)	C(3)–C(2)–H(2)	121(2)
C–Mo–C(3)	76.3(1)	C(2)–C(3)–H(3s)	122(2)
C(1)–Mo–C(2)	34.00(8)	C(2)–C(3)–H(3a)	119(1)
C(2)–Mo–C(3)	34.39(9)	H(3s)–C(3)–H(3a)	115(2)
Mo–N–O(1)	174.6(2)	C(1)–C(4)–C(5)	123.2(2)
Mo–C–O(2)	175.3(2)	C(1)–C(4)–C(9)	119.1(2)
		C(5)–C(4)–C(9)	117.7(2)
F(1)–B–F(2)	108.9(2)	C(4)–C(5)–C(6)	121.0(2)
F(1)–B–F(3)	109.7(2)	C(4)–C(5)–H(5)	118(2)
F(1)–B–F(4)	108.8(2)	C(6)–C(5)–H(5)	121(2)
F(2)–B–F(3)	110.0(2)	C(5)–C(6)–C(7)	120.1(3)
F(2)–B–F(4)	109.3(2)	C(5)–C(6)–H(6)	118(2)
F(3)–B–F(4)	110.2(2)	C(7)–C(6)–H(6)	122(2)
		C(6)–C(7)–C(8)	120.0(3)
Cp(2)–Cp(1)–Cp(5)	108.5(2)	C(6)–C(7)–H(7)	118(2)
Cp(2)–Cp(1)–Hp(1) [a]	127(1)	C(8)–C(7)–H(7)	122(2)
Cp(5)–Cp(1)–Hp(1)	124(1)	C(7)–C(8)–C(9)	120.2(3)
Cp(1)–Cp(2)–Cp(3)	107.9(2)	C(7)–C(8)–H(8)	122(2)
Cp(1)–Cp(2)–Hp(2)	133(2)	C(9)–C(8)–H(8)	117(2)
Cp(3)–Cp(2)–Hp(2)	119(2)	C(4)–C(9)–C(8)	121.1(2)
Cp(2)–Cp(3)–Cp(4)	107.3(2)	C(4)–C(9)–H(9)	117(1)
Cp(2)–Cp(3)–Hp(3)	126(2)	C(8)–C(9)–H(9)	122(1)
Cp(4)–Cp(3)–Hp(3)	127(2)		
Cp(3)–Cp(4)–Cp(5)	108.9(2)		
Cp(3)–Cp(4)–Hp(4)	122(2)		
Cp(5)–Cp(4)–Hp(4)	129(2)		
Cp(1)–Cp(5)–Cp(4)	107.4(2)		
Cp(1)–Cp(5)–Hp(5)	122(2)		
Cp(4)–Cp(5)–Hp(5)	130(2)		

[a] See footnote Table 2b.

Table 4b

Bond angles (°) for *exo-cis*-[η^5-(C_5H_5)Mo(NO)(CO)($C_6H_5C_3H_4$)]BF_4

N–Mo–C	88.4(3)	C(4)–C(5)–C(6)	119.6(8)
N–Mo–C(1)	78.5(3)	C(5)–C(6)–C(7)	121.2(9)
N–Mo–C(2)	105.7(3)	C(6)–C(7)–C(8)	120.2(9)
N–Mo–C(3)	101.8(3)	C(7)–C(8)–C(9)	118.0(9)
C–Mo–C(1)	126.7(3)	C(4)–C(9)–C(8)	124.1(8)
C–Mo–C(2)	107.0(3)	Cp(2)–Cp(1)–Cp(5)	110.2(9)
C–Mo–C(3)	72.2(3)	Cp(1)–Cp(2)–Cp(3)	106.2(9)
Mo–N–O(1)	173.8(6)	Cp(2)–Cp(3)–Cp(4)	109.8(9)
Mo–C–O(2)	177.3(8)	Cp(3)–Cp(4)–Cp(5)	107.0(9)
		Cp(1)–Cp(5)–Cp(4)	106.7(9)
C(1)–Mo–C(2)	34.0(3)		
C(2)–Mo–C(3)	35.0(3)	F(1)–B–F(2)	109.3(9)
C(2)–C(1)–C(4)	128.0(7)	F(1)–B–F(3)	108.7(0)
C(1)–C(2)–C(3)	121.8(8)	F(1)–B–F(4)	111.2(9)
C(1)–C(4)–C(5)	122.4(8)	F(2)–B–F(3)	107.0(9)
C(1)–C(4)–C(9)	120.7(7)	F(2)–B–F(4)	113(1)
C(5)–C(4)–C(9)	116.9(8)	F(3)–B–F(4)	107.9(9)

