Implicit in eqs 24 and 25 is the assumption that the volume of reaction $\Delta_r V^\infty_x$ can be approximated as a constant (for equilibrium 3) and that the reference state shall be taken to be standard conditions, specifically $P = 0.1$ MPa. It is known that the partial molar volume of dissolved CO becomes strongly pressure-dependent at temperatures in excess of approximately 400 K. Therefore, the assumption that the volume of reaction (under the present conditions) can be treated as a constant, and not a function of pressure, is not a trivial and automatic condition. A discussion of the theory regarding the reaction volume $\Delta_r V^\infty_x$ and its inclusion into the general expression for the equilibrium constant $K_x(P,T)$ determined at varying total pressures can be found in the literature.[37]

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Registry No. 3, 99572-69-7; 4, 12560-37-1; CO, 630-08-0; $CoRh(CO)_8$, 101810-30-4.

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Preparation of d^4 Molybdenum–Olefin Complexes $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (Pom-Pom = 1,2-Bis(dimethoxyphosphino)ethane) and Reactivity Studies with Carbanion Nucleophiles

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The preparation and characterization of several novel bis phosphine-substituted d^4 molybdenum-olefin complexes $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ (3) and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (4) (Pom-Pom = 1,2-bis(dimethoxyphosphino)ethane) have been carried out. Complex 3 was found to lose ethylene readily at room temperature in solution; however, complex 4 was stable for days under the same conditions. Complex 4 was further characterized by crystallographic studies. Crystal data for 4: $P2_1/c$, $a = 10.543$ (3) Å, $b = 12.055$ (2) Å, $c = 17.372$ (5) Å, $\beta = 90.54$ (3)°, $V = 2207.7$ (11) Å^3, $Z = 4$, $R(F) = 4.95\%$. The ethylene ligand is contained in the plane defined by the metal, the center of the Cp ligand, and the *trans*-phosphorus atom. The reactivity of a simple d^4 molybdenum-olefin system toward nucleophilic attack was studied as a model for the phosphine-substituted systems. Thus, reaction of $[CpMo(CO)_3(ethylene)]^+BF_4^-$ (1) with the carbanion nucleophiles $Na^+[CH(COOEt)_2]^-$ and $Na^+[CH(COOEt)(COMe)]^-$ at −80 °C gives the σ-alkyl products $Cp(CO)_3MoCH_2CH_2CH(COOEt)_2$ and $Cp(CO)_3MoCH_2CH_2CH(COOEt)(COMe)$ in good yields. The phosphine-substituted ethylene complexes 3 and 4 also react with $Na^+[CH(COOEt)_2]^-$ at −78 °C to give the σ-alkyl products $Cp(P\text{-}P)(CO)Mo(CH_2CH_2CH(COOEt)_2)$, **10a** (P-P = diphos) and **10b** (P-P = Pom-Pom).

Transition-metal–olefin complexes have been utilized extensively as reagents for organic synthesis;[1] however, only a few of the presently known systems are able to transform prochiral olefins into *chiral* organic molecules. Examples of these transformations include the Monsanto process to make L-Dopa via catalytic hydrogenation using a chiral rhodium catalyst[2] and the Sharpless epoxidation of allylic alcohols in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ and a chiral auxiliary.[3] These are important reactions that have enhanced the ability of chemists to pursue the synthesis of analogues of naturally occurring compounds that rely on chirality for their biological activity. In all of these systems, a heteroatom on the olefin is essential for bringing the olefin into the coordination sphere of the metal. An area of research that has yet to be successfully addressed is the design of transition-metal complexes that will facilitate the functionalization of prochiral olefins not necessarily containing heteroatoms.

The binding of an olefin to a transition metal has the effect of removing electron density from the bond between the unsaturated carbon atom. As a result, the ligand becomes susceptible to attack by nucleophilic reagents, including carbanion nucleophiles. This reactivity has been exploited most extensively by Hegedus with a palladium–

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olefin system[4] and Rosenblum with the $[Cp(CO)_2Fe(olefin)]^+$ system.[5] Although nucleophilic attack on the palladium–olefin complexes has been shown to be an extremely general and synthetically useful reaction, extension to the synthesis of optically active molecules is not possible because of rapid dissociation/reassociation of the olefin ligand that occurs even at low temperatures.[6] Rosenblum et al.[7] have recently succeeded in generating iron–olefin complexes $[CpFe(CO)_2(CH_2{=}CHR)]^+$ that are chiral by virtue of the asymmetry of the olefin ligand. The synthetic route to these species is lengthy for all olefins except chiral vinyl ethers, and even with the vinyl ether complexes, a dynamic equilibrium exists between diastereomers, thus making them less than ideal for chiral synthesis. Faller's work with chiral $[(NMCp)Mo(NO)(CO)(\eta^3\text{-allyl})]^+$ systems (NMCp = neomenthylcyclopentadienyl) has demonstrated that molybdenum can also be used to activate unsaturated substrates (in this case η^3-allyl ligands) toward nucleophilic attack.[8] Asymmetric induction has been achieved in these systems to produce chiral allylically substituted olefins.

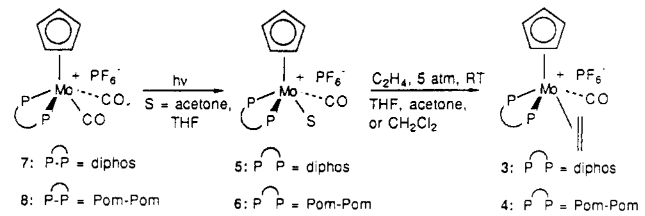
We are currently exploring the synthesis and characterization of a new class of molybdenum–olefin complexes the $[Cp(P\text{-}P)MO(CO)(olefin)]^+$ system, where P-P is a chelating phosphine ligand, that have potential for utility in the synthesis of optically active organic molecules. In addition to the site of asymmetry at the substituted carbon atom of a monosubstituted olefin ligand, there is the possibility for control of which face of the olefin will prefer to bind to the metal by virtue of the asymmetry at the metal center itself. Gladysz[9] has reported high enantiofacial selectivities in the complexation of various monosubstituted olefins to the chiral $[CpRe(NO)(PPh_3)]^+$ cation, and similar enantioselectivities have been observed in Consiglio's chiral ruthenium system $[Cp(Prophos)Ru(propylene)]^+PF_6^-$.[10]

In this paper, we report the results of our studies on molybdenum–olefin systems, specifically (a) the reactions of $[Cp(CO)_3Mo(ethylene)]^+BF_4^-$ (1) with carbanion nucleophiles, (b) the preparation of the first examples of bis phosphine-substituted achiral molybdenum–olefin complexes $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ (3) and $[Cp(Pom\text{-}Pom)MO(CO)(ethylene)]^+PF_6^-$ (4) (Pom-Pom = 1,2-bis(dimethoxyphosphino)ethane),[11] (c) crystallographic characterization of 4, and (d) the reactions of complexes 3 and 4 with carbanion nucleophiles.

