Studies on Lateral Stereocontrol Using the (π-Allyl)molybdenum System

Anthony J. Pearson,*[1a] Irina B. Neagu,[1a] A. Alan Pinkerton,[1b] Kristin Kirschbaum,[1b] and Michaele J. Hardie[1b]

Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and University of Toledo, 2801 West Bancroft Street, Toledo, Ohio 43606

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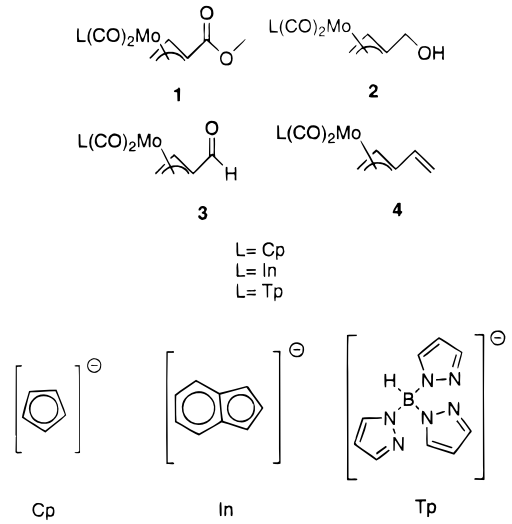
The preparation and reactions of several new (η^3-allyl)molybdenum complexes are described. Functionalization of a carbon−carbon double bond adjacent to the π-allyl unit proceeds stereoselectively, and the stereochemical outcome of this reaction is discussed in light of the Curtin−Hammett principle. It is shown that carbonyl groups can also be functionalized with moderate stereoselectivity, and this behavior is rationalized on the basis of conformational analysis using molecular mechanics calculations.

Introduction

The concept of using an organometallic group as a template for constructing stereodefined molecules has become commonplace in modern synthetic organic methodology.[2] Transition metal π-allyl complexes have been shown to effect regio- and stereocontrol during functionalization.[3] Our group has been involved in earlier investigations of the chemistry of such (π-allyl)molybdenum complexes within six-, seven-,[4,5] and eight-membered[6] rings. Stereocontrolled alkylation of six- and seven-membered rings was achieved via multiple nucleophilic addition to cationic dienemolybdenum complexes.[7] Alkylation of enolates was accomplished in the presence of a neighboring π-allyl-Mo(CO)$_2$Cp moiety,[4] with higher levels of stereocontrol in six- as opposed to seven-membered rings due to conformational effects.[5] Generation of carbanions α to the π-allyl-Mo(CO)$_2$Cp and to a CN substituent, followed by the reaction with electrophiles, proceeded in a regio- and stereocontrolled way.[8]

While most of the work was done on cyclic systems,[9] we expect that acyclic (π-allyl)molybdenum complexes present special challenges and potential synthetic opportunities. It has been shown that there can be advantages to the use of an organometallic unit to effect stereocontrol in acyclic systems.[10] This paper reports our studies on the chemistry and conformational analysis of acyclic (π-allyl)molybdenum complexes, in which we show that uncomplexed double bonds and carbonyl groups can be functionalized with reasonable degrees of stereocontrol.

Chart 1



Results and Discussion

Our initial efforts, aimed at the development of chemical methodology for the synthesis of a number of (η^5-cyclopentadienyl)(η^3-allyl)Mo(CO)$_2$ complexes (**1**−**4**, Chart 1), were disappointing, due to the difficulty in handling that we and others[11] have experienced with these compounds. Ester **1** (L = Cp) was synthesized in 89% yield but could not be stored without considerable deterioration. Alcohol **2** (L = Cp) and aldehyde **3** (L =

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(1) (a) Case Western Reserve University. (b) University of Toledo.

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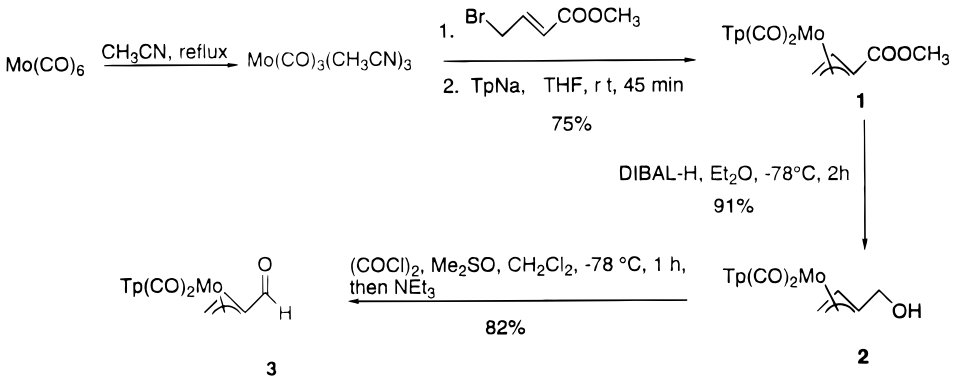
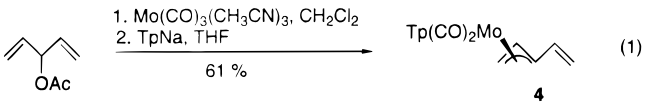
Scheme 1



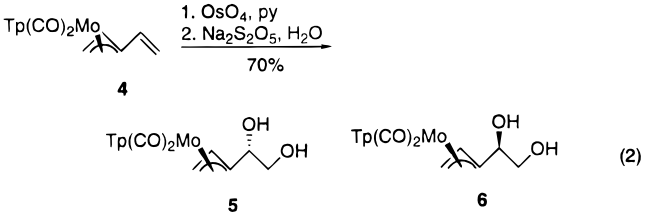
Cp) were extremely unstable under all conditions of handling and, therefore, were judged to be too problematic for further study. A search for more stable (π-allyl)-molybdenum systems was initiated, starting with the (indenyl)(η^3-allyl)$Mo(CO)_2$ complexes, which proved to be too unstable to be isolated.[12] Being aware of recent literature reports[13] regarding the excellent stability in air and in solution of the (η^3-allyl)dicarbonyl[hydridotris(1-pyrazolyl)borato]molybdenum complexes, we decided to explore this family of compounds. A modified literature[13a] procedure was developed for the synthesis of **1** (L = Tp) (Scheme 1), which relied on the use of $Mo(CO)_3(CH_3CN)_3$ and methyl 4-bromocrotonate in the step of oxidative addition, followed by ligand exchange with commercially available sodium tris(1-pyrazolyl)borohydride, thus avoiding the handling of the air-sensitive intermediate $Mo(CO)_3(DMF)_3$. Complex **1** could be reduced[14] uneventfully to the alcohol **2**, which was oxidized to aldehyde **3** using the standard Swern protocol.[15] The *syn* stereochemistry for **1**−**3** (L = Tp) was assigned by comparison with ^{1}H NMR coupling constant data reported by Liebeskind et al.[13a] While **3** could be converted to the olefin **4** (Chart 1) by standard Wittig methylenation, we decided to investigate a more direct route to **4** that would furnish significant quantities for further study, as described in the next section.

Stereocontrolled Carbon−Carbon Double Bond Construction and Functionalization. The use of allylic acetates as precursors for (π-allyl)molybdenum complexes is well documented.[16] We report here a synthesis of **4** starting with $Mo(CO)_3(CH_3CN)_3$ and 1,4-pentadien-3-yl acetate, readily obtained by acetylation of commercially available 1,4-pentadien-3-ol, followed by ligand exchange with sodium tris(1-pyrazolyl)borohydride (eq 1). The carbon−carbon double bond adjacent to the (π-allyl)molybdenum moiety was obtained exclusively in the *syn* configuration shown, according to ^{1}H NMR.



