Lateral Stereocontrol Using π-Allylmolybdenum Systems: The Use of Methyl Substitution To Effect Conformational Control Leading to High Levels of Stereoselectivity

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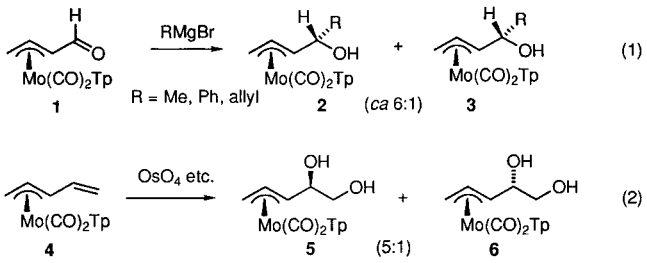
Stereocontrol exerted by a π-allyl-$Mo(CO)_2Tp$ system (Tp = hydrotris(1-pyrazolyl)borato), during addition of Grignard reagents to neighboring aldehyde functionality and during dihydroxylation of alkenes, is found to be dependent on conformational preferences of the substituent relative to the organometallic moiety. Incorporation of a methyl group at C(2) of the π-allyl ligand leads to excellent conformational control when the lateral substituent is a vinyl group, and this results in a diastereomer ratio of 25:1 for the diol that is obtained from osmylation. Poorer conformational control is observed for an aldehyde, and nucleophile additions show correspondingly lower stereoselectivity. Introduction of a methyl substituent at C(1) of the π-allyl ligand does not effect conformational control, as expected, and very poor lateral stereocontrol is observed during both alkene dihydroxylation and nucleophile additions to aldehyde.

Introduction

We have recently shown[1] that carbon−carbon double bonds and carbonyl groups adjacent to a π-allylmolybdenum unit in acyclic systems can be functionalized with modest stereocontrol, exemplified in eqs 1 and 2. Structural evidence for major diastereomeric products, correlated with molecular mechanics calculations, supported the hypothesis that the selectivities achieved result from an interplay between the directing effect of the metal and conformer populations. The major product of dihydroxylation from complex **4** has somewhat unexpected stereochemistry, which appears to result from osmylation anti to the molybdenum moiety on the higher energy *s-cis* conformation (**4A** in Figure 1). An alternate explanation for this stereochemical outcome involves attack on the double bond *syn* to the metal on the lower energy *s-trans* conformation. In an effort to shed more light on the role of steric effects from the $Mo(CO)_2Tp$ system and conformational effects in the substituted π-allyl ligand, as well as produce better stereocontrol, we undertook the studies described in the present paper, wherein the incorporation of methyl substituents is used to influence the distribution between *s-cis* and *s-trans* conformers.



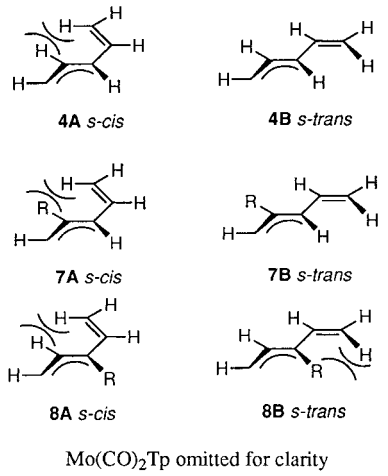


Figure 1.

We anticipated stronger nonbonded interactions between an alkyl group at C(2) of the π-allyl unit and an olefinic or aldehyde moiety adjacent to the π-allyl, interactions which would further destabilize the less preferred conformation **7A** (Figure 1). On the other hand, methylation at C(1) of the π-allyl is expected to destabilize conformer **8B**, resulting in little or no preference for *s-cis* or *s-trans* structures. Such conformational preferences, or lack thereof, are expected to be reflected in the outcome of reactions on the lateral alkene (or aldehyde) functionality.

Results and Discussion

Aldehyde complexes **10** and **13** were each prepared from (*E*)-1-acetoxy-4-chloro-3-methyl-2-butene, which is readily accessible in two steps[2] from chloroacetone via

(1) Pearson, A. J.; Neagu, I. B.; Pinkerton, A. A.; Kirschbaum, K.; Hardie, M. J. *Organometallics* **1997**, *16*, 4346−4354. For an example of the synthetic utility of cyclic π-allyl-$Mo(CO)_2Tp$ complexes, see: Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897. For examples of earlier work on side chain functionalization in acyclic π-allyl-$Mo(CO)_2Cp$ complexes, see: Vong, W. J.; Peng, S. M.; Lin, S. H.; Lin, W. J.; Liu, R. S. *J. Am. Chem. Soc.* **1991**, *113*, 573.

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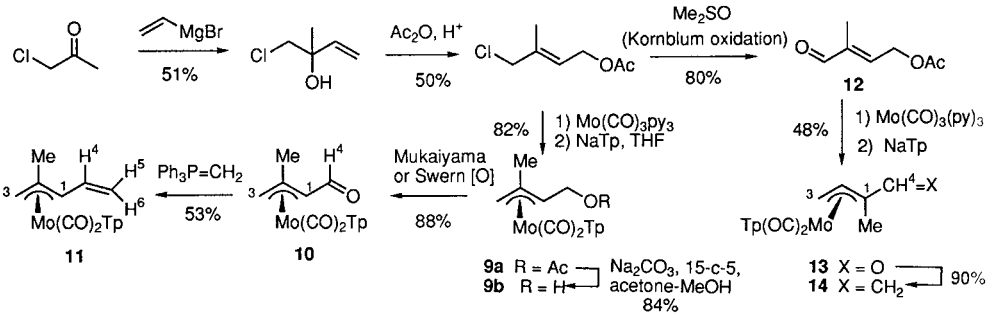
Scheme 1

