Preparation of Dicarbonyl[hydrotris(1-pyrazolyl)borato](η^3-allyl)molybdenum Complexes Bearing Electron-Donating Substituents (1-((*tert*-Butyldimethylsilyl)oxy), 1-Alkoxy, and 1-Acetoxy) via the Nucleophilic Addition of $Mo(CO)_3(DMF)_3$ to Enals and Enones

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Cyclic and acyclic dicarbonyl[hydrotris(1-pyrazolyl)borato][η^3-1-((*tert*-butyldimethylsilyl)-oxy)allyl]molybdenum complexes and a variety of their 1-acetoxy and 1-alkoxy (RO = MeO, *i*-PrO) analogues were prepared and characterized by IR and ^{1}H and ^{13}C NMR spectroscopy and, in the case of [$TpMo(CO)_2$[η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclohexen-1-yl], by X-ray crystallography. These complexes were prepared in moderate to excellent yields by the *tert*-butyldimethylsilyl chloride promoted oxidative addition of α,β-unsaturated aldehydes and acyclic and cyclic ketones to $(DMF)_3Mo(CO)_3$ followed by ligand metathesis with potassium hydrotris(1-pyrazolyl)borate. The 1-*tert*-butyldimethylsiloxy- and the 1-methoxy- and 1-isopropoxy-substituted acyclic complexes were formed solely as the *syn* isomer; however, the 1-acetoxy analogue underwent isomerization to a thermodynamic mixture of the *syn* and *anti* isomers in which the *anti* isomer predominated (3.7 : 1). The 1-((*tert*-butyldimethylsilyl)oxy)-3-alkyl- or 1-alkoxy-3-alkyl-disubstituted acyclic complexes were formed with *syn*-silyloxy/*anti*-alkyl or *syn*-alkoxy/*anti*-alkyl stereochemistry, while the disubstituted allyls bearing a 1-acetoxy substituent existed as mixtures of both possible *syn*/*anti* isomers and the *syn*/*syn* and *anti*/*anti* isomers. The conformation and configuration of the isomers was confirmed through nOe studies on several complexes and by X-ray crystallography in the case of [$TpMo(CO)_2$[η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclohexen-1-yl].

Introduction and Background

η^3-Allylic complexes of the transition metals are of great use in organic synthesis.[2−36] By far the vast majority of those π-allyl complexes that have been studied as stoichiometric reagents possess alkyl, aryl, acyl, and alkoxycarbonyl substituents, there being few general routes to (η^3-allyl)metal complexes bearing

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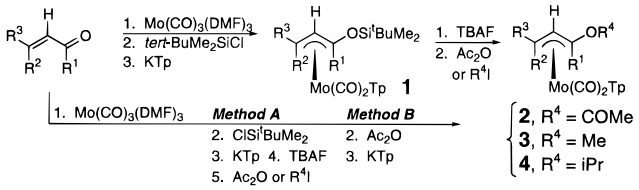
Table 1. Preparation of TpMo(CO)$_2$(η^3-allyl) Complexes Bearing Electron-Donating 1-Substituents

