by gas chromatography. After 13 h, the nickel was filtered off, and 750 μL of trifluoroacetic acid was added. The solution was evaporated to provide the trifluoroacetate ammonium salt as a white solid. The salt was dissolved in 5.0 mL of H_2O, brought to pH 10 with 5% aqueous NaOH, and extracted 3 times with 1.0 mL of toluene-d_8. The combined toluene-d_8 layers were combined and distilled to provide approximately 2.5 mL of a toluene-d_8 solution of [^{15}N]diisopropylamine. GC analysis using comparison with standardized solutions indicated a molarity of 1.39. Aliquots of solution were stored in sealed ampoules: ^{1}H NMR (200 MHz, toluene-d_8) δ 2.98 (1 H, septuplet, J = 6.2 Hz), 1.16 (6 H, dd, J_{NH} = 2.2 Hz, J_{HH} = 6.2 Hz), 1.14 (1 H, dd, J_{NH} = 3.2 Hz, J_{HH} = 6.2); ^{13}C NMR (100.58 MHz, toluene-d_8) δ 45.8 (J_{NC} = 3.9 Hz), 24.09.

Kinetics. Kinetics were run in a 50-mL, round-bottomed flask fitted with a T-joint providing access to the vacuum line and FT-IR spectrometer. The lithiation rate was monitored by using a flow system involving the following: (1) a 1.05-m length of 0.8-mm i.d. intramedic tubing leading from the reaction vessel to an FMI model RP-SY fluid pump, (2) a 0.76-m length of tubing leading from the pump to a standard solution NaCl IR cell of pathlength of 0.20 mm, and (3) a 1.05-m length of tubing leading from the cell back to the reaction vessel. The total volume of the flow system and cell external to the reaction vessel is 1.8 mL. With the pump set at 1.6 mL/min, the vessel-to-vessel turnover time is 67 s. Since the difference between the bath temperature (20.0 ± 0.3 °C) and room temperature (22-24 °C) was small and the percentage of the reaction contents external to the controlled temperature bath was also minor, the temperature fluctuations did not cause serious problems.

A typical kinetic run was effected as follows. An oven-dried, 50-mL, round-bottomed flask equipped with a T-joint is charged with LDA (321 mg, 3.00 mmol) in a glovebox. The flask is removed from the glovebox, evacuated on a vacuum line, and placed under argon. To the vessel at 0 °C is added freshly dried hexane (5.0 mL) and tetrahydrofuran (18.0 mL) via gas tight syringes. After 1 min, the flask is placed in a thermostatted bath at 20.0 ± 0.3 °C and thermally equilibrated for 5 min. The LDA solution is then pumped through the flow system for an additional 5 min. After recording a background IR spectrum (16 scans, 45-s acquisition), a stock solution of **2** in THF (90 μL, 0.875 mmol) is added to the reaction flask. The course of the reaction is monitored periodically until the reaction exceeds 95% conversion as shown by the growth in the intensity of mixed-aggregate absorbance at 1600 cm^{-1} (cf. Figure 2).

Rate Constants and Statistics. All rate constants were calculated by using first-order treatments and nonweighted, nonlinear least-squares fits on data measured to ≥5 half-lives. The reported errors correspond to one standard deviation. The numerical fits were carried out with the LTP-LOT statistical package developed in the Materials Sciences Center at Cornell University.

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Construction of Quaternary Carbon Centers Using Organomolybdenum Chemistry

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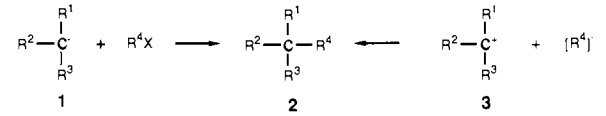
Abstract: Two approaches are described for the construction of quaternary carbon centers using organomolybdenum complexes. The first involves carbon nucleophile addition to the methylated diene terminus of dicarbonyl(η^5-indenyl)(1-4-η-1,4-dimethylcyclohexa-1,3-diene)molybdenum tetrafluoroborate (**12**). A wide range of nucleophiles add successfully to **12** giving *gem*-disubstituted cyclohexenylmolybdenum complexes. This methodology, coupled with a lactonization/decomplexation reaction, has led to a short synthesis of 2-(2-hydroxy-1,4-dimethylcyclohex-3-enyl)propionic acid lactone (**14**), which has previously been employed as a key intermediate for trichothecene synthesis. The second method involves alkylation of cyano-stabilized carbanions generated from dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-cyanocyclohexenyl)molybdenum and dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-cyanocycloheptenyl)molybdenum. While a rather limited range of electrophiles could be used in this coupling reaction, it was found that stereochemical control is excellent and allows the construction of quaternary carbon centers with defined stereochemistry relative to other substituents on the cyclohexenyl or cycloheptenyl ligand. During the course of this study it was found that treatment of the exo-cyano-substituted π-allylmolybdenum complexes with butyllithium led to a novel decyanation reaction. This allowed the generation of nonstabilized carbanion species that could be alkylated regio- and stereospecifically.

A quaternary carbon center, i.e., a molecular substructure consisting of a carbon atom bound to four other carbon atoms, is a feature of a broad range of natural products and therefore constitutes an important target in the context of general synthetic methodology. A review by Martin[1] outlines earlier work in this area and gives an overview of the types of natural products that are of general interest. More recently, Meyers' group reported methodology for the asymmetric construction of quaternary carbon centers.[2]

Using polar reactions there are two basic ways in which such centers can be introduced into an already existing molecule: (1) addition of an electrophilic alkylating agent to a trisubstituted carbanion, e.g., **1** gives **2**; (2) addition of a nucleophilic alkylating



1 2 3

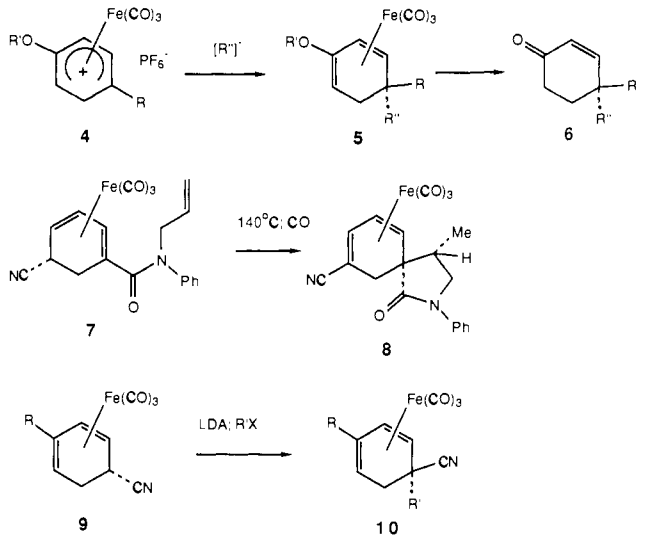
agent to a tertiary carbocation or its equivalent (e.g., a tertiary alkyl halide), as in the conversion of **3** to **2**. A combination of (1) and (2) would lead to the formation of two juxtaposed quaternary carbon centers. An example of approach 1 would be the alkylation of a substituted enolate, while the Lewis acid catalyzed alkylation of a silyl enol ether with a tertiary alkyl halide provides an example of (2). Other approaches involve rearrangement

(1) Martin, S. F. *Tetrahedron* **1980**, *36*, 419.
(2) Meyers, A. I.; Lefker, B. A. *J. Org. Chem.* **1986**, *51*, 1541.

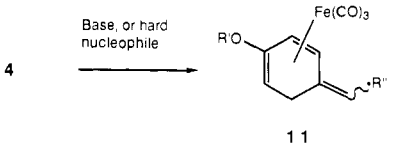
0002-7863/89/1511-6778$01.50/0

reactions, cycloaddition reactions, and oxidative or reductive coupling reactions. All of these methods are discussed in the review by Martin.[1]

Our own interest in this area has previously centered around the use of organoiron complexes. Addition of carbon nucleophiles to cyclohexadienyliron complexes[3] of type **4** generally occurs with good regiocontrol to give diene complexes **5**, which may be converted to cyclohexenone derivatives **6**. Thus, the dienyliron complex acts as a tertiary carbocation that carries (masked) enone functionality, and this has been found useful for the synthesis of a variety of natural products.[4] More recently, we have discovered a nonpolar intramolecular coupling reaction, exemplified by the conversion of **7** to **8**, that allows generation of quaternary carbon centers,[5] while Birch and co-workers[6] have shown that alkylation of cyano-substituted cyclohexadiene–$Fe(CO)_3$ complexes, e.g., **9**, can be accomplished via their carbanions.



Despite the already successful applications of some of the above technology in synthesis, there do exist limitations on these methods. For example, the range of nucleophiles that react successfully with complexes of type **4** is somewhat limited; while "soft" carbanions lead to adducts **5**, the use of harder nucleophiles, such as simple lithium enolates or Grignard reagents, results in deprotonation of **4** to give complexes of type **11**. Alkylations of complexes **9**



lead ultimately to organic products that are either cyclohexadienes or cyclohexenones. With these limitations in mind, we have investigated a series of ionic bond forming reactions using diene- and π-allylmolybdenum complexes, in anticipation that the different metal moiety might allow the development of methodology complementary to that using the organoiron systems. This paper summarizes our initial findings in the area.[7-9]

Scheme I

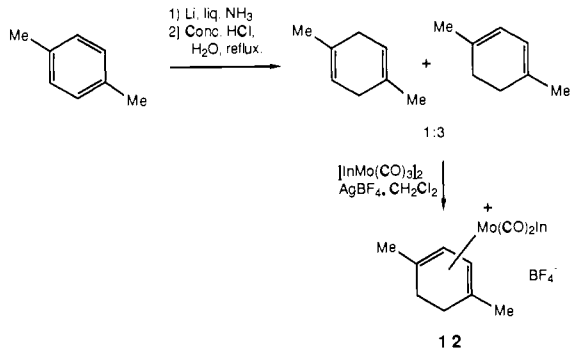
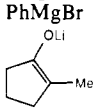


Table I. Addition of Carbon Nucleophiles to Complex **12**

nucleophile	product	yield, %
NaCN	**13a**	85
$NaCH(CO_2Me)_2$	**13b**	91
$NaCH(SO_2Ph)CO_2Me$	**13c**	87[a]
$NaCMe(SO_2Ph)CO_2Me$	**13d**	81[a]
MeMgBr	**13e**	92
Me_2CuLi	**13e**	35
$CH_2{=}CHCH_2MgBr$	**13f**	90
$CH_2{=}CHMgBr$	**13g**	37
PhMgBr	**13h**	30
	**13i**	83[b]
$CH_2{=}C(OMe)OLi$	**13j**	81
$MeCH{=}C(OMe)OLi$	**13k**	89[c]

[a] Obtained as a 3:2 mixture of diastereomers. [b] Obtained as a 2:1 mixture of diastereomers. [c] Obtained as a 4:3 mixture of diastereomers.

Results and Discussion

(1) Formation of Quaternary Carbon Centers by Nucleophile Addition to Cationic Diene–Molybdenum Complexes. In order to test the potential utility of cyclohexadiene–molybdenum complexes for generating quaternary carbon centers, the symmetrical 1,4-dimethylcyclohexadiene derivative **12** was chosen. This avoids problems of regioselectivity and allows an assessment of the types of carbon nucleophile that can be used. Green[10] has described methods for the direct complexation of 1,3-dienes to give diene–$Mo(CO)_2In$ cations (In = η^5-indenyl) and this approach was followed, as outlined in Scheme I. The requisite 1,4-dimethylcyclohexa-1,3-diene was obtained as a 3:1 mixture with 1,4-dimethylcyclohexa-1,4-diene via Birch reduction of *p*-xylene and acid-catalyzed conjugation.[11] While the mixture of dienes can be separated by chromatography on silica gel impregnated with silver nitrate, this is unnecessary since only the 1,3-diene is converted to complex **12**, which is isolated by precipitation with ether.

Table I lists the carbon nucleophiles that were examined in reaction with **12** and yields of alkylation product, i.e., π-allyl–$Mo(CO)_2In$ complexes **13**.

Of particular interest is the observation that **12** reacts satisfactorily with Grignard reagents, although in the case of vinyl and phenyl Grignard reagents, the yields were rather low. Reactive

(3) Reviews: Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, Chapter 58.

(4) Pearson, A. J.; Rees, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 1118; *J. Chem. Soc., Perkin Trans. 1* **1982**, 2467. Pearson, A. J.; Rees, D. C.; Thornber, C. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 619. Pearson, A. J.; Ham, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1421. Pearson, A. J.; Richards, I. C.; Gardner, D. V. *J. Org. Chem.* **1984**, *49*, 3887. Pearson, A. J.; Chen, Y. S. *J. Org. Chem.* **1986**, *51*, 1939. O'Brien, M. K.; Pearson, A. J.; Pinkerton, A. A.; Schmidt, W.; Willman, K. *J. Am. Chem. Soc.* **1989**, *111*, 1499.

(5) Pearson, A. J.; Zettler, M. W.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1987**, 264. Pearson, A. J.; Zettler, M. W. *J. Chem. Soc., Chem. Commun.* **1987**, 1233. Pearson, A. J.; Zettler, M. W. *J. Am. Chem. Soc.* **1989**, *111*, 3908.

(6) Birch, A. J.; Kelly, L. F. *J. Org. Chem.* **1985**, *50*, 712.

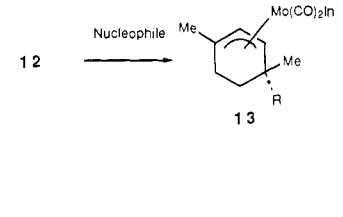
(7) Taken from: Khetani, V. D. Ph.D. Dissertation, Case Western Reserve University, 1989.

(8) Preliminary communications: Pearson, A. J.; Khetani, V. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1772; *J. Org. Chem.* **1988**, *53*, 3395.

(9) For some applications of π-allyl–molybdenum and –tungsten complexes in quaternary center construction, see: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 7757.

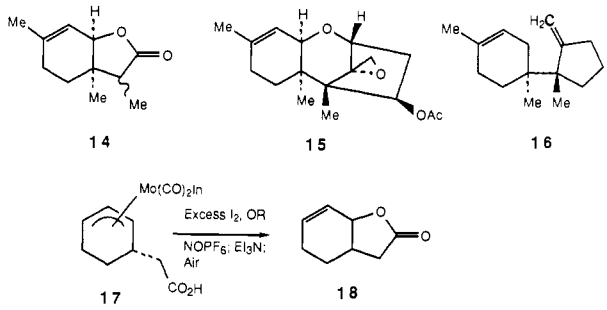
(10) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365. Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18. King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 475.

(11) Brady, W. T.; Norton, S. J.; Ko, J. *Synthesis* **1985**, 704.

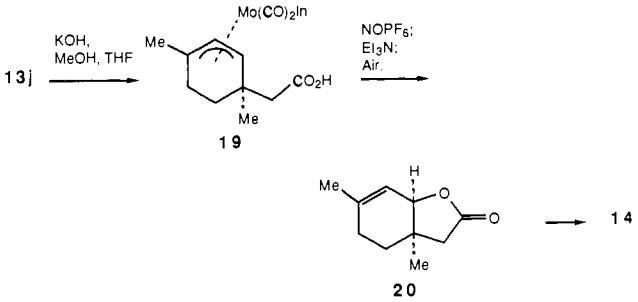


lithium enolates give uniformly high yields of **13**. Both sets of results are in sharp contrast to the behavior of iron complexes **4**, which give only the deprotonation products **11** in these reactions.[12] In order to illustrate the potential of this methodology for organic synthesis, we examined further transformations of complexes **13j** and **13k**.

