Efficient Synthesis of (η^5-Cyclopentadienyl)(η^3-allyl)Mo(CO)$_2$ Complexes from Allylic Diphenylphosphinates

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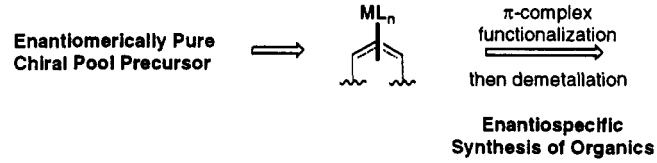
Received August 19, 1992

(η^5-Cyclopentadienyl)(η^3-allyl)Mo(CO)$_2$ complexes are readily prepared by the reaction of molybdenum hexacarbonyl or tris(acetonitrile)molybdenum tricarbonyl with allylic diphenylphosphinates followed by treatment with cyclopentadienyllithium. The yields, accessibility of precursors, and operational simplicity of this method compare favorably with existing methods based upon allylic halides.

Introduction

In recent years, stoichiometric metal π-complexes of various unsaturated ligands have been used to significant advantage in the stereocontrolled construction of substituted cyclic and acyclic hydrocarbons[1-19] and heterocycles.[20-28] A specific subset of these processes holds great promise for *enantiospecific organic synthesis*: readily available, enantiomerically pure materials from the chiral pool can be stoichiometrically converted into enantiomerically pure metal π-complexes, and these complexes can be subjected to metal-mediated *multiple sequential* stereospecific and regiospecific functionalizations. Ultimate demetalation provides *enantiomerically pure* compounds (Scheme I).[22,29]

Scheme I



Of the potential metal–ligand systems that can be probed by this chemistry, previous experience has demonstrated that CpMo(CO)$_2$-derived π-allyl and π-diene complexes are exceptionally versatile. The fundamental chemistry surrounding the synthesis and transformations of CpMo(CO)$_2$-derived π-complexes developed by Faller and Green and subsequently utilized by Pearson is acknowledged.[1,17,19,30-40]

Allylic halides are the traditional moieties used for generation of π-allylmolybdenum complexes;[41] however, the formation of allylic halides is often complicated by stereochemical and regiochemical scrambling, processes that would seriously degrade the potential of this chemistry for enantiospecific synthesis. In addition to the stereochemical difficulties associated with allylic halides, many synthetically interesting examples would be expected to have very limited shelf lives. For example, 3-chlorocy-

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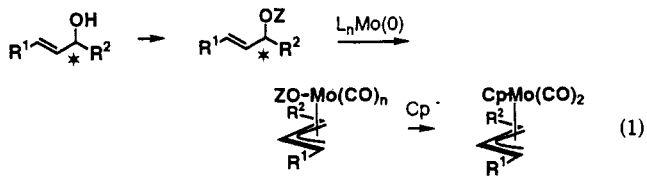
clopentene rapidly polymerizes at room temperature[42] and is usually used immediately after preparation.

The use of allylic substrates other than halides for the stoichiometric formation of π-allylmolybdenum complexes has been barely explored. Allylic tosylates and methanesulfonates are too unstable to be generally useful. Allylic acetates would be superior starting materials, but these substrates, though participating effectively in π-allylmolybdenum formation in some cases,[19,29,43] have not proven generally viable.[44] There is one literature report of allyl trifluoroacetate[45] participating in π-allylmolybdenum formation.

With this background in hand, an investigation was begun of allylic alcohol-derived leaving groups that could be used to prepare π-allylmolybdenum complexes. To meet the ultimate requirements of enantiospecific synthesis from chiral pool-derived precursors, three hurdles had to be overcome. First, the activated allylic substrates must be prepared easily and generally from diverse allylic alcohols. Second, the activated allylic substrates must react stereospecifically with a source of zerovalent molybdenum generating tractable π-allylmolybdenum intermediates that, third, would be suitable for reaction with an appropriate cyclopentadienylating reagent in order to generate the desired $(\eta^5\text{-Cp})(\eta^3\text{-allyl})\text{Mo(CO)}_2$ complexes (eq 1). These criteria led, after some preliminary experiments with allylic acetates and Mo(0) reagents, to a study of the reaction of allylic diphenylphosphinate esters with zerovalent molybdenum sources. Delineated below are the results of an initial study of the preparation of π-allylmolybdenum complexes from cyclic and acyclic allylic diphenylphosphinates, where maintenance of olefin stereochemistry (*Z*- and *E*-geometry) was confirmed. The facial stereochemistry of the formation of π-allylmolybdenum complexes from allylic diphenylphosphinate esters derived from chiral nonracemic alcohols will be addressed separately. Neither allylic phosphate nor diphenylphosphinate esters have been used in π-allylmolybdenum chemistry. The use of allylic phosphate esters for metal-mediated substitutions is increasing in frequency,[46-48] while there appears to be only one report of a palladium-catalyzed substitution of an allylic diphenylphosphinate.[49]



(1)