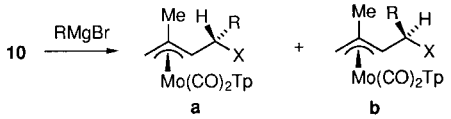


reaction with vinylmagnesium bromide, followed by acetylation with allylic inversion. We anticipated the oxidative addition to be the critical step in the synthesis, and to optimize it, we explored two molybdenum(0) sources under different reaction conditions. In an earlier attempt, (*E*)-1-acetoxy-4-chloro-3-methyl-2-butene was reacted with in situ prepared $Mo(CO)_3(CH_3CN)_3$[3] and provided, after ligand exchange, the π-allylmolybdenum complex **9a** in a modest 15% yield. The alternative route used tricarbonyltris(pyridine)molybdenum[4] as the molybdenum(0) source, allowing overall yields of 82% of **9a** after ligand exchange with sodium tris(1-pyrazolyl)-borohydride (Scheme 1). The same procedure using substrate **12** furnished complex **13** in 48% yield at 23% conversion. No attempts were made to optimize the latter complexation, as the later results indicated that this particular system did not lead to acceptable levels of stereocontrol (vide infra). Complex **9a** was converted uneventfully into alcohol **9b**, which was oxidized to aldehyde **10** in good yield using either a Swern[5] or a Mukaiyama[6] protocol. The aldehydes **10** and **13** were used for studies on nucleophile additions, and also for the preparation of vinyl-substituted derivatives (complexes **11** and **14**) by standard Wittig methylenation.[7]

The issue of *syn*−*anti* isomerism associated with these complexes deserves consideration and will be presented here in more detail. Being aware of literature reports[8] supporting the kinetic retention of olefin geometry during the oxidative addition step, we expected (*E*)-1-acetoxy-4-chloro-3-methyl-2-butene to provide the corresponding π-allyl complex **9a** exclusively in its syn configuration (shown). Unlike the unsubstituted acyclic molybdenum π-allyls described by Liebeskind,[8] the 2-methallyl complexes do not benefit from the convenience of assigning their *syn* or *anti* stereochemistry on the basis of the ^1H NMR coupling constants. However, we have convincing evidence that complexes **10**, **11**, **13**, and **14** are produced exclusively in their expected *syn* configuration, based on NOE experiments. Thus, for complex **10**, presaturation of the singlet (methyl) at 2.17 ppm resulted in an 11% enhancement of the aldehydic proton (doublet, H(4) on structure) at 10.20 ppm. Similarly, for complex **11**, presaturation of the singlet (methyl) at 2.29 ppm resulted in a 9% enhancement of the signal at 6.82 ppm (ddd) corresponding to H(4). No enhancement of the signals corresponding to H(1) was observed in either case. For complex **13**, presaturation of the doublet of doublets (H(2)) at 4.79 ppm resulted in a 12% enhancement of the aldehydic proton (singlet) at 8.81 ppm. Similarly, for complex **14**, presaturation of the doublet of doublets (H(2)) at 4.05 ppm resulted in a 5% enhancement of the signal at 5.78 ppm (dd) corresponding to H(4). No enhancement of the signals corresponding to the methyl substituent was observed for either complex.

While 1-D NOE experiments confirmed the *syn* configuration for these complexes, they could not provide conclusive evidence for the presence of the corresponding *s-cis* and *s-trans* conformers in solution. However, NOESY spectral data supported the presence of only one conformer of complex **11**. Cross-peaks were observed for H(1) ↔ H(6), as well as for the methyl ↔ H(4) signals, both consistent with the molecule existing in the expected low-energy *s-trans* conformation shown in Figure 1. No cross-peaks indicative of the presence of the higher energy *s-cis* conformer were observed. For complex **14**, cross-peaks were observed between H(2) and H(4), and between H(6) and the methyl group, indicating the presence of the *s-trans* conformer. In addition, cross-peaks were observed between H(2) and H(6), and between H(4) and the methyl group, indicative also of the presence of the *s-cis* conformer. Thus, in contrast to **11**, complex **14** exists in solution as an equilibrium mixture of *s-cis* and *s-trans* conformers (undefined ratio). NOE experiments on aldehydes **10** and **13** indicated the presence of both conformers for each complex. It is worth mentioning here that the NMR spectra of all complexes show a single set of peaks in each case, indicating rapid interconversion of *s-cis* snd *s-trans* conformers, an important property when considering the stereochemical outcome of lateral functionalization.

We expected nucleophilic additions to aldehyde **10** to provide mixtures of diastereomeric carbinols (eq 3), as a reflection of the ratio of *s-cis* and *s-trans* conformers.



(3)

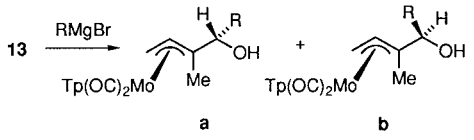
15 R = Me, X = OH (84%)
16 R = CMe=CH$_2$, X = OH (32%)
17 R = Ph, X = OH (55%)
18 R = Me, X = OAc (**a**:**b** = 4:1)
19 R = CMe=CH$_2$, X = OAc (**a**:**b** = 5:1)
20 R = Ph, X = OAc (**a**:**b** = 8:1)

(2) Tietze, L. F.; Eicher, T. Syntheses and Transformations of Functional Groups. In *Reactions and Syntheses*; University Science Books: Mill Valley, CA, 1989; Chapter G, pp 102−104.
(3) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433−434.
(4) Pearson, A. J.; Schoffers, E. *Organometallics* **1997**, *16*, 5365−5367.
(5) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480−2482.
(6) Narasaka, K.; Morikawa, A.; Saigo, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2773−2776.
(7) Boden, R. M. *Synthesis* **1975**, 784.
(8) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132−4156.

Surprisingly, the ^1H and ^{13}C NMR spectra of complexes **15**−**17** all showed single sets of peaks in three different solvents ($CDCl_3$, C_6D_6, d_6-acetone). One is tempted to present these data as evidence for exceptional selectivity in the nucleophilic addition reactions, but careful investigation revealed that this is a case of remarkably coincidental NMR shieldings.

If only one diastereomer were obtained from each Grignard reaction, Mitsunobu reaction[9] would provide us with the other diastereomer, in the form of its benzoic ester. Hydrolysis to the alcohol, followed by comparison of NMR data, would allow a comparison of the two diastereomers. In the event, the Mitsunobu reaction on these substrates was unsuccessful, as was standard benzoylation of the initial carbinols, most probably due to steric hindrance. On the other hand, good yields (70−75%) were obtained from acetylation (eq 3). The product acetates also showed single sets of resonances in their ^1H NMR spectra. Addition of lanthanide shift reagents to the NMR solutions of acetates **18**−**20** induced separation of signals in the ^1H NMR spectra, and this development allowed determination of the diastereomeric ratios listed in eq 3. For example, the ^1H NMR spectrum for complex **20**, without any shift reagent, shows peaks at 2.13 ppm (s, acetyl) and 2.11 ppm (d, H^3). Addition of $Eu(fod)_3$ to the solution induced their separation into signals corresponding to each diastereomer in the mixture. Thus, the acetyl peak was shifted and split into two singlets (δ 2.39 and 1.99, ratio 8:1), while the signal corresponding to H^3 was shifted and split into two doublets (δ 2.28 and 2.07, ratio 8:1). The major products are assigned the stereochemistry shown in structure **a** by analogy with the reactions of the unsubstituted complex (eq 1), which have been characterized by X-ray structure determination.