(1)

Several methods for the stereoselective functionalization of double bonds in the presence of an organometallic group have been reported.[17] Most work has been done on iron complexes,[10] yet the stereocontrol we recently observed during osmylation in the presence of a (π-allyl)molybdenum group[18] has laid the basis for a more thorough investigation of this reaction. Although epoxidation[19] was unsuccesful with **4** (L = Tp), both catalytic[20] and stoichiometric[21] osmylation procedures worked well, providing mixtures of two diastereomeric diols, **5** and **6** (eq 2). The best results combined



(2)

complete alkene conversion in a short reaction time (45 min) with a diastereoselectivity of 5:1, the reaction being performed in pyridine using stoichiometric amounts of OsO_4.

We expected the X-ray structure of the major diastereomeric diol to confirm the OsO_4 approach *anti* to the metal, on the preferred conformer of **4**, i.e., the one depicted in eq 2. The stereochemical outcome of the reaction, based on the X-ray structure determination of the *major* diastereomeric diol **6** (Figure 1), proved to be different from the one expected, favoring the hypothesis that this is a case where the Curtin−Hammett principle

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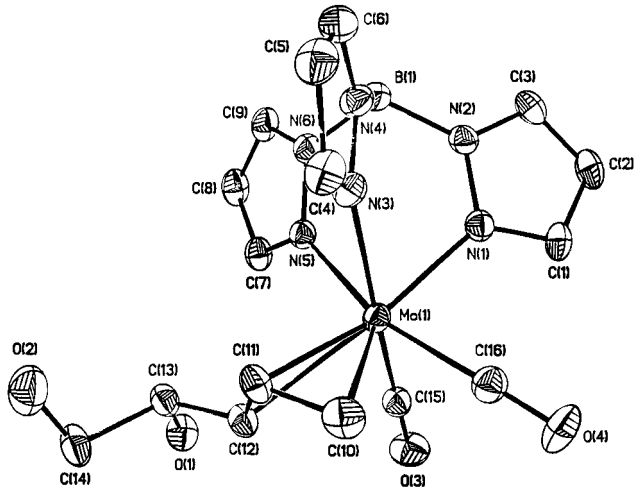


Figure 1. X-ray crystal structure of **6**. Selected bond lengths and bond angles with standard deviations are as follows. Bond lengths (Å): Mo−C10 = 2.326(5); Mo−C11 = 2.255(4); Mo−C12 = 2.464(5); C11−C10 = 1.421(7); C12−C11 = 1.409(7); C12−C13 = 1.501(7); C13−C14 = 1.533(7); O1−C13 = 1.436(6). Bond angles (deg): C15−Mo−C16 = 78.4(2); C11−Mo−C12 = 34.4(2); C12−C11−C10 = 116.6(5); C11−C12−C13 = 122.2(5); O1−C13−C12 = 109.1(4); O1−C13−C14 = 107.6(4).

comes into play. To explain the result, conformational studies were initiated.

For **4**, pseudoconjugation of the double bond with the π-allyl system leads to a planar conformation, but two of these are possible, i.e., **4A** and **4B** (Figure 2). The hypothesis that conformation **A** is destabilized by the nonbonded interaction between one olefinic proton and one π-allyl proton (an interaction that will become more important once the olefinic proton is replaced by an alkyl group) had to be verified. We expected NMR experiments, coupled with molecular mechanics calculations, to be relatively straightforward in the study of conformational equilibria of these compounds in solution.

The difference in strain energies for the two minimized conformers of **4**, as calculated using Spartan[22] molecular mechanics under a SYBYL force field, translated into a distribution of populations of 80/20, favoring conformer **B** (Figure 2). ROESY[23] experiments confirmed the existence of both conformers **A** and **B** in solution at room temperature, but the appearance of only a single set of resonances indicated rapid equilibration.

We invoked the Hammond postulate and proposed that the osmate ester intermediate should be similar in structure to the transition state. Spartan (SYBYL) molecular mechanics calculations were run for the four possible osmate ester conformers resulting from the top and side attack of OsO_4 on **4B** (Figure 3) and **4A** (Figure 4), assuming a [3 + 2] mechanism is operating. We found that one minimized conformation of the diastereomeric osmate ester, leading to the observed major product (the *RS*,*SR* configuration of the major diastereomeric diol (Figure 1) is matched by the osmate esters depicted in Figure 4), had an energy 0.16 kcal/mol higher than that of the corresponding structure leading to the minor product. This fact, correlated with a difference of 0.814 kcal/mol in the energy of the ground state reactants, suggested that the higher energy conformer of **4**, i.e., **4A**, reacted faster than the lower energy one. Our calculations indicate that the stereochemical outcome of the osmylation reaction on **4** may be explained as a result of the Curtin−Hammett principle.[24] It should be emphasized that the approximations used in the model, as well as the fact that interactions in the transition state leading to the osmate ester intermedi-

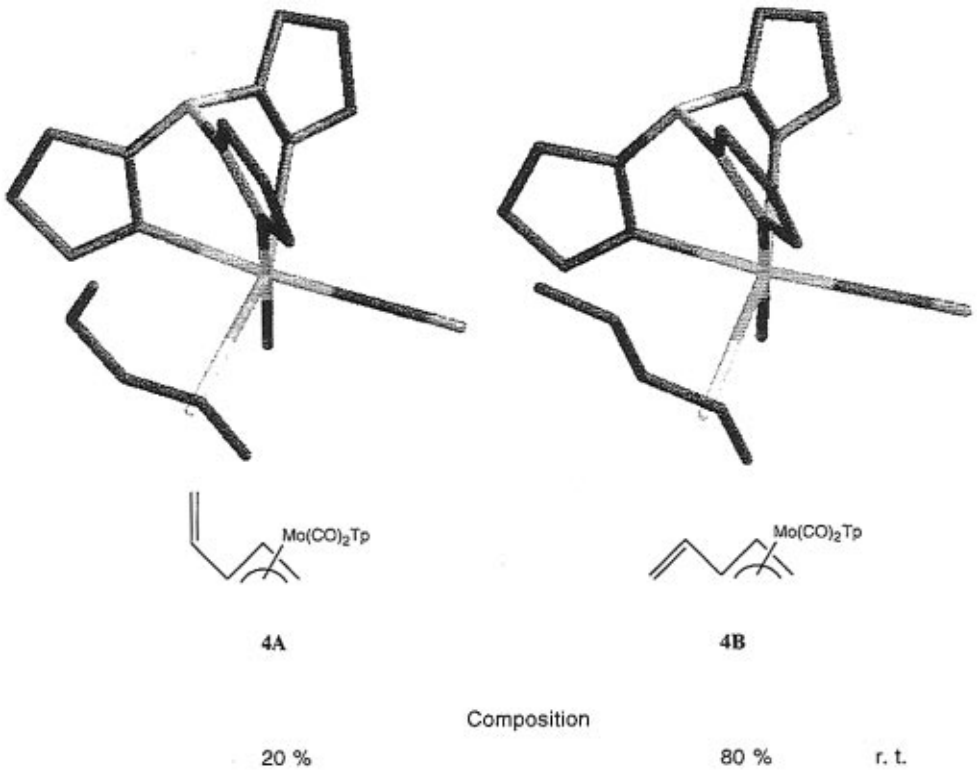


Figure 2. Molecular mechanics (SYBYL) calculations for the two preferred conformers of the CH_2=CH group adjacent to the (π-allyl)molybdenum unit (**4**).