Results and Discussion

Allylic Acetates with Mo(0) Reagents. To develop an efficient means of producing π-allylmolybdenum complexes from allylic alcohol-derived leaving groups, the reactivity of the allylic leaving group (OZ in eq 1) must be matched with that of the source of zerovalent molybdenum, L_nM^0, and with the reagent used to introduce the cyclopentadienyl group. π-Allylmolybdenum complexes are formed from allylic acetates and $Mo(CO)_3(CH_3CN)_3$ on prolonged reflux (18 h) in acetonitrile, but these conditions preclude the use of thermally sensitive substrates. In principle, the generality of the π-allylmolybdenum formation could be improved by using a more reactive source of Mo(0). (Diglyme)$Mo(CO)_3$, a known Mo(0) source[50-56] whose previous use was confined to dative-type substitutions of dienes, trienes, phosphines, etc.,[57-66] was prepared and investigated for reaction with allylic acetates. Reaction of (diglyme)$Mo(CO_3)$ with allyl acetate in THF, DME, Et_2O, and CH_2Cl_2 was rapid at room temperature, in all cases, but addition of LiCp provided only moderate yields of $(\eta^5\text{-Cp})(\eta^3\text{-allyl})\text{Mo(CO)}_2$ complexes. The weakly bound diglyme ligand is presumed to undergo ligand exchange with most of these solvents.[50,53,56] Not surprisingly, thallium cyclopentadienide was an inferior reagent for displacement of acetate. Neither (dimethylformamide)$_3$Mo(CO)$_3$[67] nor the very air-sensitive, slightly pyrophoric substance that precipitated after prolonged refluxing of $Mo(CO)_6$ in 1,2-dimethoxyethane [presumed, but not proven, to be $(DME)_2Mo_2(CO)_6$ on the basis of analogy with the diglyme-derived product] was found to offer any significant advantage in the synthesis of π-allylmolybdenum complexes from allylic acetates.

Preparation of Molybdenum π-Allyl Complexes from Diphenylphosphinate Esters of Allylic Alcohols. Attention was next turned to the reaction of zerovalent molybdenum sources with allylic phosphinates on the assumption that these substrates would be activated for departure, but still be of sufficient stability to facilitate preparation and handling. Because few allylic diphenylphosphinic esters were known,[68-70] new procedures for the synthesis of these substrates had to be developed.[71] Exposure of 2-cyclohexenyl-1 diphenylphosphinate (1) to

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(44) Simple allylic acetates that survive prolonged heating with $Mo(CO)_3(CH_3CN)_3$ in CH_3CN, or somewhat activated allylic acetates (γ-acetoxy-α,β-unsaturated carbonyls),[29] will produce π-allylmolybdenum complexes in good yields; however, it has been observed in these laboratories that more functionalized and sensitive allylic acetates are not converted efficiently into the corresponding π-allyl complexes.
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Table I. Preparation of π-Allylmolybdenum Complexes from Allylic Diphenylphosphinates

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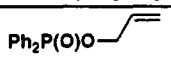
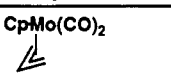
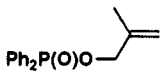
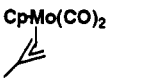
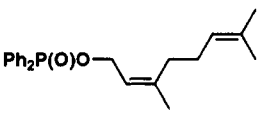
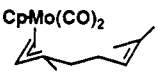
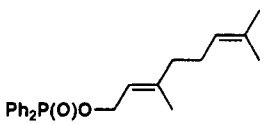
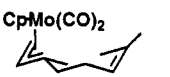
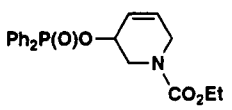
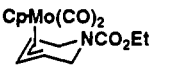
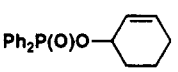
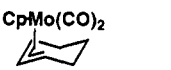
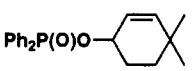
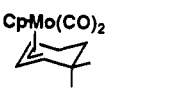
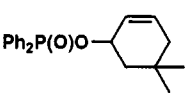
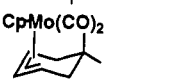
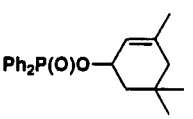
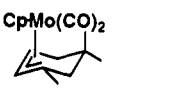
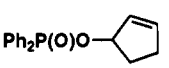
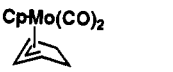
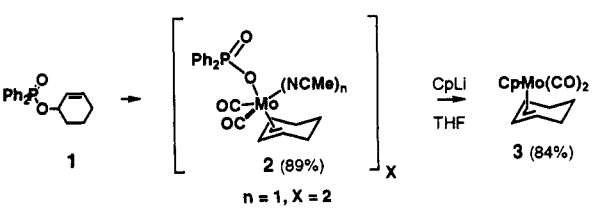
1		4a		5a	A	*70* (93, 75)
2		4b		5b	A	*86* (96, 90)
3		4c		5c	A	*55* (69, 80)
4		4d		5d	A	*55* (76, 73)
5		4e		5e	A	*80* (108, 75)
6		4f = 1		5f = 3	A	*75* (89, 84)
7		4g		5g	A	*58* (84, 69)
8		4h		5h	A	*76* (86, 88)
9		4i		5i	B	*8*[c]
10		4j		5j	B	48[c]

