# Stereoselectivity in Carbanion Addition to Coordinated Allyl Ligands. Catalytic (Exo–Endo) Isomerization of Cationic Molybdenum Complexes

W. E. VanArsdale,† R. E. K. Winter, and J. K. Kochi*†

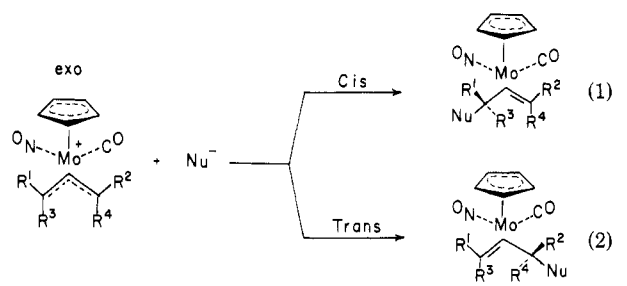
*Departments of Chemistry, University of Houston, University Park, Houston, Texas 77004, and University of Missouri—St. Louis, St. Louis, Missouri 63121*

*Received August 5, 1985*

Regio- and stereochemistry in the nucleophilic addition of various types of carbanions to coordinated allyl ligands are examined in a series of $(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^3\text{-allyl})^+$ cations II. Stereoselectivity is determined primarily by the conformational preference of the allyl ligand in the endo and exo isomers of II. Different additives, including the carbanion itself, induce an efficient catalytic equilibration of the conformational population which can be faster than nucleophilic addition. The rapidity of such a preequilibrium endo–exo interconversion can lead to a high degree of stereoselectivity in the addition of various carbanionic nucleophiles to allyl cations II. Thus the $\eta^2$-olefin product of the addition of the dimethyl benzylmalonate anion to the 1,3-dimethallyl cation IIc is a single diastereomer formed in high yields. The stereochemistry of the adduct $(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^2\text{-}C_{17}H_{22}O_4)$ (VIII) is established by X-ray crystallography. Compound VIII crystallized in the monoclinic space group $P2_1/c$ with lattice constants $a$ = 11.434 (3) Å, $b$ = 17.298 (5) Å, $c$ = 12.771 (3) Å, $\beta$ = 116.51 (1)°, and $Z$ = 4. The stereochemistry of nucleophilic addition is discussed in terms of the preferred attack on a coordinated allyl ligand.

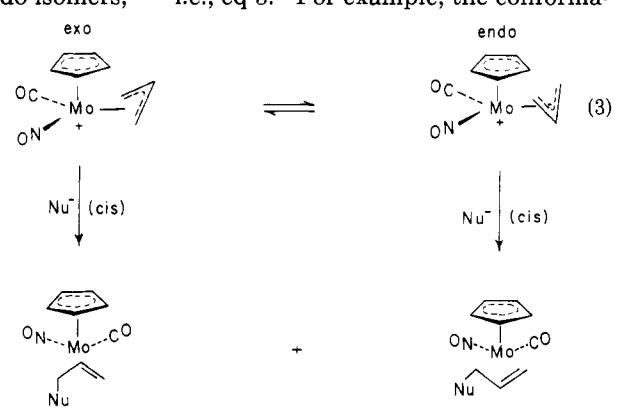
## Introduction

Nucleophilic addition to coordinated ligands is a useful strategy in organic synthesis.[1-3] Indeed extraordinary regioselectivity has been achieved in a series of cationic complexes of the general structure $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-allyl})^+$ with an asymmetric molybdenum center.[4-7] In this system, the addition of various types of nucleophiles to the allyl ligand leads to structurally diverse $\eta^2$-olefin complexes which can be isolated intact.[8] The regioselectivity has been attributed to the directing effect of the nitrosyl group—theoretical calculations supporting an electronic influence which promotes nucleophilic attachment at the allylic terminus cis to the NO ligand from the external or anti face,[9] e.g., eq 1 and 2. However, com-




(1) (2)

plications can arise from the conformational interconversion of the coordinated allyl group in the form of exo and endo isomers,[8b,10] i.e., eq 3. For example, the conforma-




(3)

tionally pure exo and endo isomers of the $\eta^3$-cyclooctenyl have been reported to undergo either regiospecific (exo) or nonselective (endo) nucleophilic addition.[11] However with other allyl derivatives, the nucleophilic addition to mixtures of exo and endo cations has led to a predominance of a single diastereomer.[5b,c,12] Such apparent inconsistencies can be rationalized by a "reagent-assisted" conformational isomerization,[5c,7,11] in which the initial interaction between the cation and the nucleophile results in a rapid equilibration of the conformational populations prior to the formation of the $\eta^2$-olefin product.

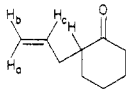
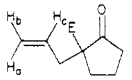
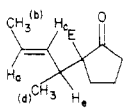
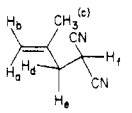
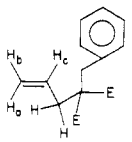
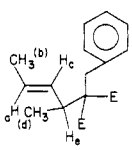
In an earlier study, we observed the nucleophilic addition of thiophenolate to the cyclooctenyl–molybdenum cation to produce in high yields only one stereoisomer, the structure of which was established by X-ray crystallography.[7] Since the cyclooctenyl cation was formed predominantly in the endo conformation,[11] the production of the

† University of Houston.

(1) (a) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (b) Alper, H. "Transition Metals in Organic Synthesis"; Academic Press; New York, 1976; Vol. 2, p 1978.
(2) Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry", Brooks-Cole: Monterey, CA, 1985.
(3) (a) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. (b) Trost, B. M. *Ibid.* **1980**, *13*, 385.
(4) Bailey, N. A.; Kita, W. F.; McCleverty, J. A.; Murray, A. J.; Mann, B. E.; Walker, N. W. J. *J. Chem. Soc., Commun.* **1974**, 592.
(5) (a) Faller, J. W.; Rosan, A. M. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 186. (b) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570. (c) Faller, J. W.; Chao, K H. *Ibid.* **1983**, *105*, 3893. (d) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.
(6) (a) Pearson, A. J.; Khan, Md. N. I. *Tetrahedron Lett.* **1985**, *26*, 1407. (b) Pearson, A. J.; Khan, Md. N. I.; Clardy, J. C.; Cunheng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.
(7) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *J. Organomet. Chem.* **1985**, *296*, 31.
(8) In the case of inorganic iodide, however, substitution at the metal center occurs (with loss of CO) to afford neutral iodo (allyl) complexes: (a) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5396. (b) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.
(9) Schilling, B. E. R.; Hoffman, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.
(10) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.
(11) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.
(12) The alternative pair of diastereomers (i.e., the same relative configuration at the metal and at C-2, but coordination through different faces of the olefin) is less likely on the basis of crystallographic data obtained on other structurally related products (cf. ref 5b,c).

0276-7333/86/2305-0645$01.50/0 

Table I. Proton Chemical Shifts in $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-olefin})]$ Complexes[a]

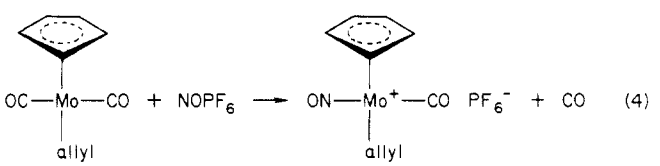
| $\eta^2$-olefin complex | olefin | Cp | $H_a$ | $H_b$ | $H_c$ | others |
|---|---|---|---|---|---|---|
| III |  | 5.48, 5.45 (s) | ~3.70 | 3.20 (br m) | 2.80 | 2.82-1.44 (br m) |
| IV |  | 5.47 (s) | ~3.40 | 2.90 (br m) | 2.50 | 3.70, 3.67 sh (s); 2.47-1.60 (br m) |
| V[b] |  | 5.53 (s) | ~3.35 (m) | 1.34 (d) | ~2.80 (bf d), $J \simeq 12$ | 3.74, 3.70 sh (s); 2.80-1.60 (br m); 1.17 (d, $H_d$) |
| VI |  | 5.49, 5.47 (s) | 3.05 (d) | 2.80 (d) | 1.76 (s) | 3.98 (dd, $H_f$); 2.48 (br d, $H_d$, $H_e$) |
| VII[c] |  | 5.40 (s) | 2.84 (dd) | 2.20 (br d) | 3.48 (m) | 7.16 (br s); 3.67, 3.65 (s); 3.34, 3.30 (s); 2.09 (d); 1.40 (dd) |
| VIII |  | 5.44 (s) | 3.09 (m) | 1.36 (d) | 2.98 (dd), $J_{ac} = 11.5$ | 7.13 (br s); 3.58, 3.56 (s); 3.31, 3.20 (s); 2.01 (dq, $H_e$) |

[a] ppm relative to $Me_4Si$; $J$ in Hz; $CDCl_3$; 25 °C, E = $CO_2CH_3$. [b] 15 °C. [c] 60 °C.

single adduct required either a trans addition or a prior nucleophile-induced (endo → exo) interconversion followed by cis addition. In order to resolve this ambiguity and to extend the synthetic utility of this organometallic system, we examined the addition of various types of carbon-centered nucleophiles to a series of $(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^3\text{-allyl})^+$ complexes with and without prochiral carbon termini.

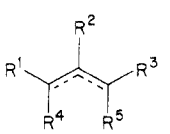
## Results and Discussion

The nucleophilic additions were carried out by a standard procedure involving the direct conversion of the stable allyldicarbonyl complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-allyl})$ I to the allyl cation II with 1 equiv of nitrosyl hexafluorophosphate in acetonitrile solutions.[4,5] The series of




I II

structurally differentiated allyl groups below are included in this study.

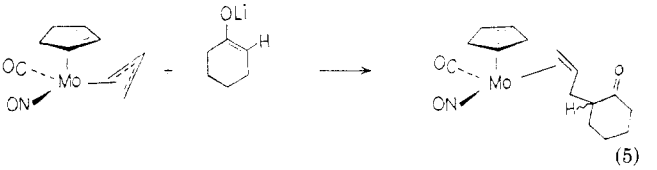


a, allyl
b, 2-methallyl ($R^2$=$CH_3$)
c, 1,3-dimethallyl ($R^1$, $R^3$=$CH_3$)
d, cyclooctenyl ($R^{4,5}$=$(CH_2)_5$)

The formation of this allyl cation II occurs cleanly and readily at −20 °C with the evolution of 1 equiv of carbon monoxide within 15 min. The conversion is readily followed by the downfield shift of the singlet Cp resonance at $\delta$ 5.2 ± 0.1 in the $^1H$ NMR spectrum of the neutral dicarbonyl complex I to $\delta$ 6.0 ± 0.2 in the cationic complex II. Furthermore, the conformational composition of II can be deduced by the appearance of a pair of resolved signals—the singlet Cp resonance due to the endo isomer being invariably located downfield relative to that of the exo isomer. Similarly the formation of a mixture of $\eta^2$-olefin products resulting from the nucleophilic addition could be readily diagnosed by the appearance of resolved singlet Cp resonances in the region of $\delta$ 5.5 ± 0.1.