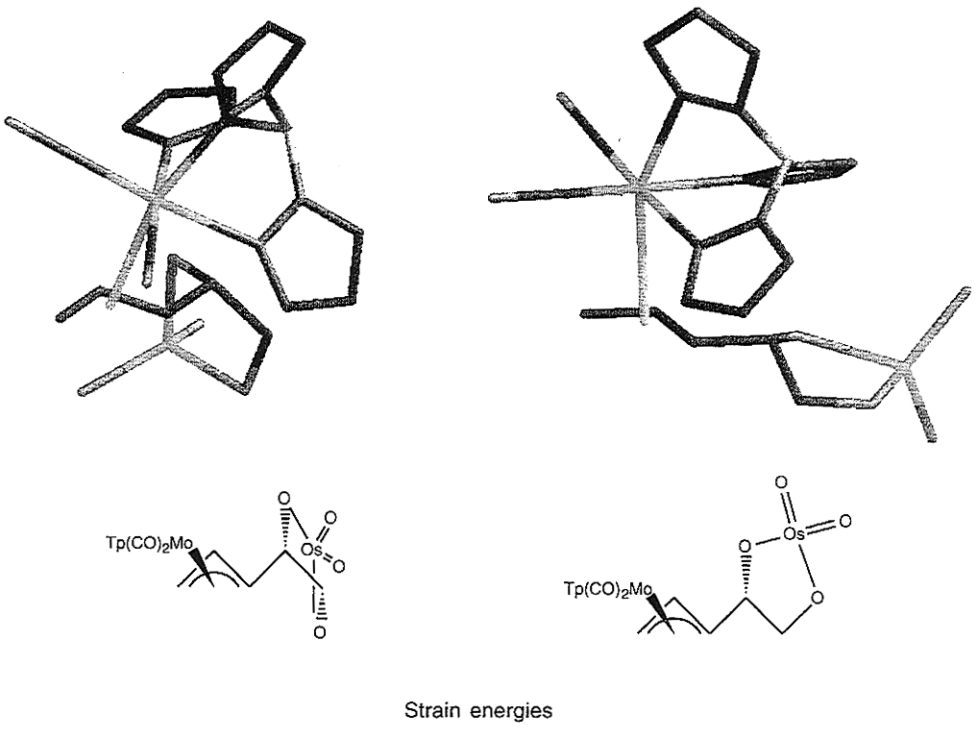


Figure 3. Molecular mechanics (SYBYL) calculations for the two preferred osmate ester conformers resulting from the top and side attack by OsO_4 on the lower energy conformer of **4**.

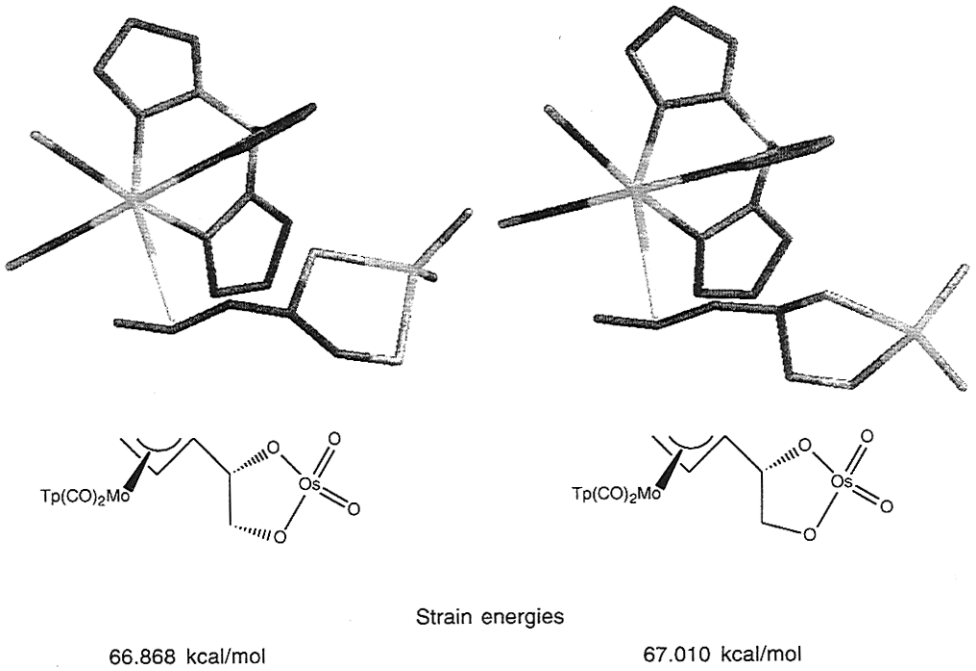
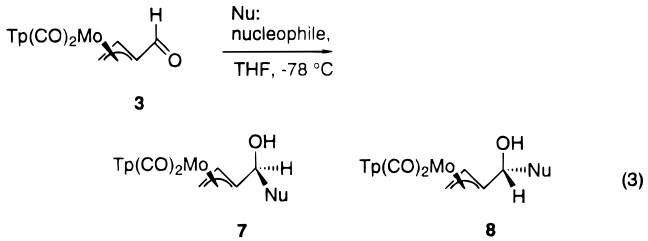


Figure 4. Molecular mechanics (SYBYL) calculations for the two preferred osmate ester conformers resulting from the top and side attack by OsO_4 on the higher energy conformer of **4**.

ate, may differ significantly from those in the intermediate, make quantitative predictions unreliable.

Nucleophile Addition to Carbonyl Groups Adjacent to the (π-Allyl)molybdenum Unit. A moderate diastereoselectivity (~6:1) was observed in the reaction of aldehyde **3** (R = H) with a series of nucleophiles (eq 3, Table 1). The conformational biasing of



(3)

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(23) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207.
(24) Maskill, H. *The physical basis of organic chemistry*; Oxford University Press: Oxford, 1985.

Table 1. Nucleophile Additions to Complex 3

nucleophile	reaction conditions: temp (°C)	time (h)	equiv of Nu/**3**	ratio of diastereomers	yield (%)
MeMgBr	−78 to −50	4	10	5.9/1	96
CH_2=CH-CH_2MgBr	−78 to −50	2.5	2	5.2/1	94
CH_2=CHMgBr	−78 to −50	4	10	5.6/1	99
PhMgBr	−78	4	10	6.3/1	97
$NaBD_4$	rt[a]	1	6	1/0	90[b]

[a] Room temperature. [b] 90% yield at 45% conversion.

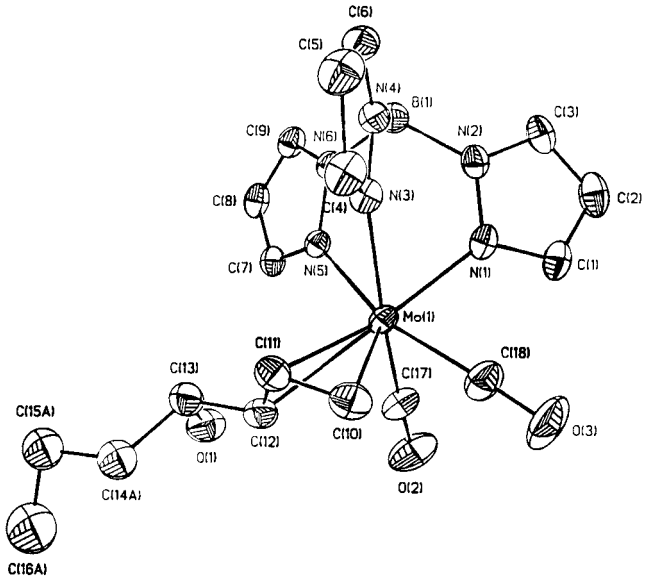
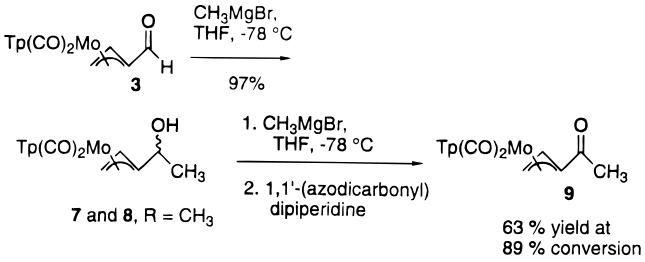


