Conformational Preferences in Molybdenum(II) π-Allyl Complexes: Role of CH/π Interaction†

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A series of isostructural complexes **1a–g** of general formula $LMo(CO)_2(\eta^3\text{-}R^1R^3C{=}CHCHR^2)$, where L = bis(3,5-dimethyl-1-pyrazolyl)phosphinate, R^1, $R^3 = CH_3$, H, and $R^2 = CH_3$, C_6H_5, $p\text{-}OCH_3C_6H_4$, $p\text{-}NO_2C_6H_4$, were prepared and their solution conformations were studied. The close proximity of phenyl and methyl groups in certain conformations was shown to result from a CH/π attractive interaction. The structure of the complex **1a** ($R^2 = C_6H_5$, R^1, R^3 = H) was determined by X-ray crystallography. The compound $C_{21}H_{23}MoN_4O_4P$ crystallized in monoclinic space group $P2_1/n$ with $a = 7.592(1)$ Å, $b = 11.134(3)$ Å, $c = 26.464(2)$ Å, $\beta = 95.02(1)°$, $V = 2228.4(6)$ Å^3, $Z = 4$, and $\mu_{calc} = 1.56$ g cm^{-3}. Using Mo Kα radiation for 2480 observed reflections ($\omega/2\theta$ scan mode, maximum $\theta = 23.5°$), the structure was refined to $R = 0.038$.

Introduction

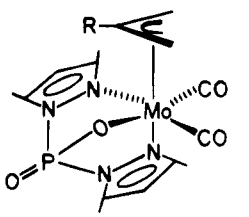
The conformation of organic compounds as well as organometallic or coordination complexes is determined by the relative magnitude of various interatomic interactions which may be stabilizing (hydrogen bond, complementary dipole, π-stacking) or destabilizing (van der Waals repulsion, dipolar repulsion). In recent times, the CH/π interaction has been identified[1] as a weak, attractive, donor–acceptor type interaction between an acidic CH group and a basic π-system, which can affect the conformation of molecules[2] and transition-state structures.[3] While most of the accumulated evidence in support of such an interaction pertains to the solid-state crystal structure data, a few instances where solution conformations were controlled by a CH/π interaction have also been documented.[4]

The magnitude of a CH/π stabilization has often been estimated[5] to be <2 kcal/mol, which is comparable to the energy of a weak hydrogen bond. Thus, it can be difficult to actually identify such an interaction and unambiguously ascribe energy values to it, particularly in the presence of other dominant structural factors. One might obtain fairly reliable estimates of CH/π contribution from a series of isostructural compounds where all other interactions remain essentially the same.

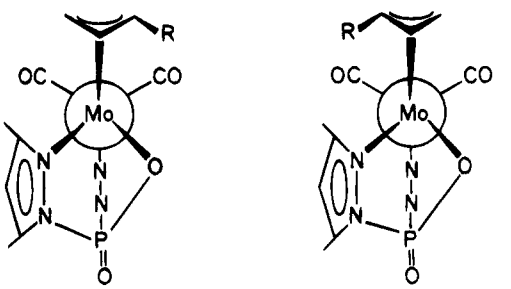
We recently reported[6] the synthesis and structure of molybdenum π-allyl complexes with an unsymmetrical ligand containing two 3,5-dimethylpyrazole moieties. These complexes have definite stereochemistry where intramolecular distances are practically invariant. Thus, the set of complexes proved to be a model system to probe subtle interatomic interactions. In this paper, we describe the synthesis and structural characterization of new, isostructural molybdenum π-allyl complexes which provide definite evidence that, other factors remaining equal, a CH/π interaction dictates conformational preferences in these molecules.

Specifically, in these complexes, one pyrazole nitrogen and one oxygen atom occupy the positions *cis* to the allyl group, as shown in conformation **I** (Chart 1). A terminally substituted allyl group, in such a case, would have two possible orientations where the substituent is either close to the oxygen (**A**) or near the pyrazole (**B**). In the

Chart 1



I



A **B**

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‡ Division of Organic Chemistry (Synthesis).
§ Division of Physical Chemistry.
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(1) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201.
(2) (a) Oki, M. *The Chemistry of Rotational Isomers*; Springer-Verlag: Berlin, Heidelberg, 1993; Chapter 2. (b) Nakai, Y.; Inoue, K.; Yamamoto, G.; Oki, M.; *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2923. (c) Subramanian, S.; Wang, L.; Zaworotko, M. J. *Organometallics* **1993**, *12*, 310.
(3) Capillon, J.; Guette, J. P. *Tetrahedron* **1979**, *35*, 1817.
(4) Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2648.
(5) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.
(6) Joshi, V. S.; Kale, V. K.; Sathe, K. M.; Sarkar, A.; Tavale, S. S.; Suresh, C. G. *Organometallics* **1991**, *10*, 2898.