The carbon-centered nucleophiles were generated in situ by proton removal from (a) cyclohexanone, (b) 2-carbomethoxycyclopentanone, (c) malononitrile, and (d) dimethyl benzylmalonate, representing a simple ketone, a $\beta$-keto ester, a nitrile, and an encumbered carbanion, as described individually below.

**I. Nucleophilic Addition of Cyclohexanone Enolate.** The addition of lithiocyclohexanone to the allyl cation IIa led to the slow formation of the corresponding olefin complex III, i.e., eq 5, the production of which was




(5)

monitored by the gradual intensification of a mobile organometallic band in the thin-layer chromatogram (TLC). The complex III isolated in 25% yield consisted of a mixture of stereoisomers, as judged by a pair of well-resolved singlet Cp resonances at $\delta$ 5.45 and 5.48 of equal intensity (Table I). Since the pyrolysis of III afforded only 2-allylcyclohexanone, the mixture of diasteromers undoubtedly relates to the attack of both enantiofaces of the enolate at either terminus of the coordinated allyl group.[12] This structural assignment is supported by the infrared data in Table II showing the coordination about the mo-

**Table II. Infrared Stretching Frequencies of CO and NO Ligands in the $\eta^2$-Olefin Products[a]**

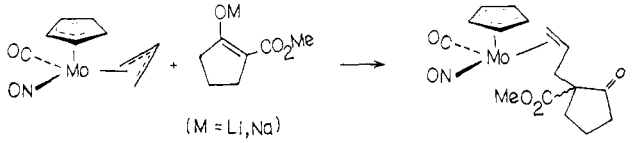
| $\eta^2$-olefin product | $\nu_{CO}$ | $\nu_{NO}$ | others |
|---|---|---|---|
| III | 1967 | 1645 | 1710 (keton) |
| IV | 1963 | 1615 | 1745 (ester) |
| | | | 1727 (ketone) |
| V[b] | 1963 | 1620 | 1742 (ester) |
| | | | 1730 (ketone) |
| VI | 1965 | 1620 | 2240 (nitrile) |
| VII | 1965 | 1630 | 1725 (ester) |
| VIII[b] | 1973 | 1621 | 1726 (ester) |

[a] Neat films, unless otherwise specified; $cm^{-1}$. [b] Dichloromethane

lybdenum center to be intact.

Although the yield and selectivity with lithiocyclohexanone were low, the formation of the olefin complex III does establish the reactivity of the carbon center in enolates toward nucleophilic addition of allyl ligands.

**II. Nucleophilic Addition β-Keto Ester Enolates.** The addition of either the sodium or lithium enolate of the β-keto ester 2-carbomethoxycyclopentanone to the allyl cation IIa afforded the olefin complex IV in ~ 60% yield (eq 6). The stereochemical outcome of the addition could




(6)

be inferred from both the $^1H$ and $^{13}C$ NMR spectra of IV. The $^1H$ NMR spectrum at 55 °C[13] exhibited a doubling of the methoxyl resonances (δ 3.70, 3.67) which is attributed to the formation of a new chiral center at C-2 of the cyclopentanone ring with no apparent stereoselectivity. This analysis was confirmed by the $^{13}C$ NMR spectrum of IV which also showed a doubling of the ketone singlet (δ 214.1, 213.8), the ester carbonyl singlet (δ 171.2, 170.8), and the quaternary singlet (δ 63.4, 63.2) as well as the allylic methylene triplet (δ 42.3, 41.9) in Table III.[14] Pyrolysis of IV produced only 2-carbomethoxy-2-allylcyclopentanone. Coupled with the NMR data, we conclude that only two diastereomers are formed in roughly equal amounts.

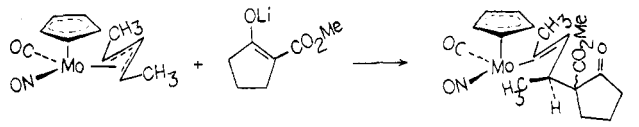
Although a X-ray crystallographic determination (vide infra) of the olefin complex IV was not undertaken, we can infer the structure on the basis of previous studies of related systems.[4,5b,c,7] Thus the available crystallographic data of complexed $\eta^2$-olefin products are consistent with exclusive nucleophilic attachment at that terminus of the allyl ligand which is cis to the nitrosyl group in the exo conformation of the cation II, as delineated by Hoffman and Faller.[2] Furthermore the approach of the nucleophile occurs exclusively from that allyl face which is external (i.e., anti) to the metal center,[15] as summarized.


(13) At this temperature olefin rotation in the complex is expected to be rapid (vide infra), so that two methoxyl signals are indicative of two noninterconvertible diastereomers rather than two rotameric isomers.

(14) This measurement was taken at 25 °C, when olefin rotation is occurring at an intermediate exchange rate. Under these conditions, the olefinic carbon resonances are too broad to be observed.

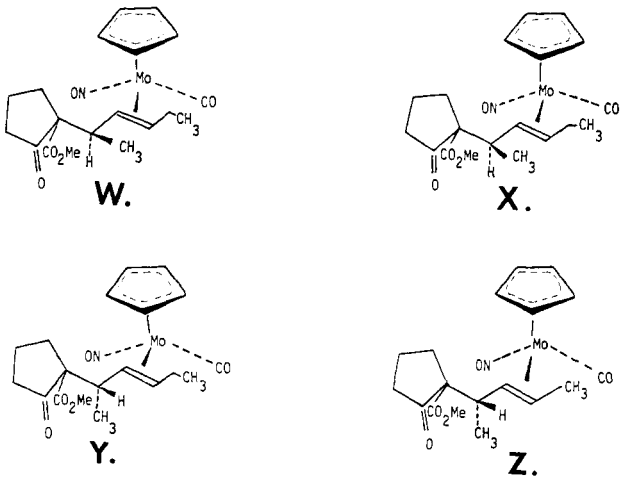
If we accept this stereochemical description, the structures of the products III and IV derived from the enolate of cyclohexanone and 2-carbomethoxycyclopentanone, respectively, correspond to the attack on the allyl cation IIa, by either enantioface of the nucleophile with more or less equal facility. Since IIa is formed kinetically in eq 4 with endo dominance,[10] the results are consistent with either a preferential addition to the exo isomer and/or equilibration of the endo isomer prior to addition.[17]

These results thus indicate that the allyl cation IIa makes no distinction as to which enantioface of the enolate is allylated. However diastereoselective addition in this system may be achieved if the affected allylic terminus (rather than the enolate) were prochiral, as previously observed by Faller and co-workers[5c] in the nucleophilic addition of an achiral enamine to the 1,3-dimethallyl cation IIc. Such a stereochemical discrimination should be augmented when a prochiral allyl ligand is coupled with a prochiral enolate. In order to test this notion, we treated the lithium enolate of 2-carbomethoxycyclopentanone with the 1,3-dimethallyl cation IIc. Indeed the nucleophilic addition proved to be quite facile, and the olefin complex V was readily obtained in ~70% yield (eq 7).




(7)

The allylated product V possesses four chiral centers, viz., the metal, the two contiguous carbon centers, and the olefin coordinated through a single face. The possibility of *E*/*Z* isomerism in the olefin was ruled out by spectroscopic analysis. Thus exclusive *E* geometry could be inferred from the large coupling constant (12 Hz) observed between the olefinic protons.[18] Accordingly the overall stereoselectivity in this nucleophilic addition may be viewed as being comprised of two parts, viz., chirality at the carbomethoxy-bearing carbon (i.e., the isomeric pairs W/X and Y/Z) and chirality at the allylic terminus (i.e., the isomeric pairs W/Y and X/Z) in the four diastereomeric $\eta^2$-olefin complexes described.[19] In fact the spectral




(15) Syn addition has been noted in other π-allyl complexes.[16]

(16) (a) Bäckvall, J. E.; Nordberg, R. E.; Bjorkman, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943. (b) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. (c) Hosokawa, T.; Imada, Y.; Murahasi, S.-I. *Tetrahedron Lett.* **1982**, *23*, 3373.

(17) Faller and co-workers suggested that both of these factors are operative with acyclic allyl ligands.[11]

(18) A similar result was obtained in enamine addition to IIc.[11]

Table III. $^{13}C$ Chemical Shifts of $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-olefin})]$ Complexes[a]

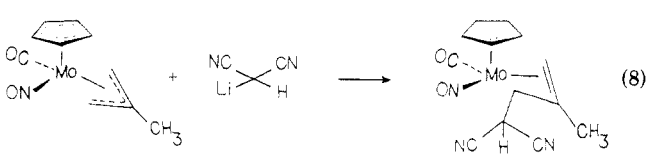
| $\eta^2$-olefin complex | CO | Cp | olefinic | others |
|---|---|---|---|---|
| IV | 230.4 (s) | 95.6 (d) | not observed | 214.1, 213.8 (s); 171.2, 170.8 (s); 63.4, 63.2 (s); 52.4 (q); 42.3, 41.9 (t); 37.9, 32.0, 19.3 (t) |
| V[b] | 232.0 (s) | 96.3 (d) | 62.1, 61.9 (br d); 60.8, 54.5 (br d) | 213.6, 212.8 (s); 171.0, 170.5 (s); 69.0, 68.1 (s); 52.3, 52.2 (q); 45.8, 45.1, 39.2, 38.7 (t); 30.2, 28.4 (d); 24.0, 23.8 (q), 19.8 (q); 19.4 (t) |
| VII[c] | 230.4 (s) | 95.4 (d) | 40.8 (br t); 52.3 (br d) | 171.1 (s); 136.0 (s); 129.9, 128.1, 126.8 (d); 62.4 (s); 51.8 (q); 42.0, 39.2 (t) |
| VIII | 232.0 (s) | 96.4 (d) | 61.6 (br d); 61.4 (br d) | 170.7 (s); 137.4 (s); 130.1 127.9, 126.7 (d); 67.4 (s); 51.7 (q); 48.7 (d); 41.5 (t); 24.0 (q); 20.7 (q) |

[a] ppm relative to $Me_4Si$; off-resonance decoupled; $CDCl_3$; 25 °C. [b] 55 °C. [c] 60 °C.

analyses of V are consistent with the formation of only a major diastereomer together with a minor one. Thus the $^1H$ NMR spectrum of complex V exhibited two methoxyl resonances ($\delta$ 3.74, 3.70) in a roughly 4:1 intensity ratio at 55 °C.[13] Of the stereochemical possibilities described above, the addition of the enolate to the cis allylic terminus (relative to NO) in the exo conformation[9] predicts that the diastereomeric mixture V is composed of either pair W/X or Y/Z. If so, the moderate preference of one member in each pair must arise from the enantioselectivity of the enolate faces during nucleophilic addition. [Such a selectivity is in contrast to the nonselective formation of the $\eta^2$-olefin complex III and IV from the parent allyl cation II.] Indeed the chiral recognition of the 1,3-dimethallyl cation for the prochiral carbanion is notable in itself.[20]