[a] Procedure A: $Mo(CO)_6$ in refluxing acetonitrile followed by LiCp in THF. Procedure B: $Mo(CO)_3(CH_3CN)_3$ in CH_3CN at room temperature followed by LiCp in THF. [b] Yield over two steps is in italics. The separate yields for reaction of the allylic diphenylphosphinate with the Mo(0) reagent and for the subsequent introduction of the cyclopentadienyl unit are given in parentheses. [c] Yields of the intermediates were not determined.

$Mo(CH_3CN)_3(CO)_3$ in CH_3CN at room temperature resulted in a change of color from yellow to orange-red, but formation of no precipitate. Heating of the reaction mixture to reflux resulted within 2 h in the formation of a copious orange precipitate, whose structure 2 is discussed below. Subsequent studies revealed that $Mo(CO)_6$ reacted directly with 2-cyclohexenyl-1 diphenylphosphinate in refluxing acetonitrile in less than 4 h to provide an identical precipitate that was smoothly converted to the desired cyclopentadienyl π-allyl complex (3) on treatment with lithium cyclopentadienide in THF in 75% overall yield from the allylic diphenylphosphinate (eq 2). These results confirmed the anticipated improved reactivity of allylic phosphinates compared to allylic acetates.

With a new access to a variety of allylic diphenylphosphinate esters,[71] a study of their conversion to π-allylmolybdenum complexes using $Mo(CO)_6$ in refluxing acetonitrile was undertaken (Table I). Although some



(2)

restrictions to the process were discovered, many allylic diphenylphosphinate esters reacted cleanly under reproducible conditions, providing a practical route to π-allylmolybdophosphinates from allylic alcohols. The procedure of choice encompassed refluxing equimolar quantities of $Mo(CO)_6$ and an allylic diphenylphosphinate in CH_3CN for a few hours to produce a nearly insoluble bright orange precipitate. Initial attempts to prepare X-ray diffraction quality single crystals of any of these precipitates has been unsuccessful, and limited solubility only in coordinating solvents has precluded definitive NMR and IR characterization. On the basis of elemental analyses,[72] the orange intermediate is tentatively assigned

(71) McCallum, J. S.; Liebeskind, L. S. *Synthesis*, in press.

a dimeric structure (2) with two bridging oxygen-bound diphenylphosphinate ligands. However, it should be noted that related $X(CH_3CN)_2(CO)_2Mo(\eta^3\text{-allyl})$ complexes, where X = Cl or Br, show a pronounced tendency to ionize in solution with liberation of CH_3CN, producing ionic aggregates.[73,74] Future studies will clarify the exact nature of the diphenylphosphinate π-allylmolybdenum system.

The orange precipitate was treated in THF with LiCp, producing the η^5-$CpMo(CO)_2(\eta^3$-allyl) complexes in the yields indicated in the table. Comparison of the ^1H NMR spectra of the allyl complexes derived from geraniol and nerol revealed that no detectable change of double bond geometry occurred during the allylation process. Neither 2-cyclopentenyl diphenylphosphinate nor 3,5,5-trimethylcyclohex-2-enyl diphenylphosphinate produced acceptable yields of π-allylmolybdenum complexes under these conditions. However, reaction of the these allylic phosphinates with preformed $Mo(CH_3CN)_3(CO)_3$ in CH_3CN at room temperature gave lower (but synthetically useful for the former substrate) yields of the intermediate product as a precipitate when run under concentrated conditions. Subsequent treatment with LiCp in THF provided the desired $CpMo(CO)_2(\eta^3$allyl) complexes. It is of interest that these two phosphinate substrates are somewhat sensitive to hydrolysis and decomposition on storage, indicating a possible correlation of the requirement for milder conditions of π-allylmolybdenum complex formation with the presumed higher propensity of these substrates to ionize. At this time it is unclear whether the low yield obtained from 3,5,5-trimethyl-2-cyclohexenyl diphenylphosphinate (Table I, entry 9) should be attributed to the limited stability of this material and/or to unfavorable steric interactions during reaction of this relatively encumbered substrate with the Mo(0) reagent. Further studies of the steric and conformational requirements of the allylation process will be reported in due course. With the exception of the parent π-allylmolybdenum complex (4a), all of the $Cp(CO)_2Mo(\eta^3$-allyl) complexes prepared exist as a single exo–endo conformer. The factors influencing the population of exo–endo conformers and their diagnostic spectral properties are documented;[37,40,75,76] proposed assignments are indicated in the Experimental Section.

