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Controlled Functionalization in the Cycloheptane Ring Using Organomolybdenum Chemistry

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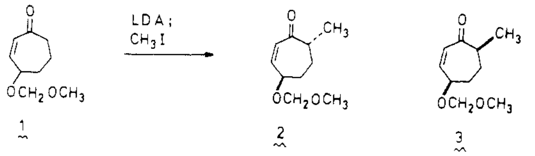
The synthesis and reactivity of a series of η^3-cycloheptenyl–Mo(CO)$_2$Cp and η^4-cycloheptadiene–Mo(CO)$_2$Cp complexes are reported. The parent π-allyl complex $(\eta^3\text{-}C_7H_{11})Mo(CO)_2Cp$ undergoes hydride abstraction on treatment with Ph_3CPF_6 to give $(\eta^4\text{-}C_7H_{10})Mo(CO)_2Cp$ cation as the PF_6^- salt. This complex reacts stereospecifically with a variety of carbon nucleophiles, including Grignard reagents and stabilized enolates, by addition to the diene ligand to give substituted π-allyl complexes $(\eta^3\text{-}C_7H_{10}R)Mo(CO)_2Cp$. With the unsymmetrical enolate from methyl 2-oxocyclopentanecarboxylate a high degree of diastereoselectivity is observed. Alkyl-substituted complexes, $(\eta^3\text{-}C_7H_{10}R)Mo(CO)_2Cp$ (R = CH_3, $CH_2CH{=}CH_2$, $C_6H_4OMe\text{-}p$), undergo regiospecific hydride abstraction to give $(\eta^4\text{-}C_7H_9R)Mo(CO)_2Cp$ cations which react with a range of nucleophiles stereospecifically at the diene ligand. The regioselectivity of this second nucleophile addition was studied. Decomplexation of the product π-allyl complexes by a cyclofunctionalization/demetalation procedure is reported.

Cycloheptane has the unenviable reputation of being an awkward ring system to deal with from a synthetic point of view, since it is difficult to determine which of several available conformations for polysubstituted derivatives is the preferred lowest energy form.[1] This results in problems of rationalizing or predicting the outcome of reactions designed to introduce new functionality, and as a consequence this ring size has been neglected as a means of constructing an array of stereocenters which may, for example, be translated to an acyclic system by ring cleavage.[2] Introduction of unsaturation, as in cycloheptene or cycloheptenone, leads to considerable improvement in the conformational bias, but reactions of such molecules are rarely stereospecific. As an example, recent studies in our own laboratory show that methylation of the 4-alkoxy-substituted cycloheptenone **1** gives a mixture of **2** and **3** in a ratio of ca. 4:1, thereby demonstrating only modest stereoselectivity.[3]



1 **2** **3**

Attachment of a transition-metal moiety to a cyclic olefinic ligand can serve a number of purposes, among which are activation of the olefinic moiety toward nucleophilic attack[4] and imposition of stereochemical and conformational bias on the ring. Such effects are particularly useful for controlled functionalization of the seven-membered ring, as shown by recent endeavors with cycloheptadienyliron[5] and (cycloheptatriene)manganese[6] complexes. In each of these systems the metal moiety spans a different number of carbon atoms, so it becomes possible to envision a set of complementary ligand types that can lead to selected organic intermediates, provided multiple functionalization can be accomplished without loss or rearrangement of the organometallic grouping. A hypothetical set of such double functionalization reactions of cycloheptadienyliron, (cycloheptatriene)manganese, and (cycloheptadiene)molybdenum complexes is illustrated in Figure 1, where it has been assumed that all nucleophile additions to such 18-electron complexes occur, for stereoelectronic reasons,[7] trans to the metal.[8] With such stereospecificity it becomes possible to introduce substituents with a cis 1,3-relationship by using the iron complexes, with a cis 1,2- (or 1,3-) relationship by using manganese systems, and with a cis 1,4- (or 1,5-) relationship using diene– and π-allyl–molybdenum chemistry. The first has been realized in our laboratory[5] and currently forms the basis for approaches to macrolide antibiotic synthesis, the second (manganese) has not been intensively investigated but will form the basis for future study,[9] and the last (molybdenum) is described in this paper.[10]

Figure 1 calls our attention to a potentially major problem with the use of diene–molybdenum chemistry. Addition of a nucleophilic species results in the formation of a π-allylmolybdenum complex that cannot be translated to an organic equivalent by direct conversion using standard demetalation techniques. Activation of the π-allyl complex, followed by external nucleophile addition is likely to be accompanied by problems of regiocontrol,[11]

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[1] Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; American Chemical Society: Washington, DC, 1981; pp 206–210 and references cited therein.

[2] For some notable uses of the seven-membered ring in constructing acyclic systems in a stereocontrolled manner, see: Masamune, S.; Kim, C. U.; Wilson, K. E.; Spessard, G. O.; Georghiou, P. E.; Bates, G. S. *J. Am. Chem. Soc.* **1975**, *97*, 3512. White, J. D.; Fukuyama, Y. *Ibid.* **1979**, *101*, 226. Stork, G.; Nair, V. *Ibid.* **1979**, *101*, 1315.

[3] Pearson, A. J.; Bansal, H. S. *Tetrahedron Lett.*, in press.

[4] Pearson, A. J. "Metallo-organic Chemistry"; Wiley: Chichester, England, 1985. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. Birch, A. J.; Jenkins, I. D. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1. Nicholas, K. M.; Nestle, M. O.; Seyferth, D. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2. Jaouen, G. In "Transition Metal Organometallics in Organic Chemistry"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2. Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: Berlin, 1975. Davies, S. G. "Organotransition Metal Chemistry. Applications to Organic Synthesis." Pergamon Press: Oxford, 1982.

[5] Pearson, A. J.; Kole, S. L.; Chen, B. *J. Am. Chem. Soc.* **1983**, *105*, 4483. Pearson, A. J.; Kole, S. L.; Ray, T. *Ibid.* **1984**, *106*, 6060.

[6] Pearson, A. J.; Bruhn, P. R.; Richards, I. C. *Isr. J. Chem.* **1984**, *24*, 93 and references cited therein.

[7] Pearson, A. J.; Khan, M. N. I.; Clardy, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

[8] See ref 4 and the following X-ray structure determinations which provide evidence for trans attack: Ireland, R. E.; Brown, G. G., Jr.; Stanford, R. H., Jr.; McKenzie, T. C. *J. Org. Chem.* **1974**, *39*, 51. Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 395. For a fuller discussion, see ref 4 and the following: Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry"; Brooks/Cole: Monterey, CA; 1985; pp 313–341.

[9] For related studies, see: Honig, E. D.; Quin-jin, M.; Robinson, W. T.; Williard, P. G.; Sweigart, D. A. *Oganometallics* **1984**, *4*, 871 and references cited therein.

[10] Preliminary communication: Pearson, A. J.; Khan, M. N. I. *Tetrahedron Lett.* **1985**, *26*, 1407.

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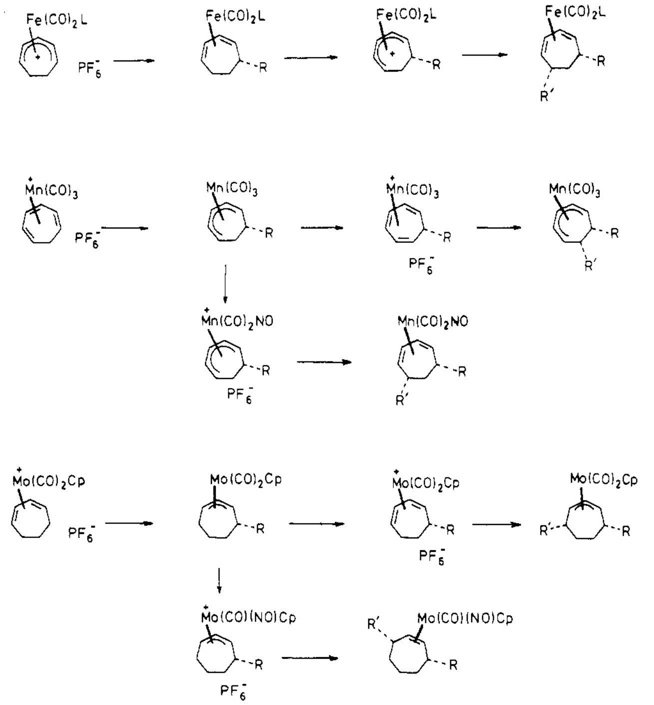
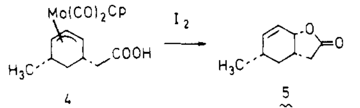


Figure 1. The complementary modes of stereocontrolled functionalization of the seven-membered ring which are accessible, at least in principle, using organoiron, organomanganese, and organomolybdenum chemistry.

and so far the most appropriate solution to this problem is the cyclofunctionalization procedure which we have developed for the corresponding cyclohexenylmolybdenum complexes,[7] illustrated here by the conversion of complex 4 to the lactone 5.



4 5

With this groundwork laid down we set out to investigate the chemistry of cycloheptadiene–Mo(CO)$_2$Cp systems, in order to determine whether comparable regioselectivity and stereoselectivity can be accomplished. It may be noted that the reactivity of diene–Mo(CO)$_2$Cp cations toward nucleophiles is very different, in terms of regiochemistry and stereochemistry, to that of uncharged diene–Fe(CO)$_3$ systems,[12] so that ultimately these complexes might allow complementary methodology for diene functionalization.

Results and Discussion

Scheme I

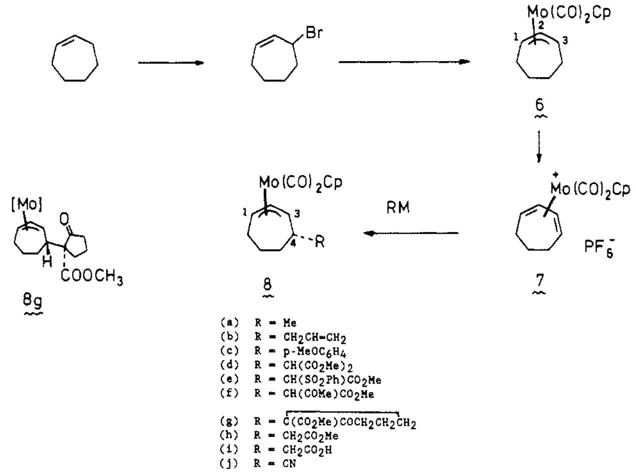


Table I. Addition of Nucleophiles to Cycloheptadiene–Mo(CO)$_2$Cp Salts 7 and 9

diene complex	nucleophile	product(s)	ratios 10:11	yield, %
7	MeMgBr	**8a**		85
7	$CH_2{=}CHCH_2MgBr$	**8b**		90
7	p-$MeOC_6H_4MgBr$	**8c**		90
7	$NaCH(CO_2Me)_2$	**8d**		95
7	$NaCH(SO_2Ph)CO_2Me$	**8e**		98
7	$NaCH(COMe)CO_2Me$	**8f**		90
7	$NaC(CO_2Me)COCH_2CH_2CH_2$	**8g**		90[a]
7	NaCN	**8j**		90
9a	MeMgBr	**10a + 11a**	2:1	85
9a	NaCN	**10b + 11b**	3:2	82
9a	p-$MeOC_6H_4MgBr$	**10c + 11c**	5:1	85
9a	$NaCH(CO_2Me)_2$	**10d + 11d**	2:1	85
9a	$NaCH(SO_2Ph)CO_2Me$	**10e**		98
9a	$NaC(CO_2Me)COCH_2CH_2CCH_2$	**10f**		95[b]
9b	$NaCH(CO_2Me)_2$	**10i**		98
9b	$NaCH(SO_2Ph)CO_2Me$	**10j**		98
9c	MeMgBr	**10m**		95
9c	$NaCH(CO_2Me)_2$	**10n**		95

[a] Obtained as ca. 9:1 mixture of diastereomers. [b] Obtained as ca. 4:1 mixture of diastereomers.

(a) Preparation and Reactions of η^4-Diene Complexes. The preparation of η^3-cycloheptenyl–Mo(CO)$_2$Cp (6) was readily accomplished by using the procedure described by Hayter and by Faller et al. for similar compounds,[11] as shown in Scheme I. The NMR spectrum of 6 is interesting in that the central allyl proton, 2-H, occurs at *higher* field than the terminal allyl protons, 1-H and 3-H. This contrasts with the related acyclic and cyclohexenyl complexes in which the central allyl proton is the lower field resonance[7,11] but is similar to the cyclooctenyl complex.[13,14] Some care is therefore required in making assignments of substituted π-allyl complexes, since the factors affecting shieldings are not well-defined. For several of the cycloheptenyl–Mo(CO)$_2$Cp complexes derived from nucleophile addition to the diene complexes in this study, NMR assignments were obtained from double resonance experiments, details of which are given in the Experimental Section.