The lactone **14** has been employed as an intermediate for the total synthesis of (±)-trichodermin[13] (**15**) and of (±)-trichodiene[14] (**16**). We previously reported[15] that π-allyl-$Mo(CO)_2Cp$ complexes such as **17** may be decomplexed by a regiocontrolled lactonization process to give **18**. Application of such a procedure to carboxylic acids derived from **13j** and **13k** could provide these lactones efficiently.



Hydrolysis of the methyl ester **13j** proceeded smoothly but slowly, using KOH in MeOH/THF at room temperature, to give **19**. On the other hand **13k**, which is sterically more hindered, was completely resistant to hydrolysis under these conditions, even after 18 days of reaction. The use of elevated temperature resulted in considerable decomposition of the complex. While the carboxylic acid **19** could be converted to **20** by treatment with $NOPF_6/Et_3N$, and this can be converted to **14** by methylation (LDA; MeI),[13] we considered that a more direct route to **14** would better serve the purpose of demonstrating the synthetic utility of complex **12**.



Accordingly, **12** was treated with the lithium enolate of trimethylsilyl propionate, followed by acidic workup (10% aqueous HCl), to give directly the carboxylic acid **21** in 93% yield. Treatment of this with $NOPF_6/Et_3N$, followed by exposure of the reaction mixture to air, afforded lactone **14** in 87% yield. This

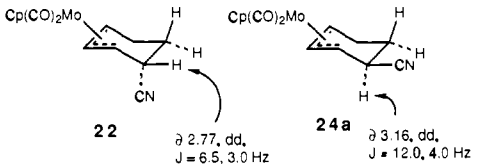
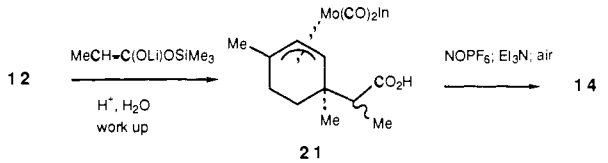


Figure 1. Conformations of complexes **22** and **24a**, showing diagnostic NMR data.

synthesis of **14** requires only five synthetic operations from *p*-xylene and is the shortest route so far reported.

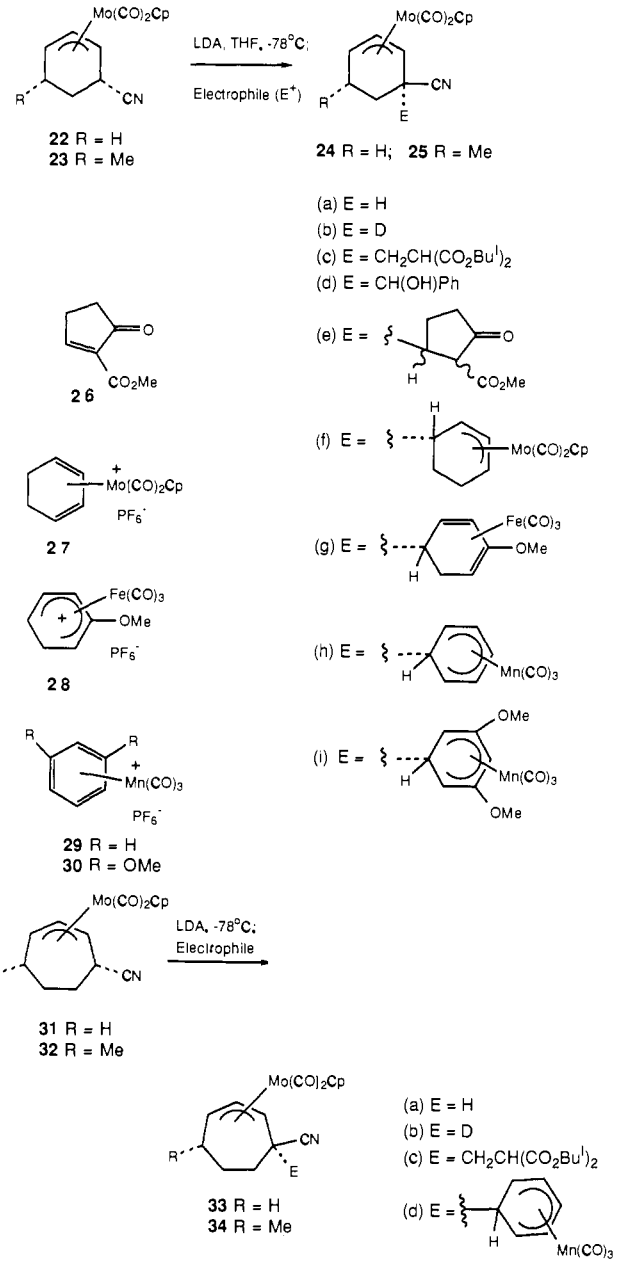


(2) Formation of Quaternary Carbon Centers Using Organomolybdenum-Substituted Carbanions. This option is expected to provide a complementary set of C–C bond forming reactions, since the placement of functionality in the moiety to be attached to the organomolybdenum complex is usually different compared with nucleophiles discussed above. The cyano functionality was chosen as a carbanion-stabilizing group, and the six- and seven-membered-ring π-allylmolybdenum complexes **22**, **23**, **31**, and **32** were readily prepared by cyanide addition to the corresponding diene complexes.[15,16] Each complex was treated with lithium diisopropylamide (LDA) in tetrahydrofuran at −78 °C to effect deprotonation, giving a burgundy-colored solution. The stereochemistry of electrophile addition was established by quenching the anions with water, giving products of inversion at the cyano-substituted carbon, i.e., **24a**, **25a**, **33a**, and **34a**, respectively. ^1H NMR spectroscopy was especially useful in assigning stereochemistry to the cyclohexenyl derivatives. X-ray crystallographic studies[15-17] have established that these complexes have a chairlike structure, and the typical axial/equatorial relationships between protons are evident in their NMR spectra. Figure 1 shows this for complexes **22** and **24a** and summarizes the relevant NMR data for H-4, from which the conclusions are obvious. Use of D_2O as electrophile gave complexes **24b**, **25b**, **33b**, and **34b**, which showed the expected loss of NMR signal for the proton α to the cyano group.

A range of electrophiles was examined in reaction with the anion from **22**, while a narrower range was used for **23**, **31**, and **32**. These are summarized in Table II, together with yields. Reactive Michael acceptors gave good results, as did benzaldehyde. Organometallic electrophiles **27**, **28**, **29**, and **30** all reacted with the carbanion, but **28** gave disappointing yields. The arene-$Mn(CO)_3$ cations **29** and **30** were examined with a view to converting the dienyl-$Mn(CO)_3$ adducts to aromatic derivatives.[18] However, all attempts to oxidatively demetalate complexes **24h**, **24i**, or **33d**, using a variety of known methods[19] (DDQ, NBS, buffered ceric ammonium nitrate), resulted only in oxidative cleavage of the interconnecting C–C bond to generate the cyclohexadiene-Mo-$(CO)_2Cp$ cation **27** (or the corresponding cycloheptadiene complex) and **29** or **30**.

Several potential electrophiles failed to react with the organomolybdenum carbanions under conditions where the anions were stable. Among these were methyl iodide, methyl triflate, allyl bromide, acetyl chloride, acid anhydrides, epoxides, and fluorobenzene-chromium tricarbonyl. We attribute this partly to the lower reactivity of the anion, which might be due to a stabilization from the neighboring π-allyl-$Mo(CO)_2Cp$ unit (see later). At-

(12) For the use of tin enolates to overcome this problem, see: Pearson, A. J.; O'Brien, M. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1445.
(13) Colvin, E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1989.
(14) Welch, S. C.; Rao, A. S. C. P.; Gibbs, C. G.; Wong, R. Y. *J. Org. Chem.* **1980**, *45*, 4077.
(15) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.
(16) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400, and references cited therein.
(17) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.
(18) Walker, P. J. C.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 622.
(19) Pearson, A. J.; Richards, I. C. *J. Organomet. Chem.* **1983**, *258*, C41. Lee, S.-H., unpublished results, this laboratory.



tempts to effect alkylation at temperatures higher than −40 °C resulted in decomposition of the complex.

In addition to the electrophiles shown in Table II, we examined Rosenblum's vinyl ether–Fp complex[20] **34** as a means of introducing a vinyl substituent onto the quaternary carbon center. The overall conversion worked extremely well, as shown in Scheme II, and allowed access to complexes **39** and **40** in good overall yield (see Experimental Section).

In summary this methodology allows the construction of quaternary carbon centers, although the range of electrophiles that can be used is rather limited. The most meritorious aspect of this approach is that the $Mo(CO)_2Cp$ group controls the stereochemistry of C–C bond formation during the alkylation and during the nucleophile additions to diene–$Mo(CO)_2Cp$ complexes that were used to prepare, e.g., **23** and **32**. Consequently, the relative stereochemical relationship between the quaternary center and other substituents can be controlled very easily. While we have illustrated this only for methyl-substituted derivatives, we anticipate few problems in the use of other groups that can be attached via nucleophile addition to the diene–molybdenum precursor complex.

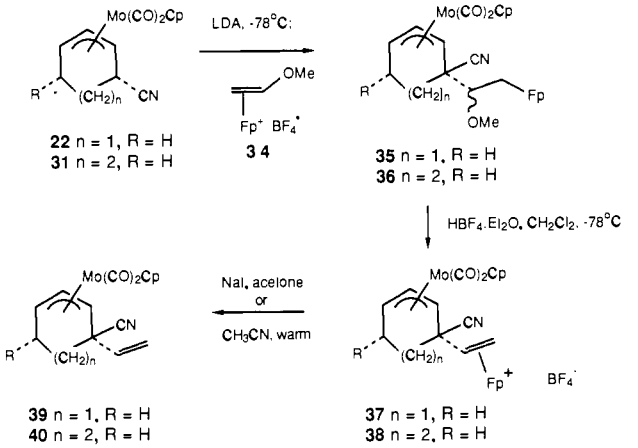
(20) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381.

Table II. Reactions of Cyano-Stabilized Organomolybdenum Carbanions with Electrophiles

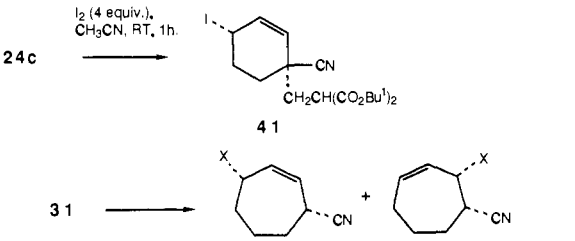
complex used to generate carbanion	electrophile	product	yield, %
22	$H_2O(D_2O)$	**24a (24b)**	96 (90)
22	$CH_2{=}C(CO_2Bu^t)_2$	**24c**	88
22	PhCHO	**24d**	78[a]
22	**26**	**24e**	70[b]
22	**27**	**24f**	86
22	**28**	**24g**	34
22	**29**	**24h**	74
22	**30**	**24i**	67
23	$H_2O(D_2O)$	**25a (25b)**	96 (90)
23	$CH_2{=}C(CO_2Bu^t)_2$	**25c**	85
31	$H_2O(D_2O)$	**33a (33b)**	90 (90)
31	$CH_2{=}C(CO_2Bu^t)_2$	**33c**	86
31	**29**	**33d**	62
32	H_2O (D_2O)	**34a (34b)**	80
32	$CH_2{=}C(CO_2Bu^t)_2$	**34c**	84

[a] Obtained as a 4:1 mixture of diastereomers. Best results were obtained with $BF_3{\cdot}OEt_2$. [b] Obtained as an ca. 8:10:9 mixture of diastereomers (fourth diastereomer not apparent in NMR spectrum).

Scheme II



In order for this chemistry to be useful in organic synthesis, it is necessary to effect clean demetalation of the π-allyl–$Mo(CO)_2Cp$ system. We have earlier described[15] lactonization methods as well as conversion of the complexes to allylic iodides. In the present case, treatment of complex **24c** with iodine gave the allylic iodide **41**, but this was very unstable, making it difficult

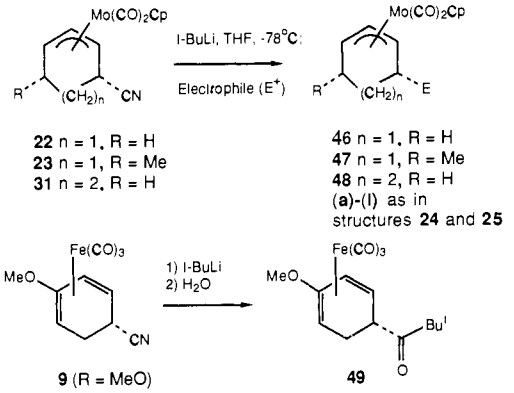


to purify and characterize. Alternative methods still need to be examined for decomplexation, but we note here that complex **31** is converted to a 5:1 mixture of bromides **42** and **43** using 1.0 equivalent of bromine in dichloromethane at low temperature. Competing bromination of the product was the major problem, which was serious when a slight excess of bromine was used. Faller[16] has shown that the π-allyl–$Mo(CO)_2Cp$ system may be activated toward nucleophilic attack by replacement of one CO ligand with NO^+. In the present study, sequential treatment of **31** with $NOPF_6$ and then water, gave the allylic alcohols **44** and **45** as a 5:1 mixture. While there still remain regiochemical

problems to be solved, this approach looks extremely promising, and remains an obvious area for future studies.

(3) Generation of Organomolybdenum Carbanion Species via a Novel Decyanation Reaction. During the course of the above studies we decided to examine the use of various alkyllithium bases to effect deprotonation of the cyano-substituted π-allyl-Mo$(CO)_2$Cp complexes. The main reason for this was that low yields of reaction product were observed during the reaction of the carbanions with dienyl-Fe$(CO)_3$ complexes such as **28**, which we felt might have been due to a competing reaction between diisopropylamine (from the LDA) and **28**, which is known to be very reactive toward secondary amine nucleophiles.[21] Even though no products from such a reaction were isolated, *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium were examined as bases, since these would give innocuous materials during the deprotonation.

Accordingly, complex **22** was treated with *n*-BuLi in THF at −78 °C, to produce a red color, typical of the desired carbanion species. However, quenching the reaction mixture with water produced the decyanated cyclohexenyl-Mo$(CO)_2$Cp complex **46a**, which was identical with an authentic sample.[15,16] When the reaction was quenched with D_2O, stereospecific incorporation of deuterium to give **46b** was observed, indicating that electrophilic attack on the intermediate carbanion (or organolithium species) occurs exclusively trans to the Mo$(CO)_2$Cp group. The stereochemistry of **46b** was readily established by comparing ^{1}H NMR data with that for **49a**, and using the complete assignments previously reported by Faller's group.[16] Thus, complex **46a** shows exo H-4 as a dddd at δ 2.03, while endo H-4 occurs as a dddd at δ 1.58. The spectrum of **46b** showed complete loss of the δ 2.03 resonance, and the signal at 1.58 (now ddd) showed the expected loss of geminal coupling (14.5 Hz). The decyanation of complexes **23** and **31** proceeded in an analogous fashion. Of particular note is the observation that protonation (deuteration) of the intermediate carbanion from **23** was both regio- and stereospecific, giving only **47a** (**47b**).



The decyanation reaction could be coupled with the addition of electrophiles to give complexes **46**, **47**, and **48**, as summarized in Table III (an extensive range was not studied for complex **23**, but we anticipate no problems with the use of carbon electrophiles). As before, attempts to alkylate the intermediate carbanion with, e.g., methyl iodide or allyl bromide failed. Attempts to effect a similar decyanation of complex **13a**, in the hope of ultimately generating quaternary carbon centers, also failed. The reactivity of the π-allyl-Mo$(CO)_2$Cp was shown to be very different from that of diene-Fe$(CO)_3$ complexes by the observation that complex **9** (*R* = MeO) gave exclusively the *tert*-butyl ketone derivative **49** on treatment with *t*-BuLi; no decyanation was observed.