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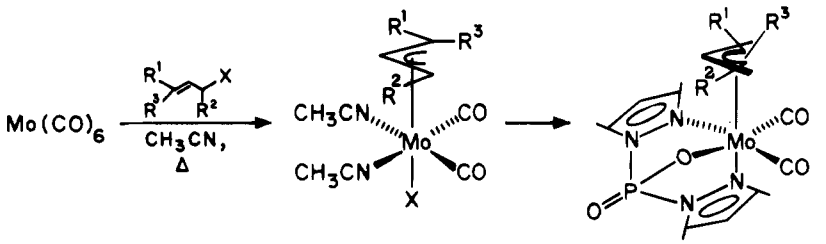
Scheme 1



	R^1	R^2	R^3
a	C_6H_5	H	H
b	CH_3	H	H
c	CH_3	H	CH_3
d	CH_3	CH_3	H
e	C_6H_5	CH_3	H
f	p-OCH_3-C_6H_4	H	H
g	p-NO_2-C_6H_4	H	H

latter, one would *a priori* anticipate an unfavorable steric interaction between the allyl substituent and the 3-methyl group of the pyrazole due to their proximity, suggesting a preference for the conformer **A** over **B**.

We have studied the conformations of these complexes in solution and determined the structure of one in the crystalline state. The results indicate that a phenyl group is better accommodated in the vicinity of the 3-methyl substituent of the pyrazole ring than is a methyl group, *i.e.* the Me/Me steric interaction appears to be less favorable than a Me/Ph interaction in these complexes. Such a conformational preference appears to be largely governed by a CH/π attractive interaction between the phenyl and the methyl groups.

Results and Discussion

The complexes were synthesized and isolated as air-stable, crystalline solids as depicted in Scheme 1, following an earlier procedure.[6]

The ^{1}H NMR spectrum of the cinnamyl complex **1a** at ambient temperature showed dynamic features. At −31 °C, the peaks were sharp and well-resolved. The spectrum clearly showed the presence of two conformers in the ratio 4:3, as determined by integration. A complete assignment of all the peaks (except those of the phenyl group) to an individual conformer was possible with the help of a COSY spectrum obtained at −31 °C. Significantly, one of the pyrazole methyl groups appeared at 1.15 ppm, uniquely shielded (about 1 ppm) by the proximal phenyl ring anisotropy. Thus, it could be immediately assigned to the minor conformer where the phenyl group was on the same side as the pyrazole (conformer **B**). This shielded methyl group was subsequently used as the diagnostic feature for such a conformer.

The X-ray structure of this complex (Table 1) revealed the presence of only one type of molecule in the unit cell, and fortuitously, it was the conformer with proximal phenyl and pyrazolyl groups (Figure 1). The orientation of these groups in the molecule was in agreement with the contention that the chemical shift of a methyl group on the pyrazole was affected by the proximal phenyl ring anisotropy, and its ^{1}H NMR signal appeared upfield compared to the other methyl signals.

Table 1. Crystal Data and Structure Refinement

compd	$C_{21}H_{23}MoN_4O_4P$
fw	522.55
space group	$P2_1/n$
a, Å	7.592(1)
b, Å	11.134(3)
c, Å	26.464(2)
β, deg	95.02(1)
V, Å^3	2228.4(6)
molecules/unit cell	4
μ_{calc}, g cm^{-3}	1.56
μ_{calc}, mm^{-1}	0.68
radiation	Mo Kα
cryst size, mm	0.09 × 0.19 × 0.30
temp, K	293
scan type	$\omega/2\theta$
scan width, deg	0.80 + 0.35 tan θ
2θ range, deg	0−47.0
std rflns	3 measd every 1 h
decay of stds	none
no. of rflns collected	3490
no. of rflns obsd, $I \geq 3.0\sigma(I)$	2480
no. of params varied	280
GOF	2.39
R	0.038
R_w	0.043

