under a nitrogen atmosphere was added *n*-butyllithium (3.42 mL of a 2.5 M solution in hexanes, 8.56 mmol). After the mixture was stirred for 15 min at 0 °C, 1-(2-thienyl)-1-propanone (**8**)[19] (1.00 g, 7.13 mmol) was added via syringe. The mixture was cooled further to −50 °C after 30 min of stirring at 0 °C, and a solution of copper triflate (2.85 g, 7.85 mmol) in dry isobutyronitrile (10 mL) was added. After 30 min at −50 °C, the mixture was stirred for 1 h at room temperature and then poured into water (50 mL). An insoluble precipitate was filtered under vacuum before the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extract was washed with water (2 × 30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo to obtain a red-brown liquid (1.27 g). Column chromatography on silica (8:1 hexanes/ethyl acetate and 6:1 hexanes/ethyl acetate) afforded 1,4-bis(2-thienyl)-2,3-dimethyl-1,4-butanedione (**9**) (0.36 g, 36.4%) as white crystals recrystallized from CH_2Cl_2/hexanes: mp 113.5–115.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) (major isomer) δ 1.35 (dd, 6 H, J = 2.1, 4.7 Hz), 3.77 (m, 2 H), 7.14 (m, 2 H), 7.62 (dd, 2 H, J = 1.0, 5.0 Hz), 7.81 (dd, 2 H, J = 1.2, 3.8 Hz), (minor isomer) δ 1.19 (dd, 6 H, J = 2.0, 4.5 Hz), 3.77 (m, 2 H), 7.18 (m, 2 H), 7.70 (dd, 2 H, J = 1.1, 5.0 Hz), 7.87 (dd, 2 H, J = 1.2, 3.8 Hz); IR (Nujol) 3100, 1650, 1520, 1420, 1240, 1220, 1060, 855, 745, 730 cm^{-1}; MS (EI) *m/e* (relative intensity) 279 (M + 1, 1.3), 278 (M$^+$, 7.0), 167 (16.0), 153 (13.3), 140 (13.8), 126 (8.2), 111 (100). Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.08. Found: C, 59.76; H, 5.07.

***N*-Methyl-2,5-bis(2-thienyl)-3,4-dimethylpyrrole (7).** A solution of 1,4-bis(2-thienyl)-2,3-dimethyl-1,4-butanedione (**9**) (1.21 g, 4.35 mmol), methylamine (0.68 g of a 40% aqueous solution, 8.75 mmol), and glacial acetic acid (0.50 mL, 8.73 mmol) in benzene (12 mL) was refluxed under nitrogen atmosphere in a round-bottom flask equipped with a Dean–Stark trap. After 24 h, additional methylamine (0.50 mL, 5.81 mmol) was added to the reaction, and the mixture was refluxed for a total of 43 h before it was poured into water (20 mL). The volatile constituents were removed under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography on silica (hexanes) and recrystallized from EtOAc/hexane to afford *N*-methyl-2,5-bis(2-thienyl)-3,4-dimethylpyrrole (**7**) (0.93 g, 78.2%) as white needles: mp 100–101.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.07 (s, 6 H), 3.46 (s, 3 H), 7.01 (dd, 2 H, J = 1.1, 3.5 Hz), 7.13 (dd, 2 H, J = 3.5, 5.2 Hz), 7.39 (dd, 2 H, J = 1.1, 5.2 Hz); UV–vis ($CHCl_3$) 314.6, 242.6 nm; MS (EI) *m/e* (relative intensity) 275 (M + 2, 59.0), 274 (M + 1, 79.8), 273 (M$^+$, 200), 272 (90.8), 259 (36.4), 258 (72.2), 147 (25.1), 137 (33.4), 109 (29.7). Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.89; H, 5.54. Found: C, 65.84; H, 5.54.

Electrochemical Studies. An EG&G PARC Model 273 potentiostat/galvanostat controlled with a PC computer using the Model 270 or 271 software packages was employed for all studies. The COOL program analysis was performed on a PC computer running at 33 MHz. An Ag^+ (0.01 M in CH_3CN)/Ag reference electrode and a Pt wire counter electrode were employed during data collection; however, all potentials are reported relative to the ferrocene/ferrocenium couple measured in CH_3CN (0.1 M NBu_4PF_6). The ferrocene/ferrocenium couple was measured at appropriate intervals to give an accurate reference potential conversion. The 1.6-mm Pt working electrode was purchased from Bioanalytical Systems. The 130-μm and 25-μm Pt microelectrodes were constructed by sealing wire (Alfa) of the appropriate diameter in glass; the Pt microdisks were exposed and polished using SiC paper and 1-, 0.5-, and 0.03-μm Al_2O_3 polishing suspensions from Buehler. Acetonitrile was distilled from CaH_2 under nitrogen immediately before use. The NBu_4PF_6 supporting electrolyte was obtained from Bioanalytical Systems and used as received. All experiments were performed under a dry nitrogen atmosphere.

Acknowledgment. We wish to thank EG&G for providing us with a beta version of the COOL program and J. G. Osteryoung, R. A. Osteryoung, and J. J. O'Dea for providing us with an earlier version of the COOL program. We also thank the National Science Foundation for a grant (CHE 9001714) in support of this work.

(19) Kooreman, H. J.; Wynberg, H. *Recl. Trav. Chim.* **1967**, *86*, 37.

Enantiospecific Synthesis by Transformations of Chiral Pool-Derived Metal π-Complexes. A Strategy for the Introduction of Substituents on a Pyranose-Derived Lateral π-Ligand either Syn or Anti to the Coordinating Metal

Almudena Rubio and Lanny S. Liebeskind*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.
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Abstract: In order to extend the use of stoichiometric transition metal π-complexes to the stereocontrolled synthesis of organic target structures bearing substituents either cis or trans to each other on a cyclic unsaturated π-ligand, new strategies for the functionalization of π-complexes are required. A first-generation approach to the stereocontrolled introduction of substituents syn or anti relative to an η^5-$CpMo(CO)_2$ unit coordinated to a lateral π-ligand is reported. The pyranone ring was chosen as the first template upon which the strategy for stereocontrolled introduction of substituents would be studied. The stereocontrol of the process relies on (1) the ability of the $CpMo(CO)_2$ unit to direct all nucleophilic attack away from itself, (2) the observation that cationic diene complexes, $CpMo(CO)_2(\eta^4$-diene)$^+$, can be generated from (η^3-allyl)molybdenum species bearing an adjacent alkoxy substituent syn to the molybdenum by treatment with $Ph_3C^+PF_6^-$, and (3) the precedented introduction of nucleophiles adjacent to the oxygen atom in $CpMo(CO)_2(2H$-pyran) cations. Using these stereocontrol features, the pyranone carbonyl group was replaced by two different substituents, R^1 and R^2. By changing the order of substituent introduction, the stereochemistry of the substituents R^1 and R^2 relative to the molybdenum unit can be influenced. This can be translated into a method for controlling the introduction of multiple substituents either cis or trans to each other on a cyclic π-template.

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[1-29] and heterocycles.[30-38] With few exceptions,[1,22,39-45] the dominant mode of functionalization is addition of a nucleophilic reactant to an electrophilic metal π-complex.

(1) Pearson, A. J.; Mallik, S.; Pinkerton, A. A.; Adams, J. P.; Zheng, S. *J. Org. Chem.* **1992**, *57*, 2910.

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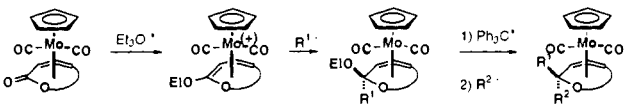
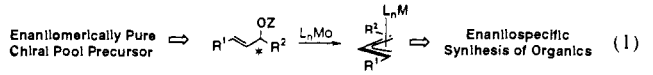
Scheme I

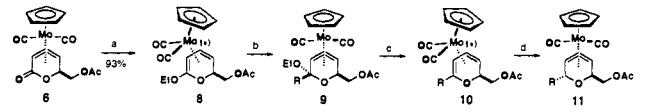


Common to all synthetically useful applications described to date is the overriding anti directing effect of the coordinatively saturated metal–auxiliary ligand unit bound to the π-ligand. That is, with few exceptions,[3,20,46,47] all incoming nucleophilic reactants are directed to the face of the π-ligand opposite the metal (eq 1). A



consequence of this mode of reaction is the introduction of multiple substituents cis to each other on a cyclic π-ligand substrate. In order to extend the use of stoichiometric metal π-complexes to the stereocontrolled synthesis of target structures bearing substituents either cis or trans to each other on a cyclic unsaturated π-ligand, new strategies for functionalization of π-complexes are required. Herein is reported a first-generation approach to the stereocontrolled introduction of substituents syn or anti relative to an η^5-CpMo(CO)$_2$ unit π-coordinated to a pyranose-derived ligand: hence, a method allowing the introduction of multiple substituents cis or trans to each other on an unsaturated cyclic ligand.

Table I. Synthesis of *trans*-2,6-Disubstituted Pyranyl Complexes



a) $Et_3O^+PF_6^-$; b) R^-; c) $Ph_3C^+PF_6^-$; d) $NaBH_4$

entry	R^-	compd	%	compd	%
1	$NaBH_4$	**9a**	94	**11a**	
2	MeMgI	**9b**	87	**11b**	85
3	EtMgBr	**9c**	74	**11c**	73
4	*p*-tolylMgBr	**9d**	84	**11d**	88
5	CH_2=$CHMgBr$	**9e**	79	**11e**	0[a]
6	C_4H_9C≡$CMgBr$	**9f**	59	**11f**	
7	C_4H_9≡CLi	**9f**	89	**11f**	75[b]
8	$MeOCOCH_2Li$	**9g**	84	**11g**	64
9	$(MeO_2C)_2CHNa$	**9h**	0[c]	**11h**	

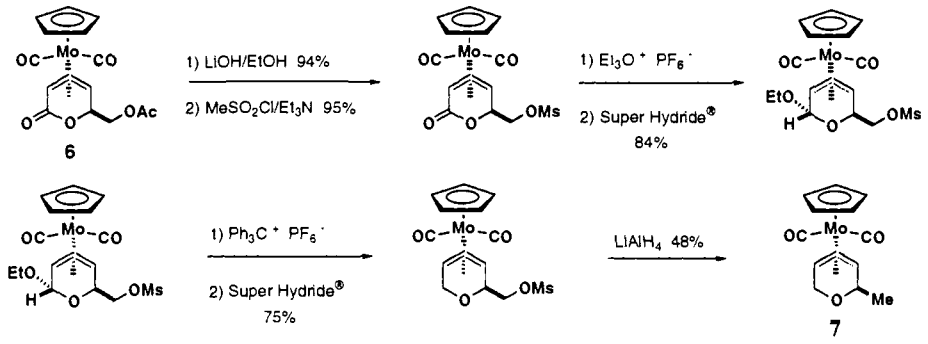
[a] $NaBH_4$ gave a complex mixture; $NaBH_3CN$ led to overreduction of the vinyl group, giving the ethyl derivative **11c** in good yield. [b] $NaBH_3CN$ was used. [c] No product is formed.

Results and Discussion

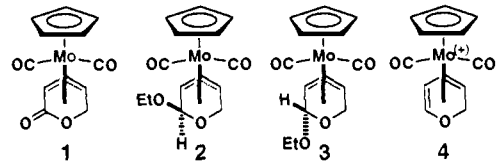
During early unpublished portions of a study of the synthesis of cationic molybdenum complexes of 2*H*-pyran,[32] it was observed that the η^3-lactonyl complex **1** (prepared from the allylic bromide derived from reaction of dihydropyrone with *N*-bromosuccinimide[48]) on reaction with $Et_3O^+PF_6^-$ followed by reduction with Super Hydride gave the *syn*-OEt isomer **2**. This kinetic product was easily epimerized in high yield to the more stable anti isomer **3** by treatment with catalytic *p*-toluenesulfonic acid in CH_2Cl_2/EtOH. Reaction of the anti isomer with a stoichiometric amount of HBF_4·Et_2O in diethyl ether caused precipitation of the racemic 2*H*-pyran molybdenum complex **4** in high yield. The syn isomer **2**, on the other hand, was not cleanly converted into the

(2) Franck-Neumann, M.; Colson, P. J.; Geoffroy, P.; Taba, K. M. *Tetrahedron Lett.* **1992**, *33*, 1903.
(3) Sheridan, J. B.; Padda, R. S.; Chaffee, K.; Wang, C. J.; Huang, Y. Z.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539.
(4) Owen, D.; Stephenson, G.; Finch, H.; Swanson, S. *Tetrahedron Lett.* **1990**, *31*, 3401.
(5) Stephenson, G. R.; Thomas, R. D.; Cassidy, F. *Syn. Lett.* **1992**, 247.
(6) Dickens, M. J.; Mowlem, T. J.; Widdowson, D. A.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 323.
(7) Mann, I. S.; Widdowson, D. A.; Clough, J. M. *Tetrahedron* **1991**, *47*, 7981.
(8) Laabassi, M.; Toupet, L.; Gree, R. *Bull. Soc. Chim. Fr.* **1992**, *129*, 47.
(9) Hachem, A.; Teniou, A.; Gree, R. *Bull. Soc. Chim. Belg.* **1991**, *100*, 625.
(10) Astruc, D. The Use of π-Organoiron Sandwiches in Aromatic Chemistry. In *Topics in Current Chemistry*; Hermann, W. A., Ed.; Springer-Verlag: Berlin, 1992; Vol. 160, p 47.
(11) Pearson, A. J.; Burello, M. P. *Organometallics* **1992**, *11*, 448.
(12) Knox, G. R.; Pauson, P. L.; Rooney, J. *J. Organomet. Chem.* **1991**, *420*, 379.
(13) Kundig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991**, *113*, 9676.
(14) Kundig, E. P.; Grivet, C.; Wenger, E.; Bernardinelli, G.; Williams, A. F. *Helv. Chim. Acta* **1991**, *74*, 2009.
(15) Uemura, M. In *Tricarbonyl(η^6-Arene)chromium Complexes in Organic Synthesis*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. II, p 195.
(16) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736.
(17) Marr, G.; Rockett, B. W. *J. Organomet. Chem.* **1991**, *416*, 399.
(18) Vong, W.-J.; Peng, S.-M.; Lin, S.-H.; Lin, W.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **1991**, *113*, 573.
(19) Baxter, J. S.; Green, M.; Lee, T. V. *J. Chem. Soc., Chem. Commun.* **1989**, 1595.
(20) Halpin, W. A.; Williams, J. C., Jr.; Hanna, T.; Sweigart, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 376.
(21) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.
(22) Pearson, A. J.; Khetani, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6778.
(23) Pearson, A. J. In *Recent Developments in the Synthetic Applications of Organoiron and Organomolybdenum Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. I, p 1.
(24) Pearson, A. J.; Kole, S. L.; Yoon, J. *Organometallics* **1986**, *5*, 2075.
(25) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645.
(26) Faller, J. W.; Lambert, C. *Tetrahedron* **1985**, *41*, 5755.
(27) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.
(28) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; He, C.-H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.
(29) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.
(30) Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 6682.
(31) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 757.
(32) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.
(33) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.
(34) Zakrzewski, J. *J. Organomet. Chem.* **1987**, *326*, C17.
(35) Felkin, H.; Zakrzewski, J. *J. Am. Chem. Soc.* **1985**, *107*, 3374.
(36) Kutney, J. P.; Kaczmarek, L.; Mostowicz, D.; Worth, B. R. *Can. J. Chem.* **1982**, *60*, 323.
(37) Kutney, J. P.; Noda, M.; Worth, B. R. *Heterocycles* **1979**, *12*, 1269.
(38) Kutney, J. P.; Mak, T. C. W.; Mostowicz, D.; Trotter, J.; Worth, B. R. *Heterocycles* **1979**, *12*, 1517.
(39) Williams, G. M.; Pino, M. J. *Organometallics* **1992**, *11*, 345.
(40) Itoh, K.; Nakanishi, S.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2965.
(41) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972.
(42) Lin, S.-H.; Yang, Y.-J.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1991**, 1004.
(43) Pearson, A. J.; Mallik, S.; Mortezaei, R.; Perry, M. W. D.; Shively, R. J., Jr.; Youngs, W. J. *J. Am. Chem. Soc.* **1990**, *112*, 8034.
(44) Brookhart, M.; Volpe, A. F., Jr.; Yoon, J. In *Carbon Electrophiles with Dienes and Polyenes Promoted by Transition Metals*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 695.
(45) Davies, S. G.; Coote, S. J.; Goodfellow, C. L. In *Synthetic Applications of Chromium Tricarbonyl Stabilized Benzylic Carbanions*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. II, p 1.
(46) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857.
(47) Ittel, S.; Whitney, J.; Chung, Y.; Williard, P.; Sweigart, D. *Organometallics* **1988**, *7*, 1323.
(48) Nakagawa, M.; Saegusa, J.; Tonozuka, M.; Obi, M.; Kiuchi, M.; Hino, T.; Ban, Y. *Org. Synth.* **1977**, *56*, 49.