Results and Discussion

Reactions of $[Cp(CO)_3Mo(ethylene)]^+BF_4^-$ (1) with Carbanion Nucleophiles. Although the chemistry of palladium- and iron–olefin complexes has been well-studied, there are surprisingly few examples of d^4 molybdenum–olefin complexes, and little is known about their reactivity with nucleophiles. The most studied example is $[Cp(CO)_3Mo(ethylene)]^+BF_4^-$ (1); however, the reactivity of even this simple system with carbanion nucleophiles had yet to be explored when we started this project. Earlier work has shown that the ethylene ligand of 1 is susceptible to attack by heteroatom nucleophiles such as ammonia and phosphines to give unusual ammonium and phosphonium salts,[12] as well as by metal anions to give ethylene-bridged dimeric species.[13] In order to determine the feasibility of using these d^4 molybdenum centers as reagents for the formation of carbon–carbon bonds, we chose to investigate the reactivity of 1 with carbanion nucleophiles, with the expectation of extending this work to the phosphine-substituted systems. Although carbon nucleophiles are significantly more reducing than heteroatom species, it seemed possible that they would react to give the σ-alkyl complexes $Cp(CO)_3MoCH_2CH_2R$ (2). We have indeed found this to be the case.

Scheme I



The ethylene complex 1 was prepared by reaction of $[CpMo(CO)_3]^+BF_4^-$ with ethylene. Attempts to extend this preparative method to substituted olefins (propylene, cyclohexene, and dimethyl maleate) gave low yields of products and was not pursued further.

The reaction of complex 1 with stabilized carbanions[14] at −80 °C in tetrahydrofuran (THF) gave good yields of the alkylated products 2a and 2b, as indicated in eq 1.

$$\underset{1}{[Cp(CO)_3Mo(ethylene)]^+} + R^- \rightarrow \underset{2}{Cp(CO)_3MoCH_2CH_2R} \quad (1)$$

$R^- = [(EtO_2C)_2CH]^-Na^+$, 67% yield, **2a**;
$[(EtO_2C)(COMe)CH]^-Na^+$, 57% yield, **2b**

The products were yellow oils that could be purified by column chromatography and were identified by ^{1}H NMR using homonuclear decoupling.

With the electrophilic reactivity of the d^4 molybdenum-coordinated olefin thus demonstrated, we proceeded to develop synthetic pathways to the phosphine-substituted systems.

Synthesis and Stability of $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ (3) and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (4). The synthetic pathway to complexes 3 and 4 is outlined in Scheme I. The starting dicarbonyl complexes $[Cp(diphos)Mo(CO)_2]^+PF_6^-$ (7) and $[Cp(Pom\text{-}Pom)Mo(CO)_2]^+PF_6^-$ (8) were prepared by using a slight modification of the method of Treichel.[15] Photolysis (through Pyrex) of 7 and 8 in a coordinating solvent such as acetone or THF resulted in loss of carbon monoxide and coordination of a solvent molecule to give the

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$[Cp(P\text{-}P)Mo(CO)(S)]^+PF_6^-$ complexes **5** (P-P = diphos) and **6** (P-P = Pom-Pom). Although both THF and acetone gave stable products, the reaction was cleaner with S = acetone. Unless the reaction is carried out in vacuo or purged with nitrogen, reassociation of carbon monoxide occurs. The yield of both products is quantitative by NMR and IR; isolated yields range from 75% to 99%.

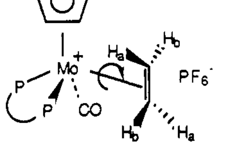
Attempts to use the neutral chloride complex Cp(P-P)Mo(CO)Cl (**9**)[16] as a precursor to the solvent complexes **5** and **6** were unsuccessful. Mixing **9** with excess $TlPF_6$, NH_4PF_6, $AlCl_3$, or $AlMe_3$ in acetone, THF, or methylene chloride resulted in no reaction. Addition of $AgBF_4$ to a THF or acetone solution of **9** resulted in oxidation of the molybdenum complex and precipitation of silver metal.

The ethylene complexes **3** and **4** were synthesized by reaction of **5** and **6** with 5 atm of ethylene in THF, acetone, or methylene chloride. At 20 °C, the red-orange color of the solvent complexes **5** and **6** fades within 5–10 min for **5** and within 15–20 min for **6**. If the preparation of **3** is carried out in THF, analytically pure orange crystals of **3** precipitate out within 5 min in 45% isolated yield. In contrast to **3**, complex **4** remains soluble even in THF solutions; however, it can be recrystallized from methylene chloride/hexane to give 64% yield of analytically pure **4**. Isolation of the intermediate solvent complexes is not necessary for the successful preparation of complexes **3** and **4**; thus, the preparation can be carried out in acetone or THF in a two-step procedure that avoids intermediate workup.

The spectral and analytical data are consistent with the formulation of complexes **3** and **4** as shown in Scheme I. The ^1H NMR spectrum of **3** at −47 °c (vide infra) shows a Cp resonance at δ 5.03. The resonances for the four ethylene protons occur as very broad peaks in the region where the ethane bridge protons of the phosphine ligand occur (2–3 ppm). The ^{13}C NMR spectrum, taken under ethylene pressure at room temperature in acetone-d_6, shows a single sharp peak at δ 43.8 for the ethylene carbons, significantly shifted from free ethylene at δ 123. The equivalence of the ethylene carbons by ^{13}C NMR implies rapid, room-temperature rotation around the molybdenum–ethylene bond.

For complex **4**, the ^{13}C NMR spectrum also shows a single resonance for the ethylene carbon atoms at δ 38.7, again indicating rapid rotation around the Mo–ethylene bond.

Two different types of ethylene protons exist when rotation is rapid, as shown by **4**. The resonances for the ethylene protons of complex **4** occur at δ 2.33 and 2.26 as apparent triplets with J = 9 Hz. The H_a protons are coupled via both geminal and cis couplings to the H_b protons.