Hydride abstraction occurred without problem to give the cycloheptadiene complex 7 in good yield. This reaction is deceptively trivial. While it proceeds smoothly for six- and seven-membered ring complexes (this work and ref 7 and 11) we have found that η^3-cyclooctenyl–Mo(CO)$_2$Cp is resistant to hydride removal using Ph_3C^+ and a variety of other techniques,[15] a result which perhaps reflects the requirement for a stable 1,3-diene–metal complex. The diene complex 7 is stable and easy to handle but is quite reactive toward a range of common nucleophiles, leading to π-allyl complexes 8 in which the substituent is assumed to be exo[16] on the basis of the literature precedent for

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[11] Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, C1.

[12] Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715. Semmelhack, M. F.; Le, H. T. M. *Ibid.* **1985**, *107*, 1455.

[13] Blystone, S., unpublished results from this laboratory.

[14] Faller, J. W.; Chao, K.-H. *Organometallics* **1985**, *3*, 927.

[15] Unpublished results from this laboratory; Faller has also found similar difficulties in hydride abstraction from η^3-cyclooctenyl–Mo(CO)$_3$Cp complexes (Faller, J. W., personal communication).

[16] Exo refers to substituents on the opposite side of the ligand to that occupied by the metal, endo to those on the same side as the metal. While not entirely satisfactory, this does conform to the currently accepted notation.

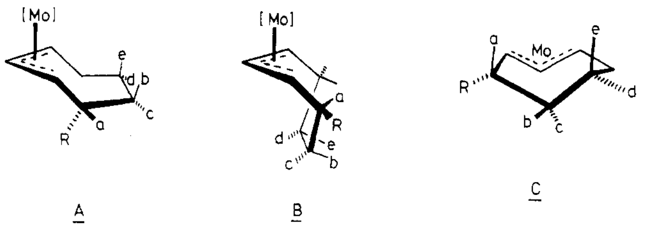


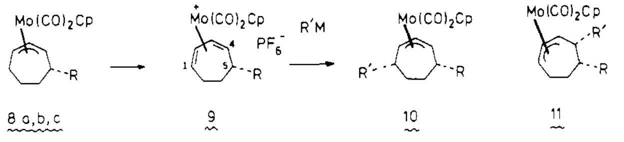
Figure 2. Possible conformations for 4-substituted η^3-cycloheptenyl–Mo(CO)$_2$Cp complexes: A, chair; B, boat; C, twist boat.

related systems.[7,11] The results are summarized in Scheme I. Stabilized enolates added cleanly and in high yield (See Table I); Grignard reagents reacted satisfactorily, but it was observed in the later experiments that some degree of reductive coupling occurred when the reactions were carried out in tetrahydrofuran (THF). This was particularly evident during the reaction of 7 with (4-methoxyphenyl)magnesium bromide, when appreciable amounts of 4,4′-dimethoxybiphenyl were observed in the product. Since this could not be removed by chromatography it became a vexing problem. Alteration of the reaction temperature was found to have no effect, but conducting the Grignard addition reaction in dichloromethane instead of THF eliminated the electron-transfer process. This is interesting in view of the similar report by Birch et al. that organolithium reagents add cleanly to cyclohexadienyliron complexes in dichloromethane (at −78 °C) whereas considerable reductive coupling of the transition-metal complex occurs in ethereal solvents,[17] suggesting a general improvement in procedures employing alkylmagnesium and related reagents.

Addition of the enolate derived from methyl 2-oxocyclopentanecarboxylate occurred with pronounced diastereoselectivity (ca. 9:1 mixture), though not as good as the same reaction with the cyclohexadiene–Mo(CO)$_2$Cp complex,[7] and we have assigned the structure **8g** to the major product by analogy with the six-membered ring. We have not at this stage attempted to analyze the factors leading to this selectivity. Reaction of 7 with NaCH(SO$_2$Ph)CO$_2$Me or NaCH(COMe)CO$_2$Me was also stereoselective, but the products readily epimerized on chromatography to give equimolar mixtures diastereomers.

Inspection of the ^{1}H NMR spectra for the π-allyl complexes 8 reveals some interesting characteristics. We discuss here the spectrum of the dimethyl malonate adduct **8d**, on which extensive spin decoupling was performed (See Experimental Section), all other complexes showing identical patterns. Complex **8d** shows a high field (δ 0.96) resonance assignable to exo 5-H (in general pseudo axial exo protons are observed at higher field than endo protons[5,7,11]), occurring as a quartet, J = 11.7 Hz. This data allows us to partially analyze the conformations adopted by these molecules; three possible conformations are shown in Figure 2. The chair conformation (A) would show the following dihedral angles connecting groups a–b (ca. 60°), a–c (ca. 60°), c–d (ca. 0°), and c–e (120°); the boat conformation (B) would give a–b (60°), a–c (180°), c–d (0°), and c–e (120°); the twist boat (C) would give a–b (60°), a–c (180°), c–d (90°), and c–e (ca. 170°). These angles are based on molecular models and are not exact, but a comparison with the NMR data shows that the chair conformation A can be ruled out immediately, since a proton in position c would show only a small coupling to a proton at a. Consequently, for this conformation exo 5-H (proton c) would not occur as a quartet with large (11.7 Hz) coupling. In the boat conformation (B) we should expect to see large couplings between a and c, between b and c, and between c and d. We should also expect to see an appreciable coupling between c and e (dihedral angle 120°), but this is not observed (compare exo 5-H pattern). On the other hand, the twist boat (C) would give large, possibly equal couplings between proton c and a, b, or e but near zero coupling between c and d (dihedral angle ca. 90°). The data at hand suggests that the twist boat conformation (C) is preferred for the substituted C$_7$H$_{10}$R–Mo(CO)$_2$Cp complexes, but this awaits the confirmation of a crystallographic study. Interestingly, conformation C places the R substituent pseudoequatorial and the 7-exo proton pseudoaxial, thereby allowing an antiperiplanar arrangement of C(1)–Mo and C(7)–H(7-exo) bonds. This is the arrangement required for hydride abstraction outlined in the next paragraph (for a fuller discussion of conformational requirements during hydride abstraction, see ref 7). It is also interesting to note that the analogous η^3-cyclohexenyl complexes adopt the chair conformation[7,11] presumably due to the lower degree of flexibility in this ring size which prevents facile C–C bond rotation necessary for conformational interconversions.

Scheme II



(a) R = Me
(b) R = CH$_2$CH=CH$_2$
(c) R = p-MeOC$_6$H$_4$

(a) R = R′ = Me
(b) R = Me, R′ = CN
(c) R = Me, R′ = C$_6$H$_4$OMe-p
(d) R = Me, R′ = CH(CO$_2$Me)$_2$
(e) R = Me, R′ = CH(SO$_2$Ph)CO$_2$Me

(f) R = Me, R′ = C(CO$_2$Me)COCH$_2$CH$_2$CH$_2$
(g) R = Me, R′ = CH$_2$CO$_2$Me
(h) R = Me, R′ = CH$_2$CO$_2$H
(i) R = CH$_2$CH=CH$_2$, R′ = CH(CO$_2$Me)$_2$
(j) R = CH$_2$CH=CH$_2$, R′ = CH(SO$_2$Ph)CO$_2$Me
(k) R = CH$_2$CH=CH$_2$, R′ = CH$_2$CO$_2$Me
(l) R = CH$_2$CH=CH$_2$, R′ = CH$_2$CO$_2$H
(m) R = C$_6$H$_4$OMe-p, R′ = Me
(n) R = C$_6$H$_4$OMe-p, R′ = CH(CO$_2$Me)$_2$

With the substituted π-allyl complexes at hand, attention was directed at further activation. Again, hydride abstraction proceeded without problem for the three complexes **8a**, **8b**, and **8c**. No attempts were made to convert other allyl complexes to the cationic diene systems. Addition of nucleophiles to the substituted diene complexes 9 turned out to be less regioselective than the corresponding reactions with the six-membered ring counterpart,[7] and dependent on the steric requirements of the substituent (R) and the nucleophile. The reactions are shown in Scheme II and the regiochemical data is given in Table I. Ratios of isomers were estimated from 200-MHz proton NMR spectra of the mixtures, usually using the singlet (ca. δ 5.2) due to the cyclopentadienyl ligand which occurred at slightly different field for each isomer. The nitriles **10b** and **11b** gave coincident resonances for Cp and for Me groups, so the ratio was estimated from the π-allyl proton resonances. Addition of (phenylsulfonyl)acetate anion was somewhat more difficult to analyze, owing to the formation of diastereomers. However, desulfonylation gave a single monoester **10f** in good yield, so we assume that the initial nucleophile addition occurs with a very high degree of regioselectivity, as expected for the bulkier phenylsulfonyl ester carbanion.

On reaction with dimethyl sodiomalonate, the methyl-substituted diene complex **9a** gave a 2:1 mixture of regioisomers **10d** and **11d**, while the allyl- and 4-methoxyphenyl-substituted derivatives **9b** and **9c** gave essentially single products **10i** and **10n** respectively. It is especially noteworthy that in our earlier work the analogous 5-methylcyclohexadiene–Mo(CO)$_2$Cp cation gave a ca. 10:1

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[17] Bandara, B. M. R.; Birch, A. J.; Khor, T.-C. *Tetrahedron Lett.* 1980, *21*, 3625.

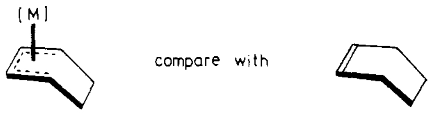
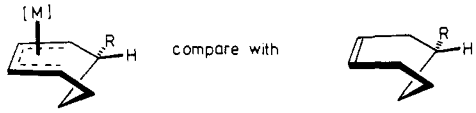


Figure 3. Comparison of cyclohexadiene–metal complexes with boat conformation of cyclohexene.



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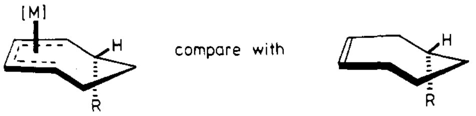

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Figure 4. Comparison of possible conformations of cycloheptadiene–metal complexes with boat and chair conformations of cycloheptene. The boat conformation diagrams are slightly distorted for ease of viewing.

mixture from reaction with $NaCH(CO_2Me)_2$, favoring addition at the diene terminus remote from the methyl group. The much poorer selectivity for this particular reaction in the seven-membered ring is most likely due to the subtle difference in conformation between the two molecules, and an analysis of this result can be made as follows. X-ray structure determinations on cyclohexadiene–metal complexes, such as diene–$Fe(CO)_3$ derivatives,[8] reveals that these molecules have a shape resembling a boat cyclohexene conformation, as shown in Figure 3.

The cycloheptadiene complexes can adopt either a boat conformation (**12**) or a chair conformation (**13**) as depicted in Figure 4. Analysis of ^{1}H NMR coupling constants for 5-substituted cycloheptadiene–*iron* complexes indicates that these adopt the boat conformation (**12**), thus avoiding a nonbonded interaction between the substituent and the diene moiety.[5] However, the molybdenum complexes **9a**, **9b**, and **9c** all show a characteristic ^{1}H NMR signal at ca. δ 2.5 due to the endo 7-H, which is observed as a doublet of quartets (J_{gem} = ca. 18 Hz, $J_{6\text{-endo},7\text{-endo}} = J_{6\text{-exo},7\text{-endo}} = J_{1,7}$ = ca. 4.5 Hz). These coupling constants are strongly indicative of the chair conformation (**13**) for these molecules, since the boat conformation would have a dihedral angle between endo 7-H and exo 6-H of ca. 180°, leading to a large coupling constant, as observed for the iron complexes.[5] Since there is no X-ray data available for the cycloheptadiene–molybdenum derivatives, the conclusions from NMR data so far remain unconfirmed. The reason for the preference of the chair conformation for the molybdenum complexes is puzzling, but evidently the transannular nonbonded interactions are less important for these cationic diene complexes than for the uncharged iron systems.

