mmol) of amino diester **4c** to 71 mg (70%) of cycloheptane **19** after Kugelrohr distillation (120 °C at 1 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.20–3.0 (m, 11 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 9.79 (d, 1 H, J = 2 Hz); IR ($CHCl_3$) 1720 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 242 (13), 215 (37), 150 (49), 145 (100), 113 (38), calcd for $C_{12}H_{18}O_5$ 242.115, found 242.113.

Cyclohexanone 20. General Procedure J. To a solution of 129 mg (0.477 mmol) of LTP in 8 mL of 1:1 methylene chloride/THF was added 250 mg of molecular sieves (4 Å) at 25 °C. To this mixture was added a solution of 105 mg (0.492 mmol) of aminoketo ester **4g** in 2 mL of 1:1 methylene chloride/THF. After the solution was stirred for 10 min at 25 °C, 61 mg of powdered potassium *tert*-butoxide was added. The mixture was stirred for 1.5 h at 25 °C, 1 mL of methanol was added, and hydrogen was bubbled through the mixture for 1.5 h. The solution was immediately placed on an MPLC column and chromatographed with 0.7% aqueous ammonia/6.3% methanol/chloroform to afford 37 mg (35%) of cyclohexanone **20**: ^{1}H NMR ($CDCl_3$) δ 1.20–1.87 (m, 3 H), 1.90–3.40 (m, 6 H), 2.27 (s, 6 H), 3.67 (s, 3 H), 6.20 (s, very br, 1 H); IR ($CHCl_3$) 1600, 1645, 2770, 2810 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 213 (20), 154 (100), 122 (55), calcd for $C_{11}H_{19}NO_3$ 213.136, found 213.139.

Cycloheptanone 21. Following procedure J, 108 mg (0.475 mmol) of aminoketo ester **9c** was converted to 70 mg (65%) of cycloheptanone **21**: ^{1}H NMR ($CDCl_3$) δ 1.17–2.03 (m, 5 H), 2.07–3.00 (m, 7 H), 2.20 (s, 5.4 H), 2.25 (s, 0.6 H), 3.07–3.60 (m, 1 H), 3.69 (s, 0.3 H), 3.75 (s, 2.7 H); IR ($CHCl_3$) 1600, 1640, 1705, 1735, 2770, 2810 cm^{-1}; mass spectrum (70 eV), m/e (rel intensity) 227 (47), 200 (8), 151 (19), 125 (10), 58 (100), calcd for $C_{12}H_{21}NO_3$ 227.151, found 227.145.

Attempted Intramolecular Carbopalladation of Sulfide Keto Ester 9e. Following procedure H, 100 mg of sulfide keto ester **9e** failed to cyclize. TLC and ^{1}H NMR analysis indicated the presence of starting olefin complex only, even after 1 month at 25 °C.

Attempted Carbopalladation of 4c. Procedure G was followed with the exception that the solution was diluted to 0.01 M in amino diester **4d** and molecular sieves (4 Å) were added prior to the addition of the amino diester **4d**. Gas chromatographic analysis after reduction of a small aliquot of the reaction mixture failed to show even traces of a new product until the solution had been stirred for 48 h at 25 °C. Within 2 weeks at 25 °C, the starting material was completely consumed. TLC analysis of the reduced reaction mixture revealed a minimum of nine materials.

Attempted Carbopalladation of Aminoketo Ester 4f. Procedure J was followed with the exception that the solution was diluted to 0.01 M in aminoketo ester **4f**. TLC analysis showed that the starting material was completely consumed in ca. 1 week. After reduction with hydrogen, as in procedure J, TLC analysis revealed at least nine products.

Acknowledgment. We thank the National Institutes of Health for generous financial support of our program. JRZ acknowledges a predoctoral fellowship from Tennessee Eastman Co. NMR spectra were obtained with the aid of the NSF Regional NMR Facility at the University of South Carolina. Special thanks are due Prof. H. C. Dorn for his aid in obtaining and interpreting NMR spectra.

Registry No. 1a, 36697-88-8; **1b**, 1002-37-5; **1c**, 1002-50-2; **1d**, 94517-78-9; **2a**, 94517-79-0; **2b**, 94517-80-3; **2c**, 94517-81-4; **2d**, 94517-82-5; **3a**, 94517-83-6; **3b**, 94517-84-7; **3c**, 94517-85-8; **3d**, 94517-86-9; **3e**, 94517-87-0; **4a**, 94517-88-1; **4b**, 94517-89-2; **4c**, 94517-90-5; **4d**, 94517-91-6; **4e**, 94517-92-7; **4f**, 94517-93-8; **4g**, 94517-94-9; **5**, 64244-47-9; **6**, 94517-95-0; **7a**, 27354-43-4; **7b**, 76047-81-9; **8a**, 94517-96-1; **8b**, 94517-97-2; **9a**, 94517-98-3; **9b**, 94517-99-4; **9c**, 94518-00-0; **9d**, 94518-01-1; **9e**, 94518-02-2; **9f**, 94518-03-3; **10a**, 94518-17-9; **10b**, 94518-18-0; **10c**, 94518-19-1; **11a**, 94518-04-4; **11b**, 94518-05-5; **12a**, 94596-00-6; **12b**, 94596-01-7; **12c**, 94596-02-8; **13** (isomer 1), 94518-06-6; **13** (isomer 2), 94518-07-7; **14**, 94518-08-8; **15**, 94518-09-9; **16**, 94518-20-4; **17**, 94518-10-2; **18**, 94518-11-3; **19**, 94518-12-4; **20**, 94518-13-5; **21**, 94518-14-6; LTP, 15525-45-8; Na-($CH_3COCHCO_2$-*t*-Bu), 64770-14-5; $NaCH(CO_2Me)_2$, 18424-76-5; $CH_2(CO_2Me)_2$, 108-59-8; $(CH_2COCHCO_2Me)^{2-}$, 30568-00-4; *cis*-tetrahydropyranyl alcohol, 57323-06-5; *cis*-allylic iodide, 94518-15-7; tetrahydropyranyl keto ester, 94518-16-8.

Alkoxide Triggered Ligand Substitution. Highly Stereoselective Formation of Unsaturated Phosphinite Ester—$Mo(CO)_4$ Chelates and the X-ray Crystal Structure of $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$

Randall T. DePue,[†] David B. Collum,*[†] Joseph W. Ziller,[‡] and Melvyn Rowen Churchill*[‡]

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, and the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received August 20, 1984*

Abstract: Treatment of $(L)Mo(CO)_4$ (L = η^2-pyridyl dimethylphosphinite) at 0 °C in diethyl ether with 1.1 equiv of lithium alkoxides (ROLi) derived from unsaturated alcohols affords $(\eta^3$-$PMe_2OR)Mo(CO)_4$ chelates. The reaction involves nucleophilic attack at the phosphorus with cleavage of the chelate bridge and subsequent rapid extrusion of the alkoxide of 2-hydroxypyridine. The procedure is illustrated by using a number of allylic, homoallylic, 1°, 2°, and 3° alkoxides. When the alkoxides contain asymmetric centers, disastereofacial coordination selectivities of 3 → 30:1 are observed. A molecular structure determination of $(\eta^3$-$PMe_2OR)Mo(CO)_4$ (**10**; R = 1-phenylallyl) was effected. Crystals of $(PMe_2OCPhCH{=}CH_2)Mo(CO)_4$ belong to the centrosymmetric triclinic space group $P\bar{1}$ with cell parameters a = 7.416 (1) Å, b = 8.649 (1) Å, c = 13.572 (2) Å, α = 98.48 (1)°, β = 94.08 (1)°, γ = 97.29 (1)°, and Z = 2. Diffraction data (Mo Kα, 2θ = 4.5–45.0°) were collected with a Syntex $P2_1$ automated diffractometer and the structure refined to R_F = 2.3% for all 2223 reflections (R_F = 1.8% for those 1984 data with $|F_o| > 6\sigma|F_o|$. The complex has a central Mo(0) atom that is octahedrally coordinated to four carbonyl ligands and with the other two (mutually cis) sites being taken up by the phosphorus atom and the terminal olefin function of the chelating $PMe_2OCHPhCH{=}CH_2$ ligand; the Mo—P distance is 2.446 (1) Å, Mo—C (olefin) distances are Mo—C(1) = 2.430 (3) Å and Mo—C(2) = 2.399 (3) Å, and the bond length of the coordinated olefin is C(1)–C(2) = 1.370 (4) Å.