The foregoing stereochemical analysis is borne out by the $^{13}C$ NMR spectrum of V, which showed a doubling of the ketonic resonances ($\delta$ 213.6, 212.8), ester carbonyl singlet ($\delta$ 171.0, 170.5), and methoxyl singlets ($\delta$ 52.3, 52.2) at 55 °C. At this temperature, the two pairs of broad resonances centered at ~62 and 57.5 ppm arising from the olefinic carbons were broadened.[21] These observatons are consistent with the presence of two diastereomers in complex V which do not interconvert but undergo olefin rotation at comparable rates. Such a conclusion can be rationalized in terms of a selective addition of the carbanion to the exo conformation of the allylic cation V, as in the stereochemical outcome of enamine additions.[5c]

**III. Nucleophilic Additions of Malononitrile Anion.** Owing to its high nucleophilic reactivity, we examined the addition of the malononitrile anion to the allyl cation II. However the addition of lithiomalonitrile to the methallyl cation IIb afforded only a modest yield (14%) of the olefin complex VI, eq 8, together with a minor byproduct the

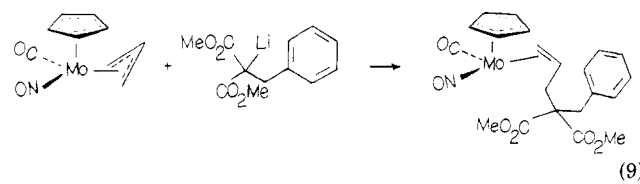



(8)

structure of which is presented separately in the Experimental Section. Most useful in the structural assignment of the olefin complex VI was the $^1H$ NMR signal due to the lone malonyl proton which appeared as a doublet of doublets as a result of splitting by the pair of diastereotopic allylic (methylene) protons. Pyrolysis of VI afforded only 2-methallylmalononitrile indicative of the presence of a single olefin ligand. However, VI consists of a mixture of two diastereomers in roughly equimolar amounts as judged by the observation in the $^1H$ NMR spectrum of a pair of well-resolved Cp singlets ($\delta$ 5.49, 5.47) with ~1:1 intensity ratio. Owing to the symmetrical (i.e., not prochiral) nature of the malononitrile, the two diastereomers must correspond to complexation of both enantiofaces of the olefin ligand. Such a stereochemical course of nucleophilic addition to the methallyl cation IIb can arise by either (1) a nonselective addition at both allylic termini of either the exo or endo conformer or (2) a cis addition to both the exo and endo conformers.[22] Since the first alternative is contrary to the previous observations, we favor the second. If so, the availability of both conformers would be modulated by the rapidity of the endo–exo preequilibration of the type alluded to above. [For example, it is known that the methallyl cation IIb is formed kinetically with exo preference while the endo isomer is dominant at equilibrium.[9-11]] It is interesting to note that although theoretical calculations of charge distribution and overlap populations clearly predict cis attack in the exo conformer, they predict no such preference in the endo conformer.[9] We thus conclude the cis addition occurs in both conformations, the generality of which could account for the mixture of diastereomers obtained in those cases where significant populations of both conformations exist.[23]

**IV. Nucleophilic Addition of Dimethyl Benzylmalonate Anion.** Dimethyl benzylmalonate anion is a prochiral highly encumbered nucleophile.[24] Nonetheless it reacted readily with the allyl cation IIa and the 1,3-dimethallyl cation IIc to afford the $\eta^2$-olefin complexes VII and VIII in ~30% and 80% yields, respectively.

The allyl adduct VII consisted of a single isomer, eq 9, the structure of which was determined by the analysis of the temperature-dependent behavior of the $^1H$ and $^{13}C$ NMR spectra as described in the Experimental Section.




(9)

(19) Assuming the addition to occur on the allylic terminus cis to NO in the exo conformer and from the external (anti) face.

(20) This type of enantiopreference has also been observed in the stereospecific oxidation of a coordinated allylic thioether.[7]

(21) Selective line broadening results from conditions approaching rapid rotation of the olefin ligand.[13] Thus upon lowering the temperature, the olefinic resonances continued to broaden until they were no longer observable below 40 °C. At the low temperatures the allylic methine resonances ($\delta$ 30.2, 28.4) were also severly broadened relative to the carbonyl and methoxyl singlets. The latter behavior supports line broadening to result from olefin rotation since the allylic methine is contiguous to an asymmetric carbon center and sufficiently close to the chiral metal center to exhibit a large chemical shift difference between rotamers.

(22) For example, Faller et al. have suggested that the rate of endo–exo interconversion of IIc is increased by the presence of enamine nucleophiles.[5c]

(23) Faller et al. have reported that mixtures of diastereomers are formed when both conformations of a cyclic allyl ligand are present. Compare ref 11.

(24) In the conjugate acid there is hindered rotation about the carbon–carbon bond linking the benzyl and malonyl moieties. Thus in the $^1H$ NMR spectrum, the lone malonyl proton appears as a doublet of doublets and the pair of benzylic protons occur as a pseudo AB system. This behavior persists up to ~80 °C, at which these pairs of multiplets resolve into a single triplet and doublet, respectively. [See: Ledon, H.; Linstrumelle, G.; Julia, S. *Bull. Soc. Chim. Fr.* **1973**, *6*, 2nd part, 2065.]

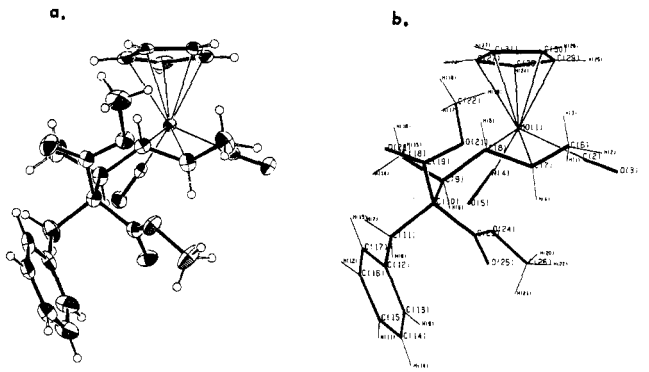
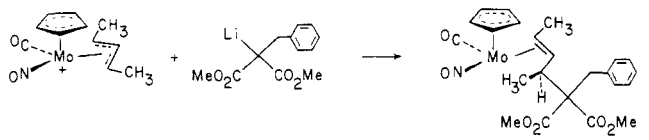



**Figure 1.** ORTEP diagram of the molecular structure of the $\eta^2$-olefin complex VIII derived from the nucleophilic addition of dimethyl lithiobenzylmalonate to the 1,3-dimethallyl cation IIc. The numbering scheme is included in the stick diagram at the right.

Liberation of the olefin from VII afforded only dimethyl allylbenzylmalonate. Similarly the $\eta^2$-olefin complex VIII obtained from the addition of dimethyl lithiobenzylmalonate to the 1,3-dimethallyl cation IIc also consisted of a single isomer (eq 10). The $^1H$ and $^{13}C$ NMR spectra




(10)

of the olefin complex VIII is comparable to those of VII (see Experimental Section). A single crystal of VIII was successfully grown, and X-ray crystallography confirmed the spectral assignments. The ORTEP diagram of the olefin complex VIII shown in Figure 1 establishes the nucleophilic addition of the malonate anion to occur at the allylic terminus which is cis to the nitrosyl group in the exo conformation and from the external or anti face of the coordinated group. We take this structure to represent clear evidence that the exo conformer of IIc is the one which is available to the carbanion. Thus the endo conformer either must be much less reactive than the exo isomer or rapidly equilibrate to a predominantly exo mixture prior to addition, or both must occur simultaneously.[25]

**V. Reagent-Assisted Isomerization of Exo–Endo Conformers.** Since the stereochemical outcome of the addition of carbanionic nucleophiles in this study has revolved around a recurrent theme of exo–endo isomerization of the allyl cations II, we undertook a separate, detailed study of this phenomenon. The 1,3-dimethallyl cation IIc is formed as a mixture of exo and endo conformations, the composition of which changes relatively little during the course of nucleophilic addition. In a system such as this which is close to equilibrium, any reagent-assisted isomerization would be experimentally difficult to establish. Therefore we concentrated our attention on the cyclooctenyl cation IId which is formed kinetically at −20 °C as the endo conformer.[11] This is readily shown in the $^1H$ NMR spectrum of IId by the appearance of a sharp singlet Cp resonance at $\delta$ 6.12 which persists indefinitely at this temperature. When the solution is allowed to warm to room temperature, the endo conformer is slowly converted to the exo isomer, the $^1H$ NMR spectrum of which is

(25) For the endo conformer, the structure of VIII requires the less likely stereoselective addition of the malonate to the allylic terminus which is trans to the nitrosyl ligand.

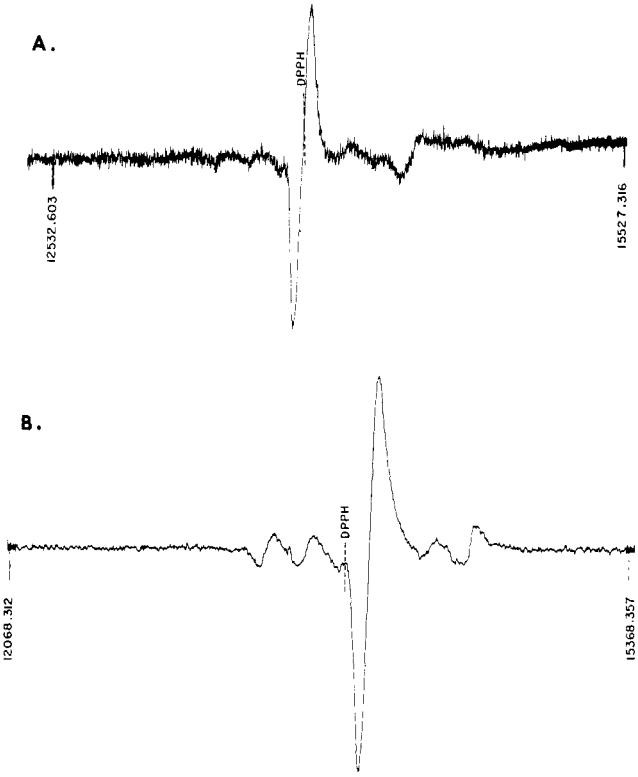



**Figure 2.** Electron paramagnetic resonance spectra obtained during the iodide-catalyzed endo/exo conversion of the cyclooctenyl cation IId: A, transient species obtained at < −100 °C; B, equilibrated species obtained at 20 °C. $^1H$ NMR field markers are in kilohertz.

characterized by a singlet Cp resonance at $\delta$ 6.03. Integration of the two signals allows the endo → exo conversion to be readily monitored over ~3 h, at which time only the exo isomer is in evidence.[26] The uncatalyzed isomerization follows first-order kinetics for at least 3 half-lives with a rate constant $k_1 = 2 \times 10^{-4}$ s$^{-1}$ ($\tau_{1/2}$ = 60 min) in acetonitrile at 25 °C.