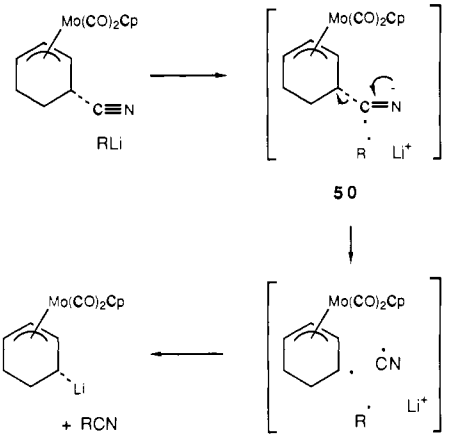
Treatment of the endo-cyano adduct **24a** with BuLi led only to deprotonation, as evidenced by the formation of **24b** on quenching the reaction mixture with D_2O. This implies that there must be an antiperiplanar relationship between the C–Mo bond

Table III. Decyanation Reactions of Complexes **22**, **23**, and **31**, Using *tert*-Butyllithium, and Addition of Electrophiles to Intermediate Carbanion

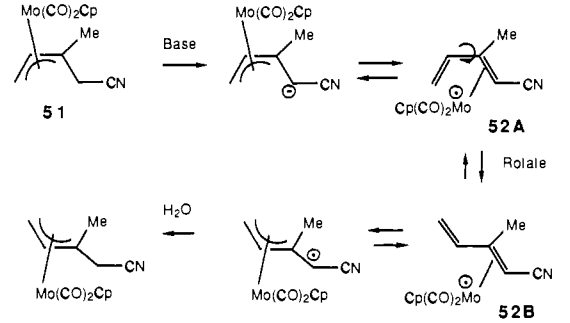
complex	electrophile	product	yield, %
22	$H_2O(D_2)$	**46a** (**46b**)	96 (84)
22	CH_2=$C(CO_2Bu^t)_2$	**46c**	86
22	PhCHO	**46d**	81[a]
22	**26**	**46e**	81[b]
22	**27**	**46f**	62
22	**28**	**46g**	64
22	**29**	**46h**	83
22	**30**	**46i**	73
23	$H_2O(D_2O)$	**47a** (**47b**)	97 (89)
31	$H_2O(D_2O)$	**48a** (**48b**)	86 (81)
31	CH_2=$C(CO_2Bu^t)_2$	**48c**	90
31	**27**	**48f**	54

[a] Obtained as a 6:5 mixture of diastereomers. [b] Obtained as a 9:5 mixture of two diastereomers.

Scheme III



Scheme IV



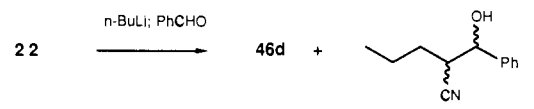
of the π-allyl-Mo$(CO)_2$Cp system and the C–CN bond, as is implied in Figure 1. An electron-transfer mechanism, shown in Scheme III, appears plausible for this reaction. The antiperiplanar arrangement is presumably required to give stabilization of the incipient carbanion, thereby lowering the activation energy for fragmentation of the radical anion intermediate **50**. It may be noted that all attempts to effect direct deprotonation of complex **46a** failed, so that the degree of stabilization of neighboring carbanion by the organomolybdenum group is very low, the fragmentation providing a lower activation barrier for this process. That the π-allyl-Mo$(CO)_2$Cp is capable of interacting with a neighboring carbanion is shown by the base-promoted rearrangement of complex **51** to give **53** (Scheme IV), which we have previously reported,[22] and which presumably involves an intermediate such as **52**, in which the negative charge is delocalized onto the metal, and in which rotation about the C–C single bond can occur. However, complete delocalization of the carbanion

(21) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882.

(22) Pearson, A. J.; Holden, M. S.; Simpson, R. *Tetrahedron Lett.* **1986**, *27*, 4121.

does not occur with the cyclic compounds, since the regiochemical integrity of the cyano-substituted complex is maintained throughout the reaction, as evidenced by the conversion of complex **23** to **47a** and **47b**. On these grounds we favor the intermediacy of an alkyllithium species rather than a free carbanion.

The mechanism outlined in Scheme III assumes that the radical pairs remain in a solvent cage sufficiently long that combination occurs to give RCN. While we did not attempt to isolate such products, we did observe indirect evidence for the formation of valeronitrile when *n*-BuLi was used as reductant. In this case, addition of benzaldehyde to the reaction mixture gave, in addition to the expected adduct **46d**, an equimolar amount of an organic byproduct that was characterized as **54**, which arises via deprotonation of the valeronitrile and subsequent condensation with benzaldehyde.



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No such byproduct was observed when *t*-BuLi was used, and so this was the reagent of choice for all other reactions. While an alternative mechanism, involving nucleophilic addition of RLi to the cyano group, followed by fragmentation of the anion, would also explain these results, it appears less likely for *t*-BuLi, which is a very hindered nucleophile. However, the conversion of **9** to **49** means that this cannot be ruled out (although such a conversion might also proceed via a single-electron-transfer mechanism[23]).

Conclusions

From this work, two approaches to the construction of quaternary carbon centers have emerged. The addition of nucleophiles to complexes of type **12** appears to be especially versatile with regard to the type of nucleophile that can be employed. However, the examples described in this paper use a symmetrical 1,4-disubstituted cyclohexadiene ligand, thus avoiding problems of regioselectivity. Very little work has been reported on methods for regiocontrol using unsymmetrically substituted complexes. From a practical point of view, this is a question that must be addressed in order to generate synthetic methodology of general utility. The approach using carbanion derivatives of the π-allyl-$Mo(CO)_2Cp$ system is promising but suffers from the disadvantage that only a limited range of electrophiles react satisfactorily with the complexes. Since the π-allylmolybdenum moiety represents a variety of masked functional groups (enone, allylic alcohol, allylic halide), such an approach may well have advantages over standard organic chemical procedures in cases where such functionality is required, and also in situations where the quaternary center is to have defined stereochemistry relative to other substituents. The fact that an operationally simple synthesis of a useful intermediate, such as the lactone **14**, can be devised, attests to the potential utility of these complexes.

Experimental Section

All reactions were performed under an inert atmosphere (using dry, oxygen-free argon). All solvents used in the reactions were freshly distilled under nitrogen as follows: tetrahydrofuran and benzene from Na/benzophenone, methylene chloride and acetonitrile from CaH_2, and diethyl ether from $LiAlH_4$. Preparative thin-layer chromatography was performed either on commercial Analtech Uniplate 20 cm × 20 cm plates with a 500-μm thickness of silica gel GF or on 20 cm × 20 cm plates prepared in-house with a layer of Kieselgel 60 PF_{254} silica gel 1.5 mm thick. Melting points were recorded either on a Fisher-Johns or on a Unimelt Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer. NMR spectra were recorded on a Varian XL-200 spectrometer. Elemental analyses were obtained through Galbraith Laboratories, Knoxville, TN. Mass spectral analyses were carried out by the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln, Lincoln, NE, by the Department of Pharmacology, CWRU, or by the Major Analytical Instruments Facility at the Department of Chemistry, CWRU.

Tricarbonylindenylmolybdenum dimer ($[InMo(CO)_3]_2$) was prepared by a modified literature procedure.[10] Indene (technical grade) was purified by stirring with 6 M hydrochloric acid at room temperature for 24 h and then refluxing with 40% sodium hydroxide for 2 h, followed by distillation of the organic layer [bp 181.6 °C (760 mm)]. A mixture of molybdenum hexacarbonyl (26.4 g, 100 mmol) and purified indene (2.16 equiv, 25 g, 216 mmol) was refluxed in ethylcyclohexane (100 mL, bp 130–132 °C) for 8 h. The reaction mixture was allowed to cool to room temperature and was filtered to give light brown needle-shaped crystals of the dimer, which were washed with pentane. Yield, 15.2 g (52%).

1,4-Dimethylcyclohexa-1,4-diene. This was prepared by Birch reduction of *p*-xylene (100 g, 0.9 mol) according to the literature procedure,[11] using lithium (2.5 equiv, 2.4 mol, 16.5 g) in liquid ammonia (1.5 L) as reductant and ethanol (3.0 equiv, 2.8 mol, 165 mL) as a proton source.

1,4-Dimethylcyclohexa-1,3-diene. Following the literature procedure,[11] 1,4-dimethyl-1,4-cyclohexadiene (68 g, 0.63 mol) was refluxed with concentrated hydrochloric acid (40 mL) in water (400 mL) for 18 h. After being cooled to room temperature, this mixture was extracted with diethyl ether (2 × 200 mL). The combined ether extracts were washed with water until neutral, dried (anhydrous $MgSO_4$), and evaporated to give an equilibrium mixture of the desired 1,4-dimethyl-1,3-cyclohexadiene and the unreacted 1,4-dimethyl-1,4-cyclohexadiene in a 3:1 ratio. Yield, 50 g (74%). Separation of the two dienes was not necessary for the complexation reaction.

Dicarbonyl(η^5-indenyl)(1–4-η-1,4-dimethylcyclohexadiene)molybdenum Tetrafluoroborate (12). Silver(I) tetrafluoroborate (2.0 equiv, 6.8 mmol, 1.33 g) was added to a stirred solution of tricarbonylindenylmolybdenum dimer (2.0 g, 3.4 mmol) and the 3:1 mixture of 1,4-dimethyl-1,3(and 1,4)-cyclohexadienes (10.0 equiv, 30 mmol, 6.48 g) in a methylene chloride (20 mL) at room temperature. Silver metal was immediately deposited, and evolution of carbon monoxide gas was observed (in the fume hood). The flask was wrapped in aluminum foil, and the solution was stirred at room temperature for 24 h. The reaction mixture was quickly filtered through Celite, and the product was washed with methylene chloride to give a clear purple solution, the volume of which was reduced to half in vacuo. Dry diethyl ether (50 mL) was added dropwise via a syringe under argon, whereupon yellow crystals of the cation complex precipitated out. The solvent was removed by filtration and the precipitate was washed with diethyl ether to give yellow needle-shaped crystals of **12**: 1.63 g, 52%; mp 125–126 °C; IR (CH_3CN) ν_{max} 2010, 1940 cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.8–7.5 (m, 4 H, indenyl H^a), 6.37 (d, 2 H, J = 2.9 Hz, indenyl H^b), 5.94 (t, 1 H, J = 2.9 Hz, indenyl H^c), 4.3 (s, 2 H, CH=CH), 2.0–1.7 (m, 4 H, CH_2CH_2), 1.84 (s, 6 H, methyl). Anal. Calcd for $C_{19}H_{19}MoO_2BF_4$: C, 49.38; H, 4.14. Found: C, 49.15; H, 4.38.

Dicarbonyl(η^5-indenyl)(1–3-η-1,4-dimethyl-4-*exo*-cyanocyclohexenyl)molybdenum (13a). Sodium cyanide (1.5 equiv, 0.16 mmol, 8.1 mg) dissolved in water (1 mL) was added dropwise to a solution of the cationic diene complex **12** (50 mg, 0.11 mmol) in acetonitrile (10 mL) at room temperature. After being stirred at room temperature for 1 h, the mixture was extracted with diethyl ether (50 mL). The combined ether extracts were washed with saturated NaCl solution and water, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/CH_2Cl_2) gave the yellow oily complex **13a**: 37 mg, 85%; IR ($CHCl_3$) ν_{max} 2220 (w), 1945, 1865 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.14 (m, 4 H, indenyl), 6.01 (m, 1 H, indenyl), 5.78 (m, 1 H, indenyl), 5.53 (t, 1 H, J = 2.9 Hz, indenyl), 2.51 (dd, 1 H, J = 7.3, 1.6 Hz, 3-H), 1.9 (m, 1 H, endo 6-H), 1.7 (m, 1 H, exo 6-H), 1.58 (s, 3 H, 1 methyl), 1.36 (s, 3 H, 4 methyl), 1.25 (dd, 1 H, J = 1.50, 6.0 Hz, endo 5-H), 0.38 (m, 1 H, exo 5-H), –0.27 (d, 1 H, J = 7.3 Hz, 2-H); HRMS, m/e (relative intensity) 403 (M^+, 9), 375 (M^+ – CO, 12), 347 (M^+ – 2CO, 13), 316 (29), 292 (19), 167 (26), 149 (69), 116 (100); M^+ calcd for ^{98}Mo in $C_{20}H_{19}NMoO_2$ 403.0471, found 403.0440.

Dicarbonyl(η^5-indenyl)(1–3-η-1,4-dimethyl-4-*exo*-(dicarbomethoxymethyl)cyclohexenylmolybdenum (13b). Dimethyl malonate (1.5 equiv, 0.16 mmol, 18.3 μL) was added to a stirred suspension of sodium hydride (1.5 equiv, 0.16 mmol, 6.4 mg of 60% oil dispersion, washed with dry THF in situ) in THF at room temperature, to give a solution of $NaCH(CO_2Me)_2$. The diene complex **12** (50 mg, 0.11 mmol) was added via a solid addition funnel. After being stirred for 0.5 h at room temperature, the reaction mixture was taken up in ether, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/CH_2Cl_2) gave the yellow oily complex **13b**: 50 mg, 91%; IR ($CHCl_3$) ν_{max} 1945, 1860, 1760, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.75 (m, 1 H), 5.55 (t, 1 H, J = 2.9 Hz), 3.72 (s, 3 H), 3.62 (s, 3 H), 3.14 (s, 1 H, $CH(CO_2Me)_2$), 2.63 (dd, 1 H, J = 7.5, 1.8 Hz, 3-H), 1.8–1.4 (m, 2 H,

(23) Ashby, E. C.; Pham, T.; Madjdabadi, A. A. *J. Org. Chem.* **1988**, *53*, 6156. Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

endo 6-H and exo 6-H), 1.52 (s. 3 H, 1-methyl), 1.25 (s, 3 H, 4-methyl), 1.1 (dd, 1 H, J = 14.0, 6.0 Hz, endo 5-H), 0.24 (m, 1 H, exo 5-H), −0.48 (d, 1 H, J = 7.5 Hz, 2-H); HRMS, m/e (relative intensity) 276 (M^+ − $CH(CO_2Me)_2$, 1), 348 (5), 320 (15), 132 (1), 116 (100).

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-[carbomethoxy(phenylsulfonyl)methyl]cyclohexenyl]molybdenum (13c). Methyl (phenylsulfonyl)acetate (1.5 equiv, 0.16 mmol, 16.7 μL) was added to a stirred suspension of sodium hydride (1.5 equiv, 0.16 mmol, 6.4 mg of 60% oil dispersion, washed with dry THF in situ) in THF at room temperature, and stirred for 15 min. The diene complex **12** (50 mg, 0.11 mmol) was added via a solid addition funnel. After being stirred for 0.5 h at room temperature, the reaction mixture was extracted with ether, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give the yellow oily complex **13c** as a 3:2 mixture of diastereomers (55 mg, 87%), which were separated by preparative TLC (silica gel/20% ethyl acetate in hexanes): IR ($CHCl_3$) ν_{max} 1945, 1860, 1745 cm^{-1}; HRMS, m/e (relative intensity) 376 (M^+ − $CH(CO_2Me)(SO_2Ph)$, 1), 348 (8), 320 (29), 213 (1), 150 (37), 116 (100).

Major diastereomer: ^1H NMR ($CDCl_3$) δ 7.9–7.5 (m, 5 H), 7.04 (m, 4 H), 6.00 (m, 1 H), 5.73 (m, 1 H), 5.51 (t, 1 H, J = 2.9 Hz), 3.65 (s, 1 H, $CH(CO_2Me)(SO_2Ph)$), 3.46 (s, 3 H), 2.08 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.9 (m, 1 H, endo 5-H), 1.65 (m, 2 H, endo 6-H and exo 6-H), 1.52 (s, 3 H, 1-methyl), 1.44 (s, 3 H, 4-methyl), 0.3 (m, 1 H, exo 5-H), −0.73 (d, 1 H, J = 7.4 Hz, 2-H).