It has become clear that transition-metal-mediated processes will play an increasingly important role in natural products synthesis.[1] Despite the often elegant work in this area, however, a surprisingly small percentage of this methodology has successfully reached the stage of being used *routinely* by the average organic synthesis practitioner. This derives in part from the paucity of information pertaining to relative stereocontrol, that is, the in-

[†] Cornell University.
[‡] State University of New York at Buffalo.

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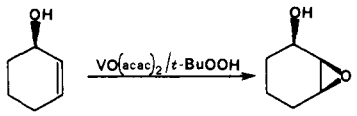
troduction into a substrate of additional stereocenters in a controlled manner relative to *preexisting* centers of asymmetry.[2]

We are intrigued by the role that neighboring group assistance has played in the application of transition-metal chemistry to organic synthesis. One prominent example involves the epoxidation of unsaturated alcohols catalyzed by high valent metals (eq 1),



(1)

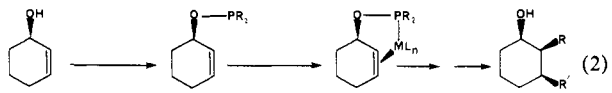
in which the orientation of the proximate hydroxyl group is determinant of the resulting epoxide stereochemistry via an as-of-yet ill-defined[3] interaction with the metal complex.[4] Recently, Crabtree[5] and Stork[6] reported procedures for Ir-catalyzed, hydroxyl-directed hydrogenations of unsaturated alcohols.

Although there are other less substantiated reports of alcohol- and alkoxide-directed transition-metal chemistry,[7,8] it can be anticipated that the number of examples will not increase dramatically in the forseeable future for the simple reason that many organometallic complexes and reactive intermediates cannot tolerate protic conditions. In a series of pioneering studies, Holton et al. circumvented this problem en route to a seven-step prostaglandin $F_{2\alpha}$ synthesis by developing an aprotic chelation technology.[9,10] Although all efforts to utilize allylic alcohols masked by ligating alcohol protecting groups failed, mandating the use of a dimethylamino moiety in place of an allylic hydroxyl function,[9b] Semmelhack recently reported a related palladium-catalyzed lactonization procedure that appeared to derive stereocontrol from a nearby hydroxyl moiety.[11]

We describe herein preliminary efforts aimed at achieving stereocontrolled chelation of unsaturated alcohols under aprotic conditions via the corresponding phosphinite esters. Our approach is illustrated by using the $Mo(CO)_4$ fragment and hinges on a novel procedure that chemically triggers a coordination site at the metal center *concomitant* to substrate attachment.

Results

Access to chelated phosphinite esters of type i could in principle put us within reach of a large number of metal-mediated olefin transformations with important stereochemical implications. There are numerous reports of chelated unsaturated phosph*ine* derivatives[12] as well as several reports by Hartwell et al. of complexes analogous to ii prepared from substitutionally labile d^8 rhodium complexes.[13] However, conversion of allylic alcohols to such

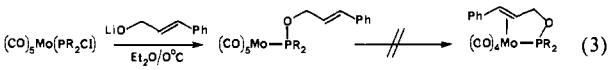


(2)

i ii

phosphinite ester chelates as depicted in eq 2 was found to be generally quite difficult due to the anticipated oxygen, moisture, and thermal lability[14] of i as well as ensuing metal-mediated Arbuzov rearrangements upon attempted chelation.[15] To circumvent these problems, we have developed an alternative strategy founded on the well-documented alcoholysis reactions of coordinated halophosphines.[16]

In preliminary studies, we found that alcoholyses of halophosphine–metal complexes could be effected under aprotic conditions by using 1.1 equiv of lithium or potassium alkoxides (eq 3). By use of aryloxy phosphines (aryl phosphinites) as



(3)

halophosphine equivalents, similar displacements could be carried out on low-valent metal complexes that normally undergo facile, irreversible oxidative additions to P–Cl bonds.[17] However, the lability of these η^1 metal complexes of allyl phosphinite esters was decisively underscored by our complete failure to induce formation of chelate **1** by using the gamut of photochemical, thermal, and redox-based CO substitution procedures.

A solution to this problem is depicted in eq 4. Hitherto unknown ligand **2** was prepared on multigram scales from dimethylchlorophosphine and 2-hydroxypyridine. Chelate complex **3** was prepared equally efficiently (70–80% yield) by heating **2** with $Mo(CO)_6$ in toluene at 110 °C for 3 h. We anticipated that upon alkoxy substitution of the pyridinyloxy group of **2**, the loss of the stabilization derived from the chelate effect and the steric congestion common to metal complexes of 2-substituted pyridines[18] would combine to make intermediate iii substitutionally quite labile. Indeed, reaction of **3** with the lithium salt of cinnamyl alcohol in ether at 0 °C for 1–2 h afforded the hitherto elusive

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(17) For example, attempts to prepare $CpCo(PR_2Cl)CO$ afforded only polymer. Alternatively, $CpCo(PR_2OAr)CO$ could be prepared and substituted with unsaturated alkoxides. Efforts to extrude CO failed in this case also, however.

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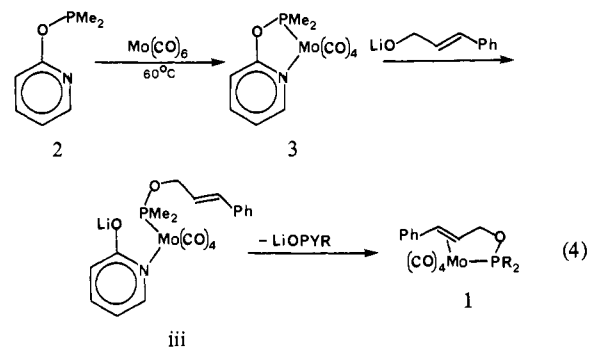
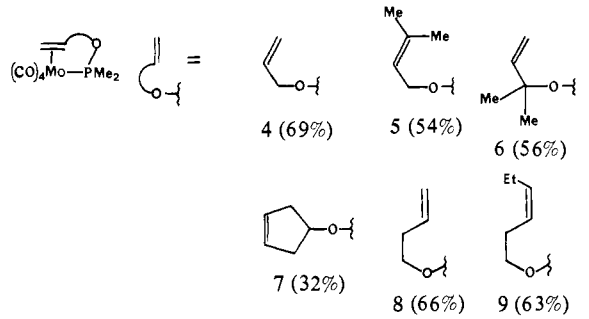


(4)

chelate **1** in 55% recrystallized yield. Labile intermediate iii was never observed.

The versatility of the procedure was illustrated by preparing a range of unsaturated phosphinite ester chelates (**4–9**). The numbers in parentheses represent isolated, recrystallized yields.