Figure 5. X-ray crystal structure of **7**, R = CH_2CH=CH_2. Selected bond lengths and bond angles with standard deviations are as follows. Bond lengths (Å): Mo−C10 = 2.326(3); Mo−C11 = 2.256(3); Mo−C12 = 2.460(3); C11−C10 = 1.413(4); C12−C11 = 1.392(4); C12−C13 = 1.503(4); C13−C14A = 1.508(8); C14A−C15A = 1.492(11); O1−C13 = 1.429(4). Bond angles (deg): C17−Mo−C18 = 78.76(12); C11−Mo−C12 = 33.98(2); C12−C11−C10 = 117.1(3); C11−C12−C13 = 121.7(3); O1−C13−C12 = 107.4(3); O1−C13−C14A = 109.6(4).

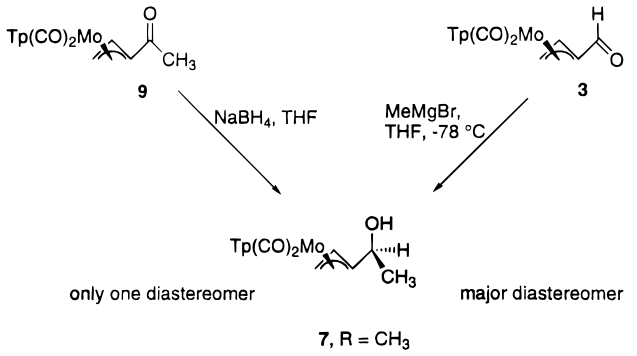
the starting complex appears to be responsible for this result. Indeed, ROESY experiments indicated the presence of both *s-cis* and *s-trans* conformers of **3** in solution at room temperature, in rapid equilibrium. The stereochemical outcome of the nucleophilic additions run on **3** was expected to reflect the conformer population of the aldehyde group, assuming that the nucleophiles attack only on the face opposite to the bulky $Mo(CO)_2Tp$ moiety. The resulting complex, **7**, identified as the major diastereomer, was assigned the *RR,SS* configuration on the basis of structural elucidation of **7** (R = CH_2CH=CH_2). An ORTEP drawing is provided in Figure 5. By analogy, we have assigned structure **7** to all major diastereomeric products of nucleophile addition to **3**. Moreover, a *single diastereomer* was obtained from the $NaBD_4$ addition on aldehyde **3**, suggesting that the stereochemical outcome of these reactions is nucleophile dependent.

To further extend our studies on more substituted carbonyl groups adjacent to (π-allyl)molybdenum systems, the methyl ketone complex **9** (R = CH_3) (Scheme 2), was prepared.[25] We were interested in the conformer distribution in **9** as a reflection of the tendency of this

Scheme 2



Scheme 3



molecule to minimize nonbonded hydrogen−hydrogen repulsions. We anticipated that the *s-cis* conformer would benefit from the lack of such nonbonded interactions between the π-allyl proton and the methyl group. It was found that sodium borohydride addition to the ketone **9** gave a *single diastereomer*, presumably arising from hydride addition to the major conformer of **9** *trans* to the $Mo(CO)_2Tp$ unit. The same stereochemistry was identified for the major product of MeMgBr addition to the aldehyde **3** (Scheme 3). This experimental result may be consistent with the aldehyde **3** and ketone **9** existing in two different preferred ground state conformations (the ones shown in Scheme 3), a hypothesis that is supported by our Spartan (SYBYL) molecular mechanics calculations. It was found that, in **3** (Figure 6), the *s-trans* isomer is favored over the *s-cis* by 0.47 kcal/mol, while the *s-cis* conformer of **9** (Figure 7) is preferred by 0.36 kcal/mol. Although the approximations used in modeling are crude and make any quantitative predictions unreliable, it appears that the conformational properties of carbonyl systems adjacent to (π-allyl)-molybdenum units have the expected consequences on the stereochemical outcome of their reactions. Further studies on the influence of alkyl substitution on stereoselectivity are now being pursued in our laboratory.

Conclusions

Moderate stereocontrol (5−6:1) was achieved during the functionalization of a C=C double bond or a carbonyl group adjacent to a (π-allyl)molybdenum unit in acyclic complexes. The result is an interplay of the directing ability of the $Mo(CO)_2Tp$ moiety and the conformer population. The unexpected stereochemical outcome of the osmylation reaction can be explained qualitatively using the Curtin−Hammett principle. An investigation of the effects of different carbonyl group substituents on the conformer population and on the diastereoselec-

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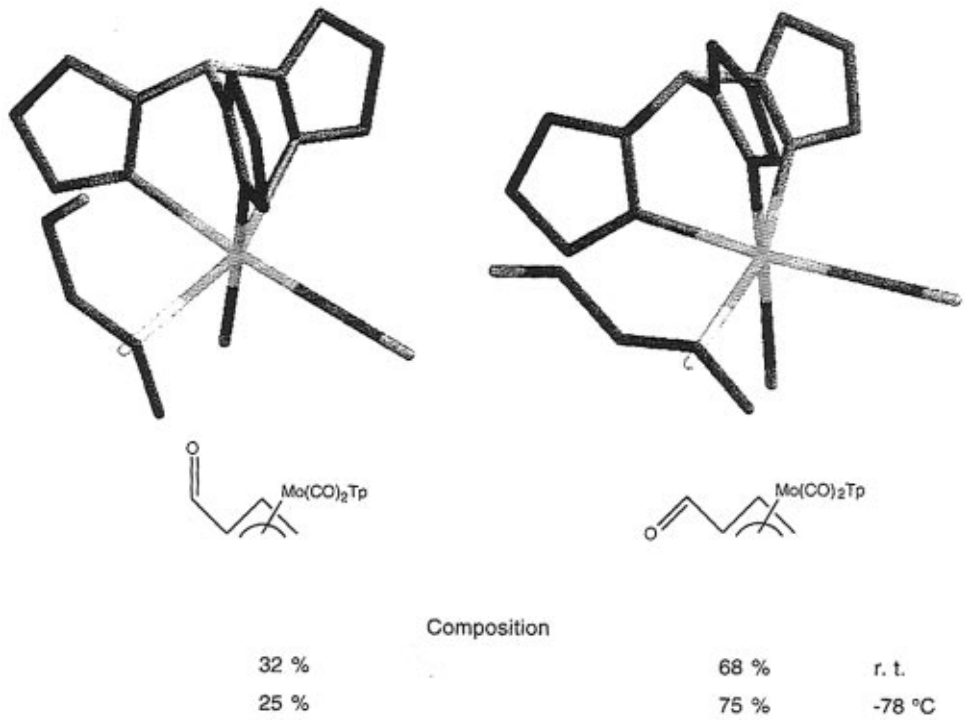

Figure 6. Molecular mechanics (SYBYL) calculations for the two preferred conformers of the aldehyde group adjacent to the (π-allyl)molybdenum unit (**3**).