4

The reactivities of the two ethylene complexes **3** and **4** are quite different. Complex **3** is stable in the solid state at room temperature and in solution below −20 °C or under pressure of ethylene; however, on warming a methylene chloride solution of **3** to room temperature, loss of ethylene occurs, and a single product with Cp at δ 4.95 is formed that has tentatively been identified as the CH_2Cl_2 complex $[Cp(P\text{-}P)Mo(CO)(ClCH_2Cl)]^+PF_6^-$. Full characterization has been hampered by the instability of the complex. Complex **3** also dissolves slowly in THF at room temperature to form the THF complex **5**. In contrast, complex **4** was stable at room temperature in methylene chloride or acetone solution for several days without an excess pressure of ethylene present.

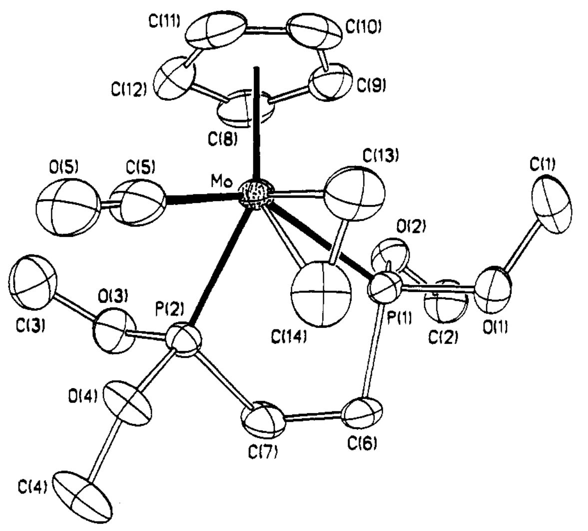


Figure 1. ORTEP drawing of $[Cp(Pom\text{-}Pom)Mo(CO)(C_2H_4)]^+PF_6^-$ (**4**). Thermal ellipsoids are drawn at the 40% probability level.

It is not yet clear whether steric or electronic differences between the two ligands are responsible for the observed differences in stability of **4** versus **3**. Cone angle measurements of the similar ligands PPh_3 (145°)[17] and $P(OMe)_3$ (128°)[18] indicate that there is a significant difference in the steric requirements of diphos versus Pom-Pom, with the decreased steric bulk of the Pom-Pom ligand enhancing the stability of complex **4** over that of **3**.

In addition to the reduced steric requirements, Pom-Pom is more electron withdrawing than diphos, as indicated by the difference in the CO stretching frequencies of $[Cp(Pom\text{-}Pom)Mo(CO)_2]^+PF_6^-$ (2000, 1943 cm^{-1}) and $[Cp(diphos)Mo(CO)_2]^+PF_6^-$ (1982, 1920 cm^{-1}). These numbers indicate that the $[Cp(Pom\text{-}Pom)Mo(CO)]^+$ moiety is a weaker π donor and a stronger σ acceptor (a stronger Lewis acid) than $[Cp(diphos)Mo(CO)]^+$, which suggests that if electronic effects are important, σ bonding is a major factor in determining the stability of the molybdenum–ethylene bond. This effect does not appear to extend to other olefins; preliminary experiments in our lab[19] indicate that a more electron-rich olefin, propylene, does not bind to either $[Cp(diphos)Mo(CO)]^+PF_6^-$ or $[Cp(Pom\text{-}Pom)Mo(CO)]^+PF_6^-$. However, extremely electron-poor olefins such as ethyl acrylate do bind successfully in both systems. This observation implies that a strong π-acceptor ligand can overcome both σ effects and steric hindrance to form a stable complex.

Crystallographic Characterization of $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (4). Complex **4** crystallizes in the monoclinic space group $P2_1/c$. An ORTEP drawing of the molecule is shown in Figure 1, and relevant crystallographic parameters are given in Tables I–III. The molecule is of the "four-legged piano stool" type, formally seven coordinate with the Cp ring at the apex of a square

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Table I. Crystallographic Data for $[Cp(Pom\text{-}Pom)Mo(CO)(C_2H_4)]^+PF_6^-$ (4)

	(a) Crystal Parameters		
formula	$C_{14}H_{25}F_6MoO_5P_3$	V, Å^3	2207.7 (11)
cryst syst	monoclinic	Z	4
space group	$P2_1/c$	D(calc), g cm^{-3}	1.706
a, Å	10.543 (3)	μ(Mo Kα), cm^{-1}	8.64
b, Å	12.055 (2)	temp, °C	20
c, Å	17.372 (5)	size, mm	0.20 × 0.27 × 0.32
β, deg	90.54 (3)	color	yellow
	(b) Data Collection		
diffractometer	Nicolet R3m	octants collected	$\pm h,+k,+l$
radiation	Mo Kα	no. of rflns collected	4227
wavelength (λ), Å	0.71073	no. of unique data	3882
monochromator	graphite	no. of obs rflns	3016
scan limits, deg	$4 \leq 2\theta \leq 50$	R(int), %	1.83
	(c) Data Reduction and Refinement		
$R(F)$, %	4.95	N_o/N_v	11.3
$R(wF)$, %	5.81	$\Delta(\rho)$, e Å^{-3}	1.01
GOF	1.374	Δ/σ	0.078

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Cp(Pom\text{-}Pom)Mo(CO)(C_2H_4)]^+PF_6^-$ (4)[a]

Mo	2094.9 (5)	6062.3 (5)	7483.8 (3)	34.4 (2)
P(1)	4285 (2)	5467 (1)	7233 (1)	38 (1)
P(2)	2410 (1)	6405 (1)	6125 (1)	38 (1)
P(3)	−2607 (1)	8035 (1)	4735 (1)	69 (1)
F(1)	−3190 (4)	7366 (4)	5375 (1)	268 (7)
F(2)	−3457 (3)	9000 (3)	4930 (3)	243 (7)
F(3)	−3599 (1)	7602 (1)	4181 (1)	189 (5)
F(4)	−2024 (4)	8705 (4)	4096 (1)	201 (5)
F(5)	−1756 (3)	7072 (3)	4540 (3)	235 (6)
F(6)	−1615 (1)	8470 (1)	5289 (1)	284 (8)
O(1)	4878 (4)	4396 (4)	7645 (3)	59 (2)
O(2)	5240 (4)	6464 (4)	7398 (2)	49 (1)
O(3)	2384 (5)	7650 (4)	5800 (3)	61 (2)
O(4)	1413 (4)	5751 (4)	5613 (2)	55 (1)
O(5)	−677 (7)	5792 (7)	6882 (5)	100 (3)
O(5′)	1702 (25)	3612 (24)	7694 (16)	56 (8)
C(1)	5037 (9)	4325 (8)	8472 (5)	92 (4)
C(2)	6577 (6)	6368 (7)	7233 (4)	65 (3)
C(3)	1324 (9)	8339 (7)	5862 (5)	94 (4)
C(4)	1412 (9)	5736 (8)	4782 (4)	82 (3)
C(5)	269 (7)	5862 (8)	7095 (5)	87 (4)
C(6)	4537 (6)	5092 (5)	6236 (3)	51 (2)
C(7)	3966 (7)	6025 (6)	5754 (4)	62 (2)
C(8)	2793 (7)	7713 (6)	7992 (4)	68 (3)
C(9)	3171 (7)	6896 (6)	8518 (4)	61 (2)
C(10)	2086 (8)	6418 (7)	8818 (4)	69 (3)
C(11)	1058 (7)	6890 (7)	8478 (4)	74 (3)
C(12)	1477 (8)	7720 (7)	7966 (5)	72 (3)
C(13)	1788 (8)	4304 (6)	7908 (5)	76 (3)
C(14)	1905 (9)	4176 (7)	7142 (6)	82 (3)