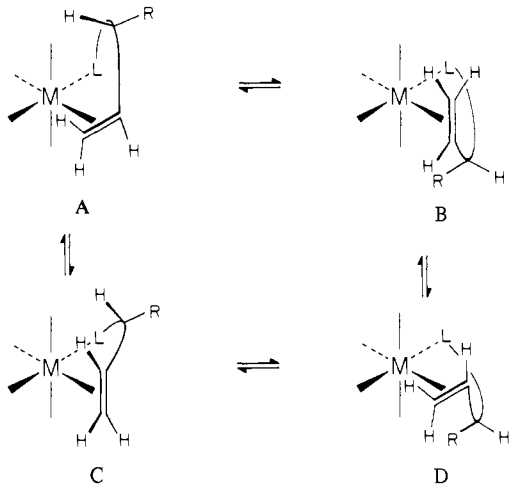


The hindered, less reactive cases required reaction times of up to 10 h. All efforts to obtain analogous chelates of cyclohexenols and cyclohexenecarbinols failed, affording complex mixtures containing appreciable amounts of the $Mo(CO)_5(\eta^1\text{-}PMe_2OR)$ derivatives.[19]

Chelates **4–9** exhibited a number of characteristic spectral features including 1.0–3.0 ppm upfield shifts of the vinyl proton resonances[20,21] as well as diastereotopic allylic and phosphinite methyl proton resonances. These features were not found in the spectra of their nonchelated $Mo(CO)_5(\eta^1\text{-}PMe_2OR)$ counterparts.[19]

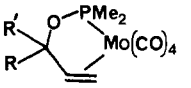
Although molecular model analysis indicated that the olefin moieties could align along either the P–Mo–CO or the CO–Mo–CO axes with equal facility for most alkenol substrates, ^{13}C and ^{31}P NMR analyses demonstrated the chelates to be stereoisomerically homogeneous. In the variable temperature $^{31}P\{^1H\}$ NMR in the spectrum (toluene-d_8) of allyl complex **4**, the single peak at 166.5 ppm (125 °C) reversibly shifted downfield to 169.6 ppm without detectable broadening upon cooling to −90 °C. The ^{31}P NMR spectrum of chelate **1** exhibited a similar temperature dependence upon cooling from 90 (166.3 ppm) to −80 °C (169.1 ppm). These subtle changes in chemical shift could have resulted from changes in distribution of a rapidly equilibrating mixture of axis alignment isomers (presumably occurring via a facile[22] nondissociative olefin rotation). A molecular structure elucidation for one complex (vide infra) exhibited olefin alignment parallel to the P–Mo–CO axis.

Chart I

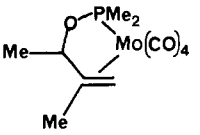


Stereoselectivity of Chelation. Because of their exceptional steric and electronic properties, transition metals have tremendous potential to interact with organic substrates highly stereoselectively. We sought insight into some of the factors that might determine the stereoselectivity of alkenol–metal interaction by investigating olefin diastereofacial coordination selectivities. In principle, four possible stereoisomeric phosphinite ester chelates can be derived from propenols or butenols containing asymmetric centers (A–D: Chart I). However, isomers corresponding to A and B coordinated to the same olefin face as well as C and D should be interconvertible by facile,[22] nondissociative olefin rotations.

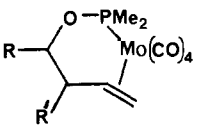
Using the procedures described above, chelates **10–16** were prepared. The poor recrystallized yield for **12** arose from its exceptional solubility in neat pentane even at reduced temperatures. The stereoisomer ratios (indicated in parentheses) were



10; R = Ph, R′ = H (30:1, 47% yield)
11; R = Me, R′ = H (22:1, 57% yield)
12; R = i-Pr, R′ = (≥30:1, 20% yield)
13; R = Me, R′ = Et(5:1, 41% yield)



14 (3:1, 67% yield)



15; R = H, R′ = Me (13:1, 66% yield)
16; R = Me, R′ = H (7:1, 69% yield)

determined from the integrations of selected resonances in the ^1H, ^{31}P, and ^{13}C NMR spectra. Since the chelations of the achiral alkenols were spectroscopically homogeneous, the minor components in **10–16** were attributed to the opposite mode of olefin face coordination. The stereoisomer ratios could not be appreciably enhanced by multiple recrystallization, indicating the diastereofacial selectivities to be thermodynamically derived. Since stereochemical assignments using standard spectroscopic arguments were not possible, a molecular structure determination of **10** was effected as described below.

Molecular Structure of $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$, 10. The complex crystallizes as discrete molecular units; there are no abnormally short intermolecular contacts. The atomic numbering scheme and the molecular stereochemistry are shown in Figures 1 and 2. A stereoview is provided in Figure 3. Selected interatomic distances and angles are given in Table I and II.

If we treat "midpt" (the midpoint of the olefinic ligand C(1)–C(2)) as occupying one coordination position, then the molecule approximates to an octahedral complex of molybdenum(0). The three trans angles are P–Mo–C(15) = 173.8 (1)°,

(19) Reaction of $(PMe_2Cl)Mo(CO)_5$ with the various unsaturated alkoxides afforded the $(\eta^1\text{-}PMe_2OR)Mo(CO)_5$ derivatives for spectral comparison.

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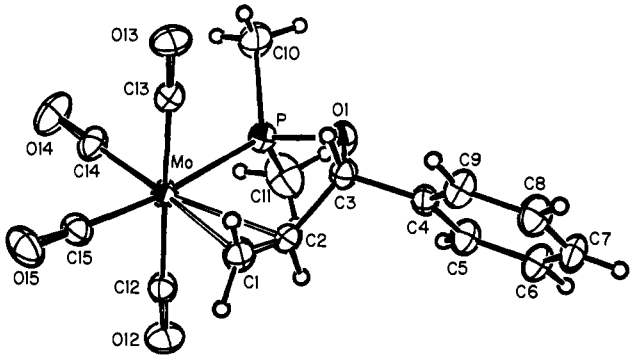

Figure 1. General view of the $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$ molecule, **10**, showing the conformation of the chelate ring (ORTEP-II diagram, 30% probability ellipsoids for all non-hydrogen atoms).

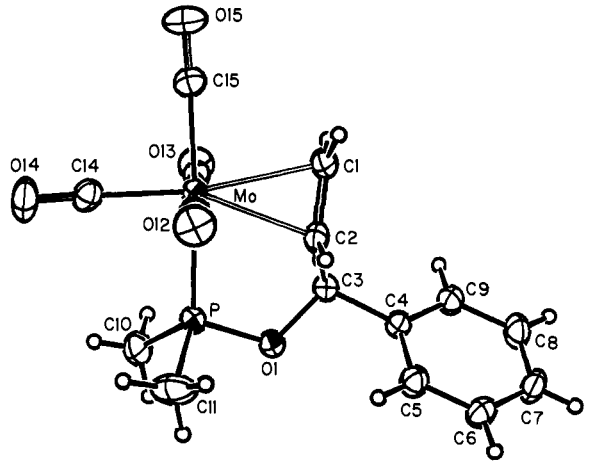

Figure 2. $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$ molecule, showing the alignment of the olefin with the P—Mo—C(15)—O(15) axis and the displacement of attached atoms from coplanarity with C(1) and C(2).

C(12)–Mo–C(13) = 178.8 (1)°, and C(14)–Mo–midpt = 173.3°.

Parameters within the $Mo(CO)_4$ moiety are within the expected ranges. Mo–CO distances are (in order) Mo–C(14) = 1.984 (3) Å, Mo–C(13) = 2.028 (3) Å, Mo–C(15) = 2.032 (3) Å, and Mo–C(12) = 2.052 (3) Å. The *shortest* of these is for the carbonyl ligand trans to the coordinated olefin; there is, here, little competition for d_π–p_π back-donation. The C–O distances range from 1.134 (4) to 1.157 (4) Å (average = 1.143 (10) Å), while Mo–C–O angles are from 176.8 (3)° to 178.5 (3)° (average = 177.5 (8)°).

We now turn our attention to the chelating $PMe_2OCHPhCH{=}CH_2$ ligand. This is linked to the Mo(0) atom via its phosphorus atom (Mo–P = 2.446 (1) Å) and the terminal olefinic function (Mo–midpt = 2.316 Å; Mo–C(1) = 2.430 (3) Å; Mo–C(2) = 2.399 (3) Å). This ligand could be regarded as forming a "$5^1/_2$"-membered chelate ring; as might be expected, this localized system has a puckered conformation. The olefin lies with its axis parallel to the O(15)–C(15)–Mo–P direction and with the phenyl group on the γ carbon atom (C(3)) in an exo configuration. All four atoms connected to the olefin are displaced from coplanarity with atoms C(1) and C(2) in a direction away from the molybdenum atom. The coordinated olefin has a bond length of 1.370 (4) Å—a value increased only slightly from the accepted C=C distance of ~1.335 Å found in noncoordinated olefins. This is consistent with rather weak Mo–olefin bonding as is also evidenced by the long Mo–C(olefin) distances and the shortening of the trans Mo–CO bond (vide supra). All other distances and angles in this system are normal, viz., P–Me = 1.808 (5)–1.816 (5) Å, P–O = 1.626 (2) Å, O–C(sp^3) = 1.447 (3) Å, C(sp^3)–C(sp^2) = 1.500 (4)–1.515 (4) Å, and C–C(phenyl) = 1.367 (5)–1.392 (5) Å. The 15 refined C–H distance range from 0.86 (3) to 0.99 (3) Å, averaging 0.93 (5) Å—in reasonable agreement with the accepted[22] X-ray value of 0.95 Å.