*Preparation of exo-cis-[CpMo(CO)(NO)(η^3-CH(Ph)CHCH$_2$)]BF_4 (exo-cis-**1**).* [CpMo(NO)(CO)(η^3-C_3H_5)]PF_6 (1.42 g, 3.5 mmol) was partially dissolved in 80 ml of THF. The suspension was cooled to −35 °C and 1.9 ml (3.8 mmol) of a 2 *M* solution of PhMgCl in THF was added under N_2. The reaction was continued for 3 h at this temperature and then hydrolyzed with water. The solvent was removed and the residue was chromatographed on deactivated alumina with 1/1 pentane/CH_2Cl_2. Elution of a yellow band and solvent removal gave 0.81 g (68%) of a yellow oil. IR (CH_2Cl_2): ν(N=O) 1662 and ν(C=O) 1972 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) broad from conformational averaging, δ 1.96–2.45 (several br m, $H_{a,b}$ and H_d or H_e), 3.2 (br m, H_d or H_e), 3.4 (br m, H_c), 5.38 (br s, Cp) 7.2–7.6 (m, Ph). This complex oxidized easily and it was used immediately in the next step.

A solution of CpMo(NO)(CO)(η^2-CH_2(Ph)CHCH$_2$) (0.81 g, 2.4 mmol) and triphenylcarbenium tetrafluoroborate (0.79 g, 2.4 mmol) in 90 ml of CH_2Cl_2 was stirred at 0 °C under N_2 for 30 min. This solution was poured into cold ether and the yellow precipitate, which formed immediately, was separated by centrifugation and washed with ether. The product was obtained in 60% yield (0.61 g) and melted at 145–146 °C (dec). IR (CH_2Cl_2): ν(N=O) 1714 and ν(C=O) 2079 cm^{-1}. ^1H NMR (acetone-d_6, 25 °C, 250 MHz): δ 3.20 (ddd, *J* 12.9, 1.6, 1.0 Hz, H_a), 4.59 (dd, *J* 8.0, 1.6 Hz, H_s), 5.65 (d, *J* 13.7 Hz, $H_{a'}$), 6.34 (ddd, *J* 13.7, 12.9, 8.0 Hz, H_c), 5.97 (s, Cp), 7.55–7.65 and 7.80–7.95 (m, Ph). A sample of this material was recrystallized from CH_2Cl_2 under slow N_2 flow and identified by single crystal X-ray diffraction analysis as the *exo-cis* isomer of **1**.

*Preparation of CpMo(NO)(CO)(η^2-2,2-dimethyl-3-phenyl-4-pentenal) (**4**).* A suspension of *exo-cis*-[CpMo(NO)(CO)(η^3-CH(Ph)CHCH$_2$)]BF_4, **1**, (0.42 g, 1 mmol) in 16 ml of THF was treated with 0.16 ml (1.1 mmol) of 1-pyrrolidino-2-methylpropene at 0 °C. After 5 min of stirring the suspension dissolved to form a yellow solution and 5 min later a yellow solid precipitated. After the reaction was allowed to stand an additional 10 min, water was added to hydrolyze the iminium salt. The solvent was removed under reduced pressure and the remaining oil was taken up in