Scheme II

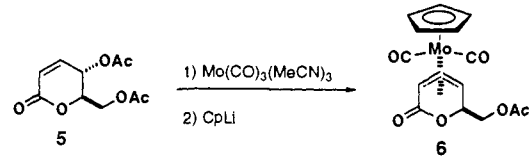


2*H*-pyran cation **4** on treatment with strong acid under identical protonation/precipitation conditions. However, the desired 2*H*-pyran complex **4** could be formed in good yield directly from *syn*-**2** by treatment with $Ph_3C^+PF_6^-$ in CH_2Cl_2 followed by precipitation with diethyl ether. The precise reason for the difference in reactivity of the syn and anti isomers is not known; however, one of two scenarios is presumed operative. Either traces of acidic impurities in Ph_3C^+ induce epimerization of *syn*-**2** to *anti*-**2**, which then undergoes abstraction of EtO by Ph_3C^+ to yield cationic diene complex **4**, or direct abstraction by Ph_3C^+ of one of the accessible methylene hydrogens on the *syn*-ethoxy group produces an oxygen-stabilized cation[49] that on loss of CH_3CHO delivers **4**. Regardless of the precise mechanism of the process, which will be looked at in greater detail in future work, this reaction became an essential element of the strategy described below for stereocontrolled introduction of substituents to molybdenum π-complexes.



Because of the large number of naturally occurring polyalkylated tetra- and dihydropyrans with significant ionophoric, antibacterial, and antifungal activity,[50,51] the pyranone ring was chosen as the first template upon which the strategy for stereocontrolled introduction of substituents was studied. Shown in Scheme I is a generalized approach to introduce substituents syn or anti to an η^5-$CpMo(CO)_2$ unit π-coordinated to a lactonyl fragment. It is based on the well-established anti addition of nucleophiles to cationic η^5-$CpMo(CO)_2(\eta^4$-diene) complexes.[16,18,23,26,32,42,52] The stereocontrol of the process relies on (1) the ability of the $CpMo(CO)_2$ unit to direct all nucleophilic attack away from itself, (2) the observation, described above, that cationic diene complexes, $CpMo(CO)_2(\eta^4$-diene)$^+$, can be generated from (η^3-allyl)molybdenum species bearing an adjacent alkoxy substituent syn to the molybdenum by treatment with $Ph_3C^+PF_6^-$, and (3) the precedented introduction of nucleophiles adjacent to the oxygen atom in $CpMo(CO)_2$(2*H*-pyran) cations.[32] By changing the order of substituent introduction, the stereochemistry of the substituents R^1 and R^2 relative to the molybdenum unit can be controlled. In principle, this can be translated into a method for controlling the introduction of multiple substituents either cis or trans to each other on a cyclic π-template.

Readily available lactone **5** was chosen as an enantiomerically pure pyranone-based allylic substrate for introduction of a $CpMo(CO)_2$ unit. It is conveniently prepared in 70% yield in one step from commercially available tri-*O*-acetyl-D-glucal by reaction with $BF_3{\cdot}Et_2O$ and *m*-chloroperbenzoic acid in CH_2Cl_2 following an established procedure.[53] Treatment of **5** in acetonitrile with $Mo(CO)_3(MeCN)_3$ at 90 °C for 16 h, removal of MeCN, and reaction of the residue with CpLi in THF gave the air-stable lactonyl complex **6** in 50% yield over the two steps (eq 2).



(2)

Formation of lactonyl complex **6** represents the second demonstration that allylic acetates react with $Mo(CO)_3(MeCN)_3$ to form (π-allyl)molybdenum complexes with retention of allylic acetate stereochemistry.[54] The absolute configuration of lactonyl complex **6** was determined by its conversion into the known pyranyl derivative **7** according to the sequence of reactions depicted in Scheme II. The spectroscopic data and optical rotation of pyranyl complex **7** were identical with those of an authentic sample previously synthesized from D-arabinose.[32]

On treatment with $Et_3O^+PF_6^-$ in CH_2Cl_2 followed by precipitation with Et_2O, **6** was converted in 93% yield into the air-stable, mustard-yellow, cationic 2*H*-pyran complex **8** (Table I). Diene complex **8** represents a common precursor from which *trans*- or *cis*-2,6-disubstituted tetrahydropyrans can be constructed enantiospecifically. Addition of nucleophiles to **8** proceeded at −78 °C in THF and provided, stereo- and regiospecifically, the neutral adducts **9** (Table I). The spectroscopic data for complexes **9** were in full accord with the occurrence of nucleophilic addition α to the pyran ring oxygen. Previous experience with the parent 2*H*-pyran π-complex allows assignment of stereochemistry anti to the molybdenum.[32] Even though an excess of nucleophile was added to a suspension of the diene complex in THF at −78 °C in entries 1–7 of Table I, no complications from addition of the nucleophile to the acetoxymethyl side chain were noted. An attempt to add $LiCH_2COOMe$ in THF to **8** in THF resulted in the formation of several products; however, reversing the order of addition led cleanly to the desired adduct **9g** in high yield. Somewhat surprising was the failure to obtain an adduct from addition of dimethyl sodiomalonate to cation **8** (entry 9, Table I), perhaps a consequence of easy departure of the malonyl unit from the anticipated product due to its anti orientation relative to molybdenum and the combined influence of the two neighboring oxygen atoms.

The adducts **9b–g** were treated with $Ph_3C^+PF_6^-$ in CH_2Cl_2 to induce ionization of the *syn*-OEt group, producing the 2*H*-pyran cations **10**. Isolation and purification of complexes **10** were not necessary; removal of CH_2Cl_2, addition of THF, cooling to −78 °C, and treatment with $NaBH_4$ or $NaBH_3CN$ in all but one case (Table I, entry 5, **11e**) led cleanly in one pot in high yield to the *trans*-2,6-disubstituted pyranylmolybdenum complexes **11b–d,f,g**. Proof that the intermediate cationic diene complexes **10** are stable was obtained by isolation and full characterization of the orange,

(49) Barton, D.; et al. *Chem. Commun.* **1971**, 861.
(50) *Polyether Antibiotics. Naturally Occurring Acid Ionophores*; Westley, J. W., Ed.; Marcel Dekker, Inc.: New York, 1982; Vol. 1: Biology.
(51) *Polyether Antibiotics. Naturally Occurring Acid Ionophores*; Westley, J. W., Ed.; Marcel Dekker: New York, 1983; Vol. 2: Chemistry.
(52) Pearson, A. J. *Philos. Trans. R. Soc. London A* **1988**, *326*, 525.
(53) Jarglis, P.; Lichtenthaler, F. W. *Tetrahedron Lett.* **1982**, *23*, 3781.
(54) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670.

Scheme III

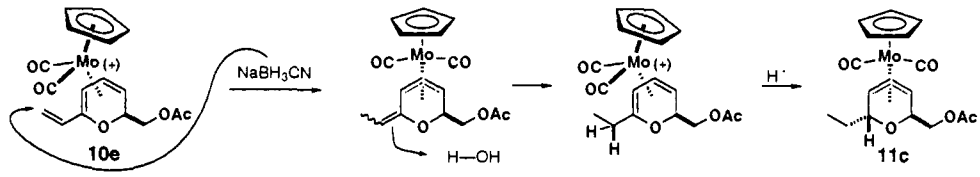
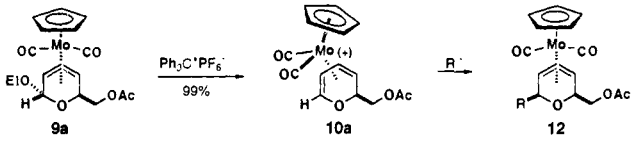


Table II. Synthesis of *cis*-2,6-Disubstituted Pyranyl Complexes



entry	R^-	compd	yield (%)
1	MeMgI	**12a**	86
2	*p*-tolylMgBr	**12b**	81
3	CH_2=$CHMgBr$	**12c**	84
4	$C_4H_9C{\equiv}CMgBr$	**12d**	51
5	$C_4H_9C{\equiv}CLi$	**12d**	83
6	$MeOCOCH_2Li$	**12e**	85
7	$(MeO_2C)_2CHNa$	**12f**	82

air-stable solid **10b** (R = Me, 99% yield).

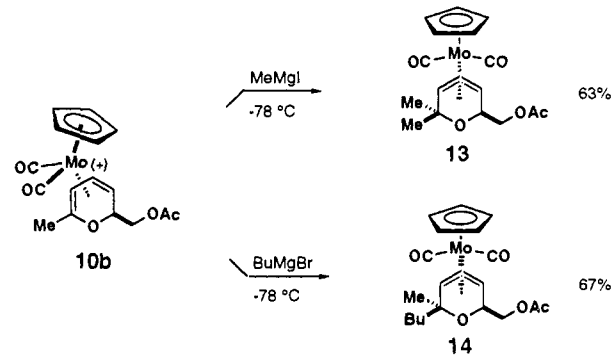
$Ph_3C^+PF_6^-$ induced ionization of **9e** led to the interesting vinyl-substituted diene complex **10e** (R = CH=CH_2). Reaction of **10e** with $NaBH_4$ gave a complex mixture of products. When $NaBH_3CN$ was used instead, a clean reaction took place; however, the observed product was identical to the ethyl-substituted pyranylmolybdenum complex **11c**. This unexpected reaction most likely proceeds via the sequence of reactions shown in Scheme III: addition of hydride to the terminal position of the vinyl substituent, rapid protonation by water of the resulting very electron-rich enol ether double bond (undefined stereochemistry) during workup, and finally stereospecific reduction by vestigial $NaBH_3CN$. Use of $NaBD_3CN$ led to incorporation of deuterium both at the vinyl terminus and at C-6, providing strong support for the proposed mechanism.

cis-2,6-Disubstituted pyranylmolybdenum complexes **12**, isomeric with the *trans*-2,6-disubstituted complexes **11**, were easily produced by reversing the order of addition of the two nucleophiles used to replace the pyranone carbonyl group. Cationic diene complex **10a** was prepared from **9a** in 99% yield by $Ph_3C^+PF_6^-$ induced ionization of the *syn*-OEt group. Addition of a variety of nucleophiles to **10a** occurred without complication and provided the *cis*-2,6-disubstituted pyranylmolybdenum complexes **12a–f** (Table II). Of note are (1) the ease with which a variety of stereoisomeric compounds can be prepared, as indicated by the synthesis of the stereoisomeric pairs **11b/12a**, **11d/12b**, **11f/12d**, and **11h/12e**, and (2) the range of carbon nucleophiles that participate in the process.

The strategy depicted in Scheme I implies the generalized introduction of two different substituents to the same carbon of the pyran ring. Construction of quaternary carbon centers using molybdenum hydrocarbon π-complexes is precedented,[22] and although not yet probed in detail with heterocycle π-complexes, quaternary carbon construction has been achieved in two cases (Scheme IV). Addition of MeMgI and *n*-BuMgBr to cationic diene complex **10b** in THF at −78 °C provided good yields of the 2,6,6-trisubstituted pyranylmolybdenum complexes **13** and **14**, respectively.

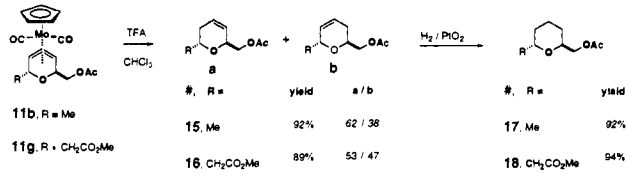
The strategy for stereocontrolled introduction of substituents to the pyranylmolybdenum template having been validated, two tasks remained to establish a synthetic method useful in organic synthesis. First, correlation of a pyranylmolybdenum-derived free organic with a known compound of established absolute configuration must be accomplished in order to confirm rigorously the overall stereochemical outcome of the transformations shown above. Second, demetalation to a free organic must occur in high

Scheme IV



yield, preferably with simultaneous regio- and stereospecific functionalization.