Table I. Interatomic Distances (Å) (with esd's) for $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$, **10**

(A) Distances Involving Molybdenum Atom			
Mo–P	2.446 (1)	Mo–C(12)	2.052 (3)
Mo–C(1)	2.430 (3)	Mo–C(13)	2.028 (3)
Mo–C(2)	2.399 (3)	Mo–C(14)	1.984 (3)
Mo–midpt[a]	2.316	Mo–C(15)	2.032 (3)
(B) Distances within the $PMe_2OCHPhCH{=}CH_2$ Chelating Ligand			
P–C(10)	1.816 (5)		
P–C(11)	1.808 (5)		
P–O(1)	1.626 (2)		
C(1)–C(2)	1.370 (4)		
C(2)–C(3)	1.500 (4)		
C(3)–O(1)	1.447 (3)		
C(3)–C(4)	1.515 (4)		
(C) C—O Distances in Carbonyl Ligands			
C(12)–O(12)	1.134 (4)	C(14)–O(14)	1.157 (4)
C(13)–O(13)	1.140 (4)	C(15)–O(15)	1.141 (4)

[a] midpt is the midpoint of the C(1)–C(2) bond.

Table II. Interatomic Angles (deg) for $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$, **10**

(A) Angles about Molybdenum Atom			
P–Mo–C(1)	102.2 (1)	C(13)–Mo–midpt	90.3
P–Mo–C(2)	70.7 (1)	C(14)–Mo–midpt	173.3
P–Mo–midpt	86.5	C(15)–Mo–midpt	96.7
P–Mo–C(12)	92.2 (1)	C(12)–Mo–C(13)	178.8 (1)
P–Mo–C(13)	87.0 (1)	C(12)–Mo–C(14)	91.3 (1)
P–Mo–C(14)	86.8 (1)	C(12)–Mo–C(15)	93.1 (1)
P–Mo–C(15)	173.8 (1)	C(13)–Mo–C(14)	89.7 (1)
C(1)–Mo–C(2)	33.0 (1)	C(13)–Mo–C(15)	87.8 (1)
C(12)–Mo–midpt	88.8	C(14)–Mo–C(15)	89.9 (1)
(B) Angles within the $PMe_2OCHPhCH{=}CH_2$ Ligand			
Mo–C(1)–C(2)	72.3 (2)	C(2)–C(3)–C(4)	111.9 (2)
Mo–P–O(1)	109.7 (1)	O(1)–C(3)–C(4)	107.2 (2)
Mo–P–C(10)	118.5 (2)	C(3)–C(4)–C(5)	121.7 (2)
Mo–P–C(11)	121.4 (2)	C(3)–C(4)–C(9)	119.8 (2)
P–O(1)–C(3)	115.3 (2)		
C(10)–P–O(1)	100.6(2)		
C(11)–P–O(1)	102.0 (2)		
C(1)–C(2)–C(3)	124.5 (3)		
C(2)–C(3)–O(1)	110.8 (2)		
(C) Carbonyl Angles			
Mo–C(12)–O(12)	177.0 (3)	Mo–C(14)–O(14)	177.8 (3)
Mo–C(13)–O(13)	178.5 (3)	Mo–C(15)–O(15)	176.8 (3)

Discussion

With the procedures described above an organic substrate can be attached to a metal fragment under aprotic conditions with concomitant release of a coordination site to effect an additional substitution at the metal center. The illustrative chelations of unsaturated alkoxides proceeded smoothly using 1°, 2°, 3°, allylic, and homoallylic alkenols, without competing Arbuzov-like formation of (η^3-allyl)Mo complexes[14] or olefin isomerizations.[20] Although we failed to obtain chelates derived from a variety of cyclohexenols and cyclohexenecarbinols, these were inordinately demanding substrates. Reports of isolable[24] or even spectro-

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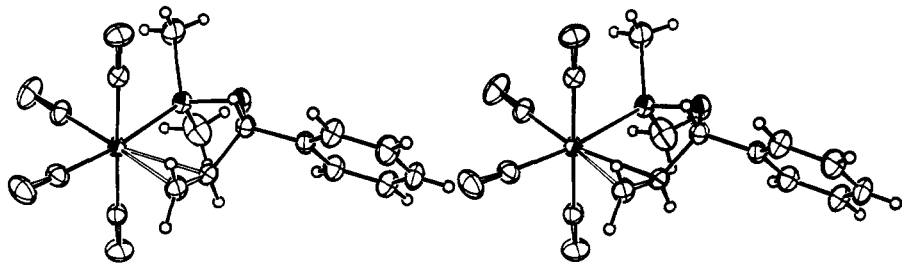

Figure 3. Stereoview of the $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$ molecule.

scopically observable[25] transition-metal complexes of cyclohexenes are surprisingly rare due to inexplicably small formation constants.[26]

From the molecular structure determination of **10**, we can begin to understand the source of the high diastereofacial coordination selectivities.[27] The molecular structure of **10** corresponds to the abstractly depicted isomer A (Chart I) in which the olefin is aligned along the P–Mo–CO axis and coordinated to the molybdenum on the olefin face that places the phenyl substituent in the least hindered exo orientation. In contrast, the isomer corresponding to isomer D in Chart I containing the same axis alignment but with the phenyl group in the endo position would encounter serious interactions between the phenyl group and the cis-disposed coordinated CO. However, it is apparent that large preferences for the olefin moieties to align parallel to the P–Mo–CO axes were prerequisites for diastereofacial coordination selectivities. The isomer corresponding to isomer C in Chart I, in which the molybdenum is coordinated to the alternative olefin face with the alternative alignment along the CO–Mo–CO axis, would also have the phenyl group in a sterically favorable exo position. Therefore, nonselective olefin alignment would have made the isomers corresponding to C and A approximately equal in energy, resulting in poor diastereofacial coordination selectivity.

Although we can assign the structure of the major stereoisomers of chelates **11–13** through analogy to **10**, the major isomers of chelates **14–16** cannot be unambiguously assigned at this time.

Metal-catalyzed epoxidation stereoselectivities are related to the coordination stereoselectivities described herein to the extent that both entail diastereoselective olefin face differentiation. At the outset of this work, we were optimistic that a direct comparison of the two would prove both interesting and instructive. For example, 3-buten-2-ol and 1-phenyl-2-propen-1-ol (the alcohols corresponding to chelates **11** and **10**) undergo $VO(acac)_2$-catalyzed epoxidation with relatively modest 4:1 and 5:1 diastereofacial selectivities, respectively.[4] However, *the major coordination stereoisomers correspond to the minor epoxide stereoisomers.* Although this underscores the lingering doubt as to whether the epoxidations proceed via direct metal–olefin and metal–hydroxyl interactions,[3] relationships between the alkenol epoxidation and coordination diastereofacial selectivities are not readily discernable at present.

Conclusions

Reactions of alkoxides with metal chelates of ligand **2** provide novel modes of triggering coordinative unsaturation at a metal center. The specific examples described herein involve the formation of $Mo(CO)_4$ chelates of unsaturated phosphinite esters and illustrate the potential of transition metals to interact highly stereoselectivity and *rationally* with organic substrates. We are currently investigating the applications of alkoxide-triggered coordinative unsaturation in organic and organometallic synthesis.

Experimental Section

Reagents and General Procedures. All preparations were carried out by using standard vacuum line and glovebox techniques under an atmosphere of argon. Solvents were dried and deoxygenated over sodium/benzophenone ketyl containing 1% tetraglyme and manipulated by vacuum transfer. The $Mo(CO)_6$ was obtained from Strem and sublimed prior to use. The 2-hydroxypyridine (Aldrich) was sublimed at full vacuum and then recrystallized from chloroform/diethyl ether. Chlorodimethylphosphine was prepared by a literature procedure (ref 28).