It now becomes possible to rationalize the observed differences in regioselectivity for the cyclohexadiene and cycloheptadiene complexes, purely on steric and conformational grounds. From the available X-ray data on cyclohexadiene–$Fe(CO)_3$ complexes[8] a Newman projection along the C(5)–C(4) bond can be constructed, as shown in Figure 5. It is evident that the bond from C(5) to the 5-exo substituent (R) is almost antiperiplanar with the C(4)–Mo bond. The same conclusion results from inspection of a boat cyclohexene molecular model. Addition of a nucleophile at C(4) is essentially a pseudo S_N2 displacement of the $Mo(CO)_2Cp$ group, so the nucleophile must approach as shown in Figure 5, thereby experiencing a severe interaction with the 5-substituent, so this approach is disfavored in comparison to attack at C(1) of the diene. Incorporation of the extra methylene group, as in the seven-membered ring leads to an appreciable change of geometry. The Newman projection along C(5)–C(4) for the chair conformation (B in Figure 5) shows that the substituent (R) is now further from the nucleophile approach trajectory (almost staggered). On the other hand, a boat conformation (C, Figure 5) places the R group and the approach vector in an almost eclipsed arrangement, as in the six-membered ring, since chair/boat interconversion involves a 60° rotation about the C(4)–C(5) bond. As a consequence the nucleophile essentially experiences the less severe gauche butane interaction with the R group during its approach to C(4) in the chair cycloheptadiene–$Mo(CO)_2Cp$ arrangement, and this would account for the observed drop in regioselectivity on changing the ring size. Interestingly, both NMR data and reactivity are more consistent with the chair than with the boat conformation. Clearly, if sterically undemanding nucleophile and 5-substituent are to be used effectively in these systems, an alternative means for regiocontrol must be sought. This will require cycloheptadiene complexes carrying substituents at C(1) or C(2) which can act as control elements, and this will form the basis for future research in our laboratories.[18]

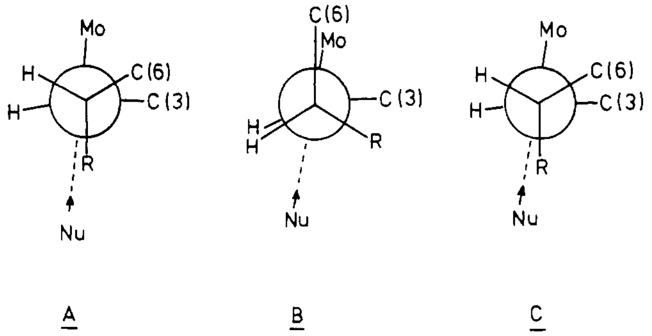

Figure 5. Newman projections along C(4)–C(5) bond for (A) cyclohexadiene–$Mo(CO)_2Cp$, (B) chair conformation of cycloheptadiene–$Mo(CO)_2Cp$, (C) boat conformation of cycloheptadiene–$Mo(CO)_2Cp$. Depicts trajectory of nucleophile (Nu) during pseudo-S_N2 attack on C(4)–Mo bond and indicates interaction between nucleophile and an exo substituent (R) at C(5).

Reaction of complex **9a** with the enolate from methyl 2-oxocyclopentanecarboxylate gave *two* products, assumed to be diastereomers of **10f**, since this relatively bulky nucleophile is expected to add exclusively at C(1) of **9a**. The mixture obtained (4:1) again indicated a pronounced diastereoselection during this reaction. This interesting phenomenon is not yet understood, and we anticipate that future studies using acyclic diene–$Mo(CO)_2Cp$ complexes will reveal whether steric or electronic factors are responsible for the effect.

(b) Demetalation of π-Allyl–$Mo(CO)_2Cp$ Complexes. In order to test the success of our cyclofunctionalization/demetalation procedure[7] on the cycloheptenyl system, the phenylsulfonyl ester adducts **8e**, **10e**, and **10j** were converted to monoesters **8h**, **10g**, and **10k**, respectively, by using standard desulfonylation techniques,[19] and then to the carboxylic acids **8i**, **10h**, and **10l**. Treatment of **8i**

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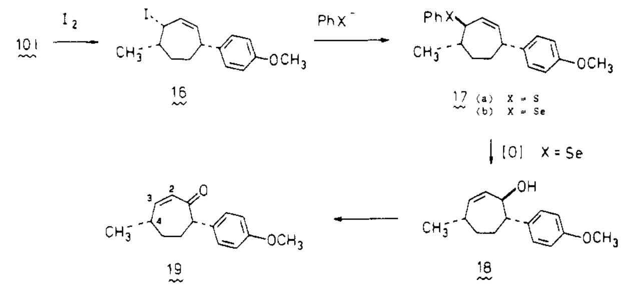
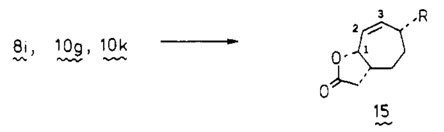
[18] Green et al. have recently reported the preparation of diene–$Mo(CO)_2(\eta^5\text{-indenyl})$ cations by reaction of the diene with $[Mo(NCMe)_2(CO)_2(\eta^5\text{-indenyl})]BF_4$. This promises access to a wide range of substituted diene complexes of potential value in organic synthesis, see: Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.

[19] Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

Scheme III



with excess iodine in acetonitrile solution resulted in good yield of the lactone **15a**, contaminated by small amounts of an unidentified byproduct. The major product was



15

(a) R = H
(b) R = Me
(c) R = CH2CH=CH2

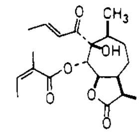
identical with a sample prepared in this laboratory[20] by the two-step sequence: (1) phenylselenolactonization of cycloheptenylacetic acid; (2) oxidation and elimination of the selenolactone,[21] thereby establishing the cis stereochemistry of the lactone. Similar treatment of **10h** with iodine again led to lactone **15b** as the major product, but a similar byproduct was evident, this time in larger amount. Alteration of reaction conditions gave no improvement, so a different procedure was investigated. Treatment of each carboxylic acid with a slight excess of nitrosyl hexafluorophosphate, followed by addition of triethylamine, aqueous workup, and ether extraction afforded directly the lactones **15a–c**, uncontaminated and in high yield. This reaction proceeds via a π-allyl–Mo(CO)(NO)Cp cationic complex[11] which undergoes cyclization to give the neutral η^2-alkene–Mo(CO)(NO)Cp complex. Evidently, the latter compound is very unstable and decomposes under the workup conditions used to give lactone **15** as the sole product in each case. Such intramolecular nucleophile addition to the π-allyl–Mo(CO)(NO)Cp system has not previously been reported and might have considerable scope with regard to the nature of the pendant nucleophile.

Treatment with iodine of π-allyl-Mo(CO)$_2$Cp complexes that do not have pendant nucleophilic groups has previously led to allylic iodides by interception of intermediate π-allyl–MoI(CO)$_2$Cp cations with iodide nucleophile.[7] In the present series, we have examined reaction of the 4-(4-methoxyphenyl)-7-methyl-substituted derivative **10m** with iodine. The product allylic iodide **16** was too unstable to purify and fully characterize, but direct reaction of the crude material with thiophenoxide gave thio ether **17a** as the only observable product (Scheme III). Similar reaction with phenylselenide anion gave **17b**, which was readily converted, via [2,3] sigmatropic rearrangement of the intermediate selenoxide, to the alcohol **18** on treatment with hydrogen peroxide. The structure and stereochemistry shown for **18** is consistent with ^{1}H NMR data (see Experimental Section). Oxidation of **18** cleanly afforded the disubstituted cycloheptenone **19**.

This sequence of iodine treatment followed by formation of allylic selenides or sulfides represents a potentially useful way to introduce functionality onto the ring in a stereo- and regiocontrolled manner. The selenoxide rearrangement is particularly useful in this respect, since hydroxy groups can be introduced stereospecifically at the position corresponding to the sterically more hindered terminus of the π-allyl-molybdenum system. So far, we have not carried out an intensive investigation into the scope of this sequence.

Conclusions

Double nucleophile additions to cycloheptadiene–Mo(CO)$_2$Cp cations provide a useful means of introducing substituents onto the seven-membered ring, although in some cases the degree of control is much poorer than with the corresponding cyclohexadiene complexes. Decomplexation of the product π-allyl–Mo(CO)$_2$Cp complexes can be accomplished by treatment with iodine, or with NOPF$_6$, to give cyclofunctionalization products or allylic iodides. One potential application of this methodology for organic synthesis is illustrated by comparison of the lactone **15b** with the compound **20**, which is a secondary metabolite



20

recently isolated from *Ratibida columnifera*,[22] and which has the same stereochemical relationship between the lactone and methyl substituent. Appropriate functionalization of the double bond in **15b** could well lead to a useful synthetic route to **20**.

Experimental Section

Infrared spectra were recorded in carbon tetrachloride solution, unless otherwise stated, on a Perkin-Elmer 1420 instrument, and NMR spectra for solutions in deuteriochloroform (unless otherwise stated) were obtained with a Varian XL-200 instrument. Field desorption mass spectra were kindly provided by Dr. Robert P. Lattimer and Dr. Bill Kroenke of the B.F. Goodrich Co., Brecksville, OH, and high-resolution electron impact mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE. For molybdenum complexes the appropriate peaks corresponding to isotopes molybdenum-92, -94, -95, -96, -97, and -98 are quoted. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Solvents were freshly distilled under nitrogen as follows: tetrahydrofuran (THF) from sodium and benzophenone; diethyl ether from lithium aluminum hydride; dichloromethane and acetonitrile from calcium hydride. Combustion analyses were carried out by Galbraith Laboratories, Knoxville, TN. Compounds that were not submitted for analysis were ascertained to be at least 95% pure by TLC, 200-MHz ^{1}H NMR, and in some cases field desorption mass spectrometry, unless otherwise stated. All reactions were carried out under an atmosphere of dry nitrogen.

Synthesis of Cp(CO)$_2$Mo(η^3-C$_7$H$_{11}$) (6). The Cp(CO)$_2$Mo(η^3-C$_7$H$_{11}$) complex was synthesized according to the method of Faller et al.[11] Mo(CO)$_6$ (10.0 g, 37.9 mmol) was charged into a three-neck round-bottom flask fitted with a magnetic stirrer and reflux condenser with nitrogen bubbler. Acetonitrile (40 mL) was added and the suspension was then refluxed for 5 h, after which 3-bromo-1-cycloheptene (6.64 g, 37.9 mmol) in THF (10 mL) was

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[20] We are grateful to Dr. H. S. Bansal for performing these experiments.

[21] Campos, M. d. M.; Petragnani, N. *Tetrahedron Lett.* **1959**, *6*, 11; *Chem. Ber.* **1960**, *93*, 317. Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884. Clive, D. L. J.; Farina, V.; Singh, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2120. Nicolaou, K. C. *Tetrahedron* **1981**, *37*, 4097.

[22] Herz, W.; Kulanthaivel, P.; Goedken, V. L. *J. Org. Chem.* **1985**, *50*, 610.

added dropwise. The resultant mixture was cooled to 0 °C to give deep orange red crystals. For complete crystallization, the mixture was left in the refrigerator at −10 °C overnight. The deep orange red crystalline compound $[(CH_3CN)_2MoBr(\eta^3\text{-}C_7H_{11})(CO)_2]$ was then separated by filtration and dried in vacuo (13 mmHg) at 25 °C to afford the product (13.16 g, 85%).

The $(CH_3CN)_2MoBr(\eta^3\text{-}C_7H_{11})(CO)_2$ complex (2 g, 4.89 mmol) was dissolved in THF (20 mL) to give a dark yellow solution. To the stirred solution, lithium cyclopentadienide solution [prepared from the reaction of cyclopentadiene (0.3 g, 4.89 mmol) and *n*-butyllithium (2.24 mL, 2.3 M) in THF under nitrogen atmosphere] was added dropwise. After complete addition of lithium cyclopentadienide, the reaction mixture becomes dark brown in color, and this was stirred at room temperature for 2 h. After evaporation of solvent in vacuo an orange red crystalline residue was obtained which was purified by chromatography (Fisher adsorption grade Al_2O_3/CH_2Cl_2). Removal of solvent from the deep yellow eluant gave a yellow crystalline product **6** (1.34 g, 88%): mp 101.5–102 °C; IR ν_{max} 1945, 1865 cm^{-1}; ^{1}H NMR δ 5.24 (5 H, s, Cp), 4.06 (2 H, td, J = 8.18, 2.09 Hz, 1-H and 3-H), 3.72 (1 H, t, J = 8.18 Hz, 2-H), 2.36 (2 H, m, endo 4-H and endo 7-H), 2.17 (1 H, m, exo 4-H and exo 7-H), 1.08 (2 H, m endo 5-H and endo 6-H), 0.81 (2 H, m, exo 5-H and exo 6-H). Decoupling experiments: irradiating δ 4.06 causes collapse of δ 3.72 to singlet and collapse of δ 2.17 to dd (J = 7.75 Hz, J = 4.01 Hz); irradiating δ 3.72 causes partial collapse of δ 4.06. Anal. Calcd for $C_{14}H_{16}O_2Mo$: C, 53.85; H, 5.16. Found: C, 53.80; H, 4.98.