Nucleophilic additions to the aldehyde group of complex **13** (eq 4) resulted in only a modest diastereomeric ratio of 1.2−1.8 to 1, which could be determined directly from the ^1H NMR spectra of the products. Overall, these

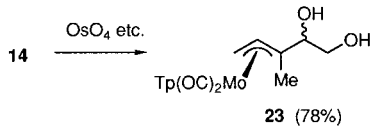


(4)

21 R = Me (97%, 1.2:1)
22 R = Ph (98%, 1.8:1)

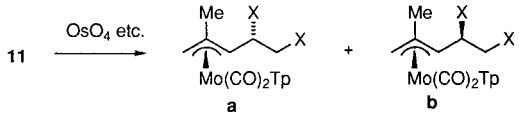
results appear to be consistent with our earlier proposition that the methyl group at C(2) of the allyl ligand will favor the *s-trans* conformer to some degree, while a C(1) methyl substituent causes a more even distribution between *s-trans* and *s-cis* arrangements. However, the observed stereoselectivities for complex **10** are no better than those observed in our earlier work for the unsubstituted π-allyl complex **1**,[1] presumably as a result of the low steric demand from the aldehyde oxygen versus the hydrogen. We anticipated that the situation would be very different for the alkene side chain in complexes **11** and **14**, as indicated from the NOE studies outlined above.

Our earlier investigations[1] showed a 5:1 selectivity during osmylation of the unsubstituted π-allyl system (eq 2). For complexes **11** and **14**, we followed Kishi's osmylation procedure,[10] which resulted in an improvement in the yield of the diols (eqs 5 and 6). The diastereomer ratio



(5)

23 (78%)



(6)

24 X = OH (98%)
25 X = OAc (85%; **a**:**b** = 25:1)

for diols **23**, from complex **14**, was 1.1:1 (by NMR spectroscopy), indicative of poor conformational control in the reactant molecule, and consistent with the NOE studies described earlier. The ratio of the diastereomeric diols **24** could not be estimated from the ^1H NMR spectrum of the mixture, as only a single set of resonances was observed. Following the approach we developed for the carbinols **15**−**17**, we achieved good separation of the ^1H NMR signals of the corresponding acetates **25**, after addition of lanthanide shift reagent. This procedure allowed us to determine a diastereomeric ratio of 25:1 for the acetates, indicating excellent selectivity in the osmylation of carbon−carbon double bonds adjacent to the 2-methallyl system.

The final task was to assign the stereochemistry of the major product. We experienced considerable difficulties in crystallizing **24**. The major diacetate isomer could be selectively crystallized from ethanol at 0 °C, but the crystals were small and twinned. X-ray structure analysis[11] showed a unit cell consisting of two identical molecules, which were assigned the *RS*,*SR* configuration **25a**, consistent with OsO_4 attack *anti* to $Mo(CO)_2Tp$ on the more favored conformation of complex **11** (corresponding to **7B** in Figure 1).

Conclusions

Within the last three years, our group has been successful in developing efficient synthetic routes toward a variety of new acyclic π-allylmolybdenum complexes,[1,4] in exploring the stereodirecting effect of molybdenum during functionalization,[1] and in developing reliable methods of demetalation.[12] In the present work, we have shown that functionalization of carbon−carbon double bonds and carbonyl groups adjacent to π-allylmolybdenum units is the result of the interplay between the directing effect of the metal and conformer populations, resulting in a 25:1 selectivity during double bond functionalization of complex **11**. While this result is significant on its own, it may also represent a useful entry into

(9) Mitsunobu, O. *Synthesis* **1981**, 1−28.

(10) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3943−3946. Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron* **1984**, *40*, 2247−2255.

(11) We are grateful to Professor A. Alan Pinkerton at the University of Toledo for X-ray structure determination on complex **25**. Owing to problems of twinning in the crystal, structural data of publishable quality could not be obtained. Nevertheless, the key structural feature, i.e., the stereochemistry of the secondary alcohol relative to the π-allylmolybdenum system, could be elucidated.

(12) Pearson, A. J.; Douglas, A. R. *Organometallics* **1998**, *17*, 1446−1448.

the field of organic synthesis, especially if correlated with access to optically pure molybdenum complexes.