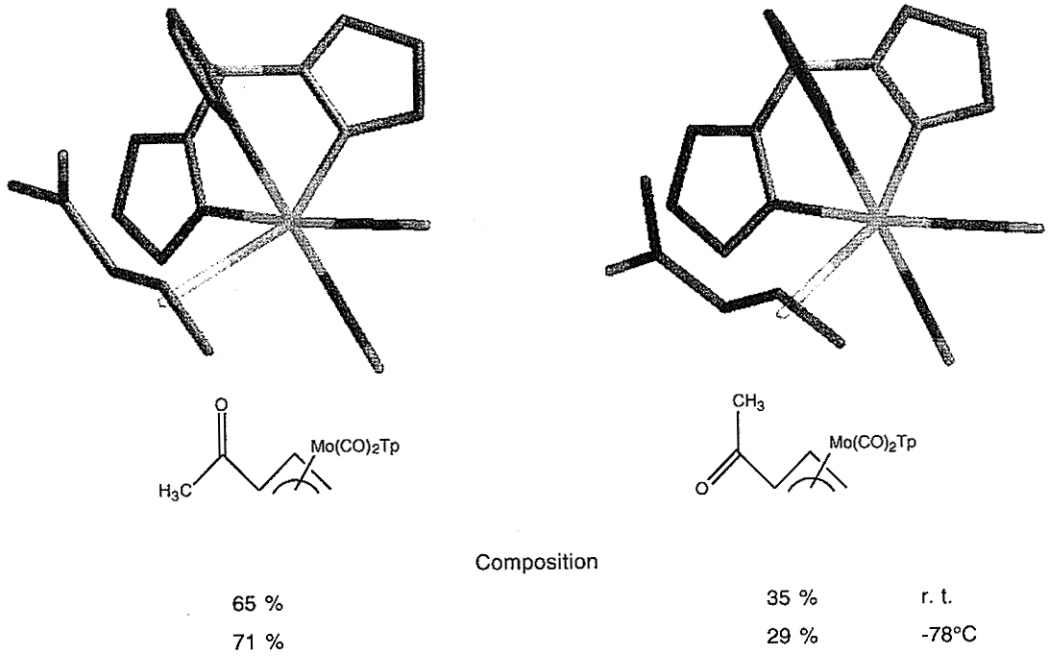

Figure 7. Molecular mechanics (SYBYL) calculations for the two preferred conformers of the methyl ketone group adjacent to the (π-allyl)molybdenum unit (**9**).

tivities obtained in nucleophilic additions has been initiated. Molecular mechanics calculations, correlated with structural evidence for the major diastereomeric product, support the idea that the stereoselectivity achieved in these reactions is a reflection of the ground state conformer distribution of the starting complexes.

To further extend our conformational studies, more substituted (π-allyl)molybdenum complexes will be synthesized, with the aim of improving the selectivities achieved during their functionalization. Coupled with the preparation of (π-allyl)molybdenum systems in optically pure form and controlled demetalation, this methodology is expected to allow stereocontrolled construction of a range of useful organic systems.

Experimental Section

General Procedures. 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 diethyl ether from sodium/benzophenone, methylene chloride and acetonitrile from CaH_2. Molybdenum hexacarbonyl, acetic anhydride, DIBAL-H, osmium tetraoxide, 1,4-pentadien-3-ol, oxalyl chloride, and all the Grignard reagents were purchased from

Aldrich Chemical Co. and used as received. DMSO and triethylamine were distilled from CaH_2 prior to use. Analytical thin-layer chromatography was performed on glass plates precoated with Merck F_{254} silica gel 60, and visualization was accomplished using UV light. Column chromatography was performed with mixtures of hexanes and ethyl acetate on Merck silica gel 60 under nitrogen pressure. Melting points were recorded on a Unimelt Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer. NMR spectra were recorded on a Varian Gemini 300 spectrometer. Mass spectral analyses were carried out by the Major Analytical Instruments Facility at the Department of Chemistry, CWRU.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(methoxycarbonyl)propenyl]molybdenum (1). To the $Br(CH_3CN)_2(CO)_2Mo(\eta^3\text{-}1\text{-}C_3H_4COOCH_3)$ complex[26] (204 mg, 0.49 mmol, 1 equiv) in THF (5 mL) was added sodium tris(1-pyrazolyl)borohydride (140 mg, 0.59 mmol, 1.2 equiv) with stirring at room temperature under an atmosphere of purified nitrogen. After 45 min, when no starting material remained, a saturated NH_4Cl solution (5 mL) was added. Stirring continued for 30 min, followed by extraction with ethyl ether (6 × 5 mL), drying ($MgSO_4$), and rotary evaporation to provide a brown oil. Flash chromatographic purification (silica gel, 4/1 hexanes/ethyl acetate) provided the desired ester, 171.6 mg (75% yield) as an orange crystalline solid, which was further purified by recrystallization from pentane/ether. When the same procedure was followed on a larger scale, 6.0 g (14.5 mmol) of the starting complex and 4.117 g (17.4 mmol) of sodium tris(1-pyrazolyl)borohydride, the desired **1**[13a] was obtained in 74% yield after recrystallization: mp 140−142 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.93 (br s, 3H), 7.53 (d, J = 2.0 Hz, 3H), 6.20 (t, J = 2.3 Hz, 3H), 4.83 (dt, J = 6.5, 9.5 Hz, 1H), 3.65 (dd, J = 6.5, 2.8 Hz, 1H), 3.55 (s, 3H), 2.49 (d, J = 9.5 Hz, 1H), 1.42 (dd, J = 9.5, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 234.5, 224.8, 171.9, 143.7, 135.4, 105.4, 85.5, 66.8, 51.3, 47.9; IR ($CHCl_3$, cm^{-1}) 2498 (w, BH), 1945 (s), 1858 (s), 1714 (s); TLC R_f 0.27 (hexanes/ethyl acetate 3/1); HRMS (EI, 20 eV) m/z calcd for $C_{16}H_{17}O_4N_6MoB$ (^{98}Mo) 466.0464, found 466.0409, 438 (M^+ − CO), 410 (M^+ − 2CO), 407 (M^+ − COOMe).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(hydroxymethylene)propenyl]molybdenum (2). The pure ester **1** (3.84 g, 8.27 mmol) was dissolved in 150 mL of dry ether at −78 °C, and 18.18 mL of a solution 1 M in DIBAL-H (18.18 mmol) was added at −78 °C. Stirring was continued for 2 h, at which time the solution was warmed to room temperature and added to a saturated solution of Na_2CO_3. The ether layer was decanted, and the aqueous solution was extracted with ethyl ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated to provide the alcohol, which crystallized from ethyl ether as a pale yellow solid (3.30 g, 91% yield): mp 148.5−150 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.00 (br s, 3H), 7.48 (d, J = 2.2 Hz, 3H), 6.15 (t, J = 2.1 Hz, 3H), 4.28 (m, 2H), 3.93 (dt, J = 6.8, 9.5 H), 3.42 (dd, J = 2.8, 6.6 Hz, 1H), 2.26 (m, 1H), 1.5 (s, 1H, OH), 1.18 (dd, J = 2.9, 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 232.3, 226.9, 144.2, 135.5, 105.5, 82.4, 77.8, 63.5, 49.4; IR ($CHCl_3$, cm^{-1}) 3406 (br), 2928 (m), 2849 (m), 2486 (w, BH), 1944 (s), 1850 (s); TLC R_f 0.13 (hexanes/ethyl acetate 3/1); HRMS (EI, 23 eV) m/z calcd for $C_{15}H_{17}O_3N_6MoB$ (^{98}Mo) 438.0515, found 438.0510, 410 (M^+ − CO), 382 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-formylpropenyl]molybdenum (3). Oxalyl chloride (291 μL, 3.33 mmol) was added to 10 mL of CH_2Cl_2, and the solution was cooled to −78 °C. To this was added DMSO (416 μL, 6.66 mmol) in 2.5 mL of CH_2Cl_2, and the solution was stirred for 2 min. The alcohol **2** (657 mg, 1.5 mmol) dissolved in 25 mL of CH_2Cl_2 was added dropwise. After 1 h at −78 °C, 2.5 mL of triethylamine (17.5 mmol) was added to the reaction mixture, the cooling bath was removed, and the solution turned orange at room temperature. It was poured into 15 mL of water, and the layers were separated. The water layer was extracted with methylene chloride (5 × 10 mL), and the combined organic extracts were dried ($MgSO_4$) and rotary evaporated. Recrystallization from methylene chloride/hexanes provided 535 mg of pure aldehyde (82% yield) as an orange crystalline solid: mp 154.5-156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 9.2 (d, J = 7.9 Hz, 1H), 7.98 (s, br, 3H), 7.58 (d, J = 2.2 Hz, 3H), 6.23 (t, J = 2.2 Hz, 3H), 4.85 (ddd, J = 9.5, 9.3, 6.8 Hz, 1H), 3.76 (dd, J = 6.8, 2.7 Hz, 1H), 2.65 (t, J = 8.7 Hz, 1H), 1.62 (dd, J = 9.7, 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) 234.1, 224.1, 200.7, 144.5, 135.7, 105.8, 88.7, 74.9, 48.9; IR ($CHCl_3$, cm^{-1}) 3142 (w), 2493 (w, BH), 1967 (s), 1867 (s), 1688 (s); TLC R_f 0.25 (hexanes/ethyl acetate 3/1); HRMS (EI, 23 eV) m/z calcd for $C_{15}H_{15}O_3N_6MoB$ (^{98}Mo) 436.0358, found 436.0354, 380 (M^+ − 2CO).