The rate of the endo → exo conversion of IId is markedly influenced by the presence of various additives in catalytic amounts as enumerated below.

**A. Iodide-Promoted Isomerization.** The presence of 5 mol % of sodium iodide is sufficient to induce the endo–exo conversion even at −40 °C.[27] For example, the isomerization is 40% complete within 90 min. [Note that at this temperature there is no thermal isomerization.] Furthermore, the initially sharp and well-defined $^1H$ NMR spectrum of the endo isomer of IId undergoes severe line broadening within 20 min of mixing at −40 °C. The latter arises from the formation of small amounts of paramagnetic molybdenum intermediates which are apparent from an examination of the EPR spectrum under equivalent conditions. For example when a frozen mixture consisting of endo IId and 5 mol % sodium iodide (which are solidified into separate layers) at −190 °C is allowed to thaw, a broad isotropic EPR signal (A) is observed at $\langle g \rangle$ = 2.0004 with partially resolved $^{95,97}$Mo hyperfine splittings of 40.0 G (Figure 2).[28] Upon continued warming, this spectrum is gradually converted to spectrum with $\langle g \rangle$ = 1.9800. After 75 min at 20 °C, the original EPR has dis-

(26) Note that during this endo → exo conversion, the sum of the intensities of the Cp resonances is constant (±10%).

(27) Compare the original observation by Faller and co-workers.[11]

(28) Any $^{14}N$ hyperfine coupling (expected for a 19-electron nitrosyl-centered radical) would be lost in the line width observed here (15 G). A typical value would be ca. 7 G: Yu, Y. S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106.

appeared completely, and it is replaced by a spectrum B ($\langle g \rangle$ = 1.9800) showing partially resolved $^{95,97}$Mo hyperfine splittings of 50.0 G. The latter persists for prolonged periods (>16 h), which is long past that required for catalysis of the endo → exo conversion. We attribute the EPR spectrum B to a stable molybdenum(V) species which is presumably formed by disproportionation of the transient species.[29] Separate experiments demonstrate that it is not responsible for the catalysis of the endo → exo conversion of the cyclooctenyl cation IId.

Assignment of the structure of the transient paramagnetic species which is responsible for the catalysis is more difficult to establish. Although electron transfer from iodide to the allyl cation II should convert a formally molybdenum(II) complex to a paramagnetic molybdenum(I) species,[30] transient electrochemical studies indicate it to be too fleeting to be an effective catalyst. Thus the cyclic voltammogram of the cyclooctenyl cation IId showed an irreversible cathodic wave at $E_p$ = −0.8 V even at scan rates of 1000 mV s$^{-1}$.[31] It is thus unlikely that the concentration of the Mo(I) species builds up under reaction conditions. We thus ascribe the transient spectrum A to a more persistent Mo(III) intermediate,[32] which may be derived by a conproportionation of the Mo(I) species with the allyl cation II.

**B. Iodine-Promoted Isomerization.** A frozen solution of the cyclooctenyl cation IId (predominantly as the endo conformer) was sealed in a NMR tube with a single crystal of iodine (5 mg, <15 mol %). When the tube was warmed to −40 °C, the conversion of the endo conformer to the exo isomer was 60% complete within 30 min. The examination of a similarly prepared solution revealed the presence of the EPR spectrum B ($\langle g \rangle$ = 1.981, $a$($^{95,97}$Mo) = 50.0 G). Since the neutral precursor I is also known to react with halogen,[6] the cyclooctenyl dicarbonyl Id was treated with a single crystal of iodine. Under the same reaction conditions we were unable to observe the EPR spectra of measureable amounts of any paramagnetic molybdenum species.

**C. Cobaltocene-Promoted Isomerization.** In order to determine whether nucleophiles are required for the endo → exo conversion, we examined the effect of the 19-electron reducing agent cobaltocene.[33] Indeed the half-life of IId was sharply decreased to 10 min at 25 °C by the presence of 5 mol % cobaltocene. Furthermore cobaltocene is an effective catalyst even at −25 °C. When larger amounts of cobaltocene are employed with IId, the cobalticenium ion is formed as judged by its characteristic singlet Cp resonance at δ 5.65 in the $^1$H NMR spectrum. A frozen mixture of endo IId and cobaltocene (8 mol %) were examined by EPR spectroscopy. Below −50 °C an intense, anisotropic signal due to cobaltocene and a broad, minor signal with $g \simeq 2.00$ are observed. At −40 °C, the cobaltocene signal is broadened beyond recognition, but the broad signal remains together with a new signal with

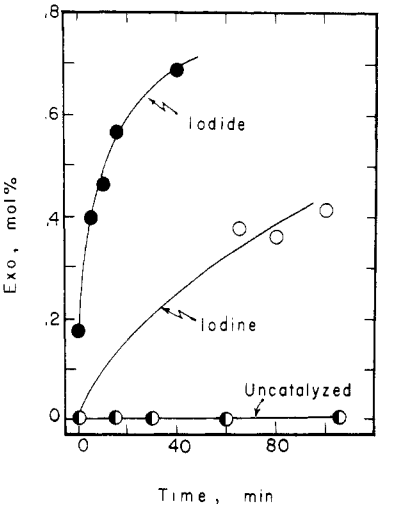



**Figure 3.** Catalysis of the endo → exo conversion of 8 × 10$^{-2}$ M cyclooctenyl cation IIc by 4.4 mol % sodium iodide (●) and <15 mol % iodine (○) in acetonitrile solution at −40 °C. The uncatalyzed conversion is represented by (◐).

$g \simeq 1.98$. Finally when the sample is warmed to 20 °C, the only remaining signal is that with $g$ = 1.981 showing partially resolved $^{95,97}$Mo hyperfine splittings of 50.0 G. This EPR spectrum identical with that (B) observed in both the iodide and iodine reactions (see Figure 2).

**D. Carbanion-Promoted Isomerization.** The addition of less than 1 equiv of a preformed carbanion (dimethyl lithiobenzylmalonate) to a $CH_3CN$ solution of endo IId at −20 °C led to a very slow rate of formation of a $\eta^2$-olefin complex. The appearance of the latter was followed by the increase in the singlet resonance at δ 5.57 over a period of 45 min. There is also a concomitant growth of the exo isomer of IId which is greatly increased as the temperature is raised. [For example, only exo IId is observed at 25 °C within 8 min.] Thus in this system, the carbanion-assisted conversion of endo IId to the exo isomer occurs more rapidly than the nucleophilic addition of the carbanion.[35]

**E. Comments on the Mechanism of the Endo–Exo Conversion.** The rate of the endo → exo conversion of the cyclooctenyl cation IId is markedly increased by the presence of additives as chemically diverse as iodide, iodine, cobaltocene, and the malonate carbanion. Under more or less comparable conditions the effectiveness of the additive decreases generally in the order iodide > iodine > cobaltocene > carbanion. Thus the endo–exo conversion is rather slow for dimethyl lithiobenzylmalonate at −20 °C. Although it is faster with cobaltocene at this temperature, at −40 °C no isomerization occurs. Iodide is somewhat more effective than iodine under comparable conditions of concentration and temperature (−40 °C) as shown in Figure 3). The results on hand favor the formation of a paramagnetic molybdenum species (see Figure 2) as a catalyst for the endo–exo conversion. If so, the effectiveness of the additives should be related to their ability to reduce the allyl cations II—provided of course that a common mechanism is applicable to all additives. However, the observed trend does not accord with this expectation since cobaltocene is generally considered to be a more efficient reducing agent than iodine. Barring this apparent anomaly, the promotion of the endo → exo conversion may lie in the facility with which the allyl ligands undero $\eta^3 \rightarrow \eta^1$ binding in the labile paramagnetic molybdenum intermediate(s).[36]

(29) For example: (a) Huang, T. J.; Haight, G. P., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 611. (b) Kadish, K. M.; Chang, D.; Malinski, T.; Ledon, H. *Inorg. Chem.* **1983**, *22*, 3492.

(30) On the basis of the nitrosyl ligand being considered a two-electron donor in these complexes. However, NO can also act as a three-electron donor. For a review, see: McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.

(31) (a) The electrochemical behavior of allyl cations II is complicated by pollution of the electrode. (b) At very fast scan rates of 20 000 V s$^{-1}$, a reversible CV wave of IIb has been observed at −0.78 V vs. SCE in acetonitrile containing 0.1 M tetraethylammonium perchlorate.

(32) For example: (a) Rossman, G. R.; Tsay, F.-D.; Gray, H. B. *Inorg. Chem.* **1973**, *12*, 824. (b) Green, M. L. H.; Knight, J.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2189.

(33) The reversible oxidation potential of cobaltocene is $E°$ = −0.945 V vs. SCE.[34]

(34) Koelle, V. *J. Organomet. Chem.* **1978**, *152*, 225.

(35) A faster rate of addition to the endo conformer is unlikely.[11]

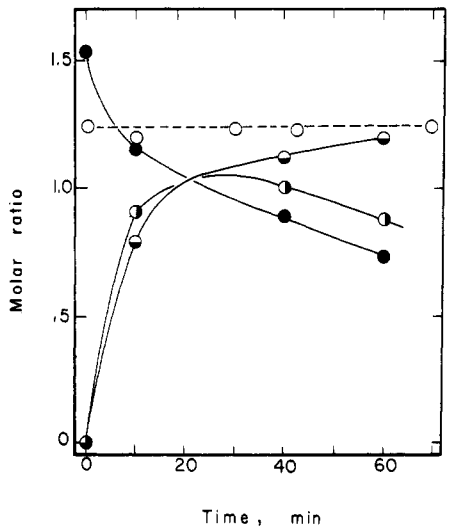



**Figure 4.** Time-dependent changes in the exo/endo ratio (●) during the nucleophilic addition $1.6 \times 10^{-2}$ M dimethyl lithiobenzylmalonate to $4.2 \times 10^{-2}$ M 1,3-dimethallyl cation IIc in acetonitrile at 23 °C. The accompanying growth of the $\eta^2$-olefin complex VIII is normalized to the exo conformer (◒) and the endo isomer (◑). The constancy of the the exo/endo ratio in the absence of carbanion is indicated by an open circle (○).

**VI. Reactivities of Endo–Exo Conformers to Carbanion Addition.** While the X-ray structural data (vide supra) have provided circumstantial evidence for the origin of the high regio- and stereoselectivity observed in the nucleophilic addition to the 1,3-dimethallyl cation IIc, we sought more direct evidence for the relative reactivity of endo and exo conformers. Unfortunately such a measure is difficult to obtain experimentally in the teeth of a facile endo ⇄ exo interconversion of the allyl cation II.

