Stereoselective Binding of Olefins to a Molybdenum Center and Synthesis of a Chiral Molybdenum–Olefin Complex

Susan E. Kegley,* Kevin A. Walter, Dirk T. Bergstrom, Darren K. MacFarland, and Bruce G. Young

Department of Chemistry, Williams College, Williamstown, Massachusetts 01267

Arnold L. Rheingold

Department of Chemistry, The University of Delaware, Newark, Delaware 19716

Received January 8, 1993

Synthesis and characterization of the molybdenum–alkene complexes [Cp(P-P)Mo(CO)(alkene)]$^+PF_6^-$ [P-P = 1,2-bis(dimethylphosphino)ethane (Dmpe), 1,2-bis(dimethoxyphosphino)ethane (Pom-Pom); alkene = methyl acrylate, ethyl acrylate, styrene, dimethyl maleate, *p*-chlorostyrene, α-methylene-γ-butyrolactone] are reported. The Mo–alkene complexes were synthesized by reaction of [Cp(P-P)Mo(CO)(acetone)]$^+PF_6^-$ with the alkenes at room temperature. X-ray crystallographic analysis of [Cp(Pom-Pom)Mo(CO)(ethyl acrylate)]$^+PF_6^-$ (**9**) was carried out. Crystal data for **9**: $P2_1/n$, a = 8.825 (2) Å, b = 27.834 (8) Å, c = 10.192 (2) Å, β = 93.03(2)°, V = 2500.0 (11) Å^3, Z = 4, $R(F)$ = 4.93%. For the Pom-Pom complexes, high kinetic stereoselectivity is observed for binding the olefin to produce only one diastereomer. In this diastereomer, orbital overlap between the metal and the alkene is maximized; i.e., the olefin ligand is contained in the plane defined by the metal, the center of the Cp ligand, and the *trans*-phosphorus atom, and the substituent on the olefin ligand lies *syn* to the Cp ring, thus minimizing steric hindrance between the phosphine and the alkene substituent. For the Dmpe complexes, reaction of [Cp(Dmpe)Mo(CO)(acetone)]$^+PF_6^-$ with styrene resulted in similar stereoselectivity for olefin binding, as demonstrated by crystallographic data from the structures of [Cp(Dmpe)Mo(CO)(styrene)]$^+PF_6^-$ (**17**) and [Cp(Dmpe)Mo(CO)(dimethyl maleate)]$^+PF_6^-$ (**15**). Crystal data for **17**: $P2_1/n$, a = 8.925 (3) Å, b = 35.824 (9) Å, c = 16.180 (5) Å, β = 102.75(2)°, V = 5045 (2) Å^3, Z = 8, $R(F)$ = 8.29%. Crystal data for **15**: $P2_12_12_1$, a = 15.821 (4) Å, b = 17.637 (3) Å, c = 8.597 (2) Å, V = 2398.8 (9) Å^3, Z = 4, $R(F)$ = 3.76%. An unusual difference was noted in the formation of [Cp(Dmpe)Mo(CO)(methyl acrylate)]$^+PF_6^-$, where a 50:50 mixture of two diastereomeric alkene complexes was obtained. On standing at room temperature, the more thermodynamically stable alkene complex is formed exclusively (>99%). The mechanism of isomerization of diastereomers is intramolecular; i.e., no dissociation of the olefin ligand occurs during the isomerization process. Synthesis of the chiral molybdenum olefin complex [Cp(P-P)Mo(CO)(methyl acrylate)]$^+PF_6^-$ [P-P = 1,2-bis[bis[(*S*)-2-methyl-1-butanoxy]phosphino]ethane] was also carried out. Again, extremely high kinetic selectivity was observed in the formation of the olefin complexes; however, when the synthesis was carried out under photolytic conditions, a 60:40 mixture of the isomeric products was obtained. Isomerization did not occur in this system.

Introduction

The selective reactivity of different enantiomers of organic molecules in biological systems makes it desirable to have ready access to synthetic methodology that will facilitate the production of only one enantiomer of a pair. Thus it is of interest to study organometallic systems that have potential for carrying out asymmetric transformations in organic systems. The ability to carry out asymmetric transformations on prochiral molecules such as olefins and carbonyl compounds depends on selective protection of one face of the prochiral substrate. Chiral organometallic complexes that will bind to unsaturated substrates can facilitate this process by acting as a protecting group for one face of the reactant. At present, there are only a limited number of chiral transition metal complexes that can both bind olefins stereoselectively and also serve to increase the reactivity of the olefin toward synthetically useful transformations such as hydrogenation,[1] epoxidation,[2,3] dihydroxylation,[4] or nucleophilic attack.[5]

In this paper, we report the synthesis and characterization of some molybdenum complexes,[Cp(P-P)Mo(CO)(η^2-olefin)]$^+PF_6^-$, that selectively bind monosubstituted olefins. The ligands P-P are chelating phosphines or phosphonites and include 1,2-bis(dimethoxyphosphino)ethane (Pom-Pom), 1,2-bis(dimethylphosphino)ethane

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. F. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 537.
(2) (a) Pedersen, S. F.; Dewan, J. C.; Eckman, R. R.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 1279. (b) Burns, C. J.; Martin, C. A.; Sharpless, K. B. *J. Org. Chem.* **1989**, *54*, 2826. (c) Carlier, P. R.; Sharpless, K. B. *J. Org. Chem.* **1989**, *54*, 4016.
(3) (a) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schroeder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968. (b) Wai, J. S. M.; Markó, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123.
(4) Zhang, W.; Loebach, J. L., Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.
(5) (a) Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927. (b) Faller, J. W.; Murray, H. H.; Chao, K.-H. *Organometallics* **1983**, *2*, 400. (c) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. (d) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670.

0276-7333/93/2312-2339$04.00/0

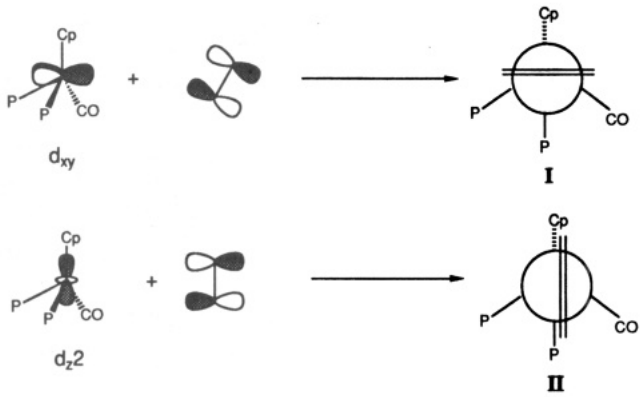
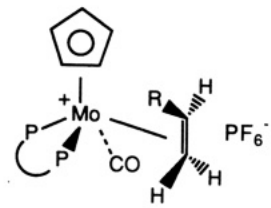


Figure 1. Possible orientations for ethylene interacting with a $CpML_3$ fragment.

(Dmpe), and a novel chiral phosphonite of our own design, 1,2-bis[bis[(*S*)-2-methyl-1-butanoxy]phosphino]ethane (Pom-Pom*).



These complexes activate metal-bound olefins to nucleophilic attack by carbanions and have the potential to be useful enantioselective reagents for the formation of carbon–carbon bonds. A prior report from this laboratory discussed the development of synthetic routes to ethylene complexes of this type [where P-P = diphos or 1,2-bis(dimethoxyphosphino)ethane], as well as studies on their reactions with carbanion nucleophiles.[6]

For complete understanding of the chirality in these systems, it is useful to consider the possible orientations of an olefin ligand on a pseudo-square pyramidal $CpML_3$ fragment. Extended Hückel calculations[7] indicate that, in an asymmetric $CpML_4$ system such as $[Cp(P\text{-}P)Mo(CO)(\eta^2\text{-ethylene})]^+$, there are two metal orbitals available for overlap with the ethylene ligand, the d_{z^2} and the d_{xy}, both of equal energy in the absence of steric considerations (see Figure 1). Our structural work with the ethylene complex $[Cp(Pom\text{-}Pom)Mo(CO)(\eta^2\text{-ethylene})]^+PF_6^-$ demonstrated that, in the solid state, overlap with the d_{z^2} orbital (II in Figure 1) is the most favorable for the ethylene ligand. In solution at room temperature, rapid rotation of the ethylene ligand around the Mo–olefin bond can be observed via ^{13}C NMR.[6]

For the case of a monosubstituted olefin, there are more possibilities, since the positioning of the substituent relative to the other ligands on the metal adds another variable to the system. Crystallographic studies of $[Cp(Pom\text{-}Pom)Mo(CO)(\eta^2\text{-olefin})]^+$ complexes that we describe in this paper indicate that, in the solid state, monosubstituted olefins adopt an orientation similar to the ethylene ligand shown in II, with the substituent on

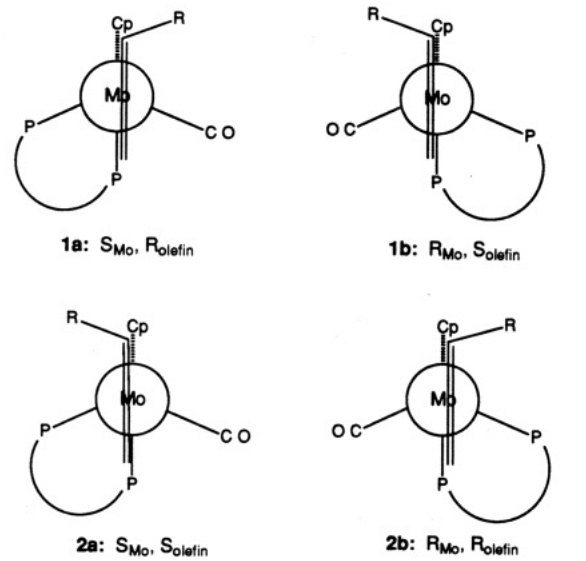


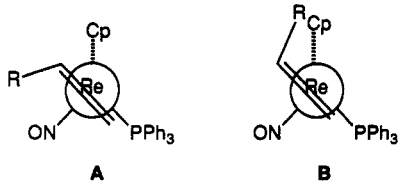
Figure 2. Newman projections for Mo–olefin complexes.

the olefin *syn* to the Cp ring[8] and between the CO and the Cp. If we assume a static orientation of the olefin ligand (lowest energy conformation), there are then four distinct isomers (**1a,b**, **2a,b**) produced on complexation of a monosubstituted olefin (see Figure 2).

There are two centers of chirality in these molecules, the molybdenum atom and the substituted carbon of the bound olefin, with the configuration of the metal specified by the rules given by Sloan[9] and that of the olefin specified by the convention used by Paiaro[10] and Gladysz.[11] These differences in stereochemistry render **1a** and **1b** (and **2a** and **2b**) related as enantiomers, while **1** and **2** are diastereomers. Although the different rotamers of **1** and **2** may be present in solution, the stereochemistry of olefin binding will not be affected by a rotation about the metal–olefin bond; however, different rotamers *can* produce distinctly different NMR spectra.

Asymmetry at the metal center is essential for stereoselective binding of an olefin to the metal. Complexes that have demonstrated such selectivity include Gladysz's $[CpRe(NO)(PPh_3)]^+BF_4^-$ cation[12] and Consiglio's $[Cp(Ph_2PCH_2CH(CH_3)PPh_2)Ru]^+PF_6^-$ system,[13] both of which have a center of asymmetry at the metal atom. In Gladysz's system, there is a mild kinetic preference for binding a particular face of an olefin, with ~2:1 (A:B) mixtures of diastereomers of $[CpRe(NO)(PPh_3)(olefin)]^+BF_4^-$ complexes A and B obtained from reaction of $[CpRe(NO)(PPh_3)]^+BF_4^-$ with a variety of olefins. Although the kinetic preference is not high, there is a strong thermodynamic preference (>97:3 A:B) for the olefins to bind the metal in such a way as to maximize orbital overlap while minimizing steric hindrance between substituents on the olefin and the ligands on the metal, as shown in A.

(6) Kegley, S. E.; Bergstrom, D. T.; Crocker, L. S.; Weiss, E. P.; Berndt, W. G.; Rheingold, A. L. *Organometallics* **1991**, *10*, 567.
(7) Hoffmann, R.; Sylvestre, J. personal communication.
(8) The *syn* and *anti* nomenclature for metal–olefin complexes is that used by Gladysz,[11] where a *syn* arrangement is that with the olefin substituent up and toward the Cp ring, while the *anti* arrangement is that with the R group down and away from the Cp ring.
(9) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.
(10) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *88*, 5148.
(11) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.
(12) Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Helv. Chim. Acta* **1992**, *75*, 442.
(13) (a) Consiglio, G.; Morandini, F. *J. Organomet. Chem.* **1986**, *310*, C66. (b) Consiglio, G.; Pregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345. (c) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761.



In Consiglio's ruthenium systems,[13] both the kinetic and thermodynamic selectivity are quite variable, depending on the nature of the olefin.

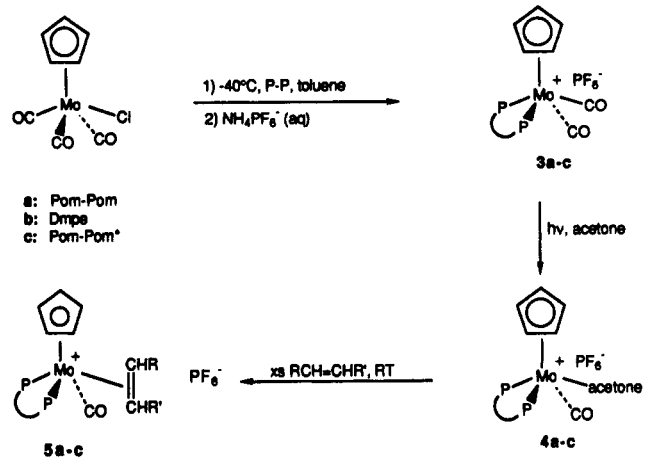
Because there is asymmetry at the molybdenum center in our systems, we presumed that there would be similar selectivity for binding an olefin such that the substituent would be positioned in the sterically least hindered position. Results of our crystallographic studies (see below) indicate that there is indeed very high kinetic and thermodynamic selectivity for olefin binding in some of these systems, with the preferred position of the substituent on the olefin ligand being between the CO and the Cp ring, as in **1** (Figure 2), instead of between the phosphorus atom and the Cp ring, as in **2**. This advantage is still not enough to enable one to carry out chiral syntheses via reaction of nucleophiles with the coordinated olefin, since complex **1** presents both *si* (**1a**) and *re* (**1b**) faces of the olefin for attack by an incoming nucleophile. When the chelating phosphine is achiral, **1a** and **1b** are enantiomeric and it is impossible to separate them by standard physical methods. To circumvent this problem, we have done some preliminary work on the introduction of a *chiral* chelating phosphonite ligand, in order to make complexes **1a** and **1b** diastereomeric.