The interatomic arrangement of the groups around molybdenum and various bond distances and angles were comparable with those of a related structure reported earlier.[6] The short contacts between some of the phenyl ring atoms and the nearest methyl carbon are noteworthy (C7—C16 = 3.373 Å, C7—C17 = 3.436 Å, C7—C21 = 3.621 Å, C7—C18 = 3.750 Å). The proximity is particularly striking (the distance between the phenyl plane and C7 is 3.306 Å) if one considers that the van der Waals radius of a methyl group is 2.0 Å and the half-thickness of a phenyl group is 1.85 Å.[7] Yet, this conformer is preferred in the crystalline state. This would imply that this conformer is less destabilized than one would imagine, despite the close approach of a methyl and a phenyl group, and lattice forces could compensate for such minimal destabilization. Alternatively, this conformer could be stabilized by an interaction which is absent in the other conformer. The CH/π interaction can be such a stabilizing factor.

(7) Cotton, F. A.; Wilkinson, G. *Basic Inorganic Chemistry*; Wiley: New York, 1976; p 88.

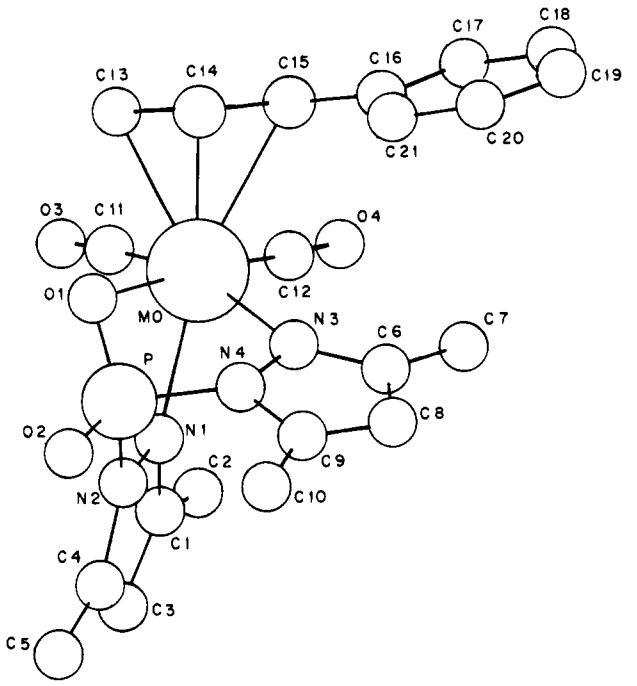


Figure 1.

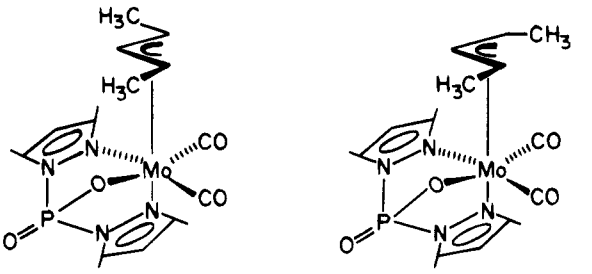
In this context, a relative assessment of Me/Ph and Me/Me interactions at comparable distances, appeared appropriate.

For the crotyl complex **1b**, only one conformer was detected by the ^{1}H NMR spectrum, and no change was observed even at −50 °C. Considering the close proximity of the allyl substituent to the pyrazolyl 3-Me group in the confomer **B**, as shown for complex **1a**, it was tentatively deduced that the methyl substituent on the allyl fragment in **1b** lies toward the oxygen (conformer **A**) in the only observed conformer of this complex. The methyl doublet of the crotyl group appeared at 2.00 ppm, while the corresponding methine multiplet appeared at 1.90 ppm.

The prenyl complex **1c** was prepared to obtain representative chemical shift values for the two methyl groups, one *syn* and the other *anti* with respect to the central proton. The ^{1}H NMR spectrum revealed the presence of a single conformer which displayed the two allyl methyl singlets at 1.05 and 2.05 ppm, the *anti* methyl being the shielded one. A positive NOE was observed for the *syn*-allyl proton when the pyrazole methyl groups were irradiated, which indicated that the unsubstituted end of the π-allyl ligand was closer to the pyrazole (conformer **A**), as one would anticipate. This is probably true for the conformation of the crotyl complex **1b** also.

When two methyl substituents are attached to two termini of the allyl group as in the complex **1d**, one of them must reside close to the 3-Me group of a pyrazole. If these groups interact repulsively, the allyl methyl group would have the option of adopting an *anti* orientation which can be readily recognized from the upfield shift in the ^{1}H NMR spectrum. In the absence of a repulsive interaction, both of the allylic methyls would remain in the more stable *syn* configuration (the *anti* configuration is destabilized by torsional strain[8]). The two isomers are shown in Chart 2.