We examined the temporal evolution of the endo/exo ratio during the course of the nucleophilic addition of dimethyl lithiobenzylmalonate to the 1,3-dimethallyl cation IIc. Figure 4 shows that the exo/endo ratio of IIc actually decreases during the course of addition. Thus under these conditions the rate of the endo ⇄ exo interconversion must be slower than addition. Accordingly, we attribute the decreasing exo/endo ratio to a faster rate of depletion of the exo conformer relative to the endo isomer. This conclusion accords with the divergent trends in the normalized yields of the $\eta^2$-olefin product to the endo and exo isomers extant. A more quantitative measure of the relative reactivities of endo and exo conformers awaits a kinetic study of the endo ⇄ exo interconversion in this system.

## Summary and Conclusions

Nucleophilic addition of carbanions to various cationic $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-allyl})^+$ complexes II may be achieved with high stereoselectivity by due consideration of several factors. The highest stereoselectivities are obtained in those systems in which the allyl cations II exist predominantly in the exo conformation.[7] Under these conditions, the cis rule described by Hoffmann and Faller[9] provides a useful guide to predict the regio- and stereochemistry of nucleophilic addition to II. Since the relative populations of endo and exo conformers are important, any enhancement of the rate of equilibration by the added nucleophile must be taken into account, especially if it occurs faster than addition. The observation of transient paramagnetic molybdenum species during the facile conversion of endo → exo conformers promoted by small amounts of iodide, iodine, and cobaltocene suggests that it occurs by electron-transfer catalysis.[37]

In those systems in which the exo and endo conformers are formed kinetically close to equilibrium (e.g., the 1,3-dimethallyl cation IIc), the stereoselectivity is dependent on the relative reactivity of the two isomers. Nonselective addition occurs when the kinetic mixture of the conformers approaches the equilibrium (thermodynamic) composition, and the reactivities of the endo and exo conformers are comparable (e.g., the 2-methallyl cation IIb). Limited selectivity is also to be expected when the rates of addition become competitive with the rates of isomerization (e.g., the addition of sodiomalonate to the cyclooctenyl cation IId).[11] Malonyl-stabilized carbanions as well as stable enolates are viable nucleophiles for stereoselective allylation by this class of chiral organometallic cations. Spectroscopic data summarized in Tables I–III provide a reliable guide to deduce the structures of the $\eta^2$-olefin products, as well as their dynamic properties.

## Experimental Section

**Materials.** Molybdenum hexacarbonyl (Aldrich) and nitrosyl hexafluorophosphate (Alfa) were used in the synthesis as received. The dicarbonyl complexes Ia–d were prepared by the method described by Hayter,[38] and they have been previously characterized.[11,39] The series of $\pi$-allyl cations $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(allyl)^+$ IIa–d were prepared as the hexafluorophospate salts from the dicarbonyl precursor I by treatment in situ with nitrosyl hexafluorophosphate.

Unless otherwise noted, the following general information applies. All reactions were performed by using standard inert-atmosphere techniques. Solvents and reagents were purified prior to use as follows. Acetonitrile was refluxed over phosphorus pentoxide followed by distillation through a fractionating column under an atmosphere of argon. Tetrahydrofuran was refluxed under argon with sodium and benzophenone and distilled. It was redistilled from lithium aluminum hydride immediately before use. *N,N*-Dimethylformamide was dried over 4A molecular sieves and distilled through a fractionating column. Dichloromethane was dried over 4A molecular sieves under argon. Cyclohexanone, 2-carbomethoxycyclopentanone, and malononitrile were distilled through a Vigreaux column at reduced pressure. Dimethyl benzylmalonate was prepared and purified according to literature methods.[40] All other reagents were used as received.

**Instrumentation.** Infrared spectra were recorded on either a Perkin-Elmer 337 or a Beckman IR-8 spectrometer. Only the principal bands are listed in Table II. Proton NMR measurements were obtained at 60, 90, or 100 MHz using either a Varian T-60, JEOL JNM-FX-90Q, or JEOL JNM-FX-100 spectrometer, respectively. Carbon-13 NMR measurements were obtained by using the pulsed Fourier transform technique at 25.05 MHz with internal deuterium operating as a field frequency lock. NMR kinetic experiments were performed by using 5.0-mm (o.d.) Pyrex tubes sealed in vacuo or 10.0-mm tubes sealed with a septum cap. Chemical shifts are reported in parts per million relative to internal tetramethylsilane in the indicated solvent. NMR spectra were routinely recorded at a probe temperature of 35 °C. Mass spectra were obtained by using an AEI MS-12 spectrometer at 60 eV or greater, and only the most characteristic and/or most intense fragments are tabulated. The parent ions of all organomolybdenum compounds were taken to be those due to $^{98}Mo$ (natural abundance, 23.78%). ESR spectra were recorded on a

(36) For a catalytic process to obtain, this isomerization must be accompanied by a electron-transfer or redox reaction. Compare: Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771 for such an electron-transfer catalysis.[37]

(37) See: Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *50*, 1007. Chanon, M. *Bull. Soc. Chim. Fr.* **1982** II, 197. Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

(38) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1.

(39) Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

(40) See Ledon et al. in footnote 24.

Varian E-12 spectrometer, with the sample sealed in 1-mm (i.d.) Pyrex tubes (in vacuo). Cyclic voltammetric experiments were performed on a Princeton Applied Research Model 175 Universal Programmer and Model 173 potentiostat equipped with a Model 176 current-to-voltage converter which provided a feedback compensation for ohmic drop between the working and reference electrodes. Voltammograms were recorded on a Houston Series 2000 X/Y recorder, using an air-free electrochemical cell.

Thin-layer chromatography was performed with Eastman No. 6060 silica gel sheets using a fluorescent indicator. Developing solvents are as indicated, and visualization was achieved by using UV irradiation, spraying with 50% (v/v) sulfuric acid in methanol or spraying with an acidic solution of 2,4-dinitrophenylhydrazine (where appropriate). Column chromatographic separations were achieved by using gravity flow columns packed with Fisher Alumina (neutral or acid-washed, 80–200 mesh), Florisil, or MCB Silica Gel (100–200 mesh). "Flash" chromatography[41] was performed by using pressurized columns packed with either EM Reagents Kieselgel 60 (200–400 mesh) or EM Reagents Aluminiumoxid 60 GF(254) (neutral, Type E), using argon pressure. Gas–liquid chromatographic analysis was accomplished by using a Varian Series 2800 instrument equipped with on-column injection capability and a flame-ionization detector on a 6 ft × $^1/_4$ in. (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$^{-1}$. Preparative separations were achieved on a Varian Model 920 instrument equipped with a thermal conductivity detector on a 5 ft × $^1/_4$ in. (o.d.) stainless-steel column packed with 3% SE-30 on Varaport 30 (100–120 mesh) using a helium carrier flow of 30 mL min$^{-1}$.

**Nucleophilic Addition of Lithiocyclohexanone to Allyl Cation IIa.** A solution of 0.379 g (1.46 mmol) of $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ (Ia) in 5 mL of degassed acetonitrile was stirred at −20 °C under argon. A volume of 1.20 mL of a 1.22 M nitrosyl hexafluorophosphate solution in acetonitrile[42] was added via syringe. The resultant yellow-orange solution was stirred at −20 °C for 30 min in order to achieve complete conversion of Ia to IIa. In a separate flask, 0.166 g (1.69 mmol) of cyclohexanone was stirred in 5 mL of acetonitrile at −20 °C under argon. Then, 1.10 mL of a 1.6 M *n*-butyllithium solution in hexane was added dropwise with constant stirring, followed by 2 mL of DMF to redissolve the precipitated salt. This mixture was allowed to warm to room temperature, recooled to −20 °C, and then transferred to the solution of IIa via syringe. The resultant mixture was stirred at −20 °C for 2 h and then at room temperature for an additional 2 hr. Thereafter, the reaction mixture was filtered quickly through a bed of Florisil and the solvent removed in vacuo, affording 0.46 g of a dark brown, semisolid. Flash chromatography of the crude product on silica gel ($CH_2Cl_2$ eluent) followed by solvent removal in vacuo afforded 0.132 g (25% yield) of $[(\eta^2\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}2\text{-allylcyclohexanone})]$ (III) as an orange, air-sensitive semisolid: homogeneous by TLC ($SiO_2$, $CH_2Cl_2$, $R_f$ 0.71); IR (neat) 3100 (w), 2960 (m), 1967 (s), 1710 (m), 1645 (s), 800 (s) cm$^{-1}$; mass spectrum (EI), *m/z* (relative intensity) 359 (0.5), 331 (12), 314 (17), 279 (4), 249 (7), 193 (10), 165 (17), 163 (19), 161 (18), 138 (42), 110 (18), 109 (38), 95 (43), 94 (92), 81 (43), 79 (54), 67 (80), 55 (45), 54 (46), 53 (35), 41 (100), 39 (75), 29 (26), 28 (54), 27 (50); $^1$H NMR ($CDCl_3$) δ 5.48 (sh), 5.45 (singlets, 5 H), 3.72–2.82 (br m, 2 H), 2.82–1.44 (br m, 12 H).

Pyrolysis of this complex in the injection port of a gas chromatograph (175 °C) yielded a single ligand signal with a retention time of 4.8 min (temperature program: initial temperature 100 °C for 5 min and then 8 °C min$^{-1}$ to a final temperature of 250 °C).

**Nucleophilic Addition of 2-Lithio-2-carbomethoxycyclopentanone to Allyl Cation IIa.** A solution of 0.665 g (2.56 mmol) of Ia in 3 mL of degassed acetonitrile was converted to IIa as before. In a separate flask, 0.367 g (2.59 mmol) of 2-carbomethoxycyclopentanone was stirred in 5 mL of acetonitrile under argon at −20 °C. Then, 1.80 mL of a 1.6 M *n*-butyllithium solution in hexane was added dropwise with constant stirring, followed by 2 mL of DMF to redissolve the precipitated salt. This mixture was allowed to warm to room temperature, recooled to −20 °C, and transferred to the solution of IIa via syringe. The resultant mixture was stirred at −20 °C for 2 h and then at room temperature for an additional 2 hr. Thereafter, the reaction mixture was filtered quickly through a bed of Florisil (using acetonitrile) and the solvent removed in vacuo. It afforded 1.52 g of a red-brown semisolid. Flash chromatography of the crude product on silica gel ($CH_2Cl_2$ eluent), followed by solvent removal in vacuo, afforded 0.632 g (61.3% yield) of $[(\eta^2\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}(2\text{-allyl})\text{-}2\text{-carbomethoxycyclopentanone})]$ (IV) as a bright yellow, air-sensitive, amorphous solid; homogeneous by TLC ($SiO_2$, $CH_2Cl_2$, $R_f$ 0.48).