Minor diastereomer: ^1H NMR ($CDCl_3$) δ 7.9–7.5 (m, 5 H), 7.19 (m, 4 H), 6.03 (m, 1 H), 5.74 (m, 1 H), 5.57 (t, 1 H, J = 2.9 Hz), 3.89 (s, 1 H, $CH(CO_2Me)(SO_2Ph)$), 3.34 (s, 3 H), 3.26 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.6 (m, 2 H, endo 6-H and exo 6-H), 1.51 (s, 3 H, 1-methyl), 1.45 (s, 3 H, 4-methyl), 0.75 (m, 1 H, endo 5-H), 0.3 (m, 1 H, exo 5-H), −0.03 (d, 1 H, J = 7.4 Hz, 2-H).

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-[1′-carbomethoxy-1′-(phenylsulfonyl)ethyl]cyclohexenyl]molybdenum (13d). Methyl (phenylsulfonyl)propionate (1.5 equiv, 0.16 mmol, 36.5 mg) was added to a stirred suspension of sodium hydride (1.5 equiv, 0.16 mmol, 6.4 mg of 60% oil dispersion) in THF (10 mL) at room temperature. After stirring for 15 min, the cation complex **12** (50 mg, 0.11 mmol) was added. After stirring for a further 0.5 h, the reaction mixture was extracted with ether, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give the yellow oily complex **13d** as a 3:2 mixture of diastereomers (53 mg, 81%), which were separated by preparative TLC (silica gel/20% ethyl acetate in hexanes): IR ($CHCl_3$) ν_{max} 1945, 1860, 1745 cm^{-1}; HRMS, m/e (relative intensity) 376 (M^+ − $CMe(CO_2Me)(SO_2Ph)$, 0.2), 348 (6), 320 (23), 228 (0.4), 141 (29), 116 (100).

Major diastereomer: ^1H NMR ($CDCl_3$) δ 7.9–7.5 (m, 5 H), 7.04 (m, 4 H), 6.00 (m, 1 H), 5.73 (m, 1 H), 5.51 (t, 1 H, J = 2.9 Hz), 3.46 (s, 3 H), 2.08 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.9 (m, 1 H, endo 5-H), 1.65 (m, 2 H, endo 6-H and exo 6-H), 1.62 (s, 3 H, 1′-methyl), 1.52 (s, 3 H, 1-methyl), 1.44 (s, 3 H, 4-methyl), 0.3 (m, 1 H, exo 5-H), −0.73 (d, 1 H, J = 7.4 Hz, 2-H).

Minor diastereomer: ^1H NMR ($CDCl_3$) δ 7.9–7.5 (m, 5 H), 7.19 (m, 4 H), 6.03 (m, 1 H), 5.74 (m, 1 H), 5.57 (t, 1 H, J = 2.9 Hz), 3.34 (s, 3 H), 3.26 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.63 (s, 3 H, 1′-methyl), 1.6 (m, 2 H, endo 6-H and exo 6-H, partially obscured), 1.51 (s, 3 H, 1-methyl), 1.45 (s, 3 H, 4-methyl), 0.75 (m, 1 H, endo 5-H), 0.3 (m, 1 H, exo 5-H), −0.03 (d, 1 H, J = 7.4 Hz, 2-H).

Dicarbonyl(η^5-indenyl)(1–3-η-1,4,4-trimethylcyclohexenyl)molybdenum (13e). Method A. Methyllithium (2.4 equiv, 0.26 mmol, 0.19 mL of a 1.4 M solution in diethyl ether) was added dropwise to a suspension of copper(I) iodide (1.2 equiv, 0.13 mmol 25 mg) in THF (5 mL) at 0 °C, to give a solution of Me_2CuLi, to which the diene complex **12** (50 mg, 0.11 mmol) was added. After the reaction mixture was stirred for 0.5 h at 0 °C, the solution was warmed to room temperature, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) gave the yellow oily complex **13e** (15 mg, 35%).

Method B. Methylmagnesium bromide (10.0 equiv, 1.1 mmol, 0.37 mL of a 3.0 M solution in diethyl ether) was added dropwise to a solution of the diene complex **12** (50 mg, 0.11 mmol) in methylene chloride (5 mL) at 0 °C. After being stirred for 15 min, the excess of Grignard reagent was quenched with water. The colloidal suspension that resulted was warmed to room temperature and filtered through Celite, and the solvent was removed in vacuo. The residue was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) gave the yellow complex **13e**: 39 mg, 92%; IR ($CHCl_3$) ν_{max} 1930, 1845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.73 (m, 1 H), 5.55 (t, 1 H, J = 2.9 Hz), 2.57 (dd, I H, J = 7.4, 1.7 Hz, 3-H), 1.6 (m, 2 H, endo 6-H and exo 6-H), 1.51 (s, 3 H, 1-methyl), 0.99 (s, 3 H, 4-methyl), 0.89 (s, 3 H, 4-methyl), 0.7 (dd, 1 H, J = 14.0, 6.0 Hz, endo 5-H), 0.3 (m, 1 H, exo 5-H), −0.37 (d, 1 H, J = 7.4 Hz, 2-H); HRMS, m/e (relative intensity) 392 (M^+, 10), 364 (M^+ − CO, 15), 336 (M^+ − 2CO, 33), 321 (23), 116 (17); M^+ calcd for ^{98}Mo in $C_{20}H_{22}MoO_2$ 392.0675, found 392.0723.

Dicarbonyl(η^5-indenyl)(1–3-η-1,4-dimethyl-4-*exo*-allylcyclohexenyl)molybdenum (13f). Allylmagnesium bromide (2.0 equiv, 0.22 mmol, 0.22 mL of a 1.0 M solution in diethyl ether) was added dropwise to a solution of the diene complex **12** (50 mg, 0.11 mmol) in methylene chloride (10 mL) at −78 °C. After stirring for 1 h, the excess Grignard reagent was quenched with water and the reaction mixture was worked up as above to give the crude product. Purification by preparative TLC (silica gel/CH_2Cl_2) gave the yellow complex **13f**: 41 mg, 90%; IR ($CHCl_3$) ν_{max} 1930, 1845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.74 (m, 1 H), 5.9–5.6 (m, 1 H, vinyl), 5.55 (t, 1 H, J = 2.9 Hz), 4.92 (m, 2 H, vinyl), 2.56 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.97 and 1.82 (AB q d, 2 H, J_{ab} = 14.0 Hz, J_{AX} = 7.3 Hz, J_{BX} = 7.8 Hz, $CH_2CH{=}CH_2$), 1.6 (m, 2 H, endo 6-H and exo 6-H), 1.50 (s, 3 H, 1-methyl), 0.94 (s, 3 H, 4-methyl), 0.8 (dd, 1 H, J = 14.0, 6.0 Hz, endo 5-H), 0.2 (m, 1 H, exo 5-H), −0.36 (d, 1 H, J = 7.4 Hz, 2-H); HRMS, m/e (relative intensity) 418 (M^+, 8), 390 (M^+ − CO, 11), 362 (M^+ − 2CO, 8), 319 (100), 149 (19); M^+ calcd for ^{98}Mo in $C_{22}H_{24}MoO_2$ 418.0831, found 418.0843.

Dicarbonyl(η^5-indenyl)(1–3-η-1,4-dimethyl-4-*exo*-vinylcyclohexenyl)molybdenum (13g). Vinylmagnesium bromide (10.0 equiv, 1.1 mmol, 1.1 mL of a 1.0 M solution in tetrahydrofuran) was added dropwise to a solution of the diene complex **12** (50 mg, 0.11 mmol) in methylene chloride (10 mL) at 0 °C. The reaction mixture was worked up and purified as described above to give the yellow complex **13g**: 18 mg, 37%; NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.73 (m, 1 H), 5.7 (dd, 1 H, J = 16.9, 9.9 Hz, vinyl), 5.55 (t, 1 H, J = 2.9 Hz), 4.95 (d, 1 H, J = 16.9 Hz vinyl), 4.78 (d, 1 H, J = 9.9 Hz, vinyl), 2.65 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.6 (m, 2 H, endo 6-H and exo 6-H), 1.55 (s, 3 H, 1-methyl), 1.1 (s, 3 H, 4-methyl), 0.9 (m, 1 H, endo 5-H), 0.3 (m, 1 H, exo 5-H), −0.45 (d, 1 H, J = 7.4 Hz, 2-H); HRMS, m/e (relative intensity) 404 (M^+, 2), 376 (M^+ − CO, 2), 348 (M^+ − 2CO, 2), 317 (11), 293 (37), 277 (43), 201 (14), 167 (25), 149 (100), 116 (86); M^+ calcd for ^{98}Mo in $C_{21}H_{22}MoO_2$ 404.0675, found 404.0649.

Dicarbonyl(η^5-indenyl)(1–3-η-1,4-dimethyl-4-*exo*-phenylcyclohexenyl)molybdenum (13h). Phenylmagnesium bromide (10.0 equiv, 1.1 mmol, 0.37 mL of a 3.0 M solution in diethyl ether) was added dropwise to a clear solution of the complex **12** (50 mg, 0.11 mmol) in methylene chloride (10 mL) at 0 °C. The reaction mixture was worked up and purified as described above to give the yellow complex **13h**: 14 mg, 30%; IR ($CHCl_3$) ν_{max} 1930, 1845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 9 H), 6.0 (m, 1 H), 5.74 (m, 1 H), 5.55 (t, 1 H, J = 2.9 Hz), 2.65 (dd, 1 H, J = 7.4, 1.7 Hz, 3-H), 1.6 (m, 2 H, endo 6-H and exo 6-H), 1.55 (s, 3 H, 1-methyl), 1.25 (s, 3 H, 4-methyl), 0.9 (m, 1 H, endo 5-H), 0.5 (m, 1 H, exo 5-H), −0.35 (d, 1 H, J = 7.4 Hz, 2-H); HRMS, m/e (relative intensity 454 (M^+, 2), 426 (M^+ − CO, 1), 398 (M^+ − 2CO, 3), 333 (24), 167 (20), 149 (100); M^+ calcd for ^{98}Mo in $C_{25}H_{24}MoO_2$ 454.0795, found 454.0781.

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-(1′-methyl-2′-oxocyclopentyl)cyclohexenyl]molybdenum (13i). Methyllithium (1.0 equiv, 0.11 mmol, 79 μL of a 1.4 M solution in diethyl ether) was added dropwise to a stirred solution of 2-methyl-1-[(trimethylsilyl)oxy]cyclopentene (1.0 equiv, 0.11 mmol, 19 mg) in THF at 0 °C. The solution was stirred at 0 °C for 15 min to generate the Li enolate. The diene complex **12** (50 mg, 0.11 mmol) was added via a solid addition funnel. After being stirred for 0.5 h, the solution was worked up and purified as described above to give the yellow complex **13i** as a 2:1 mixture of diastereomers: 42 mg, 83%; IR ($CHCl_3$) ν_{max} 1930, 1845, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.74 (m, 1 H), 5.57 (m, 1 H), 3.1 (d, J = 7.4 Hz, 3-H, minor), 2.5 (d, J = 7.4 Hz, 3-H major), 1.47 (s, 1-methyl, major), 1.44 (s, 1-methyl, minor), 1.25 (s, 1′-methyl, minor), 1.10 (s, 4-methyl, major), 1.03 (s, 4-methyl, minor), 0.95 (s, 1′-methyl, major), 2.2–0.5 (m, 10 H), −0.25 (d, J = 7.4 Hz, 2-H, minor), −0.31 (d, J = 7.4 Hz, 2-H, major); HRMS, m/e (relative intensity) 376 (M^+ − C_6H_9O, 1), 348 (6), 320 (20), 116 (100).

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-(carbomethoxymethyl)cyclohexenyl]molybdenum (13j). Freshly distilled diisopropylamine (1.2 equiv, 0.13 mmol, 18.5 μL) was added to a stirred solution of *n*-butyllithium (1.2 equiv, 0.13 mmol, 53 μL of a 2.5 M solution in hexanes) in THF (10 mL) at 0 °C. After stirring for 15 min to generate LDA, the clear solution was cooled to −78 °C. Methyl acetate (1.5 equiv, 0.165 mmol, 13 μL) was added dropwise and stirred for 0.5 h to produce the Li enolate, to which the diene complex **12** (50 mg, 0.11 mmol) was added. After being stirred for 1 h, the clear yellow solution was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by flash chromatography (silica gel/CH_2Cl_2) gave the yellow complex **13j**: 39 mg, 81%; IR ($CHCl_3$) ν_{max} 1930, 1850, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.0 (m, 1 H), 5.75 (m, 1 H), 5.55 (t, 1 H, J = 2.9 Hz), 3.61 (s, 3 H), 2.59 (dd, 1 H,

J = 7.4, 1.7 Hz, 3-H), 2.20 and 2.08 (AB q, 2 H, J_{AB} = 12.9 Hz, CH_2CO_2Me), 1.65–1.50 (m, 2 H, endo 6-H and exo 6-H), 1.51 (s, 3 H, 1-methyl), 1.09 (s, 3 H, 4-methyl), 0.94 (dd, 1 H, J = 14.0, 6.0 Hz, endo 5-H), 0.24 (m, 1 H, exo 5-H), −0.36 (d, 1 H, J = 7.4 Hz, 2-H); HRMS, m/e (relative intensity) 450 (M^+, 8), 420 (22), 394 ($M^+ - 2CO$, 33), 367 (21), 279 (31), 251 (27), 201 (49), 151 (48), 113 (74); M^+ calcd for ^{98}Mo in $C_{22}H_{24}MoO_4$ 450.0730, found 450.0719.

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-[1′-(methoxycarbonyl)ethyl]cyclohexenyl]molybdenum (13k). Methyl propionate (1.5 equiv, 0.165 mmol, 16 μL) was added to a solution of LDA as above and the mixture was stirred for 0.5 h to produce the Li enolate, to which the complex **12** (50 mg, 0.11 mmol) was added. After being stirred for 1 h, the solution was warmed to room temperature, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by flash chromatography (silica gel/CH_2Cl_2) afforded the yellow complex **13k** as a 4:3 mixture of diastereomers: 44 mg, 89%; IR ($CHCl_3$) ν_{max} 1940, 1850, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.01 (m, 1 H), 5.74 (m, 1 H), 5.55 (m, 1 H), 3.66 (s, CO_2Me, major), 3.55 (s, CO_2Me, minor), 2.62 (dd, J = 7.5, 1.8 Hz, 3-H, minor), 2.36 (dd, J = 7.5, 1.8 Hz, 3-H, major), 2.19 (q, J = 7.1 Hz, CH_3CH, minor), 1.52 (s, 1-methyl, major), 1.16 (d, J = 7.1 Hz, CH_3CH, minor), 1.03 (s, 4-methyl, major), 0.99 (s, 4-methyl, minor), 0.96 (d, J = 7.1 Hz, CH_3CH, major), −0.39 (d, J = 7.5 Hz, 2-H, major), −0.48 (d, J = 7.5 Hz, 2-H, minor), other peaks were obscured by the three methyl peaks of each of the two diastereomers; HRMS, m/e (relative intensity) 464 (M^+, 14), 436 ($M^+ - CO$, 20), 408 ($M^+ - 2CO$, 32), 321 (39), 116 (40); M^+ calcd for ^{98}Mo in $C_{23}H_{26}MoO_4$ 464.0886, found 464.0897.

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-[(hydroxycarbonyl)methyl]cyclohexenyl]molybdenum (19). Method A. Potassium hydroxide (50.0 equiv, 1.1 mmol, 62 mg) dissolved in water (0.5 mL) was added to a stirred solution of the complex **13j** (10 mg, 0.022 mmol) in a 1:1 mixture of methanol/THF (2 mL) at room temperature. The reaction was monitored by TLC, which showed that hydrolysis was complete after 2 days. A 10% aqueous HCl solution was added and the product was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the yellow acid complex **19** (10 mg, >99%).