Protodemetalation results have been obtained to address the second problem in a preliminary fashion; a thorough examination of demetalation–functionalization protocols will be studied and published separately. Treatment of the *trans*-2,6-disubstituted pyranylmolybdenum complexes **11b** and **11g** with trifluoroacetic acid in ethanol-free chloroform produced mixtures of regioisomeric dihydropyrans in high yield (eq 3). Both of these regioisomeric



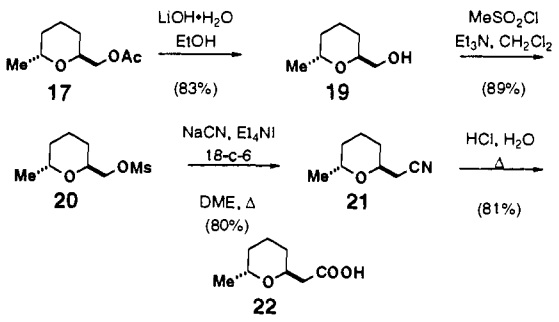
(3)

mixtures were hydrogenated in high yield to the *trans*-2,6-disubstituted tetrahydropyrans **17** and **18**. These results, when viewed in context with the previously described stereospecific manipulations of enantiomerically pure $CpMo(CO)_2$(dihydropyran) complexes,[32] validate the assumption of stereocontrolled synthesis of cyclic organic target structures bearing substituents either cis or trans to each other. At this time, no attempt has been made to affect the ratio of dihydropyran regioisomers; however, improvement of the modest regioselectivity by variation of reaction conditions and electrophile might lead to a viable regioselective synthetic method. An alternate mode of (π-allyl)molybdenum functionalization that is precedented[23,25–28,32,52,55] and might prove useful for stereo- and regiospecific demetalation–functionalization is conversion of the neutral $CpMo(CO)_2(\eta^3$-allyl) to the electrophilic nitrosyl cation, $CpMo(CO)(NO)(\eta^3$-allyl)$^+$, followed by addition of a nucleophile. Subsequent demetalation of the product η^2-alkene complex is easily accomplished by mild oxidation with ceric ammonium nitrate or, in some cases, by exposure to air. However, a thorough understanding of the scope and stereo- and regiocontrol of this means of demetalation–functionalization is not yet available.

To confirm the absolute stereochemical assignments proposed in the syntheses and transformations of the pyranylmolybdenum complexes, the chemistry shown in Scheme V was carried out. After hydrogenation of the regioisomeric pair of *trans*-2,6-disubstituted dihydropyrans (**15a,b**) obtained by protodemetalation

(55) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.

Scheme V



of the pyranylmolybdenum complex **11b** (eq 3) to *trans*-2-(acetoxymethyl)-6-methyltetrahydropyran (**17**), a standard series of transformations (**17** → **21**) was used to homologate by one carbon, providing *trans*-2-(cyanomethyl)-6-methyltetrahydropyran (**21**) in very good yield over three steps. Finally, acidic hydrolysis of the nitrile functional group of **21** delivered *trans*-(6-methyltetrahydropyran-2-yl)acetic acid (**22**). It was identical by IR and ^{1}H NMR with the known enantiomer, (2*R*,6*S*)-*trans*-(6-methyltetrahydropyran-2-yl)acetic acid,[56] but displayed opposite optical rotation [$[\alpha]_D$ = +41.0° (*c* 1.45, $CHCl_3$); lit.[56] $[\alpha]_D$ −39.5° (*c* 1.45, $CHCl_3$)], confirming the absolute stereochemistry of the material produced via the molybdenum π-complexes shown above as 2*S*,6*R*. This result validates the relative and absolute stereochemical assignments suggested above and attests to the stereochemical integrity inherent in the transformations of the $CpMo(CO)_2$(π-ligand) system.

Conclusions

A strategy for stereocontrolled introduction of substituents syn or anti relative to a π-complexed metal–ligand auxiliary has been described. The ease of introduction of various substituents coupled with the observed absolute stereocontrol suggests that enantiospecific synthesis using metal π-complexes derived from chiral pool substrates should be a fruitful new domain for exploration. After additional clarification of reaction conditions for demetalation–functionalization, the described reaction sequences could provide powerful new procedures for the enantiospecific synthesis of a variety of substituted heterocyclic systems.

Experimental Section

Materials and Methods. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise indicated. Solutions of *n*-butyllithium (Aldrich, ≈2.5 M in hexanes) were titrated with diphenylacetic acid just prior to use. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone prior to use. Dichloromethane, acetonitrile, and diisopropylamine were distilled from calcium hydride and stored under nitrogen. Lithium diisopropylamide was prepared by dropwise addition of 1 equiv of *n*-butyllithium (≈2.5 M in hexanes) to a 0.5 M solution of diisopropylamine in THF at 0 °C and stirred at the same temperature for 15 min. All reactions were performed under a positive pressure of argon unless otherwise indicated. Analytical TLC was performed on Merck TLC glass plates precoated with F_{254} silica gel 60. Visualization was accomplished using one of the following: UV; 5% phosphomolybdic acid in ethanol (PMA); 2.5% *p*-anisaldehyde and 2.5% sulfuric acid in ethanol (PAA); or 0.4% vanillin with 10% sulfuric acid and 10% water in methanol (VAN). NMR chemical shifts, recorded on a GE QE-300 instrument, are given in δ values relative to residual protio resonances of the deuterated solvent used ($CDCl_3$ 7.26, CD_3CN 1.93) or to δ values relative to the solvent (DMSO-d_6 39.5, CD_3CN 1.30) for ^{1}H and ^{13}C NMR, respectively. The following abbreviations are used in descriptions of NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, app = apparent, and *J* = coupling constant. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. The nomenclature for determining the chirality of the molybdenum complexes is straightforward.[57] Single bonds are assumed between molybdenum and π-coordinated carbons. The chirality of the carbon (bound to molybdenum) with the highest priority (CIP)[58] determines the chirality of the complex.

Syntheses and Transformations of Racemic Lactonyl Complex 1. (A) Racemic (η^5-Cyclopentadienyl)(dicarbonyl)[(3,4,5-η)-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (1). Molybdenum hexacarbonyl (4.8 g, 18 mmol) and 30 mL of CH_3CN were placed in a flame-dried Schlenk flask under argon. The flask was equipped with a condenser and flushed with argon. After 6.5 h at vigorous reflux under Ar, the reaction mixture was allowed to cool to room temperature. Under a flow of Ar, the condenser was removed, the flask was fitted with a septum cap and placed in an ice bath, and Ar was sparged through the yellow solution for a few minutes, during which time a yellow solid began to precipitate. 5-Bromo-5,6-dihydro-2*H*-pyran-2-one[48] (3.2 g, 18 mmol) in 5 mL of THF was added using an additional 5 mL of THF to rinse the syringe and the inside wall of the flask. The solution changed color from yellow to orange as the initial precipitate disappeared and gas evolved and a new yellow-orange precipitate formed. Solvent and unreacted $Mo(CO)_6$ were removed under reduced pressure, leaving 7.0 g of solid $Mo(CO)_2(CH_3CN)_2Br(C_5H_5O_2)$. To 0.5 g (1.2 mmol) of this material and 20 mL of dry THF in a flask was added cyclopentadienylthallium (0.34 g, 1.2 mmol), and the inside wall of the flask was washed with 10 mL of THF. Dimethylformamide (5 mL) was added and the reaction mixture was stirred at room temperature for 7 h. The reaction mixture was passed through a pad of silica gel with EtOAc to remove thallium salts. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc and filtered through a pad of silica gel. Removal of solvent left 0.22 g (58%) of **1** as a yellow solid: mp 219–220 °C (1:1 ethanol/ethyl acetate); ^{1}H NMR (300 MHz, DMSO-d_6, observed resonances are concentration dependent moving upfield with increasing concentration) δ 5.57 (s, 5 H), 5.04 (br t, *J* ≈ 6 Hz, 1 H), 4.48 (dd, *J* = 13.4, 2.7 Hz, 1 H), 4.12 (d, *J* = 7.1 Hz, 1 H), 3.84 (dd, *J* = 13.4, 1.0 Hz, 1 H), 3.38 (dd, *J* = 5.8, 1.9 Hz, 1 H); IR (KCl cells, CH_2Cl_2) 1968, 1919, 1895, 1694, 1664, 1387, 1207, 1073, 815 cm^{-1}. Anal. Calcd for $C_{12}H_{10}MoO_4$: C, 45.88; H, 3.21. Found: C, 45.83; H, 3.23.

(B) Racemic (η^5-Cyclopentadienyl)(dicarbonyl)[(3,4,5-η)-2-*syn*-ethoxy-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (2). A 100-mL Schlenk flask equipped with a magnetic stirrer and a gas inlet was flame dried and flushed with argon. To the flask were added 0.26 g (0.83 mmol) of **1**, $Et_3O^+PF_6^-$ with 10% diethyl ether (0.23 g, 0.83 mmol), and 5 mL of dry CH_2Cl_2. Within 5 min the solid dissolved, and by 15 min a new precipitate had formed. After 2 h the solvent was removed, leaving a bright yellow solid. THF (20 mL) was added, the suspension was cooled with stirring to −78 °C, and 1.0 M $LiEt_3BH$ in THF (0.83 mL, 0.83 mmol) was added. After 15 min the solid had dissolved, and TLC analysis indicated clean conversion to a yellow material with R_f = 0.63 (SiO_2, 1:1 hexane/ethyl acetate). The solution was stirred for an additional 40 min at −78 °C, warmed to room temperature, and then passed through a 2-cm silica gel plug. The solvent was removed in vacuo leaving a yellow-brown oil that was flash chromatographed (SiO_2, 50 g, degassed 4:1 hexane/ethyl acetate), giving 0.21 g (74%) of *syn*-ethoxy complex **2** as a mildly air-sensitive yellow solid: mp 134–135 °C (pentane/CH_2Cl_2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 5.31 (s, 5 H), 4.61 (s, 1 H), 4.24 (t, *J* = 7.2 Hz, 1 H), 3.81 (d, *J* = 11.4 Hz, 1 H), 3.74 (dq, *J* = 9.5, 7.1 Hz, 1 H), 3.62 (d, *J* = 11.4 Hz, 1 H), 3.60 (pattern obscured by peak at 3.62, 1 H), 3.42 (pattern obscured by peak at 3.40, 1 H), 3.40 (dq, *J* = 9.5, 7.1 Hz, 1 H), 1.16 (t, *J* = 7.1 Hz, 3 H); IR (KCl cell, CH_2Cl_2) 2980, 2823, 1960, 1878, 1322, 1362, 1126, 1066, 917, 819 cm^{-1}. Anal. Calcd for $C_{14}H_{16}MoO_4$: C, 48.85; H, 4.69. Found: C, 45.25; H, 4.61.

(C) Epimerization of 2 to Racemic (η^5-Cyclopentadienyl)(dicarbonyl)[(3,4,5-η)-2-*anti*-ethoxy-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (3). A dry 250-mL round-bottomed flask equipped with a magnetic stirrer was flushed with nitrogen and charged with 1.50 g (4.36 mmol) of **2** and 30 mL of CH_2Cl_2. The resulting solution was treated with 2.60 mL (43.6 mmol, 10 equiv) of absolute EtOH and 83 mg (0.44 mmol, 0.10 equiv) of *p*-toluenesulfonic acid monohydrate. After stirring at 25 °C for 3.5 h, the color of the reaction mixture had changed from yellow to yellow-brown, and TLC analysis showed complete disappearance of starting material and a new yellow component at R_f = 0.60 that streaked extensively. The reaction mixture was passed through a short plug of silica gel, and the filtrate was concentrated in vacuo to give 1.3 g (87%) of the *anti*-ethoxy complex **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (s, 5 H), 4.60 (d, *J* = 1.9 Hz, 1 H), 4.44 (t, *J* = 7.1 Hz, 1 H), 4.00 (d, *J* = 12.0 Hz, 1 H), 3.68–3.58 (overlapping multiplets, 2 H), 3.50–3.30 (overlapping multiplets, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H); IR (KCl cell, CH_2Cl_2) 2970, 2915, 2847, 1940, 1863, 1362, 1134, 1066, 1035, 985, 801. Due to the sensitivity of this compound, no further purification was attempted and the crude material was used directly in the next step.

(D) Ionization of 3 to Racemic (η^5-Cyclopentadienyl)(dicarbonyl)-

(56) Keinan, E.; Seth, K. K.; Lamed, R. *J. Am. Chem. Soc.* **1986**, *108*, 3474.

(57) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

(58) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

[(3,4,5,6-η)-2*H*-pyranyl]molybdenum Tetrafluoroborate (4). A dry 250-mL Schlenk flask equipped with a magnetic stirrer and a gas inlet tube was flushed with argon. The crude product from the epimerization step (1.00 g, 2.91 mmol) was dissolved in 15 mL of dry CH_2Cl_2 and passed through a short plug of SiO_2 directly into the Schlenk flask. This resulted in a transparent orange solution, which was then mixed with 150 mL of dry Et_2O. To this solution with stirring was added $HBF_4{\cdot}Et_2O$ (0.47 g, 2.9 mmol) dropwise via syringe. A yellow solid immediately precipitated. The solid was allowed to settle and the supernatant ether was removed via cannula. The product was then washed successively with three 50-mL portions of ether leaving, after drying under vacuum, 1.0 g (89%) of **4**: mp 180–200 °C dec (acetone/ether); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (dd, J = 4.6, 2.3 Hz, 1 H), 6.18 (m, 1 H), 5.94 (s, 5 H), 5.14 (ddd, J = 4.3, 4.3, 2.3 Hz, 1 H), 4.60 (d mult, J = 7.5 Hz, 1 H), 3.94 (br d, $J \approx 13$ Hz, 1 H), 3.57 (dd, J = 12.9, 2.3 Hz, 1 H); IR (KBr pellet) 3010, 2000, 1960, 1460, 1395, 1213, 1193, 1050, 825 cm^{-1}. Anal. Calcd for $C_{12}H_{11}MoO_3BF_4$: C, 37.34; H, 2.87. Found: C, 37.34; H, 2.90.