Chart 2



C **D**

The ^{1}H NMR spectrum of a freshly prepared sample of complex **1d** displayed two sets of signals corresponding to two isomers in unequal proportions (3:1). The major component had two allyl methyl signals (1.82 and 2.04 ppm) significantly broadened, presumably due to a slow *trigonal twist*[9] involving the ligand. The corresponding signals of the minor isomer were sharp doublets (1.19 and 2.08 ppm, J = 6.3 Hz). When the solution was cooled to −50 °C, the broad signals were resolved as sharp doublets (J = 6.3 Hz). The assignment of the protons corresponding to each isomer was possible with the help of a COSY spectrum. It was observed that the major isomer had two *syn* methyl groups on the allyl fragment (isomer **C**), while the minor isomer had one *syn* and one *anti* methyl group on the allyl ligand (isomer **D**). The *syn* proton on the allyl group (isomer **D**) appeared downfield as a multiplet at 4.17 ppm. It was presumed that the *anti* methyl group of the minor isomer was on the allyl terminus closer to the pyrazole group.

In order to determine the equilibrium population of isomers of the complex **1d**, a solution of the complex in benzene was heated under reflux for 6 h. When the ^{1}H NMR spectrum of this sample was recorded, it showed that the ratio of the isomers was 1:1; the population of the minor isomer **D** (with an *anti* methyl group on the allyl ligand) had increased considerably. This implied that the interaction of an allylic *syn* methyl group with the neighboring 3-Me group of pyrazole was repulsive in nature and tilted the balance slightly in favor of isomer **D**, despite the strain inherent in that conformation.

The complex **1e** lent further support to this observation. The ^{1}H NMR spectrum at room temperature showed sharp signals corresponding to a single conformer. The upfield singlet of the pyrazole methyl group (1.25 ppm) confirmed the proximity of the phenyl group and the pyrazole. No change of the spectral pattern was observed after heating the complex in benzene under reflux for 6 h. Thus, in this molecule, the repulsive Me/Me interaction and the presumably attractive Ph/Me interaction worked in the same direction to stabilize the observed conformation.

It appears that numerous instances are scattered in the literature where the unusual proximity of a π-system with an alkyl group is noted. Similar orientation preference and proximity between two phenyl rings (edge to face) have also been observed in several molecules. Only recently have these examples been identified with the term CH/π interaction by Nishio and Hirota.[1] Anisotropic shielding by an aromatic group

(8) Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

(9) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

Table 2. Relative Conformer Populations and Free Energies

complex	conformer ratio (A/B)	$\Delta G°_{A-B}$(233 K), kcal/mol
1f	1	0
1a	1.3	0.12
1g	5	0.74

could serve as a structural index which could unambiguously characterize the proximity of such groups in a given molecular structure. The proximity of groups *per se* does not represent a CH/π interaction. If the proximity results from CH/π stabilization, the species should be further stabilized when the aromatic group is more electron-rich and should be destabilized when the aromatic ring (or any donor π-system) is depleted of electron density.[10]

In order to ascertain that a CH/π type attractive interaction is indeed operative in this class of complexes, one must be able to predictably perturb the conformational balance by tuning the electron density on the aromatic ring, thereby altering its donor character. The presence of an electron-releasing or an electron-withdrawing substituent at the *para* position of the aromatic ring would have negligible steric contribution but should exert a contrasting effect on the donor property of the aromatic ring. If a CH/π interaction is a deciding factor in the conformational equilibrium, a *p*-methoxyphenyl group would stabilize the conformer **B** (Chart 1), whereas a *p*-nitrophenyl group would strongly disfavor such a conformation.

The conformer ratio A:B was determined to be 1:1 for the *p*-methoxycinnamoyl complex **1f** and 5:1 for the *p*-nitrocinnamoyl complex **1g**, from the integration of well-resolved signals at −35 °C. Thus, a *p*-nitro substituent actually destabilized the conformer **B** to a much larger extent than a *p*-methoxy substituent could reinforce CH/π interaction. This, in light of precedents,[10] is acceptable evidence that the preferred proximity of the phenyl and the methyl groups in these complexes results from a CH/π stabilization, although the magnitude of the stabilization energy is less than 1 kcal/mol (Table 2).

Summary

Conformational studies on a class of isostructural organometallic complexes suggest a definite role of the CH/π interaction in determining conformational preferences.