1,4-Pentadien-3-yl Acetate. 1,4-Pentadien-3-ol (0.5 g, 0.578 mL, 5.94 mmol) in 5 mL of dry ethyl ether was treated with DMAP (0.881 g, 7.13 mmol) and freshly distilled acetic anhydride (0.672 mL, 0.727 g, 7.13 mmol) with stirring for 3 days at room temperature. The resulting reaction mixture was washed with water (5 mL), 10% HCl solution (3 × 5 mL), and water again (3 × 5 mL) and then dried ($MgSO_4$). The ether was removed by distillation to provide 0.4 g (53% yield) of acetylated product (bp 112.5−114 °C), which was pure according to the capillary GC analysis: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 5.84 (ddd, J = 16.8, 10.6, 6.1 Hz, 2H), 5.72 (t, J = 5.9 Hz, 1H), 5.31 (d, J = 17.3 Hz, 2H), 5.23 (d, J = 10.3 Hz, 2H), 2.2 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 169.8, 134.9, 117.3, 74.9, 21.1; IR ($CHCl_3$, cm^{-1}) 1734 (s), 1381 (m), 1250 (s), 919 (s); TLC R_f 0.67 (hexanes/ethyl acetate 4/1).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-vinylpropenyl]molybdenum (4). (A) From 1,4-pentadien-3-yl Acetate. $Mo(CO)_6$ (0.734 g, 2.78 mmol, 1 equiv) was heated at reflux with 2.9 mL of dry acetonitrile for 14 h. The reaction mixture was cooled to room temperature, and the unreacted acetonitrile was evaporated under a nitrogen stream. Dry methylene chloride (10 mL) was added, and the solution turned green. The color changed to orange when 1,4-pentadien-3-yl acetate (0.382 g, 3.03 mmol, 1.09 equiv) was added with stirring at room temperature. After 30 min, the methylene chloride was evaporated under nitrogen, and dry THF (10 mL) was added. Sodium tris(1-pyrazolyl)borohydride (0.656 g, 2.78 mmol, 1 equiv) was added, and the reaction was judged to be complete in 20 min. The reaction mixture was subjected to flash chromatography (silica gel, 4/1 hexanes/ethyl acetate) to provide the desired complex, which was recrystallized from methylene chloride/hexanes as an orange crystalline solid (0.735 g, 61% yield).

(B) From Aldehyde 3. To a stirred mixture of methyltriphenylphosphonium bromide (0.428 g, 1.1 mmol) and potassium *tert*-butoxide (1.1 mL of a 1.0 M solution in THF) in THF (2.5 mL) were added **3** (0.436 g, 1 mmol) and 18-crown-6 (15 mg) in 5 mL of THF. After the mixture was stirred for 6 h at room temperature, water (7 mL) was added, and the solvent was removed *in vacuo*. The residue was extracted with ethyl acetate, washed with water, dried ($MgSO_4$), and concentrated to provide the crude product. Flash chromatographic separation (silica gel, hexanes/ethyl acetate 4/1, then 2/1) provided the desired complex (0.170 g, 44% yield based on 89% conversion): mp 167−168 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.9 (s, br, 3H), 7.45 (s, br, 3H), 6.14 (s, br, 3H), 5.92 (ddd, J = 17.0, 10.4, 10.1 Hz, 1H), 5.48 (dd, J = 17.0, 1.5 Hz, 1H), 5.24 (dd, J = 10.0, 1.4 Hz, 1H), 3.92 (ddd, J = 10.1, 9.1, 6.6 Hz, 1H), 3.40 (dd, J = 6.6, 3.3 Hz, 1H), 2.86 (t, J = 10.5 Hz, 1H), 1.18 (dd, J = 9.1, 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 233.5, 227.3, 139.8, 135.7, 116.7, 105.2, 86.9, 79.7, 47.7; IR ($CHCl_3$, cm^{-1}) 3157 (m), 2490 (m, BH), 1943 (s), 1843 (s), 1616 (w); TLC R_f 0.36 (hexanes/ethyl acetate 3/1); HRMS (EI,

(26) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.