Conclusions

Diphenylphosphinate esters of allylic alcohols are readily converted in a high yield, operationally simple, one-pot operation to $(\eta^5$-cyclopentadienyl$)(\eta^3$-allyl$)Mo(CO)_2$ complexes with retention of double bond geometry. The accessibility and the greater stability of the requisite diphenylphosphinate esters offer significant advantages over the usually employed allylic bromides.

Experimental Section

General Methods. Molybdenum hexacarbonyl was purchased from Aldrich Chemical Co. and used as received. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. Anhydrous dimethylformamide and 1,2-dimethoxyethane were purchased from Alrich Chemical Co. and sparged with dry argon or nitrogen for at least 15 min prior to use. Acetonitrile was distilled from calcium hydride prior to use. Solid lithium cyclopentadienide was purchased from Aldrich Chemical Co. and manipulated under an inert atmosphere using standard Schlenk techniques. Alternatively, solutions of lithium cyclopentadienide prepared from freshly cracked cyclopentadiene and *n*-butyllithium gave identical results. All reactions were performed under a positive pressure of dry argon or nitrogen. Analytical tlc was performed on glass plates precoated with Merck F_{254} silica gel 60. Visualization was accomplished using one of the following: UV, 5% phosphomolybdic acid in ethanol, or 2.5% *p*-anisaldehyde and 2.5% sulfuric acid in ethanol. Column chromatography of π-allylmolybdenum complexes was performed with degassed solvents (sparging with argon or nitrogen) on Merck silica gel 60 under nitrogen pressure, and fractions were collected in nitrogen-flushed Schlenkware. Activity I basic alumina refers to Merck basic aluminum oxide 90 (art no. 1076) which was used as received. ^1H NMR spectra were recorded on GE QE-300 (300 MHz), GE/Nicolet NT-360 (360 MHz), and GE GN-500 (500 MHz) instruments, and chemical shifts are reported in δ referenced to the chemical shift of the residual protiated solvent. ^{13}C NMR spectra were recorded on a GE QE-300 (75-MHz) instrument with chemical shifts in δ referenced to the chemical shift of the solvent. Infrared spectra were recorded on a Nicolet 510 Fourier transform instrument. Melting points are uncorrected and were obtained in open capillary tubes using a Hoover oil-immersion apparatus.

Starting Materials. All allylic diphenylphosphinate esters (4a–4j) were prepared and are fully described in a recent article.[71] $Mo(CH_3CN)_3(CO)_3$ and $Mo(DMF)_3(CO)_3$ were prepared according to literature procedures.[67,77–79] (Diglyme)$Mo(CO)_3$ was prepared by a slight modification of the Werner/Coffield procedure as described below.[50–52]

$Mo(CO)_6$ (12 g, 0.046 mol) suspended in a mixture of 40 mL of diglyme (distilled from CaH_2) and 12 mL of benzene with rigorous exclusion of oxygen was slowly heated to reflux over 1 h and then vigorously refluxed (oil bath maintained at 130–140 °C) for 12 h to produce a yellow-tan precipitate. Superheating of the reaction vessel is avoided by ensuring that the heating bath meniscus is below that of the solvent; failure to observe this precaution results in some decomposition of the product. Early in the reaction, sublimed $Mo(CO)_6$ was occasionally returned to the reaction flask by inserting a long spatula or wire through the condensor with argon purging. The product was isolated by cooling the reaction flask to 0 °C and removing the supernatant via cannula, then washed with hexanes, and put on the vacuum line. Any unreacted $Mo(CO)_6$ was removed by room-temperature sublimination onto a water-cooled cold finger inserted into the reaction flask. The product was not characterized due to extreme air sensitivity (decomposition in air within 15 s). Yield: 74%.

$(DME)_2Mo_2(CO)_6$ was prepared as follows: A suspension of molybdenum hexacarbonyl in 1,2-dimethoxyethane (2.5 g/10 mL) was heated to vigorous reflux (oil bath temperature 130–140 °C) for 36–48 h. During this time the white molybdenum hexacarbonyl was slowly replaced by a pale greenish-yellow solid. When no remaining molybdenum hexacarbonyl could be seen, the solution was allowed to cool and the solvent removed by cannula. The remaining solid was briefly dried on the vacuum line; then any residual molybdenum hexacarbonyl was removed by sublimination onto a cold finger inserted into the reaction flask to provide 45–65% yields of a pyrophoric powder which was used without further purification.

Preparation of π-Allylmolybdenum Complexes from Allyl Phosphinates. Procedure A. The allyl diphenylphosphinate

(72) Yellow prisms crystallized from warm acetone. Anal. Calcd for $[Mo(CO)_2(CH_3CN)(\eta^3\text{-}2\text{-cyclohexen-1-yl})(\mu\text{-}OPOPh_2)]_2$, $C_{44}H_{44}N_2O_8P_2Mo_2$: C, 53.78; H, 4.51; N, 2.85. Found: C, 53.81; H, 4.59; N, 3.30.

(73) Brisdon, B. J.; Cartwright, M. J. *J. Organomet. Chem.* **1979**, *164*, 83.