In this paper, we describe (a) the synthesis and characterization of achiral Mo–olefin species, (b) X-ray crystallographic characterization of [Cp(Pom-Pom)Mo(CO)(η^2-ethyl acrylate)]$^+PF_6^-$, [Cp(Dmpe)Mo(CO)(η^2-styrene)]$^+PF_6^-$, and [Cp(Dmpe)Mo(CO)(dimethyl maleate)]$^+PF_6^-$, (c) studies on the stereochemistry and solution dynamics of these complexes, and (d) synthesis and characterization of *chiral* Mo–olefin complexes.

Synthesis of Achiral Olefin Complexes

The synthesis of the monosubstituted olefin complexes [Cp(P-P)Mo(CO)(η^2-olefin)]$^+PF_6^-$ (P-P = Pom-Pom, Dmpe) is analogous to that used for the preparation of the ethylene complexes previously reported[6] and is summarized in Scheme I.

Scheme I. Synthetic Route to Olefin Complexes



[Cp(Pom-Pom)Mo(CO)(η^2-olefin)]$^+PF_6^-$ Complexes: The solvent complex[Cp(Pom-Pom)Mo(CO)(acetone)]$^+PF_6^-$ (**4a**) reacts cleanly in acetone solution (and successfully, but not as cleanly, in methylene chloride solution) with monosubstituted and cis-1,2-disubstituted electron-deficient olefins to give the complexes [Cp(Pom-Pom)Mo(CO)(η^2-CHR=CHR′)]$^+PF_6^-$ in good yields (R = H, R′ = CO_2Me, **8**; R = H, R′ = CO_2Et, **9**; R = CO_2Me, R′ = CO_2Me, **10**) (see Table I). Infrared analysis indicates that the olefins are indeed bound η^2 to the C=C bond, as demonstrated by the observation of the ester C=O stretch between 1700 and 1740 cm^{-1}, as expected for uncomplexed ester carbonyl groups. The acrylate complexes **8** and **9** and the dimethyl maleate complex **10** are yellow crystalline solids that are stable for days in acetone solution at room temperature in the absence of air. Even extended periods of heating (50 °C for 30 h) in acetone solution cause little decomposition. Attempts to extend the scope of reactivity to 1,1′-disubstituted electron-deficient olefins such as α-methylene-γ-butyrolactone were unsuccessful.

Reaction of **4a** with electron-*rich* olefins did not result in the formation of metal–olefin complexes. With propylene, no reaction was observed, while with ethyl vinyl ether, immediate polymerization of the olefin occurred, an observation that is not too surprising considering the Lewis acidity of the 16-electron species[Cp(Pom-Pom)Mo(CO)]$^+PF_6^-$ that is presumably the reactive intermediate in this reaction.

Quantification of the stability of the [Cp(Pom-Pom)Mo(CO)(η^2-olefin)]$^+$ complexes with respect to the electron-donating capability of the olefin was attempted by reaction of **4a** with para-substituted styrenes of varying electronic properties. Thus, **4a** was allowed to react with styrene, *p*-Cl-styrene, and *p*-OMe-styrene. Although no reaction occurred with any styrene in acetone solution (presumably due to the greater ability of the solvent to coordinate to the metal), formation of [Cp(Pom-Pom)Mo(CO)(η^2-*p*-X-styrene)]$^+PF_6^-$ (X = H, **11**; X = Cl, **12**) was rapid in methylene chloride. When X = OMe, polymerization occurred, as with ethyl vinyl ether. Full characterization of **11** and **12** was hampered by the reactivity of these complexes with NMR solvents that successfully solubilize them, e.g., THF, acetone, and CD_2Cl_2 (in the absence of excess *p*-X-styrene). Decomposition of **11** (and to a lesser extent **12**) in solution over relatively short periods of time precluded any spectral analyses requiring long (>5–10-min) acquisition times.

Clearly, the styrene complexes **11** and **12** are thermodynamically not as stable as the acrylate species **8–10**. Whether this is due entirely to the electronic properties of the olefins or to a combination of sterics and electronics is not totally clear. However, the fact that the solution stability of **11** and **12** is markedly different, with the more electron-deficient *p*-Cl-styrene forming a more stable complex, suggests that electronics are a major factor in determining the strength of the metal–olefin bond. The more electron-deficient the olefin, the more stable the complex.

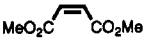
[Cp(Dmpe)Mo(CO)(η^2-olefin)]$^+PF_6^-$ Complexes. The reaction of [Cp(Dmpe)Mo(CO)(acetone)]$^+PF_6^-$ (**4b**) with olefinic substrates produced results similar to those observed for the Pom-Pom species, albeit with some significant differences (see Table II). Thus, reaction of **4b** with monosubstituted and *cis*-1,2-disubstituted electron-deficient olefins in acetone successfully produced [Cp(Dmpe)Mo(CO)(η^2-CHR=CHR′)]$^+PF_6^-$ (R = H, R′

Table I. Reaction of [Cp(Pom-Pom)Mo(CO)(acetone)]$^+PF_6^-$ (4a) with Olefins

olefin	reaction conditions[a]	product[b]	yield[c] (%)
ethyl vinyl ether	RT,[d] 1 min, CH_2Cl_2	polymer	
propylene	RT, 2 wk, CH_2Cl_2	no reaction	0
methyl acrylate, CH_2=$CHCO_2Me$	RT, 2 h, actone	[Cp(Pom-Pom)Mo(CO)(η^2-methyl acrylate)]$^+$ (**8**)	88
ethyl acrylate, CH_2=$CHCO_2Et$	RT, 2 h, acetone	[Cp(Pom-Pom)Mo(CO)(η^2-ethyl acrylate)]$^+$ (**9**)	80
dimethyl maleate 	RT, 26 h, acetone	[Cp(Pom-Pom)Mo(CO)(η^2-dimethyl maleate)]$^+$ (**10**)	86
styrene	RT, 30 min, CH_2Cl_2	[Cp(Pom-Pom)Mo(CO)(η^2-styrene)]$^+$ (**11**)	*e*
p-Cl-styrene	RT, 30 min, CH_2Cl_2	[Cp(Pom-Pom)Mo(CO)(η^2-*p*-Cl-styrene)]$^+$ (**12**)	82
p-OMe-styrene	RT, 5 min, CH_2Cl_2	polymer	
α-methylene-γ-butyrolactone 	RT, 55 h, acetone	no reaction	0

[a] Excess (10–20 equiv) olefin was used in all reactions. [b] All complexes contain PF_6^- as the counterion. [c] After recrystallization. [d] RT, room temperature. [e] Decomposes on workup.

Table II. Reaction of [Cp(Dmpe)Mo(CO)(acetone)]$^+PF_6^-$ (4b) with Olefins

olefin	reaction conditions[a]	product[b]	yield[c] (%)
ethyl vinyl ether	RT,[d] 14 h, acetone	no reaction	0
ethyl vinyl ether	RT, 1 min, CH_2Cl_2	polymer	0
methyl acrylate, CH_2=$CHCO_2Me$	RT, 15 min, acetone	[Cp(Dmpe)Mo(CO)(η^2-methyl acrylate)]$^+$ (**13**)	87
ethyl acrylate, CH_2=$CHCO_2Et$	RT, 15 min, acetone	[Cp(Dmpe)Mo(CO)(η^2-ethyl acrylate)]$^+$ (**14**)	88
dimethyl maleate 	RT, 26 h, acetone	[Cp(Dmpe)Mo(CO)(η^2-dimethyl maleate)]$^+$ (**15**)	89
α-methylene-γ-butyrolactone 	RT, 8.5 h, acetone	[Cp(Dmpe)Mo(CO)(η^2-α-methylene-γ-butyrolactone)]$^+$ (**16**)	75
5,6-dihydro-2*H*-pyran-2-one 	RT, 55 h, acetone	no reaction	
2-cyclohexene-1-one 	RT, 55 h, acetone	no reaction	0
styrene	RT, 30 min, acetone	[Cp(Dmpe)Mo(CO)(η^2-styrene)]$^+$ (**17**)	78
p-Cl-styrene	RT, 30 min, acetone	[Cp(Dmpe)Mo(CO)(η^2-*p*-Cl-styrene)]$^+$ (**18**)	82

[a] Excess (10–20 equiv) olefin was used in all reactions. [b] All complexes contain PF_6^- as the counterion. [c] After recrystallization. [d] RT, room temperature.

= CO_2Me, 13; R = H, R′ = CO_2Et, 14; R = CO_2Me, R′ = CO_2Me, 15). Interestingly, the rate of formation of these species was significantly faster than that of the corresponding Pom-Pom derivative in the same reaction solvent. When the reaction of **4b** with either methyl or ethyl acrylate was carried out at room temperature, formation of product was complete within 10–15 min, as compared to the 2 h necessary for the analogous Pom-Pom derivatives. Once formed, the acrylate complexes **13** and **14** and the dimethyl maleate complex **15** exhibit stability comparable to that of the Pom-Pom complexes. Compounds **13–15** exist as yellow crystalline solids that are stable for days in acetone solution at RT in the absence of air, and as with the Pom-Pom derivatives, extended periods of heating (50 °C for 30 h) in acetone solution cause little decomposition. In methylene chloride solution, decomposition occurs within several hours at room temperature.

Attempts to extend the scope of reactivity to 1,1′-disubstituted electron-deficient olefins such as α-methylene-γ-butyrolactone proved successful in this case, and good yields of [Cp(Dmpe)Mo(CO)(η^2-α-methylene-γ-butyrolactone)]$^+PF_6^-$ (**16**) were obtained. Reaction of **4b** with cis-1,2-disubstituted olefins such as 5,6-dihydro-2*H*-pyran-2-one and 2-cyclohexen-1-one did not give olefin complexes.

Synthesis of the styrene complexes [Cp(Dmpe)Mo(CO)(η^2-*p*-X-styrene)]$^+PF_6^-$ (X = H, 17; X = Cl, 18) was successful, even in acetone solution; however, because the styrene complexes **11** and **12** could not be prepared in acetone, the relative reactivity of **4a** and **4b** with styrenes could not be judged. The styrene complexes **17** and **18** proved to be somewhat more stable than **11** and **12**, although decomposition in coordinating solvents also occurred for the Dmpe species. Again, there was a marked difference in stability between the complex formed with the relatively electron-rich styrene ligand and that formed with the more electron-deficient *p*-Cl-styrene ligand, with the more electron-deficient styrene forming a more stable complex.

The enhanced reactivity of **4b** over **4a** (in acetone solution) is likely due to a combination of the different electron-donating abilities and steric properties of the two bidentate ligands. Table III lists both the cone angles[14] of the ligands used in this study (from X-ray data in this work) and the CO stretching frequencies for the dicarbonyl species [Cp(P-P)Mo(CO)$_2$]$^+PF_6^-$.

Comparison of the cone angles of Pom-Pom versus Dmpe indicates that the Pom-Pom ligand has the potential to

(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table III. Comparison of Cone Angles and Electronic Parameters for Representative Phosphine and Phosphonite Ligands

ligand	cone angle (deg)	electronic parameter (ν, cm^{-1})[a]
Dmpe	90[b]	1913, 1983
Pom-Pom	90–134[c]	1943, 2000
Pom-Pom*	*d*	1930, 1990
diphos	125[e]	1920, 1982

[a] For the dicarbonyl complexes $[Cp(P\text{-}P)Mo(CO)_2]^+PF_6^-$ in CH_2Cl_2. [b] From X-ray data obtained for complex **15**. [c] From X-ray data obtained for complex **9**. [d] No crystallographic data available. [e] From ref 14.

be a much bulkier ligand than Dmpe. The fact that rotation can occur around the P–O bond in the Pom-Pom ligand provides a means by which the cone angle can increase from a minimum value of 90° (identical to that of Dmpe in these systems), when the methyl groups are pointing down and away from the molybdenum atom, to a maximum value of 134° when the methyl groups are pointing up and toward the molybdenum atom. Access to the metal center will certainly be restricted to a greater degree when the cone angle is at its maximum; however, the fact that the methyl group is two atoms removed from the metal center certainly lessens the effect of this increase in steric bulk on the binding of an olefin to the metal.

The greater reactivity of the Dmpe complex can also be attributed to electronic effects. The high-energy CO stretching frequency of $[Cp(Dmpe)Mo(CO)_2]^+PF_6^-$ is 30 wavenumbers lower than that of the corresponding Pom-Pom complex, indicative of a much greater level of electron density at the metal. Thus, although the more electron-rich Dmpe ligand reduces the Lewis acidity of the complex, it facilitates backbonding between the metal and the olefin. There is no quantitative method available for separating these effects; however, it seems that a combination of sterics and electronics is responsible for the differences in reactivity observed.

Stereochemistry of Olefin Binding: Crystallographic Analyses and Solution Dynamics

$[Cp(Pom\text{-}Pom)Mo(CO)(\eta^2\text{-}CH_2{=}CHR)]^+PF_6^-$ Complexes. In contrast to the previously-studied Re and Ru systems,[12,13] extremely high *kinetic* selectivity is observed in the formation of the metal–olefin bonds in $[Cp(Pom\text{-}Pom)Mo(CO)(\eta^2\text{-olefin})]^+PF_6^-$ complexes **8** and **9**, and only a *single* diastereomer is observed, corresponding to configuration **1** shown in Figure 2. This fact is demonstrated by the observation of only two phosphorus resonances in the ^{31}P NMR, for the phosphorus atoms cis and trans to the CO. This spectroscopic evidence is particularly convincing because of the great sensitivity of ^{31}P chemical shifts to very slight changes in molecular structure (*vide infra*). Although **11** and **12** are not stable enough to be analyzed by ^{31}P NMR at room temperature, **12** was stable enough to examine by ^1H NMR and was found to exhibit only one Cp resonance in the ^1H NMR spectrum, suggesting that *p*-Cl-styrene also binds stereoselectively to the metal.