$[Cp(CO)_2Mo(\eta^4\text{-}C_7H_{10})]PF_6$ (7). To a stirred solution of complex **6** (0.81 g, 2.59 mmol) in CH_2Cl_2 (3 mL) was added Ph_3CPF_6 (0.98 g, 2.54 mmol) in one portion at 0 °C. The resultant mixture was stirred for 1 h, after which the crystalline solid was precipitated by addition of dry ether. The crude crystalline compound was purified by reprecipitation from CH_2Cl_2 with ether to yield the yellow crystalline product **7** (1.12 g, 95%): mp >300 °C dec; IR (CH_2Cl_2) ν_{max} 2016, 1960 cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.78 (2 H, dd, J = 7.34, 3.34 Hz, 2-H and 3-H), 5.64 (5 H, s, Cp), 4.81 (2 H, dt, J = 7.32, 3.47 Hz, 1-H and 4-H), 2.28 (2 H, m, endo 5-H and endo 7-H), 2.07 (2 H, m, exo 5-H and exo 7-H), 1.35 (1 H, m, endo 6-H), 1.15 (1 H, m, exo 6-H). Anal. Calcd for $C_{14}H_{15}O_2PF_6Mo$: C, 36.86; H, 3.31. Found: C, 36.75; H, 3.29.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_{10}\text{-}4\text{-}CH(CO_2Me)_2]$ (8d). A solution of $NaCH(CO_2Me)_2$ in THF was prepared in the usual way by addition of $CH_2(CO_2Me)_2$ (0.06 g, 0.46 mmol) to a stirred suspension of sodium hydride (0.46 mmol, from 0.022 g of NaH 50% suspension in mineral oil, washed with dry THF in situ). The reaction flask was opened briefly with back-flushing of nitrogen, and the diene complex **7** (0.2 g, 0.44 mmol) was added in one portion. The reaction could be monitored by dissolution of the THF-insoluble complex **7** (ca. 30 min), after which the mixture was poured into water (40 mL) and extracted with ether (2 × 20 mL). The combined extracts were washed with water (3 × 20 mL), dried ($MgSO_4$), and evaporated in vacuo to yield the crude product, which was purified by chromatography (silica gel/CH_2Cl_2) to give **8d** as a yellow oil (0.18 g, 95%): IR ν_{max} 1950, 1870, 1740 cm^{-1}; ^{1}H NMR δ 5.25 (5 H, s, Cp), 4.14 (1 H, dd, J = 6.84, 3.15 Hz, 1-H), 3.77 (3 H, s, CO_2Me), 3.75 (2 H, m, obscured, 2-H and 3-H), 3.74 (3 H, s, CO_2Me), 3.51 (1 H, d, J = 6.35 Hz, 8-H), 2.91 (1 H, m, endo 4-H), 2.17 (2 H, m, endo 5-H and endo 7-H), 1.26 (2 H, m, 6-H and exo 7-H), 0.99 (1 H, q, $J_{gem} = J_{5,6} = J_{4,5}$ = 11.72 Hz, exo 5-H), 0.35 (1 H, m, 6-H). Decoupling experiment: irradiating δ 4.14 causes partial collapse of δ 3.75; irradiating δ 3.51 causes collapse of δ 2.91 to dd (J = 10.90, 3.25 Hz); irradiating δ 2.91 causes collapse of δ 3.51 to singlet, simplification of δ 3.75 and 1.16, and collapse of δ 0.99 to t (J = 11.72 Hz); irradiating δ 1.26 causes collapse of δ 2.91 to dd (J = 9.22, 6.56 Hz), partial modification of δ 2.17, and collapse of δ 0.99 to t (J = 11.72 Hz) and δ 0.35 to td (J = 10.25, 5.59 Hz); irradiating δ 0.99 causes modification of δ 1.26 and collapse of δ 2.91 to d (J = 6.46 Hz); irradiating δ 0.35 causes partial modification of δ 2.17 and 1.26, collapse of δ 0.99 to t (J = 11.72 Hz). FDMS, *m/e* (relative intensity) 445 (12), 442 (60), 441 (55) [M]; M$^+$ calcd for ^{98}Mo in $C_{19}H_{22}O_6Mo$ 445, found 445. The FD mass spectrum showed no other peaks, indicating a high degree of purity for this compound.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_{10}\text{-}4\text{-}CH(CO_2Me)(SO_2Ph)]$ (8e). The diene complex **7** (0.2 g, 0.44 mmol) was added to a stirred solution of $NaCH(CO_2Me)(SO_2Ph)$ [prepared in THF from the reaction of methyl (phenylsulfonyl)acetate (0.11 g, 0.5 mmol) and NaH (0.22 g, 0.44 mmol)] in THF (10 mL). The reaction was judged to be complete after 30 min of stirring and was worked up as described above. ^{1}H NMR study on the crude product indicated ca. 2:1 mixture of diastereomers. Purification by preparative TLC afforded an equimolar mixture of diastereomers **8e** as a yellow foam (0.23 g, 98%) due to epimerization. This compound could not be crystallized: IR ν_{max} 1950, 1870, 1750 cm^{-1}; ^{1}H NMR δ 7.96, 7.64 (5 H, m, Ar H), 5.28 (s, minor isomer, Cp), 5.21 (s, major isomer, Cp), 4.19 (2 H, m, 1-H and 3-H), 3.90 (1 H, d, J = 7.32 Hz, 8-H), 3.76 (s, major isomer, CO_2Me), 3.68 (1 H, t, J = 7.81 Hz, 2-H), 3.60 (s, minor isomer CO_2Me), 3.07 (1 H, m, major isomer, endo 4-H), 2.90 (1 H, m, minor isomer, endo 4-H), 2.11 (2 H, m, endo 5-H and endo 7-H), 1.28 (2 H, m, 6-H and exo 7-H), 0.96 (1 H, q, $J_{gem} = J_{5,6} = J_{4,5}$ = 13.37 Hz, exo 5-H), 0.30 (1 H, m, 6-H) [rigorous assignment of multiplicities in some regions was prevented by spectral overlap of the two isomers]; FDMS, *m/e* (relative intensity) 425 (3.5), 526 (4), 524 (4), 523 (3.5) [M]; M$^+$ calcd for ^{98}Mo in $C_{23}H_{24}O_6SMo$ 526, found 526. The FD mass spectrum showed no other peaks, indicating a high degree of purity for this compound.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_{10}\text{-}4\text{-}CH(CO_2Me)(COMe)]$ (8f). A solution of $NaCH(CO_2Me)(COMe)$ was prepared in THF under N_2 as described above. To the stirred solution was added the diene complex **7** (0.2 g, 0.44 mmol) in one portion at room temperature. After 30 min the reaction was worked up in the usual way to afford complex **8f** as a 2:1 mixture of diastereomers. Purification by preparative TLC gave an equimolar mixture of isomers as an oily product (0.17 g, 90%), which could not be crystallized: IR ν_{max} 1950, 1870, 1720 (br) cm^{-1}; ^{1}H NMR δ 5.24 (5 H, s, Cp), 4.17 (1 H, m, 1-H), 3.76 (s, minor isomer, CO_2Me), 3.75 (1 H, m, partially obscured, 2-H), 3.70 (s, major isomer, CO_2Me), 3.52 (2 H, 4 overlapping d, diastereomers, $J_{2,3}$ = 8.19 Hz, $J_{4,8}$ = 6.35 Hz, 3-H and 8-H), 2.94 (1 H, m, endo 4-H), 2.31 (s, minor isomer, COMe) 2.23 (s, major isomer, COMe), 2.13 (2 H, m, partially obscured, endo 5-H and endo 7-H), 1.23 (2 H, br, d, J = 10.96 Hz, 6-H and exo 7-H), 0.89 (1 H, 2 × q, $J_{gem} = J_{5,6} = J_{4,5}$ = 10.35 Hz, exo 5-H, diastereomers), 0.34 (1 H, 2 × qd, diastereomers J_q = 10.8 Hz, J_d = 3.64 Hz, 6-H). Decoupling experiment: irradiating δ 3.52 causes collapse of δ 2.94 to dd (J = 10.68 Hz, J = 3.36 Hz) and simplification of δ 3.75; irradiating δ 2.94 causes collapse of δ 3.52 to d (J = 9.0 Hz), and collapse of δ 0.89 to 2 × t (J = 11.04 Hz); irradiating δ 1.23 causes collapse of δ 0.89 to 2 overlapping t (J = 10.8 Hz) and δ 0.34 collapse to td (J = 10.06 Hz, J = 3.66 Hz). FDMS, *m/e* (relative intensity) 426 (3.5), 425 (3.8), 424 (2.5), 423 (1.2) [M]; M$^+$ calcd for ^{98}Mo in $C_{19}H_{22}O_5Mo$ 426, found 426. The FD mass spectrum showed no other peaks, indicating a high purity of this compound.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_{10}\text{-}4\text{-}\overline{C(CO_2Me)CH_2CH_2CH_2C}{=}O]$ (8g). The diene complex **7** (0.2 g, 0.44 mmol) was added to a stirred solution of methyl 2-oxo-1-sodiocyclopentane carboxylate (prepared in situ as described above) in THF (10 mL) at room temperature. After 30 min, the reaction was worked up in the usual manner and evaporated to give a yellow crystalline solid **8g** (0.18 g, 90%). ^{1}H and ^{13}C NMR on the crude product indicated ca. 9:1 mixture of diastereomers. The major diastereomer was obtained pure by recrystallization from a solution in $CHCl_3$ (1 mL) and Et_2O (2 mL) by addition of pentane (5 mL) followed by cooling: mp 135–137 °C dec; IR ν_{max} 1950, 1875, 1755, 1725 cm^{-1}; ^{1}H NMR δ 5.23 (5 H, s, Cp), 4.17 (1 H, m, 1-H), 3.75 (3 H, s, CO_2Me), 3.69 (1 H, dd, partially obscured, J = 8.73, 4.61 Hz, 2-H), 3.56 (1 H, dd, J = 8.73, 0.98 Hz, 3-H), 3.00 (1 H, dd, J = 12.11, 2.26 Hz, endo 4-H), 2.62 (1 H, dtd, J_{gem} = 13.34 Hz, J_t = 5.57 Hz, J_d = 1.77 Hz, endo 7-H), 2.37 (1 H, dtd, J_{gem} = 18.54 Hz, J_t = 6.54 Hz, J_d = 1.41 Hz, endo 5-H), 2.15 (3 H, m, 6-H, 10-H), 1.91 (3 H, m, exo 7-H, 12-H), 1.22 (2 H, m, 11-H), 0.78 (1 H, q, $J_{gem} = J_{5,6} = J_{4,5}$ = 11.71 Hz, exo 5-H), 0.16 (1 H, m, 6-H); ^{13}C NMR (run to 280 ppm) 212.0, 170.0, 92.60 (Cp), 65.45, 64.78, 60.37, 58.84, 52.50, 45.56, 39.27, 30.61, 29.69, 29.20, 23.55, 19.49 ppm. Anal. Calcd for $C_{21}H_{24}O_5Mo$: C, 55.75; H, 5.34. Found C, 55.68; H, 5.30.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_{10}\text{-}4\text{-}CH_3]$ (8a). Methylmagnesium bromide solution in THF (13.6 mL, 43.8 mmol = 5.22 g) was added dropwise to a stirred solution of the diene complex **7** (2 g, 4.38 mmol) in THF (40 mL) at 0 °C. After 20 min the excess MeMgBr was destroyed with H_2O (10 mL) followed by workup in the usual manner, to yield a brown crystalline solid **8a**. The crude product was purified by chromatography (Fisher adsorption grade Al_2O_3/CH_2Cl_2) and evaporation of the yellow eluant afforded a yellow crystalline solid (1.21 g, 85%): mp 70–71 °C; IR ν_{max} 1950, 1870 cm^{-1}; ^{1}H NMR δ 5.24 (5 H, s, Cp), 4.08 (1 H, m, 1-H), 3.73 (1 H, d, J = 9.49 Hz, 3-H), 3.66 (1 H, t, J = 9.49 Hz, 2-H), 2.21 (3 H, m, endo 4-H, endo 5-H, and endo 7-H), 1.24 (2 H, m, partially obscured, 6-H and exo 7-H), 1.16 (3 H, d, J = 6.84 Hz, 4-CH$_3$), 0.71 (1 H, q, $J_{gem} = J_{5,6} = J_{5,4}$ = 10.11 Hz, exo 5-H), 0.40 (1 H, m, 6-H). Decoupling experiment: irradiating δ 4.08 causes collapse of δ 3.66 to d (J = 9.01 Hz) and simplification of δ 2.21; irradiating δ 3.73 or 3.66 causes modification of δ 4.08 and 0.84; irradiating δ 2.21 causes collapse of δ 4.08 to t (J = 9.64 Hz) and collapse of δ 1.16 to s and δ 0.40 to dd (J = 13.67 Hz, J = 10.74 Hz). Anal. Calcd for $C_{15}H_{18}O_2Mo$: C, 55.22; H, 5.56. Found: C, 55.29; H, 5.51.