(74) Drew, M. G. B.; Brisdon, B. J.; Cartwright, M. *Inorg. Chim. Acta* **1979**, *36*, 127.

(75) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752.

(76) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.

(77) Kubas, G. J. *Inorg. Chem.* **1982**, *22*, 692.

(78) Kubas, G. J.; Wasserman, H.; Ryan, R. R. *Organometallics* **1985**, *4*, 2012.

(79) Kubas, G. J.; Vandersluys, L. S. In *Tricarbonyltris(Nitrile) Complexes of Cr, Mo, and W*; Angelici, R. J., Ed.; Inorganic Syntheses; John Wiley & Sons Inc. 605 3rd Ave., New York, NY 10016, 1990; Vol. 28, pp 29.

(1.0 equiv) and molybdenum hexacarbonyl (1.1 equiv) were combined in a tared Schlenk flask, and an inert atmosphere was introduced. Acetonitrile was added (2.5 mL/g Mo(CO)$_6$), and the mixture was slowly heated to vigorous reflux over about 30 min. Reflux was continued for 3$^1/_2$–5 h. Within 1 h of reflux, formation of an orange solid was usually apparent. The reaction mixture was cooled, and the orange solid was isolated by removal of the (usually brown) mother liquor by cannula, washed several times with cold acetonitrile, and then placed on the vacuum line. The crude yields of this intermediate complex, when determined, are reported by assuming a formulation of [Cp(CO)$_2$(CH$_3$CN)(O$_2$P(Ph)$_2$)Mo(π-allyl)]$_2$ and appear after the overall yield in parentheses accompanied by the yield for cyclopentadienide addition. The crude material was then suspended in tetrahydrofuran (15 mL/g), and excess lithium cyclopentadienide (1.2–1.5 equiv) was added as a solution in tetrahydrofuran. Small-scale reactions (1 mmol or less) were alternatively conducted by combining the crude π-allyl complex with solid cyclopentadienyllithium followed by addition of tetrahydrofuran. A lightening of the reaction mixture, accompanied by the formation of a white precipitate, occurred within 15 min. The reaction was allowed to stir for 1 h, diluted with two volumes of diethyl ether, and subjected to rapid vacuum filtration in the air through a plug of silica gel covered with activity I basic alumina, using diethyl ether as the eluant. Often, no further purification was required, and the product was obtained by the addition of a small amount of heptane, followed by removal of the more volatile polar solvents under vacuum, usually inducing crystallization. Where noted, further chromatographic purification, recrystallization, or sublimation was employed. The complexes are best stored under an inert atmosphere.

Procedure B. The allyl diphenylphosphinate (1.0 equiv) and trisacetonitrile molybdenum tricarbonyl (1.0 equiv) were combined in a tared Schlenk flask under an inert atmosphere. Acetonitrile was added (2.5 mL/g Mo(CO)$_6$), and the mixture was stirred for 12–18 h. Within 1–3 h, formation of a yellow precipitate was usually apparent. The yellow solid was isolated by removal of the (usually brown) mother liquor by cannula, washed several times with cold acetonitrile, and then placed on the vacuum line. The crude yields of this intermediate complex, when determined, are reported by assuming a formulation of [(CO)$_2$(CH$_3$CN)(O$_2$P(Ph)$_2$)Mo(π-allyl)]$_2$ and appear after the overall yield in parentheses accompanied by the yield for cyclopentadienide addition. The crude material was then suspended in tetrahydrofuran (15 mL/g), and excess lithium cyclopentadienide (1.2–1.5 equiv) was added as a solution in tetrahydrofuran. Small-scale reactions (1 mmol or less) were alternatively conducted by combining the crude π-allyl complex with solid cyclopentadienyllithium followed by addition of tetrahydrofuran. A lightening of the reaction mixture, accompanied by the formation of a white precipitate, occurred within 15 min. The reaction was allowed to stir for 1 h, diluted with two volumes of diethyl ether, and subjected to rapid vacuum filtration in the air through a plug of silica gel covered with activity I basic alumina, using diethyl ether as the eluant. Often, no further purification was required, and the product was obtained by the addition of a small amount of heptane, followed by removal of the more volatile polar solvents under vacuum, usually inducing crystallization. Where noted, further chromatographic purification, recrystallization, or sublimation was employed. The complexes are best stored under an inert atmosphere.

(η^5-Cyclopentadienyl)dicarbonyl(η^3-propenyl)molybdenum (5a). Procedure A: yield, 70% overall (93,75); yellow microcrystals, mp = 135–138 °C (diethyl ether/heptane). Material exhibited ^{1}H NMR, IR, and mp data that correspond to those previously reported by Cousins and Green[80] (^{1}H NMR, IR, EA, mp) and Faller et al.[40] (^{1}H NMR, IR). (Note that the melting point of 134 °C dec reported by Green corresponds to that obtained for our material; that reported by Faller is 165–168 °C.)