Microanalyses were performed by Alfred Bernhardt Analytisches Laboratorien, Elbach, West Germany. Infrared spectra were run on a Perkin-Elmer Model 137 spectrometer. Proton NMR were run on Varian CFT-20 80-MHz or a Bruker 300-MHz spectrometer. ^{31}P and ^{13}C NMR spectra were recorded on a JEOL FX 90Q 90-MHz spectrometer with chemical shifts reported in parts per million relative to 85% H_3PO_4 and tetramethylsilane, respectively. Low-resolution mass spectral data were obtained by using chemical ionization (CI) on a Finnigan Model 3300 mass spectrometer. The reported peaks represent the central peaks of seven peak isotopic envelopes.

2-Pyridyl Dimethylphosphinite (2). To a solution of 2-hydroxypyridine (75.5 g, 0.794 mol) in anhydrous tetrahydrofuran (1.10 L) under nitrogen was added sequentially dimethylchlorophosphine (73.1 g, 0.758 mol) at 0 °C and *N,N,N',N'*-tetramethylethylenediamine (60.0 mL, 0.398 mol, added slowly over a 30-min period). Following stirring at 0 °C for 1 h, the resulting thick, white mixture was stirred for an additional 15 h at room temperature. The mixture was filtered under nitrogen and the supernatant was stripped to a pale yellow oil. Vacuum distillation afforded 48.0 g of **2** (41% yield) as a pyrophoric colorless oil (bp 55–57 °C at 0.1 mm): ^1H NMR (C_6D_6) δ 8.06 (m, 1 H), 7.03 (m, 1 H), 6.56 (m, 2 H), 1.34 (d, J_{PC} = 7.1 Hz, 6 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 116.4 (s). Despite the apparent spectroscopic homogeneity of **2**, acceptable elemental analysis could not be obtained.

Tetracarbonyl(2-pyridyl dimethylphosphinite-*N*,*P*)molybdenum (3). A mixture of molybdenum hexacarbonyl (7.93 g, 30.0 mmol) in toluene (50 mL) under nitrogen was treated with ligand **2** (3.70 mL, 30.0 mmol) and then heated to 110 °C for 3 h. After cooling to room temperature, the solution was concentrated to an approximate 40-mL volume and layered with hexane (90 mL). Further cooling to −55 °C and filtering afforded 6.82 g of **3** as pale yellow plates. Concentration of the filtrate and further layering with hexane afforded an additional 0.97 g of **3** (total yield: 71%): mp 107.0–108.5 °C; ^1H NMR (C_6D_6) δ 8.16 (m, 1 H), 6.59 (m, 1 H), 6.18 (m, 1 H), 5.82 (m, 1 H), 1.30 (d, J_{PH} = 4.5 Hz, 6 H): $^{31}P\{^1H\}$ NMR (C_6D_6) δ 168.1 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 163.7 (d, J_{PC} = 7.3 Hz), 152.8 (d, J_{PC} = 5.4 Hz), 140.4 (s), 118.1 (s), 112.1 (d, J_{PC} = 4.0 Hz), 23.9 (d, J_{PC} = 18.8 Hz), CO's not observed; IR ($CHCl_3$) ν_{CO} 2025 (m), 1925 (s), 1900 (s), 1865 (m) cm^{-1}; mass spectrum (CH_4), *m/e* 363 (M + 1), 335, 307, 279, 156, 96, 79, 61. Anal. Calcd for $C_{11}H_{10}MoNOP$: C, 36.39; H, 2.78; N, 3.86; P, 8.53. Found: C, 36.27; H, 2.87; N, 3.72; P, 8.77.

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Representative Procedure: Tetracarbonyl(η^2-3-phenyl-2-propen-1-yl-dimethylphosphinite-*P*)molybdenum (1). The following is a typical experimental procedure for alkoxide reaction with chelate **3**. The hindered tertiary alkoxides required stirring at 25 °C for up to 6 h. A solution of cinnamyl alcohol (285 mg, 2.13 mmol) in diethyl ether (30 mL) at −78 °C under nitrogen was treated with 2.50 M *n*-BuLi (0.85 mL, 2.13 mmol) and allowed to warm to room temperature. After 10 min at room temperature, the vessel was cooled to 0 °C and treated with chelate **3** (0.73 g, 2.01 mmol) by a side arm. Within 10 min of stirring at 0 °C, the lithium alkoxide of 2-hydroxypyridine precipitated. After layering with pentane, the precipitate was filtered and the supernatant was concentrated in vacuo to a yellow solid. Recrystallization from pentane at −40 °C with slow cooling to −78 °C afforded 0.447 g of **1** (55% yield) as a pale yellow solid: mp 83–84 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 6.88–7.12 (m, 5 H), 5.06 (dddd, J_{PH} = 6.1, J_{HH} = 13.4, 10.0, 3.8 Hz, 1 H), 4.87 (d, J_{HH} = 13.4 Hz, 1 H), 4.29 (dddd, J_{PH} = 44.1, J_{HH} = 11.4, 3.8, 1.0 Hz, 1 H), 2.61 (ddd, J_{PH} = 2.5, J_{HH} = 11.4, 10.0 Hz, 1 H), 1.37 (d, J_{PH} = 7.5 Hz, 3 H), 1.35 (d, J_{PH} = 7.9 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 167.2 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 218.6 (d, J_{PC} = 10.3 Hz), 213.9 (d, J_{PC} = 23.4 Hz), 206.6 (d, J_{PC} = 7.3 Hz), 206.5 (d, J_{PC} = 11.7 Hz), 140.5, 128.8, 127.0, 125.5, 87.6, 84.4 (d, J_{PC} = 2.9 Hz), 73.3 (d, J_{PC} = 8.8 Hz), 25.5 (d, J_{PC} = 22.0 Hz), 22.5 (d, J_{PC} = 26.4 Hz); IR ($CDCl_3$) ν_{CO} 2030 (m), 1950 (m), 1920 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 195, 117, 79. Anal. Calcd for $C_{15}H_{15}MoO_5P$: C, 44.80; H, 3.76; Mo, 23.85; P, 7.70. Found: C, 44.67; H, 3.81; Mo, 23.70; P, 7.65.

Tetracarbonyl(η^2-2-propen-1-yl dimethylphosphinite-*P*)molybdenum (4): 69% yield, mp 87–88 °C dec; ^{1}H NMR (C_6D_6) δ 3.65–4.60 (m, 2 H), 2.75–3.20(m, 2 H), 2.30 (m, 1 H), 1.28 (d, J_{PH} = 6.0 Hz, 6 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 166.1 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.3 (d, J_{PC} = 10.3 Hz), 215.4 (d, J_{PC} = 22.0 Hz), 206.6 (d, J_{PC} = 8.8 Hz), 206.3 (d, J_{PC} = 13.2 Hz), 93.3 (d, J_{PC} = 2.9 Hz), 72.8 (d, J_{PC} = 7.3 Hz), 62.6, 25.4 (d, J_{PC} = 23.4 Hz), 22.8 (d, J_{PC} = 26.8 Hz); IR ($CDCl_3$) ν_{CO} 2025 (m), 1945 (s), 1910 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 327 (M + 1), 299, 271, 119, 79. Anal. Calcd for $C_9H_{11}MoO_5P$: C, 33.15; H, 3.40. Found: C, 33.06; H, 3.41.