Experimental Section

General Comments. All reactions were carried out under a positive pressure of dry argon. Acetonitrile was purified by distillation from calcium hydride. The progress of the reaction was monitored by analytical thin-layer chromatography with TLC plates precoated with silica gel 60 F_{254} (Merck). Column chromatography of molybdenum complexes was carried out with silica gel obtained from Merck (230−400 mesh, 9385 grade) under argon or nitrogen pressure. The IR spectra were recorded as chloroform solutions on a Perkin-Elmer Infracord spectrophotometer, Model 599B or 1600 FT-IR. The ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker AC-200, MSL-300, or AM-500 spectrometers; ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 FT NMR spectrometer at 50.3 MHz all NMR data were expressed as parts per million downfield of tetramethylsilane. All melting points (recorded on a Thermonik Campbell melting point apparatus) are uncorrected and are recorded on the Celsius scale. Elemental analyses (C, H, N) were performed by Dr. S. Y. Kulkarni and his group at NCL on a Carlo-Erba 1100 automatic analyzer. Allyl halides were distilled prior to complexation unless otherwise mentioned. Cinnamoyl, crotyl, and prenyl chlorides were purchased from Aldrich. Molybdenum hexacarbonyl was purchased from Aldrich and used as received. The ligand precursor tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide (L′) was prepared as reported earlier[6] (L = bis(3,5-dimethyl-1-pyrazolyl)phosphinate).

Preparation of 1a: Standard Procedure. Molybdenum hexacarbonyl (0.528 g, 2 mmol) was placed in a two-necked flask fitted with a septum and a reflux condenser under argon cover. Cinnamoyl chloride (0.5 mL, excess) and acetonitrile (20 mL) were added to the flask through a syringe. The reaction mixture was heated under reflux for 5 h to obtain a red solution of the bis(acetonitrile) complex. The reaction mixture was cooled to room temperature, and a solution of the ligand L′ (0.996 g, 3 mmol) in acetonitrile (10 mL) was added with a syringe. After this mixture was stirred at room temperature for 10 min, degassed water (2 mL) was added and was preserved under argon at 0 °C for 48 h. The orange crystals that deposited in the flask were filtered, washed with 50% aqueous acetonitrile (10 mL), and dried in vacuo to obtain complex **1a** (0.505 g, 48%) as an orange crystalline solid, mp 239 °C dec. IR: 1938 (s), 1843 (s), 1559 (m), 1166 (m) cm^{-1}. ^{1}H NMR (−31 °C, 300 MHz): conformer **A**, δ 1.95 (d, 1H, J = 10 Hz), 2.32 (s, 3H), 2.45 (s, 3H), 2.50 (s, 3H), 2.58 (s, 3H), 2.65 (d, 1H, J = 10 Hz), 3.85 (d, 1H, J = 6 Hz), 4.60 (m, 1H), 5.90 (d, 1H, J = 2.0 Hz), 5.97 (d, 1H, J = 2.0 Hz); conformer **B**, δ 1.15 (s, 3H), 1.55 (d, 1H, J = 10 Hz), 2.44 (s, 3H), 2.80 (s, 3H), 2.83 (s, 3H), 3.15 (d, 1H, J = 10 Hz), 3.45 (d, 1H, J = 6 Hz), 4.60 (m, 1H), 5.65 (d, 1H, J = 2.0 Hz), 5.95 (s, 1H). The aromatic protons for both conformers appear as a complex multiplet from 6.60 to 7.7. ^{13}C NMR (−31 °C): δ 11.7, 12.1, 14.6, 49.4, 62.3, 89.2, 109.2, 110.3, 125.2, 127.4, 127.9, 128.3, 130.3, 136.9, 137.7, 145.6, 146.0, 147.2, 147.3, 148.0, 155.7, 156.6, 157.1, 159.1, 229.3, 230.0, 230.1, 231.7. Anal. Calcd for $C_{21}H_{23}MoN_4O_4P$: C, 48.27; H, 4.4; N, 10.73. Found: C, 48.55; H, 4.39; N, 10.6.