23 eV) *m*/*z* calcd for $C_{14}H_{17}N_6MoB$ (^{98}Mo) ($M^+ - 2CO$) 378.0667, found 378.0636.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(1′,2′-dihydroxyethyl)propenyl]molybdenum (5 and 6). To a solution of **4** (200 mg, 0.46 mmol, 1 equiv) in pyridine (6 mL) was added dropwise a 2.5 wt % solution of OsO_4 in 2-methyl-2 propanol (8.5 mL, 0.69 mmol, 1.5 equiv) under nitrogen. After 2 h at room temperature, the reaction mixture was stirred with an aqueous solution of $Na_2S_2O_5$ (2.3 g, 18 equiv) for 16 h. The dark red solution was transferred to a separatory funnel containing 25 mL of 3% HCl and was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with saturated aqueous NH_4Cl (2 × 15 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography (silica gel, hexanes/ethyl acetate, gradual elution with 2.5/1, 2/1, 1.5/1) provided a mixture of diastereomeric diols as a yellow solid (152 mg, 70% yield, diastereomeric ratio of 5:1 by ^1H NMR): mp 125−127 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), major diastereomer, 8.22 (s, br, 3H), 7.48 (d, *J* = 2.2 Hz, 3H), 6.15 (t, *J* = 2.1 Hz, 3H), 4.05 (m, 1H), 3.91 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.82 (m, 2H, overlap with 3.91), 3.35 (dd, *J* = 6.7, 3.2 Hz, 1H), 2.70 (s, br, 1H, OH), 1.86 (t, *J* = 9.4 Hz, 1H), 0.97 (dd, *J* = 8.6, 3.1 Hz, 1H); ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), minor diastereomer, 8.00 (s, br, 3H), 7.51 (d, *J* = 2.1 Hz, 3H), 6.17 (t, *J* = 2.2 Hz, 3H), 4.57 (m, 1H), 4.14 (dt, *J* = 7.1, 9.9 Hz, 1H), 3.71 (m, 2H), 3.51 (dd, *J* = 6.9, 2.6 Hz, 1H), 2.27 (dd, *J* = 10.4, 2.2 Hz, 1H), 1.5 (s, br, 1H, OH), 1.31 (dd, *J* = 9.5, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), major diastereomer, 231.8, 226.5, 144.1, 135.4, 105.6, 83.5, 77.9, 72.2, 70.05, 48.2; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), minor diastereomer, 231.8, 226.5, 144.1, 135.9, 105.9, 82.2, 79.2, 71.3, 68.5, 49.9; IR ($CHCl_3$, cm^{-1}) 3429 (s, br), 2940 (m), 2492 (m, BH), 2259 (w), 1939 (s), 1859 (s); TLC R_f 0.16 (hexanes/ethyl acetate 1/1); HRMS (FAB) *m*/*z* calcd for $C_{16}H_{19}O_4N_6MoB$ (^{98}Mo) 468.06149, found 468.06475.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(1′-hydroxyethyl)propenyl]molybdenum (7, R = CH_3). Methylmagnesium bromide (0.31 mL of a 3.0 M solution in diethyl ether, 0.92 mmol) was added dropwise to a solution of **3** (40 mg, 0.092 mmol) in THF (3 mL) at −78 °C. After the solution was stirred for 4 h, the excess 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 diethyl ether, washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 33% ethyl acetate in hexanes) gave the complex (42.2 mg, 96% yield, diastereomeric ratio of 5.9:1 by ^1H NMR) as a yellow solid: mp 119−119.5 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), major diastereomer, 8.28 (s, br, 3H), 7.54 (d, *J* = 2.1 Hz, 3H), 6.21 (t, *J* = 2.2 Hz, 3H), 4.24 (m, 1H), 3.69 (ddd, *J* = 9.3, 8.7, 6.5 Hz, 1H), 3.40 (dd, *J* = 6.3, 3.0 Hz, 1H), 2.08 (t, *J* = 9.3 Hz, 1H), 1.95 (d, *J* = 5.4 Hz, 1H), 1.62 (d, *J* = 6.1 Hz, 3H), 1.05 (dd, *J* = 8.7, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), major diastereomer, 231.9, 227.2, 144.4, 135.3, 105.5, 90.9, 73.2, 68.2, 48.4, 29.1; IR ($CHCl_3$, cm^{-1}) 3440 (s, br), 3147 (m), 3130 (m), 2973 (m), 2481 (m, BH), 1937 (s), 1839 (s), 1508 (m, CH_3); TLC R_f 0.46 (hexanes/ethyl acetate 2/1); HRMS (EI, 23 eV) *m*/*z* calcd for $C_{16}H_{19}O_3N_6MoB$ (^{98}Mo) 452.0665, found 452.0659, 434 ($M^+ - H_2O$), 406 ($M^+ - H_2O - CO$), 378 ($M^+ - H_2O - 2CO$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(1′-hydroxybuten-3′-yl)propenyl]molybdenum (7, R = $CH_2CH{=}CH_2$). Allylmagnesium bromide (0.18 mL of a 1.0 M solution in diethyl ether, 0.18 mmol) was added dropwise to a solution of **3** (40 mg, 0.092 mmol) in THF (3 mL) at −78 °C. After the solution was stirred for 2.5 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, 33% ethyl acetate in hexanes) gave the complex as a yellow solid (41.3 mg, 94% yield, ratio of diastereomers 5.2:1 by ^1H NMR): mp 136−137 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), major diastereomer, 8.30 (s, br, 3H), 7.55 (d, *J* = 2.1 Hz, 3H), 6.21 (t, *J* = 2.1 Hz, 3H), 5.97−5.16 (lines of the $CH_2{=}CH$ system; 5.97−5.77 X part, 5.26−5.16 AB part), 4.05 (m, 1H), 3.74 (ddd, *J* = 10.3, 8.7, 6.4 Hz, 1H), 3.41 (dd, *J* = 6.4, 3.1 Hz, 1H), 2.59 (m, 2H), 2.20 (d, *J* = 4.8 Hz, 1H, OH), 2.07 (dd, *J* = 9.9, 9.0 Hz, 1H), 1.04 (dd, *J* = 8.6, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), major diastereomer, 229.4, 226.7, 144.4, 135.4, 133.9, 119.6, 105.5, 88.8, 76.6, 73.3, 70.4, 47.9, 47.3; IR ($CHCl_3$, cm^{-1}) 2478 (m, BH), 1946 (s), 1849 (s), 1054 (s, vinyl); TLC R_f 0.48 (hexanes/ethyl acetate 2/1); HRMS (EI, 23 eV) *m*/*z* calcd for $C_{18}H_{21}O_3N_6MoB$ (^{98}Mo) 478.0822, found 478.0807, 460 ($M^+ - H_2O$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(1′-hydroxypropen-2′-yl)propenyl]molybdenum (7, R = $CH{=}CH_2$). Vinylmagnesium bromide (0.92 mL of a 1.0 M solution in THF, 0.92 mmol) was added dropwise to a solution of **3** (40 mg, 0.092 mmol) in THF (3 mL) at −78 °C. After the solution was stirred for 4 h, the excess Grignard reagent was quenched with water, and the reaction mixture was worked up and purified as described above to give the complex as a 5.6:1 mixture of diastereomers (42.2 mg, 99% yield): mp 132−134 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), major diastereomer, 8.31 (s, br, 3H), 7.56 (d, *J* = 2.1 Hz, 3H), 6.21 (t, *J* = 2.1 Hz, 3H), 6.15 (overlapping with 6.21, m, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.49 (app t, *J* = 7.1 Hz, 1H), 3.74 (ddd, *J* = 9.4, 8.6, 6.5 Hz, 1H), 3.42 (dd, *J* = 6.5, 3.2 Hz, 1H), 2.15 (s, br, 1H, OH), 2.02 (t, *J* = 9.4 Hz, 1H), 1.06 (dd, *J* = 8.6, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), major diastereomer, 232.0, 226.7, 142.6, 135.5, 135.4, 113.9, 105.5, 81.2, 73.8, 73.4, 48.1; IR ($CHCl_3$, cm^{-1}) 3356 (br), 2971 (m), 2914 (m), 2484 (m, BH), 1946 (s), 1849 (s), 1055 (s, vinyl); TLC R_f 0.45 (hexanes/ethyl acetate 2/1); HRMS (EI, 23 eV) *m*/*z* calcd for $C_{15}H_{19}ON_6MoB$ (^{98}Mo) ($M^+ - 2CO$) 408.07675, found 408.07785, 391 ($M^+ - 2CO - OH$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(hydroxybenzyl)propenyl]molybdenum (7, R = Ph). Phenylmagnesium bromide (0.153 mL of a 3.0 M solution in diethyl ether, 0.46 mmol) was added dropwise to a solution of **3** (20 mg, 0.046 mmol) in THF (2 mL) at −78 °C. After the solution was stirred for 4 h, the excess Grignard reagent was quenched with water, and the reaction mixture was worked up and purified as described above to give 24.4 mg (97% yield) of the complex as a 6.3:1 mixture of diastereomers: mp 135−137 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm), major diastereomer, 8.34 (s, br, 3H), 7.57 (d, *J* = 2.1 Hz, 3H), 7.37 (m, 5H), 6.21 (t, *J* = 2.0 Hz, 3H), 5.02 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.74 (ddd, *J* = 9.5, 8.6, 6.4 Hz, 1H), 3.33 (dd, *J* = 6.4, 3.2 Hz, 1H), 2.47 (d, *J* = 2.7 Hz, 1H, OH), 2.34 (t, *J* = 9.5 Hz, 1H), 1.01 (dd, *J* = 8.7, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm), major diastereomer, 231.9, 226.9, 146.6, 144.7, 135.5, 128.9, 128.0, 126.1, 105.6, 89.1, 74.8, 73.5, 48.4; IR ($CHCl_3$, cm^{-1}) 3361 (br), 3070 (m), 1945 (s), 1850 (s), 1599 (m), 1497 (m), 1477 (m); TLC R_f 0.50 (hexanes/ethyl acetate 2/1); HRMS (EI, 23 eV) *m*/*z* calcd for $C_{21}H_{20}O_2N_6MoB$ (^{98}Mo) ($M^+ - OH$) 498.0873, found 498.0844.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(hydroxymethylene-*d*)-propenyl]molybdenum (7, R = D). Complex **3** (20 mg, 0.046 mmol) was stirred with $NaBD_4$ (10.5 mg, 0.25 mmol) in THF (0.7 mL) at room temperature for 1 h. The reaction was quenched by addition of a saturated NH_4Cl solution. Stirring continued for 10 min, followed by extraction with ethyl ether, drying ($MgSO_4$), and rotary evaporation. Purification by preparative TLC (silica gel, 33% ethyl acetate in hexanes) gave 11 mg of unreacted aldehyde **3**, together with **7**, R = D (8 mg, 90% yield based on 45% conversion), as a single diastereomer: ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.07 (s, br, 3H), 7.55 (d, *J* = 2.2 Hz, 3H), 6.21 (t, *J* = 2.1 Hz, 3H), 4.37 (m, 1H), 4.02 (ddd, *J* = 10.2, 8.9, 6.7 Hz, 1H), 3.48 (dd, *J* = 6.6, 2.9 Hz, 1H), 2.32 (dd, *J* = 10.4, 5.5 Hz, 1H), 1.58 (s, br, 1H, OH), 1.26 (dd, *J* = 9.4, 2.9 Hz, 1H);