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, and methylene chloride and acetonitrile from CaH_2. Molybdenum hexacarbonyl, acetic anhydride, DIBAL-H, osmium tetroxide, 1,4-pentadien-3-ol, oxalyl chloride, sodium tris(1-pyrazolyl)borohydride, $Eu(fod)_3$, 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. ^{1}H NMR spectra were recorded at 300 MHz. Mass spectral analyses were carried out in-house by the Major Analytical Instruments Facility at the Department of Chemistry.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(acetoxymethylene)-2-methylpropenyl]molybdenum (9a). $Mo(CO)_3py_3$[4] (233 mg, 0.559 mmol, 1 equiv) was stirred with (*E*)-1-acetoxy-4-chloro-3-methyl-2-butene[2] (100 mg, 0.615 mmol, 1.1 equiv) in methylene chloride (5 mL) at reflux for 1 h (TLC monitoring, silica gel, 3/1 hexanes/ethyl acetate). The solvent was evaporated, and potassium tris(1-pyrazolyl)-borohydride[13] (169 mg, 0.671 mmol, 1.2 equiv) in THF (5 mL) was added. The reaction was quenched after 3 h of stirring at room temperature, by addition of a saturated NH_4Cl solution (5 mL). Stirring was 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, 3/1 hexanes/ethyl acetate) provided the desired complex (227 mg, 82% yield) as a yellow crystalline solid, which was further purified by recrystallization from methylene chloride/hexanes: mp 159.5−162 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.06 (d, *J* = 2.0 Hz, 3H), 7.54 (d, *J* = 2.2 Hz, 3H), 6.20 (t, *J* = 2.2 Hz, 3H), 5.21 (dd, *J* = 12.0, 7.7 Hz, 1H), 4.85 (dd, *J* = 12.0, 7.0 Hz, 1H), 3.58 (d, *J* = 1.8 Hz, 1H), 2.17 (s, 3H), 1.76 (dd, *J* = 7.7, 7.2 Hz, 1H), 1.66 (s, 3H), 1.36 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.7, 227.5, 171.0, 144.9, 135.7, 105.4, 84.2, 71.2, 64.0, 58.2, 20.9, 14.9; IR ($CHCl_3$, cm^{-1}) 2991 (w), 2480 (w, B−H), 1939 (s), 1854 (s), 1743 (s); TLC R_f 0.19 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{18}H_{21}O_4N_6MoB$ (^{98}Mo) 494.07715, found 494.07681; 438 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(hydroxymethylene)-2-methylpropenyl]molybdenum (9b). Complex **9a** (105 mg, 0.212 mmol) in methanol (4 mL)−acetone (3.6 mL) was stirred overnight at room temperature with 4 mL of a saturated Na_2CO_3 solution containing 15-crown-5 (50 μL). Addition of 5 mL of a 10% solution of HCl at 0 °C, followed by extraction into ethyl acetate, drying ($MgSO_4$), and rotary evaporation, provided the crude product, which was purified by recrystallization from chloroform/hexanes to give a yellow solid (80 mg, 84% yield): mp 142−144 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.11 (s, br, 3H), 7.54 (d, *J* = 2.0 Hz, 3H), 6.20 (t, *J* = 2.0 Hz, 3H), 4.70 (dd, *J* = 12.2, 6.6 Hz, 1H), 4.46 (dd, *J* = 12.2, 7.4 Hz, 1H), 3.55 (d, *J* = 2.0 Hz, 1H), 1.76 (dd, *J* = 7.4, 6.6 Hz, 1H), 1.64 (s, 3H), 1.24 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.6, 227.5, 145.0, 135.7, 105.4, 77.9, 77.2, 62.2, 57.6, 14.8; IR ($CHCl_3$, cm^{-1}) 3555 (br), 2491 (m, B−H), 1930 (s), 1844 (s); TLC R_f 0.09 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{16}H_{19}O_3N_6MoB$ (^{98}Mo) 452.06656, found 452.06820; 396 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-formyl-2-methylpropenyl]molybdenum (10). A (Mukaiyama Oxidation). To a solution of isopropenylmagnesium bromide (0.5 mL of a 0.5 M solution, 0.25 mmol, 1.36 equiv) was added dropwise a solution of alcohol **9b** (80 mg, 0.177 mmol, 1 equiv) in THF (4 mL) at −78 °C under argon atmosphere. A solution of 1,1′-(azodicarbonyl)dipiperidine (54 mg, 0.212 mmol, 1.2 equiv) in THF (1.5 mL) was then added dropwise to the mixture at −78 °C. The cooling bath was removed, the mixture was allowed to warm to room temperature, and the reaction was quenched after 1 h 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 crystallized from chloroform/hexanes as an orange solid (70 mg, 88% yield).

B (Swern Oxidation). Oxalyl chloride (291 μL, 3.33 mmol) was added to 10 mL of CH_2Cl_2 and 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 **9b** (681 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. Purification by flash chromatography (silica gel, 20% ethyl acetate in hexanes), followed by recrystallization from methylene chloride/hexanes, provided 537 mg of pure aldehyde **10** (79% yield) as an orange crystalline solid: mp 139−141 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 10.08 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 2.0 Hz, 3H), 7.56 (d, *J* = 2.2 Hz, 3H), 6.20 (app t, *J* = 2.2 Hz, 3H), 3.73 (d, *J* = 2.2 Hz, 1H), 2.05 (s, 3H), 1.91 (d, *J* = 8.0 Hz, 1H), 1.29 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.9, 227.0, 202.2, 145.4, 136.1, 105.6, 91.4, 68.5, 58.7, 16.0; IR ($CHCl_3$, cm^{-1}) 2482 (m, B−H), 1958 (s), 1872 (s), 1674 (s); TLC R_f 0.17 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{16}H_{17}O_3N_6MoB$ (^{98}Mo) 450.05093, found 450.05197; 394 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-vinyl-2-methylpropenyl]molybdenum (11). To a stirred mixture of methyltriphenylphosphonium bromide (0.086 g, 0.24 mmol, 3 equiv) and potassium *tert*-butoxide (0.24 mL of a 1.0 M solution in THF, 0.24 mmol, 3 equiv) in CH_2Cl_2 (2 mL) were added complex **10** (0.036 g, 0.08 mmol, 1 equiv) and 18-crown-6 (2 mg) in 2 mL of CH_2Cl_2. After the resulting mixture was stirred for 3 h at room temperature, water (2 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the extract was washed with water, dried ($MgSO_4$), and concentrated to afford the crude product. Flash chromatographic separation (silica gel, 5/1 hexanes/ethyl acetate) provided the desired complex **11** (0.0190 g, 53% yield): mp 159−161 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.12 (s, br, 3H), 7.53 (s, br, 3H), 6.59 (ddd, *J* = 16.9, 10.8, 10.2 Hz, 1H), 6.17 (t, *J* = 2.1 Hz, 3H), 5.62 (d, *J* = 17.0, 1H), 5.43 (d, *J* = 9.9 Hz, 1H), 3.57 (d, *J* = 2.2 Hz, 1H), 2.35 (d, *J* = 10.9 Hz, 1H), 1.68 (s, 3H), 1.38 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 229.4, 228.7, 144.9, 137.1, 135.6, 117.4, 105.1, 83.8, 80.9, 56.9, 15.4; IR ($CHCl_3$, cm^{-1}) 2479 (m, B−H), 1936 (s), 1851 (s); TLC R_f 0.42 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{17}H_{19}O_2N_6MoB$ (^{98}Mo) 448.07222, found 448.07012.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1−3)-η-*syn*-(1-formyl)-*anti*-(1-methyl)propenyl]molybdenum (13). $Mo(CO)_3py_3$[4] (133.5 mg, 0.32 mmol, 1 equiv) was stirred with (*E*)-4-acetoxy-2-methyl-2-butenal (50 mg, 0.352 mmol, 1.1 equiv) in methylene chloride (2.5 mL) at reflux for 2 h (TLC monitoring, silica gel, 3/1 hexanes/ethyl acetate). The solvent was removed in vacuo, the residue was dissolved in THF (2 mL), and sodium tris(1-pyrazolyl)borohydride (91 mg, 0.384 mmol, 1.2 equiv) in THF (2 mL) was added. The reaction mixture was stirred at room temperature for 16 h, and the resulting crude product was purified by filtration through a plug of alumina (CH_2Cl_2). Preparative TLC separation (silica gel, 4/1 hexanes/ethyl acetate) provided the desired complex (16 mg, 48% yield at 23% conversion) and 39.5 mg of unreacted (*E*)-4-acetoxy-2-methyl-2-butenal: mp 153.5−156 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.81 (s, 1H), 7.80 (s, br, 3H), 7.57 (s, 3H), 6.24 (s, 3H), 4.79 (dd, *J* = 10.3, 7.2 Hz, 1H), 3.93

(13) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170−3177.