Preparation of Complex 1b. With a solution of a bis(acetonitrile) π-crotyl complex from molybdenum hexacarbonyl (0.528 g, 2 mmol) and crotyl chloride (1 mL, excess) in acetonitrile (20 mL), ligand exchange was carried out (0.835 g, 2.5 mmol of ligand L′ in 10 mL of acetonitrile) in a manner as described above. The reaction mixture was stirred for 10 min and concentrated to about 10 mL. It was poured into cold water (100 mL), and the yellow sticky mass was extracted with dichloromethane (25 mL). The residue obtained after the removal of dichloromethane was crystallized from acetone−water to furnish yellow crystals of complex **1b** (0.228 g, 25%), mp 260 °C dec. IR: 1940 (s), 1850 (s), 1560 (m), 1180 (s) cm^{-1}. ^{1}H NMR (25 °C, 200 MHz): δ 1.55 (s, 1H), 1.90 (m, 1H), 2.00 (d, 3H, J = 6 Hz), 2.30 (bm, 9H), 2.70 (s, 3H), 3.50 (d, 1H, J = 6 Hz), 3.70 (m, 1H), 5.75 (d, 1H, J = 2.0 Hz), 5.85 (d, 1H, J = 2.0 Hz). ^{13}C NMR (25 °C): δ 11.4, 11.7, 14.2, 14.4, 16.0, 62.1, 73.9, 81.6, 109.2, 109.3, 109.9, 110.0, 145.9, 146.1, 147.2, 147.4, 155.5, 155.7, 157.2, 157.4, 228.9, 229.8. Anal. Calcd for $C_{16}H_{21}MoN_4O_4P$: C, 41.75; H, 4.56; N, 12.17. Found: C, 41.73; H, 4.52; N, 11.84.

Preparation of Complex 1c. A mixture of molybdenum hexacarbonyl (0.528 g, 2 mmol), prenyl chloride (0.418 g, 4 mmol), and acetonitrile (20 mL) was heated under reflux for 5 h to afford an orange solution of the bis(acetonitrile) π-allyl complex. The reaction mixture was cooled to room temperature, and the ligand L′ (0.996 g, 3 mmol) in aceonitrile (10 mL) was syringed in. This mixture was stirred for 1 h and then concentrated to about 5 mL. The pure yellow complex **1c** obtained by column chromatography (25% ethyl acetate −75% petroleum ether) was recrystallized from dichlo-

(10) (a) Nakai, Y.; Yamamoto, G.; Oki, M. *Chem. Lett.* **1987**, 89. (b) Nakamura, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3377. (c) Karatsu, M.; Suezawa, H.; Abe, K.; Hirota, M.; Nishio, M.; *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3529.

romethane–petroleum ether to obtain orange crystals (0.168 g, 17.8%), mp 234 °C dec. IR: 1931 (s), 1834 (s), 1555 (m), 1165 (m) cm^{-1}. ^1H NMR (25 °C, 200 MHz): δ 1.05 (s, 3H), 2.05 (s, 3H), 2.37 (dd, 1H, J = 11.3, 1.1 Hz), 2.40 (s, 3H), 2.45 (s, 3H), 2.47 (s, 3H), 2.80 (s, 3H), 3.57 (dd, 1H, J = 7.5, 1.1 Hz), 3.97 (dd, 1H, J = 11.2, 7.5 Hz), 5.87 (d, 1H, J = 3.0 Hz), 5.92 (d, 1H, J = 3.0 Hz). ^{13}C NMR (25 °C): δ 11.4, 11.7, 14.2, 14.4, 22.3, 25.4, 61.3, 84.0, 86.8, 109.3, 109.9, 146.1, 147.3, 155.6, 157.4, 229.1, 232.3. Anal. Calcd for $C_{17}H_{23}MoN_4O_4P$: C, 43.02; H, 4.85; N, 11.81. Found: C, 42.85; H, 4.76; N, 11.51.