Enantiomerically Pure Molybdenum Complex Studies. (η^5-Cyclopentadienyl)(dicarbonyl)[(3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (6). A mixture of $Mo(CO)_6$ (6.94 g, 26.3 mmol) in dry deoxygenated acetonitrile (30 mL) was refluxed under Ar for 5 h at 90 °C. The allylic acetate **5**[53] (5.8 g, 26.8 mmol) in dry THF (20 mL) was added, and the reaction mixture was kept at 90 °C for 16 h. The solvent was evaporated, THF (40 mL) was added, and the reaction mixture was cooled to approximately −40 °C. In another flask, cyclopentadienyllithium (43.34 mmol in 50 mL of THF) was prepared by dropwise addition of *n*-BuLi (15.76 mL, 2.5 M in hexanes, 39.4 mmol) to freshly distilled cyclopentadiene (2.86 g, 3.54 mL, 43.34 mmol) in dry THF (50 mL) at −30 °C. This mixture was stirred for 20 min, allowed to warm to 0 °C with stirring for 10 min, and then added via cannula to the flask containing the (η^3-allyl)molybdenum complex. The reaction mixture was stirred between −40 and 0 °C for 1 h and was then quenched with saturated ammonium chloride solution (100 mL). Extraction with ether (4 × 200 mL), drying over Na_2SO_4, filtration, and concentration on the rotary evaporator followed by flash chromatography (3:1, ethyl acetate/hexanes, 16 × 5 cm, R_f = 0.28) gave 4.9 g (50%) of a yellow solid. Analytically pure material was obtained by recrystallization from a mixture of ether and dichloromethane: mp 137–8 °C; $[\alpha]_D$ +25.9° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.46 (s, 5 H), 4.94 (br mult, 1 H), 4.26 (app t, J = 4.1 Hz, 1 H), 4.16 (app d, J = 4.1 Hz, 2 H), 3.83 (br d, $J \approx 6.5$ Hz, 1 H), 3.45 (dd, J = 1.6, 5.8 Hz, 1 H), 2.03 (s, 3 H); ^{13}C NMR (acetone-d_6, 75.1 MHz) δ 234.1, 233.3, 169.8, 168.2 (br), 93.1, 75.6 (br), 67.6, 62.7 (br), 50.4 (br), 39.5, 19.9; IR (KCl cell, CH_2Cl_2) 2989, 1997, 1980, 1935, 1904, 1742, 1708, 1424, 1370, 1237, 1210, 1080, 1044, 822 cm^{-1}. Anal. Calcd for $C_{15}H_{14}MoO_6$: C, 46.65; H, 3.65. Found: C, 46.56; H, 3.64.

Confirmation of Syn Introduction of $CpMo(CO)_2$ to Allylic Acetate 5 Producing 6. Conversion of 6 into 7. (A) (η^5-Cyclopentadienyl)(dicarbonyl)[(3*S*,6*R*)-(3,4,5-η)-6-(hydroxymethyl)-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (see Scheme II). The complex **6** (1.677 g, 4.34 mmol) was dissolved in ethanol (20 mL), and $LiOH{\cdot}H_2O$ (0.55 g, 13.0 mmol) was added at room temperature. After 30 min the reaction was complete and part of the product crystallized out from the reaction mixture. The reaction mixture was quenched with water (200 mL) and extracted with CH_2Cl_2 (6 × 100 mL). Drying over Na_2SO_4, filtration, and evaporation of the solvents gave 1.4 g of a yellow solid (94%) that was used without further purification. An analytically pure sample of the alcohol was obtained by recrystallization from ethanol: mp >190 °C dec; $[\alpha]_D$ +145.0° (c 1.0, DMSO); ^{1}H NMR (CD_3CN, 360 MHz) δ 5.46 (s, 5 H), 4.92 (br m, 1 H), 4.08 (app t, $J \approx$ 4.2 Hz, 1 H), 3.93 (d, $J \approx$ 7 Hz, 1 H), 3.59 (dd, J = 4.2, 11.6 Hz, 1 H), 3.53 (dd, J = 4.3, 11.6 Hz, 1 H), 3.42 (br d, $J \approx 6$ Hz, 1 H), 3.05 (br s, 1 H); ^{13}C NMR (DMSO-d_6, 75.1 MHz) δ 236.0, 234.9, 169.4, 93.4, 78.7, 66.4, 63.2 (br), 53.9 (br), 39.3; IR (KCl cell, CH_2Cl_2) 3600, 3062, 2987, 1939, 1978, 1932, 1901, 1732, 1705, 1678, 1374, 1216, 1080, 1046 cm^{-1}. Anal. Calcd for $C_{13}H_{12}MoO_5$: C, 45.37; H, 3.51. Found: C, 45.46; H, 3.54.

(B) (η^5-Cyclopentadienyl)(dicarbonyl)[(3*S*,6*R*)-(3,4,5-η)-6-[(methylsulfonyl)oxy]methyl]-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (see Scheme II). A solution of methanesulfonyl chloride (265 μL, 392.6 mg, 3.43 mmol) in 15 mL of CH_2Cl_2 was added to a solution of the alcohol (0.718 g, 2.285 mmol), prepared in the preceding procedure, and Et_3N (0.95 mL, 0.69 mg, 6.85 mmol) in 15 mL of CH_2Cl_2 at 0 °C. The reaction mixture was stirred for 30 min at room temperature and then quenched with water (50 mL). Extraction with CH_2Cl_2 (3 × 30 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent gave 0.912 g (95%) of a yellow solid that was used without further purification. An analytically pure sample of the mesylate was obtained by recrystallization from a mixture of CH_2Cl_2 and ether: mp 184–189 °C dec; $[\alpha]_D$ +28.4° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.48 (s, 5 H), 4.99 (br m, 1 H), 4.38–4.30 (m, 2 H), 4.20 (part B of a ABX system, J_{AB} = 11.5 Hz, J_{BX} = 5.4 Hz, 1 H), 3.84 (br d, J = 6.7 Hz, 1 H), 3.47 (dd, J = 1.4, 5.7 Hz, 1 H), 3.03 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 234.9, 234.6, 169.8, 94.3, 76.5 (br), 73.9, 63.8 (br), 50.3 (br), 40.1, 37.8; IR (KCl cell, CH_2Cl_2) 3060, 2989, 2001, 1982, 1939, 1906, 1711, 1362, 1177, 965 cm^{-1}. Anal. Calcd for $C_{14}H_{14}MoO_7S$: C, 39.82; H, 3.34. Found: C, 39.77; H, 3.38.

(C) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-2-ethoxy-6-[[(methylsulfonyl)oxy]methyl]-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (see Scheme II). To the molybdenum complex prepared in the preceding experiment (296 mg, 0.70 mmol) in dry CH_2Cl_2 (7 mL) in a Schlenk flask was added triethyloxonium hexafluorophosphate (191 mg, 0.77 mmol). The solution was stirred at room temperature for 1 h, during which time the initial yellow color of the solution turned to orange-red. The solvent was evaporated at high vacuum pump, THF (15 mL) was added, and the solution was cooled to −78 °C. Super Hydride (4.95 mL, 4.95 mmol, 3 equiv) was added dropwise via a syringe. The mixture became yellow within ~5 min. After 15 min the reaction was quenched by the addition of saturated ammonium chloride solution (50 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried over Na_2SO_4, concentrated on a rotary evaporator, and flash chromatographed (1:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.44) to yield 266 mg (84%) of a yellow syrup that was crystallized from a degassed mixture of diethyl ether and hexanes: mp 93–95 °C; $[\alpha]_D$ −66.2° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.36 (s, 5 H), 4.91 (s, 1 H), 4.48 (br app t, $J \approx$ 7 Hz, 1 H), 4.17 (app d, J = 5.6 Hz, 2 H), 3.91 (dt, J = 0.9, 5.6 Hz, 1 H), 3.57 (qd, J = 7.0, 9.4 Hz, 1 H), 3.54 (br d, $J \approx$ 7 Hz, 1 H), 3.42 (br d, $J \approx$ 7 Hz, 1 H), 3.32 (qd, J = 7.0, 9.4 Hz, 1 H), 3.01 (s, 3 H), 1.03 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 238.8, 235.1, 93.71, 93.2, 73.4, 72.0 (br), 64.1, 59.0 (br), 54.7 (br), 52.2, 37.8, 15.5; IR (KCl cell, CH_2Cl_2) 3062, 1981, 1875, 1964, 1883, 1358, 1177, 961, 816 cm^{-1}. Anal. Calcd for $C_{16}H_{20}MoO_7S$: C, 42.48; H, 4.46. Found: C, 42.62; H, 4.46.

(D) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*)-(3,4,5-η)-2-[[(methylsulfonyl)oxy]methyl]-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (see Scheme II). To the molybdenum complex prepared in the preceding experiment (266 mg, 0.588 mmol) and dissolved in dichloromethane (5 mL) was added a solution of triphenylcarbenium hexafluorophsphate (251 mg, 0.647 mmol) in dichloromethane (2 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C, during which time a yellow precipitate was formed. The solvent was evaporated at high vacuum and THF (5 mL) was added. To this suspension stirred at −78 °C was added Super Hydride (1.47 mL, 1.47 mmol, 2.5 equiv). The mixture became clear within 1 min. After 15 min the reaction was quenched with a saturated ammonium chloride solution (30 mL) and extracted with dichloromethane (3 × 15 mL). The combined organic phases were dried over Na_2SO_4, concentrated on a rotary evaporator, and flash chromatographed (1:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.54) to yield 180 mg (75%) of yellow syrup that was crystallized from a degassed mixture of diethyl ether and hexanes: mp 92–94 °C; $[\alpha]_D$ −36.0° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.40 (s, 5 H), 4.47 (app t, $J \approx$ 7.2 Hz, 1 H), 4.21 (app d, J = 5.7 Hz, 2 H), 3.92 (d, J = 12.6 Hz, 1 H), 3.70 (app dt, J = 1.3, 5.7 Hz, 1 H), 3.57 (dd, J = 1.54, 7.2 Hz, 1 H), 3.33 (dd, J = 1.4, 12.6 Hz, 1 H), 3.30 (br d, $J \approx$ 7 Hz, 1 H), 3.0 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 236.7, 236.4, 93.6, 72.5, 69.0, 57.8, 55.6, 54.0, 49.2, 37.8; IR (KCl cell, CH_2Cl_2) 3058, 2989, 2834, 1953, 1874, 1358, 1177, 961, 814. Anal. Calcd for $C_{14}H_{16}MoO_6S$: C, 41.19; H, 3.95. Found: C, 41.28; H, 3.98.

(E) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*)-(3,4,5-η)-2-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (7). The molybdenum complex prepared in the preceding experiment (54 mg, 0.132 mmol) dissolved in THF (2 mL) was treated with a 1 M solution of lithium aluminum hydride in ether (0.264 mL, 0.264 mmol). The reaction mixture was heated at 60 °C for 3 h and then quenched with ammonium chloride solution (10 mL) at 0 °C. After extraction with dichloromethane (3 × 10 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was purified by flash chromatography (5:1, degassed hexanes/ethyl acetate mixture) to give 20 mg (48%) of **7**. This compound was found to be identical (NMR, IR, optical rotation) with an authentic sample synthesized earlier in these laboratories.[32]

Synthesis of *trans*-2,6-Disubstituted Pyranyl Complexes. (A) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,6*S*)-(3,4,5,6-η)-2-(acetoxymethyl)-6-ethoxy-2*H*-pyranyl]molybdenum Hexafluorophosphate (8). To the molybdenum complex **6** (2.0 g, 5.18 mmol) stirred in 36 mL of dichloromethane in a Schlenk flask at room temperature was added triethyloxonium hexafluorophosphate (1.57 g, 5.70 mmol). The mixture was stirred for 1 h at room temperature, and then the solvent was evaporated at high vacuum. The syrup was dissolved in THF (25 mL), diethyl ether (75 mL) was added, and a yellow precipitate formed. The solid was allowed to settle and the supernatant was removed by cannula.

The solid was washed with ether (3 × 25 mL) and dried in vacuo to give 2.71 g (93%) of a mustard-yellow powder: mp 125 °C dec; $[\alpha]_D$ = +485° (*c* 1.0, acetone); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.65 (s, 5 H), 5.39 (br m, 1 H), 4.67 (br m, 1 H), 4.42 (m, 2 H), 4.38 (dd, *J* = 2.7, 12.6 Hz, 1 H), 4.28 (dd, *J* = 5.1, 12.6 Hz, 1 H), 4.11 (br m, 1 H), 3.87 (dd, *J* = 1.3, 4.9 Hz, 1 H), 2.05 (s, 3 H), 1.34 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 234.2 (br), 230.1 (br), 184.6, 171.2, 95.9, 83.7, 70.8, 65.9, 64.1 (br), 54.2 (br), 35.5, 20.5, 14.1; IR (KCl cell, CH_2Cl_2) 3112, 3064, 2995, 2036, 2001, 1935, 1752, 1517, 1476, 1221, 847 cm^{-1}. Anal. Calcd for $C_{17}H_{19}O_6PF_6Mo$: C, 36.45; H, 3.42. Found: C, 36.50; H, 3.43.

(B) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,5*S*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-ethoxy-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9a). To a solution of the molybdenum complex **8** (400 mg, 0.714 mmol) in THF (7 mL) stirred at −78 °C was added sodium borohydride (81 mg, 2.14 mmol). The solution was stirred for 45 min at −78 °C and then quenched with saturated ammonium chloride solution (30 mL). The mixture was allowed to warm up to room temperature and then extracted with 3 × 20 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, concentrated on a rotary evaporator, and flash chromatographed (1:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.23) to yield 278.2 mg (94%) of **9a** as a yellow solid that was recrystallized from a degassed mixture of diethyl ether and hexanes: mp 107–8 °C; $[\alpha]_D$ −97.5° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.34 (s, 5 H), 4.87 (s, 1 H), 4.44 (app t, *J* ≈ 7 Hz, 1 H), 4.26 (dd, *J* = 7.7, 11.5 Hz, 1 H), 3.92 (dd, *J* = 3.6, 11.5 Hz, 1 H), 3.81 (br dd, *J* = 3.6, 7.7 Hz, 1 H), 3.53 (overlapped br d, *J* = 7.0 Hz, 1 H), 3.53 (overlapped dq, *J* = 9.5, 7.1 Hz, 1 H), 3.44 (br d, *J* = 7.0 Hz, 1 H), 3.27 (qd, *J* = 7.1, 9.5 Hz, 1 H), 1.98 (s, 3 H), 1.02 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.0, 235.0, 171.1, 93.3, 93.1, 71.8 (br), 67.4, 63.7, 58.6 (br), 54.4, 53.8, 21.1, 15.6; IR (KCl cell, CH_2Cl_2) 3062.2, 2981.1, 2934.8, 2875.0, 1960.4, 1879.4, 1738.5, 1375.7, 1233.0, 1126.8, 1067.0, 1040.0, 1020.7, 814.3. Anal. Calcd for $C_{17}H_{20}MoO_6$: C, 49.05; H, 4.84. Found: C, 49.12; H, 4.89.