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

Table III. Selected Bond Distances and Angles for $[Cp(Pom\text{-}Pom)Mo(CO)(C_2H_4)]^+PF_6^-$ (4)

	(a) Bond Distances, Å		
Mo–P(1)	2.461 (2)	Mo–C(11)	2.283 (8)
Mo–P(2)	2.423 (7)	Mo–C(12)	2.265 (8)
Mo–C(5)	2.048(7)	Mo–C(13)	2.268 (8)
Mo–C(8)	2.295 (7)	Mo–C(14)	2.358 (9)
Mo–C(9)	2.343 (7)	Mo–CNT[a]	1.984 (7)
Mo–C(10)	2.358 (7)	C(13)–C(14)	1.347 (14)
	(b) Bond Angles, deg		
P(1)–Mo–P(2)	74.9 (1)	Mo–P(2)–O(3)	120.0 (2)
P(1)–Mo–C(5)	142.0 (3)	Mo–P(2)–O(4)	111.5 (2)
P(2)–Mo–C(5)	80.6 (2)	O(3)–P(2)–O(4)	105.1 (2)
P(1)–Mo–C(13)	85.5 (2)	Mo–P(2)–C(7)	115.6 (2)
P(2)–Mo–C(13)	119.8 (2)	O(3)–P(2)–C(7)	97.1 (3)
C(5)–Mo–C(13)	82.0 (4)	O(4)–P(2)–C(7)	105.7 (3)
P(1)–Mo–C(14)	75.6 (2)	CNT–Mo–P(1)[a]	108.6 (3)
P(2)–Mo–C(14)	86.1 (3)	CNT–Mo–P(2)[a]	129.2 (3)
C(5)–Mo–C(14)	74.1 (4)	CNT–Mo–C(5)[a]	109.4 (4)
C(13)–Mo–C(14)	33.8 (3)	CNT–Mo–C(13)[a]	111.0 (4)
Mo–P(1)–O(1)	121.3 (2)	CNT–Mo–C(14)[a]	144.7 (4)
Mo–P(1)–O(2)	109.9 (2)	P(1)–C(6)–C(7)	106.3 (4)
O(1)–P(1)–O(2)	106.5 (2)	P(2)–C(7)–C(6)	110.1 (4)
Mo–P(1)–C(6)	112.8 (2)	Mo–C(13)–C(14)	76.8 (5)
O(1)–P(1)–C(6)	99.6 (3)	Mo–C(14)–C(13)	69.4 (5)
O(2)–P(1)–C(6)	105.2 (3)	Mo–C(5)–O(5)	177.5 (9)

[a] CNT = centroid of Cp ring, C(8)–C(12).

pyramid. An interesting feature of the molecule is that the ethylene 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, a relationship that is easily seen by looking down the molybdenum–ethylene bond (see Figure 2). Extended Huckel calculations[20] on the molecule $[Cp(PH_3)_2(CO)Mo(C_2H_4)]^+$ indicate that in the absence of any steric effects there is no energy difference between the observed orientation and the one where the ethylene ligand is rotated by 90°, corresponding to overlap with the d_{xy} and d_{z^2} orbitals, respectively.[21] However, the observed orientation is higher in energy by 2–3 kcal/mol than the lowest possible energy conformation predicted by the calculations (see Figure 3).

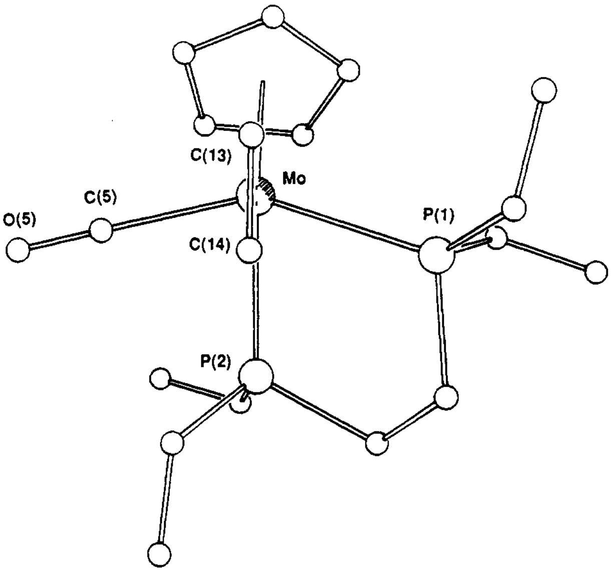

Figure 2. View down the Mo–ethylene bond of $[Cp(Pom\text{-}Pom)Mo(CO)(C_2H_4)]^+PF_6^-$ (4), showing the orientation of the olefin ligand.

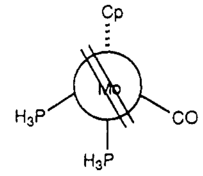

Figure 3. Lowest energy conformation calculated for $[Cp(PH_3)_2Mo(CO)(C_2H_4)]^+$.

The C–C bond length for the bound ethylene in 4 is 1.347 (14) Å, only slightly longer than that for free ethylene

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(20) Hoffmann, R.; Sylvestre, J. Private communication.

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at 1.33 Å,[22] which implies that there is little backbonding involved in the molybdenum–olefin bond. This bond length is similar to that observed for ethylene bound to Pt(II) in Zeiss's salt, $[Cl_3Pt(C_2H_4)]^-$ (1.37 Å)[23] or ethylene bound to iron in $[Cp(CO)(PPh_3)Fe(C_2H_4)]^+AsF_6^-$ (1.39 Å)[24] but is significantly shorter than that for ethylene bound to Pt(0) in $(PPh_3)_2Pt(C_2H_4)$ (1.43 Å),[23] where backbonding plays an important role. The C–C bond distances observed for a d^6 Mo(0) complex, *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$, 1.39 and 1.41 Å, are significantly longer than those observed for our d^4 Mo(II) complex.[25]

The molybdenum–carbon distances of 2.268 (8) and 2.358 (9) Å for the ethylene carbon atoms are different, with the carbon atom that is nearer the Cp ring closer to the metal by 0.1 Å. The Mo–P bond distances of 2.461 (2) and 2.423 (2) Å for **4** are slightly shorter than the mean distance of 2.50 Å observed for $[Cp(diphos)Mo(\eta^4\text{-}C_6H_8)]^+PF_6^-$,[26] which indicates that Pom-Pom is more electron withdrawing than diphos, in accordance with the infrared data obtained for **3** and **4** (vide supra).