Ca. 4:1 mixture of exo and endo conformers: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.81 (b-d, J = 11 Hz, 2 H, exo *anti*-π-allyl), 1.43 (b-d, J = 9 Hz, 2 H, endo *anti*-π-allyl), 3.42 (b–m, 1 H and 1 H, exo and endo central π-allyl), 4.53 (b-s, 5 H, exo Cp), 4.57 (b-s, 5 H, endo Cp); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 36.2 (exo), 39.6 (endo), 67.2 (exo), 86.1 (endo), 90.1 (endo), 91.2 (exo), 237.4 (exo), 240.6 (endo); IR (cyclohexane) 1966 and 1958 (vs, metal C=O), 1899 and 1883 (vs, metal C=O), (KBR pellet) 1939 (vs, metal C=O), 1854 cm^{-1} (vs, metal C=O).

(η^5-Cyclopentadienyl)dicarbonyl(η^3-2-methylpropenyl)molybdenum (5b). Procedure A: yield, 86% overall (96, 90); fine yellow needles (ethyl acetate/heptane), mp = 81–83 °C, further purification not required. Material exhibits ^{1}H NMR, IR, and mp data that correspond to those previously reported.[40,81]

endo conformer: ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.71 (s, 3 H, CH$_3$), 1.95 (s, 2H, *anti*-π-allyl), 2.79 (s, 2 H, *syn*-π-allyl); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 23.7, 38.7, 90.5, 105.2, 241.4; IR (KBr) 1938 (vs, metal C=O), 1836 cm^{-1} (vs, metal C=O). Anal. Calcd for C$_{11}$H$_{12}$MoO$_2$: C, 48.55; H, 4.44. Found: C, 48.38; H, 4.51.

(η^5-Cyclopentadienyl)dicarbonyl[(1,2,3-η)-*trans*-3,7-dimethyl-2,6-octadien-1-yl]molybdenum (5c). Procedure A: yield, 55% overall (69, 80); yellow needles (methanol), mp = 46–48 °C, initially isolated as an oil after chromatography (silica gel, 1:8 ethyl acetate/hexane), crystallized from methanol.

exo conformer: ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 0.49 (m, 1 H, C$_\pi$(CH$_3$)—C*H*H), 1.19 (dd, J = 10.5, 3.0 Hz, 1 H, *anti*-π-allyl), 1.52 (S, 3 H, (C*H*$_3$)(CH$_3$)C=C), 1.63 (s, 3 H, (CH$_3$)(C*H*$_3$)C=C), 1.67 (s, 3 H, π-allyl—CH$_3$), 1.85 (m, 1 H, C$_\pi$(CH$_3$)—CH*H*), 2.20 (m, 2 H, C=CH—C*H*$_2$), 2.35 (dd, J = 7.3, 3.0 Hz, 1 H, *syn*-π-allyl), 3.55 (dd, J = 10.5, 7.4 Hz, 1 H, central π-allyl), 4.59 (s, 5 H, Cp), 5.03 (b-t, J = 6.5 Hz, 1 H, (CH$_3$)$_2$C=C*H*); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 17.6, 25.8, 27.3, 30.4, 31.0, 36.9, 68.5, 84.3, 91.8, 124.6, 131.3, 236.2, 242.8; IR (KBr) 1934 (vs, metal C=O), 1848 cm^{-1} (vs, metal C=O). Anal. Calcd for C$_{17}$H$_{22}$MoO$_2$: C, 57.63; H, 6.26. Found: C, 57.69; H, 6.29.

(η^5-Cyclopentadienyl)dicarbonyl[(1,2,3-η)-*cis*-3,7-dimethyl-2,6-octadien-1-yl]molybdenum (5d). Procedure A: yield, 55% overall (76, 73); yellow needles (methanol), mp = 59–60.5 °C, initially isolated as an oil after chromatography (silica gel, 1:8 ethyl acetate/hexane), crystallized from methanol.

exo conformer: ^{1}H NMR (360 MHz, C$_6$D$_6$) δ 1.05 (s, 3 H, π-allyl—C*H*$_3$), 1.20 (dd, J = 10.5, 2.9 Hz, 1 H, *anti*-π-allyl), 1.57 (b-s, 3 H, (C*H*$_3$)(CH$_3$)C), 1.60 (m, 1 H, C$_\pi$(CH$_3$)—C*H*H), 1.71 (b-s, 3 H, (CH$_3$)(C*H*$_3$)C), 2.13–2.27 (m, 3 H, C=C(C*H*$_2$)—CH*H*), 2.33 (dd, J = 7.3, 3.0 Hz, 1 H, *syn*-π-allyl), 3.62 (dd, J = 10.5, 7.3 Hz, 1 H, central π-allyl), 4.58 (s, 5 H, Cp), 5.21 (b-m, 1 H, (CH$_3$)$_2$C=C*H*); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 17.7, 18.9, 25.8, 29.4, 30.9, 44.8, 68.8, 85.7, 91.8, 124.4, 131.7, 236.4, 242.6; IR (KBr) 1914 (vs, metal C=O), 1840 cm^{-1} (vs, metal C=O). Anal. Calcd for C$_{17}$H$_{22}$MoO$_2$: C, 57.63; H, 6.26. Found: C, 57.65; H, 6.30.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-(*N*-ethoxycarbonyl)-1,2,5,6-tetrahydropyridin-5-yl]molybdenum (5e). Procedure A: yield, 80% overall (108, 75); fine yellow needles (ethyl acetate/heptane), mp = 139.5–141 °C, further purification not required.