Method B. Trimethylsilyl acetate (1.5 equiv, 0.0825 mmol, 12.24 μL) was added to a solution of LDA at −78 °C as above and stirred for 0.5 h to generate the Li enolate. The enolate was transferred dropwise via a cannula to a stirred suspension of the diene complex **12** (25 mg, 0.055 mmol) in THF (5 mL) at −78 °C. After stirring for 0.5 h, the flask was warmed to room temperature, the product was extracted with ether, and the combined extracts were washed with 10% aqueous HCl solution to remove the trimethylsilyl group and generate the acid derivative. The ether layer was washed with water, dried ($MgSO_4$), and concentrated to give the yellow acid complex **19**: 20 mg, 85%; IR ($CHCl_3$) ν_{max} 2940 (br), 1935, 1855, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.01 (m, 1 H), 5.75 (m, 1 H), 5.56 (t, 1 H, J = 1.9 Hz), 2.62 (dd, 1 H, J = 7.5, 1.7 Hz, 3-H), 2.24 and 2.12 (AB q, 2 H, J_{AB} = 12.9 Hz, CH_2CO_2H), 1.64–1.50 (m, 2 H, endo 6-H and exo 6-H), 1.51 (s, 3 H, 1-methyl), 1.14 (s, 3 H, 4-methyl), 0.95 (dd, 1 H, J = 14.0, 6.0 Hz, endo 5-H), 0.23 (m, 1 H, exo 5-H), −0.34 (d, 1 H, J = 7.5 Hz, 2-H); HRMS, m/e (relative intensity) 436 (M^+, 2), 408 ($M^+ - CO$, 1), 380 ($M^+ - 2CO$, 1), 375 (10), 347 (8), 319 (43), 279 (33), 183 (39), 167 (80), 149 (100), 116 (28); M^+ calcd for ^{98}Mo in $C_{21}H_{22}MoO_4$ 436.0573, found 436.0037.

Dicarbonyl(η^5-indenyl)[1–3-η-1,4-dimethyl-4-*exo*-[1′-(hydroxycarbonyl)ethyl]cyclohexenyl]molybdenum (2j). Trimethylsilyl propionate (1.5 equiv, 0.165 mmol, 30 μL; prepared by treating propionic acid with triethylamine and trimethylsilyl chloride in diethyl ether) was added to LDA in THF (1.2 equiv), and the mixture was stirred for 0.5 h to generate the Li enolate, to which the diene complex **12** (50 mg, 0.11 mmol) was added. After being stirred for 0.5 h, the reaction mixture was warmed to room temperature, and worked up as described for complex **19** to give the acid complex **21** as a 2:1 mixture of diastereomers: 45 mg, 93%; IR ($CHCl_3$) ν_{max} 2940 (br), 1935, 1844, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.02 (m, 1 H), 5.74 (m, 1 H), 5.55 (m, 1 H), 2.62 (dd, J = 7.5, 1.8 Hz, 3-H, major), 2.55 (dd, J = 7.5, 1.8 Hz, 3-H minor), 2.19 (q, J = 7.1 Hz, CH_3CH, major), 2.11 (q, J = 7.1 Hz, CH_3CH, minor), 1.52 (s, 1-methyl, major), 1.49 (s, 1-methyl, minor), 1.20 (d, J = 7.1 Hz, CH_3CH, major), 1.05 (s, 4-methyl, minor), 1.02 (s, 4-methyl, major), 0.99 (d, J = 7.1 Hz, CH_3CH, minor), −0.26 (d, J = 7.5 Hz, 2-H, minor), −0.48 (d, J = 7.5 Hz, 2-H, major), other peaks were obscured by the three methyl peaks of each of the two diastereomers; HRMS, m/e (relative intensity) 450 (M^+, 1), 422 ($M^+ - CO$, 3), 394 ($M^+ - 2CO$, 3), 321 (9), 116 (100); M^+ calcd for ^{98}Mo in $C_{22}H_{24}MoO_4$ 450.0730, found 450.0731.

2-Hydroxy-1,4-dimethylcyclohex-3-enyl Acetic Acid Lactone (20). Nitrosyl hexafluorophosphate (1.5 equiv, 0.7 mmol, 12 mg) was added to a stirred solution of the acid complex **19** (20 mg, 0.045 mmol) in acetonitrile (10 mL) at 0 °C. After the resultant mixture was stirred for 15 min, freshly distilled triethylamine (1.5 equiv, 0.07 mmol, 9.6 μL) was added dropwise, and the mixture was stirred for an additional 15 min. The reaction mixture was warmed to room temperature, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the pale yellow oily product **20** (6 mg, 82%). The spectral data of the lactone were identical with that reported in literature:[13] IR ($CHCl_3$) ν_{max} 1760, 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (m, 1 H, C*H*=C), 4.2 (m, 1 H, C*H*O), 2.2 (s, 2 H, CH_2CO), 1.8 (s, 3 H, CH_3C=C), 1.2 (s, 3 H, CH_3C).

2-(2-Hydroxy-1,4-dimethylcyclohex-3-enyl)propionic Acid Lactone (14). The acid complex **21** (20 mg, 0.045 mmol) was treated with $NOPF_6$ as described above to give the pale yellow oily product **14** (7 mg, 87%). The spectral data of the lactone were identical with that reported in the literature:[13] IR ($CHCl_3$) ν_{max} 1760, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (m, 1 H, C*H*=C), 4.3 (m, 1 H, C*H*—O), 2.4 (q, 1 H, J = 8.0 Hz, CH_3—C*H*), 1.75 (s, 3 H, CH_3C=C), 1.1 (d, 3 H, J = 8.0 Hz, CH_3CH), 1.0 (s, 3 H, CH_3C); HRMS, m/e (relative intensity) 180 (M^+, 49), 171 (27), 165 (70), 152 (26), 147 (21), 136 (54), 121 (100), 108 (79), 101 (87); M^+ calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1152.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-4-*exo*-cyanocyclohexenyl)molybdenum (22). Sodium cyanide (1.5 equiv, 3.38 mmol, 166 mg) dissolved in water (2 mL) was added to a stirred suspension of the diene complex **27** (1.0 g, 2.26 mmol) in acetonitrile (20 mL) at room temperature. After being stirred for 1 h, the reaction mixture was extracted with diethyl ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by flash chromatography (silica gel/CH_2Cl_2) yielded the yellow crystalline complex **22** (600 mg, 82%). An analytical sample of the complex was obtained by recrystallization from a 1:1 mixture of pentane and petroleum ether to give needle-shaped crystals: mp 155–156 °C; IR ($CHCl_3$) ν_{max} 2215 (w), 1950, 1870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (s, 5 H, Cp), 4.36 (t, 1 H, J = 7.1 Hz, 2-H), 3.86 (m, 1 H, 3-H), 3.59 (br, d, 1 H, J = 6.8 Hz, 1-H), 2.77 (dd, 1 H, J = 6.5, 3.0 Hz, endo 4-H), 2.17 (dt, 1 H, J = 13.5, 4.0 Hz, endo 6-H), 1.75 (td, 1 H, J = 12.3, 4.0 Hz, exo 6-H), 1.30 (dd, 1 H, J = 14.5, 5.8 Hz, endo 5-H), 0.64 (m, 1 H, exo 5-H). Anal. Calcd for $C_{14}H_{13}NMoO_2$: C, 52.03; H, 4.05; N, 4.33. Found: C, 52.13; H, 4.23; N, 4.43.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-4-*endo*-cyanocyclohexenyl)molybdenum (24a). General Procedure for Carbanion Generation. THF (1.0 mL) was added to a flame-dried 4-mL reaction vial equipped with a nitrogen-filled balloon and cooled to 0 °C. Freshly distilled diisopropylamine (1.2 equiv, 0.186 mmol, 25 μL) was added, followed by dropwise addition of *n*-butyllithium (1.2 equiv, 0.186 mmol, 75 μL of a 2.5 M solution in hexanes). After stirring for 15 min to generate LDA, the reaction vessel was cooled to −78 °C. The cyano complex **22** (50 mg, 0.155 mmol) dissolved in THF (0.5 mL) was added dropwise, to give a dark red solution. After stirring for 0.5 h, the carbanion was quenched with water (0.1 mL) and the reaction vessel was warmed to room temperature, whereby the solution turned yellow. The reaction mixture was extracted with diethyl ether (10 mL), washed with a 10% aqueous HCl solution (2 × 5 mL) and brine (2 × 5 mL), dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) yielded the yellow crystalline complex **24a** (48 mg, 96%). An analytical sample was obtained by recrystallization from 1:1 mixture of petroleum ether/pentane: mp 172–174 °C; IR ($CHCl_3$) ν_{max} 2240 (w), 1955, 1875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.34 (s, 5 H, Cp), 4.20 (t, 1 H, J = 7.3 Hz, 2-H), 3.75 (m, 1 H, 3-H), 3.61 (br, d, 1 H, J = 7.3 Hz, 1-H), 3.16 (dd, 1 H, J = 12.0, 4.0 Hz, exo 4-H), 1.85 (m, 2 H, endo 6-H and exo 6-H), 1.45 (m, 1 H, endo 5-H), 0.72 (m, 1 H, exo 6-H). Anal. Calcd for $C_{14}H_{13}NMoO_2$: C, 52.03; H, 4.05; N, 4.33. Found: C, 52.32; H, 4.00; N, 4.36.

Dicarbonyl(η^5-cyclopentadienyl)[1–3-η-4-*endo*-cyano-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]cyclohexenyl]molybdenum (24c). LDA was generated at 0 °C as described above by using diisopropylamine (1.2 equiv, 0.186 mmol, 25 μL of 2.5 M solution in hexanes) in THF (1.0 mL), cooled to −78 °C. The cyano complex **22** (50 mg, 0.155 mmol) was converted to the carbanion as described above. This was treated with di-*tert*-butyl methylenemalonate (1.2 equiv, 0.186 mmol, 42 μL; prepared by literature procedure[24]), and the resultant mixture was stirred for 1 h. After being warmed to room temperature, the reaction mixture was extracted with ether and purified as described above, to yield the yellow crystalline complex **24c** (75 mg, 88%). An analytical sample was obtained by recrystallization from a 1:1 mixture of pentane/petroleum ether: mp 185 °C; IR ($CHCl_3$) ν_{max} 2230 (w), 1955, 1870, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.32 (s, 5 H, Cp), 4.17 (t, 1 H, J = 7.2 Hz, 2-H), 3.78 (m, 1 H, 3-H), 3.53 (m, 2 H, 1-H and CH_2CH), 2.45 and 2.30 (AB q d, 2 H, J_{AB} = 14.4 Hz, J_{AX} = 6.05 Hz, J_{BX} = 6.35 Hz, CH_2CH), 2.0 (m, 1 H, endo 6-H), 1.74 (m, 1 H, exo 6-H), 1.49 (s, 9 H, *tert*-butyl),

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1.46 (s, 9 H, *tert*-butyl), 1.24 (m, 1 H, endo 5-H), 0.9 (m, 1 H, exo 5-H). Anal. Calcd for $C_{26}H_{33}NMoO_6$: C, 56.62; H, 6.03; N, 2.54. Found: C, 56.36; H, 6.23; N, 2.49.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-(hydroxybenzyl)cyclohexenyl]molybdenum (24d). Following the general procedure, the cyano complex **22** (100 mg, 0.310 mmol) was deprotonated and treated with benzaldehyde (1.2 equiv, 0.372 mmol, 39 mg) premixed with boron trifluoride etherate (1.2 equiv, 0.372 mmol, 53 mg) in THF (0.5 mL). After 2 h at −78 °C the reaction mixture was warmed to room temperature. The usual workup yielded a 4:1 mixture of diastereomers of the complex **24d** (104 mg, 78%), which were separated by preparative TLC (silica gel/40% ethyl acetate in hexanes): IR ($CHCl_3$) ν_{max} 3400 (OH), 2240 (w), 1945, 1850 cm^{-1}; HRMS, *m/e* (relative intensity) 430 (M^+, 1), 402 (M^+ − CO, 2), 353 (30), 266 (40), 194 (22), 144 (29); M^+ calcd for ^{98}Mo in $C_{21}H_{19}MNoO_3$ 430.0475, found 430.0465.

Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.25 (s, 5 H, Cp), 4.38 (d, 1 H, J = 4.0 Hz, PhC*H*OH), 4.22 (t, 1 H, J = 7.2 Hz, 2-H), 3.82 (m, 1 H, 1-H), 2.82 (br d, 1 H, J = 7.2 Hz, 3-H), 2.35 (d, 1 H, J = 4.0 Hz, CHO*H*), 2.0 (m, 1 H, endo 6-H), 1.85 (m, 1 H, exo 6-H), 0.9 (m, 2 H, endo 5-H and exo 5-H). ^{1}H NMR after D_2O shake shows disappearance of hydroxyl resonance at δ 2.35, collapse of α-proton resonance at 4.38 to a singlet, and appearance of HOD resonance at 4.8.

Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 5 H, Cp), 4.61 (d, 1 H, J = 4.0 Hz, PhC*H*OH), 4.37 (t, 1 H, J = 7.2 Hz, 2-H), 4.10 (br d, 1 H, J = 7.2 Hz, 3-H), 3.91 (m, 1 H, 1-H), 2.34 (d, 1 H, J = 4.0 Hz, CHO*H*), 2.0 (m, 1 H, endo 6-H), 1.8 (m, 1 H, exo 6-H), 1.0 (dd, 1 H, J = 15.0, 6.0 Hz, endo 5-H), 0.8 (m, 1 H, exo 5-H). ^{1}H NMR after D_2O shake shows disappearance of hydroxyl resonance at δ 2.34, collapse of α-proton resonance at 4.61 to a singlet, and appearance of HOD resonance at 4.8.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-(2-carbomethoxy-3-oxocyclopentyl)cyclohexenyl]molybdenum (24e). The cyano complex **22** (50 mg, 0.155 mmol) was converted to the carbanion as above, and 2-carbomethoxy-2-cyclopenten-1-one (**26**; 1.2 equiv, 0.186 mmol, 26 mg; prepared by the literature procedure[25]) was added; the resultant mixture was stirred for 1 h and warmed to room temperature. The usual ether workup yielded a 8:10:9 mixture of three diastereomers of the complex (50 mg, 70%). The "major" diastereomer was separated by preparative TLC (silica gel/40% ethyl acetate in hexanes): IR ($CHCl_3$) ν_{max} 2200 (w), 1940, 1855, 1755, 1725 cm^{-1}; HRMS, *m/e* (relative intensity) 440 (M^+ − CN, 11), 412 (8), 382 (100), 350 (28), 320 (44), 241 (44), 192 (22); (M^+ − CN); calcd for ^{98}Mo in $C_{20}H_{21}MoO_5$ 440.0522, found 440.0512.

Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 5 H, Cp), 4.25 (t, 1 H, J = 7.2 Hz, 2-H), 3.73 (s with overlapping m, 5 H, 1-H, 3-H, and CO_2Me), 3.26 (d, 1 H, J = 10.4 Hz, C*H*CO_2Me), 2.93 (dt, 1 H, J = 12.0, 10.4 Hz, CH_2CHCHCO_2Me), 2.7–2.3 (m, 3 H), 2.05 (m, 2 H, CH_2), 1.75 (m, 1 H), 0.95 (m, 2 H, CH_2).