Crystallographic analysis of $[Cp(Pom\text{-}Pom)Mo(CO)(\eta^2\text{-}CH_2{=}CHCO_2Et)]^+PF_6^-$ (**9**) was carried out. Complex **9** crystallizes in the monoclinic space group $P2_1/n$. An ORTEP drawing of the molecule is shown in Figure 3, and relevant crystallographic parameters are given in Tables IV–VI. The molecule is of the "four-legged piano stool" type, formally 7-coordinate with the Cp ring at the apex of a square pyramid. The olefin ligand is oriented such that it is contained in the plane defined by the metal, the center of the Cp ring, and the *trans*-phosphorus atom, identical to that observed for $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (see ref 6). The isomer formed in the reaction is that with the substituent on the olefin *syn* to the Cp ring and lying between the Cp and the CO (Figure 4), corresponding to **1** in Figure 2.

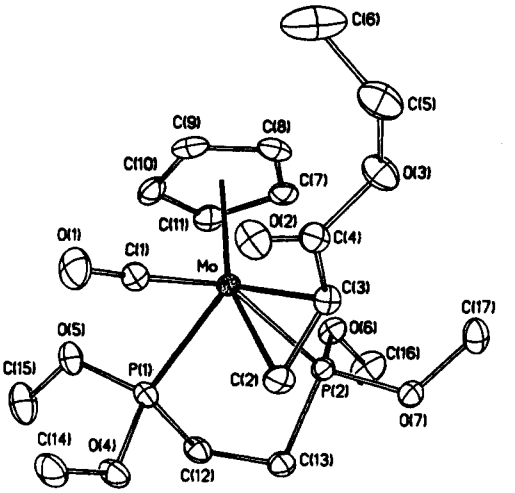


Figure 3. ORTEP drawing of $[Cp(Pom\text{-}Pom)Mo(CO)(H_2C{=}CHCO_2Et)]^+PF_6^-$ (**9**). Thermal ellipsoids are drawn at the 40% probability level.

Table IV. Crystallographic Data for 9, 15, and 17

	9	15	17
	(a) Crystal Parameters		
formula	$C_{17}H_{29}F_6MoO_7P_3$	$C_{18}H_{29}F_6MoO_5P_3$	$C_{20}H_{29}F_6MoOP_3$
mol wt	648.26	628.28	588.30
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a, Å	8.825(2)	8.925(3)	15.821(4)
b, Å	27.834(8)	35.824(9)	17.637(3)
c, Å	10.192(2)	16.180(5)	8.597(2)
α, deg			
β, deg	93.03(2)	102.75(2)	
γ, deg			
V, Å^3	2500.0(11)	5045(2)	2398.8(9)
Z	4	8	4
cryst dimens, mm	0.32 × 0.38 × 0.40	0.32 × 0.28 × 0.28	0.26 × 0.40 × 0.40
cryst color	yellow	yellow	yellow
D(calc), g cm^{-3}	1.722	1.654	1.629
μ(Mo Kα), cm^{-1}	7.76	7.47	7.86
temp, K	295	295	295
	(b) Data Collection		
diffractometer	Nicolet R3m		
monochromator	graphite		
radiation	Mo Kα (λ = 0.71073 Å)		
2θ scan range, deg	4–55	4–50	4–50
data collected (h, k, l)	±12, +37, +14	±11, +43, +20	+19, +21, +11
rflns collected	6187	9403	2433
indpt rflns	5737	8896	2411
indpt obsd rflns [$F_o \geq 5\sigma(F_o)$]	4261	5349	2087
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1	<1
	(c) Refinement		
$R(F)$, %	4.93	8.29	3.76
$R(wF)$, %	5.36	9.63	4.09
Δ/σ(max)	0.021	0.065	0.044
$\Delta(\rho)$, eÅ^{-3}	1.09	1.08	0.53
N_o/N_v	13.9	9.0	7.7
GOF	1.31	1.69	1.08

Table V. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 9

	x	y	z	U[a]
Mo	867.6(4)	6115.6(1)	7299.0(4)	24.2(1)
P(1)	-1442(1)	6439(1)	8170(1)	31(1)
P(2)	-684(1)	6368(1)	5292(1)	30(1)
P(3)	771(2)	1727(1)	2665(2)	42(1)
F(1)	1468(6)	1325(2)	3577(4)	106(2)
F(2)	574(5)	2074(2)	3864(5)	99(2)
F(3)	57(5)	2126(2)	1713(5)	99(2)
F(4)	974(4)	1378(2)	1454(4)	72(1)
F(5)	2389(4)	1944(2)	2478(6)	105(2)
F(6)	-875(4)	1518(2)	2785(4)	84(2)
O(1)	1114(5)	5562(2)	10028(4)	57(1)
O(2)	2024(4)	4876(1)	7917(4)	45(1)
O(3)	3281(4)	5007(1)	6110(4)	47(1)
O(4)	-2746(4)	6097(1)	8687(4)	43(1)
O(5)	-1023(4)	6805(1)	9322(4)	45(1)
O(6)	-142(4)	6879(1)	4784(3)	39(1)
O(7)	-894(4)	6031(1)	4031(3)	39(1)
C(1)	1000(5)	5740(2)	9025(5)	36(1)
C(2)	-488(5)	5436(2)	6777(5)	38(2)
C(3)	975(5)	5399(2)	6258(5)	31(1)
C(4)	2098(5)	5074(2)	6880(5)	35(1)
C(5)	4444(6)	4671(2)	6596(7)	55(2)
C(6)	5540(7)	4899(3)	7524(9)	95(4)
C(7)	2555(5)	6605(2)	6262(5)	38(2)
C(8)	3415(5)	6228(2)	6816(6)	42(2)
C(9)	3302(6)	6242(2)	8182(6)	45(2)
C(10)	2370(6)	6644(2)	8477(5)	44(2)
C(11)	1900(6)	6861(2)	7309(5)	39(2)
C(12)	-2643(5)	6750(2)	6947(5)	40(2)
C(13)	-2643(5)	6452(2)	5676(5)	40(2)
C(14)	-2535(7)	5795(2)	9831(5)	52(2)
C(15)	-2134(8)	7106(2)	9894(6)	66(3)
C(16)	-969(7)	7146(2)	3759(6)	61(2)
C(17)	315(7)	5986(2)	3130(5)	47(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Distances and Bond Angles for [Cp(Pom-Pom)Mo(CO)(CH₂=CHCO₂Et]⁺PF₆⁻ (9)

	(a) Bond Distances (Å)		
Mo–CNT[a]	1.968(4)	Mo–C(2)	2.286(5)
Mo–C(1)	2.045(5)	Mo–C(3)	2.264(4)
Mo–P(1)	2.438(1)	C(2)–C(3)	1.425(7)
Mo–P(2)	2.502(1)		
	(b) Bond Angles (deg)		
CNT–Mo–P(1)	118.3(2)	P(1)–Mo–P(2)	76.2(1)
CNT–Mo–P(2)	107.6(2)	P(1)–Mo–C(1)	83.4(1)
CNT–Mo–C(1)	103.4(2)	P(2)–Mo–C(1)	148.3(1)

[a] CNT = center of the Cp ring.

Experiments to determine the solution configuration of 8 and 9 by looking for NOE between the hydrogens on the olefin ligand and the hydrogens on the Cp ring revealed none; however, extensive coupling of the olefinic hydrogen resonances to ^{31}P and ^{1}H nuclei and concomitant broadening of the signal could have obscured any enhancement.

[Cp(Dmpe)Mo(CO)(η²-*p*-X-styrene)]⁺PF₆⁻ Complexes. For the formation of the styrene complexes 17 and 18, the stereoselectivity of olefin binding remains high, and only one isomer is observed for each of these complexes, as indicated by ^{1}H and ^{31}P NMR. Crystallographic analysis of 17 was carried out and indicates that, as with 9, the substituent on the olefin ligand lies between the Cp ring and the CO, again corresponding to the set of isomers 1 shown in Figure 2. Complex 17 crystallizes in the orthorhombic space group $P2_12_12_1$. An ORTEP drawing of 17 is shown in Figure 5, and relevant crystallographic parameters are given in Tables IV, VII, and VIII. The orientation of the olefin ligand is identical to that of 9 as

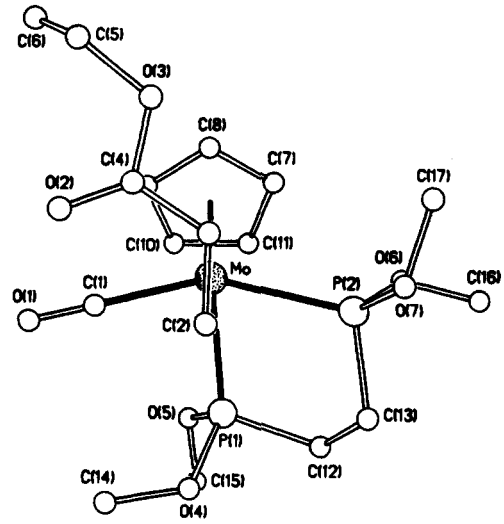


Figure 4. A view down the Mo–ethyl acrylate bond of 9 showing the orientation of the olefin and the position of the substituent *syn* to the Cp ring.

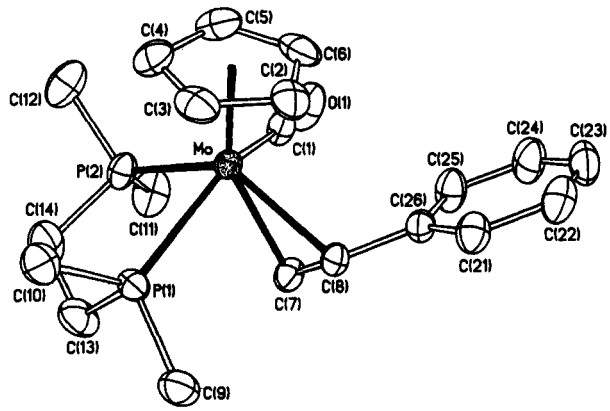


Figure 5. ORTEP drawing of [Cp(Dmpe)Mo(CO)(H₂C=CHPh)]⁺PF₆⁻ (17). Thermal ellipsoids are drawn at the 40% probability level.

well, with the substituent *syn* to the Cp ring and between the Cp and the CO.

NOE experiments on 17 show significant enhancement of all three olefinic hydrogens on irradiation of the Cp ring, indicative of rapid rotation about the metal–styrene bond.

[Cp(Dmpe)Mo(CO)(η²-dimethyl maleate)]⁺PF₆⁻ (15). Chelation of the disubstituted olefin dimethyl maleate to the molybdenum center proceeded smoothly to give complex 15. Because of the symmetry of the olefin, there is no possibility of obtaining diastereomeric products. Observation of the ^{31}P NMR spectrum indicated a near equivalence of the chemical shifts of the two phosphorus atoms ($\Delta\nu$ = 36 Hz), a feature only observable at high field strength (202.31 MHz). Variable-temperature proton NMR (25 to -40 °C) revealed little change in the chemical shifts of the two methyl resonances over this temperature range, suggesting that rotation about the Mo–olefin bond is rapid even at low temperatures.

An X-ray crystallographic analysis of 15 was carried out. Complex 15 crystallizes in the monoclinic space group $P2_1/n$. An ORTEP drawing of 15 is shown in Figure 6, and relevant crystallographic parameters are given in Tables IV, IX, and X. This complex exhibits the same four-legged piano stool geometry found for monosubstituted olefin complexes. The olefin ligand is oriented such

Table VII. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å²×10³) for 17

	x	y	z	U[a]
Mo(1)	6274.8(13)	1148.0(3)	9173.6(7)	32.0(4)
Mo(1′)	8589.7(13)	1336.0(3)	4546.8(6)	30.8(4)
P(1)	7987(4)	1571(1)	10189(2)	45(1)
P(2)	8037(5)	698(1)	10147(2)	46(1)
P(1′)	6083(4)	1216(1)	4981(2)	36(1)
P(2′)	7618(5)	1974(1)	4777(2)	43(1)
P(3)	1461(7)	2370(1)	12695(3)	75(2)
P(3′)	6924(8)	−282(2)	7507(5)	100(3)
F(1)	892(27)	2754(4)	12359(10)	183(12)
F(2)	1130(22)	2237(5)	11761(9)	160(9)
F(3)	2972(22)	2455(8)	12584(18)	260(17)
F(4)	−158(25)	2291(6)	12716(18)	229(16)
F(5)	1684(34)	2505(7)	13563(10)	250(15)
F(6)	1953(25)	1965(4)	12972(10)	162(10)
F(1′)	7236(26)	91(5)	7035(10)	177(11)
F(2′)	5888(28)	−44(6)	7892(21)	250(18)
F(3′)	6309(47)	−619(6)	7839(17)	328(25)
F(4′)	7983(25)	−516(6)	7117(17)	231(14)
F(5′)	5728(24)	−369(6)	6658(15)	216(13)
F(6′)	8216(27)	−159(5)	8203(12)	206(12)
O(1)	4115(14)	1849(3)	9122(8)	71(5)
O(2)	2146(14)	1094(3)	8516(7)	70(5)
O(3)	2524(13)	479(3)	8339(7)	63(4)
O(4)	2455(14)	1294(5)	10187(8)	107(7)
O(5)	4540(14)	1393(4)	11209(7)	77(5)
O(1′)	11708(12)	1795(3)	4906(7)	66(4)
O(2′)	12232(12)	901(3)	5359(7)	61(5)
O(3′)	10944(13)	375(3)	5399(8)	69(5)
O(4′)	11962(14)	1443(4)	6589(7)	86(6)
O(5′)	9930(14)	1692(3)	6996(7)	72(5)
C(1)	4839(16)	1588(4)	9131(9)	46(5)
C(2)	5681(21)	868(5)	7842(9)	59(6)
C(3)	5440(17)	1255(5)	7738(9)	61(7)
C(4)	6866(18)	1436(4)	8048(8)	47(5)
C(5)	8009(17)	1163(4)	8336(9)	51(6)
C(6)	7256(16)	816(4)	8168(8)	44(5)
C(7)	4369(16)	772(4)	9376(9)	44(5)
C(8)	4824(17)	992(5)	10116(9)	54(6)
C(9)	2903(17)	816(4)	8721(9)	45(5)
C(10)	1257(21)	480(5)	7617(11)	82(8)
C(11)	3795(17)	1234(4)	10461(9)	51(6)
C(12)	3577(25)	1611(7)	11636(13)	110(11)
C(13)	9266(21)	1306(5)	11034(9)	66(7)
C(14)	8693(19)	924(4)	11181(9)	53(6)
C(15)	9359(20)	1846(5)	9764(11)	67(7)
C(16)	7113(22)	1937(6)	10723(13)	103(10)
C(17)	9864(18)	576(4)	9862(10)	56(6)
C(18)	7286(20)	247(5)	10438(12)	72(8)
C(1′)	10650(15)	1607(4)	4800(9)	44(5)
C(2′)	9767(18)	1173(4)	3454(8)	50(6)
C(3′)	8930(20)	848(5)	3619(9)	58(6)
C(4′)	7418(19)	952(5)	3433(9)	54(6)
C(5′)	7254(16)	1313(5)	3172(10)	53(6)
C(6′)	8647(20)	1454(5)	3211(8)	57(6)
C(7′)	9588(13)	902(4)	5491(7)	29(4)
C(8′)	9392(15)	1236(4)	5955(8)	39(5)
C(9′)	11064(16)	747(4)	5442(8)	42(5)
C(10′)	12310(21)	174(5)	5310(16)	106(11)
C(11′)	10572(17)	1462(4)	6540(8)	50(5)
C(12′)	10946(21)	1929(6)	7605(12)	86(9)
C(13′)	5709(17)	1589(4)	5657(8)	47(5)
C(14′)	5932(21)	1966(4)	5235(10)	58(6)
C(15′)	4361(16)	1228(5)	4128(9)	55(6)
C(16′)	5882(18)	793(4)	5552(11)	61(7)
C(17′)	6937(22)	2263(5)	3822(11)	75(8)
C(18′)	8901(22)	2301(5)	5426(13)	89(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

that the C=C bond is contained in the plane defined by the metal, the center of the Cp ring, and the *trans*-phosphorus atom. The substituents on the olefin ligand lie on the CO side of the molecule.