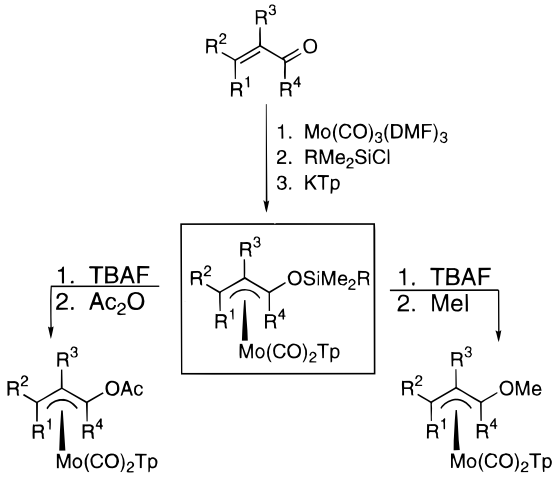


substrate	complex	configuration R^1	R^2	R^3	R^4	yield (%)
2-propenal	1a	H	H	H	Si^{t}BuMe$_2$	67
E-2-butenal	1b	H	H	Me	Si^{t}BuMe$_2$	82
E-2-pentenal	1c	H	H	Et	Si^{t}BuMe$_2$	87
E-cinnamaldehyde	1d	H	H	Ph	Si^{t}BuMe$_2$	78
3-buten-2-one	1e	Me	H	H	Si^{t}BuMe$_2$	66
2-cyclohexenone	1f	$-CH_2CH_2CH_2-$		H	Si^{t}BuMe$_2$	61
2-cyclopentenone	1g	$-CH_2CH_2-$		H	Si^{t}BuMe$_2$	63
3-methyl-2-cyclopentenone	1h	$-CH_2CH_2-$		Me	Si^{t}BuMe$_2$	37
2-propenal	2a	H	H	H	COMe	67 (B)
E-2-butenal	2b	H	H	Me	COMe	88 (B)
2-cyclohexenone	2f	$-CH_2CH_2CH_2-$		H	COMe	54 (A)
2-cyclopentenone	2g	$-CH_2CH_2-$		H	COMe	50 (A)
2-propenal	3a	H	H	H	Me	64 (A)
E-2-butenal	3b	H	H	Me	Me	64 (A)
E-2-pentenal	3c	H	H	Et	Me	30 (A)
3-buten-2-one	3e	Me	H	H	Me	65 (A)
2-cyclohexenone	3f	$-CH_2CH_2CH_2-$		H	Me	78 (A)
2-cyclopentenone	3g	$-CH_2CH_2-$		H	Me	60 (A)
4,4-dimethyl-2-cyclohexenone	3i	$-CMe_2CH_2CH_2-$		H	Me	38 (A)
2-propenal	4a	H	H	H	*i*-Pr	56 (A)
E-2-butenal	4b	H	H	Me	*i*-Pr	23 (A)
2-cyclohexenone	4f	$-CH_2CH_2CH_2-$		H	*i*-Pr	19 (A)

electron-donating substituents.[37−39] As part of an ongoing study of the synthesis, properties, and synthetic utility of TpMo(CO)$_2$(η^3-allyl) complexes[40−42] (Tp = hydrotris(1-pyrazolyl)borato),[43,44] a general preparative route to TpMo(CO)$_2$(η^3-allyl) complexes possessing electron-donating substituents was desired.

α,β-Unsaturated aldehydes and ketones have served as precursors to 1-((trialkylsilyl)oxy)allyl substituted η^3-allyl complexes of a number of metals.[37,39] For example, Mackenzie and co-workers showed that enone and enal substrates on treatment with bis(1,5-cyclooctadiene)-nickel(0) and then with chlorotrialkylsilanes gave [η^3-1-((trialkylsilyl)oxy)allyl]nickel chloride dimers in excellent yield.[39] Described herein is a variant of that procedure using Mo(CO)$_3$(DMF)$_3$ that allows the construction of (η^3-allyl)molybdenum complexes possessing 1-(*tert*-butyldimethylsiloxy), 1-alkoxy, and 1-acetoxy substituents.

Scheme 1



Results

Treatment of a variety of cyclic and acyclic α,β-unsaturated enals and enones in CH_2Cl_2 with (DMF)$_3$-Mo(CO)$_3$[45] followed by addition of *tert*-BuMe$_2$SiCl generated a cherry-red solution from which the stable *tert*-butyldimethylsiloxy-substituted (η^3-allyl)molybdenum complexes **1** were obtained after addition of K^+Tp^- and purification of the reaction mixture by flash chromatography (Scheme 1) (Table 1). Use of Me_3SiCl produced similar results, but *tert*-BuMe$_2$SiCl was preferred for ease of purification and stability of the product toward moisture. The general procedure involved addition of the neat α,β-unsaturated carbonyl compound to a solu-

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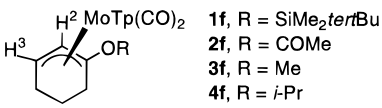
tion of 1 equiv of $(DMF)_3Mo(CO)_3$ in dry, degassed dichloromethane (*ca.* 0.2 M) under an inert atmosphere. Addition of 1.1 equiv of solid *tert*-$BuMe_2SiCl$ followed by stirring of the reaction mixture at room temperature (0.5 h for enals and 2−24 h for enones) led to a clear orange solution in most cases (the reaction mixture from the highly substituted cyclic enones changed very little in color). Addition of 1.1 equiv of solid potassium hydrotris(1-pyrazolyl)borate[43] produced a gelatinous reaction mixture (formation of KCl) from which the yellow to orange products were easily obtained after purification by flash chromatography on SiO_2 and/or recrystallization from hexane (Table 1). The solid (*tert*-butyldimethylsilyl)oxy-substituted allyls were stable in air under anhydrous conditions for months; however, atmospheric moisture caused noticeable degradation within days or weeks, especially for the highly substituted complex **1h**.