Two minor diastereomers: ^{1}H NMR ($CDCl_3$) δ 5.32 (s, Cp, minor), 5.28 (s, Cp, major), 4.21 (t, J = 7.2 Hz, 2-H, minor), 4.09 (t, J = 7.2 Hz, 2-H major), 3.79 (s, CO_2Me, major), 3.74 (s, CO_2Me, minor), 3.70 (m, 1 H, 3-H), 3.43 (m, 1 H, 1-H), 3.10 (d, J = 11.2 Hz, C*H*CHCO_2Me, major), 2.93 (d, J = 11.2 Hz, C*H*CO_2Me, minor), 2.7 (m, 1 H, CH_2CHCHCO_2Me), 2.4 (m, 3 H), 1.95 (m, 1 H), 1.5 (m, 2 H, CH_2), 1.05 (m, 1 H), 0.6 (m, 1 H).

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-protiocyclohexenyl)molybdenum]cyclohexenyl]molybdenum (24f). The cyano complex **22** (200 mg, 0.62 mmol) dissolved in THF (0.5 mL) was added dropwise to LDA as above. After being stirred for 0.5 h, the solution was added via a cannula to a stirred suspension of the diene complex **27** (1.5 equiv, 0.93 mmol, 412 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The usual workup, ether extraction, and purification by flash chromatography yielded the yellow oily complex **24f** as an equimolar mixture of diastereomers: 251 mg, 66%; IR ($CHCl_3$) ν_{max} 2240 (w, CN), 1950, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.32 (s, 5 H, Cp), 5.28 (s, 5 H, Cp), 4.57 (t, 1 H, J = 7.2 Hz, 2-H), 4.35 (t, 1 H, J = 7.2 Hz, 2-H), 4.15 (m, 1 H, 3-H), 4.0 (m, 1 H, 3-H), 3.88 (m, 1 H, 1-H), 3.80 (m, 1 H, 1-H), 2.4 (m, 1 H, endo 4-H), 1.9–0.5 (m, 8 H); HRMS, *m/e* (relative intensity) 621 (M^+, 1), 565 (M^+ − 2CO, 1), 537 (M^+ − 3CO, 2), 509 (M^+ − 4CO), 1), 323 (5), 298 (16), 295 (14), 270 (13), 267 (28), 242 (53); M^+ calcd for ^{98}Mo in $C_{27}H_{25}NMo_2O_4$ 620.9884, found 620.9863.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[tricarbonyl(2′-5′-η-4′-methoxy-1′-*endo*-protiocyclohexadienyl)iron]cyclohexenyl]molybdenum (24g). The cyano complex **22** (50 mg, 0.155 mmol) dissolved in THF (0.5 mL) was treated with LDA as above. After being stirred for 0.5 h, the solution was added via a cannula to a stirred suspension of the dienyliron complex **28** (1.5 equiv, 0.232 mmol, 92 mg; prepared by literature methods[21]) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The usual workup and purification by preparative TLC yielded the yellow oily complex **24g** (30 mg, 34%): IR ($CHCl_3$) ν_{max} 2240 (w), 2040, 1960, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 5 H, Cp), 5.15 (dd, 1 H, J = 6.4, 2.3 Hz, 3′-H), 4.16 (t, 1 H, J = 7.3 Hz, 2-H), 3.76 (m, 1 H, 1-H), 3.66 (5, 3 H, OMe), 3.48 (m, 1 H, 3-H), 3.26 (m, 1 H, 5′-H), 2.54 (dd, 1 H, J = 6.4, 3.0 Hz, 4′-H), 2.2–0.8 (m, 7 H, 1′-H and 3 CH_2); HRMS, *m/e* (relative intensity) 573 (M^+, 0.4), 461 (M^+ − 4CO, 0.7), 433 (M^+ − 5CO, 2.5), 324 (11), 296 (10), 268 (8), 249 (100), 221 (69), 165 (62); M^+ calcd for ^{98}Mo in $C_{24}H_{21}NO_6MoFe$ 572.9773, found 572.9784.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[tricarbonyl(1′-5′-η-6′-*endo*-protiocyclohexadienyl)manganese]cyclohexenyl]molybdenum (24h). The cyano complex **22** (50 mg, 0.155 mmol) dissolved in THF (0.5 mL) was treated with LDA as above and added via a cannula to a stirred suspension of the arene manganese complex **29** (1.5 equiv, 0.232 mmol, 84 mg)[18,26] in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The usual workup and purification by preparative TLC (silica gel/70% ethyl acetate in hexanes) yielded the yellow complex **24h**: 62 mg, 74%; IR ($CHCl_3$) ν_{max} 2230 (w), 2020, 1950, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.85 (t, 1 H, J = 5.4 Hz, 3′-H), 5.31 (s, 5 H, Cp), 5.09 (t, 1 H, J = 6.1 Hz, 2′-H), 5.01 (t, 1 H, J = 6.1 Hz, 4′-H), 4.22 (t, 1 H, J = 7.2 Hz, 2-H), 3.76 (m, 1 H, 1-H), 3.58 (br t, 1 H, J = 5.4 Hz, 1′-H), 3.47 (d, 1 H, J = 7.2 Hz, 3-H), 3.26 (br t, 1 H, J = 5.4 Hz, 5′-H), 2.70 (t, 1 H, J = 5.6 Hz, 6′-H), 1.84 (m, 1 H, endo 6-H), 1.73 (m, 1 H, exo 6-H), 1.24 (dd, 1 H, J = 14.5, 5.8 Hz, endo 5-H), 0.55 (m, 1 H, exo 5-H) (The dienyl–Mn group shows diastereotopic proton resonances.); HRMS, *m/e* (relative intensity) 541 (M^+, 2), 429 (M^+ − 4CO, 3), 367 (5), 325 (21), 297 (17), 267 (100), 240 (71), 189 (24), 161 (20), 105 (16); M^+ calcd for ^{98}Mo in $C_{23}H_{18}NO_5MoMn$ 540.9620, found 540.9627.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[tricarbonyl(1′-5′-η-2,4-dimethoxy-6′-*endo*-protiocyclohexadienyl)manganese]cyclohexenyl]molybdenum (24i) was prepared by the same procedure as above, but using the arenemanganese complex **30** (1.5 equiv): 67%; IR ($CHCl_3$) ν_{max} 2230 (w), 2020, 1940, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.72 (s, 1 H, 3′-H), 5.32 (s, 5 H, Cp), 4.26 (t, 1 H, J = 7.2 Hz, 2-H), 3.74 (m, 1 H, 1-H), 3.64 (s, 3 H, 2′-methoxy), 3.55 (s, 3 H, 4′-methoxy), 3.47 (m, 1 H, 3-H), 3.3 (br d, 1 H, J = 5.9 Hz, 1′-H), 3.1 (br d, 1 H, J = 5.9 Hz, 5′-H), 2.85 (t, 1 H, J = 5.9 Hz, 6′-H), 1.9 (m, 1 H, endo 6-H), 1.7 (m, 1 H, exo 6-H), 1.1 (m, 1 H, endo 5-H), 0.6 (m, 1 H, exo 5-H); HRMS, *m/e* (relative intensity) 601 (M^+, 0.2), 573 (M^+ − CO, 0.3), 545 (M^+ − 2CO, 0.4), 489 (M^+ − 4CO, 0.5), 461 (M^+ − 5CO, 1), 299 (42), 241 (100), 151 (21); M^+ calcd for ^{98}Mo in $C_{25}H_{22}NO_7MoMn$ 600.9832, found 600.9822.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-cyano-6-*exo*-methylcyclohexenyl)molybdenum (23). Sodium cyanide (1.5 equiv, 0.493 mmol, 24 mg) dissolved in water (0.5 mL) was added dropwise to a stirred suspension of dicarbonyl(η^5-cyclopentadienyl)(1-4-η-5-*exo*-methylcyclohexadiene)molybdenum hexafluorophosphate (150 mg, 0.329 mmol) in acetonitrile (5 mL) at room temperature. After being stirred for 1 h, the reaction mixture was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by flash chromatography (silica gel/CH_2Cl_2) gave the yellow crystalline complex **23** (105 mg, 95%). An analytical sample was obtained by recrystallization from a 1:1 mixture of petroleum ether/pentane: mp 145–147 °C; IR ($CHCl_3$) ν_{max} 2240 (w), 1950, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 5 H, Cp), 4.31 (t, 1 H, J = 7.1 Hz, 2-H), 3.82 (m, 1 H, 3-H), 3.62 (m, 1 H, 1-H), 2.75 (dd, 1 H, J = 6.5, 3.0 Hz, endo 4-H), 2.10 (m, 1 H, endo 6-H), 1.40 (d, 3 H, J = 7.1 Hz, methyl), 1.2 (m, 1 H, endo 5-H), 0.8 (m, 1 H, exo 5-H). Anal. Calcd for $C_{15}H_{15}NMoO_2$: C, 53.42; H, 4.48; N, 4.15. Found: C, 52.79; H, 4.39; N, 4.14.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-cyano-6-*exo*-methylcyclohexenyl)molybdenum (25a). The cyano complex **23** (50 mg, 0.148 mmol) dissolved in THF (0.5 mL) was added dropwise to LDA (1.2 equiv) in THF at −78 °C. After being stirred for 0.5 h, the carbanion solution was quenched with water (0.1 mL) and warmed to room temperature. The usual workup and purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) yielded the yellow crystalline complex **25a**: 48 mg, 95%; mp 139–141 °C (from petroleum ether/pentane); IR ($CHCl_3$) ν_{max} 2230 (w), 1950, 1870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 5 H, Cp), 4.19 (t, 1 H, J = 7.1 Hz, 2-H), 3.67 (m, 2 H, 1-H and 3-H),

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3.27 (dd, 1 H, J = 12.0, 4.0 Hz, exo 4-H), 2.1 (m, 1 H, endo 6-H), 1.14 (d, 3 H, J = 6.8 Hz, methyl), 1.1 (m, 1 H, endo 5-H), 0.89 (m, 1 H, exo 5-H). Anal. Calcd for $C_{15}H_{15}NMoO_2$: C, 53.42; H, 4.48; N, 4.15. Found: C, 53.92; H, 4.76; N, 4.02.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]-6-*exo*-methylcyclohexenyl]molybdenum (25c). By an identical procedure as for **24c**, the cyano complex **23** (50 mg, 0.148 mmol) was converted to complex **25c**. An analytical sample was obtained by recrystallization from a 1:1 mixture of petroleum ether/pentane: mp 140–142 °C; IR ($CHCl_3$) ν_{max} 2230 (w), 1955, 1875, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (s, 5 H, Cp), 4.15 (t, 1 H, J = 7.1 Hz, 2-H), 3.81 (td, 1 H, J = 7.1, 2.1 Hz, 3-H), 3.62 (dd, 1 H, J = 7.1, 1.7 Hz, 1-H), 3.56 (dd, 1 H, J = 7.9, 4.0 Hz, CH_2CH), 2.14 (m, 1 H, endo 6-H), 1.50 (s, 9 H, *tert*-butyl), 1.47 (s, 9 H, *tert*-butyl), 1.30 (d, 3 H, J = 7.4 Hz, methyl), 1.21 (m, 1 H, endo 5-H), 0.9 (m, 1 H, exo 5-H). Anal. Calcd for $C_{27}H_{35}NMoO_6$: C, 57.27; H, 6.36; N, 2.47. Found: C, 57.21; H, 6.36; N, 2.35.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-cyanocycloheptenyl)molybdenum (33a). The cyano complex **31**, prepared as described earlier[15] (50 mg, 0.148 mmol) and dissolved in THF (0.5 mL), was added dropwise to LDA (1.2 equiv) in THF at −78 °C. After being stirred for 0.5 h, the carbanion solution was quenched with water (excess, 0.1 mL) and warmed to room temperature. The usual workup and purification by preparative TLC yielded the yellow crystalline complex **33a**: 45 mg, 90%; mp 156–158 °C; IR ($CHCl_3$) ν_{max} 2240 (w), 1950, 1870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.31 (s, 5 H, Cp), 4.29 (t, 1 H, J = 8.5 Hz, 1-H), 4.08 (td, 1 H, J = 8.7, 1.5 Hz, 3-H), 3.81 (t, 1 H, J = 8.7 Hz, 2-H), 3.53 (td, 1 H, J = 11.2, 3.36 Hz, exo 4-H), 2.6 (m, 1 H, endo 5-H), 2.2 (m, 1 H, endo 7-H), 1.7 (m, 1 H, exo 7-H), 1.55 (m, 1 H, endo 6-H), 0.9 (m, 1 H, exo 5-H), 0.8 (m, 1 H, exo 6-H). Anal. Calcd for $C_{15}H_{15}NMoO_2$: C, 53.41; H, 4.45; N, 4.15. Found: C, 53.25; H, 4.55; N, 3.96.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]cycloheptenyl]molybdenum (33c). The cyano complex **31** (50 mg, 0.148 mmol) dissolved in THF (0.5 mL) was added dropwise to LDA (1.2 equiv) in THF at −78 °C. After stirring for 0.5 h to generate the carbanion, di-*tert*-butyl methylenemalonate (1.2 equiv, 0.178 mmol, 40 mg) was added. After 1 h the mixture was warmed to room temperature, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) gave the yellow crystalline complex **33c** (72 mg, 86%). An analytical sample was obtained by recrystallization from 1:1 petroleum ether/pentane: mp 170 °C; IR ($CHCl_3$) ν_{max} 2240 (w), 1950, 1870, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (s, 5 H, Cp), 4.46 (br, t, 1 H, J = 8.1 Hz, 1-H), 3.90 (d, 1 H, J = 8.5 Hz, 3-H), 3.75 (t, 1 H, J = 8.5 Hz, 2-H), 3.54 (t, 1 H, J = 5.8 Hz, CH_2CH), 2.61 (dd, 2 H, J = 5.8, 3.0 Hz, CH_2CH), 2.55 (m, 1 H, endo 5-H), 2.15 (m, 1 H, endo 7-H), 1.49 (s, 9 H, *tert*-butyl), 1.46 (s, 9 H, *tert*-butyl), 1.3 (m, 2 H, exo 5-H and exo 6-H), resonances for endo 6-H and exo 7-H are obscured by the two *tert*-butyl peaks. Anal. Calcd for $C_{27}H_{35}NMoO_6$: C, 57.34; H, 6.24; N, 2.48. Found: C, 57.05; H, 6.31; N, 2.53.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[tricarbonyl(1′-5′-η-6′-*endo*-protiocyclohexadienyl)manganese]cycloheptenyl]molybdenum (33d). The cyano complex **31** (100 mg, 0.296 mmol) dissolved in THF (0.5 mL) was added dropwise to LDA (1.2 equiv) in THF at −78 °C. After being stirred for 0.5 h, the red carbanion solution was transferred via cannula to a stirred suspension of the arene–$Mn(CO)_3$ complex **29** (1.5 equiv, 0.444 mmol, 161 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature and extracted with ether; the extracts were washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) afforded the yellow complex **33c**: 101 mg, 62%; IR ($CHCl_3$) ν_{max} 2230 (w), 2020, 1950, 1865 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (t, 1 H, J = 5.4 Hz, 3′-H), 5.3 (s, 5 H, Cp), 5.2 (t, 1 H, J = 6.1 Hz, 2′-H), 5.05 (t, 1 H, J = 6.1 Hz, 4′-H), 4.4 (br t, 1 H, J = 7.3 Hz, 1-H), 3.75 (m, 2 H, 2-H and 3-H), 3.65 (t, 1 H, J = 5.4 Hz, 1′-H), 3.25 (t, 1 H, J = 5.4 Hz, 5′-H), 3.10 (t, 1 H, J = 5.6 Hz, 6′-H), 2.5 (m, 1 H, endo 5-H), 2.2 (m, 1 H, endo 7-H), 1.4 (m, 2 H, endo 6-H and exo 7-H), 1.2 (m, 1 H, exo 5-H), 0.9 (m, 1 H, exo 6-H); HRMS, m/e (relative intensity) 529 (M^+ − CN, 0.1), 441 (0.3), 311 (16), 279 (100), 252 (48); (M^+ − CN) calcd for ^{98}Mo in $C_{23}H_{20}O_5MoMn$ 528.9777, found 528.9624.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-cyano-7-*exo*-methylcycloheptenyl)molybdenum (32). This was obtained as a single regioisomer and not as the mixture of adducts previously described.[15] Sodium cyanide (1.5 equiv, 2.03 mmol, 99 mg) dissolved in water (1 mL) was added to a stirred suspension of dicarbonyl(cyclopentadienyl)(5-*exo*-methylcycloheptadiene)molybdenum hexafluorophosphate[15] (636 mg, 1.35 mmol) in acetonitrile (10 mL) at room temperature. After being stirred for 1 h, the reaction mixture was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by flash chromatography (silica gel/CH_2Cl_2) gave the yellow crystalline complex **32** (375 mg, 79%). An analytical sample was obtained by recrystallization from a 1:1 mixture of petroleum ether/pentane: mp 136–138 °C; IR ($CHCl_3$) ν_{max} 2240 (w), 1945, 1860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.31 (s, 5 H, Cp), 4.02 (br d, 1 H, J = 7.9 Hz, 1-H), 3.89 (d, 1 H, J = 7.9 Hz, 3-H), 3.78 (t, 1 H, J = 8.5 Hz, 2-H), 3.22 (m, 1 H, endo 4-H), 2.34 (m, 1 H, endo 5-H), 1.51 (m, 1 H, endo 7-H), 1.35 (m, 1 H, endo 6-H, partially obscured), 1.22 (d, 3 H, J = 6.9 Hz, methyl), 1.13 (m, 1 H, exo 5-H, partially obscured), 0.78 (m, 1 H, exo 6-H). Anal. Calcd for $C_{16}H_{17}NMoO_2$: C, 54.71; H, 4.88; N, 3.99. Found: C, 54.85; H, 5.05; N, 3.65.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-cyano-7-*exo*-methylcycloheptenyl)molybdenum (34a). The cyano complex **32** (50 mg, 0.142 mmol) dissolved in THF (0.5 mL) was added dropwise to LDA (1.2 equiv) in THF at −78 °C. After being stirred for 0.5 h, the solution was quenched with water (excess, 0.1 mL) and warmed to room temperature. The usual workup and purification by preparative TLC as described above yielded the yellow crystalline complex **34a** (45 mg, 90%). An analytical sample was obtained by recrystallization from petroleum ether/pentane: mp 166–168 °C; IR ($CHCl_3$) ν_{max} 2250 (w), 1955, 1870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (s, 5 H, Cp), 4.05 (br d, 1 H, J = 8.7 Hz, 1-H), 3.98 (d, 1 H, J = 8.7 Hz, 3-H), 3.76 (t, 1 H, J = 8.7 Hz, 2-H), 3.53 (td, 1 H, J = 11.6, 3.0 Hz, exo 4-H), 2.3 (m, 1 H, endo 5-H), 1.7–1.4 (m, 2 H, endo 6-H and endo 7-H), 1.14 (d, 3 H, J = 7.0 Hz, methyl), 0.9–0.6 (m, 2 H, exo 5-H and exo 6-H). Anal. Calcd for $C_{16}H_{17}NMoO_2$: C, 54.70; H, 4.84; N, 3.99. Found: C, 54.40; H, 5.00; N, 4.15.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]-7-*exo*-methylcycloheptenyl]molybdenum (34c). The procedure was the same as for complex **33c**. Purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) afforded the yellow complex **34c**: 84%; IR ($CHCl_3$) ν_{max} 2240 (w), 1950, 1870, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (s, 5 H, Cp), 4.17 (d, 1 H, J = 8.8 Hz, 1-H), 3.92 (d, 1 H, J = 8.8 Hz, 3-H), 3.72 (t, 1 H, J = 8.8 Hz, 2-H), 3.53 (t, 1 H, J = 5.9 Hz, CH_2CH), 2.63 (d, 2 H, J = 5.9 Hz, CH_2CH), 2.22 (m, 1 H, endo 5-H), 1.49 (s, 9 H, *tert*-butyl), 1.46 (s, 9 H, *tert*-butyl), 1.12 (d, 3 H, J = 7.1 Hz, methyl), other resonances are obscured by methyl and *tert*-butyl peaks; HRMS, m/e (relative intensity) 553 (M^+ − CO, 1), 525 (M^+ − 2CO, 4), 451 (29), 386 (40), 340 (100), 120 (40); (M^+ − CO) calcd for ^{98}Mo in $C_{28}H_{37}NMoO_6$ 553.1726, found 553.1720.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[1-methoxy-2-(η^1-Fp)ethyl]cyclohexenyl]molybdenum (35). Using the general procedure the carbanion solution from **22** (0.5 g, 1.55 mmol) was added via a cannula to a stirred suspension of Fp(η^2-methyl vinyl ether)PF_6 (1.2 equiv, 1.85 mmol, 707 mg; prepared by a literature procedure[20]) in THF (5 mL) at −78 °C; the resultant mixture was stirred for 1 h, warmed to room temperature, extracted with diethyl ether, washed with a 10% aqueous HCl solution, brine, and water, dried ($MgSO_4$), and concentrated to give the dark red crude complex **35** (862 mg, 100%). The complex proved to be unstable, hence it was taken directly to the next step without purification: IR ($CHCl_3$) ν_{max} 2240 (w), 2010, 1950, 1870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (s, 5 H, Mo–Cp), 4.85 (s, 5 H, Fe–Cp), 4.3 (t, 1 H, J = 7.1 Hz, 2-H), 3.85 (m, 1 H, 1-H), 3.65 (d, 1 H, J = 7.1 Hz, 3-H), 3.5 (s, 3 H, OMe), 3.1 (m, 1 H, $CHOMe$), 2.0–0.5 (m, 6 H).