(C) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethoxy-2-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9b). To a solution of the molybdenum complex **8** (300 mg, 0.535 mmol) in THF (5 mL) stirred at −78 °C was added a 3 M solution of methyl magnesium iodide (0.54 mL, 1.61 mmol, 3 equiv). The mixture was stirred for 15 min at −78 °C and then quenched with saturated ammonium chloride solution (30 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, and the crude residue was flash chromatographed (2:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.50) to give 200 mg (87%) of **9b** as a yellow brownish solid: mp 80–82 °C; $[\alpha]_D$ +46.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.30 (s, 5 H), 4.61 (br app t, *J* ≈ 5 Hz, 1 H), 4.01 and 3.94 (AB part of ABX system, J_{AB} = 10.9 Hz, J_{AX} = 7.0 Hz, J_{BX} = 5.3 Hz, 2 H), 3.90 (br d, *J* = 3.59, 1 H), 3.84 (app t, *J* ≈ 7 Hz, 1 H), 3.59 (br d, *J* = 6.8 Hz, 1 H), 3.33 (q, *J* = 7.0 Hz, 2 H), 1.98 (s, 3 H), 1.49 (s, 3 H), 1.01 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 240.1, 236.1, 171.3, 97.1, 93.2, 71.6 (br), 69.6, 61.9, 61.1 (br), 57.4, 53.2, 30.3, 21.0, 15.5; IR (KCl cell, CH_2Cl_2) 3058, 2983, 2935, 2887, 1960, 1877, 1738, 1385, 1368, 1237, 1152, 1050, 812 cm^{-1}. Anal. Calcd for $C_{18}H_{22}MoO_6$: C, 50.24; H, 5.15. Found: C, 50.01; H, 5.19.

(D) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethoxy-2-ethyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9c). To a solution of molybdenum complex **8** (500 mg, 0.892 mmol) in THF (10 mL) stirred at −78 °C was added a 3 M solution of ethyl magnesium bromide (0.89 mL, 2.68 mmol, 3 equiv). The mixture was stirred for 15 min at −78 °C and then quenched with saturated ammonium chloride solution (30 mL) and extracted with dichloromethane (3 × 30 mL). Drying over Na_2SO_4, filtration, evaporation of the solvent, and flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm) gave 292.5 mg (74%) of **9c** as a yellow syrup: $[\alpha]_D$ = +73.0° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.29 (s, 5 H), 4.67 (app t, *J* ≈ 7 Hz, 1 H), 4.06 (dd, *J* = 1.5, 7.2 Hz, 1 H), 3.95 (app d, *J* = 5.7 Hz, 2 H), 3.83 (app t, *J* = 5.7 Hz, 1 H), 3.56 (d, *J* = 6.6 Hz, 1 H), 3.24 (m, 2 H), 1.97 (s, 3 H), 1.80 and 1.65 (AB part of ABX_3 system, J_{AB} = 13.9, J_{AX} = 7.3, J_{BX} = 7.3 Hz, 2 H), 0.99 (t, *J* = 7.0 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 240.3, 236.0, 171.2, 99.2, 93.2, 71.4 (br), 69.5, 62.6 (br), 59.8, 57.0, 52.8, 34.4, 21.0, 15.3, 8.8; IR (KCl cell, CH_2Cl_2) 3062, 2979, 2939, 2885, 1960, 1875, 1738, 1383, 1366, 1235, 1194, 1154, 1054, 1053, 812 cm^{-1}; MS (high resolution) no molecular ion was observed.

(E) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethoxy-2-*p*-tolyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9d). To a solution of the molybdenum complex **8** (300 mg, 0.535 mmol) in THF (5 mL) stirred at −78 °C was added dropwise a 1 M solution of *p*-tolylmagnesium bromide in diethyl ether (1.61 mL, 1.61 mmol, 3 equiv). The mixture was stirred for 15 min at −78 °C and then quenched by addition of saturated ammonium chloride solution (30 mL). The mixture was extracted with 3 × 20 mL of dichloromethane, dried over Na_2SO_4, filtered, concentrated, and flash chromatographed (4:1, degassed hexanes/ethyl acetate mixture, 140 × 2.5 cm, R_f = 0.50) to give 231.6 mg (85%) of a yellow solid that was recrystallized from degassed hexanes: mp 114–118 °C dec; $[\alpha]_D$ +128.6° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 7.34 and 7.17 (AA'BB' system, *J* = 8.1 Hz, 4 H), 5.29 (s, 5 H), 4.72 (app t, *J* ≈ 7 Hz, 1 H), 4.12 (dd, *J* = 2.4, 7.0 Hz, 1 H), 4.10–3.97 (m, 3 H), 3.62 (dd, *J* = 1.7, 6.5 Hz, 1 H), 3.03 (qd, *J* = 7.2, 9.3 Hz, 1 H), 2.85 (qd, *J* = 7.1, 9.3 Hz, 1 H), 2.30 (s, 3 H), 1.98 (s, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 240.4, 236.4, 171.4, 144.3, 137.9, 129.7, 126.9, 99.5, 93.5, 71.6, 69.0, 64.0, 63.2 (br), 59.1, 51.9, 21.1, 21.0, 15.1; IR (KCl cell, CH_2Cl_2) 3054, 2979, 2929, 2887, 1962, 1877, 1738, 1385, 1366, 1235, 1086, 1073, 1044, 812 cm^{-1}. Anal. Calcd for $C_{24}H_{26}MoO_6$: C, 56.92; H, 5.17. Found: C, 57.01; H, 5.23.

(F) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethenyl-2-ethoxy-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9e). To a solution of the molybdenum complex **8** (300 mg, 0.535 mmol) in THF (5 mL) was added dropwise a 1 M solution of vinylmagnesium bromide in THF (1.59 mL, 1.59 mmol, 3 equiv). The mixture was stirred at −78 °C for 15 min and then quenched by addition of saturated ammonium chloride solution (30 mL). The mixture was extracted with 3 × 20 mL of dichloromethane, dried over Na_2SO_4, filtered, concentrated, and flash chromatographed (4:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.36) to give 188 mg (79%) of a yellow solid: mp 83–84 °C; $[\alpha]_D$ +121.0° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.90 (dd, *J* = 10.6, 17.4 Hz, 1 H), 5.33 (dd, *J* = 1.2, 17.4 Hz, 1 H), 5.32 (s, 5 H), 5.15 (dd, *J* = 1.2, 10.6 Hz, 1 H), 4.64 (app t, *J* ≈ 6 Hz, 1 H), 4.00 (m, 2 H), 3.91 (m, 2 H), 3.62 (d, *J* = 6.8 Hz, 1 H), 3.25 (app q, *J* = 7.0 Hz, 2 H), 1.97 (s, 3 H), 0.97 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 240.1, 236.0, 171.3, 144.1, 115.4, 97.1, 93.3, 72.0 (br), 69.3, 61.2 (br), 59.2, 58.1, 53.5, 21.0, 15.4; IR (KCl cell, CH_2Cl_2) 3062, 2981, 2930, 2890, 1962, 1879, 1738, 1383, 1368, 1236, 1069, 1041, 814 cm^{-1}. Anal. Calcd for $C_{19}H_{22}MoO_6$: C, 51.59; H, 5.01. Found: C, 51.69; H, 5.06.

(G) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethoxy-2-(1-hexyn-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9f). Hexynyllithium was prepared by dropwise addition of *n*-BuLi (0.43 mL, 1.08 mmol, 2.5 M in hexanes) to a stirred solution of 1-hexyne (136.5 μL, 97.6 mg, 1.19 mmol) in THF (4 mL) at −78 °C. The solution was stirred at −78 °C for 1 h, and then a solution of the molybdenum complex **8** (200 mg, 0.36 mmol) in THF (4 mL) was added by cannula. The mixture was stirred for 15 min at −78 °C and then quenched with saturated ammonium chloride solution (30 mL) and extracted with 3 × 20 mL of dichloromethane. Drying over Na_2SO_4, filtration, and evaporation of the solvent followed by flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.48) gave 158 mg (89%) of a yellow syrup: $[\alpha]_D$ +79.5° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.34 (s, 5 H), 4.47 (app t, *J* ≈ 6 Hz, 1 H), 4.40 (dd, *J* = 11.0, 7.5 Hz, 1 H), 4.17 (dd, *J* = 11.0, 5.8 Hz, 1 H), 3.88 (app t, *J* ≈ 7 Hz, 1 H), 3.75 (dd, *J* = 0.8, 7.2 Hz, 1 H), 3.68 (br d, *J* = 7.2 Hz, 1 H), 3.65–3.45 (m, 2 H), 2.19 (br t, *J* = 6.6 Hz, 2 H), 1.98 (s, 3 H), 1.50–1.30 (m, 4 H), 1.02 (t, *J* = 6.9 Hz, 3 H), 0.88 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.2, 235.1, 171.3, 93.3, 91.0, 85.3, 84.0, 72.3, 68.9, 59.6, 58.9, 57.7 (br), 55.4, 31.1, 22.6, 21.0, 18.7, 15.3, 13.9; IR (KCl cell, CH_2Cl_2) 3060, 2962, 2935, 2217, 1964, 1883, 1738, 1381, 1368, 1243, 1175, 1146, 1121, 1069, 1040, 814 cm^{-1}. Anal. Calcd for $C_{23}H_{28}MoO_6$: C, 55.65; H, 5.68. Found: C, 55.71; H, 5.70.

(H) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*S*,3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-ethoxy-2-[(methoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (9g). Methyl acetate (140.3 μL, 130.8 mg, 1.76 mmol) was added dropwise to a lithium diisopropylamide solution (1.61 mmol) in THF (20 mL) at −78 °C and stirred for 30 min. A solution of the molybdenum complex **8** (300 mg, 0.535 mmol) in THF (20 mL) was then added by cannula. The reaction mixture was stirred for 15 min at −78 °C and was then quenched by addition of a saturated ammonium chloride solution (30 mL). Extraction with dichloromethane (3 × 20 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent followed by flash column chromatography (1:1, degassed hexanes/ether mixture, 14 × 2.5 cm, R_f = 0.27) gave 220 mg (84%) of a yellow syrup that was crystallized from a degassed mixture of ethyl ether and hexanes: mp 74–75 °C; $[\alpha]_D$ = +11.0° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.31 (s, 5 H), 4.63 (br app t, *J* ≈ 6 Hz, 1 H), 4.30 (br d, *J* = 6.4 Hz, 1 H), 4.05–3.87 (m, 3 H), 3.61 (s, 3 H), 3.59 (d, 1 H), 3.38 (q, *J* = 7.0 Hz, 2 H), 2.94 and 2.72 (AB system, *J* = 13.5 Hz, 2 H), 1.98 (s, 3 H), 0.96 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.9, 235.5, 171.3, 170.5, 97.2, 93.3, 72.3 (br), 69.4, 60.8 (br), 59.2,

57.9, 53.1, 52.0, 48.1, 21.0, 15.1; IR (KCl cell, CH_2Cl_2) 3062, 2983, 2954, 2902, 1964, 1879, 1738, 1439, 1229, 1144, 1096, 1073, 1044, 1007, 814 cm^{-1}. Anal. Calcd for $C_{20}H_{24}MoO_8$: C, 49.19; H, 4.95. Found C, 49.04; H, 4.90.

(I) (η^5-Cyclopentadienyl)(dicarbonyl)[(3*R*,6*R*)-(3,4,5,6-η)-2-(acetoxymethyl)-6-methyl-2*H*-pyranyl]molybdenum Hexafluorophosphate (10b). To the molybdenum complex **9b** (1.875 g, 4.36 mmol) stirred in 40 mL of dichloromethane in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (1.86 g, 4.79 mmol). The mixture was stirred for 30 min at 0 °C, diethyl ether (60 mL) was added, and a precipitate formed. The solid was allowed to settle and the supernatant was removed. The solid was washed with diethyl ether (3 × 20 mL) and dried in vacuo to give 2.30 g (99%) of an orange solid: mp 147 °C dec; $[\alpha]_D$ = 619.8° (*c* 1.0, acetone); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.06 (br m, 1 H), 5.78 (s, 5 H), 4.72 (dd, *J* = 1.6, 4.1 Hz, 1 H), 4.46 (br d, *J* ≈ 4 Hz, 1 H), 4.25 (app d, *J* = 4.0 Hz, 2 H), 4.12 (dt, *J* = 1.2, 4.3 Hz, 1 H), 2.36 (s, 3 H), 2.12 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 231.5 (br), 225.9 (br), 175.1, 171.2, 96.1, 78.6, 69.6, 65.6 (br, 2 C), 60.1 (br), 24.6, 21.0; IR (KCl cell, CH_2Cl_2) 3070, 2956, 2055, 1953, 1750, 1511, 1424, 1407, 1221, 1046, 1021, 847 cm^{-1}. Anal. Calcd for $C_{16}H_{17}MoO_5PF_6$: C, 36.24; H, 3.22. Found: C, 36.14; H, 3.23.

(J) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*R*)-(3,4,5-η)-2-(acetoxymethyl)-6-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (11b). To a suspension of the molybdenum complex **10b** (1.12 g, 2.11 mmol) in THF (30 mL) at −78 °C was added sodium borohydride (239 mg, 6.33 mmol). The mixture was allowed to warm from −78 to 0 °C over 30 min and then was quenched by addition of saturated ammonium chloride solution (100 mL). The mixture was extracted with dichloromethane (3 × 50 mL), dried over Na_2SO_4, filtered, concentrated in the rotary evaporator, and flash chromatographed (2:1, degassed hexanes/ethyl acetate mixture, 14 × 3 cm, R_f = 0.48) to give 0.73 g (89%) of a yellow syrup: $[\alpha]_D$ = −9.6° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 5.32 (s, 5 H), 4.52 (app t, *J* ≈ 7 Hz, 1 H), 4.20 (dd, *J* = 8.2, 11.6 Hz, 1 H), 4.05 (q, *J* = 6.3 Hz, 1 H), 3.99 (dd, *J* = 3.8, 11.6 Hz, 1 H), 3.77 (br d, *J* = 8.2 Hz, 1 H), 3.71 (d, *J* = 6.9 Hz, 1 H), 3.38 (d, *J* = 6.9 Hz, 1 H), 1.97 (s, 3 H), 1.03 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.3, 238.2, 171.3, 93.0, 71.2, 66.7, 64.3, 61.1, 58.9 (br), 52.7, 21.1, 20.7; IR (KCl cell, CH_2Cl_2) 3060, 2979, 2941, 1951, 1874, 1737, 1381, 1368, 1235, 1082, 1040, 816 cm^{-1}. Anal. Calcd for $C_{16}H_{18}MoO_5$: C, 49.75; H, 4.70. Found: C, 49.65; H, 4.72.