The (*tert*-butyldimethylsilyl)oxy-substituted allyl complexes in Table 1 underwent desilylative alkylation and acylation producing 1-acetoxy- and 1-alkoxy-substituted η^3-allyls when treated with tetra-*n*-butylammonium fluoride (TBAF) followed by the addition of electrophiles (Ac_2O, MeI, *i*-PrI). It proved possible to carry out these transformations without isolation and purification of the intermediate *tert*-butyldimethylsilyl ether. For example, treatment of the reaction mixture with 2.0−2.5 equiv of tetra-*n*-butylammonium fluoride (TBAF) followed by 2−20 equiv of the electrophile provided the desired η^3-allyl complexes after workup (Table 1, method A). Furthermore, the acyclic 1-acetoxy derivatives **2a**,**b** can be directly obtained by acylation of the initial enal−Mo complex with Ac_2O followed by metathesis with KTp (Table 1, method B). Unlike their (*tert*-butyldimethylsilyl)oxy counterparts, the 1-acetoxy-substituted allyls were stable indefinitely to moisture and air.

Discussion

Substituent Configuration and η^3-Allyl Conformation of Acyclic Allyls. The *syn*/*anti* configuration of the terminal substituents of the acyclic η^3-allyl was readily assigned on the basis of the coupling constants and chemical shifts of the *syn* and *anti* protons, as previously described.[40] In addition, the *exo* conformation was assigned to each of the new complexes on the basis of ^{1}H nOe experiments (*exo*: the terminal carbon atoms of the allyl eclipse the carbonyl carbon atoms and the central carbon of the allyl eclipses the Mo) and by X-ray crystallography in the case of complex **3a**. Solution spectra (IR, ^{1}H NMR, ^{13}C NMR) revealed no evidence of the *endo* rotamer, supporting the recent observation that all $TpMo(CO)_2(\eta^3$-allyl) complexes that have been structurally characterized assume the *exo* conformation in the solid state as well as in solution.[40] In direct contrast, both *exo* and *endo* rotamers of η^3-allyl complexes possessing the CpMo(CO)L fragment (L = CO, NO) have been characterized and their interconversion studied by temperature-dependent NMR.[46−49]

2-Propenal-Derived Complexes 1a−4a. Assignment of the ^{1}H NMR resonances of the acyclic 2-propenal-derived complexes **1a**−**4a** rested upon the unequivocal assignment of the ^{1}H NMR spectra of the cyclohexenyl complexes **1f**−**4f**. In these cyclic complexes the protons H2 and H3 possess an unambiguous *cis* (*syn*) relationship (Figure 1) and absorb in the range 3.89−4.07 ppm with coupling constants between 7.5 and 8.1 Hz. These values are similar to *syn*-related protons of non-heteroatom-substituted allyls in both the $MoTp(CO)_2$ and $MoCp(CO)_2$ series.[40,50]



1f, R = $SiMe_2$*tert*Bu
2f, R = COMe
3f, R = Me
4f, R = *i*-Pr

Figure 1.

Table 2. Chemical Shifts of Allyl Protons of 2-Propenal-Derived Complexes 1a-4a and the Magnitude of Coupling to the Central Proton (H^2)

complex	H^1		H^2	H^3		H^4	
	shift (ppm)	coupling (Hz)	shift (ppm)	shift (ppm)	coupling (Hz)	shift (ppm)	coupling (Hz)
1a	4.57	7.8	3.77	3.24	7.2	1.22	9.0
2a	5.42	7.2	4.05	3.38	7.2	1.49	9.4
3a	4.59	8.0	3.81	3.31	7.0	1.26	9.0
4a	4.67	8.0	3.75	3.27	7.0	1.30	9.0

The propenal-derived complexes **1a**−**4a** displayed four common sets of resonances: (1) doublets resonating in the range 4.57−5.42 ppm with coupling to the central proton in the range 7.2−8.0 Hz which were assigned to the H1 proton (Table 2), (2) doublets of triplets or doublet of doublet of doublets resonating in the range 3.75−4.05 ppm which were assigned to the H2 central protons (Table 2), (3) doublets of doublets resonating in the range 3.24−3.38 ppm with a coupling to the central proton in the range 7.0−7.2 Hz which were assigned to the *syn*-H3 protons, and (4) doublets of doublets resonating in the range 1.22−1.49 ppm with coupling to the central proton in the range 9.0−9.4 Hz which was assigned to the H4 *anti* proton (Table 2).[33] With H2, H3, and H4 securely assigned, the H1 protons were tentatively assigned as *anti* on the basis of the observed coupling constants of 7.2−8.0 Hz to H2.[40] Protons in the *anti* position of symmetrically substituted and *syn*-alkyl-substituted allyls exhibited coupling to the central proton in the range 8.7−12.0 Hz; however, the attachment of an electron-withdrawing heteroatom lowers the magnitude of such couplings in both *syn* and *anti* protons.[38,39]