[Cp(Dmpe)Mo(CO)(η^2-CH₂=CHCO₂R)]⁺PF₆⁻ (13, R = CH₃; 14, R = CH₂CH₃). In contrast to the reactions

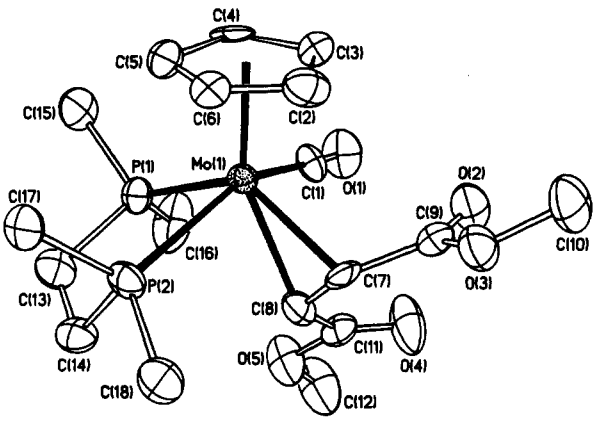


Figure 6. ORTEP drawing of [Cp(Dmpe)Mo(CO)-((MeO₂C)CH=CHCO₂Me)]⁺PF₆⁻ (15). Thermal ellipsoids are drawn at the 40% probability level.

Table VIII. Selected Bond Distances and Bond Angles for [Cp(Dmpe)Mo(CO)(CH₂=CHPh)]⁺PF₆⁻ (17)

(a) Bond Distances (Å)

Mo–CNT[a]	1.973(6)	Mo–C(7)	2.316(7)
Mo–C(1)	1.986(7)	Mo–C(8)	2.321(6)
Mo–P(1)	2.544(2)	C(7)–C(8)	1.437(9)
Mo–P(2)	2.474(2)		

(b) Bond Angles (deg)

CNT–Mo–P(1)	110.7(2)	P(1)–Mo–P(2)	77.0(1)
CNT–Mo–P(2)	120.1(2)	P(1)–Mo–C(1)	142.3(2)
CNT–Mo–C(1)	106.2(2)	P(2)–Mo–C(1)	78.3(2)

[a] CNT = center of the Cp ring.

Table IX. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 15

	x	y	z	U[a]
Mo	129.5(3)	6208.6(3)	4291.0(6)	31.8(1)
P(1)	1342(1)	6192(1)	6235(2)	40(1)
P(2)	601(1)	7546(1)	4325(3)	45(1)
P(3)	−1476(1)	8250(1)	−637(3)	50(1)
O(1)	−1535(3)	7084(3)	3431(8)	78(2)
F(1)	−696(4)	8669(6)	−1167(9)	182(5)
F(2)	−1038(6)	7509(4)	−403(10)	201(5)
F(3)	−1279(5)	8472(3)	1095(7)	113(3)
F(4)	−1698(4)	8016(4)	−2361(6)	94(2)
F(5)	−1953(5)	9020(3)	−852(12)	149(4)
F(6)	−2345(5)	7905(4)	−138(9)	144(4)
C(1)	−933(4)	6753(4)	3771(9)	47(2)
C(2)	160(5)	4994(4)	3161(9)	52(2)
C(3)	988(5)	5271(4)	3090(9)	54(3)
C(4)	998(5)	5952(4)	2199(9)	56(3)
C(5)	152(5)	6081(4)	1679(9)	64(3)
C(6)	−360(5)	5486(5)	2305(8)	58(3)
C(7)	−591(4)	6372(4)	6612(8)	44(2)
C(8)	−600(4)	5578(4)	6243(8)	38(2)
C(9)	1295(5)	5619(4)	8009(9)	57(3)
C(10)	2393(4)	5958(5)	5517(11)	65(3)
C(11)	−132(5)	8266(4)	4957(12)	75(3)
C(12)	953(6)	7927(4)	2477(11)	74(4)
C(13)	1483(6)	7161(4)	6956(11)	67(3)
C(14)	1507(5)	7697(4)	5577(12)	76(4)
C(21)	−1322(2)	4360(2)	5831(6)	49(2)
C(22)	−2021	3927	5397	61(3)
C(23)	−2761	4284	4905	63(3)
C(24)	−2803	5073	4848	66(3)
C(25)	−2104	5506	5283	57(3)
C(26)	−1364	5150	5775	39(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

described above, *two* products are observed when **4b** is allowed to react with either methyl or ethyl acrylate. Thus, **13k** and **13t** (or **14k** and **14t**) are formed in approximately a 50:50 ratio. The thermodynamic products are **13t** and

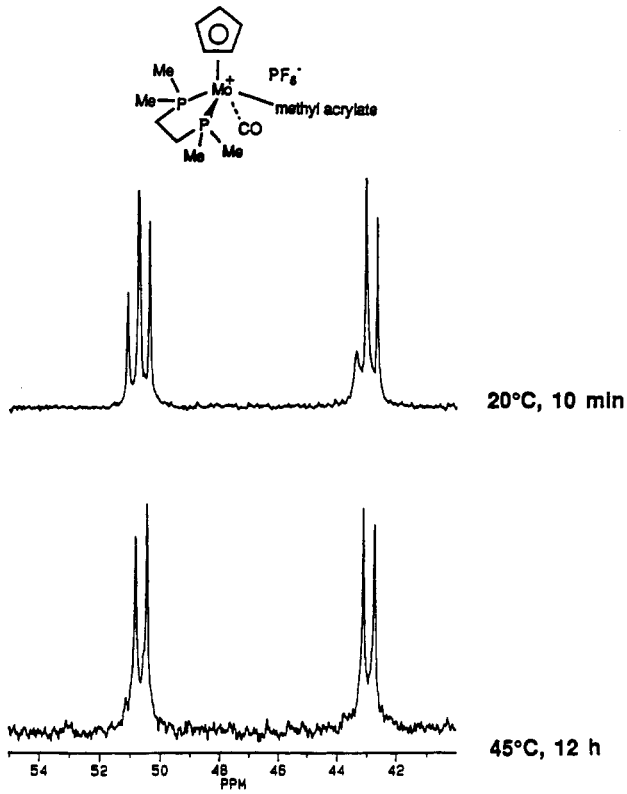


Figure 7. ^{31}P NMR spectra of [Cp(Dmpe)Mo(CO)(CH_2=$CHCO_2Me$)]$^+PF_6^-$ (**13**) prepared at 20 °C and at 45 °C.

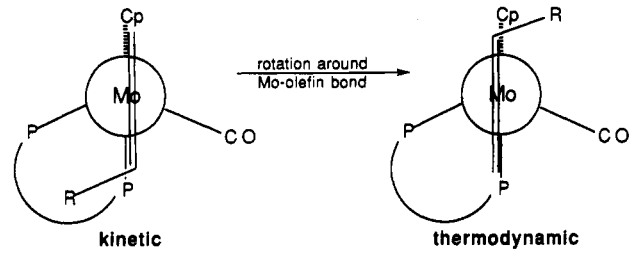
Table X. Selected Bond Distances and Bond Angles for [Cp(Dmpe)Mo(CO)(dimethyl maleate)]$^+PF_6^-$ (15)

	molecule A	molecule B
	(a) Bond Distances (Å)	
Mo–CNT[a]	1.962(11)	1.980(10)
Mo–C(1)	2.023(15)	2.040(13)
Mo–P(1)	2.495(4)	2.525(4)
Mo–P(2)	2.541(4)	2.502(4)
Mo–C(7)	2.250(15)	2.223(1)
Mo–C(8)	2.277(16)	2.261(13)
C(7)–C(8)	1.414(20)	1.442(18)
	(b) Bond Angles (deg)	
CNT–Mo–P(1)	117.4(5)	108.3(5)
CNT–Mo–P(2)	109.1(5)	119.6(5)
CNT–Mo–C(1)	105.3(5)	103.7(5)
P(1)–Mo–P(2)	76.8(1)	75.9(1)
P(1)–Mo–C(1)	80.8(4)	147.2(4)
P(2)–Mo–C(1)	144.7(4)	82.1(4)

[a] CNT = center of the Cp ring.

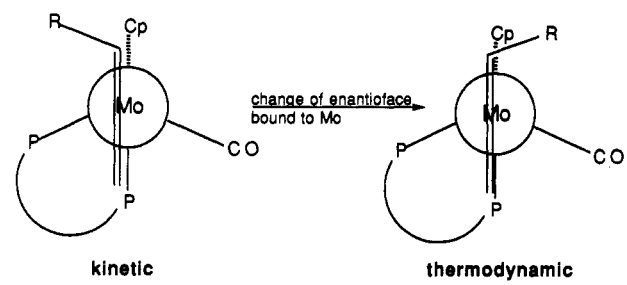
14t, and over the course of several days, **13k** and **14k** are transformed completely into **13t** and **14t** with a half-life of 385 h at 28 °C for both **13** and **14** [k_{obs} = 5(1) × 10^{-6} s^{-1}]. The progress of these interconversion reactions was monitored by observation of the changing integrals of the Cp resonances corresponding to the two isomers in the ^1H NMR spectrum. If the reaction of **4b** with methyl or ethyl acrylate is carried out at elevated temperatures (45 °C) over a 12-h period, only **13t** and **14t** are formed (see Figure 7).

At present, there are several possible explanations for this behavior (for the sake of ease of discussion, we will consider only **13**, but the same logic applies to **14** as well). One possibility is that **13k** and **13t** are two different rotamers of **1** (shown below is a single enantiomer of **1** for simplicity), where the process that interconverts the two is a simple rotation around the Mo–olefin bond.



The rate constant for isomerization provides a measure of the activation energy for the process. Using the Arrhenius equation, we obtain a value of 25 kcal/mol for the free energy of activation. If the process that interconverts the two isomers is indeed rotation around the M–olefin bond, the activation energy should be similar to that observed for rotation around other M–olefin bonds. A look at a summary of such data[15] gives a range for $\Delta G^{\ddagger}$ of 8–20 kcal/mol for rotation around a wide variety of M–olefin bonds. The dissimilarity of these values with our value suggest that our value for $\Delta G^{\ddagger}$ is too high for such a process. Indeed, the observation of a healthy population of both rotamers of the styrene complex (**17**) in solution at room temperature suggests that rotation for the acrylate complexes is also quite rapid and the difference in NMR spectra is likely due to other factors.

A more reasonable explanation for the observed products is that there is no kinetic stereoselectivity for binding these particular olefins to a Dmpe-coordinated metal center. Compounds **13k** and **13t** are thus diastereomers that correspond to **1** and **2** in Figure 2. For a given configuration at Mo, conversion to the lower energy form **13t** would necessarily involve a change in the face of the olefin bound to Mo.



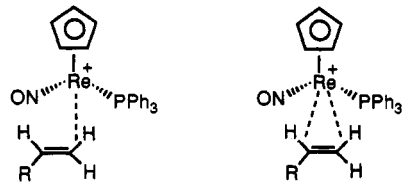
Isomerization could occur via two possible pathways: (1) dissociation of the olefin ligand and reassociation in a different conformation, or (2) via an intramolecular mechanism.

In order to test the possibility of a dissociative mechanism, a solution of **13k/t** (~50:50) was allowed to stir for a week at room temperature in the presence of a large excess of *ethyl* acrylate in acetone. Aliquots of the solution were taken over time and analyzed by proton NMR to test for the presence of the ethyl acrylate complex, **14**, one of the expected products if dissociative exchange were occurring. At no time, even after 7 days, was any **14** detected. The reverse reaction was also carried out. Thus, a solution of **14k/t** (~50:50) was stirred with a large excess of *methyl* acrylate. Again, no cross product **13** was formed. For both of these reactions, the isomerization process occurred at the same rate as it did in the absence of added olefin, as measured by monitoring a control reaction where

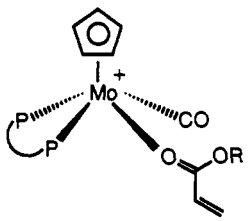
(15) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press, 1982; Vol. 3, p 99.

a solution containing only **13k/t** was stirred at room temperature in acetone. No formation of acetone complex **4b** was noted even after a week. These experiments prove that the mechanism of interconversion is not dissociative.

The question of how the isomers interconvert without dissociation of the olefin is similar to that encountered by Gladysz and Peng in their study of the isomerization of $[Cp(PPh_3)(NO)Re(styrene)]^+$.[16,17] Their use of a chiral rhenium complex and some clever labeling experiments enabled them to determine that the interconversion did *not* go via a simple rotation around the metal–olefin bond, or by formation of a rhenium-bound benzylic carbocation, or via an $[L_nRe{=}CH(CH_2Ph)]^+$ intermediate, or via an η^2-arene complex. Instead, they postulated a σ-bond complex as a reaction intermediate, where one or two of the vinylic C–H bonds are coordinated to the metal, as shown below.