A comparable yield of IV was obtained by the use of the sodium enolate prepared as follows. A stirred suspension of sodium hydride (previously washed free of paraffin oil using hexane and carefully dried in vacuo) in 5 mL of DMF was stirred under argon at 0 °C. A solution of the carbon acid in acetonitrile was added dropwise and the resultant mixture heated to 60 °C and stirred at that temperature 2 h (a bright yellow supernatant solution was observed). Thereafter, this enolate mixture was transferred to the solution of IIa via syringe, maintaining the reaction mixture between −20 and 0 °C. The final reaction mixture was then allowed to warm to room temperature and stirred 2 h. Filtration through Florisil and flash chromatography as before afforded IV in 49% yield: IR (neat) 3108 (w), 2955 (m), 1963 (s), 1745 (m), 1725 (m), 1615 (s), 1228 (m), 1157 (s), 1005 (m), 808 (s); mass spectrum (EI), *m/z* (relative intensity) 403 (14), 345 (10), 314 (18), 182 (32), 154 (50), 122 (40), 95 (63), 94 (58), 80 (85), 69 (93), 67 (95), 55 (54), 41 (100), 39 (85), 28 (57), 27 (55), 15 (38); $^1$H NMR ($CDCl_3$, 25 °C) δ 5.47 (br s, 5 H), 3.70 (sh), 3.67 (singlets, 3 H), 3.40–2.47 (br m, 3 H), 2.47–1.68 (br m, 8 H); $^{13}$C NMR ($CDCl_3$, 25 °C) δ 230.4 (s), 214.1 (sh), 213.8 (singlets), 171.2 (sh), 170.8 (singlets), 95.6 (br d), 63.4 (sh), 63.2 (singlets), 52.4 (q), 42.3 (sh), 41.9 (triplets) 37.9 (t), 32.0 (t), 19.3 (t) (olefinic signals too broad to be observed).

Pyrolysis of this complex in the injection port of a gas chromatograph (175 °C) yielded a single ligand signal with a retention time of 8.3 min (temperature program: initial temperature 100 °C for 5 min and then 8 °C min$^{-1}$ to a final temperature of 250 °C).

**Nucleophilic Addition of 2-Lithio-2-carbomethoxycyclopentanone to 1,3-Dimethallyl Cation IIc.** A solution of 0.280 g (0.97 mmol) of $CpMo(CO)_2(\eta^3\text{-}C_5H_9)$ (Ic) in 5 mL of degassed acetonitrile was stirred at −20 °C under argon. Conversion of Ic to IIc was effected in a manner similar to that described previously. Then, a mixture of acetonitrile and DMF containing 1.14 mmol of lithio-2-carbomethoxycyclopentanone (prepared as described previously) was added via syringe at −20 °C. The final reaction mixture was stirred at −20 °C for 30 min and then at room temperature for an additional 1 h. Thereafter, the solvent was removed in vacuo and the brown residue taken up in $CH_2Cl_2$ and filtered quickly through a bed of Florisil. Removal of solvent in vacuo afforded 0.45 g of an orange semisolid. Flash chromatography of the crude product on silica gel (hexane/$CH_2Cl_2$ (1:1) eluent), followed by solvent removal in vacuo afforded 0.282 g (67.3% yield) of $[(\eta^2\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}2\text{-}(4\text{-methyl-2-butenyl})\text{-}2\text{-carbomethoxycyclopentanone})]$ (V) as a bright yellow, air-sensitive amorphous solid: homogeneous by TLC ($SiO_2$, $CH_2Cl_2$, $R_f$ 0.48); IR ($CH_2Cl_2$) 1963 (s), 1742 (m), 1730 (m), 1620 (s), 804 (s), cm$^{-1}$; mass spectrum (EI), *m/z* (relative intensity) 431 (15), 403 (0.8), 373 (15), 210 (38), 195 (21), 95 (66), 94 (60), 81 (44), 80 (80), 69 (85), 67 (95), 55 (75), 54 (60), 43 (66), 41 (100), 39 (94), 28 (64), 27 (50), 15 (30); $^1$H NMR ($CDCl_3$, 15 °C) δ 5.53 (br s, 5 H), 3.74, (sh), 3.7 0 (singlets, 3 H), 3.37–2.80 (br m, containing a br dd, $J \simeq 12$, 5 Hz, 2 H), 2.80–1.60 (br m, 7 H), 1.34 (br d, $J$ = 4.9 Hz, 3 H), 1.17 (br d, $J$ = 6.4 Hz, 3 H). No appreciable change in this spectrum was observed over the temperature range −78 to 55 °C. In particular, no coalescence or further splitting of the methoxy signals (δ 3.74, 3.70) was noted. $^{13}$C NMR ($CDCl_3$, 55 °C): δ 232.0 (s), 213.6, 212.8 (singlets), 171.0, 170.5 (singlets), 96.3 (d), 69.0, 68.1 (singlets), 62.1 (sh), 61.9 (doublets), 60.8, 54.5 (doublets), 52.3 (sh), 52.2 (quartets), 45.8, 45.1 (triplets), 39.2, 38.7 (triplets), 30.2, 28.4 (doublets), 24.0 (sh), 23.8 (quartets), 19.8 (q), 19.4 (t); pairs of signals centered at ~62.0 and ~57.5 ppm appeared to broaden significantly when the temperature was lowered.

(41) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(42) This standard solution may be successfully stored in all-glass containers under argon at −15 °C for several weeks and aliquots withdrawn as needed against a countercurrent of argon.

Also, the methine signals at 30.2 and 28.4 ppm were broadened at lower temperatures.

Pyrolysis of this complex in the injection port of a gas chromatograph (175 °C) yielded two ligand signals with retention times of 10.5 and 11.4 min, in a ratio of 4:1, respectively (temperature program: initial temperature 125 °C for 5 min and then 4 °C/min to a final temperature of 240 °C).

**Reaction of IIb with Lithiomalononitrile.** A solution of 0.865 g (3.16 mmol) of Ib in 3 mL of degassed acetonitrile was stirred at 0 °C under argon. Conversion of IIa to cation IIb was accomplished by the addition of 1.0 equiv of $NOPF_6$ as before. In a separate flask, 0.21 g (3.17 mmol) of malononitrile was stirred in 3 mL of acetonitrile at −20 °C under argon. The 2.0 mL of a 1.6 M *n*-butyllithium solution in hexane was added dropwise with constant stirring, and the resulting mixture was allowed to warm to room temperature. This solution was then transferred to the solution IIb with the aid of an additional 10 mL of acetonitrile. The final reaction mixture was stirred at 0 °C for a period of 2 h. Most of the solvent was removed in vacuo, the residue exhausted with chloroform, and the chloroform solution percolated quickly through acid-washed alumina (activity V). Removal of solvent afforded 1.05 g of a dark brown, semisolid. The crude product was fractionated on an acid-washed alumina column (activity II–III), eluting with hexane/chloroform (1:1), affording two fractions. The faster moving fraction, after solvent removal, yielded 0.151 g of [($\eta^5$-$C_5H_5$)Mo(CO)(NO)($\eta^2$-(2-methylallyl)malononitrile)] (VI) (14% yield), as an orange, air-sensitive, semisolid. TLC analysis ($SiO_2$, hexane/$CH_2Cl_2$, 1:1) indicated the presence of the major product only ($R_f$ 0.71): IR (neat) 3050 (w), 2955 (w), 2900 (w), 2240 (w), 1965 (s), 1620 (s), 812 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 5.49 (major), (sh), 5.47 (s, 5 H), 3.98 (dd, $J$ = 6.9, 4.5 Hz, 1 H), 3.05 (br d, $J$ = 4.5 Hz, 1 H), 2.80 (br d, $J$ = 4.5 Hz, 1 H), 2.48 (br d, $J$ = 4.8 Hz, 2 H), 1.76 (br s, 3 H).

High-performance liquid chromatography of the slower moving fraction on a Partisil column (detecting at 360 nm, $CH_2Cl_2$) indicated the presence of both the major product and ~17.5% of the slower moving organometallic compound. Pyrolysis of this fraction in the injection port of a gas chromatograph (175 °C) yielded a peak with the retention time expected (2.5 min) for (2-methylallyl)malonitrile and a peak of approximately the same size for a higher boiling component (retention time 7.0 min, column temperature 100 °C). The higher boiling material was isolated by preparative gas chromatography and characterized by mass spectral analysis: mass spectrum, $m/z$ (relative intensity) 174 (3), 159 (5), 146 (20), 81 (10), 56 (61), 55 (100), 53 (19), 43 (20), 41 (30), 39 (41), 29 (18), 27 (41). The mass spectral cracking pattern is consistent with that of an olefinic ligand composed of two methallyl moieties for each malononitrile unit, i.e., $[CH_2{=}C(CH_3)CH_2]_2C(CN)_2$. The formation of such a bisallylated product, while not remarkable in classical organic alkylations, is worthy of note in an organometallic system.

**Nucleophilic Addition of Dimethyl Lithiobenzylmalonate to Allyl Cation IIa.** A solution of 0.528 g (2.03 mmol) of Ia in 3 mL of degassed acetonitrile was stirred at −20 °C under argon. Conversion of Ia to IIa was effected by the addition of 1 equiv of $NOPF_6$ as before. In a separate flask, 0.380 g (1.71 mmol) of dimethyl benzylmalonate was stirred with 5 mL of acetonitrile and 5 mL of THF at 0 °C under argon. Then, 1.10 mL of a 1.6 M *n*-butyllithium solution in hexane was added dropwise with constant stirring and the resultant mixture allowed to warm to room temperature and then stirred 30 min. After being recooled to −20 °C, this mixture was transferred to the solution of IIa via syringe and the final reaction mixture stirred at −20 °C for 1 h and then at room temperature for an additional 2 h. Thereafter, the solvent was removed in vacuo and the residue taken up in $CH_2Cl_2$ and filtered quickly through a bed of neutral alumina (activity III). Solvent removal in vacuo afforded 1.04 g of a light brown semisolid. Flash chromatography of the crude product on silica gel (hexane/$CH_2Cl_2$ (1:1) eluent)), followed by solvent removal in vacuo afforded 0.226 g (27% yield) of [($\eta^5$-$C_5H_5$)Mo(CO)(NO)($\eta^2$-dimethyl allylbenzylmalonate)] (VII), as a yellow-orange semisolid: homogeneous by TLC ($SiO_2$, $CH_2Cl_2$, $R_f$ 0.58); IR (neat) 3100 (w), 2960 (m), 1965 (s), 1725 (m), 1630 (s), 805 (s), $cm^{-1}$; mass spectrum (EI), $m/z$ (relative intensity) 483 (<0.05), 455 (0.3), 387 (0.2), 358 (0.6), 221 (44), 189 (88), 143 (44), 91 (100),

**Table IV. Experimental Data for X-ray Diffraction Study of (Cyclopentadienyl)carbonylnitrosyl($\eta^2$-dimethyl (4-methyl-2-butenyl)benzylmalonate)molybdenum (VIII)**

(A) Crystal Parameters at −159 °C

| | | | |
|---|---|---|---|
| space group | $P2_1/c$ | $V$, Å$^3$ | 2260.28 |
| $a$, Å | 11.434 (3) | $Z$ | 4 |
| $b$, Å | 17.298 (5) | mol wt | 509.41 |
| $c$, Å | 12.771 (3) | $\rho$ (calcd), g cm$^{-3}$ | 1.497 |
| β, deg | 116.51 (1) | | |