^{1}H nOe studies on complex **1a** confirmed these assignments (Figure 2). Irradiation of *syn*-H^3 produced a 7% enhancement of the central-H^2 and a 27% enhancement of the geminal *anti*-H^4. Irradiation of H^4 produced a 15% enhancement of the geminal H^3 and an 11% enhancement of H^1 with no enhancement of H^2 observed. Presaturation of H^1 produced a 10% enhancement of H^4, while irradiation of H^2 revealed 5% enhancement of H^3. In addition, the recently determined solid-state stucture of methoxy complex **3a** revealed the methoxy group in the *syn* orientation.[40] (*tert*-Butyldimethylsilyl)oxy complex **1a** and alkoxy complexes **3a** and **4a** were configurationally stable at elevated temperatures (C_6D_6, >125 °C). *syn*-acetoxy complex **2a**, however, equilibrated at elevated temperature (C_6D_6, 120 °C) to a 3.7 to 1.0 *anti* vs *syn* mixture of isomers.[40]

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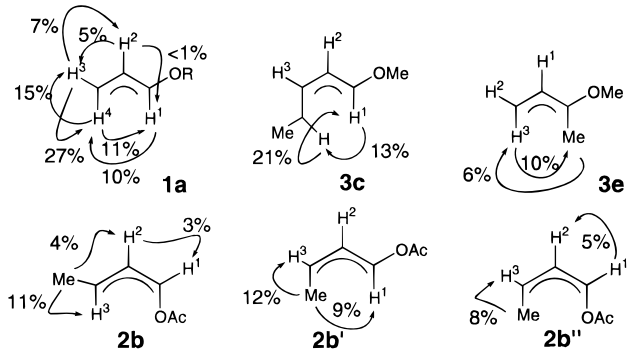

Figure 2. ^{1}H nOe studies.

Table 3. Complexes 1b, 3b, 4b, 1c, and 3c and the Magnitude of Coupling to the Central Proton (H^2)

complex	H^1		H^2		H^3	
$MoTp(CO)_2$	shift (ppm)	coupling (Hz)	shift (ppm)	coupling (Hz)	shift (ppm)	coupling (Hz)
1b	5.29	6.8	H^2 and H^3 overlapped at 3.90−3.83			
3b	5.30	9.0	H^2 and H^3 overlapped at 3.89			
4b	5.27	7.8	H^2 and H^3 overlapped at 3.90−3.83			
1c	5.23	8.3	3.78		3.87	8.3
3c	5.22	8.6	3.79		3.90	8.6

2-Butenal- and 2-Pentenal-Derived Complexes 1b, 2b, 3b, 4b, 1c, and 3c. The orientation of the methyl and ethyl groups of complexes **1b**, **3b**, **4b**, **1c**, and **3c** was easily assigned on the basis of the coupling constants and chemical shifts of the allyl signals in the ^{1}H NMR spectra (Table 3). The Me and Et groups were assigned *anti* on the basis of (1) the chemical shifts of H^3 in the range 3.78−3.92 ppm and (2) couplings of H^3 to the central proton in the range 8.3−8.6 Hz. The silyloxy and alkoxy groups were assigned *syn* on the basis of the series of doublets in the range 5.22−5.30 ppm with couplings to the central proton in the range 6.8−9.0 Hz (Table 3). ^{1}H nOe studies on complex **3c** confirmed these analyses (Figure 2, above). Irradiation of the methylene signal of **3c** at 0.52 ppm produced a 21% enhancement of H^1 at 5.22 ppm.

Treatment of *E*-2-butenal with $(DMF)_3Mo(CO)_3$ in CH_2Cl_2 followed by the addition of acetic anhydride then KTp (method B) gave three isomeric products (14.8/2.2/1.0). The major isomer was purified by column chromatography and assigned the structure **2b** (*syn*-methyl/*anti*-acetoxy) on the basis of ^{1}H nOe experiments (Figure 2). Presaturation of the methyl doublet at 2.30 ppm produced an 11% enhancement of H^3 (δ 3.15) and a 4% enhancement of H^2 (δ 3.87). Irradiation of H^2 also enhanced H^1 (δ 7.62) by 3%.