CH_2Cl_2 and chromatographed on alumina with CH_2Cl_2/pentane (4/1). The elution of the yellow band yielded a yellow oil (0.75 g, 75% yield). IR (CH_2Cl_2): ν(N=O) 1624 and 1667, ν(C=O) 1729, 1758 and 1894 cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): broad from conformational averaging, δ 0.90 (s, Me), 1.20 (s, Me), 2.19 (dd, J 12.0, 3.5 Hz, H_a), 2.35 (dd, J 12.0, 3.5 Hz, H_b), 2.67 (d, J 10.4 Hz, H_d), 3.41 (ddd, J 12.0, 10.4, 9.5 Hz, H_c), 5.09 (s, Cp), 7.25–7.45 (m, Ph), 9.60 (s, CHO).

Preparation of 2,2-dimethyl-3-phenyl-4-pentenal. CpMo(NO)(CO)(η^2-2,2-dimethyl-3-phenyl-4-pentenal) (0.28 g, 0.70 mmol) was dissolved in 10 ml of $CHCl_3$ and the solution allowed to stand in the air for 4 days, after which the metal complex had completely decomposed. The free olefin was chromatographed on alumina with CH_2Cl_2. The yield was 0.12 g (90%). The 2,4-dinitrophenylhydrazone melted at 162.5–163°C (lit. [6] 164°C).

Preparation of CpMo(NO)(CO)[η^2-(dimethyl 3-phenyl-1-butene-4,4-dicarboxylate)] (5). To a suspension of *exo-cis*-[CpMo(NO)(CO)(η^3-CH(Ph)CHCH$_2$)]BF_4 (0.42 g, 1 mmol) in 16 ml of THF at −78°C was added 4 ml of a ~0.5 *M* solution of $NaCH(CO_2CH_3)_2$ in THF. After being stirred for 20 min at −78°C the mixture was allowed to warm to room temperature and the solvent was removed under vacuum. The crude material was purified by chromatography on deactivated alumina and the elution with CH_2Cl_2 gave 0.35 g (75% yield) of a yellow oil. IR (CH_2Cl_2): ν(N=O) 1624, ν(C=O) 1796, 1756, 1986 cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): δ 2.06, 2.33, 3.20 (3 br m, H vinylic and benzylic), 3.37, 3.42, 3.71, 3.80 (4 s, Me), 3.98 (br d, J 10.7 Hz, H malonate), 5.02 (br s, Cp), 7.20–7.45 (m, Ph).

Preparation of dimethyl 3-phenyl-1-butene-4,4-dicarboxylate (6). This procedure followed that for 2,2-dimethyl-3-phenyl-4-pentenal given above. Evaporation of the eluant from chromatography on alumina gave the free olefin as a pale yellow oil with a 90% yield. IR (CH_2Cl_2): ν(C=O) 1757, 1791 cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): δ 3.47 (s, Me), 3.72 (s, Me), 3.85 (d, J 12.5 Hz, H malonate), 4.10 (dd, J 12.5, 8.1 Hz, H benzylic), 5.04–5.14 (AB part of an ABX system of geminal protons), 5.98 (m, H vinylic), 7.19–7.30 (m, Ph).

Preparation of (−)-dimethyl 3-phenyl-1-butene-4,4-dicarboxylate. (−)-NMCpMo(NO)(CO)(η^2-dimethyl-3-phenyl-1-butene-4,4-dicarboxylate) was prepared in 30% yield by following an analogous procedure to that described for the racemic mixture, but starting with (+)-[NMCpMo(NO)(CO)(η^3-C_3H_5)]PF_6 [1b,7] instead of [CpMo(NO)(CO)(η^3-C_3H_5)]PF_6. The chromatographic purifications in this case required an initial elution with pentane to separate some organic materials from the metal complex, which was eluted with CH_2Cl_2. A solution of (−)-NMCpMo(NO)(CO)[η^2-(dimethyl 3-phenyl-1-butene-4,4-dicarboxylate)] in $CHCl_3$ was allowed to stand in the air for 15 days after which the free olefin was chromatographed on alumina with CH_2Cl_2. Complete separation from minor impurities (to assure absence of any impurities with a high optical rotation) required subsequent repeated (3 times) chromatography on silica gel with CH_2Cl_2 and $CHCl_3$. The enantiomeric purity of the (−)-dimethyl 3-phenyl-1-butene-4,4-dicarboxylate was determined by using Eu(tfc)$_3$ in benzene-d_6. The addition of the chiral shift reagent induced a separation in both of the diastereotopic methyl singlets (the intensities of the outer resonances at δ 3.08 and 3.40 were much larger than those at δ 3.14 and 3.34). The relative positions of the methyl resonances of the enantiomers in the ^1H NMR in the presence of Eu(tfc)$_3$ were confirmed by adding a racemic mixture of the olefin to