While a similar intermediate could be proposed for the isomerization of **13** and **14**, a more likely possibility in this system is the formation of an η^1-acrylate complex where the olefin is now bound through an unshared pair on the carbonyl oxygen atom.



The rate of isomerization in our system is significantly faster than that observed in the Re systems,[17] where isomerization of $[Cp(NO)(PPh_3)Re(styrene)]^+$ occurs at a comparable rate only when the temperature is significantly higher, e.g., $t_{1/2}$ = 210 h at 86.6 °C for $[Cp(NO)(PPh_3)Re(styrene)]^+$ compared to $t_{1/2}$ = 385 h at 28 °C for $[Cp(Dmpe)Mo(CO)(methyl\ acrylate)]^+$.

Mechanistic Considerations. The mechanism for initial formation of the olefin complexes is proposed to be S_N1-like, with dissociation of the acetone ligand occurring rapidly at room temperature (eq 1). Evidence in support of this hypothesis is the observation of free acetone in all NMR spectra of **4** acquired in acetone-d_6, where exchange of acetone-d_6 with protioacetone occurs. The rate-determining step is reaction of the 16-electron species $[Cp(P\text{-}P)Mo(CO)]^+$ with the olefin (eq 2), and it is in this step

$$[Cp(P\text{-}P)Mo(CO)(acetone)]^+PF_6^- \textbf{ (4)} \rightleftharpoons [Cp(P\text{-}P)Mo(CO)]^+PF_6^- + \text{acetone} \quad (1)$$

$$[Cp(P\text{-}P)Mo(CO)]^+PF_6^- + RO_2C\text{-}CH{=}CH_2 \rightarrow [Cp(P\text{-}P)Mo(CO)(RO_2CCH{=}CH_2)]^+PF_6^- \textbf{ (5)} \quad (2)$$

that transition-state selectivities appear. The observation of a 50:50 mixture of products for the reaction of **4b** with ethyl or methyl acrylate suggests that there is little selectivity for binding the olefin in a particular way in the transition state, i.e., the transition state must be an early one that largely resembles the reactants. The very high selectivity observed for reaction of **4a** with the acrylates (and **4b** with styrenes) indicates that the transition state is late in the progress of the reaction and closely resembles the products.

The differences in the relative rates of reaction of **4a** and **4b** with olefins can also be explained on the basis of eq 2 as the rate-determining step. As mentioned above, there are several somewhat inseparable effects that govern the *thermodynamic* stability of the M–olefin bond, including the σ acceptor capability (or Lewis acidity) of the metal fragment, the σ donor capability of the olefin, the π donating ability of the metal fragment, and the π accepting capability of the olefin. However, the *kinetics* of these reactions seem to be controlled largely by π interactions between the metal and the olefin. Because the olefins are identical in these examples, the only properties we are comparing in the acrylate systems are those relating to the metal center. With a change from the relatively electron-poor Pom-Pom ligand to the more electron-rich Dmpe ligand, a faster reaction with olefins (10 min vs 2 h) is clearly observed. Thus, the enhancement of the π donating ability of the metal fragment by introduction of an electron-rich ligand such as Dmpe has a significant effect on reactivity, even though the presence of such an electron-rich ligand seriously compromises the Lewis acidity of the 16-electron intermediate. The steric differences between the two ligands may also contribute to the increased reactivity of the Dmpe species (see Table III).

Synthesis and Characterization of Chiral Molybdenum–Olefin Complexes

Preparation of the optically active ligand 1,2-bis[bis[(*S*)-2-methyl-1-butanoxy]phosphino]ethane (Pom-Pom*) was readily achieved by reaction of $Cl_2PCH_2CH_2PCl_2$ with 99% optically pure (*S*)-(−)-2-methyl-1-butanol in the presence of Et_3N, analogous to the preparation of 1,2-bis(dimethoxyphosphino)ethane (Pom-Pom) reported by King.[18] The product was obtained analytically pure from the reaction and was in the form of an oily liquid whose boiling point was >300 °C at 1 mmHg pressure. Because of the hydrophobic properties of this ligand, all of the organometallic complexes containing Pom-Pom* exist as oils, even though they are ionic species. They are all at least partially soluble in a wide range of solvents, including both water and pentane, a characteristic which makes them easy to chromatograph, but impossible to crystallize.

The synthetic scheme for the optically active complexes was exactly analogous to that for the achiral systems (see Scheme I). Preparation of the chiral dicarbonyl species $[Cp(Pom\text{-}Pom^*)Mo(CO)_2]^+PF_6^-$ (**3c**) was carried out by reaction of the optically active ligand Pom-Pom* with $CpMo(CO)_3Cl$ at −40 °C, followed by ion exchange to produce the PF_6^- salt. The proton NMR spectrum of **3c** is unremarkable; however, the ^{31}P spectrum deserves mention. If the complex is viewed from the top of the square pyramid (see Figure 8), it is clear that there is no

(16) Peng, T.-S.; Gladysz, J. A. *Chem. Commun.* **1990**, 902.
(17) Peng, T.-S., Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, 4174.
(18) King, R. B.; Rhee, W. M. *Inorg. Chem.* **1978**, *17*, 2961.

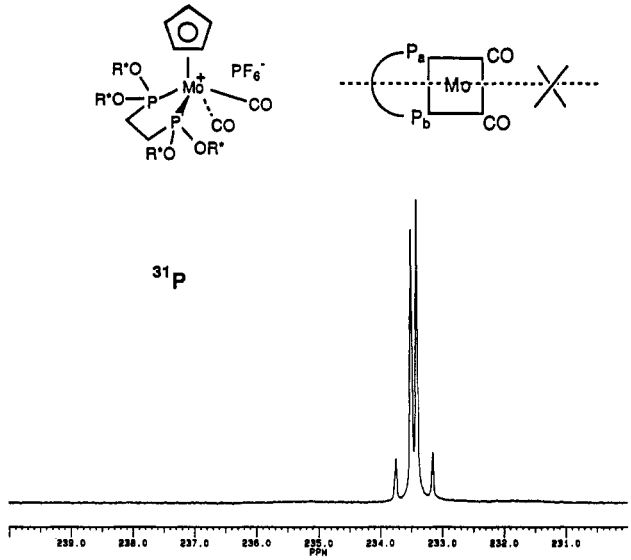


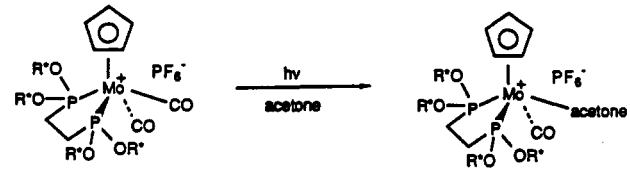
Figure 8. ^{31}P NMR spectrum of [Cp(Pom-Pom*)Mo-$(CO)_2$]$^+PF_6^-$ (**3c**), and a view of the molecule from the top of the square pyramidal structure with the Cp ring omitted.

plane of symmetry bisecting the molecule, due to the fact that all alkoxy groups on the phosphorus atoms are of the *S* configuration. The spectroscopic result of this inequivalence in the ^{31}P spectrum is an AB pattern that is typical for two nuclei when the chemical shift difference between the nuclei is quite small.[19] This spectroscopic feature could only be observed at high field (202 MHz for ^{31}P) and is indicative of the high sensitivity of ^{31}P NMR for detecting different diastereomers of these types of molecules.

Photolysis of **3c** in acetone produced the acetone complex **4c**. The proton NMR spectrum of **4c** shows only one Cp resonance for the two diastereomers obtained; however, the ^{31}P spectrum obtained with a narrow sweep width (~50–100 ppm) indicates clearly the presence of two diastereomers with very similar chemical shifts and coupling constants (see Figure 9). Although the spectrum resembles a doublet of doublets for each phosphorus atom, each major group of four peaks is actually two doublets produced by the phosphorus atoms of different diastereomers, which are shifted slightly away from each other and have nearly identical coupling constants. The fact that the splitting was due to a chemical shift difference and not to a coupling to another nucleus was proven by acquiring the ^{31}P spectra at two different field strengths (81 and 202 MHz), where at the higher field strength, greater separation was observed between the resonances.

Synthesis of the methyl acrylate complex [Cp(Pom-Pom*)Mo(CO)(η^2-methyl acrylate)]$^+PF_6^-$ (**19**) could be carried out via two different methods. Reaction of the acetone complex **4c** with methyl or ethyl acrylate at room temperature for 2–3 h gives good yields of only one pair of diastereomers (>97%), **19a,b**. The ^{31}P spectrum of **19** clearly indicates the presence of only two diastereomers that have similar chemical shifts and coupling constants (see Figure 10). The proton NMR spectrum showed no difference in the chemical shifts observed for both the Cp and OCH_3 resonances of the two diastereomers.

Because of the high solubility of the ionic dicarbonyl species **3c** in relatively nonpolar solvents, it was also



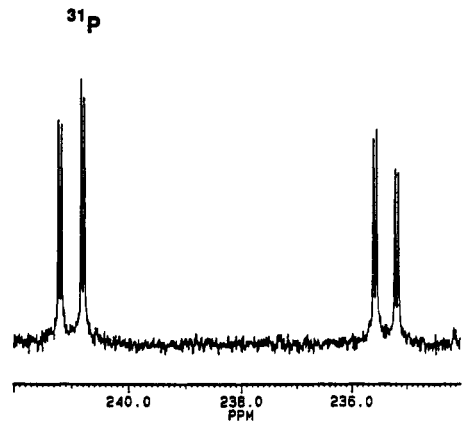


Figure 9. ^{31}P NMR spectrum of [Cp(Pom-Pom*)Mo(CO)-(acetone)]$^+PF_6^-$ (**4c**).

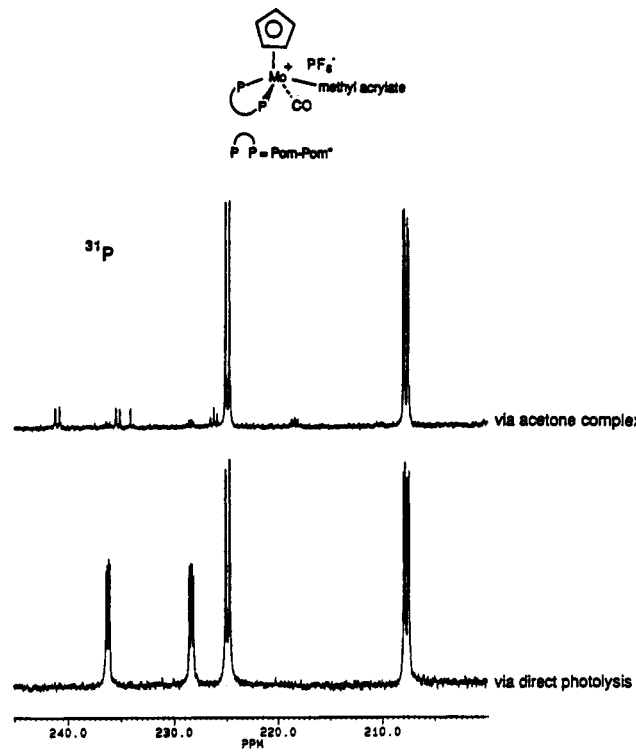


Figure 10. ^{31}P NMR spectra of [Cp(PomPom*)Mo-(CO)(methyl acrylate)]$^+PF_6^-$ (**19** and **20**), prepared via **4c** and via direct photolysis of **3c** in methyl acrylate.

possible to photolyze **3c** directly, using methyl acrylate as the solvent. An interesting consequence of this preparatory method is that all *four* diastereomers of [Cp(Pom-Pom*)Mo(CO)(methyl acrylate]$^+PF_6^-$, **19a,b** and **20a,b**, are produced. Photolysis of the starting dicarbonyl complex **3c** in methyl acrylate results in loss of CO to form a 16-electron intermediate which reacts rapidly and indiscriminately with the olefin and exhibits little stereoselectivity in binding the olefin in a particular orientation. The formation of **19** and **20** is similar to the formation of **13k** and **13t**, in that little kinetic selectivity is exhibited

(19) Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy. An Integrated Approach*; Heyden and Son Ltd.: London, 1978; pp 65–69.

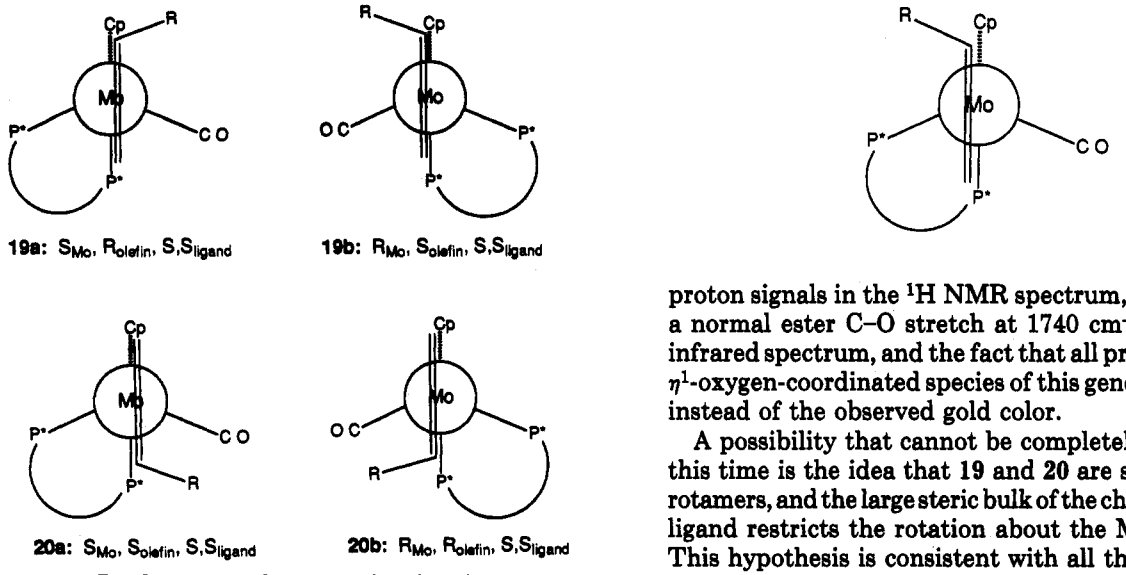


Figure 11. Products **19** and **20** from the photolytic reaction of $[Cp(Pom\text{-}Pom^*)Mo(CO)_2]^+PF_6^-$ (**3c**) with methyl acrylate.

and all possible diastereomers are obtained. A difference between the two reactions is that introduction of the chiral ligand makes it possible to distinguish **1a** from **1b** and **2a** from **2b** (see Figure 2). Thus, the four possible diastereomeric products are formed in roughly equal amounts. The slight (10%) excess of **19a,b** over **20a,b** is likely due to the concurrent thermal reaction taking place during the 40 min of the photolysis reaction.