(dd, J = 7.1, 3.2 Hz, 1H), 2.20 (dd, J = 10.2, 3.2 Hz, 1H), 1.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 235.6, 224.9, 200.8, 144.7, 135.9, 105.9, 92.5, 86.1, 48.2, 13.7; IR ($CHCl_3$, cm^{-1}) 2493 (m, B−H), 1950 (s), 1866 (s), 1678 (s); TLC R_f 0.28 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{16}H_{17}O_3N_6MoB$ (^{98}Mo) 450.05093, found 450.04963; 394 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1−3)-*η*-*syn*-(1-vinyl)-*anti*-(1-methyl)propenyl]molybdenum (14). To a stirred mixture of methyltriphenylphosphonium bromide (0.052 g, 0.13 mmol, 3 equiv) and potassium *tert*-butoxide (0.13 mL of a 1.0 M solution in THF, 0.13 mmol, 3 equiv) in CH_2Cl_2 (1 mL) at 0 °C were added complex **13** (0.020 g, 0.044 mmol, 1 equiv) and 18-crown-6 (1 mg) in 1 mL of CH_2Cl_2. After the resulting mixture was stirred for 3 h at room temperature, water (2 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extract was washed with water, dried ($MgSO_4$), and concentrated to provide the crude product. Flash chromatographic separation (silica gel, 5/1 hexanes/ethyl acetate) provided the desired complex **14** (0.018 g, 90% yield). mp 100−102 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.45 (s, br, 3H), 7.54 (d, J = 2.3 Hz, 3H), 6.19 (t, J = 2.0 Hz, 3H), 5.78 (dd, J = 17.5, 10.6 Hz, 1H), 5.44 (d, J = 17.2 Hz, 1H), 5.24 (d, J = 10.9 Hz, 1H), 4.05 (dd, J = 10.0, 7.1 Hz, 1H), 3.62 (dd, J = 7.1, 4.1 Hz, 1H), 1.88 (dd, J = 9.9, 4.2 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.6, 228.5, 145.6, 135.7, 113.8, 105.2, 84.3, 75.6, 45.5, 16.2; IR ($CHCl_3$, cm^{-1}) 1832 (s), 1926 (s); TLC R_f 0.43 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{17}H_{19}O_2N_6MoB$ (^{98}Mo) 448.07222, found 448.05165; 392 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-*η*-1-(1′-hydroxyethyl)-2-methylpropenyl]molybdenum (15). Methylmagnesium bromide (0.21 mL of a 3 M solution in ethyl ether, 0.63 mmol) was added dropwise to a solution of the complex **10** (27 mg, 0.060 mmol) in THF (1.5 mL) at −78 °C. After the mixture was stirred for 5 h, the excess of Grignard reagent was destroyed 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, and the organic solution was washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 17% ethyl acetate in hexanes) gave the complex as a yellow solid, which was recrystallized from $CHCl_3$/hexanes (23.4 mg, 84% yield): mp 179.5−181 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.22 (s, br, 3H), 7.47 (s, br, 3H), 6.12 (t, J = 2.2 Hz, 3H), 4.55 (m, 1H), 3.44 (d, J = 2.2 Hz, 1H), 2.15 (s, br, 1H, OH), 1.58 (d, J = 9.8 Hz, 1H, overlapping with 1.54), 1.54 (d, J = 6.1 Hz, 3H), 1.46 (s, 3H), 1.11 (d, J = 2.0 Hz, 1H); ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm) 8.30 (s, br, 3H), 7.15 (s, br, 3H), 5.76 (s, br, 3H), 4.46 (ddd, J = 9.7, 6.7, 6.6 Hz, 1H), 3.29 (d, J = 2.0 Hz, 1H), 1.84 (d, J = 7.4 Hz, 1H, OH), 1.48 (d, J = 9.7 Hz, 1H), 1.31 (s, 3H), 1.25 (d, J = 6.1 Hz, 3H), 1.11(d, J = 2.0 Hz, 1H); ^{1}H NMR (d_6-acetone, 300 MHz) δ (ppm) 8.29 (s, br, 3H), 7.58 (s, br, 3H), 6.13 (t, J = 2.2 Hz, 3H), 4.40 (dd, J = 9.7, 5.9 Hz, 1H), 3.52 (d, J = 2.2 Hz, 1H), 2.68 (s, br, 1H, OH), 1.68 (d, J = 9.8 Hz, 1H), 1.48 (d, J = 6.1 Hz, 3H), 1.40 (s, 3H), 0.91 (d, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 229.8, 228.0, 146.7, 135.7, 105.4, 86.3, 81.2, 66.9, 57.3, 25.9, 14.8; IR ($CHCl_3$, cm^{-1}) 2479 (m, B−H), 1937 (s), 1842 (s); TLC R_f 0.26 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{17}H_{21}O_3N_6MoB$ (^{98}Mo) 466.08221, found 466.08057; 410 (M^+ − 2CO), 392 (M^+ − 2CO − H_2O).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-*η*-1-(1′-hydroxyisobuten-2′-yl)-2-methylpropenyl]molybdenum (16). Isopropenylmagnesium bromide (0.88 mL of a 0.5 M solution in diethyl ether, 0.44 mmol) was added dropwise to a solution of the complex **10** (20 mg, 0.044 mmol) in THF (1.5 mL) at −78 °C. After the mixture was stirred for 2.5 h, the excess of Grignard reagent was destroyed 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 **16** as a yellow solid, which was recrystallized from $CHCl_3$/hexanes (7 mg, 32% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.26 (s, br, 3H), 7.47 (s, 3H), 6.13 (d, J = 1.7 Hz, 3H), 4.95 (s, 1H), 4.89 (s, 1H), 4.75 (d, J = 9.9 Hz, 1H), 3.45 (d, J = 2.01 Hz, 1H), 2.10 (s, 1H, OH), 1.85 (s, 3H), 1.70 (d, J = 10.0 Hz, 1H), 1.44 (s, 3H), 1.17 (d, J = 2.0 Hz, 1H); ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm) 8.30 (s, br, 3H), 7.15 (s, br, 3H), 5.76 (s, br, 3H), 4.81−4.73 (overlap of 3H), 3.32 (s, 1H), 2.05 (d, J = 5.1 Hz, 1H, OH), 1.79 (d, J = 10.3 Hz, 1H), 1.70 (s, 3H), 1.43 (s, 3H), 1.16 (s, 1H); ^{1}H NMR (d_6-acetone, 300 MHz) δ (ppm) 8.33 (s, br, 3H), 7.61 (s, br, 3H), 6.13 (d, J = 2.1 Hz, 3H), 4.85 (s, 1H), 4.78 (s, 1H), 4.66 (d, J = 9.7 Hz, 1H), 3.54 (d, J = 2.2 Hz, 1H), 2.70 (s, br, 1H, OH), 1.85 (d, J = 9.9 Hz, 1H), 1.79 (s, 3H), 1.37 (s, 3H), 0.97 (d, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 227.2, 220.9, 146.7, 146.5, 135.8, 112.8, 105.5, 81.9, 76.3, 74.7, 57.2, 17.5, 15.3; TLC R_f 0.24 (hexanes/ethyl acetate, 2/1); HRMS (EI, 23 eV) calcd for $C_{19}H_{23}O_3N_6MoB$ (^{98}Mo) 492.09787 found 492.09785; 436 (M^+ − 2CO).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-*η*-1-(hydroxybenzyl)-2-methylpropenyl]molybdenum (17). Phenylmagnesium bromide (1.11 mL of a 1 M solution in THF, 1.11 mmol) was added dropwise to a solution of the complex **10** (50 mg, 0.111 mmol) in THF (3 mL) at −78 °C. After the mixture was stirred for 6 h, the excess of Grignard reagent was destroyed 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, and the extract was washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 17% ethyl acetate in hexanes) gave the complex **17** as a yellow solid, which was recrystallized from $CHCl_3$/hexanes (32 mg, 55% yield): mp 164−166 °C dec; ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm) 8.30 (s, br, 3H), 7.26−7.09 (overlap of 8H), 5.78 (d, J = 2.9 Hz, 3H), 5.32 (dd, J = 9.8, 5.2 Hz, 1H), 3.24 (d, J = 2.2 Hz, 1H), 2.19 (d, J = 4.9 Hz, 1H, OH), 2.07 (d, J = 9.9 Hz, 1H), 1.40 (s, 3H), 1.11 (d, J = 2.1 Hz, 1H); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.38 (s, br, 3H), 7.49−7.15 (8H overlapping), 6.22 (t, J = 2.0 Hz, 3H), 5.42 (dd, J = 10.1, 4.6 Hz, 1H), 3.47 (d, J = 2.1 Hz, 1H), 2.63 (d, J = 4.6 Hz, 1H, OH), 2.02 (d, J = 10.1 Hz, 1H), 1.50 (s, 3H), 1.18 (d, J = 1.9 Hz, 1H); ^{1}H NMR (d_6-acetone, 300 MHz) δ (ppm) 8.40 (s, br, 3H), 7.61 (d, J = 1.8 Hz, 3H), 7.44−6.67 (5H overlapping), 6.15 (t, J = 2.2 Hz, 3H), 5.22 (d, J = 9.9 Hz, 1H), 3.47 (d, J = 2.3 Hz, 1H), 2.69 (s, br, 1H, OH), 2.10 (d, J = 9.6 Hz, 1H), 1.33 (s, 3H), 0.91 (d, J = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 229.8, 228.0, 144.3, 135.7, 128.8, 128.1, 126.9, 105.5, 84.2, 82.0, 73.2, 57.3, 15.7; IR ($CHCl_3$, cm^{-1}) 2489 (m, B−H), 1940 (s), 1843 (s); TLC R_f 0.27 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{22}H_{23}O_3N_6MoB$ (^{98}Mo) 528.09784, found 528.09444; 472 (M^+ − 2CO).