(B) Measurement of Intensity Data

| | |
|---|---|
| radiation Mo Kα | 0.710 69 Å |
| monochromator | graphite |
| detector aperture | 3.0 × 4.0 mm |
| reflctns measd | $+h$, $+k$, $\pm l$ |
| max 2θ, deg | 45 |
| min 2θ, deg | 6 |
| scan type | moving crystal–moving detector |
| ω scan rate, deg min$^{-1}$ | 4.0 |
| ω scan width, deg min$^{-1}$ | 2.0 + dispersion |
| background time, s | 8 at extremes of scan |
| reflcts measd. | 3448 |
| data used ($F > 3\sigma(F)$) | 2612 |

(C) Treatment of Data

| | |
|---|---|
| abs coeff $\mu$, cm$^{-1}$ | 6.019 |
| $\Delta/\sigma$ final cycle (max) | 0.05 |
| final residuals $R(F)$, $R_w(F)$ | 0.0257, 0.0297 |
| goodness of fit for last cycle | 0.788 |

28 (90). This complex exhibited temperature-dependent NMR spectra (both $^1H$ and $^{13}C$) as follows. $^1H$ NMR ($CDCl_3$): (−50 °C), δ 7.28 (br m, 5 H), 5.49 (sh), 5.46 (singlets 5 H), 3.78, 3.75, 3.72 (sh), 3.69 (singlets, 6 H), 3.40 (br m, 1 H), 3.10–1.00 (br m, 5 H); (+26 °C), δ 7.22, 5.43, 3.72, 3.68, 3.36, 3.23–1.21; (+60 °C), δ 7.16 (br s, 5 H), 5.40 (s, 5 H), 3.67 (s, 3 H), 3.65 (s, 3 H), 3.48 (m, 1 H), 3.34 (s, 1 H), 3.30 (s, 1 H), 2.84 (dd, $J$ = 14.2, 2.5 Hz, 1 H), 2.20 (br d, $J$ = 12.8 Hz, 1 H), 2.09 (br d, $J$ = 9.7 Hz, 1 H), 1.40 (br dd, $J \cong$ 14, 12 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): (−50 °C), δ 230.7 (s), 230.1 (s), 171.4 (sh), 171.3, 171.0 (sh), 170.8 (singlets), 135.3 (s), 134.9 (s), 129.5 (d), 128.2 (d), 126.9 (d), 95.5 (br d), 62.1 (s), 61.5 (s), 57.2 (br d), 47.5 (br d), 52.7 (sh), 52.5 (sh), 52.3 (sh), 52.1 (quartets), 43.0, 41.5 (br triplets), 39.3 (br t), 36.5 (br t), 35.0 (br t); (+60 °C), δ 230.4 (s), 171.1 (s), 136.0 (s), 129.9 (d), 128.1 (d), 126.8 (d), 95.4 (d), 62.4 (s), 52.3 (br d), 51.8 (q), 42.0 (t), 40.8 (br t), 39.2 (t). Pyrolysis of this complex in the injection port of a gas chromatograph (175 °C) yielded a single ligand signal with retention time of 18.4 min (temperature program: initial temperature 100 °C and then 8 °C min$^{-1}$ to a final temperature of 250 °C).

The $\eta^2$-olefin complex VII is a mixture of rotameric isomers, which exhibit Cp resonances at δ 5.49 and 5.43 in the $^1H$ NMR spectrum at −50 °C. Similarly the methoxyl groups were diastereotopic appearing as four singlets (δ 3.78, 3.75, 3.72, 3.69), two for each rotamer. Upon warming the sample to 26 °C the Cp resonance collapsed into a single peak (δ 5.43) and the methoxyl resonance collapsed into a pair of singlets, which indicated that olefin rotation was already becoming rapid at this temperature. Further heating served merely to sharpen the upfield resonances by accelerating the carbon–carbon bond rotational process. The $^{13}C$ NMR spectrum of VII was also temperature dependent. At −50 °C, two carbon monoxide resonances (δ 230.7, 230.1) were obseved which is an unusual observation for rotamers in this series. It is most probably due to the stereoelectronic effects produced by the phenyl ring—the CO ligands experiencing quite different environments in the two stable conformations. This pair of signals collapses to a single resonance at higher temperatures. Similarly four separate ester carbonyl signals (δ 171.4, 171.3, 171.0, 170.8) and four methoxyl signals (δ 52.7, 52.5, 52.3, 52.1) were observed at low temperatures. Both sets of resonances collapse to a pair of (apparent) singlets at 60 °C. [The singlets resonances are somewhat misleading since the carbomethoxy groups are diastereotopic and are probably due to accidental degeneracy.] The proton spectrum of VII at 60 °C still exhibits two methoxy signals.

**Nucleophilic Addition of Dimethyl Lithiobenzylmalonate to 1,3-Dimethallyl Cation IIc.** A solution of 0.359 g (1.25 mmol) of Ic in 3 mL of degassed acetonitrile was stirred at −20 °C under

**Table V. Fractional Coordinates and Isotropic Thermal Parameters for ($\eta^5$-$C_5H_5$)Mo(NO)(CO)($\eta^2$-$CH_3CH$=$CHCH(CH_3)C(CO_2Me)_2CH_2Ph$(VIII)[a-c]**

| atom | x | y | z | $B_{iso}$, Å$^2$ | atom | x | y | z | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| M0(1) | 4998.9 (2) | 2224.2 (1) | 3224.6 (2) | 12 | H(1) | 404 (4) | 455 (2) | 270 (3) | 39 (9) |
| C(2) | 6302 (3) | 2145 (2) | -476 (3) | 17 | H(2) | 552 (4) | 427 (2) | 349 (3) | 34 (8) |
| O(3) | 7093 (2) | 1173 (1) | 227 (2) | 23 | H(3) | 465 (4) | 401 (2) | 211 (4) | 43 (9) |
| N(4) | 4439 (2) | 3273 (1) | -850 (2) | 14 | H(4) | 401 (3) | 352 (2) | 393 (3) | 21 (7) |
| O(5) | 4055 (2) | 1355 (1) | 4737 (2) | 21 | H(5) | 295 (3) | 302 (2) | 158 (3) | 14 (6) |
| C(6) | 4619 (4) | 4111 (2) | 2846 (4) | 29 | H(6) | 222 (3) | 249 (2) | 335 (3) | 17 (6) |
| C(7) | 4074 (3) | 3426 (2) | 3218 (3) | 19 | H(7) | 925 (3) | 261 (2) | 179 (3) | 27 (8) |
| C(8) | 3140 (3) | 2929 (2) | 2389 (3) | 17 | H(8) | 998 (3) | 269 (2) | 308 (3) | 29 (8) |
| C(9) | 1953 (3) | 2626 (2) | 2499 (3) | 19 | H(9) | -50 (4) | 378 (2) | 405 (3) | 36 (8) |
| C(10) | 883 (3) | 3284 (2) | 2177 (3) | 17 | H(10) | 196 (4) | -21 (3) | 115 (4) | 64 (12) |
| C(11) | 9672 (3) | 2986 (2) | 2322 (4) | 24 | H(11) | 653 (4) | 527 (2) | 210 (3) | 36 (8) |
| C(12) | -1268 (3) | 3619 (2) | 2259 (3) | 20 | H(12) | 620 (4) | 464 (2) | 30 (3) | 39 (9) |
| C(13) | -1188 (4) | 3978 (2) | 3269 (3) | 31 | H(13) | 772 (4) | 364 (2) | 49 (3) | 44 (9) |
| C(14) | 2002 (4) | -412 (3) | 1799 (4) | 33 | H(14) | 65 (4) | 167 (2) | 184 (3) | 32 (8) |
| C(15) | 7063 (4) | 4841 (2) | 2123 (3) | 27 | H(15) | 200 (3) | 148 (2) | 202 (3) | 31 (8) |
| C(16) | 6950 (3) | 4481 (2) | 1118 (3) | 23 | H(16) | 120 (3) | 197 (2) | 95 (3) | 29 (8) |
| C(17) | 7770 (3) | 3872 (2) | 1181 (3) | 22 | H(17) | 14 (5) | 54 (3) | 416 (4) | 55 (11) |
| C(18) | 1406 (4) | 1897 (2) | 1767 (4) | 28 | H(18) | 99 (4) | 127 (3) | 416 (4) | 59 (12) |
| C(19) | 445 (3) | 3514 (2) | 893 (3) | 17 | H(19) | 159 (4) | 46 (2) | 461 (3) | 44 (9) |
| O(20) | 9547 (2) | 1789 (2) | 5092 (2) | 30 | H(20) | 847 (4) | 76 (3) | 199 (4) | 52 (10) |
| O(21) | -1242 (2) | -975 (1) | 4240 (2) | 22 | H(21) | 888 (3) | 30 (2) | 114 (3) | 31 (8) |
| C(22) | 942 (5) | 802 (3) | 4554 (3) | 35 | H(22) | 743 (4) | 17 (2) | 92 (3) | 35 (8) |
| C(23) | 8556 (3) | -1069 (2) | 1917 (3) | 17 | H(23) | 414 (3) | 90 (2) | 156 (3) | 28 (7) |
| O(24) | 1227 (2) | 4641 (1) | 2637 (2) | 23 | H(24) | 643 (3) | 86 (2) | 318 (3) | 21 (7) |
| O(25) | 1963 (2) | 1197 (1) | 9126 (2) | 23 | H(25) | 760 (3) | 210 (2) | 324 (3) | 27 (7) |
| C(26) | 8343 (5) | 271 (2) | 1527 (4) | 36 | H(26) | 595 (3) | 294 (2) | 166 (3) | 24 (7) |
| C(27) | 4808 (3) | 1289 (2) | 1791 (3) | 22 | H(27) | 384 (4) | 220 (2) | 61 (3) | 30 (8) |
| C(28) | 6103 (4) | 1260 (2) | 2711 (3) | 24 | | | | | |
| C(29) | 6717 (3) | 1964 (2) | 2733 (3) | 21 | | | | | |
| C(30) | 5819 (3) | 2439 (2) | 1843 (3) | 18 | | | | | |
| C(31) | 4637 (3) | 2020 (2) | 1259 (3) | 19 | | | | | |

[a] Fractional coordinates are $\times 10^{-4}$ for non-hydrogen atoms and $\times 10^{-3}$ for hydrogen atoms. $B_{iso}$ values are $\times 10$. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. [c] Parameters marked by an asterisk (*) were not varied.