Reaction of $[Cp(diphos)Mo(CO)(ethylene)]^+PF_6^-$ (3) and $[Cp(Pom\text{-}Pom)Mo(CO)(ethylene)]^+PF_6^-$ (4) with Carbanion Nucleophiles. Preliminary studies on the reactivity of the bisphosphine-substituted ethylene complexes **3** and **4** with a carbanion nucleophile are promising. Thus, reaction of sodium diethyl malonate with **3** (**4**) in THF solution at −80 °C (20 °C) for 20 min (45 min) gives 52% (40%) unoptimized isolated yields of the alkylated products $Cp(P\text{-}P)Mo(CO)(CH_2CH_2CH(CO_2Et)_2)$, **10a** (P-P = diphos) and **10b** (P-P = Pom-Pom). The products are easily isolated and can be purified by a simple extraction and recrystallization. Demonstration of reactivity of this type indicates that these complexes compare favorably to other metal–olefin systems as reagents for the formation of carbon–carbon bonds.

Conclusions

Representative members of a new class of molybdenum–olefin complexes have been synthesized and characterized by spectroscopic and crystallographic means, and the reactivity of these complexes with carbanion nucleophiles has been demonstrated. Studies on the reactivity of the olefin complexes **3** and **4** with a variety of carbanions is presently under investigation, and the work is being extended to include *chiral* chelating phosphonite ligands and substituted olefins that are prochiral. Recent work with optically active rhenium[9] and ruthenium[10] systems has shown that chiral metal centers can retain configuration during ligand substitution reactions and can subsequently bind a prochiral olefin stereoselectively. Thus, it seems likely that these chiral molybdenum–olefin complexes will be able to produce optically active organic molecules on reaction with nucleophilic reagents. We are presently working toward that goal.

Experimental Section

General Comments. All reactions were carried out in the absence of oxygen, either in a nitrogen-filled drybox or by using standard Schlenk techniques. Solvents were freshly distilled from an appropriate drying agent (THF, Na/K/benzophenone; hexane, calcium hydride; pentane, calcium 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. Potassium hydride was obtained as a 60% suspension in mineral oil and was washed with hexane to remove the oil prior to use. Ethylene was received from Matheson Gas Co. and was passed through 4A molecular sieves before use. The dimer $[Cp(CO)_3Mo]_2$ was purchased from Pressure Chemical Co. and was used to prepare $Cp(CO)_3Mo(Cl)$ by the literature method.[27] $[Cp(diphos)Mo(CO)_2]^+PF_6^-$ [28] and $Cp(diphos)Mo(CO)Cl$[16] were prepared by literature methods. 1,2-Bis(dichlorophosphino)ethane was purchased from Strem Chemical Co. and was used without further purification. 1,2-Bis(dimethoxyphosphino)ethane was prepared by the method of King et al.[11]

NMR solvents were dried over an 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). ^1H NMR spectra were taken on either an IBM WP-200SY operating at 200.132 MHz or a Bruker AM-500 operating at 500 MHz. ^{31}P NMR spectra were obtained on an IBM WP-200SY operating at 80.96 MHz. ^{13}C NMR spectra were taken on a Bruker AM-500 operating at 125.95 MHz. 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 by using a Perkin-Elmer Model 283 spectrometer. Elemental analyses were performed by Desert Analytics, Tuscon, AZ.

$[Cp(CO)_3Mo(ethylene)]^+BF_4^-$ (1). This preparation is a new route to a previously known complex.[29] To a solution of $[Cp(CO)_3Mo]_2$ (5.0 g, 0.010 mol) in 250 mL of methylene chloride was added 3.91 g (0.020 mol) of $AgBF_4$. The reaction mixture was stirred for 5 h at room temperature, during which time the solution changed from a cherry red to a deep purple. The progress of the reaction was followed by monitoring the carbonyl region of the infrared spectrum (ν_{CO} $[Cp(CO)_3Mo]_2$ (in CH_2Cl_2): 2010 (m), 1960 (s), 1920 (s) cm^{-1}; ν_{CO} $[Cp(CO)_3Mo]^+BF_4^-$ (in CH_2Cl_2): 2070 (m), 1990 (s) cm^{-1}).[30] The solution was filtered, 100 mL of hexane was added, and the solution was cooled to −60 °C until dark purple crystals began to form. Addition of an additional 150 mL of hexane induced further precipitation. The supernatant was removed and the solid dried under vacuum to leave 1.7 g (0.0052 mol, 26%) of $[Cp(CO)_3Mo]^+BF_4^-$. The cation was then dissolved in 30 mL of methylene chloride and 5 atm of ethylene was introduced. The reaction mixture was stirred overnight, the solvent evaporated, and the yellow product recrystallized from acetone/Et_2O to yield 1.17 g (0.00325 mol, 52% based on $[Cp(CO)_3Mo]^+BF_4^-$, 18% based on $AgBF_4$) of **1**. ^1H NMR (acetone-d_6): δ 6.30 (s, 5 H Cp), 3.60 (s, 4 H, ethylene). IR (in acetone): 2105 (w), 2060 (s), 2005 (m) cm^{-1}, metal carbonyls.[31]

$Cp(CO)_3MoCH_2CH_2CH(COOEt)_2$ (2a). A suspension of 50 mg (2 mmol) of NaH in 10 mL of THF was cooled to −40 °C, 0.8 mL (0.84 g, 0.005 mol) of diethyl malonate was added dropwise, and the solution was stirred for 30 min. This solution was added to a suspension of 250 mg (0.69 mmol) of **1** in 10 mL of THF at −40 °C. When the two solutions were mixed, the bright yellow suspension of **1** changed to a homogeneous dark gold solution. This solution was stirred and allowed to warm to 0 °C over a 1-h period. The mixture was extracted with pentane (4 × 15 mL), and the extracts were filtered and cooled to −60 °C to precipitate an oily liquid. The supernatant was removed at −60 °C, and the residual solvent was removed under vacuum to yield 0.2 g (0.47 mmol, 68% based on **1**) of **2a**. Recovered product: 0.12 g (0.27 mmol, 40%). Further purification could be effected by chromatography on neutral alumina (Activity III), using 2:1 diethyl ether:pentane as the eluent. ^1H NMR (benzene-d_6): δ 4.61 (s, 5 H, Cp), 4.00 (m, 4 H, OCH_2CH_3 of ester groups), 3.45 (t, J = 7 Hz, 1 H, $MoCH_2CH_2CH(COOEt)_2$), 2.41 (m, 2 H,

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[23] Reference 1, p 150.