IR ($CHCl_3$, cm^{-1}) 3406 (br), 2928 (m), 2849 (m), 2486 (w, BH), 1944 (s), 1850 (s); TLC R_f 0.13 (hexanes/ethyl acetate 3/1).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3-η)-1-(carbomethyl)propenyl]molybdenum (9). To a solution of methylmagnesium bromide (160 μL of a 3 M solution, 0.480 mmol, 1.36 equiv) was added dropwise a solution of alcohol **7**, R = CH_3 (160 mg, 0.352 mmol, 1 equiv), in THF (6 mL) at −78 °C under argon atmosphere. A solution of 1,1′-(azodicarbonyl)dipiperidine (112 mg, 0.424 mmol, 1.2 equiv) in THF (2 mL) was then added dropwise to the mixture at −78 °C. The mixture was left to warm to room temperature and was quenched after 30 min by addition of brine. Extraction with ethyl acetate, followed by washing of the organic layer with saturated aqueous $NaHCO_3$ and brine, drying (Na_2SO_4), and removal of solvent, gave the crude product, which was separated by preparative TLC (2.5/1 hexanes/ethyl acetate) to provide 89 mg of ketone **9** (63% yield based on 89% conversion) as an orange solid (mp 122−124 °C dec), together with 17.5 mg of unreacted starting material: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.91 (s, br, 3H), 7.55 (d, J = 1.8 Hz, 3H), 6.21 (t, J = 2.2 Hz, 3H), 4.75 (dt, J = 6.9, 9.7 Hz, 1H), 3.67 (dd, J = 6.9, 2.6 Hz, 1H), 2.59 (d, J = 9.9 Hz, 1H), 1.83 (s, 3H), 1.49 (dd, J = 9.6, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 231.9, 227.0, 205.3, 144.2, 135.7, 105.8, 86.1, 75.8, 48.5, 28.4; IR ($CHCl_3$, cm^{-1}) 2492 (m, BH), 1952 (s), 1869 (s), 1712 (s); TLC R_f 0.24 (hexanes/ethyl acetate 2/1); HRMS (EI, 23 eV) m/z calcd for $C_{16}H_{17}O_3N_6MoB$ (^{98}Mo) 450.05093, found 450.05023.

X-ray Crystal Data for 6: $C_{18}H_{25}BMoN_6O_5$, triclinic, space group $P\bar{1}$, a = 8.1109(2), b = 17.2013(4), and c = 18.0843(3) Å, α = 62.404(1)°, β = 83.015(1)°, γ = 81.562(1)°, V = 2207.70(8) Å^3, Z = 4, D_c = 1.541, λ = 0.710 73 Å, F(000) = 1048. A total of 12 691 reflections (8890 unique) were collected at 293(1) K on a plate-shaped crystal with approximate dimensions of 0.38 mm × 0.22 mm × 0.08 mm using a Siemens Smart Platform diffractometer. Data collection was performed using three different ϕ settings and 0.3° increment ω scans, corresponding to a nominal hemisphere of data; 2θ < 55.42°. Frame time was set to 15 s. Corrections for absorption and decay were applied using SADABS.[27] Solution was by direct methods[28] and refinement by full-matrix least-squares on F^2 using all 8890 unique data.[29] The asymmetric unit contains two disordered ethanol molecules. The atoms C(33), C(34), O(9) and C(35), C(36), O(10) are disordered over two positions with equal occupancies and refined with isotropic thermal parameters. Chemically similar bonds of the different components were restrained to have similar lengths. No hydrogen positions were calculated for the disordered solvent molecules. All other hydrogen atoms were included in the refinement as riding atoms. The final refinements included anisotropic thermal pareameters for all other non-hydrogen atoms and converged to wR_2 = 0.1455 (F^2, all data) and R_1 = 0.0504 (F, 6516 reflections with $I > 2\sigma(I)$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

X-ray Crystal Data for 7 (R = $CH_2CH{=}CH_2$): $C_{18}H_{21}BMoN_6O_3$, monoclinic, space group $P2_1/n$, a = 9.5554(1), b = 10.4674(1), and c = 21.9773(3) Å, β = 96.762(1)°, V = 2182.88(4) Å^3, Z = 4, D_c = 1.449, λ = 0.710 73 Å, F(000) = 968. A total of 9734 reflections (3121 unique) were collected at 293(1) K on a chunky crystal with approximate dimensions of 0.40 mm × 0.35 mm × 0.25 mm using a Siemens Smart Platform diffractometer. Data collection was performed using three different ϕ settings and 0.3° increment ω scans, corresponding to a nominal hemisphere of data; 2θ < 46.46°. Frame time was set to 10 s. Corrections for absorption and decay were applied using SADABS.[27] Solution was by direct methods[28] and refinement by full-matrix least-squares on F^2 using all 3121 unique data.[29] The terminal propenyl group is disordered over four positions. The refined model contained two positions with equal occupancies for the atoms C(14) and C(15) and four positions with equal occupancies for C(16). All disordered carbon atoms were refined with isotropic thermal parameters. Only the positions of the hydrogen atoms bonded to C(14A) and C(14B) were included. The four chemically similar bonds between the individual C(15)═C(16) groups were restrained to have similar lengths. The final refinements included anisotropic thermal parameters for all other non-hydrogen atoms and isotropic thermal parameters for all other hydrogen atoms and converged to wR_2 = 0.0614 (F^2, all data) and R_1 = 0.0229 (F, 2825 reflections with $I > 2\sigma(I)$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **6** and **7** (R = $CH_2CH{=}CH_2$) (18 pages). Ordering information is given on any current masthead page.

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