General Procedure for the Acetylation of Hydroxyl Groups in Dicarbonyl[hydrotris(1-pyrazolyl)borato]-[syn-(1−3)-*η*-2-methylpropenyl]molybdenum complexes. Preparation of 18, 19, and 20. The complex (0.05 mmol, 1 equiv) in 1 mL of dry ethyl ether was treated with DMAP (1.2 equiv) and freshly distilled acetic anhydride (1.2 equiv) with stirring for 30 min at reflux. The resulting reaction mixture was washed with water (1 mL), 10% HCl solution (3 × 1 mL), and water (3 × 1 mL), then dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 20% ethyl acetate in hexanes) gave the complex as a yellow solid, which was recrystallized from $CHCl_3$/hexanes.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-*η*-1-(1′-acetoxyethyl)-2-methylpropenyl]molybdenum (18) was obtained in 71% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.99 (s, br, 3H), 7.54 (d, J = 2.1 Hz, 3H), 6.20 (t, J = 2.2 Hz, 3H), 5.67 (dd, J = 10.4, 5.9 Hz, 1H), 3.56 (d, J = 1.7 Hz, 1H), 2.16 (s, 3H), 1.80 (d, J = 10.3 Hz, 1H), 1.66 (d, J = 5.9 Hz, 3H), 1.58 (s, 3H), 1.39 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.5, 228.2, 171.0, 144.7, 135.7, 105.5, 81.5, 79.4, 71.4, 59.1, 22.6, 21.3, 15.0; IR ($CHCl_3$, cm^{-1}) 3199 (m), 2993 (m), 2483 (m, B−H), 1950 (s), 1852 (s), 1740 (s); TLC