exo conformer: ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.16 (t, J = 7 Hz, 3 H, CH$_3$), 3.26 (b-d, J = 14 Hz, 1 H, C*H*H—N—CH$_2$), 3.31 (b-d, J = 14 Hz, 1 H, CH$_2$—N—C*H*H), 3.58 (dddd, J = 7.0, 2.5, 2.5, 2.0 Hz, 1 H, *syn*-π-allyl), 3.65 (dddd, J = 7.0, 2.5, 2.5, 2.0 Hz, 1 H, *syn*-π-allyl), 3.85 (dd, J = 14.0, 2.5 Hz, CH*H*—N—CH$_2$), 3.93 (dd, J = 14.0, 2.5 Hz, CH$_2$—N—CH*H*), 3.99 (m, 1 H, C*H*H—CH$_3$), 4.06 (m, 1 H, CH*H*—CH$_3$), 4.19 (J = 7.0 Hz, central π-allyl), 5.30 (s, 5 H, Cp); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.6, 39.9, 40.1, 50.9, 51.2, 53.9 (br), 60.9, 91.9, 155.3, 233.6, 234.1; IR (KBr pellet) 1930 (vs, metal C=O), 1849 (vs, metal C=O), 1686 cm^{-1} (s, carbamate C=O). Anal. Calcd for C$_{15}$H$_{17}$Mo NO$_4$: C, 48.53; H, 4.62. Found: C, 48.37; H, 4.57.

(η^5-Cyclopentadienyl)dicarbonyl[(1,2,3-η)-cyclohexen-1-yl]molybdenum (5f = 3). Procedure A: yield 75% overall (89, 94); yellow needles (ethyl acetate/heptane), mp = 94–95 °C,

(80) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1963**, 889.

(81) Luh, T.-Y.; Wong, C. S. *J. Organomet. Chem.* **1985**, *287*, 231.

further purification not required. This material exhibited ^{1}H NMR, IR, and mp data that correspond to those previously reported for this material.[37] (These authors report ^{1}H NMR, IR, mp and elemental analysis.)

exo conformer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.31 (dtt, J = 14.0, 11.8, 7.4 Hz, 1 H, CH_2—C*H*H—CH_2), 0.94 (dtm, J = 14.0, 6.2 Hz, 1 H, CH_2—CH*H*—CH_2), 1.66 (dm, J = 17.5 Hz, 2 H, C*H*H—CH_2—C*H*H), 1.89 (dddm, J = 14.6, 11.8, 6.0 Hz, 2 H, CH*H*—CH_2—CH*H*), 3.66 (dm, J = 7.2 Hz, 2 H, *syn*-π-allyl), 4.15 (apparent tq, J = 7.2, 1.0 Hz, 1 H, central π-allyl), 5.28 (s, 5 H, Cp); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 21.2, 54.9, 57.2, 91.9, 235.6; IR (KBr pellet) 1925 (vs, metal C=O), 1852 cm^{-1} (vs, metal C=O).

(η^5-Cyclopentadienyl)dicarbonyl[4,4-dimethyl-(1,2,3-η)-cyclohexen-1-yl]molybdenum (5g). Procedure A: yield, 58% overall (84, 69); yellow needles (heptane/diethyl ether), mp 83.5–85 °C, purified by sublimation (75 °C, 0.5 mmHg).

exo conformer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.41 (b-ddd, J = 6.2, 11.6, 13.0 Hz, 1 H, $C(Me)_2$C*H*H)), 0.78 (b-dd, J = 6.0, 13.0 Hz, 1 H, $C(Me)_2$H*H*), 1.03 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.74 (dddd, J = 1.0, 3.0, 6.2, 15.2 Hz, 1 H, C_πH—C*H*H), 2.02 (ddddd, J = 1.0, 2.6, 6.0, 11.6, 15.2 Hz, C_πH—CH*H*), 3.63 (ddd, J = 1.6, 2.6, 7.2 Hz, 1 H, CMe_2—C_π*H*), 3.74 (dddd, J = 2.6, 2.6, 3.0, 7.2 Hz, 1 H, C_π*H*—CH_2), 4.23 (b-dd, J = 7.2, 7.2, 1 H, central π-allyl), 5.24 (s, 5 H, Cp); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 28.3, 32.4, 33.8, 35.2, 57.0, 59.1, 67.1, 91.9, 236.5, 239.4; IR (CH_2Cl_2) 1934 (vs, metal C=O), 1850 cm^{-1} (vs, metal C=O). Anal. Calcd for $C_{15}H_{18}MoO_2$: C, 55.22; H, 5.56. Found: C, 55.27; H, 5.58.