the sample of the enantiomerically enriched product. The ee, taken from the integrated areas, was 97%. A sample of the free olefin gave $[\alpha]_D^{21} \approx -24°$ (c 0.12, $CHCl_3$). The absolute configuration should be (S) based on our understanding of the mechanism of formation. Note also that the rotation of $[\alpha]_D^{20} + 38.5°$ for the methyl-substituted olefin analogue, (+)-(R)-dimethyl 4-phenyl-2-butene-5,5-dicarboxylate [14], supports this assignment of absolute configuration.

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References

1 (a) J.W. Faller, K-H. Chao, and H.H. Murray, Organometallics, 3 (1984) 1231; (b) J.W. Faller and K-H. Chao, ibid, 927; (c) J.W. Faller and K-H. Chao, J. Am. Chem. Soc., 105 (1983) 3893; (d) J.W. Faller and C. Lambert, Tetrahedron, 41 (1985) 5755.
2 J.W. Faller, D. Linebarrier and C. Lambert, in preparation.
3 W.E. VanArsdale, R.E.K. Winter and J.K. Kochi, Organometallics, 5 (1986) 645.
4 J.W. Faller, C.C. Chen, M.J. Mattina and A. Jakubowski, J. Organomet. Chem., 52 (1973) 361.
5 (a) J.W. Faller, H.H. Murray, D.L. White and K-H. Chao, Organometallics, 2 (1983) 400; (b) J.W. Faller and A.M. Rosan, Ann. N.Y. Acad. Sci., 295 (1977) 186; (c) J.W. Faller and A.M. Rosan, J. Am. Chem. Soc., 99 (1977) 4858.
6 P. Cresson, Bull. Soc. Chim. France, (1964) 2618.
7 J.W. Faller and Y. Shvo, J. Am. Chem. Soc., 102 (1980) 5396.
8 (a) B.E.R. Schilling, R. Hoffman and J.W. Faller, J. Am. Chem. Soc., 101 (1979) 592; (b) R.D. Adams, D.F. Chodosh, J.W. Faller and A.M. Rosan, J. Am. Chem., Soc., 101 (1979) 2570.
9 W.A. Kiel, G.-Y. Lin, A.G. Constable, F.B. McCormick, C.E. Strouse, O. Eisenstein, and J.A. Gladysz, J. Am. Chem. Soc., 104 (1982) 4865.
10 (a) J.W. Faller and Y. Ma, Organometallics, 7 (1988) 559; (b) J.W. Faller and Y. Ma, ibid, 8 (1989) 609.
11 (a) J.W. Faller and B.V. Johnson, J. Organomet. Chem., 88 (1975) 101; (b) J.W. Faller, B.V. Johnson, and C.D. Schaeffer, Jr., J. Am. Chem. Soc., 98 (1976) 1395.
12 D.T. Cromer and J.T. Waber, International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1975; Vol IV; (a) Table 2.2B, p. 99–101; (b) Table 2.3.1, p. 149–150.
13 J.A. Ibers and W.C. Hamilton, Acta Crystallog., 17 (1964) 781.
14 T. Hayashi, A. Yamamoto and T. Hagihara, J. Org. Chem., 51 (1986) 723.