(K) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*R*)-(3,4,5-η)-2-(acetoxymethyl)-6-ethyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (11c). To the molybdenum complex **9c** (100 mg, 0.225 mmol) stirred in 2 mL of dichloromethane in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (96 mg, 0.247 mmol). The mixture was stirred for 30 min at 0 °C, and then the solution was concentrated at high vacuum and THF (3 mL) was added. This solution was cooled to −78 °C and sodium borohydride (25 mg, 0.67 mmol) was added. The mixture was allowed to warm from −78 to 0 °C over 30 min and then was quenched with saturated ammonium chloride solution (20 mL). Extraction with dichloromethane (3 × 10 mL), drying over Na_2SO_4, filtration, evaporation of the solvents, and flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 1 cm) gave 66 mg (73%) of a yellow syrup: $[\alpha]_D$ = −6.2° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 5.32 (s, 5 H), 4.51 (app t, *J* ≈ 7 Hz, 1 H), 4.26 (dd, *J* = 8.5, 11.5 Hz, 1 H), 3.95 (dd, *J* = 3.7, 11.5 Hz, 1 H), 3.82–3.70 (m, 3 H), 3.38 (br d, *J* = 7.0 Hz, 1 H), 1.96 (s, 3 H), 1.43 (app p, *J* = 7.4 Hz, 2 H), 0.78 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.3, 238.1, 171.3, 93.0, 71.0, 70.1, 66.5, 59.9, 58.8, 52.6, 28.0, 21.0, 10.8; IR (KCl cell, CH_2Cl_2) 3056, 2977, 2937, 1951, 1872, 1735, 1422, 1374, 1233, 1152, 1073, 1038, 812 cm^{-1}. Anal. Calcd for $C_{17}H_{20}MoO_5$: C, 51.01; H, 5.04. Found: C, 51.13; H, 5.09.

(L) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*R*)-(3,4,5-η)-2-(acetoxymethyl)-6-*p*-tolyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (11d). To the molybdenum complex **9d** (175 mg, 0.345 mmol) stirred in dichloromethane (4 mL) in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (147.6 mg, 0.38 mmol) in dichloromethane (2 mL). The solution was stirred for 30 min at 0 °C, and then the solvent was evaporated at high vacuum. The resulting syrup was dissolved in THF (5 mL) at −78 °C, and sodium borohydride (39 mg, 1.0 mmol) was added. The mixture was allowed to warm from −78 to 0 °C over 1 h and then was quenched with saturated ammonium chloride solution (30 mL). After extraction with dichloromethane (3 × 20 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was subjected to flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.24) to give 140.2 mg (88%) of a yellow syrup that was crystallized from a degassed mixture of ethyl ether and hexanes: mp 50–52 °C; $[\alpha]_D$ = −14.6° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 7.17 and 7.15 (AA′BB′ system *J* = 8.1 Hz, 4 H), 5.28 (s, 5 H), 5.05 (s, 1 H), 4.59 (app t, *J* = 7.1 Hz, 1 H), 4.34 (dd, *J* = 8.4, 11.6 Hz, 1 H), 4.17–3.97 (m, 3 H), 3.41 (td, *J* = 1.7, 7.1 Hz, 1 H), 2.25 (s, 3 H), 1.98 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 238.2, 235.9, 171.4, 139.5, 136.9, 129.0, 126.6, 92.9, 71.5, 67.9, 66.7, 60.9, 59.8, 58.3 (br), 51.4, 21.1; IR (KCl cell, CH_2Cl_2) 3056, 2929, 1956, 1877, 1737, 1383, 1368, 1233, 1080, 1040, 812 cm^{-1}. Anal. Calcd for $C_{22}H_{22}MoO_5$: C, 57.15; H, 4.80. Found: C, 57.17; H, 4.84.

(M) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*R*)-(3,4,5-η)-2-(acetoxymethyl)-6-(1-hexyn-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (11f). To a solution of the molybdenum complex **9f** (153 mg, 0.31 mmol) in dichloromethane (6 mL) in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (131.6 mg, 0.34 mmol) in dichloromethane (2 mL). The mixture was stirred for 30 min at 0 °C, and then the solvent was evaporated at high vacuum and THF (6 mL) was added. This solution was cooled to −78 °C, and sodium cyanoborohydride (58.4 mg, 0.93 mmol) was added. The mixture was allowed to warm from −78 to 0 °C over 1 h and then was quenched with saturated ammonium chloride solution (30 mL). After extraction with dichloromethane (3 × 20 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was subjected to flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 10 × 2.5 cm, R_f = 0.34) to give 105 mg of a yellow solid: mp 68–69 °C; $[\alpha]_D$ = −150.3° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 5.36 (s, 5 H), 4.74 (s, 1 H), 4.41 (app t, *J* ≈ 7 Hz, 1 H), 4.13 and 4.02 (AB part of ABX system, J_{AB} = 11.7 Hz, J_{AX} = 8.1 Hz, J_{BX} = 3.6 Hz, 2 H), 3.74 (d m, *J* = 6.9 Hz, 1 H), 3.57 (d, *J* = 7.2 Hz, 1 H), 3.38 (td, *J* = 6.9, 1.5 Hz, 1 H), 2.10 (dt, *J* = 1.5, 6.9 Hz, 2 H), 1.98 (s, 3 H), 1.45–1.25 (m, 4 H), 0.85 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 238.4, 235.4 (br), 171.3, 93.2, 85.6, 79.7, 70.9 (br), 66.5, 59.1 (br), 57.1 (br), 54.8 (br), 53.0, 31.2, 22.56, 21.1, 18.8, 13.8; IR (KCl cell, CH_2Cl_2) 3064, 2962, 2937, 2875, 1960, 1881, 1738, 1381, 1368, 1233, 1148, 1071, 1038, 1013, 814 cm^{-1}. Anal. Calcd for $C_{21}H_{24}MoO_5$: C, 55.76; H, 5.35. Found: C, 55.71; H, 5.39.

(N) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*R*)-(3,4,5-η)-2-(acetoxymethyl)-6-[(methoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (11g). To a solution of the molybdenum complex **9g** (108 mg, 0.221 mmol) stirred in dichloromethane (4 mL) in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (94.5 mg, 0.243 mmol) in dichloromethane (2 mL). The mixture was stirred for 30 min at 0 °C, and then the solvent was evaporated at high vacuum. The residue was dissolved in THF (4 mL), and sodium borohydride (25 mg, 0.66 mmol) was added at −78 °C. The reaction mixture was allowed to warm from −78 to 0 °C over 1 h and then was quenched with saturated ammonium chloride solution (30 mL). The mixture was extracted with dichloromethane (3 × 20 mL), dried over Na_2SO_4, filtered, concentrated in vacuo, and flash chromatographed (3:2, degassed hexanes/ethyl acetate mixture, 14 × 1 cm, R_f = 0.35) to yield 62.6 mg (64%) of a yellow solid: mp 130–2 °C; $[\alpha]_D$ = −12.4° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 5.34 (s, 5 H), 4.56 (app t, *J* ≈ 7 Hz, 1 H), 4.31 (app, t, *J* ≈ 6 Hz, 1 H), 4.24 (dd, *J* = 8.2, 11.6 Hz, 1 H), 3.97 (dd, *J* = 3.7, 11.6 Hz, 1 H), 3.75 (m, 2 H), 3.55 (s, 3 H), 3.42 (td, *J* = 1.6, 7.1 Hz, 1 H), 2.50 and 2.40 (AB part of ABX system, J_{AB} = 15.6 Hz, J_{AX} = 5.0 Hz, J_{BX} = 8.1 Hz, 2 H), 1.96 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.6, 237.8, 172.4, 171.3, 93.2, 71.1, 66.5, 65.7, 59.0, 57.9, 53.0, 52.0, 40.0, 21.1; IR (KCl cell, CH_2Cl_2) 3060, 3000, 2954, 2850, 1953, 1874, 1738, 1440, 1378, 1233, 1177, 1150, 1077, 1040, 814 cm^{-1}. Anal. Calcd for $C_{21}H_{24}MoO_5$: C, 48.66; H, 4.54. Found: C, 48.76; H, 4.54.

Preparation and Reactions of Vinyl Diene Complex 10e. Generation of 10e and Reaction with $NaBH_3CN$ and $NaBD_3CN$. To the molybdenum complex **9e** (53 mg, 0.12 mmol) stirred in dichloromethane (2 mL) in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (51 mg, 0.12 mmol), producing a deep red solution. The mixture was stirred for 30 min at 0 °C, diethyl ether (7 mL) was added, and an orange-brown precipitate formed. The solid was allowed to settle, the supernatant was removed via cannula, and the resulting residue was washed two times with 5 mL of diethyl ether, leaving crude **10e**: ^1H NMR (300 MHz, CD_3CN) δ 6.26 (dd, *J* = 17.1, 10.8 Hz, 1 H), 5.95 (br d, *J* = 17.1 Hz), 5.77 (br m, 2 H), 5.55 (br s, 5 H), 5.15 (br m, 1 H), 4.35–4.15 (m, 4 H), 2.05 (s, 3 H); IR (CH_2Cl_2) 3114, 3071, 2954, 2055, 2014, 1956, 1748, 1622, 847 cm^{-1}. A portion of crude **10e** (28 mg, 0.05 mmol) in 2 mL of THF at −78 °C was treated with $NaBH_3CN$ (9.7 mg, 0.15 mmol). Within 5 min the red color of the solution turned to yellow, and the reaction mixture was quenched with aqueous NH_4Cl, extracted with dichloromethane (3 × 10 mL), dried over Na_2SO_4, filtered, evaporated, and flash chromatographed (4:1, degassed hexanes/ethyl acetate mixture, 14 × 1 cm, R_f = 0.5), giving 9 mg (44%) product identical with **11c**, described above. An identical reaction of **10e** (28 mg) with $NaBD_3CN$ produced a dideuterio **11c**, whose ^1H NMR spectrum was consistent with introduction of deuterium at the vinyl terminus and at C-6 of the pyran ring: ^1H NMR (300 MHz, $CDCl_3$) δ 5.28 (s, 5 H),

4.40 (apparent t, J = 7.2 Hz, 1 H), 4.33 (dd, J = 11.5, 8.5 Hz, 1 H), 3.98 (dd, J = 11.5, 3.7 Hz, 1 H), 3.93 (br m, 1 H), 3.74 (br d, J = 7.0 Hz, 1 H), 3.32 (br d, J = 7.0 Hz, 1 H), 2.04 (s, 3 H), 1.47 (apparent t, J = 7.4 Hz, 2 H), 0.83 (apparent t, J = 7.4, 2 H).

Synthesis of *cis*-2,6-Disubstituted Pyranyl Complexes. (A) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,6*R*)-(3,4,5,6-η)-2-(acetoxymethyl)-2*H*-pyranyl]molybdenum Hexafluorophosphate (10a). To the molybdenum complex **9a** (764 mg, 1.835 mmol) stirred in dichloromethane (15 mL) in a Schlenk flask at 0 °C was added triphenylcarbenium hexafluorophosphate (780 mg, 2.02 mmol, 1.1 equiv) in dichloromethane (10 mL). The mixture was stirred for 30 min at 0 °C, diethyl ether (50 mL) was added, and a yellow precipitate formed. The solid was allowed to settle and the supernatant was removed. The solid was washed three times with 10 mL of diethyl ether and dried in vacuo to give 936 mg (99%) of a yellow air-stable solid: mp 158 °C dec; $[\alpha]_D$ = +389.5° (c 1.0, acetone); ^{1}H NMR (CD_3CN, 300 MHz) δ 7.34 (dd, J = 2.3, 4.4 Hz, 1 H), 5.93 (m, 1 H), 5.74 (s, 5 H), 5.15 (dt, J = 1.9, 4.5 Hz, 1 H), 4.24 (dd, J = 2.6, 11.4 Hz, 1 H), 4.15–3.95 (m, 3 H), 2.01 (s, 3 H); IR (KCl cell, CH_2Cl_2) 3114, 1062, 2061, 2018, 1972, 1748, 1607, 1491, 1422, 1368, 1221, 1046, 847 cm^{-1}. Anal. Calcd for $C_{15}H_{15}MoO_5PF_6$: C, 34.90; H, 2.93. Found: C, 34.99; H, 2.97.

(B) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12a). A suspension of **9a** (65 mg, 0.126 mmol) was stirred at −78 °C in 2 mL of THF, and a 3 M solution of methylmagnesium iodide in diethyl ether (125 μL, 0.38 mmol, 3 equiv) was added dropwise. The mixture was stirred for 1 h at −78 °C and then quenched with saturated ammonium chloride solution (30 mL) and extracted with dichloromethane (3 × 15 mL). Drying over Na_2SO_4, filtration, and evaporation of the solvent on a rotary evaporator followed by flash chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 1 cm, R_f = 0.22) gave 42 mg (86%) of **12a** as a yellow solid that was recrystallized from a degassed mixture of hexanes and ether: mp 115–6 °C; $[\alpha]_D$ +22.7° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.37 (s, 5 H), 4.48 (app t, $J \approx 7$ Hz, 1 H), 4.11–3.98 (AB part of ABX system, J_{AB} = 10.9, J_{AX} = 6.9, J_{BX} = 5.7 Hz, 2 H), 3.72–3.61 (m, 3 H), 3.59 (br d, J = 7.2 Hz, 1 H), 1.98 (s, 3 H), 1.29 (dd, J = 6.6 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 237.5, 237.3, 171.3, 93.5, 71.2, 69.8, 68.0, 59.5, 56.3 (br), 51.9, 28.2, 21.0; IR (KCl cell, CH_2Cl_2) 3060, 2981, 2929, 1949, 1868, 1738, 1366, 1237, 1165, 1038, 812 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_5Mo$: C, 49.75; H, 4.70. Found: C, 49.84; H, 4.72.

(C) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-*p*-tolyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12b). To a suspension of the molybdenum complex **9a** (46 mg, 0.089 mmol) in THF (2 mL) stirred at −78 °C was added dropwise a 1 M solution of *p*-tolylmagnesium bromide in diethyl ether (0.27 mL, 0.27 mmol, 3 equiv). The mixture was stirred for 30 min at −78 °C and then quenched by addition of saturated ammonium chloride solution (20 mL). The mixture was extracted with dichloromethane (3 × 10 mL), dried over Na_2SO_4, filtered, concentrated, and flash chromatographed (4:1, degassed hexanes/ethyl acetate mixture, 14 × 1 cm, R_f = 0.26) to give 33.2 mg (81%) of **12b** as a yellow solid: mp 118–9 °C; [α] [illegible] (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 7.42 and [illegible] AA′BB′ system, J = 8.1 Hz, 4 H), 5.42 (s, 5 H), 4.78 (app t, [illegible], 1 H), 4.53 (s, 1 H), 3.94 (br d, J = 7.2 Hz, 1 H), 3.73–3.6[illegible]), 3.52 (dd, J = 8.9, 12.3 Hz, 1 H), 2.29 (s, 3 H), 1.87 (s, 3 H); ^{13}C NMR (CD_3CN, 75 MHz) δ 237.6, 237.6, 171.1, 143.4, 138.0, 129.6, 128.2, 93.8, 72.6, 70.6, 69.9, 57.7 (br), 55.8, 53.0, 21.1, 20.9; IR (KCl cell, CH_2Cl_2) 3058, 2987, 2927, 1951, 1870, 1737, 1256, 1040, 814 cm^{-1}. Anal. Calcd for $C_{22}H_{22}MoO_5$: C, 57.15; H, 4.80. Found: C, 57.24; H, 4.84.