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[30] Beck[29b] reports ν_{CO} for $[Cp(CO)_3Mo]^+BF_4^-$ (CH_2Cl_2) as 2071, 1988 cm^{-1}.

[31] This agrees well with Beck's spectral data[29b] for **1**. IR (Nujol): 2104, 2053, 2001 cm^{-1}. ^1H NMR (acetone-d_6): δ Cp 6.35.

MoCH$_2$CH_2CH(COOEt)$_2$), 1.51 (m, 2 H, MoCH_2CH$_2$CH(COOEt)$_2$), 0.87 (m, 6 H, OCH$_2$CH_3 of ester groups). IR (THF): 2000 (m), 1900 (s) cm^{-1}, metal carbonyls, 1730 (s) cm^{-1}, ester carbonyls. Anal. Calcd for C$_{17}$H$_{20}$MoO$_7$: C, 47.24; H, 4.66. Found: C, 47.54; H, 4.74.

Cp(CO)$_3$MoCH$_2$CH$_2$CH(COOEt)(COMe) (2b). A suspension of 100 mg (4.2 mmol) of NaH in 10 mL of THF was cooled to −40 °C, 1.5 mL (1.53 g, 0.012 mol) of ethyl acetoacetate was added dropwise, and the solution was stirred for 30 min. This solution was added to a suspension of 630 mg (1.75 mmol) of **1** in 15 mL of THF at −40 °C. When the two solutions were mixed, the bright yellow suspension of **1** changed to a homogeneous dark gold solution. This solution was stirred and allowed to warm to 0 °C over a 1-h period, and the reaction was quenched by adding 5 mL of degassed water. The mixture was extracted with ether (4 × 15 mL), and the extracts were dried over anhydrous sodium sulfate, filtered, and cooled to −60 °C to precipitate an oily solid. The supernatant was removed at −60 °C and the residual oil was dissolved in ether and chromatographed on a neutral alumina column (Activity III), using 1:1 ether:hexane as the eluent. The product came off as a yellow band and 0.40 g (1.0 mmol, 57% based on **1**) of **2b** was obtained. ^{1}H NMR (benzene-d_6): δ 4.64 (s, 5 H, Cp), 3.89 (quartet, J = 7 Hz, 2 H, OCH_2CH$_3$ of ester group), 3.33 (t, J = 7 Hz, 1 H, MoCH$_2$CH$_2$CH(COOEt)(COOCH$_3$)), 2.20 (m, 2 H, MoCH$_2$CH_2CH(COOEt)$_2$), 1.92 (s, 3 H, COCH_3), 1.40 (m, 2 H, MoCH_2CH$_2$CH(COOEt)$_2$), 0.91 (t, J = 7 Hz, 3 H, OCH$_2$CH_3 of ester group). IR (benzene): 2040 (m), 1924 (s) cm^{-1}, metal carbonyls, 1745 (m), 1715 (m) cm^{-1}, ester and ketone carbonyls.

[CpMo(diphos)(CO)(ethylene)]$^+$PF$_6^-$ (3). Complex **5** (64 mg, 0.097 mmol) was dissolved in 4 mL of THF and freeze–pump–thaw-degassed twice. A measured amount of predried ethylene (passed through 4A molecular sieves) equal to 5 atm was condensed into the reaction vessel, and the mixture was allowed to warm to room temperature and stir for 20 min, gradually turning from maroon to gold and slowly precipitating out gold crystals of **3**. The reaction mixture was cooled to −10 °C overnight to ensure complete recrystallization. The ethylene pressure was released, the supernatant was removed at −80 °C, and the residual solvent was removed under vacuum to yield 27 mg (0.044 mmol, 45%) of analytically pure **3**. ^{1}H NMR (CD$_2$Cl$_2$ at −47 °C): δ 7.9–7.0 (m, 20 H, Ph's), 5.03 (s, 5 H, Cp), 2.88 (br m, 2 H, ethane bridge), 2.44 (br m, 6 H, ethane bridge and coordinated ethylene). ^{13}C NMR (acetone-d_6 under 5 atm of ethylene pressure): δ 135–128 (m, Ph's), 94.1 (s, Cp), 43.8 (s, coordinated ethylene), 32.4, 29.2 (m, ethane bridge). ^{31}P NMR (CD$_2$Cl$_2$ under 5 atm of ethylene pressure): δ 88.5 (d, $J_{\text{P-P}}$ = 33 Hz, P cis to CO), 66.2 (d, $J_{\text{P-P}}$ = 33 Hz, P trans to CO), −146.2 (sept, $J_{\text{P-F}}$ = 708 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$): 1888 (s) cm^{-1}, Mo–CO. Anal. Calcd for C$_{34}$H$_{33}$F$_6$MoOP$_3$: C, 53.70; H, 4.37. Found: C, 54.05; H, 4.87.