Tetracarbonyl(η^2-3,3-dimethyl-2-propene-1-yl dimethylphosphinite-*P*)molybdenum (5): 54% yield, mp 75–77 °C dec; ^{1}H NMR (C_6D_6) δ 3.50–4.35 (m, 2 H), 3.05 (m, 1 H), 1.72 (d, 2.5 Hz, 3 H); 1.66 (d, J 2.2 Hz, 3 H), 1.38 (d, J_{PH} = 5.5 Hz, 3 H), 1.32 (d, J_{PH} = 5.2 Hz, 3 H): ^{31}P {^{1}H} NMR (C_6D_6) δ 163.0 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 217.8 (d, J_{PC} = 8.8 Hz), 217.4 (d, J_{PC} = 26.4 Hz), 207.1 (d, J_{PC} = 11.7 Hz), 206.7 (d, J_{PC} = 10.3 Hz), 109.6 (d, J_{PC} = 2.9 Hz), 95.6 (d, J_{PC} = 2.9 Hz), 68.7 (d, J_{PC} = 7.3 Hz), 32.3, 25.2 (d, J_{PC} = 22.0 Hz), 22.8 22.6 (d, J_{PC} = 24.9 Hz); IR ($CDCl_3$) ν_{CO} 2020 (m), 1925 (s), 1895 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 355 (M +), 326, 298, 147, 79, 69. Anal. Calcd for $C_{11}H_{15}MoO_5P$: C, 37.31; H, 4.27. Found: C, 37.25; H, 4.26.

Tetracarbonyl(η^2-1,1-dimethyl-2-propen-1-yl dimethylphosphinite-*P*)-molybdenum (6): 56% yield, mp 59.0–60.5 °C; ^{1}H NMR (C_6D_6) δ 4.82 (ddd, *J* 3.2, 9.3, 14.6 Hz, 1 H), 3.25 (d, *J* 9.3 Hz, 1 H), 2.96 (d, *J* 1.8, 14.6 Hz, 1 H), 1.32 (d, J_{PH} = 6.0 Hz, 3 H), 1.24 (d, J_{PH} = 6.3 Hz, 3 H), 1.15 (s, 3 H), 0.77 (s, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 151.6 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.0 (d, J_{PC} = 10.3 Hz), 214.4 (d, J_{PC} = 22.0 Hz), 208.0 (d, J_{PC} = 11.7 Hz), 207.2 (d, J_{PC} = 8.8 Hz), 104.5, 82.2 (d, J_{PC} = 5.9 Hz), 61.5, 31.5 (d, J_{PC} = 10.3 Hz), 26.0 (d, J_{PC} = 24.9 Hz), 24.5 (d, J_{PC} = 26.4 Hz), 23.0; IR ($CDCl_3$) ν_{CO} 1930 (s), 1905 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 355 (M + 1), 326, 298, 270, 242, 147, 79, 69.

Tetracarbonyl(η^2-3-cyclopenten-1-yl dimethylphosphinite-*P*)molybdenum (7): 32% yield: mp 122.5–123.0 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 4.52 (s, 2 H), 3.88 (dt, J_{PH} = 22.1 Hz, J_{HH} = 6.8 Hz, 1 H), 2.22 (d, *J* 17.0 Hz, 2 H), 1.84 (ddd, J_{PH} = 1.8 Hz, J_{HH} = 17.0, 6.8 Hz, 2 H), 1.08 (d, J_{PH} = 5.0 Hz, 6 H), ^{31}P {^{1}H} NMR (C_6D_6) δ 113.9 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 218.6 (d, J_{PC} = 5.9 Hz), 212.8 (d, J_{PC} = 10.3 Hz), 211.1 (d, J_{PC} = 35.2 Hz), 85.8, 75.6, 42.1 (d, J_{PC} = 8.8 Hz), 25.5 (d, J_{PC} = = 26.4 Hz); IR ($CDCl_3$) ν_{CO} 2020 (m), 1925 (s), 1905 (s), 1875 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 353 (M + 1), 324, 296, 268, 240, 145, 79, 67.

Tetracarbonyl(η^2-3-buten-1-yl dimethylphosphinite-*P*)molybdenum (8): 66% yield; mp 72–73 °C dec; ^{1}H NMR (C_6D_6) δ 1.70–3.75 (m, 6 H), 1.52 (d, J_{PH} = 5.7 Hz, 3 H), 1.26 (d, J_{PH} = 4.9 Hz, 3 H), 0.65–1.35 (m, 1 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 139.3 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.9 (d, J_{PC} = 22.0 Hz), 216.8 (d, J_{PC} = 8.8 Hz), 205.8 (d, J_{PC} = 8.8 Hz), 205.7 (d, J_{PC} = 13.2 Hz), 75.5 (d, J_{PC} = 4.4 Hz), 64.9, 57.8, 35.3 (d, J_{PC} = 5.9 Hz), 24.9 (d, J_{PC} = 32.3 Hz), 23.0 (d, J_{PC} = 16.1 Hz); IR ($CDCl_3$) ν_{CO} 2020 (m), 1935 (s), 1910 (s) cm^{-1}; mass spectrum (CH_4), *m/e* 341 (M + 1), 313, 285, 133, 79. Anal. Calcd for $C_{10}H_{13}MoO_5P$: C, 35.31; H, 3.85. Found: C, 35.18; H, 3.82.

Tetracarbonyl(η^2-4-ethyl-3-buten-1-yl dimethylphosphinite-*P*)molybdenum (9): 63% yield: mp 33.5–35.5 °C; ^{1}H NMR (C_6D_6) δ 2.75–4.30 (m, 4 H), 1.15–2.55 (m, 4 H), 1.54 (d, J_{PH} = 5.6 Hz, 3 H), 1.24 (d, J_{PH} = 4.7 Hz, 3 H), 0.84 (t, 7.3 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 138.0 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 218.2 (d, J_{PC} = 22.0 Hz), 217.2 (d, J_{PC} = 11.7 Hz), 206.5 (d, J_{PC} = 13.2 Hz), 205.7 (d, J_{PC} = 10.3 Hz), 86.4, 75.9 (d, J_{PC} = 4.4 Hz), 65.4, 29.6 (*d*, J_{PC} = 4.4 Hz), 26.0 (d, J_{PC} = 26.4 Hz), 23.6 (d, J_{PC} = 19.1 Hz), 22.5, 15.5; IR ($CDCl_3$) ν_{CO} 2020 (m), 1900 (s) cm^{-1}: mass spectrum (CH_4), *m/e* 369 (M + 1), 340, 312, 284, 161, 95, 83, 79.

Table III. Experimental Data for the X-ray Diffraction Study of $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$, **10**.

(A) Crystal Parameters at 23 °C (296 K)

cryst. system: triclinic	space group: $P\bar{1}$ (C_i^1; no. 2)
a = 7.416 (1) Å	V = 850.4 (2)Å^3
b = 8.649 (1) Å	formula: $C_{15}H_{15}O_5PMo$
c = 13.572 (2) Å	M_r 402.21
α = 98.48 (1)°	Z = 2
β = 94.08 (1)°	D(calcd) = 1.57 g/cm^3
γ = 97.29 (1)°	

(B) Data Collection

diffractometer: Syntex $P2_1$
radiation Mo Kα ($\bar{\lambda}$ 0.710730 Å)
monochromator: pyrolytic graphite, equatorial geometry, 2θ (m) = 12.2°, assumed 50% perfect
scan type: coupled θ (crystal) − 2θ (counter)
scan speed: 2.0 deg min^{-1} (in 2θ)
scan width: symmetrical [1.8 + $\Delta(\alpha_2 - \alpha_1)$]°
relfections measured: $+h,\pm k,\pm l$ for 2θ = 5.0°–45.0°; 2433 total reflections were merged to 2223 unique independent data; file name MOPO
absorption correction: μ(Mo Kα) = 8.7 cm^{-1}; all data were corrected by interpolation in 2θ and ϕ between ψ scans of four close to axial reflections

Tetracarbonyl(η^2-1-phenyl-2-propen-1-yl dimethylphosphinite-*P*)molybdenum (10): 47% yield; ^{1}H NMR (C_6D_6) δ 7.12 (s, 5 H), 4.45 (m, 1 H), 3.88 (m, 1 H), 2.85–3.10 (m, 2 H), 1.36 (d, J_{PH} = 6.1 Hz, 6 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 158.8 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 215.9 (d, J_{PC} = 10.2 Hz), 215.1 (d, J_{PC} = 20.5 Hz), 206.3 (d, J_{PC} = 11.7 Hz), 206.0 (d, J_{PC} = 8.8 Hz), 140.5 (d, 16.1 Hz), 128.6, 128.1, 126.6, 97.1, 87.4 (d, J_{PC} = 8.8 Hz), 60.2, 25.6 (d, J_{PC} = 23.4 Hz), 22.9 (d, J_{PC} = 27.8 Hz); approximate isomer ratio, 30/1. Anal. Calcd for $C_{15}H_{15}MoOP$: C, 44.80; H, 3.73; P, 7.70. Found: C, 44.83; H, 3.72; P, 7.91.