(D) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-ethenyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12c). To a suspension of the molybdenum complex **9a** (100 mg, 0.194 mmol) in THF (3 mL) was added dropwise a 1 M solution of vinylmagnesium bromide in THF (0.58 mL, 0.58 mmol, 3 equiv). The mixture was stirred at −78 °C for 30 min and then quenched by addition of saturated ammonium chloride solution (30 mL). Extraction with dichloromethane (3 × 15 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent followed by flash chromatography (3:1, degassed hexanes/ethyl acetate mixture, 10 × 2.5 cm, R_f = 0.32) gave 65 mg (84%) of a yellow oil that was crystallized from a degassed mixture of ether and hexanes: mp 83–84 °C; $[\alpha]_D$ = +58.2° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 6.01 (ddd, J = 6.9, 10.3, 17.3 Hz, 1 H), 5.39 (s, 5 H), 5.22 (d, J = 17.5 Hz, 1 H), 5.05 (d, J = 10.3 Hz, 1 H), 4.53 (app t, $J \approx 7$ Hz, 1 H), 4.02 (app d, J = 6.3 Hz, 2 H), 3.93 (d, J = 6.9 Hz, 1 H), 3.70 (t, J = 6.3 Hz, 1 H), 3.62 (d, J = 7.3 Hz, 1 H), 3.56 (d, J = 7.3 Hz, 1 H), 1.98 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 237.0 (2 C), 171.2, 144.8, 116.1, 93.6, 72.2, 70.9, 69.5, 55.6, 55.4, 52.1, 21.0; IR (KCl cell, CH_2Cl_2) 3060, 2985, 2929, 1951, 1872, 1738, 1422, 1383, 1237, 1040, 182.3 cm^{-1}. Anal. Calcd for $C_{17}H_{18}MoO_5$: C, 51.27; H, 4.55. Found: C, 51.00; H, 4.60.

(E) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-(1-hexyn-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12d). Hexynyllithium was prepared by dropwise addition of *n*-BuLi (116 μL, 0.291 mmol, 2.5 M in hexanes) to a stirred solution of 1-hexyne (26.3 mg, 37 μL, 0.320 mmol) in THF (1.5 mL) at −78 °C. The solution was stirred at −78 °C for 1 h and then transferred via cannula to a suspension of the molybdenum complex **9a** (50 mg, 0.097 mmol) in THF (1.5 mL) at −78 °C. The mixture was stirred for 15 min at −78 °C and then quenched by addition of saturated ammonium chloride solution (30 mL). The mixture was extracted with dichloromethane (3 × 20 mL), dried over Na_2SO_4, filtered, concentrated on the rotary evaporator, and flash chromatographed (4:1, degassed hexanes/ethyl acetate, 14 × 1 cm, R_f = 0.36) to give 36.5 mg (83%) of a yellow syrup: $[\alpha]_D$ = +79.4° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.40 (s, 5 H), 4.48 (app t, $J \approx 7$ Hz, 1 H), 4.43 (dd, J = 7.9, 11.1 Hz, 1 H), 4.24 (dd, J = 5.2, 11.1 Hz, 1 H), 4.11 (br d, J = 1.7 Hz, 1 H), 3.72–3.61 (m, 2 H), 3.55 (td, J = 7.3, 1.5 Hz, 1 H), 2.17 (dt, J = 1.7, 6.7 Hz, 2 H), 1.97 (s, 3 H), 1.50–1.30 (m, 4 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 236.4, 236.2, 171.3, 93.7, 86.0, 84.2, 69.7, 69.5, 59.6, 55.7, 54.1 (br), 52.5, 31.3, 22.6, 21.0, 18.9, 13.9; IR (KCl cell, CH_2Cl_2) 3056, 2962, 2937, 2306, 1953, 1874, 1738, 1424, 1370, 1258, 1040, 814 cm^{-1}. Anal. Calcd for $C_{21}H_{24}MoO_5$: C, 55.75; H, 5.35. Found: C, 55.67; H, 5.42.

(F) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-[(methoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12e). Methyl acetate (46 μL, 43.1 mg, 0.58 mmol) was added dropwise to a lithium diisopropylamide solution (0.58 mmol) in THF (2 mL) at −78 °C and stirred for 30 min. The lithium enolate solution was then transferred via cannula into a suspension of the molybdenum complex **9a** (100 mg, 0.194 mmol) stirred in THF (2 mL) at −78 °C. The reaction mixture was stirred for 15 min at −78 °C and was then quenched by addition of saturated ammonium chloride solution (30 mL). The mixture was extracted with dichloromethane (3 × 20 mL), dried over Na_2SO_4, filtered, concentrated on a rotary evaporator, and subjected to flash chromatography (1:1, degassed hexanes/ethyl acetate mixture, 10 × 2.5 cm, R_f = 0.48) to give 73.6 mg (85%) of **12e** as a yellow solid: mp 106–7 °C; $[\alpha]_D$ = +13.4° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.39 (s, 5 H), 4.47 (app t, $J \approx 7$ Hz, 1 H), 4.16–3.94 (m, 3 H), 3.74–3.62 (m, 2 H), 3.57 (s, 3 H), 3.60–3.52 (overlapped app d, $J \approx 7$ Hz, 1 H), 2.63 and 2.55 (AB part of ABX system, J_{AB} = 15.0 Hz, J_{AX} = 5.9 Hz, J_{BX} = 8.5 Hz, 2 H), 1.99 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 237.1, 236.8, 171.9, 171.3, 93.7, 71.0, 69.3, 68.6, 55.9, 55.6, 52.0, 51.5, 47.0, 21.0; IR (KCl cell, CH_2Cl_2) 3060, 2989, 2956, 1953, 1874, 1738, 1437, 1368, 1237, 1179, 1150, 1082, 1040, 812 cm^{-1}. Anal. Calcd for $C_{18}H_{20}MoO_7$: C, 48.66; H, 4.54. Found: C, 48.65; H, 4.60.

(G) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-(1,3-dioxo-1,3-dimethoxy-2-propyl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (12f). Sodium malonate [0.58 mmol, prepared in THF (2 mL) by treatment of dimethyl malonate (65.8 μL, 65.8 mg, 0.58 mmol) with NaH (18 mg) for 30 min at room temperature] was added to a suspension of the molybdenum complex **9a** (100 mg, 0.194 mmol) in THF (3 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and then quenched by addition of saturated ammonium chloride solution (30 mL). Extraction with dichloromethane (3 × 20 mL), drying over Na_2SO_4, filtration, and concentration on the rotary evaporator followed by flash chromatography (1:1, degassed hexanes/ethyl acetate mixture, 10 × 2.5 cm, R_f = 0.28) gave 80 mg (82%) of a yellow solid that was recrystallized from a degassed mixture of hexanes and dichloromethane: mp 171 °C dec; $[\alpha]_D$ = +3.5° (c 1.0, CH_2Cl_2); ^{1}H NMR (CD_3CN, 300 MHz) δ 5.40 (s, 5 H), 4.47 (app t, $J \approx 7$ Hz, 1 H), 4.16 (d, J = 10.6 Hz, 1 H), 3.97 (app d, J = 5.2 Hz, 2 H), 3.74 (t, J = 5.2 Hz, 1 H), 3.70–3.57 (overlapped m, 2 H), 3.68 (s, 3 H), 3.59 (s, 3 H), 3.54 (d, J = 7.3 Hz, 1 H), 2.02 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 236.8 (2 C), 171.3, 168.3, 168.0, 93.8, 70.9, 70.5, 69.6, 62.8, 55.9, 53.2, 53.0, 52.4, 51.6, 21.1; IR (KCl cell, CH_2Cl_2) 3064, 2956, 1955, 1877, 1737, 1437, 1252, 1200, 1156, 1040, 814 cm^{-1}. Anal. Calcd for $C_{20}H_{22}MoO_9$: C, 47.82; H, 4.41. Found: C, 47.79; H, 4.45.

Stereospecific Construction of Quaternary Carbon Centers. (A) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*)-(3,4,5-η)-2-(acetoxymethyl)-6,6-dimethyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (13). To a suspension of the molybdenum complex **10b** (229 mg, 0.43 mmol) in THF (8 mL) at −78 °C was added a 3 M solution of methylmagnesium iodide in diethyl ether (0.43 mL, 0.129 mmol, 3 equiv). The reaction mixture was stirred at −78 °C for 4 h and then quenched with ammonium chloride solution (30 mL). Extraction with dichloromethane (3 × 30 mL), drying over Na_2SO_4, filtration, evaporation of the solvent, and flash column chromatography (4:1, degassed hexanes/ethyl acetate mixture, 14 × 2.5 cm, R_f = 0.32) gave 109 mg (63%) of **13** as a yellow syrup:

$[\alpha]_D$ = −119° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_3CN, 300 MHz) δ 5.29 (s, 5 H), 4.57 (app t, *J* ≈ 7 Hz, 1 H), 4.13 (dd, *J* = 7.1, 10.7 Hz, 1 H), 4.05 (obscured m, 1 H), 4.04 (dd, *J* = 5.8, 10.7 Hz, 1 H), 3.91 (app t, *J* ≈ 6 Hz, 1 H), 3.47 (d, *J* = 6.9 Hz, 1 H), 1.99 (s, 3 H), 1.37 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.6, 237.3, 171.3, 92.5, 72.9, 71.2, 71.1, 69.9, 58.4 (br), 50.5, 37.2, 30.5, 21.1; IR (KCl cell, CH_2Cl_2) 3062, 2977, 2927, 1953, 1874, 1737, 1432, 1381, 1370, 1360, 1237, 1190, 1152, 1092, 1067, 1038, 812 cm^{-1}. Anal. Calcd for $C_{17}H_{20}MoO_5$: C, 51.01; H, 5.04. Found: C, 51.12; H, 5.15.

(B) (η^5-Cyclopentadienyl)(dicarbonyl)[(2*R*,3*R*,6*S*)-(3,4,5-η)-2-(acetoxymethyl)-6-*n*-butyl-6-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (14). To a suspension of the molybdenum complex **10b** (195 mg, 0.368 mmol) in THF (7 mL) at −78 °C was added a 2 M solution of *n*-butylmagnesium chloride in THF (0.55 mL, 1.10 mmol, 3 equiv). The reaction mixture was stirred for 1 h at −78 °C and then quenched with saturated ammonium chloride solution (30 mL). After extraction with dichloromethane (3 × 20 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was subjected to flash column chromatography (5:1, degassed mixture of hexanes/ethyl acetate, 14 × 2.5 cm, R_f = 0.33) to give 125 mg (67%) of **14** as a yellow syrup; $[\alpha]_D$ = +119.5° (*c* 1.0, CH_2Cl_2); ^1H NMR (CD_2Cl_2, 300 MHz) δ 5.23 (s, 5 H), 4.52 (br m, 1 H), 4.20–3.95 (m, 4 H), 4.35 (br m, 1 H), 2.03 (s, 3 H), 1.70–1.15 (m, 6 H), 1.07 (s, 3 H), 0.87 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (CD_3CN, 75.1 MHz) δ 239.6, 237.6, 171.4, 92.4, 75.2, 71.2, 71.1, 70.3, 59.0 (br), 50.5, 50.13, 27.7, 27.1, 24.0, 21.0, 14.4; IR (KCl cell, CH_2Cl_2) 3056, 2987, 2960, 2875, 1953, 1874, 1737, 1422, 1380, 1256, 1038, 816 cm^{-1}; MS (high resolution, EI) calcd for $C_{20}H_{26}O_5Mo$ 444.083 429 2, found 444.083 990 1.

Protodemetalation and Hydrogenation to Enantiomerically Pure *trans*-2,6-Disubstituted Tetrahydropyrans. (A) (2*R*,6*S*)-6-(Acetoxymethyl)-2-methyl-5,6-dihydro-2*H*-pyran and (2*S*,6*R*)-2-(Acetoxymethyl)-6-methyl-5,6-dihydro-2*H*-pyran (15a and 15b). To the complex **11b** (2.164 g, 5.60 mmol) dissolved in 100 mL of chloroform (Aldrich, HPLC quality, stabilized with amylenes; *chloroform-containing ethanol is not useful for the reaction*) was added trifluoroacetic acid (2.16 mL, 25 mmol, 5 equiv). The mixture was stirred at room temperature for 2.5 h. It was then quenched with saturated sodium bicarbonate solution (100 mL) and extracted with dichloromethane (2 × 50 mL). Drying over Na_2SO_4, filtration, evaporation of the solvent, and flash column chromatography (30:1, dichloromethane/ether, 14 × 3 cm, R_f = 0.31) gave 882 mg (92%) of a 38:62 mixture of **15a** and **15b** as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz, mixture of isomers) δ 5.94 (m, 0.38 H), 5.77 (br d, *J* = 10.5 Hz, 0.62 H), 5.68 (br d, *J* = 10.5 Hz, 0.62 H), 5.62 (br d, *J* = 10.2 Hz, 0.38 H), 4.45–4.24 (m, 1.38 H), 4.11 (d, *J* = 5.10 Hz, 1.24 H), 4.00–3.95 (m, 1 H), 3.87 (m, 0.38 H), 2.08 (s, 3 H), 2.03–1.90 (m, 2 H), 1.26 (d, *J* = 6.3 Hz, 1.86 H), 1.20 (d, *J* = 6.3 Hz, 1.14 H); IR (KCl cell, CH_2Cl_2) 3058, 2977, 2931, 2900, 1738, 1449, 1426, 1368, 1237, 1192, 1104, 1040 cm^{-1}.