[CpMo(Pom-Pom)(CO)(ethylene)]$^+$PF$_6^-$ (4). Complex **6** (1.0 g, 1.65 mmol) was dissolved in 20 mL of CH$_2$Cl$_2$ or acetone and freeze–pump–thaw-degassed twice. A measured amount of predried ethylene (passed through 4A molecular sieves) equal to 5 atm was condensed into the reaction vessel, and the mixture was allowed to warm to room temperature and stirred for 2 h, gradually turning from maroon to bright yellow. The solvent was removed under vacuum to yield 0.942 g (1.63 mmol, 99%) of pure **4**. Further purification could be effected by recrystallization from CH$_2$Cl$_2$/hexane. ^{1}H NMR (acetone-d_6): δ 5.51 (t, J = 0.9 Hz, 5 H, Cp), 3.91 (d, $J_{\text{P-H}}$ = 11.4 Hz, 3 H, OCH$_3$), 3.82 (d, $J_{\text{P-H}}$ = 11.4 Hz, 3 H, OCH$_3$), 3.74 (d, $J_{\text{P-H}}$ = 11.0 Hz, 3 H, OCH$_3$), 3.60 (d, $J_{\text{P-H}}$ = 11.2 Hz, 3 H, OCH$_3$), 2.5–2.1 (m, 4 H, ethane bridge), 2.33, 2.26 (app t, $J_{\text{H-H}}$ = 9.0 Hz, ethylene protons). ^{13}C NMR (acetone-d_6): δ 90.1 (s, Cp), 55.0 (d, $J_{\text{P-C}}$ = 6.6 Hz, POCH$_3$), 54.5 (d, $J_{\text{P-C}}$ = 11.1 Hz, POCH$_3$), 54.42 (d, $J_{\text{P-C}}$ = 11.5 Hz, POCH$_3$), 54.38 (d, $J_{\text{P-C}}$ = 7.7 Hz, POCH$_3$), 38.7 (s, coordinated ethylene), 27.7 (dd, $J_{\text{P1-C1}}$ = 32.5 Hz, $J_{\text{P2-C1}}$ = 17.2 Hz, bridge C), 25.1 (dd, $J_{\text{P1-C2}}$ = 34.2 Hz, $J_{\text{P2-C2}}$ = 19.1 Hz, bridge C). ^{31}P NMR (acetone-d_6): δ 232.9 (d, $J_{\text{P-P}}$ = 33 Hz, P trans to CO), 224.3 (d, $J_{\text{P-P}}$ = 33 Hz, P cis to CO), −146.3 (sept, $J_{\text{P-F}}$ = 708 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$): 2000 (s) cm^{-1}, Mo-CO; 1010 cm^{-1}, C–O of POCH$_3$. Anal. Calcd for C$_{14}$H$_{25}$F$_6$MoO$_5$P$_3$: C, 29.18; H, 4.37. Found: C, 29.35; H, 4.27.

[CpMo(diphos)(CO)(THF)]$^+$PF$_6^-$ (5). Complex **7** (305 mg, 0.496 mmol) was dissolved in 75 mL of THF, and the yellow solution was transferred to a photolysis "collar" (see Figure 4). 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 × 10 min (to avoid overheating), while purging with a stream of nitrogen gas to remove CO.[32] After photolysis, the maroon solution was evaporated to dryness, and the resulting solid was recrystallized from THF/hexane to give 202 mg (0.306 mmol, 62% yield) of **5**. ^{1}H NMR (THF-d_8): δ 8.1–7.12 (m, 20 H, Ph's), 5.44 (d, J = 2.7 Hz, 5 H, Cp), 3.61 (m, 4 H, coordinated THF), 3.10, 2.88 (br m, ethane bridge), 1.77 (m, 4 H, coordinated THF). ^{13}C NMR (THF-d_8): 136–128 (m, Ph's), 95.5 (s, Cp), 30.6, 36.8 (m, ethane bridge), coordinated THF under solvent resonances. IR (in CH$_2$Cl$_2$): 1850 cm^{-1}, metal carbonyl.

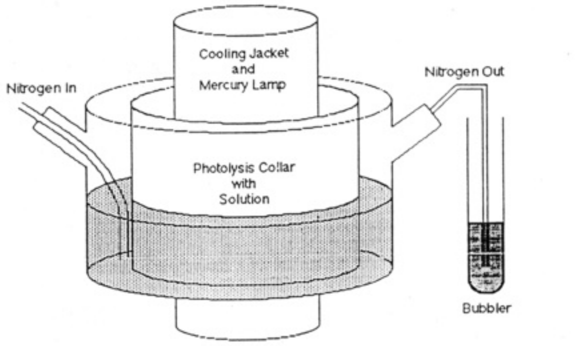

Figure 4. Photolysis apparatus used to prepare compounds **5** and **6**.

[CpMo(Pom-Pom)(CO)(acetone)]$^+$PF$_6^-$ (6). Complex **8** (2.50 g, 4.34 mmol) was dissolved in 125 mL of acetone, and the pale yellow solution was transferred to a photolysis collar (see Figure 4). 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.[32] After photolysis, the maroon solution was evaporated to dryness and the resulting solid was recrystallized from acetone/hexane to give 2.55 g (42.1 mmol, 97% yield) of **6**. ^{1}H NMR (acetone-d_6): δ 5.56 (d, J = 2.0 Hz, 5 H, Cp), 3.76 (d, $J_{\text{P-H}}$ = 11.5 Hz, 3 H, OCH$_3$), 3.69 (d, $J_{\text{P-H}}$ = 12.3 Hz, 3 H, OCH$_3$), 3.62 (d, $J_{\text{P-H}}$ = 10.6 Hz, 3 H, OCH$_3$), 3.54 (d, $J_{\text{P-H}}$ = 10.7 Hz, 3 H, OCH$_3$), 2.80, 2.70, 2.61, 2.52 (m, 4 H, ethane bridge), 2.08 (s, 6 H, coordinated acetone). ^{31}P NMR (benzene-d_6): δ 241.2 (d, $J_{\text{P-P}}$ = 33 Hz, P trans to CO), 235.8 (d, $J_{\text{P-P}}$ = 33 Hz, P cis to CO), −147.4 (sept, $J_{\text{P-F}}$ = 708 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$): 1895 (s) cm^{-1}, Mo-CO; 1662 (s) cm^{-1}, coordinated acetone; 1008 cm^{-1}, C–O of POCH$_3$. Anal. Calcd for C$_{15}$H$_{28}$F$_6$MoO$_6$P$_3$: C, 29.67; H, 4.65. Found: C, 29.73; H, 4.58.

[CpMo(Pom-Pom)(CO)$_2$]$^+$PF$_6^-$ (8). A solution of 3.86 g (13.8 mmol, 1.3 equiv relative to Pom-Pom) of Cp(CO)$_3$MoCl in 150 mL of toluene was chilled to −40 °C by using an ethyl acetate/liquid N$_2$ slush bath. Pom-Pom (2.3 g, 2.3 mL, 10.6 mmol) was added via syringe, and the solution was stirred for 1 h, during which time the solution changed from red-orange to light orange with the formation of a yellow precipate. The mixture was allowed to warm to room temperature, the supernatant was filtered off, and the pale yellow crystals of [CpMo(Pom-Pom)(CO)$_2$]$^+$Cl$^-$ were dried under vacuum. To effect the anion exchange, [CpMo(Pom-Pom)(CO)$_2$]$^+$Cl$^-$ was dissolved in 750 mL of degassed water, and a saturated aqueous solution of ammonium hexafluorophosphate was added to precipitate out the desired product. The solution was then filtered, the precipitate was dissolved in methylene chloride (25 mL), and the methylene chloride layer was washed twice with 50-mL portions of water and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent produced 5.05 g (8.76 mmol, 83% yield based on Pom-Pom) of **8**. ^{1}H NMR (acetone-d_6): δ 5.82 (s, 5 H, Cp), 3.83 (m, 4 lines, 12 H, OCH$_3$), 2.51 (m, 2 H, ethane bridge), 2.44 (m, 2 H, ethane bridge). ^{31}P NMR (acetone-d_6): δ 234.3 (s, Pom-Pom), −146.4 (sept, $J_{\text{P-F}}$ = 708 Hz, PF$_6^-$). IR (CH$_2$Cl$_2$): 2000 (s), 1943 (s) cm^{-1}, Mo–CO; 1008 cm^{-1}, C–O of POCH$_3$.