R_f 0.33 (hexanes/ethyl acetate, 2/1); HRMS (EI, 23 eV) calcd for $C_{19}H_{23}O_4N_6MoB$ (^{98}Mo) 508.09277, found 508.09216; 450 ($M^+ - 2CO$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(1′-acetoxyisobuten-2′-yl)-2-methylpropenyl]molybdenum (19) was obtained in 72% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.01 (s, br, 3H), 7.53 (d, J = 2.1 Hz, 3H), 6.20 (t, J = 2.1 Hz, 3H), 5.95 (d, J = 10.5 Hz, 1H), 5.14 (s, 1H), 5.04 (d, J = 1.4 Hz, 1H), 3.57 (d, J = 1.5 Hz, 1H), 2.15 (s, 3H), 1.86 (d, J = 9.8 Hz, 1H, overlapping with 1.84 ppm), 1.84 (s, 3H), 1.58 (s, 3H), 1.42 (app s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.8, 228.2, 170.5, 142.9, 135.7, 114.8, 105.5, 82.0, 77.8, 75.9, 59.5, 21.1, 17.6, 15.6; IR ($CHCl_3$, cm^{-1}) 2941 (m), 2498 (m, B−H), 1949 (s), 1861 (s), 1735 (s); TLC R_f 0.34 (hexanes/ethyl acetate, 2/1); HRMS (EI, 23 eV) calcd for $C_{21}H_{25}O_4N_6MoB$ (^{98}Mo) 534.10846, found 534.11162.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(1′-acetoxybenzyl)-2-methylpropenyl]molybdenum (20) was obtained in 75% yield: mp 154−155 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.03 (s, br, 3H), 7.56 (d, J = 2.1 Hz, 3H), 7.40−7.38 (2H overlapping), 7.35−7.31 (3H overlapping), 6.40 (d, J = 10.5 Hz, 1H), 6.22 (t, J = 2.1 Hz, 3H), 3.48 (app s, 1H), 2.12 (s, 3H), 2.10 (d, J = 9.7 Hz, 1H overlapping with 2.12 ppm), 1.53 (s, 3H), 1.30 (d, J = 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 228.8, 228.2, 170.5, 144.8, 141.5, 135.7, 128.6, 128.2, 127.3, 127.2, 105.5, 82.3, 78.3, 76.1, 59.2, 21.2, 15.8; IR ($CHCl_3$, cm^{-1}) 2484 (m, B−H), 1945 (s), 1856 (s), 1736 (s); TLC R_f 0.30 (hexanes/ethyl acetate, 2/1); HRMS (EI, 23 eV) calcd for $C_{24}H_{25}O_4N_6MoB$ (^{98}Mo) 570.10846, found 570.10696.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1−3)-η-*syn*-(1-(1′-hydroxyethyl))-*anti*-(1-methyl)propenyl]molybdenum (21). Methylmagnesium bromide (0.15 mL of a 3 M solution in ethyl ether, 0.45 mmol, 10 equiv) was added dropwise to a solution of the complex **13** (20 mg, 0.044 mmol) in THF (1 mL) at −78 °C. After the mixture was stirred for 6 h, the excess of Grignard reagent was destroyed 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, and the extract was washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 12.5% ethyl acetate in hexanes) gave the complex **21** (20 mg, 97% yield, diastereomeric ratio of 1.2:1 by ^{1}H NMR) as a yellow solid: mp 106−108 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) (major diastereomer) 8.03 (s, br, 3H), 7.58 (s, 3H), 6.24 (t, J = 2.1 Hz, 3H), 4.45 (m, 1H), 4.12 (dd, J = 12.9, 6.3 Hz, 1H), 3.71 (dd, J = 7.5, 3.5 Hz, 1H), 1.84 (dd, J = 10.6, 3.5 Hz, 1H), 1.48 (d, J = 6.2 Hz, 3H), 1.39 (s, 3H); (minor diastereomer) 8.30 (s, br, 3H), 7.55 (s, 3H), 6.21 (app t, J = 2.1 Hz, 3H), 4.42 (m, 1H), 3.83 (dd, J = 9.3, 7.1 Hz, 1H), 3.52 (dd, J = 6.9, 4.2 Hz, 1H), 1.68 (dd, J = 9.4, 4.1 Hz, 1H), 1.55 (d, J = 6.5 Hz, 3H), 1.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) (major diastereomer) 229.3, 228.1, 144.3, 136.2, 106.1, 80.2, 75.8, 71.1, 45.2, 22.8, 13.8; (minor diastereomer) 229.3, 228.1, 144.1, 135.4, 105.5, 80.2, 75.8, 72.0, 45.2, 26.1, 14.1; IR ($CHCl_3$, cm^{-1}) 2472 (m, B−H), 1925 (s), 1838 (s); TLC R_f 0.22 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{17}H_{21}O_3N_6MoB$ (^{98}Mo) 466.08221, found 466.08108; 410 ($M^+ - 2CO$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][(1−3)-η-*syn*-(1-(1′-hydroxybenzyl))-*anti*-(1-methyl)propenyl]molybdenum (22). Phenylmagnesium bromide (0.44 mL of a 1 M solution in THF, 0.44 mmol, 10 equiv) was added dropwise to a solution of the complex **13** (20 mg, 0.044 mmol) in THF (1 mL) at −78 °C. After the mixture was stirred for 6 h, the excess of Grignard reagent was destroyed 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, and the extract was washed with brine, dried ($MgSO_4$), and concentrated to give the crude product. Purification by preparative TLC (silica gel, 12.5% ethyl acetate in hexanes) gave the complex **22** (23 mg, 98% yield, diastereomeric ratio of 1.8:1 by ^{1}H NMR) as a yellow solid: mp 127−129 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) (major diastereomer) 8.13 (s, br, 3H), 7.61−7.28 (8H overlapping), 6.28 (d, J = 2.0 Hz, 3H), 5.23 (s, 1H), 4.81 (dd, J = 10.5, 7.6 Hz, 1H), 3.78 (dd, J = 7.6, 3.6 Hz, 1H), 1.76 (dd, J = 10.5, 3.6 Hz, 1H), 1.14 (s, 3H); (minor diastereomer) 8.50 (s, br, 3H), 7.61−7.28 (8H overlapping), 6.24 (d, J = 2.1 Hz, 3H), 4.99 (s, 1H), 4.15 (dd, J = 9.3, 7.0 Hz, 1H), 3.52 (dd, J = 6.9, 4.3 Hz, 1H), 1.64 (dd, J = 9.3, 4.3 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) (major diastereomer) 235.4, 227.7, 144.3, 141.4, 136.2, 128.5, 128.0, 127.4, 105.5, 78.4, 77.2, 75.9, 44.9, 14.1; (minor diastereomer) 233.5, 229.3, 144.3, 141.4, 136.1, 128.5, 127.8, 125.9, 105.5, 79.7, 78.4, 77.2, 45.3, 14.5; IR ($CHCl_3$, cm^{-1}) 2492 (m, B−H), 1933 (s), 1842 (s); TLC R_f 0.27 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{22}H_{23}O_3N_6MoB$ (^{98}Mo) 528.09784, found 528.09813; 472 ($M^+ - 2CO$).