(η^5-Cyclopentadienyl)dicarbonyl[5,5-dimethyl-(1,2,3-η)-cyclohexen-1-yl]molybdenum (5h). Procedure A: yield, 76% overall (86, 88); yellow needles (heptane/diethyl ether), mp = 119–120 °C.

exo conformer: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.65 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.64 (d, J = 16 Hz, 2 H, C*H*H—C-$(Me)_2$—C*H*H)), 1.98 (dd, J = 16, 7 Hz, 2 H, CH*H*—C-$(Me)_2$—CH*H*), 3.83 (b-t, J = 7 Hz, 2 H, *syn*-π-allyl), 4.69 (t, J = 6.6 Hz, 1 H, central π-allyl), 5.26 (s, 5 H, Cp); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.9, 29.6, 30.8, 39.6, 52.5, 68.0, 92.0, 238.7; IR (KBr) 1909 (vs, metal C=O), 1843 cm^{-1} (vs, metal C=O). Anal. Calcd for $C_{15}H_{18}MoO_2$: C, 55.22; H, 5.56. Found: C, 55.29; H, 5.55.

(η^5-Cyclopentadienyl)dicarbonyl[2,5,5-trimethyl-(1,2,3-η)-cyclohexen-1-yl]molybdenum (5i). Procedure B: yield, 8% overall, extensive decomposition in first step; fine yellow needles (ethyl acetate/heptane), mp = 109.5–110 °C, purification by chromatography (silica gel, 1:32 ethyl acetate/hexane 1:32).

exo conformer: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.64 (s, 3 H, (CH_3)(CH_3)C), 1.01 (s, 3 H, (CH_3)(CH_3)C), 1.59 (dd, J = 16, 2 Hz, 1 H, CH=CH—C*H*H), 1.66 (d, J = 16 Hz, 1 H, CH=CMe—CH*H*), 1.75 (d, J = 16 Hz, 1 H, CH=C(Me)—CH*H*), 1.81 (s, 3 H, CH_3C=C), 1.92 (ddd, J = 16.8, 1.5 Hz, 1 H, CH=CH—CH*H*), 3.45 (ddd, J = 8.7, 1.5 Hz, 1 H, *syn*-π-allyl), 5.58 (d, J = 7 Hz, 1 H, central π-allyl), 5.23 (s, 5 H, Cp); ^{13}C NMR (75 MHz, C_6D_6) δ 28.6, 30.4, 30.7, 30.8, 37.9, 44.0, 48.6, 68.9, 77.8, 92.5, 237.1, 242.4; IR (KBr pellet) 1906 (vs, metal C=O), 1837 cm^{-1} (vs, metal C=O). Anal. Calcd for $C_{15}H_{18}$ MoO_2: C, 55.22; H, 5.56. Satisfactory elemental analysis could not be obtained.

(η^5-Cyclopentadienyl)dicarbonyl[(1,2,3-η)-cyclopenten-1-yl]molybdenum (5j). Procedure B: yield, 48% overall; fine yellow needles (hexane), mp = 116.5–117.5 °C, purified by flash chromatography (silica gel, 1:8 ethyl acetate/hexane). Cannot be prepared by procedure A. This material exhibited ^{1}H NMR, IR, and mp data that correspond to those previously reported for this material.[82] (These authors report ^{1}H NMR, IR, mp, and elemental analysis.)

exo conformer: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.55 (dm, J = 11 Hz, 2 H, C*H*H—C*H*H), 2.01 (b-d, J = 11 Hz, 2 H, CH*H*—CH*H*), 3.74 (m, 2 H, *syn*-π-allyl), 4.18 (t, J = 4 Hz, 1 H, central π-allyl), 5.28 (s, 5 H, Cp); ^{13}C NMR (75 MHz, C_6D_6) δ 30.1, 57.9, 60.5, 91.4, 235.8; IR (KBr pellet) 1926 (vs, metal C=O), 1840 cm^{-1} (vs, metal C=O).

Acknowledgment. This investigation was supported by Grant No. GM43107, awarded by the National Institute of General Medical Science. We acknowledge the use of a VG 70-S mass spectrometer purchased through funding from the National Institutes of Health, S10-RR-02478, and a 300-MHz NMR and 360-MHz NMR purchased through funding from the National Science Foundation, NSF CHE-85-16614 and NSF CHE-8206103, respectively. We thank Dr. Nicholas Cosford, Mr. Claes Löfström, and Ms. Sonha Payne for their assistance with this project.

Note Added in Proof. Some allylic trifluoroacetates were studied as precursors to π-allylmolybdenum complexes in: Lambert, C. Ph.D. Thesis, Wesleyan University, 1986. We thank Professor Jack Faller of Yale University for bringing this information to our attention.

OM9205105

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