Preparation of Complex 1d. 4-Chloropent-2-ene was prepared by following reported procedures.[11,12] The complex **1d** was prepared using the same procedure as for **1c**. From molybdenum hexacarbonyl (0.528 g, 2 mmol), 4-chloropent-2-ene (0.418 g, 4 mmol), the ligand L′ (0.996 g, 3 mmol), and acetonitrile (30 mL) the complex **1d** (0.252 g, 26.7%) was obtained as orange crystals from dichloromethane-petroleum ether, mp 212 °C dec. IR: 1927 (s), 1827 (s), 1556 (m), 1166 (s) cm^{-1}. ^1H NMR (−50 °C, 500 MHz): isomer **C**, δ 1.68 (m, 1H), 1.82 (d, 3H, J = 3.6 Hz), 2.04 (d, 3H, J = 6.3 Hz), 2.33 (s, 3H), 2.40 (m, 1H), 2.42 (s, 3H), 2.44 (s, 3H), 2.73 (s, 3H), 3.81 (bt, 1H, J = 9.7 Hz), 5.92 (bs, 2H); isomer **D**, δ 1.19 (d, 3H, J = 6.3 Hz), 2.08 (d, 3H, J = 6.3 Hz), 2.35 (s, 3H), 2.39 (s, 3H), 2.40 (s, 3H), 2.45 (m, 1H), 2.81 (s, 3H), 3.74 (bt, 1H, J = 9.6 Hz), 4.17 (m, 1H), 5.96 (bs, 2H). ^{13}C NMR (25 °C): δ 11.7, 12.0, 14.4, 14.8, 14.9, 15.6, 16.3, 17.2, 70.1, 75.6, 81.9, 86.9, 109.6, 110.4, 146.2, 147.6, 156.1, 157.2, 157.8, 229.8, 230.5. Anal. Calcd for $C_{17}H_{23}MoN_4O_4P$: C, 43.02; H, 4.85; N, 11.81. Found: C, 42.59; H, 4.90; N, 11.56.

Preparation of Complex 1e. 3-Chloro-1-phenylbutene was prepared from the corresponding alcohol by the PPh_3–CCl_4 method.[13] 1-Phenylbuten-3-ol was prepared by $CeCl_3$/$NaBH_4$ reduction[14] of 1-phenylbuten-3-one. The procedure for preparing this complex is the same as that described for **1c**, using molybdenum hexacarbonyl (0.396 g, 1.5 mmol), the butenyl chloride (0.191 g, 1.5 mmol), the ligand L′ (0.747 g, 2.2 mmol), and acetonitrile (25 mL). The complex **1e** (0.150 g, 14%) was obtained as red crystals, mp 227 °C dec. IR: 1933 (s), 1827 (s), 1561 (m), 1167 (m) cm^{-1}. ^1H NMR (25 °C, 200 MHz): δ 1.25 (s, 3H), 2.00 (m, 1H), 2.20 (d, 3H, J = 9.0 Hz), 2.35 (s, 3H), 2.45 (s, 3H), 2.70 (s, 3H), 3.05 (d, 1H, J = 11.2 Hz), 4.50 (dd, 1H, J = 9.0, 11.2 Hz), 5.55 (d, 1H, J = 2.6 Hz), 5.90 (d, 1H, J = 2.9 Hz), 7.00 (bs, 5H). ^{13}C NMR (25 °C): δ 11.4, 11.9, 12.5, 14.3, 16.2, 66.4, 83.6, 85.0, 109.1, 110.1, 126.7, 127.9, 138.7, 146.0, 147.9, 156.7, 158.5, 231.6, 233.1. Anal. Calcd for $C_{22}H_{25}MoN_4O_4P$: C, 49.25; H, 4.66; N, 10.44. Found: C, 49.99; H, 4.30; N, 9.70.

Preparation of Complex 1f. The Reformatsky reaction of *p*-anisaldehyde with ethyl bromoacetate, dehydration, and LAH reduction furnished *p*-methoxycinnamyl alcohol, which was converted to the chloride by the PPh_3–CCl_4 method. To a dark red solution of bis(acetonitrile) π-*p*-methoxycinnamyl complex obtained from molybdenum hexacarbonyl (0.264 g, 1 mmol), *p*-methoxycinnamyl chloride (0.31 g, 1.7 mmol), and acetonitrile (15 mL), maintained under reflux, was added the ligand L′ (0.5 g, 1.5 mmol) in acetonitrile (10 mL). Cooling and partial removal of solvent afforded a dark brown liquid which was added to ice-cold degassed water (100 mL). The gummy solid was extracted in toluene (100 mL). The toluene solution was concentrated to 5 mL and preserved in a closed chamber containing petroleum ether for recrystallization. The complex **1f** (0.049 g, 9%) was obtained as brown crystals after 48 h; MP 260 °C dec. IR: 1920 (s), 1840 (s), 1560 (m), 1180 (s) cm^{-1}. ^1H NMR (−15 °C, 200 MHz): conformer **A**, δ 1.90 (d, 1H, J = 10 Hz), 2.30 (s, 3H), 2.48 (s, 3H), 2.50 (s, 3H), 2.55 (s, 3H), 2.80 (bs, 1H), 3.80 (bs, 1H), 3.85 (s, 3H), 4.50 (m, 1H), 5.90 (d, 1H, J = 2.0 Hz), 5.95 (bs, 1H), 6.92 (d, 2H, J = 9.5 Hz), 7.60 (d, 2H, J = 9.5 Hz); conformer **B**, δ 1.25 (s, 3H), 1.55 (d, 1H, J = 10 Hz), 2.45 (s, 3H), 2.80 (s, 3H), 2.82 (s, 3H), 3.30 (d, 1H, J = 10 Hz), 3.45 (m, 1H), 3.85 (s, 3H), 4.50 (m, 1H), 5.70 (d, 1H, J = 2.0 Hz), 5.95 (bs, 1H), 6.92 (d, 2H, J = 9.5 Hz), 7.60 (d, 2H, J = 9.5 Hz). The ^{13}C NMR spectrum was not recorded due to the paucity of the sample. Anal. Calcd for $C_{22}H_{25}MoN_4O_5P$: C, 47.82; H, 4.52; N, 10.14. Found: C, 48.55; H, 4.39; N, 10.6.