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-*syn*-(1-(1′,2′-dihydroxyethyl))-*anti*-(1-methyl)propenyl]molybdenum (23). To a solution of complex **14** (5 mg, 0.011 mmol, 1 equiv) in pyridine (0.5 mL) was added dropwise a 2.5 wt % solution of OsO_4 in 2-methyl-2 propanol (0.25 mL, 0.016 mmol, 1.5 equiv) under nitrogen. After 2 h at room temperature, the reaction mixture was diluted with methanol (2 mL). H_2S was bubbled through[10] for 2 min, and the resulting black precipitate was removed by filtration through Celite. The clear filtrate was diluted with ethyl acetate, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Preparative TLC (silica gel, 1/1 hexanes/ethyl acetate) provided a mixture of diastereomeric diols **23** as a pale yellow solid (4.2 mg, 78% yield, diastereomeric ratio of 1.1:1 by ^{1}H NMR): mp 120−122 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) (major diastereomer) 8.35 (s, br, 3H), 7.59 (d, J = 2.2 Hz, 3H), 6.26 (t, J = 2.2 Hz, 3H), 4.41 (m, 1H), 4.08−3.82 (3H overlapping), 3.75 (dd, J = 7.6, 3.6 Hz, 1H), 1.83 (dd, J = 10.6, 3.7 Hz, 1H), 1.56 (s, br, OH), 1.37 (s, 3H); (minor diastereomer) 8.03 (s, br, 3H), 7.54 (d, J = 2.2 Hz, 3H), 6.21 (t, J = 2.2 Hz, 3H), 4.41 (m, 1H), 3.86−3.82 (2H overlapping), 3.80−3.70 (1H, overlapping with 3.75 ppm (major diastereomer)), 3.55 (dd, J = 7.0, 4.2 Hz, 1H), 1.66 (dd, J = 9.4, 4.2 Hz, 1H), 1.56 (s, br, OH), 1.37 (s, 3H); IR ($CHCl_3$, cm^{-1}) 3585 (br, OH), 2934 (m), 2848 (m), 2486 (m, B−H), 1920 (s), 1835 (s); TLC R_f 0.33 (hexanes/ethyl acetate, 1/1); HRMS (EI, 23 eV) calcd for $C_{15}H_{19}N_6MoB$ (^{98}Mo) 392.08182, found 392.08357.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(1′,2′-dihydroxyethyl)-2-methylpropenyl]molybdenum (24). To a solution of complex **11** (20 mg, 0.045 mmol, 1 equiv) in pyridine (1 mL) was added dropwise a 2.5 wt % solution of OsO_4 in 2-methyl-2 propanol (1 mL, 0.067 mmol, 1.5 equiv) under nitrogen. After 2 h at room temperature, the reaction mixture was diluted with methanol (2 mL). H_2S was bubbled through[10] for 2 min, and the resulting black precipitate was removed by filtration through Celite. The clear filtrate was diluted with ethyl acetate, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Preparative TLC (silica gel, 1/1 hexanes/ethyl acetate) provided a mixture of diastereomeric diols **24** as a pale yellow solid (21.1 mg, 98% yield): mp 102−104 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.02 (s, br, 3H), 7.56 (d, J = 2.2 Hz, 3H), 6.21 (d, J = 1.9 Hz, 3H), 4.71 (ddd, J = 16.9, 7.1, 2.9 Hz, 1H), 4.34 (dd, J = 11.7, 2.7 Hz, 1H), 4.03 (dd, J = 11.7, 7.0 Hz, 1H), 3.68 (d, J = 1.8 Hz, 1H), 1.79 (s, 3H), 1.59 (s, br, OH), 1.48 (d, J = 10.1 Hz, 1H), 1.45 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 229.0, 228.6, 144.9, 135.8, 105.5, 84.9, 75.4, 71.4, 66.6, 60.4, 15.3; IR ($CHCl_3$, cm^{-1}) 2486 (m, B−H), 1946 (s), 1844 (s); TLC R_f 0.26 (hexanes/ethyl acetate, 1/1); HRMS (EI, 23 eV) calcd for $C_{15}H_{19}N_6MoB$ (^{98}Mo) 392.08182, found 392.08225.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][*syn*-(1−3)-η-1-(1′,2′-diacetoxyethyl)-2-methylpropenyl]molybdenum (25). Complex **24** (11 mg, 0.023 mmol, 1 equiv) in 1 mL of dry ethyl ether was treated with DMAP (6.2 mg, 0.050 mmol, 2.2 equiv) and freshly distilled acetic anhydride (5 μL, 0.050 mmol, 2.2 equiv) with stirring for 30 min at reflux. The resulting reaction mixture was washed with water (1 mL), 10% HCl solution (3 × 1 mL), and water (3 × 1 mL), then dried ($MgSO_4$), and concentrated to give the crude product. Purifica-

tion by preparative TLC (silica gel, 17% ethyl acetate in hexanes) gave the complex **25** (8.1 mg, 63% yield) as a yellow solid: mp 145−146.5 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.10 (s, 3H), 7.55 (d, J = 2.2 Hz, 3H), 6.24 (app t, J = 2.2 Hz, 3H) overlapping with 6.24 (m, 1H), 4.99 (dd, J = 12.5, 2.8 Hz, 1H), 4.30 (dd, J = 12.4, 8.0 Hz, 1H), 3.65 (s, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 1.62 (s, 3H), 1.47 (s, 1H), 1.43 (d, J = 10.4 Hz, 1H); IR ($CHCl_3$, cm^{-1}) 2967 (m), 2919 (m), 2494 (m, B−H), 1950 (s), 1861 (s), 1743 (s); TLC R_f 0.19 (hexanes/ethyl acetate, 3/1); HRMS (EI, 23 eV) calcd for $C_{21}H_{25}O_6N_6MoB$ (^{98}Mo) 566.09883, found 566.09903.

General Procedure for the Determination of the Diastereomeric Ratio in Complexes 18, 19, 20, and 25. The substrate was weighed in a 1 mL volumetric flask, and the correct amount of $CDCl_3$ was added via pipet. The shift reagent was added in portions of 10 μL from a freshly prepared stock solution of $Eu(fod)_3$ (50 mM in $CDCl_3$). The mixture was vigorously shaken prior to the ^{1}H NMR spectrum being recorded.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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