**Table VI. Selected Bond Distances (Å) and Angles (deg) for VIII**

| A | B | dist | A | B | C | angle |
|---|---|---|---|---|---|---|
| Mo(1) | N(4) | 1.7954 (25) | N(4) | Mo(1) | C(2) | 93.92 (11) |
| Mo(1) | C(2) | 1.989 (3) | Mo(1) | N(4) | O(5) | 176.35 (22) |
| O(5) | N(4) | 1.209 (3) | Mo(1) | C(2) | O(3) | 175.53 (26) |
| O(3) | C(2) | 1.146 (4) | N(4) | Mo(1) | C(7) | 97.74 (12) |
| Mo(1) | C(7) | 2.331 (3) | N(4) | Mo(1) | C(8) | 91.87 (11) |
| Mo(1) | C(8) | 2.262 (3) | C(2) | Mo(1) | C(7) | 71.56 (12) |
| | | | C(2) | Mo(1) | C(8) | 107.13 (12) |

argon. Conversion of Ic to IIc was effected by the addition of 1 equiv of $NOPF_6$ as before. In a separate flask, 0.278 g (1.25 mmol) of dimethyl benzylmalonate was stirred with 2 mL of THF at -70 °C under argon. Then, 0.80 mL of a 1.6 M *n*-butyllithium solution in hexane was added dropwise with constant stirring and the resultant mixture allowed to warm to room temperature and then stirred 30 min. After being recooled to -20 °C, this mixture was transferred via syringe to the solution of IIc. The final reaction mixture was allowed to warm to room temperature and stirred 2 h. Thereafter, the solvent was removed in vacuo and the residue taken up in $CH_2Cl_2$ and filtered quickly through a bed of Florisil. Removal of solvent in vacuo afforded 0.70 g of a yellow-orange semisolid. Flash chromatography of the crude product on silica gel (hexane/either (1:1) eluent), followed removal in vacuo, afforded 0.493 g (77% yield) of [($\eta^5$-$C_5H_5$)Mo(CO)(NO)($\eta^2$-dimethyl (4-methyl-2-butenyl)benzylmalonate)] (VIII) as a bright yellow semisolid: homogeneous by TLC ($SiO_2$, $CH_2Cl_2$, $R_f$ 0.37); IR ($CH_2Cl_2$) 3045 (w), 2945 (m), 1973 (s), 1726 (m), 1621 (s), 805 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 25 °C) $\delta$ 7.13 (br s, 5 H), 5.44 (s, 5 H), 3.58, 3.56 (singlets 6 H), 3.31, 3.20 (br singlets 2 H), 3.15–3.03 (m, 1 H), 2.98 (dd, $J$ = 11.5, 9.3 Hz, 1 H), 2.01 (dq, $J$ = 8.7, 3.0 Hz, 1 H), 1.36 (d, $J$ = 6.1 Hz, 3 H), 1.28 (d, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR ($CDCl_3$, 25 °C) $\delta$ 232.1 (s), 170.7 (s), 137.4 (s), 130.1 (d), 127.9 (d), 126.7 (d), 96.4 (d), 67.4 (s), 61.6 (br d), 61.4 (br d), 51.7 (q), 48.7 (d), 41.5 (t), 24.0 (q), 20.7 (q). Heating this sample to 58 °C produced no further sharpening or collapse of the signals.

Unlike the behavior of the $\eta^2$-olefin complex VII (vide supra), the $^1$H NMR and $^{13}$C NMR spectra of VIII were little changed upon varying the temperature from 22 to 58 °C—in all cases displaying a single set of resonances. These include a Cp singlet at $\delta$ 5.44 and methoxyl singlets at $\delta$ 3.58 and 3.56 in the $^1$H NMR spectrum and a CO singlet ($\delta$ 232.0), an ester carbonyl singlet ($\delta$ 170.7), a single quaternary carbon signal ($\delta$ 67.4), and only slightly broadened olefinic carbon resonances ($\delta$ 61.6 and 61.4) in the $^{13}$C NMR spectrum at 25 °C. Complex VIII was therefore formed either in a single rotameric conformation (i.e., directly from the exo conformation of cation IIc), possessing an extraordinarily high barrier to olefin rotation, or as a mixture of rotameric isomers in which one conformation is only sparsely populated at all experimental temperatures. The more highly substituted VIII is expected to possess a higher barrier to rotation compared to VII.

**X-ray Crystallography of $\eta^2$-Olefin Complex VIII.** Crystals of CpMO(NO)(CO)($\eta^2$-dimethyl (4-methyl-2-butenyl)benzylmalonate) (VIII) were grown from a mixture of ether and hexane (containing a trace of dichloromethane) by slowly cooling to -20 °C under an argon atmosphere. The diffractometer utilized for data collection was designed and constructed locally.[43] A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator is interfaced to a TI 980 minicomputer, with Slo-Syn stepping motors to drive angles. Measurements are taken by using Mo K$\alpha$ radiation, and centering is accomplished by using top/bottom-left/right slit assemblies.

(43) See: Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.

The minicomputer is interfaced by low-speed data lines to a CYBER 170-855 (NOS operating system) where all computations are performed.

A crystal of dimensions 0.12 mm × 0.12 mm × 0.11 mm was selected and affixed to a goniometer with silicone grease and then transferred to the goniostat where it was cooled to −159 °C for characterization and data collection. (Table IV). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry which could be indexed as the unique space group $P2_1/c$. From a total of 3448 reflections, 2612 reflections ($F > 3\sigma(F)$) were used in the structure solution and refinement. The structure was solved by direct methods (MULTAN 78) and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined isotropically (non-hydrogens anisotropically.) A final difference Fourier was featureless, the largest peak being 0.27 e Å$^{-3}$. Psi scans of several reflections were flat, and no absorption correction was deemed necessary. Final atomic coordinates and thermal parameters are listed in Table V. Selected bond distances and angles are listed in Table VI.

**Kinetics of Endo → Exo Conversion of Allyl Cations II.** For the purpose of obtaining rates of conformational equilibration, relative rates of addition, and ESR measurements, substoichiometric amounts of $NOPF_6$ were added to cations IIc and IId. The residual precursor signals (due to Ic and Id) were used as internal standards in NMR experiments. Typical experimental conditions are as follows.

A solution of 38.9 mg (0.135 mmol) of Ic in 1 mL of $CH_3CN$ was treated with 0.062 mmol of $NOPF_6$ (as a standard solution) at −20 °C and stirred 5 min at that temperature. Then, 100 μL of a 0.44 M dimethyl lithiobenzylmalonate solution (in $CH_3CN$, prepared as described above) was added and stirred quickly, and aliquots of the resultant mixture were transferred to 5.0-mm (o.d.) Pyrex NMR tubes against a countercurrent of argon, frozen at dry ice temperature, and sealed under vacuum. (An appropriate volume of acetonitrile-$d_3$ or acetone-$d_6$ was added prior to sealing to provide an internal lock signal.)

Alternatively, a solution of 29.8 mg (0.091 mmol) of Id in 1 mL of $CH_3CN$ was treated with 0.045 mmol of $NOPF_6$ (as a standard solution) at −20 °C and stirred 5 min at that temperature. Then, 5 μL of a 0.40 M NaI solution in $CH_3CN$ was added and stirred quickly, and aliquots of the resultant solution were transferred to either 5.0-mm (o.d.) Pyrex NMR tubes or 1-mm (i.d.) Pyrex ESR tubes, which were frozen at −78 °C and sealed as before.

**Acknowledgment.** We thank J. C. Huffman for the crystallographic determination of VIII and the National Science Foundation and the Robert A. Welch Foundation for financial support.

**Registry No.** *exo*-Ia, 100296-52-4; *endo*-Ia, 100296-53-5; *exo*-Ib, 95781-86-5; *endo*-Ib, 95781-86-5; *exo*-Ic, 63976-37-4; *endo*-Ic, 39015-45-7; Id, 81923-02-6; *exo*-IIa, 100296-44-4; *endo*-IIa, 100296-46-6; *exo*-IIb, 100296-48-8; *endo*-IIb, 100296-50-2; *exo*-IIc, 100296-51-3; *endo*-IIc, 100348-11-6; *exo*-IId, 90081-05-3; *endo*-IId, 90129-01-4; III (isomer 1), 100229-40-1; III (isomer 2), 100296-54-6; IV (isomer 1), 100229-41-2; IV (isomer 2), 100348-12-7; V (isomer 1), 100229-42-3; V (isomer 2), 100296-55-7; VI (isomer 1), 100229-43-4; VI (isomer 2), 100296-56-8; VII, 100229-44-5; VIII, 100243-60-5; sodium iodide, 7681-82-5; iodine, 7553-56-2; cyclohexanone, 108-94-1; 2-carbomethoxycyclopentanone, 10472-24-9; malononitrile, 109-77-3; diemthyl benzylmalonate, 49769-78-0; cobaltocene, 1277-43-6.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, complete bond distances and bond angles, and final observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

# Reaction of $(C_5H_5)_2Mo_2(CO)_4$ with Carbodiimides: Structural Characterization of $C_5H_5(CO)_2Mo(CNPh)Mo(NPh)C_5H_5$, a Novel Complex Containing a Terminal Phenylimido and a Bridging Phenyl Isocyanide Ligand, and Its Reaction with $P(OMe)_3$[1]

Ivan Bernal* and Madeleine Draux

*Department of Chemistry, University of Houston—University Park, Houston, Texas 77004*

Henri Brunner, Beate Hoffmann, and Joachim Wachter*

*Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, F.R.G.*

*Received July 3, 1985*

One of the products of the reaction of $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (Cp = $\eta^5$-$C_5H_5$) with an excess of diphenylcarbodiimide is characterized by X-ray crystallography. The substance crystallizes in the space group $P2_1/c$ with cell constants $a$ = 14.123 (2) Å, $b$ = 12.228 (1) Å, $c$ = 12.772 (1) Å, $\beta$ = 96.09 (1)°, and $V$ = 2193.2 Å$^3$. $R$ is 0.023 for 3003 reflections ($I > 4.5\sigma(I)$). The structure is identified as $Cp(CO)_2Mo$-[$\mu$-($\eta^1$:$\eta^2$-C=NPh)]Mo(NPh)Cp (II) containing an unprecedented combination of a complexed phenylimido ligand and a $\eta^2$, ($\sigma + \pi$)-bonded isocyanide bridge. Complex II undergoes a substitution reaction with excess $P(OMe)_3$ to form $Cp(CO)Mo[P(OMe)_3]Mo(CNPh)Mo(NPh)Cp$ and a related compound in which the terminal imido ligand is replaced by an oxo ligand.

## Introduction

The addition of small molecules to the metal–metal triple bond in the cyclopentadienylcarbonylmolybdenum derivatives $(\eta^5$-$C_5R_5)_2Mo_2(CO)_4$ (R = H, Me) has been the subject of several investigations. Whereas allenes add in a symmetrical fashion across the Mo≡Mo bond,[2] heteroallenes, X=C=Y, give various products depending on the nature of the heteroatoms X and Y. Thus, carbon disulfide is incorporated into $(C_5R_5)_2Mo_2(CO)_4$ (R = H, Me) as a

(1) "Reactivity of the Metal-Metal Multiple Bond in Metalcarbonyl Derivatives. 11." For part 10 see: Riess, J. G.; Klement, U.; Wachter, J. *J. Organomet. Chem.* **1985**, *280*, 215.

(2) Chisholm, M. H.; Rankel, L. A.; Bailey, W. J., Jr.; Cotton, F. A.; Murillo, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 802.

0276-7333/86/2305-0655$01.50/0 