Preparation of Complex 1g. Molybdenum hexacarbonyl (0.264 g, 1 mmol) was taken up in acetonitrile (15 mL) and heated under reflux for 6 h to afford a golden yellow solution of the tris(acetonitrile) $Mo(CO)_3$ complex. *p*-Nitrocinnamyl bromide[15] (0.266 g, 1.1 mmol) in acetonitrile (10 mL) was injected into the reaction mixture at 60–70 °C, which was then stirred for 1 h. The color of the reaction mixture changed from yellow to deep red, and the solution was then cooled to room temperature. The ligand L′ (0.498 g, 1.5 mmol) in acetonitrile (10 mL) was added, and the solution was stirred for 1 h. The complex **1g** was purified by column chromatography using 2.5% MeOH –98% EtOAc. Crimson red crystals were obtained from dichloromethane–petroleum ether (0.210 g, 37%), mp 195 °C dec. IR: 1944 (s), 1852 (s), 1553 (m), 1167 (m) cm^{-1}. ^1H NMR (−35 °C, 200 MHz): conformer **A**, δ 2.05 (d, 1H, J = 10.3 Hz), 2.30 (s, 3H), 2.45 (s, 3H), 2.47 (d, 1H, J = 11.7 Hz), 2.50 (s, 3H), 2.80 (s, 3H), 3.95 (d, 1H, J = 6.9 Hz), 4.65 (m, 1H), 5.92 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 2.9 Hz), 7.67 (d, 2H, J = 8.8 Hz), 8.17 (d, 2H, J = 8.8 Hz); conformer **B**, δ 1.25 (s, 3H), 1.62 (d, 1H, J = 8.8 Hz), 2.40 (s, 3H), 2.25 (s, 3H), 2.75 (s, 3H), 2.97 (d, 1H, J = 11.3 Hz), 3.55 (d, 1H, J = 5.9 Hz), 4.65 (m, 1H), 5.70 (d, 1H, J = 2.3 Hz), 5.95 (d, 1H, J = 2.3 Hz), 7.67 (d, 2H, J = 8.8 Hz), 8.17 (d, 2H, J = 8.8 Hz). ^{13}C NMR (25 °C): δ 11.7, 11.9, 14.6, 63.2, 70.9, 79.5, 109.9, 110.6, 123.2, 128.7, 146.3, 146.6, 147.9, 156.6, 157.8, 228.7, 230.6. Anal. Calcd for $C_{21}H_{22}MoN_5PO_6$: C, 44.44; H, 3.88; N, 12.34. Found: C, 44.02; H, 3.71; N, 11.95.

X-ray Structure Solution of Complex 1a. The crystals were grown from toluene–hexane. Diffraction data were collected on an Enraf-Nonius CAD-4F-11.M single-crystal X-ray diffractometer. Unit cell dimensions were determined using 25 machine-centered reflections in the range $18 < \theta < 23°$. Reflections were measured with the following index range: h, 0–8; k, 0–12; l, −29 to +29 (average scan speed 1° min^{-1}). The structure was solved[16] using the heavy-atom method. Least-squares refinement of scale factor, positional and anisotropic thermal parameters for non-hydrogen atoms was carried out. Coordinates of hydrogen atoms were geometrically determined and held fixed during refinement. A Cruickshank weighting scheme of the type $w = (a + b|F_o| + c|F_o|^2]^{-1}$ with a = 10.0, b = 1.0, and c = 0.008 was applied. The refinement converged to R = 0.038 for 2480 observed reflections.

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Supplementary Material Available: Tables of bond distances and angles, atomic positional parameters, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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