Because the complexes containing the Pom-Pom* ligand do not form crystals suitable for X-ray analysis, comparison of spectral data proved to be the best method for supporting this hypothesis. The proton NMR spectra of both the thermal and photochemical reaction mixtures are identical, with the exception that the spectrum of the photolysis reaction shows *two* OCH_3 resonances for coordinated methyl acrylate, one at δ 3.62 corresponding to **19a,b** and another at δ 3.76 for **20a,b**. The ^{31}P spectrum of the products is quite informative and clearly shows the presence of two diastereomeric pairs in ~60:40 ratio (**20**:**19**) (see Figure 10).

Comparison of the ^{31}P spectra of **13k** and **13t** to those of **19** and **20** reveals an interesting difference. Both diastereomers **13k** and **13t** show nearly the same 8 ppm difference in the chemical shifts, $\Delta\delta$, for the two phosphorus atoms in the complex. In contrast, complex **19** has a $\Delta\delta$ of 17.1 ppm, while **20** shows a $\Delta\delta$ of 8.1 ppm.

The $\Delta\delta$ observed for the ^{31}P chemical shifts of **19** and **20** can be explained if a difference in the preferred orientation of the substituent on the olefin ligand exists between **19** and **20**. For all complexes for which we have crystallographic data, the preferred orientation of the olefin is such that the substituent is *syn* to the Cp ring and between the Cp and the CO, as in **19a,b** (see Figure 11). However, if the olefin binds with a *syn* orientation of the substituent, steric interaction is possible between the substituent and the bulky phosphonite ligand.
It thus seems plausible that the preferred location of the substituent in **20a,b** is *anti* to the Cp ring (see Figure 11), a position which places the substituent between the phosphonite ligand and a CO instead of between the phosphonite ligand and the Cp ring.

The possibility that one of the products was an η^1-methyl acrylate complex was ruled out by the absence of olefinic proton signals in the ^1H NMR spectrum, the presence of a normal ester C–O stretch at 1740 cm^{-1} (THF) in the infrared spectrum, and the fact that all previously-known η^1-oxygen-coordinated species of this general type are red instead of the observed gold color.

A possibility that cannot be completely eliminated at this time is the idea that **19** and **20** are simply different rotamers, and the large steric bulk of the chiral phosphonite ligand restricts the rotation about the Mo–olefin bond. This hypothesis is consistent with all the spectral data; however, it seems unlikely in light of the low rotational barriers observed for the other complexes discussed in this paper (*vide supra*).

Although **19a,b** were chromatographically separable from **20a,b**, attempts to interconvert them were unsuccessful. Thus, photolysis of a pure sample of **19** resulted in no change in the ^{31}P NMR spectrum, a result that implies that binding of the olefin to the 16-electron intermediate created by loss of CO from **3c** is irreversible under the reaction conditions ($h\nu$, room temperature, 40 min). Thermal interconversion of the two sets of diastereomers also did not occur; thus, heating a pure sample of either **19** or **20** to 40 °C for 12 h resulted in no change in the ^{31}P NMR spectrum. Heating to higher temperatures resulted in decomposition of the material. It is interesting to note that interconversion of diastereomers *is* possible for the Dmpe complex **13k** → **13t** but not for **19** → **20**. This suggests that the intermolecular mechanism by which **13k** converts to **13t** is not accessible to the Pom-Pom* complexes.

Conclusions

The work presented here lends some interesting insights into the formation and stability of transition metal–olefin complexes. The formally seven-coordinate d^4 molybdenum systems we are studying appear to form stable bonds to a variety of relatively electron-deficient olefinic substrates, in contrast to d^6 rhenium,[11,12] ruthenium,[13] and iron[20] systems, which usually bind only electron-rich olefins. When the ligand is a phosphonite $[(RO)_2PCH_2CH_2P(OR)_2]$ and the preparation is carried out under thermal conditions, there is very high kinetic selectivity for binding the olefin in a manner that minimizes steric interactions between the olefin ligand and the other substituents on the metal. In the solid state, this configuration results in the olefinic substituent occupying a position *syn* to the Cp ring and between the Cp ring and the CO group. However, this kinetic selectivity nearly disappears under two conditions: (1) when the metal center is bound to the electron-rich Dmpe ligand, and (2) when the metal center is bound to the optically-active phosphonite, Pom-Pom* *and* the preparation is carried out by photolysis of $[Cp(Pom\text{-}Pom^*)Mo(CO)_2]^+$ (**3c**) in the

(20) Begum, M. K.; Chu, K.-H.; Coolbaugh, T. S.; Rosenblum, M.; Zhu, X.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 5252 and references therein.

presence of the olefin. For the Dmpe complexes, the reaction of $[Cp(Dmpe)Mo(CO)(acetone)]^+$ (**4b**) with methyl or ethyl acrylate produces a 50:50 mixture of diastereomers **13** and **14** on initial reaction, but isomerizes to the more thermodynamically stable diastereomer exclusively. For the Pom-Pom* complexes, the direct reaction of **3c** with light produces an intermediate that reacts rapidly and irreversibly with the solvent methyl acrylate to give a 60:40 mixture of **19a,b** and **20a,b**. Interconversion between **19** and **20** does not occur. The photolytic pathway to the Pom-Pom* complexes thus provides access to all possible diastereomers in this system, which can provide potentially useful intermediates for organic synthesis.

Experimental Section

General Comments. All reactions were carried out in the absence of oxygen, either in a nitrogen-filled drybox or using standard Schlenk techniques. Solvents were freshly distilled from the appropriate drying agent (THF, Na/K/benzophenone; hexane, lithium aluminum hydride; toluene, Na/benzophenone; diethyl ether, Na/K/benzophenone; acetone, potassium carbonate). Water was degassed by boiling for 10 min and cooling under nitrogen. All reagents were obtained from Aldrich Chemical Co. unless otherwise stated and were used as received. Methyl and ethyl acrylate were purified by drying over molecular sieves (4 Å) and freeze–pump–thaw degassing before use. Ammonium hexafluorophosphate (from Alfa) was dried by dissolving the solid in THF and drying the solution over 4-Å molecular sieves. The dimer $[Cp(CO)_3Mo]_2$ was purchased from Pressure Chemical Co. and was used to prepare $Cp(CO)_3MoCl$ by the literature method.[21] 1,2-Bis(dichlorophosphino)ethane and 1,2-Bis(dimethylphosphino)ethane were purchased from Strem Chemical Co. and were used without further purification. 1,2-Bis(dimethoxyphosphino)ethane was prepared by the method of King *et al.*[18] Complexes $[Cp(Pom\text{-}Pom)Mo(CO)_2]^+PF_6^-$ (**3a**) and $[Cp(Pom\text{-}Pom)Mo(CO)(acetone)]^+PF_6^-$ (**4a**) were prepared as described in ref 6.

NMR solvents were dried over the appropriate drying agent (C_6D_6 and THF-d_8 over Na/benzophenone; $(CD_3)_2CO$ over P_2O_5; CD_2Cl_2 over CaH_2). All proton NMR spectra were taken on an IBM WP-200SY operating at 200.132 MHz. All carbon NMR spectra were taken on a Bruker AM-500 operating at 125.95 MHz. Phosphorus NMR spectra were obtained either on an IBM WP-200SY operating at 80.96 MHz or on a Bruker AM-500 operating at 202.46 MHz. In order to obtain maximum resolution on the ^{31}P spectra of the chiral complexes, the spectra were acquired with a sweep width of 50–100 ppm. All chemical shifts are referenced to residual proton or carbon signals in the deuterated solvents (^1H and ^{13}C NMR) or to external phosphoric acid (^{31}P NMR). Infrared spectra were obtained using a Perkin-Elmer Model 283 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ, and the UC Berkeley Analytical Facility.

General Preparation of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-olefin})]^+PF_6^-$ Complexes. The following procedure, given for the preparation of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-methyl acrylate})]^+PF_6^-$ (**8**), is representative of the general procedure used to synthesize the olefin complexes. Details of reaction times, solvents used, and yields for each complex are given in Table I, and any differences in procedure are noted with the spectral data for each complex given below.

A solution of 225 mg (0.371 mmol) of **4a** in 5–7 mL of acetone was treated with ~1.5–2 mL of methyl acrylate and stirred at room temperature for 2 h. At the end of the reaction time, the solvent and olefin were removed under vacuum. The product was recrystallized from acetone/pentane at −35 °C.

Characterization of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-methyl acrylate})]^+PF_6^-$ (8). ^1H NMR (acetone-d_6): δ 5.45 (s, Cp), 3.95 (d, $J_{P\text{-}H}$ = 11.4 Hz, 3 H, $-POCH_3$), 3.87 (d, $J_{P\text{-}H}$ = 11.4 Hz, 3 H, $-POCH_3$), 3.78 (d, $J_{P\text{-}H}$ = 10.9 Hz, 6 H, 2 coincident $-POCH_3$ signals), 3.61 (s, $-COOCH_3$), 3.0–2.5 (m, 3 H, olefinic protons), 2.4–1.8 (m, 4 H, ethane bridge). ^{31}P NMR (acetone-d_6): δ 233.07 (d, $J_{P\text{-}P}$ = 27.7 Hz, P trans to CO), 217.42 (d, $J_{P\text{-}P}$ = 27.7 Hz, P cis to CO), −140.00 (sept, $J_{P\text{-}F}$ = 709 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 2017 (s) cm^{-1}, $\nu_{C=O}$ 1700 (s) cm^{-1}.

Characterization of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-ethyl acrylate})]^+PF_6^-$ (9). ^1H NMR (acetone-d_6): δ 5.46 (s, Cp), 4.13 and 4.01 (m, 2 H, $-COOCH_2CH_3$), 3.96 (d, $J_{P\text{-}H}$ = 11.2 Hz, 3 H, $-POCH_3$), 3.88 (d, $J_{P\text{-}H}$ = 11.3 Hz, 3 H, $-POCH_3$), 3.80 (d, $J_{P\text{-}H}$ = 11.0 Hz, 3 H, $-POCH_3$), 3.79 (d, $J_{P\text{-}H}$ = 10.4 Hz, 3 H, $-POCH_3$), 2.9–2.6 (m, 3 H, olefinic protons), 2.4-1.8 (m, 4 H, ethane bridge), 1.23 (t, $J_{H\text{-}H}$ = 7.0 Hz, $-CO_2CH_2CH_3$). ^{31}P NMR (acetone-d_6): δ 233.97 (d, $J_{P\text{-}P}$ = 24.0 Hz, P trans to CO), 217.95 (d, $J_{P\text{-}P}$ = 24.0 Hz, P cis to CO), −140.00 (sept, $J_{P\text{-}F}$ = 709 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 2015 (s) cm^{-1}, $\nu_{C=O}$ 1690 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{29}F_6MoO_7P_3$: C, 31.59; H, 4.47. Found: C, 31.36; H, 4.47.

Characterization of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-dimethyl maleate})]^+PF_6^-$ (10). The synthesis was carried out as indicated above, with the following exception. When the reaction was complete, pentane was added to precipitate the product, which was then filtered, washed with pentane, and dried under vacuum. ^1H NMR (acetone-d_6): δ 5.56 (dd, $J_{P\text{-}H}$ = 1.4, 1.4 Hz, Cp), 3.98 (d, $J_{P\text{-}H}$ = 11.4 Hz, 3 H, $-POCH_3$), 3.88 (d, $J_{P\text{-}H}$ = 11.3 Hz, 3 H, $-POCH_3$), 3.82 (d, $J_{P\text{-}H}$ = 10.6 Hz, 3 H, $-POCH_3$), 3.76 (d, $J_{P\text{-}H}$ = 11.4, 3 H, $-POCH_3$), 3.63 and 3.58 (s, 6 H, $-CO_2CH_3$), 3.01 and 2.92 (m, 2 H, olefinic protons), 2.9–2.2 (m, 4 H, ethane bridge). ^{31}P NMR (acetone-d_6): δ 229.24 (d, $J_{P\text{-}P}$ = 23.2 Hz, P trans to CO), 222.42 (d, $J_{P\text{-}P}$ = 22.0 Hz, P cis to CO), −140.03 (sept, $J_{P\text{-}F}$ = 710 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 2045 (s) cm^{-1}, $\nu_{C=O}$ 1720 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{27}F_6MoO_9P_3$: C, 31.32; H, 3.94. Found: C, 31.22; H, 4.24.

Characterization of $[CpMo(Pom\text{-}Pom)(CO)(\eta^2\text{-}p\text{-Cl-styrene})]^+PF_6^-$ (12). The synthesis was carried out as indicated above, with the following exception. When the reaction was complete, pentane was added to precipitate the product, which was then filtered, washed with pentane, and dried under vacuum. ^1H NMR (acetone-d_6): δ 7.1–7.3 (m, 4 H, Ph), 5.20 (s, Cp), 3.95 (d, $J_{P\text{-}H}$ = 11.3 Hz, 3 H, $-POCH_3$), 3.89 (d, $J_{P\text{-}H}$ = 11.0 Hz, 3 H, $-POCH_3$), 3.84 (d, $J_{P\text{-}H}$ = 11.4 Hz, 3 H, $-POCH_3$), 3.82 (d, $J_{P\text{-}H}$ = 10.8 Hz, 3 H, $-POCH_3$), 2.9–2.0 (m, 7 H, ethane bridge and olefinic protons). Note: One olefinic proton was hidden under the $P-OCH_3$ resonances. ^{31}P NMR and IR were not obtainable due to instability of the complex in solution (see text).