Tetracarbonyl(η^2-1-methyl-2-propen-yl dimethylphosphinite-*P*)molybdenum (11): 57% yield; ^{1}H NMR (C_6D_6) δ 4.05–4.55 (m, 1 H), 2.65–3.20 (m, 3 H), 1.30 (d, J_{PH} = 6.0 Hz, 6 H), 1.05 (d, J = 6.1 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 157.2 (s), 156.5 (s, minor isomer); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.1 (d, J_{PC} = 13.2 Hz), 215.3 (d, J_{PC} = 20.5 Hz), 206.6 (d, J_{PC} = 8.8 Hz), 98.3 97.7 (minor isomer), 82.1 (d, J_{PC} = 7.3 Hz), 74.8 (d, J_{PC} = 5.9 Hz, minor isomer), 61.2 (d, J_{PC} = 2.9 Hz), 60.0 (minor isomer), 25.7 (d, J_{PC} = 23.4 Hz), 23.2 (d, J_{PC} = 14.7 Hz), 23.0 (d, J_{PC} = 24.9 Hz); approximate isomer ratio, 22/1.

Tetracarbonyl[η^2-1-(2-propyl)-2-propen-1-yl dimethylphosphinite-*P*]-molybdenum (12): 20% yield; ^{1}H NMR (C_6D_6) δ 4.30 (m, 1 H), 3.06 (m, 1 H), 2.88 (m, 1 H), 2.58 (m, 1 H), 1.45 (m, 1 H), 1.32 (d, J_{PC} = 5.9 Hz, 6 H), 0.78 (d, *J* 6.5 Hz, 3 H), 0.70 (d, *J* = 7.6 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 156.7 (s). No minor isomer was detectable.

Tetracarbonyl(η^2-1-ethyl-1-methyl-2-propen-1-yl dimethylphosphinite-*P*)molybdenum (13): 41% yield; ^{1}H NMR (C_6D_6) δ 4.55–5.0 (m, 1 H), 3.25 (d, *J* = ~10 Hz, 1 H), 2.88 (dd, *J* ~15, 2 Hz, 1 H), 1.34 (d, J_{PH} = 5.6 Hz, 3 H), 1.26 (d, J_{PH} = 5.9 Hz, 3 H), 1.1–1.55 (m, 2 H), 0.70 (s, 3 H), 0.66 (t, *J* = 7.0 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 151.9 (s), 150.4 (s, minor isomer); ^{13}C{^{1}H} NMR (C_6D_6) δ 215.8 (d, J_{PC} = 10.3 Hz), 214.5 (d, J_{PC} = 22.0 Hz), 207.9 (d, J_{PC} = 11.7 Hz), 206.9 (d, J_{PC} = 10.3 Hz), 104.4 (minor isomer), 103.4, 85.1 (d, J_{PC} = 5.9 Hz), 83.9 (d, J_{PC} = 4.4 Hz, minor isomer), 62.5 (d, J_{PC} = 2.9 Hz), 60.8 (minor isomer), 36.7 (d, J_{PC} = 10.3 Hz), 29.2 (minor isomer), 28.3 (d, J_{PC} = 26.4 Hz, minor isomer), 27.3 (minor isomer), 26.0 (d, J_{PC} = 24.9 Hz), 24.6 (d, J_{PC} = 26.4 Hz), 24.1 (d, J_{PC} = 26.4 Hz, minor isomer), 19.7, 9.6; 8.0 (minor isomer); approximate isomer ratios, 5/1.

Tetracarbonyl(η^2-1,2-dimethyl-2-propen-1-yl dimethylphosphinite-*P*)-molybdenum (14): 67% yield; ^{1}H NMR (C_6D_6) δ 3.26 (s, 1 H), 3.23 (s, 1 H), 3.05-3.35 (m, 1 H), 1.58 (d, 0.7 Hz, 3 H), 1.36 (d, J_{PH} = 5.5 Hz, 3 H), 1.30 (d, J_{PH} = 5.6 Hz, 3 H), 0.96 (d, 6.3 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 156.9 (s), 148.3 (s, minor isomer); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.8 (d, J_{PC} = 8.8 Hz), 215.1 (d, J_{PC} = 24.9 Hz), 207.5 (d, J_{PC} = 8.8 Hz), 206.9 (d, J_{PC} = 11.7 Hz), 122.7, 121.4 (minor, isomer), 83.0 (d, J_{PC} = 7.3 Hz), 77.8 (d, J_{PC} = 4.4 Hz, minor isomer), 69.3, 61.8 (minor isomer), 24.1 (d, J_{PC} = 24.9 Hz), 23.7 (d, J_{PC} = 24.9 Hz), envelope of five peaks from 22.8–20.2 (undetermined coupling pattern), 21.0, 20.6, 20.5; approximate isomer ratio, 3.5/1.

Table IV. Final Refined Parameters for $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$

atom	*x*	*y*	*z*	*B*, Å²
Mo	0.854 06 (3)	0.294 10 (3)	0.178 40 (2)	
P	0.603 57 (9)	0.424 60 (8)	0.243 70 (5)	
O(1)	0.442 71 (24)	0.293 07 (20)	0.267 83 (15)	
O(12)	1.099 66 (32)	0.408 35 (29)	0.384 78 (17)	
O(13)	0.598 22 (31)	0.183 39 (27)	−0.023 29 (16)	
O(14)	0.982 50 (38)	0.611 75 (28)	0.101 57 (18)	
O(15)	1.160 44 (30)	0.133 87 (31)	0.066 50 (18)	
C(1)	0.778 20 (44)	0.027 86 (35)	0.214 70 (27)	
C(2)	0.679 33 (37)	0.123 94 (32)	0.271 92 (22)	
C(3)	0.479 92 (35)	0.131 56 (30)	0.249 72 (21)	
C(4)	0.363 57 (34)	0.039 87 (29)	0.314 79 (19)	
C(5)	0.350 15 (42)	0.098 77 (38)	0.414 69 (23)	
C(6)	0.248 63 (45)	0.011 47 (38)	0.472 90 (24)	
C(7)	0.160 50 (43)	−0.136 12 (40)	0.433 95 (25)	
C(8)	0.171 47 (47)	−0.194 24 (39)	0.335 59 (27)	
C(9)	0.272 72 (43)	−0.107 19 (34)	0.276 13 (24)	
C(10)	0.474 98 (61)	0.527 49 (53)	0.161 67 (37)	
C(11)	0.637 15 (69)	0.564 13 (63)	0.358 73 (38)	
C(12)	1.016 40 (38)	0.366 21 (33)	0.310 14 (23)	
C(13)	0.689 02 (39)	0.221 48 (31)	0.049 84 (22)	
C(14)	0.938 44 (40)	0.493 69 (37)	0.129 38 (20)	
C(15)	1.052 39 (39)	0.190 37 (35)	0.109 36 (22)	
H(1A)	0.886 9 (44)	−0.006 9 (35)	0.246 6 (22)	5.32 (71)
H(1B)	0.733 0 (43)	−0.028 7 (39)	0.150 0 (26)	5.97 (86)
H(2)	0.717 6 (38)	0.154 7 (32)	0.339 5 (23)	4.36 (67)
H(3)	0.449 3 (31)	0.088 5 (27)	0.178 3 (19)	2.66 (49)
H(5)	0.405 5 (37)	0.195 0 (34)	0.437 0 (21)	4.12 (65)
H(6)	0.233 2 (40)	0.045 4 (36)	0.538 3 (24)	4.95 (71)
H(7)	0.098 0 (36)	−0.188 7 (31)	0.471 6 (21)	3.76 (62)
H(8)	0.108 4 (46)	−0.288 1 (40)	0.308 8 (25)	6.69 (93)
H(9)	0.276 7 (39)	−0.143 5 (35)	0.208 3 (23)	5.06 (73)
H(10A)	0.448 2 (55)	0.455 4 (51)	0.097 0 (33)	8.7 (13)
H(10B)	0.548 1 (45)	0.606 4 (41)	0.149 5 (25)	5.80 (87)
H(10C)	0.370 8 (54)	0.556 9 (43)	0.192 7 (28)	7.5 (10)
H(11A)	0.528 1 (45)	0.590 1 (37)	0.377 7 (24)	5.47 (80)
H(11B)	0.686 8 (46)	0.517 3 (40)	0.408 0 (27)	5.4 (10)
H(11C)	0.724 0 (62)	0.652 7 (53)	0.345 7 (33)	9.9 (13)