Upon standing in $CDCl_3$ at room temperature for 4 days, **2b** equilibrated to a mixture of four isomers (9.3/6.0/4.1/1.0) in which complex **2b** predominated. ^{1}H nOe experiments confirmed that the second most abundant isomer was *syn*-acetoxy/*anti*-methyl complex **2b′** (Figure 2). Irradiation of the methyl doublet at 1.33 ppm produced a 12% nOe enhancement of H^3 (δ 4.13) and a 9% enhancement of the H^1 doublet at 6.14 ppm. The third species was assigned the *anti*-methyl/*anti*-acetoxy structure, **2b″**. Presaturation of the methyl doublet at 1.72 ppm produced an 8% enhancement of H^3 (δ 4.67) with no other enhancements observed. When H^1 of **2b″** was presaturated, a 5% enhancement of a doublet of doublets at 3.24 ppm (H^2) as well as 12% enhancement of a Tp signal at 7.59 ppm was observed. The minor isomer was tentatively assigned the *syn*-methyl/*syn*-acetoxy structure **2b‴**. Presaturation of the methyl doublet at 1.94 ppm resulted in a 17% enhancement of a Tp signal at 8.12 ppm. A very small nOe enhancement of a doublet of doublets (<2%) at 4.20 ppm was observed, and suggests that this is the central allyl proton of **2b‴**.

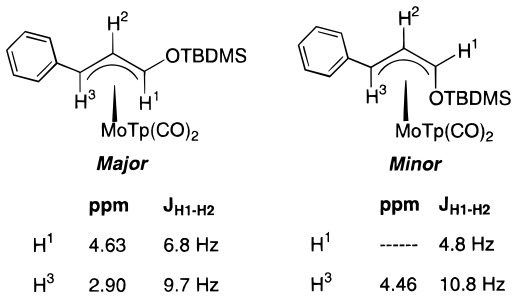

Figure 3.

When **1b** was treated withTBAF and then Ac_2O (method A), **2b′**, **2b**, and **2b‴** (3.6/3.0/1.0) were observed in the ^{1}H NMR spectrum. After several days, the fourth isomer (**2b″**) grew in, and the isomer ratio was nearly identical to that observed when **2b** was allowed to equilibrate. As was the case for **2a**, the acetoxy group displayed a thermodynamic preference for the *anti* position.[40]

3-Phenyl-2-propenal-Derived Allyl 1d. Unlike the other silyloxy complexes, **1d** was formed as a mixture of two isomers in approximately a 10 to 1 ratio. In the ^{1}H NMR spectrum the presence of doublets at 4.63 and 2.90 ppm along with coupling to the central proton of 6.8 and 9.7 Hz, respectively, revealed the *syn*-phenyl/*syn*-(*tert*-butyldimethylsilyl)oxy configuration of the major isomer. On the basis of the chemical shifts and coupling constants, the upfield doublet was assigned to the *anti* proton on the phenyl bearing carbon, while the downfield doublet was identified as an *anti* proton on the oxygen bearing carbon. The *anti* orientation of these two protons was confirmed by ^{1}H nOe experiments. Irradiation of the doublet at 2.90 ppm produced an 18% enhancement of the doublet at 4.63 ppm. Attempts to irradiate the doublet at 4.63 were complicated by the presence of the central proton resonance at 4.54 ppm.

The ^{1}H NMR spectrum of the minor isomer displayed a doublet at 4.46 ppm with coupling to the central proton of 10.8 Hz, indicating an *anti* orientation. The location of the other doublet could not be determined (obscured by Tp resonances), but its coupling to the central proton (at 4.33 ppm) was 4.8 Hz. The doublet at 4.46 ppm was identified as an *anti* proton on the allyl carbon bearing the phenyl group based on its coupling constant. The other coupling to the central proton (4.8 Hz) suggested that the proton responsible for this coupling was *syn* to the central proton, and that the minor isomer was the *syn*-phenyl/*anti*-silyloxy allyl complex (Figure 3).