Preparation of $[CpMo(Dmpe)(CO)_2]^+PF_6^-$ (3b). A solution of 2.05 g (7.33 mmol, 1.1 equiv relative to Dmpe) of $Cp(CO)_3MoCl$ in 125 mL of toluene was chilled to −80 °C using an ethyl acetate/liquid N_2 slush bath. Dmpe (1.0 g, 6.6 mmol) was added via syringe, and the solution was stirred for 15 min at −80 °C, during which time rapid evolution of CO occurred, the solution changed from red-orange to light orange, and a yellow precipitate formed. The mixture was allowed to warm slowly to room temperature and stir for an additional hour. The supernatant was removed, the precipitate was washed with 2 × 40 mL of toluene to remove any unreacted $Cp(CO)_3Mo$-Cl, and the bright yellow crystals of $[CpMo(Dmpe)(CO)_2]^+Cl^-$ were dried under vacuum. To effect the anion exchange, $[CpMo(Dmpe)(CO)_2]^+Cl^-$ was extracted with 4 × 100 mL of degassed water, the extracts were filtered through glass wool, and a saturated solution of ammonium hexafluorophosphate was added to the golden-yellow solution to precipitate out the desired product. The lemon-yellow precipitate was allowed to settle, the supernatant was removed via cannula, and the precipitate was washed with 2 × 100 mL of degassed water. The solid was then dissolved in acetone and filtered through a 3-in. column of Celite and sodium sulfate. Evaporation of the solvent produced 3.29 g (6.42 mmol, 88% yield based on Dmpe) of **3b**. ^1H NMR (acetone-d_6): δ 5.67 (s, 5 H, Cp), 2.19 (app q, $J \simeq 1.7$ Hz, 2 H, ethane bridge), 2.10 (app q, $J \simeq 1.6$ Hz, 2 H, ethane bridge), 1.86 (m, 6 H, PMe_2), 1.78 (m, 6 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 55.28 (s, Dmpe), −140.13 (sept, $J_{P\text{-}F}$ = 708 Hz,

(21) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1983 (s), 1913 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{21}F_6MoO_2P_3$: C, 30.49; H, 4.13. Found: C, 30.22; H, 4.00.

Preparation of [CpMo(Dmpe)(CO)(acetone)]$^+PF_6^-$ (4b). Complex **3b** (1.16 g, 2.26 mmol) was dissolved in 110 mL of acetone, and the lemon-yellow solution was transferred to a photolysis collar.[6] The collar was placed around a Pyrex Hanovia photolysis well, and the solution was photolyzed with a mercury vapor lamp at 457 nm for 2 × 15 min (to avoid overheating), while purging with a stream of nitrogen gas to remove CO.[22] The resulting maroon solution was transferred to a flask via cannula and the solvent removed under vacuum to give 1.16 g (2.14 mmol, 95% yield) of **4b**. ^1H NMR (acetone-d_6): δ 5.30 (d, J_{P-H} = 2.5 Hz, 5 H, Cp), 2.08 (s, free acetone),[23] 2.15–2.35 (m, 4 H, ethane bridge), 1.82 (d, J_{P-H} = 8.3 Hz, 3 H, PMe_2), 1.78 (d, J_{P-H} = 9.4 Hz, 3 H, PMe_2), 1.36 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2), 1.24 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 56.0 (d, J_{P-P} = 34 Hz, P trans to CO), 60.0 (d, J_{P-P} = 34 Hz, P cis to CO), −140.1 (sept, J_{P-F} = 708 Hz, PF_6^-). IR (acetone): $\nu_{C\equiv O}$ 1847 cm^{-1}.

General Preparation of [CpMo(Dmpe)(CO)(η²-olefin)]$^+PF_6^-$ Complexes. The following procedure, given for the preparation of [CpMo(Dmpe)(CO)(η²-methyl acrylate)]$^+PF_6^-$ (**13**), is representative of the general procedure used to synthesize the olefin complexes. Details of reaction times, solvents used, and yields for each complex are given in Table II, and any differences in procedure are noted with the spectral data for each complex given below.

A solution of 100 mg (0.184 mmol) of **4b** in 5 mL of acetone was treated with ~1.5–2 mL of methyl acrylate and stirred at room temperature for 15 min. At the end of the reaction time, the solvent and olefin were removed under vacuum. The product was recrystallized from acetone/pentane at −35 °C.

Characterization of [CpMo(Dmpe)(CO)(η²-methyl acrylate)]$^+PF_6^-$ (13). Two products were formed initially, **13k** and **13t** in a 47:53 ratio (see text). The pure kinetic isomer **13k** could be isolated by recrystallization from acetone/pentane.

Data for 13k: ^1H NMR (acetone-d_6): δ 5.46 (dd, J_{P-H} = 1.4, 1.8 Hz, 5 H, Cp), 3.63 (s, 3 H, $-CO_2CH_3$), 2.6–1.9 (m, 7 H, ethane bridge and olefinic protons), 1.88 (d, J_{P-H} = 9.6 Hz, 3 H, PMe_2), 1.76 (d, J_{P-H} = 9.5 Hz, 3 H, PMe_2), 1.56 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2), 1.35 (d, J_{P-H} = 9.9 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 51.0 (d, J_{P-P} = 28 Hz, P trans to CO), 43.2 (d, J_{P-P} = 26 Hz, P cis to CO), −140.1 (sept, J_{P-F} = 708 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1994 cm^{-1}, $\nu_{C=O}$ 1695 cm^{-1}. Anal. Calcd for $C_{16}H_{27}F_6MoO_3P_3$: C, 33.70; H, 4.77. Found: C, 33.66; H, 4.73.

Data for 13t: ^1H NMR (acetone-d_6): δ 5.36 (dd, J_{P-H} = 1.7, 1.6 Hz, 5H, Cp), 3.61 (s, 3 H, $-CO_2CH_3$), 2.6–1.9 (m, 7 H, ethane bridge and olefinic protons), 1.94 (d, J_{P-H} = 9.4 Hz, 3 H, PMe_2), 1.78 (d, J_{P-H} = 9.7 Hz, 3 H, PMe_2), 1.63 (d, J_{P-H} = 8.9 Hz, 3 H, PMe_2), 1.22 (d, J_{P-H} = 9.8 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 50.6 (d, J_{P-P} = 30 Hz, P trans to CO), 42.8 (d, J_{P-P} = 31 Hz, P cis to CO), −140.1 (sept, J_{P-F} = 708 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1994 cm^{-1}, $\nu_{C=O}$ 1695 cm^{-1}.

[CpMo(Dmpe)(CO)(η²-ethyl acrylate)]$^+PF_6^-$ (14). Two products were formed initially, **14k** and **14t** in a 54:46 ratio (see text). The pure kinetic isomer **14k** could be isolated by recrystallization from acetone/pentane.

Data for 14k: ^1H NMR (acetone-d_6): δ 5.47 (dd, J_{P-H} = 1.4, 1.7 Hz, 5 H, Cp), 4.10 (m, 9 lines, 2 H, $-CO_2CH_2CH_3$), 2.7–1.7 (m, 7 H, ethane bridge and olefinic protons), 1.90 (d, J_{P-H} = 9.6 Hz, 3 H, PMe_2), 1.76 (d, J_{P-H} = 9.5 Hz, 3 H, PMe_2), 1.56 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2), 1.36 (d, J_{P-H} = 9.9 Hz, 3 H, PMe_2), 1.24 (t, J_{H-H} = 7.1 Hz, 3 H, $-CO_2CH_2CH_3$. IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1993 cm^{-1}, $\nu_{C=O}$ 1695 cm^{-1}.

Data for 14t: ^1H NMR (acetone-d_6): δ 5.37 (dd, J_{P-H} = 1.7, 1.6 Hz, 5 H, Cp), 4.06 (m, 2 H, $-CO_2CH_2CH_3$), 2.6–1.9 (m, 7 H, ethane bridge and olefinic protons), 1.94 (d, J_{P-H} = 9.4 Hz, 3 H, PMe_2), 1.78 (d, J_{P-H} = 9.7 Hz, 3 H, PMe_2), 1.63 (d, J_{P-H} = 8.9 Hz, 3 H, PMe_2), 1.24 (d, J_{P-H} = 9.8 Hz, 3 H, PMe_2), 1.25 (t, J = 7.0 Hz, 3 H, $-CO_2CH_2CH_3$). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1993 cm^{-1}, $\nu_{C=O}$ 1695 cm^{-1}.

Characterization of [CpMo(Dmpe)(CO)(η²-dimethyl maleate)]$^+PF_6^-$ (15). ^1H NMR (acetone-d_6): δ 5.42 (app t, J_{P-H} = 1.3, 1.5 Hz, 5H, Cp), 3.600 (s, 3 H, $-CO_2CH_3$), 3.598 (s, 3 H, $-CO_2CH_3$), 2.54 (d, J = 2.7 Hz, 2 H, olefinic protons), 2.6–2.0 (m, 4 H, ethane bridge), 1.95 (d, J_{P-H} = 10.3 Hz, 3 H, PMe_2), 1.75 (d, J_{P-H} = 9.8 Hz, 3 H, PMe_2), 1.66 (d, J_{P-H} = 9.3 Hz, 3 H, PMe_2), 1.32 (d, J_{P-H} = 10.1 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 47.82 (d, J_{P-P} = 26.3 Hz), 47.58 (d, J_{P-P} = 26.3 Hz), −140.1 (sept, J_{P-F} = 709 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 2030 cm^{-1}, $\nu_{C=O}$ 1720, 1700 cm^{-1}. Anal. Calcd for $C_{18}H_{27}F_6MoO_5P_3$: C, 34.52; H, 4.34. Found: C, 34.31; H, 4.02.

Characterization of [CpMo(Dmpe)(CO)(η²-α-methylene-γ-butyrolactone)]$^+PF_6^-$ (16). ^1H NMR (acetone-d_6): δ 5.46 (d, J_{P-H} = 1.9, 1.8 Hz, 5 H, Cp), 4.34 (m, 2 H, $-OCH_2CH_2-$), 2.95 (m, 1 H, olefinic proton), 2.6–2.0 (m, 5 H, ethane bridge and olefinic proton), 1.97 (d, J_{P-H} = 9.5 Hz, 3 H, PMe_2), 1.74 (d, J_{P-H} = 9.6 Hz, Hz, 3 H, PMe_2), 1.62 (d, J_{P-H} = 8.8 Hz, 3 H, PMe_2), 1.38 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2). Anal. Calcd for $C_{17}H_{27}F_6MoO_3P_3$: C, 35.07; H, 4.67. Found: C, 34.81; H, 4.75.

Characterization of [CpMo(Dmpe)(CO)(η²-styrene)]$^+PF_6^-$ (17). The synthesis was carried out as indicated above, with the following exception. When the reaction was complete, pentane was added to precipitate the product, which was then filtered, washed with pentane, and dried under vacuum. ^1H NMR (acetone-d_6): δ 7.3–7.1 and 7.0–6.9 (m, 5 H, Ph), 5.04 (dd, J_{P-H} = 1.4, 1.4 Hz, 5 H, Cp), 3.50 (app br t, J = 8 Hz, olefinic H_α to Ph), 2.65 (m, 1 H, olefinic proton cis to Ph), 2.05 (m, 1 H, olefinic proton trans to Ph), 2.5–1.8 (m, 4 H, ethane bridge), 1.98 (d, J_{P-H} = 9.1 Hz, 3 H, PMe_2), 1.76 (d, J_{P-H} = 9.6 Hz, 3 H, PMe_2), 1.64 (d, J_{P-H} = 8.8 Hz, 3 H, PMe_2), 1.32 (d, J_{P-H} = 9.7 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 52.5 (d, J_{P-P} = 32 Hz, P trans to CO), 41.2 (d, J_{P-P} = 32 Hz, P cis to CO), −140.1 (sept, J_{P-F} = 708 Hz, PF_6^-). IR (acetone): $\nu_{C\equiv O}$ 1958 cm^{-1}. Anal. Calcd for $C_{20}H_{29}F_6MoOP_3$: C, 40.83; H, 4.97. Found: C, 40.76; H, 4.87.

Characterization of [CpMo(Dmpe)(CO)(η²-p-Cl-styrene)]$^+PF_6^-$ (18). The synthesis was carried out as indicated above, with the following exception. When the reaction was complete, pentane was added to precipitate the product, which was then filtered, washed with pentane, and dried under vacuum. ^1H NMR (acetone-d_6): δ 7.25–7.08 (m, 4 H, Ph), 5.08 (dd, J_{P-H} = 1.4, 1.4 Hz, 5 H, Cp), 3.46 (app br t, J = 10 Hz, olefinic H_α to Ph), 2.7 (m, 1 H, olefinic proton cis to Ph), 2.5–1.7 (m, 5 H, olefinic proton trans to Ph and ethane bridge), 1.98 (d, J_{P-H} = 9.2 Hz, 3 H, PMe_2), 1.76 (d, J_{P-H} = 9.6 Hz, 3 H, PMe_2), 1.64 (d, J_{P-H} = 8.8 Hz, 3 H, PMe_2), 1.32 (d, J_{P-H} = 9.8 Hz, 3 H, PMe_2). ^{31}P NMR (acetone-d_6): δ 52.1 (d, J_{P-P} = 33 Hz, P trans to CO), 41.3 (d, J_{P-P} = 34 Hz, P cis to CO), −140.1 (sept, J_{P-F} = 708 Hz, PF_6^-).

Isomerization of 13k to 13t. A solution consisting of an ~50:50 mixture of **13k**:**13t** was placed in the NMR probe at 28.5 °C.[24] Spectra were acquired automatically every 2 h for 50 h. The intensities of the two methyl resonances and the integrals of the two Cp resonances were measured. The sum of the two intensities (or integrals) was calculated, as well as the percentage that each peak contributed to the total. Plots of ln(% CH_3 **13k**) vs time and ln(% Cp **13t**) were constructed, which gave k_{obs} = 4.1 × 10^6 s^{-1} (R = 0.9990) and 6.3 × 10^6 s^{-1} (R = 0.9935), respectively.

Isomerization of 14k to 14t. A solution consisting of an ~50:50 mixture of **14k**:**14t** was placed in the NMR probe at 27.8 °C.[24] Spectra were acquired automatically every 2 h for 50 h. The integrals of the two Cp resonances were measured, and the sum of the two integrals was calculated, as well as the percentage that each peak contributed to the total. Plots of ln(% Cp **14k**) vs

(22) The time necessary for complete conversion of **3b** to **4b** is variable, depending on the thickness of the glass and the number of hours on the lamp. It is best to monitor the disappearance of the starting material by IR.

(23) Free acetone is always observed because of rapid exchange with acetone-d_6 in solution.

(24) The temperature of the NMR probe was calculated using ethylene glycol and the method described by Van Geet (*Anal. Chem.* **1968**, *40*, 2227).

time and ln(% Cp **14t**) were constructed, which gave $k_{obs} = 6.1 \times 10^{6}$ s^{-1} ($R = 0.9672$) and 5.0×10^{6} s^{-1} ($R = 0.9987$), respectively.