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[32] The time necessary for complete conversion of **7** to **5** or **8** to **6** is variable from 5 to 30 min, 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.

CpMo(diphos)(CO)($CH_2CH_2CH(COOEt)_2$) (10a). A solution of NaH (8 mg, 0.33 mmol) in 3 mL of THF was cooled to −80 °C, and 77.6 μL (0.50 mmol, 82 mg) of diethyl malonate was added. This solution was stirred for 30 min and then added to a suspension of 75 mg (0.123 mmol) of **3** in THF at −80 °C. The resulting mixture was allowed to stir at −80 °C for 20 min, during which time the solution changed from a yellow suspension to a homogeneous yellow solution of the product. The solution was allowed to warm to 0 °C, with stirring continued for an additional 30 min. The solvent was removed under vacuum, and the product was washed with cold hexane (2 × 1 mL). Chromatography on a short (~3 in. × 0.25 in.) neutral alumina (Activity I) column using 1:1 Et_2O:THF as eluent yielded 42 mg (0.067 mol, 54%) of bright yellow **10a**. ^1H NMR (benzene-d_6): 8–6.8 (m, 20 H, Ph), 4.42 (d, J = 1.8 Hz, 5 H, Cp), 3.89 (m, 4 H, OCH_2CH_3 of ethyl groups), 3.39 (t, J = 7.0 Hz, $MoCH_2CH_2CH(COOEt)_2$), 2.6–1.8 (m, 6 H, ethane bridge on diphos and $MoCH_2CH_2$), 1.12 (t, J = 7 Hz, 2 H, $MoCH_2CH_2$), 0.88 (m, 6 H, OCH_2CH_3 of ethyl groups). IR (CH_2Cl_2): 1840 (s) cm^{-1}, Mo–CO; 1740, 1719 (m) cm^{-1}, ester carbonyls. Anal. Calcd for $C_{39}H_{40}MoO_5P_2$: C, 63.57; H, 5.72. Found: C, 63.35; H, 5.79.

CpMo(Pom-Pom)(CO)($CH_2CH_2CH(COOEt)_2$) (10b). A solution of KH (13.3 mg, 0.34 mmol) in 5 mL of THF was cooled to −80 °C, and 69 mL (0.44 mmol) of diethyl malonate was added. This solution was stirred for 50 min and then added to a suspension of 100 mg (0.17 mmol) of **4** in THF at −80 °C. The resulting mixture was allowed to warm to room temperature and stirred for 45 min, during which time the solution went from a yellow suspension to a homogeneous yellow solution of the product. The solvent was removed under vacuum, and the product was washed with cold hexane (3 × 1 mL) to yield 80 mg (0.136 mmol, 80%) of crude CpMo(Pom-Pom)(CO)($CH_2CH_2CH(COOEt)_2$). Recrystallization from hexane yielded 40 mg (0.068 mmol, 40%) of analytically pure product. ^1H NMR (benzene-d_6): δ 4.97 (s, 5 H, Cp), 4.08–3.95 (m, OCH_2CH_3 of ethyl groups), 3.70 (dd, J_{H-H} = 5.9, 6.1 Hz, $MoCH_2CH_2CH(COOEt)_2$), 3.53 (d, J_{P-H} = 12.4 Hz, 3 H, OCH_3), 3.30 (d, J_{P-H} = 10.6 Hz, 3 H, OCH_3), 3.09 (d, J_{P-H} = 10.9 Hz, 3 H, OCH_3), 2.94 (d, J_{P-H} = 10.0 Hz, 3 H, OCH_3), 2.90, 2.48 (m, 2 H, $MoCH_2CH_2$), 2.02, 1.93, 1.78, 1.71 (m, 4 H, ethane bridge), 1.79, 1.23 (m, 2 H, $MoCH_2CH_2$), 1.02–0.92 (m, 6 H, OCH_2CH_3 of ethyl groups). ^{13}C NMR (acetone-d_6): δ 89.4 (s, Cp), 60.7, 60.6 (s, $-OCH_2CH_3$ of ethyl groups), 58.7 (s, $MoCH_2CH_2CH(COOEt)_2$), 52.0 (m, 2 overlapping $POCH_3$), 51.3 (d, J_{P-C} = 5.1 Hz, $POCH_3$), 50.6 (d, J_{P-C} = 12.6 Hz, $POCH_3$), 37.5, 37.6 (s, $MoCH_2CH_2$), 30.4 (dd, J_{P-C} = 21.0, 22.0 Hz, ethane bridge carbon), 28.5 (dd, J_{P-C} = 18.7, 19.2 Hz, ethane bridge carbon), 14.2, 14.1 (s, OCH_2CH_3 of ethyl groups). ^{31}P NMR (benzene-d_6): δ 262.6 (s), 247.1 (s). IR (CH_2Cl_2): 1855 (s) cm^{-1}, Mo–CO; 1742, 1722 (m) cm^{-1}, ester carbonyls; 1013 cm^{-1}, C–O of $POCH_3$. Anal. Calcd for $C_{21}H_{36}MoO_9P_2$: C, 42.72; H, 6.15. Found: C, 41.48; H, 6.15.

Crystallographic Characterization of [Cp(Pom-Pom)-Mo(CO)(C_2H_4)]$^+PF_6^-$ (4). Crystallographic data are collected in Table I. Systematic absences in the diffraction data unambiguously determined the monoclinic space group as $P2_1/n$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were treated as idealized isotropic contributions. A persistent feature of difference maps late in the refinement process was a peak, O(5′), located approximately in the Mo–C(13)–C(14) plane at a distance from the Mo equal to the Mo···O(5) distance. This was interpreted as a alternative position for the CO ligand, requiring, as well, an alternative position for the ethylene molecule. The additional C_2H_4 and CO carbon atom sites were not resolved. The O(5′) occupancy was refined to 18(1)%.

All software is contained on the SHELXTL (5.1) library (O. Sheldrick, NicoletXR, Madison, WI).

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Supplementary Material Available: Complete listings of bond lengths and angles, anisotropic thermal parameters, and H atom coordinates and their isotropic thermal parameters (6 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.