(B) (2*R*,6*S*)-6-(Acetoxymethyl)-2-[(methoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran and (2*S*,6*R*)-2-(Acetoxymethyl)-6-[(methoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran (16a and 16b). To the molybdenum complex **11g** (88 mg, 0.198 mmol) dissolved in 4 mL of chloroform (Aldrich, HPLC quality, stabilized with amylenes) was added trifluoroacetic acid (76.3 μL, 0.99 mmol, 5 equiv). The reaction mixture was stirred for 7 h at room temperature and then quenched with saturated sodium bicarbonate solution (10 mL). After extraction with dichloromethane (2 × 15 mL), drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was subjected to flash column chromatography (30:1, dichloromethane/ether) to yield 40 mg (89%) of a 47:53 mixture of **16a** and **16b** as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz, mixture of isomers) δ 5.92 (m, 0.47 H), 5.84 (m, 0.53 H), 5.71 (br d, *J* = 10.5 Hz, 0.53 H), 5.62 (br d, *J* = 10.5 Hz, 0.47 H), 4.67 (br m, 0.53 H), 4.36 (br m, 0.47 H), 4.23 (dd, *J* = 8.1, 11.7 Hz), 4.14 (m, 0.47 H), 4.07 (m, 1.06 H), 3.99 (dd, *J* = 3.3, 11.7 Hz, 0.47 H). 3.89 (m, 0.53 H), 3.67 (s, 1.59 H), 3.65 (s, 1.41 H), 2.7–2.4 (overlapping AB parts of 2 ABX systems, 2 H); IR (KCl cell, CH_2Cl_2) 3062, 3043, 2956, 2927, 2904, 1738, 1439, 1368, 1239, 1202, 1163, 1088, 1040 cm^{-1}.

(C) (2*S*,3*R*)-2-(Acetoxymethyl)-6-methyltetrahydropyran (17). A mixture of **15a** and **15b** (882 mg, 5.15 mmol) was stirred together with PtO_2 (117 mg, 0.515 mmol) in 40 mL of ethyl acetate. Hydrogen (1 atm) was introduced, and the heterogeneous mixture was stirred at room temperature for 90 min. The mixture was filtered through a pad of Celite and evaporated to give 820.2 mg (92%) of **17** as a colorless oil. Analytically pure material was obtained after bulb-to-bulb distillation (760 mmHg, 225 °C): $[\alpha]_D$ = +26.6° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.22 (dd, *J* = 11.1, 7.2 Hz, 1 H), 4.06–3.91 (m, 3 H), 2.06 (s, 3 H), 1.75–1.50 (m, 4 H), 1.45–1.20 (m, 2 H), 1.17 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.1 MHz) δ 170.7, 68.5, 67.4, 65.0, 30.8, 26.4, 20.6, 19.0, 18.0; IR (KCl cell, CH_2Cl_2) 3056, 2977, 2942, 2873, 1737, 1445, 1372, 1241, 1210, 1131, 1048, 911 cm^{-1}. Repeated attempts to obtain satisfactory high-resolution mass spectra (FAB and EI) were unsuccessful.

(D) (2*S*,6*R*)-2-(Acetoxymethyl)-6-[(methoxycarbonyl)methyl]tetrahydropyran (18). A mixture of **16a** and **16b** (37 mg, 0.162 mmol) was stirred together with PtO_2 (3.7 mg, 0.016 mmol) in 2 mL of ethyl acetate. Hydrogen (1 atm) was introduced, and the heterogeneous mixture was stirred at room temperature for 90 min. The mixture was filtered through a pad of Celite and evaporated to give 35 mg (94%) of **18** as a colorless oil: $[\alpha]_D$ = +41.8° (*c* 1.04, CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.24 (m, 1 H), 4.18 (dd, *J* = 7.5, 11.4 Hz, 1 H), 4.05–3.87 (m, 2 H), 3.64 (s, 3 H), 2.66 (A part of ABX system, J_{AB} = 14.7 Hz, J_{AX} = 8.4 Hz, 1 H), 2.39 (B part of ABX, J_{AB} = 14.7 Hz, J_{BX} = 5.7 Hz, 1 H), 2.03 (s, 3 H), 1.77–1.55 (m, 4 H), 1.45–1.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.1 MHz) δ 171.4, 170.9, 69.1, 68.7, 64.9, 51.6, 38.4, 29.0, 26.2, 20.8, 18.1; IR (neat) 2938, 2864, 1731, 1430, 1365, 1285, 1234, 11207, 1162, 1095, 1047, 1022 cm^{-1}; MS (high resolution, FAB) calcd for $C_{11}H_{18}O_5$·Li 237.1314, found 237.1311 (1.4 ppm).

Determination of Absolute Stereochemistry. Correlation with (2*S*,6*R*)-*trans*-(6-Methyltetrahydropyran-2-yl)Acetic Acid (22). (A) (2*S*,6*R*)-2-(Hydroxymethyl)-6-methyltetrahydropyran (19). The compound **17** (200 mg, 1.16 mmol) was dissolved in ethanol (5 mL), and LiOH·H_2O (146 mg, 3.48 mmol) was added at room temperature. After 30 min water (25 mL) was added and the mixture was extracted with dichloromethane (4 × 20 mL). After drying over Na_2SO_4, filtration, and evaporation of the solvent, the crude product was subjected to flash column chromatography (1:1, hexanes/ethyl ester, 14 × 2.5 cm, R_f = 0.14) to give 124.5 mg (83%) of **19** as a colorless oil: $[\alpha]_D$ = +38.8° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.98 (m, 1 H), 3.81 (m, 1 H), 3.66 (app t, *J* ≈ 11 Hz, 1 H), 3.45 (br d, *J* ≈ 10 Hz, 1 H), 2.20 (br s, 1 H), 1.75–1.50 (m, 4 H), 1.45–1.25 (m, 2 H), 1.19 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 70.9, 67.5, 63.8, 30.7, 26.2, 18.7, 17.9; IR (KCl cell, CH_2Cl_2) 3579, 3056, 2977, 2942, 2875, 1445, 1378, 1202, 1131, 1100, 1055, 1017 cm^{-1}.

(B) (2*S*,6*R*)-2-[[(Methylsulfonyl)oxy]methyl]-6-methyltetrahydropyran (20). A solution of methanesulfonyl chloride (131 μL, 194 mg, 1.69 mmol) in 5 mL of dichloromethane was added to a solution of the alcohol **19** (200 mg, 1.54 mmol) and triethylamine (674 μL, 466 mg, 4.61 mmol) in 10 mL of dichloromethane at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then was quenched with water (30 mL). Extraction with dichloromethane (2 × 30 mL), drying (Na_2SO_4), evaporation of solvent, and flash chromatography (1:2 hexanes/diethyl ether, 12 × 2 cm, R_f = 0.26) gave 284 mg (89%) of a colorless oil that crystallized on standing: mp 56 °C; $[\alpha]_D$ = +22.7° (*c* 1, CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.34 (dd, *J* = 7.7, 11.0 Hz, 1 H), 4.15 (dd, *J* = 3.8, 11.0 Hz, 1 H), 4.01 (m, 2 H), 3.05 (s, 3 H), 1.75–1.52 (m, 4 H), 1.46–1.12 (m, 2 H), 1.19 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.1 MHz) δ 70.7, 68.4, 67.9, 37.5, 30.4, 26.0, 18.6, 17.7; IR (neat) 2924, 1446, 1349, 1207, 1171, 1128, 1083, 1056, 1027, 964, 820 cm^{-1}.

(C) (2*S*,6*R*)-2-(Cyanomethyl)-6-methyltetrahydropyran (21). To a solution of compound **20** (52 mg, 0.25 mmol) in dimethoxyethane (2 mL) were added sodium cyanide (100 mg, 2.04 mmol), tetra-*n*-butylammonium iodide (10 mg, 0.027 mmol), and 18-crown-6 (5 mg, 0.020 mmol). The reaction mixture was heated at reflux in a sealed tube for 8 days. The reaction mixture was quenched with water (10 mL), extracted with diethyl ether (3 × 10 mL), dried (Na_2SO_4), evaporated, and chromatographed (6:1, dichloroethane/hexanes, 12 × 1.5 cm, R_f = 0.25), giving 28 mg (80%) of a colorless oil: $[\alpha]_D$ = +45.3° (*c* 0.85, ethanol); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.05 (dq, *J* = 3.3, 6.6 Hz, 1 H), 3.96 (m, 1 H), 2.55 (AB part of ABX, J_{AB} = 16.5, J_{AX} = J_{BX} = 6.6 Hz, 2 H), 1.80–1.58 (m, 4 H), 1.43 (m, 1 H), 1.27 (m, 1 H), 1.20 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.1 MHz) δ 118.1, 68.5, 67.0, 30.6, 29.5, 23.0, 19.0, 17.9; IR (neat) 2927, 2864, 2247, 1441, 1377, 1201, 1134, 1193, 1049, 1012 cm^{-1}.

(D) (2*S*,6*R*)-*trans*-(6-Methyltetrahydropyran-2-yl)acetic Acid (22). Compound **21** (27 mg, 0.194 mmol) was dissolved in concentrated hydrochloric acid (2 mL), and the solution was heated at 80 °C for 2 h. The reaction mixture was diluted with 15 mL of water and extracted with diethyl ether (3 × 10 mL). The ether solution was washed with brine and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was subjected to Kugelrohr distillation (150 °C, 0.1 mmHg) to give 25 mg (81%) of **22**. The compound was found to be spectroscopically identical (NMR and IR) with its enantiomer[56] and displayed opposite optical rotation, $[\alpha]_D$ = +41.0° (*c* 1.45, $CHCl_3$) [lit.[56] $[\alpha]_D$ of the enantiomer = −39.52° (*c* 1.45, $CHCl_3$)].

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Mechanism of the Reaction of Methylene with Benzene: A Study of Kinetic Hydrogen Isotope Effects and Theoretical Calculations

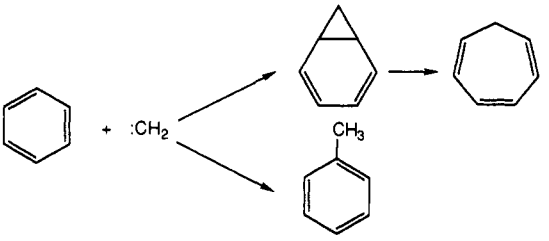
Nikolai Hartz, G. K. Surya Prakash, and George A. Olah*

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661. *Received February 19, 1991. Revised Manuscript Received November 10, 1992*

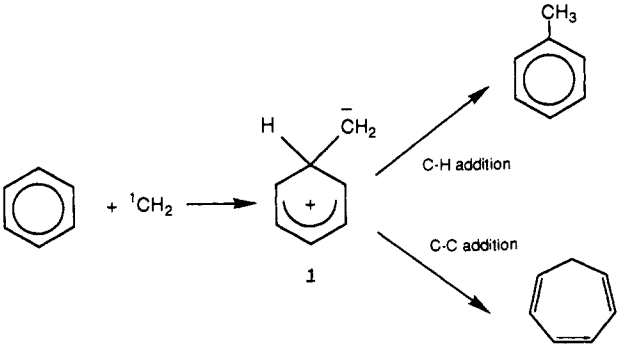
Abstract: The reaction mechanism of singlet and triplet methylene with benzene and related aromatic compounds was investigated by kinetic isotope effects (KIEs), solvent effects, and product studies. The results are further rationalized by a series of ab initio calculations at MP2/6-31G*//RHF/6-31G* and UMP2/6-31G*//UHF/6-31G* levels of theory. The proposed **1c** intermediate for the triplet reaction was found by means of the calculations, whereas no singlet analog **1** could be found.

Introduction

The reaction of diazomethane with aromatic compounds is well-known in organic chemistry.[1] Various ratios of cycloheptatriene (via norcaradiene) and toluene are obtained depending on the reaction conditions. Although the reactivity of benzene with electrophiles and the mechanism of many methylene reactions are well established in the literature,[2] no detailed study of this particular reaction mechanism has been reported so far.



In general, two possible pathways are conceivable for the attack of singlet methylene on the aromatic ring: (i) direct C—H and C=C bond reaction giving products by two independent concerted mechanisms (similar to the singlet methylene reaction with aliphatic and olefinic compounds),[3] and (ii) a multistep reaction mechanism involving a distinct intermediate that subsequently rearranges to the products. The intermediate in the latter path would resemble the Wheland intermediate of the typical electrophilic aromatic substitution mechanism. It can be depicted as a neutral zwitterionic species, **1** (i.e., benzeniummethylide).



The effect of different solvents on the reaction of methylene with a variety of substrates has been studied[4] previously. The changes in product distribution in aromatic and aliphatic solvents were discussed in terms of the formation of complexes between the carbene and the solvent. Schoeller[5] has calculated structures analogous to **1** as possible transition states for the 1,5-walk rearrangement of norcaradienes, but so far no stable intermediate with a comparable structure has been reported. At this point it should be mentioned that the concerted thermal walk rearrangement does not show toluene derivatives as significant side products.[4b] However, experimental evidence for a distinct intermediate was found in pyrolysis studies of norcaradiene[6] and norbornadiene,[7] where toluene was predominantly formed. The pyrolysis reactions carried out at temperatures around 475 °C in the gas phase suggest the presence of a diradical intermediate.[8]

We wish to report now an investigation of the reaction between methylene and benzene as well as some other aromatics. Kinetic isotope effects (KIEs), reaction product ratios for different substrates and spin states, and solvent effects were studied to in-

(1) (a) Meerwein, H.; Disselnkötter, H.; Rappen, F.; v. Rintelen, H.; van de Vloed, H. *Liebigs Ann. Chem.* **1957**, 151-154. (b) Lemmon, R. M.; Strohmeier, W. *J. Am. Chem. Soc.* **1959**, *81*, 106-108. (c) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1950**, *72*, 2305-2306. (d) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 297-303.

(2) Lowry, T. H.; Schueller Richardson, K. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; pp 553-562, 623-639.

(3) (a) Doering, W. v. E.; Prinzbach, H. *Tetrahedron* **1959**, *6*, 24-30. (b) Dobson, R. C.; Hayes, D. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6188-6192. (c) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475-1485. (d) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496-4497.

(4) (a) Russell, G. A.; Hendry, D. G. *J. Org. Chem.* **1963**, *28*, 1933-1934. (b) Neugebauer, S. M.; DeLuca, J. P. *Tetrahedron Lett.* **1989**, *30*, 7169-7172. (c) Tomioka, H.; Ozaki, Y.; Izawa, Y. *Tetrahedron* **1985**, *41*, 4987-4993.

(5) Schoeller, W. W. *J. Am. Chem. Soc.* **1975**, *97*, 1978-1980.

(6) Klump, K. N.; Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 130-132.

(7) Woods, W. G. *J. Org. Chem.* **1958**, *23*, 110-112.

(8) Wentrup, C. *Reaktive Zwischenstufen*; Georg Thieme Verlag: Stuttgart, 1979; Vol. 1, p 55.

0002-7863/93/1515-901$04.00/0