Cp(CO)$_2$Mo[η^3-C$_7$H$_{10}$-4-CN] (8j). To a stirred suspension of the diene complex **7** (0.5 g, 1.09 mmol) in CH_3CN (10 mL) at 20 °C was added dropwise NaCN (0.08 g, 1.64 mmol) in H_2O (1 mL). The resultant mixture was stirred for 17 h, monitored by TLC (silica gel/40% EtOAc in hexane), followed by workup in the usual way to yield a yellow oily compound. The crude product was purified by preparative TLC which afforded yellow crystalline compound (0.33 g, 90%) **8j**: mp 94.5–95.5 °C; IR ν_{max} 2220, 1955, 1875 cm^{-1}; ^{1}H NMR δ 5.31 (5 H, s, Cp), 4.19 (1 H, br t, J = 7.3 Hz, 1-H), 3.96 (1 H, d, J = 7.3 Hz, 3-H), 3.82 (1 H, t, J = 7.3 Hz, 2-H), 3.23 (1 H, m, endo 4-H), 2.45 (1 H, dm, J_{gem} = 16.5 Hz, endo 5-H), 2.16 (2 H, dm, J_{gem} = 18.5 Hz, endo 7-H and 6-H), 1.38 (1 H, m, 7-H), 1.20 (1 H, m, exo 5-H), 0.88 (1 H, m, 6-H). Decoupling experiment: irradiating δ 4.19 causes collapse of δ 3.82 to d (J = 8.79 Hz) and collapse of δ 2.16 to ddd (J_{gem} = 18.5 Hz, J = 8.13 Hz, J = 4.11 Hz); irradiating δ 3.96 or 3.82 causes collapse of δ 3.23 to dd (J = 7.16, 4.28 Hz); irradiating δ 2.45 or 2.16 causes collapse of δ 4.19 to d (J = 8.63 Hz) and partial collapse of δ 0.88; irradiating δ 1.38 causes collapse of δ 2.16 to br d, (J = 18.5 Hz), partial collapse of δ 2.45 and 1.20, and collapse of δ 0.88 to t (J = 6.45 Hz); irradiating δ 0.88 causes collapse of δ 2.16 to dd (J = 18.5, 8.85 Hz). Anal. Calcd for $C_{15}H_{15}O_2NMo$: C, 53.42; H, 4.48; N, 4.15. Found: C, 53.21; H, 4.53; N, 4.05.

Cp(CO)$_2$Mo(η^3-C$_7$H$_{10}$-4-CH$_2$CH═CH$_2$) (8b). To a stirred suspension of the diene complex **7** (0.10 g, 0.22 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of allylmagnesium bromide in THF (0.03 g, 0.26 mmol). The resultant reaction mixture was stirred for 30 min, the excess allyl magnesium bromide was quenched with H_2O (1 mL), and the product was worked up as usual. After evaporation, the yellow crystalline solid **8b** was purified by chromatography (silica gel/CH_2Cl_2). The yellow eluant yielded pure crystalline solid (0.07 g, 90%): mp 71–71.5 °C. IR ν_{max} 1950, 1860 cm^{-1}; ^{1}H NMR δ 5.83 (1 H, m, vinyl), 5.24 (5 H, s, Cp), 5.04 (1 H, d, J = 15.74 Hz, vinyl trans), 5.03 (1 H, d, J = 10.94 Hz, vinyl), 4.14 (1 H, m, 1-H), 3.80 (1 H, d, J = 8.8 Hz, 3-H), 3.68 (1 H, t, J = 8.79 Hz, 2-H), 2.16 (5 H, m, endo 5-H, endo 4-H, endo 7-H, and side chain CH$_2$), 1.22 (2 H, m, 6-H, exo 7-H), 0.76 (1 H, m, 6-H), 0.34 (1 H, m, exo 5-H). Anal. Calcd for $C_{17}H_{20}O_2Mo$: C, 57.98; H, 5.72. Found: C, 57.75; H, 5.84.

Cp(CO)$_2$Mo(η^3-C$_7$H$_{10}$-4-C$_6$H$_4$OMe) (8c). To a stirred solution of the diene complex **7** in CH_2Cl_2 (100 mL) at room temperature was added a solution of (*p*-methoxyphenyl)magnesium bromide (1.21 mL, 0.20 g, 1.09 mmol) [prepared from the reaction of Mg (0.2 g) and 4-BrC$_6$H$_4$OMe (1.69 g) in THF (10 mL) and standardized by titration]. The resultant reaction mixture was stirred for 30 min and then poured into H_2O (200 mL) and extracted with ether (3 × 20 mL), and the combined extracts were washed with H_2O (2 × 50 mL), dried ($MgSO_4$), and evaporated to give a brown solid, which was purified by chromatography (silica gel/40% EtOAc in hexane). Evaporation of the eluant afforded yellow crystalline solid **8c** (0.41 g, 90%); mp 112–113 °C. This reaction was also carried out in THF which resulted in considerable contamination by 4,4′-dimethoxybiphenyl and difficulty in purification: IR ν_{max} 1945, 1865 cm^{-1}; ^{1}H NMR δ 7.37 (2 H, d, J = 8.60 Hz, Ar H), 6.88 (2 H, d, J = 8.60 Hz, Ar H), 5.26 (5 H, s, Cp), 3.94 (3 H, m, 1-H, 2-H, and 3-H), 3.79 (3 H, s, OMe), 3.50 (1 H, m, endo 4-H), 2.36 (2 H, m, endo 7-H and endo 5-H), 1.38 (1 H, m, partially obscured, 6-H), 1.25 (3 H, d, J = 6.95 Hz, exo 7-CH$_3$), 1.04 (1 H, m, exo 5-H), 0.77 (1 H, m, 6-H). Anal. Calcd for $C_{29}H_{22}O_5Mo$: C, 60.29; H, 5.26. Found: C, 60.47; H, 5.37.

Cp(CO)$_2$Mo(η^3-C$_7$H$_{10}$-4-CH$_2$CO$_2$Me) (8h). To a stirred solution of phenylsulfonyl ester complex **8e** (0.25 g, 0.47 mmol) in MeOH/THF (20 mL, 4:1) was added Na_2HPO_4 (0.27 g, 1.88 mmol) at room temperature. After 15 min the mixture was cooled to 0 °C, and 6% NaHg amalgam (1.26 g, 5.64 mmol) was added in small portions, the reaction course being monitored by TLC (silica gel/40% EtOAc in hexane). When complete, the reaction mixture was acidified with aqueous HCl (10%), poured into H_2O (100 mL), and extracted with ether (2 × 50 mL). The combined extracts were washed with H_2O (2 × 20 mL), dried ($MgSO_4$), and evaporated to afford pure **8h** as a yellow crystalline solid (0.15 g, 80%): mp 125–126 °C; IR ν_{max} 1950, 1870, 1740 cm^{-1}; ^{1}H NMR δ 5.20 (5 H, s, Cp), 4.15 (1 H, m, 1-H), 3.71 (2 H, m, partially obscured, 2-H and 3-H), 3.69 (3 H, s, CO$_2$Me), 2.61 (1 H, m, endo 4-H), 2.47 (2 H, d, J = 7.82 Hz, 8-H), 2.16 (2 H, m, endo 7-H and endo 5-H), 1.24 (2 H, m, 6-H and exo 7-H), 0.84 (1 H, m, exo 5-H), 0.45 (1 H, m, 6-H). Anal. Calcd for $C_{17}H_{20}O_4Mo$: C, 53.13; H, 5.24. Found: C, 53.10; H, 5.29.

Cp(CO)$_2$Mo(η^3-C$_7$H$_{10}$-4-CH$_2$COOH) (8i). The monoester complex **8h** (0.2 g, 0.52 mmol) was stirred at room temperature in CH_3OH/THF (20 mL, 1:1), and a solution of KOH (0.47 g, 8.33 mmol) in H_2O (2 mL) was added. The mixture was stirred for 60 h and then was judged to be complete by TLC in the usual manner. Acidification, followed by the usual extractive workup afforded the pure complex **8i** as a yellow crystalline solid (0.18 g, 95%): mp 190 °C dec; IR ν_{max} 1945, 1860, 1720 cm^{-1}; ^{1}H NMR δ 5.24 (5 H, s, Cp), 4.14 (1 H, dm, J = 7.24 Hz, 1-H), 3.7 (2 H, m, 2-H and 3-H), 2.63 (1 H, m, endo 4-H), 2.50 (2 H, d, J = 6.35 Hz, 8-H), 2.15 (2 H, m, endo 7-H and 6-H), 1.21 (1 H, m, exo 7-H, obscured), 0.84 (2 H, m, endo 5-H and exo 5-H), 0.46 (1 H, m, 6-H). Anal. Calcd for $C_{16}H_{18}O_4Mo$: C, 51.90; H, 4.90. Found: C, 51.70; H, 5.01.

[Cp(CO)$_2$Mo(η^4-C$_7$H$_9$-5-CH$_3$)]PF$_6$ (9a). To a stirred solution of the complex **8a** (1.12 g, 3.44 mmol) in CH_2Cl_2 (20 mL), at 0 °C was added Ph_3CPF_6 (1.33 g, 3.44 mmol). The reaction mixture was stirred for 1 h. A greenish yellow solid was obtained on addition of dry ether. The crude compound was dissolved in CH_2Cl_2 or CH_3CN and recrystallized by addition of ether to afford pure diene complex **9a** (1.45 g, 90%): mp 170 °C dec; IR (CH_2Cl_2) ν_{max} 2016, 1960, 850 cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.88 (2 H, dd, J = 7.57 Hz, J = 3.55 Hz, 2-H and 3-H), 5.75 (5 H, s, Cp), 4.81 (2 H, m, 1-H and 4-H), 2.55 (1 H, dq, J_{gem} = 18.12 Hz, J_q = 4.94 Hz, endo 7-H), 2.22 (2 H, m, endo 5-H, exo 7-H), 1.55 (1 H, m, endo 6-H), 1.20 (1 H, m, exo 6-H), 1.07 (3 H, d, J = 6.94 Hz, exo 5-CH$_3$). Anal. Calcd for $C_{15}H_{17}O_2PF_6Mo$: C, 38.32; H, 3.64. Found: C, 37.98; H, 3.37.

Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-CH(CO$_2$Me)$_2$-7-CH$_3$] (10d) and Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-CH(CO$_2$Me)$_2$-5-CH$_3$] (11d). The diene complex **9a** (0.2 g, 0.42 mmol) was added to a stirred solution of NaCH(CO$_2$Me)$_2$ (prepared in situ as described above) in THF (10 mL) at room temperature. The reaction mixture was stirred for 1.5 h and judged to be complete from the dissolution of THF insoluble diene complex **9a**. The reaction was worked up in the usual manner to afford a 2:1 mixture of regioisomers **10d** and **11d** as a yellow foam (1.56 g, 85%). The crude compound was purified by chromatography (silica gel/CH_2Cl_2) to afford yellow crystalline solid (regioisomers not separated): IR ν_{max} 1950, 1870, 1740 cm^{-1}; ^{1}H NMR δ 5.26 (s, minor isomer, Cp), 5.25 (s, major isomer, Cp), 4.17 (1 H, m, 1-H), 3.90 (1 H, m, 2-H and 3-H), 3.79 (s, major isomer, CO$_2$Me), 3.77 (s, minor isomer, CO$_2$Me), 3.65 (1 H, d, J = 8.30 Hz, malonate CH) 3.58 (1 H, d, J = 8.30 Hz, malonate CH regioisomer), 2.91 (2 H, m, endo 4-H), 2.29 (1 H, m, endo 7-H or endo 5-H), 2.18 (1 H, m, endo 5-H or endo 7-H), 1.25 (1 H, m, partially obscured, 6-H), 1.19 (3 H, d, J = 6.95 Hz, CH$_3$), 0.88 (1 H, m, exo 5-H or exo 7-H), 0.39 (1 H, m, 6-H) [assignments of multiplicities prevented by spectral overlap for of regioisomers]. Anal. Calcd for $C_{20}H_{24}O_6Mo$: C, 52.63; H, 5.26. Found: C, 52.60; H, 5.13.

Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-CH(SO$_2$Ph)(CO$_2$Me)-7-CH$_3$] (10e). To a stirred solution of NaCH(CO$_2$Me)(SO$_2$Ph) [prepared in situ as described above] in THF (10 mL) was added the diene complex **9a** (0.2 g, 0.43 mmol) at room temperature. The reaction was stirred for 1 h followed by workup in the usual manner to yield yellow foamy product **10e** (0.22 g, 98%). Purification was carried by chromatography (silica gel/CH$_2$Cl$_2$); the yellow eluant after evaporation afforded a solid mixture of diastereomers: mp 150 °C dec; IR ν_{max} 1950, 1860, 1750 cm^{-1}; ^{1}H NMR δ 7.97 (2 H, m, Ar H), 7.63 (3 H, m, Ar H), 5.29 (s, minor isomer, Cp), 5.21 (s, major isomer, Cp), 4.23 (1 H, m, 1-H), 3.92 (1 H, m, 2-H), 3.77 (s, minor isomer, CO$_2$Me), 3.73 (s, major isomer, CO$_2$Me), 3.69 (1 H, m, 3-H), 3.65 (1 H, m, 8-H), 3.01 (1 H, m, endo 4-H), 2.27 (1 H, m, endo 7-H), 2.13 (1 H, endo 5-H), 1.32 (1 H, m, 6-H), 1.17 (d, J = 6.97 Hz, minor isomer, CH$_3$), 1.15 (d, J = 6.97 Hz, major isomer, CH$_3$), 0.92 (1 H, m, exo 5-H), 0.31 (1 H, m, 6-H). Anal. Calcd for C$_{24}$H$_{26}$O$_6$SMo: C, 53.53; H, 4.88. Found: C, 53.01; H, 4.88. The compound appeared to be a single regioisomer, but a mixture of diastereomers.

Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CN-7-CH$_3$) (10b) and Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CN-5-CH$_3$) (11b). The diene complex **9a** (0.2 g, 0.47 mmol) was dissolved in CH$_3$CN (5 mL), and a solution of NaCN (0.03 g, 0.70 mmol) in H$_2$O (1 mL) was added while stirring at room temperature. The reaction was judged to be complete after 17 h and worked up and chromatographed as usual to afford a yellow oil (0.12 g, 82%) containing a mixture (ca. 3:2) of regioisomers **10b** and **11b**: IR ν_{max} 2220, 1955, 1875 cm^{-1}; ^{1}H NMR δ 5.30 (5 H, s, Cp), 4.18 (1 H, tm, J = 6.3 Hz, 3-H of minor isomer), 3.96 (1 H, tm, J = 6.3 Hz, 3-H of major isomer), 3.9–3.7 (2 H, m, 1-H and 2-H), 3.22 (1 H, m, endo 4-H), 2.34 (1 H, m, endo 5-H), 2.08 (1 H, m, endo 7-H), 1.34 (1 H, m, 6-H), 1.20 (3 H, d, J = 6.94 Hz, CH$_3$), 1.13 (1 H, m, partially obscured, exo 5-H), 0.78 (1 H, m, 6-H); HRMS, m/e (relative intensity) 353 (10.42), 352 (10.42), 351 (6.61), 350 (6.61), 349 (3.79), 347 (4.88) [M$^+$]; M$^+$ calcd for ^{98}Mo in C$_{16}$H$_{17}$O$_2$NMo 353.0322, found 353.0309. Separation of isomers was not possible.

Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CH$_3$-7-CH$_3$) (10a) and Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CH$_3$-5-CH$_3$) (11a). A solution of MeMgBr (0.33 mL, 1.06 mmol) in hexane was added dropwise to a stirred suspension of diene complex **9a** (0.5 g, 0.11 mmol) in THF (3 mL) at 0 °C. The reaction mixture was stirred for 20 min, after which time excess MeMgBr was destroyed with H$_2$O (1 mL), and workup as previously described yielded a mixture (ca. 2:1) of regioisomers **10a** and **11a** (0.03 g, 85%). The crude compound was purified by chromatography (silica gel/CH$_2$Cl$_2$) to afford a yellow solid when dried in high vacuum, mp 91–93 °C. Regioisomers were not separated: IR ν_{max} 1950, 1860 cm^{-1}; ^{1}H NMR δ 5.21 (s, minor isomer, Cp), 5.20 (s, major isomer, Cp), 4.07 (1 H, m, 1-H), 3.80 (1 H, d, J = 9.26 Hz, 3-H, regioisomer), 3.66 (1 H, d, J = 9.26 Hz, 3-H, regioisomer), 3.54 (1 H, t, J = 9.26 Hz, 2-H), 2.16 (m, endo 4-H and endo 7-H), 1.15 (d, J = 6.80 Hz, major isomer, CH$_3$) 1.13 (d, J = 6.80 Hz, minor isomer, CH$_3$), 0.95 (1 H, m, endo 5-H), 0.88 (1 H, m, 6-H), 0.66 (1 H, m, exo 5-H), 0.36 (1 H, m, 6-H). Anal. Calcd for C$_{16}$H$_{20}$MoO$_2$: C, 56.48; H, 5.88. Found: C, 56.55; H, 5.75.

Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-$\overline{\text{C(CO}_2\text{Me)CH}_2\text{CH}_2\text{CH}_2\text{C}}$=O-7-CH$_3$] (10f). The diene complex **9a** (0.2 g, 0.43 mmol) was added to a stirred solution of methyl 2-oxo-1-sodiocyclopentane carboxylate in THF (10 mL) at room temperature. After 30 min the reaction was worked up in the usual manner to yield a yellow foamy product (0.19 g, 95%), as a mixture (ca. 4:1) of diastereomers. Purification by preparative TLC (silica gel/40% EtOAc in hexane) afforded a yellow solid **10f** (diastereomers not separated): mp 157–161 °C; IR ν_{max} 1950, 1875, 1755, 1725 cm^{-1}; ^{1}H NMR δ 5.23 (s, minor isomer, Cp), 5.22 (s, major isomer, Cp), 4.17 (1 H, m, 1-H), 3.99 (1 H, m, 1-H), 3.75 (s, major isomer, CO$_2$Me), 3.69 (s, minor isomer, CO$_2$Me), 3.66 (1 H, m, 3-H), 3.56 (1 H, m, 2-H), 2.93 (1 H, dd, J = 11.28, 3.58 Hz, endo 4-H), 2.64 (1 H, m, endo 7-H), 2.42 (1 H, m, endo 5-H), 2.20 (3 H, m, 6-H and 10-H), 1.95 (2 H, m, 12-H), 1.23 (3 H, d, J = 7.11 Hz, CH$_3$), 1.18 (2 H, m, 11-H), 0.9 (1 H, m, exo 5-H), 0.18 (1 H, m, 6-H) [assignment of multiplicities was prevented by overlapping spectra of diastereomers]. Anal. Calcd for C$_{22}$H$_{26}$O$_5$Mo: C, 47.20; H, 5.58. Found: C, 47.30; H, 5.50.

Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CH$_2$CO$_2$Me-7-CH$_3$) (10g). To a stirred solution of phenylsulfonyl ester complex **10e** (0.5 g, 0.93 mmol) in MeOH (20 mL) was added Na$_2$HPO$_4$ (0.79 g, 5.51 mmol). After 15 min at room temperature, the mixture was cooled to 0 °C, and a large excess of NaHg amalgam was added in small portions. When the reaction was judged to be complete by TLC, it was worked up in the usual manner, to yield **10g** as a yellow foam (0.22 g, 70%). The crude compound was purified by preparative TLC (silica gel/40% EtOAc in hexane) to afford a yellow crystalline solid: mp 70–72 °C; IR ν_{max} 1950, 1860, 1750 cm^{-1}; ^{1}H NMR δ 5.25 (5 H, s, Cp), 3.86 (1 H, d, J = 8.15 Hz, 1-H), 3.75 (1 H, d, J = 8.15 Hz, 3-H), 3.69 (3 H, s, CO$_2$Me), 3.60 (1 H, t, J = 8.15 Hz, 2-H), 2.63 (1 H, m, endo 4-H), 2.52 (2 H, d, J = 9.11 Hz, 8-H), 2.21 (2 H, m, endo 5-H and endo 7-H), 1.25 (1 H, m, 6-H), 1.18 (3 H, d, J = 6.94 Hz, CH$_3$), 1.05 (1 H, m, exo 5-H), 0.91 (1 H, m, 6-H). Anal. Calcd for C$_{18}$H$_{22}$O$_4$Mo: C, 54.27; H, 5.52. Found: C, 54.30; H, 5.49.

Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CH$_2$COOH-7-CH$_3$) (10h). The monoester complex **10g** (0.16 g, 0.40 mmol) was stirred in MeOH (10 mL) with a solution of KOH (0.36, 6.4 mmol) in H$_2$O (1.5 mL) at room temperature for 36 h. The reaction was worked up as described for complex **8i**, to afford a yellow crystalline solid **10h** (0.15 g, 95%): mp 140–140.5 °C; IR ν_{max} (CH$_2$Cl$_2$) 3500, 1950, 1860, 1710 cm^{-1}; ^{1}H NMR δ 5.26 (5 H, s, Cp), 3.85 (1 H, m, 1-H), 3.73 (1 H, d, J = 8.77 Hz, 3-H), 3.62 (1 H, t, J = 8.77 Hz, 2-H), 2.80 (2 H, m, endo 7-H and endo 4-H), 2.16 (2 H, m, endo 5-H and 6-H), 1.19 (3 H, d, J = 6.96 Hz, CH$_3$), 1.06 (1 H, m, exo 5-H), 0.96 (1 H, m, 6-H). Anal. Calcd for C$_{17}$H$_{20}$O$_4$Mo: C, 53.13; H, 5.24. Found: C, 52.94; H, 5.13.

[Cp(CO)$_2$Mo(η^4-C$_7$H$_9$-5-CH$_2$CH=CH$_2$)]PF$_6$ (9b). A solution of allyl complex **8b** (0.43 g, 1.22 mmol) was stirred with Ph$_3$CPF$_6$ (0.47 g, 1.22 mmol) in CH$_2$Cl$_2$ (5 mL) at 0 °C for 1 h. The diene complex was precipitated with ether and purified by recrystallization from CH$_2$Cl$_2$/ether to afford **9b** (0.55 g, 90%): mp 140–141 °C; IR ν_{max} (CH$_2$Cl$_2$) 2016, 1955 cm^{-1}; ^{1}H NMR δ 6.02 (2 H, m, 2-H and 3-H), 5.80 (5 H, s, Cp), 5.73 (1 H, m, vinyl), 5.12 (1 H, d, J = 10.04 Hz, vinyl), 5.10 (1 H, d, J = 18.67 Hz, vinyl), 4.94 (1 H, m, 1-H or 4-H), 4.73 (1 H, br d, J = 9.17 Hz, 1-H or 4-H), 2.63 (1 H, m, endo 5-H), 2.24 (2 H, m, endo 7-H and one of 8-H), 2.12 (1 H, q, J_{gem} = $J_{5,8}$ = $J_{8,9}$ = 13.37 Hz, one of 8-H), 1.28 (3 H, m, 6-H$_2$ and exo 7-H). Anal. Calcd for C$_{17}$H$_{19}$O$_2$PF$_6$Mo: C, 41.44; H, 3.83. Found: C, 41.05; H, 3.85.

Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-CH(CO$_2$Me)$_2$-7-CH$_2$CH=CH$_2$] (10i). To a stirred solution of NaCH(CO$_2$Me)$_2$ in THF (10 mL) was added the diene complex **9b** (0.025 g, 0.05 mmol). After 10 min the reaction was worked up in the usual way, and the product was purified by preparative TLC (silica gel/40% EtOAc in hexane), to afford a yellow crystalline solid **10i** (0.020 g, 98%) (single regioisomer): mp 127–128 °C; IR ν_{max} 1940, 1870, 1740 cm^{-1}; ^{1}H NMR δ 5.78 (1 H, m, vinyl), 5.24 (5 H, s, Cp), 5.04 (1 H, d, J = 16.98 Hz, vinyl), 5.03 (1 H, d, J = 8.24 Hz, vinyl), 3.96 (1 H, d, J = 8.79 Hz, 1-H), 3.85 (1 H, d, J = 9.06 Hz, 3-H), 3.65 (1 H, dd, J = 8.79, 9.06 Hz, 2-H, partially obscured), 3.56 (1 H, d, J = 8.3 Hz, 11-H), 2.90 (1 H, m, endo 4-H), 2.19 (3 H, m, endo 5-H and allyl CH$_2$), 1.15 (2 H, m, 6-H and exo 7-H), 0.73 (2 H, m, exo 5-H and 6-H). Anal. Calcd for C$_{22}$H$_{26}$O$_6$Mo: C, 54.77; H, 5.39. Found: C, 54.76; H, 5.35.

Cp(CO)$_2$Mo[η^3-C$_7$H$_9$-4-CH(SO$_2$Ph)(CO$_2$Me)-7-CH$_2$CH=CH$_2$] (10j). The diene complex **9a** (0.025 g, 0.05 mmol) was added to a stirred solution of NaCH(SO$_2$Ph)(CO$_2$Me) in THF (5 mL). The reaction mixture was stirred for 10 min at room temperature and then worked up as above to afford a 1.5:1 mixture of diastereomers **10j** (0.026 g, 98%) as a yellow foam. The crude product was purified by chromatography (silica gel/CH$_2$Cl$_2$): IR ν_{max} 1945, 1865, 1745 cm^{-1}; ^{1}H NMR δ 7.95 (m, Ar H), 7.57 (m, Ar H), 5.76 (1 H, m, 9-H), 5.29 (s, minor isomer, Cp), 5.21 (s, major isomer, Cp), 5.08 (2 H, m, 10-H), 4.46 (d, J = 8.45 Hz, 1-H, diastereomers), 4.27 (d, J = 8.45 Hz, 1-H, diastereomers), 4.11 (1 H, d, J = 8.45 Hz, 3-H), 3.98 (1 H, t, J = 8.45 Hz, 2-H), 3.87 (1 H, d, J = 8.96 Hz, sulfonylacetate CH), 3.73 (s, major isomer, CO$_2$Me), 3.70 (s, minor isomer, CO$_2$Me), 3.62 (1 H, m, endo 4-H), 3.02 (1 H, m, endo 7-H), 2.17 (3 H, m, endo 5-H and 8-CH$_2$), 1.34 (1 H, m, 6-H), 0.90 (2 H, m, 6-H and exo 5-H) [assignment of multiplicities was prevented by overlap of spectra of diastereomers]; MS, m/e (relative intensity) 568 (1.63), 566 (4.18), 563 (1.95) [M]; M$^+$ calcd for ^{98}Mo in C$_{26}$H$_{28}$O$_6$SMo 568.0645, found 568.0581.

Cp(CO)$_2$Mo(η^3-C$_7$H$_9$-4-CH$_2$CO$_2$Me-7-CH$_2$CH=CH$_2$) (10k). Treatment of the phenylsulfonyl ester complex **10j** (0.30 g, 0.57 mmol) with Na$_2$HPO$_4$ (0.40 g, 2.85 mmol) and NaHg (1.27 g, 5.2 mmol) in CH$_3$OH/THF (20 mL, 2:1) was carried out as for **8e**. The reaction was judged complete after 8 h (monitored by TLC) and afforded a yellow oily product **10k** (0.18 g, 78%), which was sufficiently pure for the next step: IR ν_{max} 1950, 1860, 1740 cm^{-1}; ^{1}H NMR δ 5.75 (1 H, m, vinyl), 5.18 (5 H, s, Cp), 4.98 (1 H, d,

J = 16.6 Hz, vinyl trans), 4.96 (1 H, d, J = 11.12 Hz, vinyl), 3.85 (1 H, d, J = 8.35 Hz, 1-H), 3.81 (1 H, d, J = 8.35 Hz, 3-H), 3.62 (3 H, s, CO_2Me), 3.55 (1 H, t, J = 8.35 Hz, 2-H), 2.58 (1 H, m, endo 4-H), 2.45 (2 H, dd, J = 9.88, 7 Hz, CH_2CO_2Me, diastereotopic), 2.11 (4 H, m, endo 7-H, endo 5-H, and 8-CH_2), 0.80 (3 H, 6-H_2, exo 5-H); HRMS, *m/e* (relative intensity) 428 (1.52), 424 (3.20), 423 (3.01), 420 (2.31) [M]; M^+ calcd for ^{98}Mo in $C_{20}H_{24}O_4Mo$ 424.0726, found 424.0719.

$Cp(CO)_2Mo(\eta^3\text{-}C_7H_9\text{-}4\text{-}CH_2COOH\text{-}7\text{-}CH_2CH{=}CH_2)$ (10l). The monoester complex **10k** (0.11 g, 2.16 mmol) was treated with a solution of KOH (0.12 g, 17.28 mmol, H_2O, 0.5 mL) in MeOH/THF (10 mL, 4:1) and stirred for 24 h. The reaction was worked up as usual to afford a yellow crystalline solid **10l** (0.10 g, 98%): mp 141–142 °C; IR ν_{max} 1950, 1860, 1720 cm^{-1}; ^1H NMR δ 5.77 (1 H, m, vinyl), 5.26 (5 H, s, Cp), 5.05 (1 H, d, J = 16.5 Hz, vinyl), 5.03 (1 H, d, J = 11.02 Hz, vinyl), 3.90 (2 H, m, 1-H and 3-H), 3.63 (1 H, t, J = 8.76 Hz, 2-H), 2.66 (1 H, m, endo 4-H), 2.56 (2 H, dd, J = 10.8, 6.75 Hz, CH_2CO_2H diastereotopic), 2.15 (4 H, m, endo 7-H, endo 5-H, and 8-CH_2), 1.16 (1 H, m, 6-H), 0.87 (2 H, m, exo 5-H, 6-H). Anal. Calcd for $C_{19}H_{22}O_4Mo$: C, 55.61; H, 5.59. Found: C, 55.32; H, 5.45.

$[Cp(CO)_2Mo(\eta^4\text{-}C_7H_9\text{-}4\text{-}C_6H_4OMe)]PF_6$ (9c). Treatment of the complex **8c** (0.39 g, 0.94 mmol) with Ph_3CPF_6 (0.36 g, 0.94 mmol) in CH_2Cl_2 (10 mL) at 0 °C for 40 min followed by addition of ether and filtration afforded crude product. This was purified by recrystallization from CH_2Cl_2/ether to afford the diene complex **9c** as yellow crystals (0.47 g, 90%): mp >155 °C dec; IR ν_{max} (CH_2Cl_2) 2021, 1960 cm^{-1}; ^1H NMR δ 7.07 (2 H, d, J = 7.92 Hz, Ar H), 6.83 (2 H, d, J = 7.92 Hz, Ar H), 6.07 (2 H, m, 2-H and 3-H), 3.78 (5 H, s, Cp), 4.94 (1 H, m, 1-H), 4.58 (1 H, br d, J = 9.38 Hz, 4-H), 3.75 (3 H, s, OMe), 3.31 (1 H, dd, J = 9.95 Hz, J = 4.69 Hz, endo 5-H), 2.75 (1 H, m, endo 7-H), 2.31 (1 H, m, endo 6-H), 1.55 (1 H, m, exo 7-H), 1.26 (1 H, m, exo 6-H). Anal. Calcd for $C_{21}H_{21}O_3PF_6Mo$: C, 44.77; H, 3.73. Found: C, 44.64; H, 3.78.

$Cp(CO)_2Mo[\eta^3\text{-}C_7H_9\text{-}4\text{-}CH(CO_2Me)_2\text{-}7\text{-}C_6H_4OMe]$ (10n). To a stirred solution of $NaCH(CO_2Me)_2$ in THF (5 mL) was added the diene complex **9c** (0.05 g, 0.088 mmol). After 30 min the reaction was worked up as usual to yield a yellow oily product (0.046 g, 95%). The crude product was purified by chromatography (silica gel/CH_2Cl_2) to afford a yellow crystalline complex (**10n**) (single regioisomer): mp 58–59 °C; IR ν_{max} 1950, 1868, 1738 cm^{-1}; ^1H NMR δ 7.37 (2 H, d, J = 8.59 Hz, Ar H), 6.88 (2 H, d, J = 8.59 Hz, Ar H), 5.28 (5 H, s, Cp), 3.91 (3 H, m, 1-H, 2-H, and 3-H), 3.80 (6 H, s, CO_2Me and OMe), 3.70 (3 H, s, CO_2Me), 3.60 (1 H, d, J = 7.48 Hz, malonate methine), 3.45 (1 H, m, endo 7-H), 2.97 (1 H, m, endo 4-H), 1.27 (2 H, m, endo 5-H and 6-H), 1.10 (1 H, m, exo 5-H), 0.83 (1 H, m, 6-H). Anal. Calcd for $C_{26}H_{28}O_7Mo$: C, 56.94; H, 5.11. Found: C, 56.92; H, 5.10.

$Cp(CO)_2(\eta^3\text{-}C_7H_9\text{-}4\text{-}CH_3\text{-}7\text{-}C_6H_4OMe)$ (10m). A solution of MeMgBr (0.13 g, 0.44 mmol) was added to a stirred suspension of the diene complex **9c** (0.05 g, 0.088 mmol) in CH_2Cl_2 (3 mL) at room temperature. The reaction mixture was stirred for 30 min and worked up in the usual manner to afford a yellow oily product (0.036 g, 95%). Purification was carried out by chromatography (silica gel/30% EtOAc in hexane) to yield pure **10m**. When THF was used as a solvent for this reaction the product was always contaminated with products from reductive coupling which could not be removed: IR ν_{max} 1945, 1860 cm^{-1}; ^1H NMR δ 7.37 (2 H, d, J = 8.60 Hz, Ar H), 6.88 (2 H, d, J = 8.60 Hz, Ar H), 5.26 (5 H, s, Cp), 3.94 (3 H, m, 1-H, 2-H, and 3-H), 3.81 (3 H, s, OMe), 3.60 (1 H, m, endo 7-H), 2.36 (2 H, m, endo 4-H and endo 5-H), 1.38 (1 H, m, partially obscured, 6-H), 1.25 (3 H, d, J = 6.95 Hz, CH_3), 1.04 (1 H, m, exo 5-H), 0.77 (1 H, m, 6-H); HRMS, *m/e* (relative intensity) 434 (3.20), 432 (2.24), 431 (1.98), 428 (1.51) [M]; M^+ calcd for ^{98}Mo in $C_{22}H_{24}O_3Mo$ 434.0783, found 434.0777.

Reaction of the methyl substituted diene complex **9a** with (*p*-methoxyphenyl)magnesium bromide afforded approximately 5:1 mixture of **10c** (same as **10m**) and **11c** (Cp ^1H NMR resonance for **11c** at δ 5.28).

Decomplexation Experiments. The general procedure is as follows. The course of each reaction was followed by infrared spectroscopy. The acid complex (0.3 mmol) was stirred in CH_3CN (10 mL) at room temperature, while I_2 (0.148 g, 1.2 mmol) was added in one portion. After being stirred 40 min, the reaction mixture was poured into H_2O (50 mL) and extracted with ether (2 × 30 mL). The combined extracts were washed with aqueous sodium thiosulfate solution (2 × 20 mL) and then with H_2O (2 × 10 mL), dried ($MgSO_4$), and evaporated to give crude product. The crude product was purified by preparative TLC (silica gel/40% EtOAc in hexane).