Isomerization of 13 in the Presence of Ethyl Acrylate. A solution containing a mixture of **13k** and **13t** (200 mg, 0.369 mmol) was prepared in 5 mL of acetone. This solution was divided into two flasks, and 1.5 mL of ethyl acrylate was added to one of the flasks. The other flask served as a control. Both flasks were allowed to stir at room temperature (~20 °C), and aliquots were removed at 12, 18.5, 35, 64.5, and 85.5 h. These aliquots were evaporated to dryness, washed with pentane to remove any excess olefin, dried under vacuum, and analyzed by NMR spectroscopy. The isomerization occurred with no noticeable change in rate. No **14** was observed in any of the spectra, indicating that no crossover had occurred.

Isomerization of 14 in the Presence of Methyl Acrylate. A solution containing a mixture of **14k** and **14t** (100 mg, 0.184 mmol) was prepared in 2 mL of acetone, and 1.5 mL of methyl acrylate was added. The flask was allowed to stir at room temperature (~20 °C) for several days, and the reaction mixture was evaporated to dryness, washed with pentane to remove any excess olefin, dried under vacuum, and analyzed by NMR spectroscopy. No **13** was observed in the spectrum of the final product, indicating that no crossover had occurred.

Preparation of 1,2-Bis[bis[(*S*)-2-methyl-1-butanoxy]phosphino]ethane (Pom-Pom*). Bubble degassed (*S*)-(−)-2-methyl-1-butanol [24.67 mL, 20 g, 226 mmol, 1.2 equiv based on 1,2-bis(dichlorophosphino)ethane] and triethylamine (31.50 mL, 226 mmol, 1.2 equiv) were placed in a three-neck round-bottom flask equipped with an overhead stirrer, nitrogen inlet, and a pressure-equalized dropping funnel. Diethyl ether (100 mL) was added and the flask chilled to −84 °C. 1,2-Bis(dichlorophosphino)ethane (7.38 mL, 10.54 g, 45 mmol, 1 equiv) was added dropwise to the reaction flask over the course of ~10 min. The walls of the dropping funnel were washed down with 2 × 5 mL of diethyl ether. Almost immediately upon addition of phosphine, formation of white ammonium salts was observed. The solution was stirred for 2 h while being warmed gradually to room temperature (melting ice bath). Additional ether (100 mL) was then added to homogenize the solution. The solution was allowed to stir for an additional hour to ensure complete reaction and then transferred via a Teflon cannula with 2.5-mm bore through a fritted funnel packed with glass wool into a clean Schlenk flask. The ammonium salt cake was washed with 2 × 25 mL of diethyl ether, and the washings were filtered as before and added to the solution containing the product. The solvent was then removed under vacuum to yield 18.38 g (41.8 mmol, 93%) of viscous, yellow liquid. Density: 0.910 g/mL. $[\alpha]^{24}_{D}$ +7.6° (toluene). ^{1}H NMR (acetone-d_6): δ 3.65 (m, 8 H, POCH_2–), 1.61 (m, 4 H, POCH$_2$CH(CH$_3$)CH$_2$CH$_3$), 1.57 (app t, J_{P-H} = 6.6 Hz, 4 H, ethane bridge), 1.44 and 1.18 (m, 8 H, POCH$_2$CH(CH$_3$)CH_2CH$_3$), 0.90 (m, 24 H, POCH$_2$CH(CH_3)CH$_2$CH_3). ^{31}P NMR (acetone-d_6): 184.16 (s). Anal. Calcd for $C_{22}H_{48}O_4P_2$: C, 60.25; H, 11.03. Found: C, 60.50; H, 11.30.

Preparation of [CpMo(Pom-Pom*)(CO)$_2$]$^+$PF$_6^-$ (3c). A solution of 2.80 g (10 mmol, 1.3 equiv relative to Pom-Pom*) of Cp(CO)$_3$MoCl in 110 mL of toluene was chilled to −40 °C using an acetonitrile/liquid N_2 slush bath. A solution of 3.70 mL (3.38 g, 7.66 mmol) of Pom-Pom* in 30 mL of toluene was chilled to −40 °C and was added to the reaction mixture via cannula. The solution was stirred for 1 h at −40 °C, then placed in an ice bath, and stirred for an additonal hour. Over the 2-h period, evolution of CO was noted and the solution changed from red-orange to golden-orange. The solvent was removed under vacuum to leave crude [CpMo(Pom-Pom*)(CO)$_2$]$^+$Cl$^-$. To effect the anion exchange, [CpMo(Pom-Pom*)(CO)$_2$]$^+$Cl$^-$ was stirred for 30 min with each of 4 × 250 mL of degassed water. The extracts were filtered through glass wool, and a saturated solution of ammonium hexafluorophosphate was added to the golden-yellow solution to give a resinous precipitate of the desired product **3c**. One hundred fifty milliliters of methylene chloride was added to the flask, and the mixture was stirred for 5 min and then allowed to settle overnight to ensure complete separation of the two layers. After this period, the methylene chloride layer was a rich yellow color and was transferred via cannula into a flask containing anhydrous Na_2SO_4. The aqueous layer was washed with 2 × 50 mL of CH_2Cl_2, and these washings were added to the product. The mixture was stirred for 15 min, then transferred into a clean flask through a frit containing 3 in. of anhydrous Na_2SO_4. The solvent was removed under vacuum to leave 4.18 g (5.22 mmol, 68% yield based on Pom-Pom*) of **3c**. ^{1}H NMR (acetone-d_6): 5.79 (s, 5 H, Cp), 3.95 (m, POCH_2–), 1.80 (m, 4 H, POCH$_2$CH(CH$_3$)CH$_2$CH$_3$), 1.53 and 1.24 (m, 8 H, POCH$_2$CH(CH$_3$)CH_2CH$_3$), 1.05–0.85 (m, 24 H, POCH$_2$CH(CH_3)CH$_2$CH_3). ^{31}P NMR (acetone-d_6): 233.61 (d, J_{P-P} = 50.9 Hz, MoP), 233.28 (d, J_{P-P} = 50.8 Hz, MoP; see Figure 8), −140.04 (sept, J_{P-F} = 710 Hz, PF$_6^-$). $[\alpha]^{26}_{D}$ +6.8° (THF). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1990 (s), 1930 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{53}F_6MoO_6P_3$: C, 43.51; H, 6.67. Found: C, 43.29; H, 6.58.

Preparation of [CpMo(Pom-Pom*)(CO)(acetone)]$^+$PF$_6^-$ (4c). Complex **3c** (0.91 g, 1.14 mmol) was dissolved in 110 mL of acetone, and the golden-yellow solution was transferred to a photolysis collar.[6] The collar was placed around a Pyrex Hanovia photolysis well, and the solution was photolyzed with a mercury vapor lamp at 457 nm for 3 × 20 min (to avoid overheating), while purging with a stream of nitrogen gas to remove CO.[22] The resulting maroon solution was transferred to a flask via cannula and the solvent removed under vacuum to give 0.91 g (1.10 mmol, 96% yield) of **4c**. ^{1}H NMR (acetone-d_6): δ 5.55 (d, J_{P-H} = 1.9 Hz, 5 H, Cp), 4.1–3.6 (m, 8 H, POCH_2–), 3.0–2.4 (br, m, 4 H, ethane bridge), 2.3–1.1 (m, 12 H, POCH$_2$CH(CH$_3$)CH_2CH$_3$), 1.1–0.8 (m, 24 H, POCH$_2$CH(CH_3)CH$_2$CH_3). ^{31}P NMR (acetone-d_6) (see Figure 9): Diastereomer 1: δ 241.04 (d, J_{P-P} = 32 Hz, P cis to CO), 235.42 (d, J_{P-P} = 32 Hz, P trans to CO), −148.7 (sept, J_{P-F} = 708 Hz, PF$_6^-$). Diastereomer 2: δ 240.98 (d, J_{P-P} = 32 Hz, P cis to CO), 235.36 (d, J_{P-P} = 32 Hz, P trans to CO), −148.7 (sept, J_{P-F} = 708 Hz, PF$_6^-$). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 1890 cm^{-1}.

Preparation of [CpMo(Pom-Pom*)(CO)(η^2-methyl acrylate)]$^+$PF$_6^-$ (19) via Direct Reaction. A solution of 91 mg (0.11 mmol) of **4c** in 5 mL of acetone was treated with ~1.5–2 mL of methyl acrylate and stirred at room temperature for 2–3 h. At the end of the reaction time, the solvent and olefin were removed under vacuum. The product was then washed with pentane and dried under vacuum to yield 90 mg (0.105 mmol, 95% yield) of **19**. ^{1}H NMR (acetone-d_6): δ 5.40 (s, 5 H, Cp), 4.2–3.8 (m, 8 H, POCH_2–), 3.62 (s, –CO$_2$CH_3), 3.1–2.0 (br, m, 7 H, ethane bridge and olefinic protons), 1.9–1.1 (m, 12 H, POCH$_2$CH(CH$_3$)CH_2CH$_3$), 1.1–0.7 (m, 24 H, POCH$_2$CH-(CH_3)CH$_2$CH_3). ^{31}P NMR (acetone-d_6) (see Figure 10): Diastereomer 1: δ 224.93 (d, J_{P-P} = 31 Hz, P trans to CO), 207.76 (d, J_{P-P} = 31 Hz, P cis to CO), −140.09 (sept, J_{P-F} = 709 Hz, PF$_6^-$). Diastereomer 2: δ 224.88 (d, J_{P-P} = 31 Hz, P trans to CO), 207.62 (d, J_{P-P} = 31 Hz, P cis to CO), −140.09 (sept, J_{P-F} = 708 Hz, PF$_6^-$). IR (CH_2Cl_2): $\nu_{C\equiv O}$ 2020 cm^{-1}, ν_{C-O} 1705 cm^{-1}. Anal. Calcd for $C_{32}H_{53}F_6MoO_7P_3$: C, 44.76; H, 6.93. Found: C, 45.06; H, 6.93.

Preparation of [CpMo(Pom-Pom*)(CO)(η^2-methyl acrylate)]$^+$PF$_6^-$ (19 and 20), via Photolysis of 3c. A solution of 130 mg (0.162 mmol) of **3c** in 10 mL of methyl acrylate was placed in a glass vial sealed with a Teflon stopcock. The solution was freeze–pump–thawed 3 times and photolyzed for 15 min through a Pyrex Hanovia photolysis well using a mercury vapor lamp operating at 457 nm. The solution changed from a yellow color to a light gold during the reaction. At the end of the reaction time, approximately half of the methyl acrylate was removed under vacuum, and then pentane was added to precipitate any methyl acrylate polymer that had formed during the reaction. The resulting solution was then filtered through Celite, more methyl acrylate was removed under vacuum, and more pentane was added to precipitate the product as an oil. The supernatant was removed and the product was washed with pentane and dried under vacuum to yield 125 mg (0.146 mmol, 90% yield) of a 64:46 mixture of **19** and **20**. Separation of **19** and **20** was effected by chromatography on a 6 in. × 1 in. neutral alumina column (activity I) using THF as the eluting solvent. See above for spectral data for **19**. Spectral data for **20**: ^{1}H NMR (acetone-d_6): δ 5.40 (s, 5 H, Cp), 4.2–3.8 (m, 8 H, POCH_2–), 3.76 (s, –CO$_2$CH_3), 3.1–2.0 (br,

m, 7 H, ethane bridge and olefinic protons), 1.9–1.1 (m, 12 H, $POCH_2CH(CH_3)CH_2CH_3$), 1.1–0.7 (m, 24 H, $POCH_2CH(CH_3)CH_2CH_3$). ^{31}P NMR (acetone-d_6) (see Figure 10): Diastereomer 1: δ 235.97 (d, J_{P-P} = 23 Hz, P trans to CO), 226.84 (d, J_{P-P} = 23 Hz, P cis to CO), −140.09 (sept, J_{P-F} = 709 Hz, PF_6^-). Diastereomer 2: δ 235.89 (d, J_{P-P} = 23 Hz, P trans to CO), 226.63 (d, J_{P-P} = 23 Hz, P cis to CO), −140.09 (sept, J_{P-F} = 708 Hz, PF_6^-). IR (CH_2Cl_2): $\nu_{C=O}$ 2020 cm^{-1}, $\nu_{C=O}$ 1705 cm^{-1}.

Attempted Interconversion of 19 and 20. *Via photolysis*: An NMR tube containing 80 mg of **19** was dissolved in 0.5 mL of methyl acrylate. The sample was photolyzed for 10 min, and a ^{31}P NMR spectrum was taken. No change was noted. The solution was then photolyzed for 30 min and analyzed by ^{31}P NMR again. No change had occurred in the spectrum. The same procedure was carried out using **20** as the starting material. Again, no change was noted in the ^{31}P NMR spectrum. *Via thermal methods*: An NMR tube containing a 60:40 mixture of **19**:**20** dissolved in acetone-d_6 was heated to 40 °C for 12 h. A ^{31}P NMR spectrum taken at the end of the heating period indicated that no change had taken place.

Crystallographic Characterization of Complexes 9, 15, and 17. Crystallographic data are collected in Table IV. All specimens were mounted on glass fibers and photographically characterized. The space groups were uniquely determined by systematic absences in the data. All data sets were corrected for minor absorption effects by empirical procedures. In all cases, the Mo atom was located from a Patterson synthesis, and the remainder of the non-hydrogen atoms were located from subsequent difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. The correctness of the hand reported for **17** was determined by refinement of a multiplicative term for $\Delta f''$.

For the dimethyl maleate complex **15**, two crystallographically independent molecules make up the asymmetric unit. The differences between the molecules are small and within the range of packing effects. All computations used SHELXTL (version 5.1) software (G. Shledrick, Nicolet (Siemens) XRD, Madison, WI). Atomic coordinates are given in Tables V, VII, and IX, and selected bond distances and angles in Tables VI, VIII, and X.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE#-8905392) and the Williams College Bronfman Science Center Funds. We are grateful to Professor D. M. Heinekey and Yale University for assistance in obtaining 500-MHz NMR spectra of key compounds and to Professor John Gladysz for communicating his prepublication results to us. We are also grateful to Professor Robert G. Bergman for helpful comments on the manuscript and for the use of his laboratory facilities for some of this work.

Supplementary Material Available: Tables giving complete listings for complexes **9**, **15**, and **17** of atomic coordinates and their isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates and their isotropic thermal parameters (19 pages). Ordering information is given on any current masthead page.

OM930019T