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[Fp(η^2-vinyl)]cyclohexenyl]molybdenum Tetrafluoroborate (37). The crude complex **35** from the previous step (862 mg, 1.55 mmol) was dissolved in methylene chloride (10 mL) at −78 °C. Tetrafluoroboric acid–diethyl ether complex (1.0 equiv, 1.55 mmol, 0.36 mL) was added dropwise and the mixture was stirred for 1 h and then warmed to room temperature. The dark brown solution was added dropwise to dry diethyl ether (50 mL), agitated by nitrogen flow. The yellow cationic Fp–olefin complex **33** precipitated out immediately. The precipitate was filtered, washed with ether, and dried to give the yellow crystals of the complex **37**: 808 mg, 85%; IR (CH_3CN) ν_{max} 2080, 2040, 1950, 1870 cm^{-1}; ^1H NMR (CD_3CN) δ 5.8–5.2 (m, 3 H, Fp–vinyl), 5.65 (s, 5 H, Mo–Cp), 5.45 (s, 5 H, Fe–Cp), 4.5 (t, 1 H, J = 7.1 Hz, 2-H), 4.0 (m, 2 H, 1-H and 3-H), 2.5–0.8 (m, 4 H).

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-cyano-4-*exo*-vinylcyclohexenyl)molybdenum (39). Method A. Sodium iodide (1.2 equiv, 0.489 mmol, 73 mg) was added to a stirred yellow solution of the Fp–vinyl complex **37** (250 mg, 0.408 mmol) in acetone (5 mL) at room temperature. After being stirred for 1 h, the dark brown solution was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification was attempted using several different solvent mixtures, but failed to separate the Fp iodide side product from the desired complex **41**.

Method B. The Fp–vinyl complex **37** (250 mg, 0.408 mmol) dissolved in acetonitrile (5 mL) was refluxed gently for 15 min. After being cooled

to room temperature, the reaction mixture was extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the pure complex **39**: 131 mg, 92%; IR ($CHCl_3$) ν_{max} 2230 (w), 1955, 1875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (dd, 1 H, J = 16.9, 9.9 Hz), 5.56 (d, 1 H, J = 16.9 Hz), 5.34 (s, 5 H, Cp), 5.19 (d, 1 H, J = 9.9 Hz), 4.28 (t, 1 H, J = 7.2 Hz, 2-H), 3.82 (m, 1 H, 1-H), 3.49 (d, 1 H, J = 7.2 Hz, 3-H), 1.98 (m, 1 H, endo 6-H), 1.79 (m, 1 H, exo 6-H), 1.31 (dd, 1 H, J = 13.7, 5.9 Hz, endo 5-H), 0.99 (m, 1 H, exo 5-H); HRMS, m/e (relative intensity) 351 (M^+, 12), 323 ($M^+ - CO$, 3), 295 ($M^+ - 2CO$, 21), 268 (100), 189 (22), 151 (16); M^+ calcd for ^{98}Mo in $C_{16}H_{15}NMoO_2$ 351.0158, found 351.0161.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[1-methoxy-2-(η^1-Fp)ethyl]cycloheptenyl]molybdenum (36). Complex **31** (0.5 g, 1.48 mmol) was converted to the dark red crude complex **36** (847 mg, 100%) by using the procedure described earlier. The complex was taken directly to the next step without purification: IR ($CHCl_3$) ν_{max} 2240 (w), 2020, 1960, 1875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (s, 5 H, Mo–Cp), 4.85 (s, 5 H, Fe–Cp), 4.39 (m, 1 H, 1-H), 3.80 (m, 2 H, 2-H and 3-H), 3.67 (s, 3 H, OMe), 3.30 (m, 1 H, C*H*OMe), 2.3–0.9 (m, 8 H).

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*endo*-cyano-4-*exo*-[Fp(η^2-vinyl)]cycloheptenyl]molybdenum Tetrafluoroborate (38). The crude complex **36** from the previous step (847 mg, 1.48 mmol) was dissolved in methylene chloride (10 mL) at −78 °C. Tetrafluoroboric acid–diethyl ether complex (1.0 equiv, 1.48 mmol, 0.34 mL) was added dropwise and the resultant mixture was stirred for 1 h. The dark brown solution was added dropwise to dry diethyl ether (50 mL) being agitated with nitrogen. The precipitate of the cationic Fp–olefin complex was filtered, washed with ether, and dried to give the yellow crystals of the complex **38**: 705 mg, 76%; IR (CH_3CN) ν_{max} 2070, 2040, 1950, 1860 cm^{-1}; ^1H NMR (CD_3CN) δ 6.3–5.2 (m, 3 H, Fp–vinyl), 5.78 (s, 5 H, Mo–Cp), 5.41 (s, 5 H, Fe–Cp), 4.53 (m, 1 H, 1-H), 4.01 (m, 2 H, 2-H and 3-H), 2.5–1.2 (m, 6 H); HRMS, m/e (relative intensity) 365 ($M^+ - FpBF_4$, 3), 309 (10), 280 (36), 185 (100), 121 (30).

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-cyano-4-*exo*-vinylcycloheptenyl)molybdenum (40). The Fp–vinyl complex **38** (300 mg, 0.478 mmol) dissolved in acetonitrile (10 mL) was refluxed gently for 15 min, cooled to room temperature, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the yellow crystalline complex **40**: 162 mg, 93%; mp 148–150 °C; IR ($CHCl_3$) ν_{max} 2230 (w), 1955, 1870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.11 (dd, 1 H, J = 16.9, 10.1 Hz), 5.64 (d, 1 H, J = 16.9 Hz), 5.30 (s, 5 H, Cp), 5.29 (d, 1 H, J = 10.1 Hz), 4.47 (br t, 1 H, J = 8.0 Hz, 1-H), 3.86 (m, 2 H, 2-H and 3-H), 2.51 (m, 1 H, endo 5-H), 2.17 (m, 1 H, endo 7-H), 1.57 (m, 1 H, exo 7-H), 1.30 (m, 3 H, exo 5-H, endo 6-H and exo 6-H). Anal. Calcd for $C_{17}H_{17}NMoO_2$: C, 56.21; H, 4.72; N, 3.85. Found: C, 56.64; H, 5.18; N, 3.50.

Di-*tert*-Butyl (1-Cyano-4-iodo-2-cyclohexenyl)methylenemalonate (41). Iodine (4.0 equiv, 0.36 mmol, 92 mg) dissolved in acetonitrile (2 mL) was added to a stirred solution of the π-allyl complex **24c** (50 mg, 0.09 mmol) in acetonitrile (2 mL) at room temperature. The reaction was monitored by IR, which indicated complete decomplexation after 1 h. The mixture was extracted with ether, and the combined ether extracts were washed with sodium thiosulfate and water, dried ($MgSO_4$), and concentrated to give the crude product **41** (34 mg, 81%). Attempts to purify this material chromatographically led to decomposition: IR ($CHCl_3$) ν_{max} 2240, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19 (dd, 1 H, J = 9.5, 5.1 Hz), 5.42 (d, 1 H, J = 9.5 Hz), 5.03 (m, 1 H), 3.38 (t, 1 H, J = 6.1 Hz), 2.36 (dd, 2 H, J = 6.1, 3.4 Hz), 2.3–1.5 (m, 4 H), 1.49 (s, 9 H, *tert*-butyl), 1.45 (s, 9 H, *tert*-butyl). Instability of the complex prevented further characterization.

7-Bromo-3-cyanocyclohept-1-ene and Isomer (42 and 43). Bromine (1.0 equiv, 0.15 mmol, 0.24 g of 10% solution in methylene chloride) was added dropwise to a stirred solution of the π-allyl complex **31** (50 mg, 0.15 mmol) in THF (10 mL) at −78 °C. The reaction was monitored by IR, which indicated complete decomplexation after 2 h. The reaction mixture was warmed to room temperature and extracted with ether. The combined ether extracts were washed with saturated NaCl solution and water, dried ($MgSO_4$), and concentrated to give the crude product as a 5:1 mixture of two regioisomers, **42** and **43**. Purification by flash chromatography (silica gel/40% ethyl acetate in hexanes) gave the mixture of isomers (19 mg, 64%) free from impurities: IR ($CHCl_3$) ν_{max} 2240 (w), 1410, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.13 (ddd, 1 H, J = 11.5, 5.7, 1.9 Hz, CH=C*H*CHBr), 5.73 (dd, 1 H, J = 11.5, 4.9 Hz, CH=C*H*CHCN), 4.85 (m, 1 H, CHBr), 3.55 (m, 1 H, CHCN), 2.3–1.8 (m, 6 H). The minor isomer showed peaks at δ 5.9 (vinyl), 4.8 (CHBr), and 3.4 (CHCN).

3-Cyano-7-hydroxycyclohept-1-ene and Isomer (44 and 45). Nitrosyl hexafluorophosphate (1.0 equiv, 0.15 mmol, 26 mg) was added to a stirred solution of the π-allyl complex **31** (50 mg, 0.15 mmol) in acetonitrile (10 mL) at 0 °C. After stirring for 15 min, water (100 equiv, 1.5 mmol, 27 mg) was added dropwise and stirring was continued for 1 h at room temperature. The reaction mixture was extracted with ether, washed with water, dried ($MgSO_4$), and concentrated to give the crude product as a 5:1 mixture of two regioisomers, **44** and **45**. Purification by preparative TLC (silica gel/70% ethyl acetate in hexanes) gave the mixture of isomers (12 mg, 61%) free from impurities: IR ($CHCl_3$) ν_{max} 3400 (br, OH), 2240 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95 (br d, 1 H, J = 12.0 Hz), 5.71 (m, 1 H), 4.38 (m, 1 H, C*H*OH), 3.35 (m, 1 H, C*H*CN), 2.2–1.5 (m, 6 H).