Lactonization of Monoacid Complex 8i. Treatment of the monoacid complex **8i** (0.10 g, 0.27 mmol) with I_2 (0.10 g, 0.81 mmol) was carried out as described above to afford lactone **15a** (0.03 g, 85%). The compound was purified by preparative TLC (silica gel/40% EtOAc in hexane): IR ν_{max} 1790 cm^{-1}; ^1H NMR δ 5.67 (1 H, dtd, J_d = 12 Hz, J_t = 5.7 Hz, J_d = 1.97, 3-H), 5.59 (1 H, dt, J_d = 12 Hz, J_t = 2.09 Hz, 2-H), 5.33 (1 H, dm, J_d = 11.72 Hz, 1-H), 2.71 (2 H, m, 8-H and 7-H), 2.23 (3 H, m, 8-H, 4-CH_2), 1.65 (4 H, m); HRMS, M^+ calcd for $C_9H_{12}O_2$ M = 152.0843, found M = 152.0836.

Lactonization of Monoacid Complex 10h with $NOPF_6$. To a stirred solution of the monoacid complex **10h** (0.02 g, 0.065 mmol) in CH_3CN (5 mL) at 0 °C was added $NOPF_6$ (0.017 g, 0.097 mmol) in one portion. The resultant mixture was stirred for 20 min, after which Et_3N (0.015 mL, 0.097 mmol, 1.5 equiv) was added dropwise and the reaction was stirred for a further 15 min. The mixture was poured into H_2O (20 mL) and the product extracted with ether (2 × 15 mL). The ether extracts were washed with aqueous NaCl (10 mL), 10% aqueous HCl (10 mL), and H_2O (2 × 10 mL), dried ($MgSO_4$), and evaporated to yield an oil (0.0097 g, 90%). The crude product was purified by preparative TLC (silica gel/40% EtOAc in hexane) to afford a single lactone **15b**. When this reaction was carried out with I_2, appreciable impurities always contaminated the product which could not be purified: IR ν_{max} 1785 cm^{-1}; ^1H NMR δ 5.58 (1 H, m, 3-H), 5.45 (1 H, m, 2-H), 5.36 (1 H, m, 1-H), 2.70 (1 H, dd, J_{gem} = 16.71 Hz, $J_{8,7}$ = 9.05 Hz, 8-H), 2.7 (1 H, m, 4-H), 2.38 (1 H, m, 7-H), 2.23 (1 H, dd, J_{gem} = 16.71 Hz, $J_{8,7}$ = 4.28 Hz, 8-H), 1.71 (2 H, m), 1.59 (1 H, m), 1.29 (1 H, m), 1.05 (3 H, d, J = 6.83 Hz, CH_3); HRMS, M^+ calcd for $C_{10}H_{14}O_2$ M = 166.1005, found M = 166.0991.

Lactonization of Monoacid Complex 10l with $NOPF_6$. Treatment of the monoacid **10l** (0.025 g, 0.06 mmol) with $NOPF_6$ (0.016 g, 0.09 mmol) and Et_3N (0.015 g, 0.09 mmol) as described above afforded lactone **15c**. The pure lactone (0.011 g, 98%) was obtained as a colorless oil after purification by preparative TLC: IR ν_{max} 1785 cm^{-1}; ^1H NMR δ 5.75 (1 H, m, vinyl), 5.62 (1 H, m, 3-H), 5.50 (1 H, m, 2-H), 5.36 (1 H, dd, J = 7.40, 1.92 Hz, 1-H), 5.04 (1 H, d, J = 16.33 Hz, vinyl), 5.03 (1 H, d, J = 10.75 Hz vinyl), 2.78 (1 H, dd, J_{gem} = 16.77 Hz, $J_{8,7}$ = 9.17 Hz, 8-H), 2.64 (1 H, m, 4-H), 2.33 (1 H, m, 7-H), 2.21 (1 H, dd, J_{gem} = 16.77 Hz, $J_{8,7}$ = 4.53 Hz, 8-H), 2.12 (2 H, t, J = 6.92 Hz, allyl CH_2), 1.72 (2 H, m), 1.58 (1 H, m), 1.32 (1 H, m); HRMS, M^+ calcd for $C_{12}H_{16}O_2$ M = 192.1157, found M = 192.1149.

Demetalation of Complex 10m with I_2. To a stirred solution of the complex **10m** (0.025 g, 0.057 mmol) in CH_3CN (2 mL) was added I_2 (0.017 g, 0.14 mmol) at 0 °C. The reaction mixture was stirred for 30 min, followed by workup as usual to afford the crude iodide **16** (0.016 g, 90%). Attempted chromatographic purification led to decomposition: ^1H NMR (C_6D_6) [on crude product] δ 6.98 (2 H, d, J = 8.68 Hz, Ar H), 6.78 (2 H, d, J = 8.68 Hz, Ar H), 5.69 (2 H, m, vinyl), 4.56 (1 H, dd, J = 8.68, 7.16 Hz, CHI), 3.71 (1 H, br d, J = 10.63 Hz, benzylic CH), 3.33 (3 H, s, OCH_3), 2.55 (1 H, m), 2.15 (1 H, m), 1.87 (1 H, m), 1.65 (1 H, m), 1.41 (2 H, m), 1.23 (3 H, d, J = 6.96 Hz, CH_3).

Reaction of Iodide 16 with PhSH. To a stirred solution of iodide **16** (0.029 g, 0.064 mmol) in benzene (3 mL) at 0 °C was added NEt_3 (0.015 mL, 1.5 equiv) dropwise. The resultant mixture was stirred for 15 min, after which C_6H_5SH (0.008 mL, 1.2 eq) was added and stirred for 1 h at 0 °C. The reaction was worked up as usual to afford **17a** (0.018 g, 90%) as an oil. The compound was purified by preparative TLC (silica gel/30% EtOAc in hexane) afforded the pure compound as a colorless oil (0.014 g, 70%): ^1H NMR δ 7.47 (2 H, m, Ar H), 7.30 (3 H, m, Ar H), 7.07 (2 H, d, J = 8.3 Hz, Ar H), 6.82 (2 H, d, J = 8.38 Hz, Ar H), 5.81 (2 H, m, 2-H and 3-H), 3.78 (3 H, s, OMe), 3.70 (1 H, t, J = 6.29 Hz, 4-H), 3.53 (1 H, br d, J = 11.72 Hz, 1-H), 2.26 (1 H, m, 5-H), 2.13 (1 H, m, endo 7-H), 1.93 (1 H, m, endo 6-H), 1.80 (1 H, m, exo 7-H), 1.65 (1 H, m, exo 6-H), 1.13 (3 H, d, J = 6.89 Hz, CH_3).

Reaction of Iodide 16 with PhSeNa. To a stirred solution of PhSeNa in EtOH [prepared in situ from the reaction of PhSeSePh and $NaBH_4$ in EtOH] under inert atmosphere was added the iodide **16** (0.01 g, 0.03 mmol). The mixture was stirred for 1 h, poured into H_2O (10 mL), and extracted with ether (2 × 15 mL), and the extracts were washed with 10% aqueous HCl (5 mL) and H_2O (2 × 10 mL), dried ($MgSO_4$), and evaporated to yield a crude product **17b** heavily contaminated with PhSeSePh. Purification was not possible, and the crude product was used directly for the next reaction: ^1H NMR δ 7.50 (2 H, m, Ar H), 7.34 (3 H, m, Ar H), 7.1 (2 H, d, J = 8.35 Hz, Ar H), 6.85 (2 H, d, J = 8.38 Hz, Ar H), 5.83 (2 H, m, 2-H and 3-H), 3.80 (3 H, s, OMe), 3.55 (2 H, m, 1-H and 4-H), 2.30 (2 H, m, 5-H and 7-H), 1.95 (2 H, m, 6-H and 7-H), 1.65 (1 H, m, 6-H), 1.15 (3 H, d, J = 6.90 Hz, CH_3).

Conversion of Phenyl Selenide 17b to Alcohol 18. The crude product **17b** from above was stirred in THF (2 mL) while a large excess of 30% H_2O_2 (1 mL) was added. The reaction mixture was stirred for 1 h at 0 °C, and then a large excess of Et_3N was added. The mixture was allowed to reach room temperature over a period of 15 min and worked up as usual to afford the alcohol as an oil, which was purified by preparative TLC (silica gel/30% EtOAc in hexane) afforded pure alcohol **18** (0.04 g, 90%): IR ν_{max} ($CHCl_3$) 3600, 3520 cm^{-1} (OH); ^1H NMR δ 7.18 (2 H, d, J = 8.63 Hz, Ar H), 6.89 (2 H, d, J = 8.63 Hz, Ar H), 5.66 (2 H, m, vinyl), 4.49 (1 H, br d, J = 10.31 Hz, C*H*OH), 3.81 (3 H, s, OCH_3), 2.83 (1 H, td, J_t = 10.3 Hz, J_d = 4.2 Hz, benzylic CH), 2.49 (1 H, m, 4-H), 1.90 (2 H, m), 1.68 (2 H, m), 1.55 (1 H, s, OH), 1.07 (3 H, d, J = 7.22 Hz, CH_3); HRMS, M^+ calcd for $C_{15}H_{20}O_2$ M = 232.1467, found M = 232.1462.

Oxidation of Alcohol 18 to Enone 19 with Pyridinium Chlorochromate. To a stirred solution of the alcohol **18** (0.0052 g, 0.024 mmol) in CH_2Cl_2 (1 mL) was added PCC ($C_5H_5NHCrO_3Cl$) (0.0103 g, 0.048 mmol). The resultant mixture was stirred for 2 h in the dark at room temperature, then diluted with ether (10 mL), and filtered through Florisil. The filtrate was washed with H_2O (2 × 5 mL), dried ($MgSO_4$), and evaporated to afford enone **19** (0.005 g, 98%). The crude product was purified by preparative TLC (silica gel/30% EtOAc in hexane) to yield a pure solid enone **19** (0.004 g, 78.4%) when dried in high vacuum: mp 59–60 °C; IR ν_{max} 1685, 1610 cm^{-1}; ^1H NMR (C_6D_6) δ 7.13 (2 H, d, J = 8.76 Hz, Ar H), 6.84 (2 H, d, J = 8.76 Hz, Ar H), 6.02 (1 H, dd, J = 11.92, 2.71 Hz, 3-H), 5.81 (1 H, dd, J = 11.92, 3.12 Hz, 2-H), 3.64 (1 H, dd, J = 10.44, 5.88 Hz, 7-H), 3.34 (3 H, s, OMe), 2.07 (1 H, m, 4-H), 1.74 (2 H, m), 1.34 (2 H, m), 0.75 (3 H, d, J = 7.33 Hz, CH_3). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.82. Found C, 78.34; H, 7.80.

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Structures and Energies of the Tricyclo[4.1.0.0^{1,3}]heptanes and the Tetracyclo[4.2.1.0^{2,9}0^{5,9}]nonanes. Extended Group Equivalents for Converting ab Initio Energies to Heats of Formation

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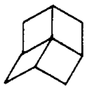
The structures of the two isomeric tricyclo[4.1.0.0^{1,3}]heptanes have been calculated by using the 3-21G basis set. The cis isomer was found to be 46 kcal/mol less stable than the known trans isomer. The calculated structures are compared with that obtained from an electron diffraction study. The modes of deformation of spiropentane were examined, and bending was found to be energetically more favorable than twisting. The structures and relative energies of three of the five isomeric tetracyclo[4.2.1.0.^{2,9}0.^{5,9}]nonanes also have been calculated. Group equivalents have been derived that permit the conversion of calculated total energies to heats of formation with reasonable accuracy, and the effect of basis set on both calculated energies and structures are examined. Equivalents for oxygen-containing groups also have been obtained.

The question of how far carbon may be deformed toward planarity[1] has led to considerable interest in tetracyclo[5.1.1.0^{3,8}0.^{5,8}]nonane (**1**),[2-4] otherwise known as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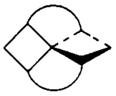
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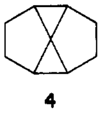
"fenestrane"[2] or "windowpane".[3] One way in which to think about **1** is to consider it as formed from spiro[3.3]heptane (**2**) by the introduction of rings **3** that will try to force the two four-membered rings into planarity. From this viewpoint, tetracyclo[4.2.1.0.^{2,9}0.^{5,9}]nonane (**4**) also is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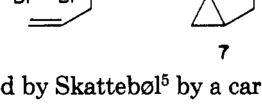
of interest. Again, starting with spiropentane (**5**), introduction of bridges **6** would tend to twist the two three-membered rings into planarity. A related compound, **7**,



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has been prepared by Skattebøl[5] by a carbene ring closure:

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