Tetracarbonyl(μ^2-2-methyl-3-buten-1-yl dimethylphosphinite-*P*)molybdenum (15): 66% yield; ^{1}H NMR (C_6D_6) δ 3.36 (ddd, $J \sim 25$, 12, 4 Hz, 1 H), 2.2–3.1 (m, 4 H), 1.56 (d, J_{PC} = 5.8 Hz, 3 H), 1.24 (d, J_{PC} = 4.9 Hz, 3 H), 0.7–1.5 (m, 1 H), 0.58 (d, J = 6.6 Hz, 3 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 142.7 (s); ^{13}C {^{1}H} NMR (C_6D_6) δ 216.9 (d, J_{PC} = 24.9 Hz), 216.8 (d, J_{PC} = 5.9 Hz), 205.7 (d, J_{PC} = 8.8 Hz), 205.5 (d, J_{PC} = 13.2 Hz), 87.1 (d, J_{PC} = 2.9 Hz, minor isomer), 80.7 (d, J_{PC} = 5.9 Hz), 70.4, 69.7 (d, J_{PC} = 2.9 Hz, minor isomer), 58.9 (minor isomer), 55.0, 40.7 (d, J_{PC} = 5.9 Hz), 34.0 (d, J_{PC} = 2.9 Hz, minor isomer), 24.8 (d, J_{PC} = 33.7 Hz), 24.0, 22.9 (d, J_{PC} = 13.2 Hz); approximate isomer ratio, 13/1.

Tetracarbonyl(μ^2-1-methyl-3-buten-1-yl dimethylphosphinite-*P*)molybdenum (16): 69% yield; ^{1}H NMR (C_6D_6) δ 2.35–3.45 (m, 4 H), 2.08 (m, 1 H), 1.55 (d, J_{PH} = 5.8 Hz, 3 H), 1.24 (d, J_{PH} = 4.9 Hz, 3 H), 0.86 (d, J = 6.3 Hz, 3 H), 0.55–1.10 (m, 1 H); ^{31}P {^{1}H} NMR (C_6D_6) δ 140.0 (s), 141.5 (s, minor isomer), ^{13}C {^{1}H} NMR (C_6D_6) δ 217.2 (d, J_{PC} = 23.4 Hz), 217.0 (d, J_{PC} = 7.3 Hz), 205.9 (d, J_{PC} = 7.3 Hz), 205.5 (d, J_{PC} = 11.7 Hz), 78.6 (d, J_{PC} = 2.9 Hz, minor isomer), 76.2 (d, J_{PC} = 4.4 Hz), 78.6 (d, J_{PC} = 2.9 Hz), 72.8 (d, J_{PC} = 2.9 Hz, minor isomer), 71.7, 62.6 (minor isomer), 56.3, 42.2 (d, J_{PC} = 5.9 Hz), 41.0 (d, J_{PC} = 2.9 Hz, minor isomer), 25.3 (d, J_{PC} = 35.2 Hz), 24.4 (d, J_{PC} = 22.0 Hz, minor isomer), 23.4 (d, J_{PC} = 13.2 Hz), 23.4 (d, J_{PC} = 7.3 Hz), 22.6 (d, J_{PC} = 8.8 Hz, minor isomer); approximate isomer ratio, 6.5/1.

Collection of X-ray Diffraction Data for $(PMe_2OCHPhCH{=}CH_2)Mo(CO)_4$, 10. An opaque yellow crystal of approximate dimensions 0.1 × 0.2 × 0.3 mm³ was sealed into a thin-walled capillary in an inert-atmosphere (Ar) KSE drybox which has been modified by adding a protruding transparent section between the gloves (thereby allowing inspection of the crystals through an externally mounted binocular microscope). The capillary was inserted into an aluminum pin which was set in an XYZ goniometer and mounted on the Syntex $P2_1$ automated four-circle diffractometer of SUNY—Buffalo. Crystal alignment, determination of unit cell parameters and orientation matrix, and data collection were carried out as previously described.[29] (See Table III.) All data were corrected for absorption (μ = 8.7 cm^{-1}) and for Lorentz and polarization effects and were converted to unscaled $|F_o|$ values. Those reflections with I (net) < 0 were assigned a value of $|F_o| = 0$. The data were placed on an approximate absolute scale by means of a Wilson plot. No datum was rejected.

All calculations were performed on the SUNY—Buffalo modified version of the Syntex XTL system. The analytical form of the appropriate neutral atom scattering factor was corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[30] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma|F_o|)^2 + 0.015\ |F_o|^2]^{-1}$.

The position of the molybdenum atom was readily determined from an unsharpened, three-dimensional Patterson map. A series of three difference Fourier syntheses revealed the positions of all remaining atoms. The model was refined by full-matrix least-squares techniques. Convergence was reached[31] with R_F = 2.3%, R_{wF} = 2.5%, and GOF = 1.21 for all 2223 reflections refined against 259 variables (R_F = 2.0% and R_{wF} = 2.5% for those 2078 reflections with $|F_o| > 3.0\ \sigma|F_o|$; R_F = 1.8% and R_{wF} = 2.4% for those 1984 reflections with $|F_o| > 6.0\ \sigma\ |F_o|$)).

The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependence on $|F_o|$, $\sin\theta/\lambda$, sequence number, identity, or parity class of the Miller indices; the weighting scheme is therefore satisfactory. Final positional parameters are collected in Table IV; anisotropic thermal parameters (Table IV-S) have been deposited.

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Registry No. 1, 94820-78-7; **2**, 94843-07-9; **3**, 94820-79-8; **4**, 94843-08-0; **5**, 94843-09-1; **6**, 94820-80-1; **7**, 94820-81-2; **8**, 94820-82-3; **9**, 94820-83-4; **10**, 94820-84-5; **11**, 94820-85-6; **12**, 94820-86-7; **13**, 94820-87-8; **14**, 94820-88-9; **15**, 94820-89-0; **16**, 94820-90-3; 2-propen-1-ol, 107-18-6; 3-methyl-2-buten-1-ol, 556-82-1; 2-methyl-3-buten-2-ol, 115-18-4; 3-cyclopenten-1-ol, 14320-38-8; 3-buten-1-ol, 627-27-0; 3-hexen-1-ol, 544-12-7; 1-phenyl-2-propen-1-ol, 4393-06-0; 3-buten-2-ol, 598-32-3; 2-propyl-2-propen-1-ol, 4364-51-6; 3-methylpenten-3-ol, 918-85-4; 3-methyl-3-buten-2-ol, 10473-14-0; 3-methyl-2-buten-2-ol, 4516-90-9; 4-penten-2-ol, 625-31-0; 2-hydroxypyridine lithium alkoxide, 94820-77-6; 2-hydroxypyridine, 142-08-5; dimethylchlorophosphine, 811-62-1; molybdenum hexacarbonyl, 13939-06-5; cinnamyl alcohol, 104-54-1.

Supplementary Material Available: Table IV-S (anisotropic thermal parameters for **10**) and a listing of observed and calculated structure factor amplitudes for **10** (12 pages). Ordering information is given on any current masthead page.

(29) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(30) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

(31) $R_F = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = 100[\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$; GOF = $[\sum_w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO = number of observations and NV = number of variables.