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-cyclohexenyl)molybdenum (46a). General Procedure for Decyanation. The cyano complex **22** (50 mg, 0.155 mmol) dissolved in THF (1.0 mL) was added to a flame-dried 4-mL reaction vial equipped with a nitrogen-filled balloon at −78 °C. *n*-Butyllithium (1.2 equiv, 0.186 mmol, 75 μL of a 2.5 M solution in hexanes), *or sec*-butyllithium (1.2 equiv, 0.186 mmol, 0.14 mL of a 1.3 M solution in cyclohexane), *or tert*-butyllithium (1.2 equiv, 0.186 mmol, 0.11 mL of a 1.7 M solution in pentane) was added dropwise. The solution changed from yellow to orange as the decyanated carbanion was generated. After stirring for 0.5 h, water (excess, 0.1 mL) was added, and the reaction vessel was warmed to room temperature, whereby the solution became yellow. Extraction with ether, washing with brine, drying ($MgSO_4$), and concentration gave the crude product. Purification was by preparative TLC (silica gel/50% ethyl acetate in hexanes) to give the yellow crystalline complex **46** (44 mg, 96%). The IR and the ^1H NMR spectra of the product were identical with that reported in literature.[15,16]

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-deuteriocyclohexenyl)molybdenum (46b). The general procedure was followed. After stirring for 0.5 h to generate the decyanated carbanion, deuterium oxide (excess, 0.1 mL) was added, and the reaction vessel was warmed to room temperature. The usual ether workup and purification by preparative TLC yielded the yellow complex **46b** (35 mg, 84%).

The IR and the ^1H NMR spectra of the monodeuterio complex compared well with the perprotio parent complex. The loss of vicinal J_{HH} coupling (14.5 Hz) at the endo-4-H resonance and decreased intensity of the exo-4-H resonance were the major differences between the ^1H NMR spectra of the parent perprotio and the monodeuterio derivative.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-*exo*-methylcyclohexenyl)molybdenum (47a). Following the general procedure, complex **23** (50 mg, 0.148 mmol) yielded the yellow crystalline complex **47a** (45 mg, 97%). The IR and the ^1H NMR spectra of the product were identical with that reported in literature.[15,16]

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*exo*-deuterio-6-*exo*-methylcyclohexenyl)molybdenum (47b). Following the general procedure, with D_2O quench, complex **23** (50 mg) gave the yellow complex **47b** (41 mg, 89%). The IR and the ^1H NMR spectra of the monodeuterio complex compared well with the perprotio parent complex. The loss of vicinal couplings at the endo-5-H and exo-5-H resonances, loss of geminal coupling at the endo-4-H resonance, and the loss of resonance for exo 4-H at 2.03 ppm were the major differences between the ^1H NMR spectra of the parent perprotio and the monodeuterio derivative.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]cyclohexenyl]molybdenum (46c). The general procedure was used to generate the decyanated carbanion from complex **22** (50 mg). Di-*tert*-butyl methylenemalonate (1.2 equiv, 0.1866 mmol, 42 mg) was added, and the resultant mixture was stirred for 1 h. The mixture was warmed to room temperature and extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification was by preparative TLC (silica gel/50% ethyl acetate in hexanes) to yield the yellow complex **46c**: 70 mg, 86%; IR ($CHCl_3$) ν_{max} 1935, 1850, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (s, 5 H, Cp), 4.15 (t, 1 H, J = 7.2 Hz, 2-H), 3.69 (m, 1 H, 3-H), 3.61 (m, 1 H, 1-H), 3.30 (t, 1 H, J = 7.6 Hz), 2.46 (m, 1 H, endo 4-H), 2.0 (m, 2 H), 1.45 (s, 18 H, *tert*-butyl), 0.9 (m, 1 H, endo 5-H), 0.5 (m, 1 H, exo 5-H), other resonances are obscured by the two *tert*-butyl peaks; HRMS, m/e (relative intensity) 528 (M^+), 500 ($M^+ - CO$, 5), 472 ($M^+ - 2CO$, 36), 414 (35), 358 (100), 312 (30); M^+ calcd for ^{98}Mo in $C_{25}H_{34}MoO_6$ 528.1410, found 528.1430.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-(hydroxybenzyl)cyclohexenyl]molybdenum (46d). The general procedure was used to generate the decyanated carbanion. Benzaldehyde (1.2 equiv, 0.186 mmol, 19 μL) was added, and the resultant mixture was stirred for 2 h. The mixture was warmed to room temperature and extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated to give a 6:5 mixture of two diastereomers of the complex **46d** (51 mg, 81%). The two diastereomers were separated by preparative TLC (40% ethyl acetate in hexanes): IR ($CHCl_3$) ν_{max} 3500, 1945, 1860 cm^{-1}; HRMS, m/e (relative intensity) 405 (M^+, 2), 377 ($M^+ - CO$, 1), 328 (29), 241 (35), 169 (22), 131 (34), 119 (29), 69 (100); M^+ calcd for ^{98}Mo in $C_{20}H_{20}MoO_3$ 405.0470, found 405.0465.

Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.27 (s, 5 H, Cp), 4.53 (d, 1 H, J = 7.4 Hz, PhC*H*OH), 4.30 (t, 1 H, J = 7.2 Hz, 2-H), 3.76 (m, 2 H, 1-H and 3-H), 2.0 (m, 3 H, endo 4-H, endo 6-H, and OH exchanged D_2O), 1.6 (m, 1 H, exo 5-H), 0.7 (dd, 1 H, J = 15.0, 6.0 Hz, endo 5-H), 0.4 (m, 1 H, exo 5-H).

Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.22 (s, 5 H, Cp), 4.43 (d, 1 H, J = 7.4 Hz, PhC*H*OH), 4.17 (t, 1 H, J = 7.2 Hz, 2-H), 3.74 (m, 1 H, 1-H), 3.05 (m, 1 H, 3-H), 2.0 (m, 3 H, endo 4-H, endo 6-H, and OH exchanged D_2O), 1.6 (m, 1 H, exo 6-H), 1.3 (dd, 1 H, J = 15.0, 6.0 Hz, endo 5-H), 0.4 (m, 1 H, exo 5-H).

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[2-(methoxycarbonyl)-3-oxocyclopentyl]cyclohexenyl]molybdenum (46e). By use of the general procedure, followed by reaction with **26** (1.2 equiv, 0.186 mmol, 26 mg) and purification by TLC (silica gel/40% ethyl acetate in hexanes), there was obtained a 9:5 mixture of two diastereomers of the complex **46e**: 52 mg, 81%; IR ($CHCl_3$) ν_{max} 1945, 1865, 1755, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.31 (s, Cp, minor), 5.28 (s, Cp, major), 4.21 (t, J = 7.2 Hz, 2-H, minor), 4.10 (t, J = 7.2 Hz, 2-H, major), 3.79 (s, CO_2Me, major), 3.73 (s, CO_2Me, minor), 3.70 (m, 1 H, 3-H), 3.44 (m, 1 H, 1-H), 3.11 (d, J = 11.2 Hz, C*H*CO_2Me, major), 2.94 (d, J = 11.2 Hz, C*H*CO_2Me, minor), 2.7 (m, 1 H, $CH_2CHCHCO_2Me$, major), 2.4 (m, 4 H), 1.95 (m, 1 H), 1.6 (m, 2 H), 1.05 (m, 1 H), 0.6 (m, 1 H); HRMS, *m/e* (relative intensity) 440 (M^+, 1.6), 384 (M^+ - 2CO, 3.4), 361 (58), 329 (50), 301 (38), 273 (20), 241 (22), 141 (73), 109 (100); M^+ calcd for ^{98}Mo in $C_{20}H_{22}MoO_5$ 440.0522, found 440.0532.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[tricarbonyl(2-5-η-4-methoxy-1-*endo*-protiocyclohexadienyl)iron]cyclohexenyl]molybdenum (46g). After being stirred for 0.5 h at −78 °C, the orange decyanated carbanion solution, obtained by the general procedure, was transferred via a cannula to a suspension of the dienyl iron complex **28** (1.5 equiv, 0.232 mmol, 92 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The usual ether workup and purification by preparative TLC (silica gel/40% ethyl acetate in hexanes) yielded the yellow oily complex **46g**: 54 mg, 64%; IR ($CHCl_3$) ν_{max} 2040, 1955, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.28 (s, 5 H, Cp), 5.06 (dd, 1 H, J = 6.4, 2.3 Hz, 3′-H), 4.23 (t, 1 H, J = 7.3 Hz, 2-H), 3.68 (m, 1 H, 1-H), 3.52 (m, 1 H, 3-H), 3.46 (s, 3 H, OMe), 3.32 (m, 1 H, 5′-H), 2.65 (m, 2 H, endo 4-H and exo 1′-H), 2.0–0.5 (m, 6 H); HRMS, *m/e* (relative intensity) 548 (M^+, 2.5), 520 (M^+ - CO, 2), 464 (M^+ - 3CO, 1), 436 (M^+ - 4CO, 4), 408 (M^+ - 5CO, 6), 299 (88), 271 (41), 249 (11), 243 (3), 221 (96), 165 (40); M^+ calcd for ^{98}Mo in $C_{23}H_{22}O_6MoFe$ 547.9820, found 547.9816.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[tricarbonyl(1-5-η-6-*endo*-protiocyclohexadienyl)manganese]cyclohexenyl]molybdenum (46h). After being stirred for 0.5 h, the orange solution of the decyanated carbanion was added via a cannula to a stirred suspension of the arenemanganese complex **29** (1.5 equiv, 0.232 mmol, 84 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The usual ether workup and purification by preparative TLC (silica gel/70% ethyl acetate in hexanes) yielded the yellow crystalline complex **46h** (66 mg, 83%). An analytical sample was obtained by recrystallization from a 1:1 mixture of petroleum ether and pentane: mp 300 °C; IR ($CHCl_3$) ν_{max} 2020, 1950, 1860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.75 (t, 1 H, J = 5.4 Hz, 3′-H), 5.27 (s, 5 H, Cp), 4.88 (t, 1 H, J = 6.1 Hz, 2′-H), 4.77 (t, 1 H, J = 6.1 Hz, 4′-H), 4.12 (t, 1 H, J = 7.2 Hz, 2-H), 3.67 (m, 1 H, 1-H), 3.47 (m, 2 H, 3-H and 1′-H), 3.21 (t, 1 H, J = 5.4 Hz, 5′-H), 2.2 (m, 2 H, endo 4-H and 6′-H), 1.8 (m, 1 H, endo 6-H), 1.5 (m, 1 H, exo 6-H), 1.2 (m, 1 H, endo 5-H), 0.8 (m, 1 H, exo 5-H). Anal. Calcd for $C_{22}H_{19}O_5MoMn$: C, 51.88; H, 3.72. Found: C, 52.00; H, 4.09.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[tricarbonyl(1-5-η-2,4-dimethoxy-6-*endo*-protiocyclohexadienyl)manganese]cyclohexenyl]molybdenum (46i). After being stirred for 0.5 h, the orange solution of the decyanated carbanion was added via a cannula to a stirred suspension of the arenemanganese complex **30** (1.5 equiv, 0.232 mmol, 98 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction mixture was warmed to room temperature and submitted to the usual workup and purification by preparative TLC (silica gel/70% ethyl acetate in hexanes) to yield the yellow complex **46i**: 65 mg, 73%; IR ($CHCl_3$) ν_{max} 2010, 1935, 1855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.69 (s, 1 H, 3′-H), 5.27 (s, 5 H, Cp), 4.15 (t, 1 H, J = 7.2 Hz, 2-H), 3.66 (m, 1 H, 1-H), 3.56 (s, 3 H, 2′-methoxy), 3.44 (s, 3 H, 4′-methoxy, diastereotopic), 3.42 (m, 1 H, 3-H), 3.27 (br d, 1 H, J = 5.9 Hz, 1′-H), 3.11 (br d, 1 H, J = 5.9 Hz, 5′-H), 2.52 (m, 2 H, endo 4-H and 6′-H), 1.9 (m, 1 H, endo 6-H), 1.6 (m, 1 H, exo 6-H), 0.8 (m, 1 H, endo 5-H), 0.1 (m, 1 H, exo 5-H); HRMS, *m/e* (relative intensity) 576 (M^+, 0.2), 548 (M^+ - CO, 0.4), 520 (M^+ - 2CO, 0.2), 464 (M^+ - 4CO, 0.3), 436 (M^+ - 5CO, 1.1), 378 (8), 277 (100), 221 (57), 194 (10), 138 (8); M^+ calcd for ^{98}Mo in $C_{24}H_{23}O_7MoMn$ 575.9880, found 575.9863.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[dicarbonyl(η^5-cyclopentadienyl)(1-3-η-4-*endo*-protiocyclohexenyl)molybdenum]cyclohexenyl]molybdenum (46f). After being stirred for 0.5 h, the orange solution of the decyanated carbanion was added via a cannula to a stirred suspension of the dienemolybdenum complex **27** (1.5 equiv, 0.232 mmol, 103 mg) in THF (5 mL) at −78 °C. After being stirred for 1 h, the reaction was worked up as above, and the product **46f** was purified by preparative TLC (silica gel/40% ethyl acetate in hexanes): 57 mg, 62%; IR ($CHCl_3$) ν_{max} 1940, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 5 H, Cp), 5.29 (s, 5 H, Cp), 4.32 (m, 2 H, 2-H), 3.76 (m, 4 H, 1-H and 3-H), 2.0 (m, 2 H, endo 6-H), 1.75 (m, 2 H, endo 4-H), 1.6 (m, 2 H, exo 6-H), 1.05 (m, 2 H, endo 5-H), 0.4 (m, 2 H, exo 5-H); HRMS, *m/e* (relative intensity) 596 (M^+, 1.5), 568 (M^+ - CO, 1.2), 540 (M^+ - 2CO, 1.3), 523 (M^+ - 3CO, 1.6), 484 (M - 4CO, 1.7), 474 (22), 298 (38), 270 (22), 241 (100); M^+ calcd for ^{98}Mo in $C_{26}H_{26}Mo_2O_4$ 595.9932, found 595.9930.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-cycloheptenyl)molybdenum (48a). *tert*-Butyllithium (1.2 equiv, 0.178 mmol, 0.11 mL of a 1.7 M solution in pentane) was added to a stirred solution of the cyano complex **31** (50 mg, 0.148 mmol) in THF (2 mL) at −78 °C. After stirring for 0.5 h, the orange solution of the decyanated carbanion was quenched with water (excess, 0.1 mL), and the reaction vessel was warmed to room temperature. The usual workup and purification by preparative TLC as described above yielded the yellow crystalline complex **48a** (40 mg, 86%). The IR and the ^{1}H NMR spectra of the product were identical with that reported in literature.[15] The IR and the ^{1}H NMR spectra of the monodeuterio complex **48b** compared well with the perprotio parent complex. The loss of vicinal couplings at the 3-H, endo-5-H, and exo-5-H resonances, loss of geminal coupling at the endo-4-H resonance, and decreased intensity of the exo-4-H resonance were the major differences between the ^{1}H NMR spectra of the parent perprotio and the monodeuterio derivative.

Dicarbonyl(η^5-cyclopentadienyl)[1-3-η-4-*exo*-[2,2-bis(*tert*-butoxycarbonyl)ethyl]cycloheptenyl]molybdenum (48c). Subjection of **31** (50 mg, 0.148 mmol) to the general procedure yielded **48c**: IR ($CHCl_3$) ν_{max} 1935, 1850, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.24 (s, 5 H, Cp), 4.13 (m, 1 H, 1-H), 3.7 (m, 2 H, 2-H and 3-H), 3.29 (t, 1 H, J = 7.2 Hz, CH_2CH), 2.53 (m, 1 H, endo 4-H), 2.5–2.0 (m, 4 H, endo 5-H, endo 7-H, and CH_2CH), 1.46 (s, 9 H, *tert*-butyl), 1.45 (s, 9 H, *tert*-butyl), 1.2 (m, 2 H, endo 6-H and exo 7-H), 0.8 (m, 1 H, exo 5-H), 0.4 (m, 1 H, exo 6-H); HRMS, *m/e* (relative intensity) 542 (M^+, 8), 486 (M^+ - 2CO, 8), 271 (100), 326 (32), 183 (19), 105 (19); M^+ calcd for ^{98}Mo in $C_{26}H_{36}MoO_6$ 542.1567, found 542.1580.

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