The minor isomer vanished when a C_6D_6 solution of **1d** was warmed to 60 °C for 3 h. Unlike other 1,3-disubstituted η^3-allyls in this and previous studies based on the $TpMo(CO)_2$ fragment, complex **1d** existed predominately as the all-*syn* rather than the *syn*/*anti* isomer, which presumably is a function of the more efficient donation of the aryl and oxygen substituents

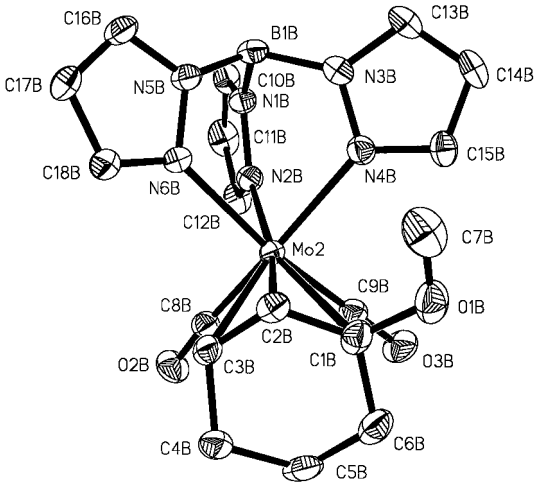

Figure 4. ORTEP diagram of **3f**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 3f

Mo(2)−C(1B)	2.664(4)	O(3B)−C(9B)	1.174(5)
Mo(2)−C(9B)	1.920(4)	O(1B)−C(1B)	1.359(5)
Mo(2)−C(8B)	1.933(4)	C(3B)−C(2B)	1.435(6)
Mo(2)−N(2B)	2.220(3)	O(2B)−C(8B)	1.165(5)
Mo(2)−N(4B)	2.243(3)	O(1B)−C(7B)	1.435(6)
Mo(2)−C(2B)	2.256(4)	C(3B)−C(4B)	1.508(6)
Mo(2)−N(6B)	2.307(3)	C(2B)−C(1B)	1.377(6)
Mo(2)−C(3B)	2.300(4)	C(5B)−C(6B)	1.523(7)
N(1B)−B(1B)	1.552(6)	C(5B)−C(4B)	1.519(6)
N(3B)−B(1B)	1.536(6)	C(1B)−C(6B)	1.508(6)
N(5B)−B(1B)	1.522(6)		

C(9B)−Mo(2)−C(8B)	82.5(2)	C(6B)−C(5B)−C(4B)	113.6(4)
C(9B)−Mo(2)−N(2B)	94.67(14)	O(1B)−C(1B)−C(2B)	124.4(4)
C(8B)−Mo(2)−N(2B)	82.73(14)	O(1B)−C(1B)−C(6B)	109.5(4)
C(9B)−Mo(2)−N(4B)	89.69(14)	C(2B)−C(1B)−C(6B)	123.0(4)
C(8B)−Mo(2)−N(4B)	159.32(14)	N(5B)−B(1B)−N(3B)	111.2(4)
C(9B)−Mo(2)−N(6B)	172.10(14)	N(5B)−B(1B)−N(1B)	107.9(3)
C(8B)−Mo(2)−N(6B)	102.48(13)	N(3B)−B(1B)−N(1B)	107.1(3)
C(1B)−O(1B)−C(7B)	118.0(4)	C(3B)−C(4B)−C(5B)	112.5(3)
C(2B)−C(3B)−C(4B)	118.2(3)	O(2B)−C(8B)−Mo(2)	174.2(3)
C(1B)−C(2B)−C(3B)	116.6(4)	C(1B)−C(6B)−C(5B)	115.6(4)

into the π-system of the allyl when both are in a *syn* orientation.[40]

3-Buten-2-one-Derived Allyls 1e and 3e. The configurations of η^3-allylic complexes **1e** and **3e** were determined by nOe studies of the methoxy complex **3e** (Figure 2). Irradiation of *anti* H^3 (1.63 ppm) produced enhancement of the geminal H^2 signal (which overlapped with the absorption of the central proton in the ^{1}H NMR) and a 10% enhancement of the allyl methyl group. Irradiation of the allyl methyl group produced a 6% enhancement of the *anti* H^3 and a 0% enhancement of the central H^1 or *syn* H^2 protons leading to assignment of **1e** and **3e** as the *syn*-silyloxy and *syn*-methoxy complexes.

X-ray Crystallographic Studies. A crystal of **3f** suitable for a diffraction study was grown from CH_2Cl_2/hexane at 0 °C. The thermal ellipsoid plot is depicted in Figure 4, with bond lengths and angles given in Table 4. The diffraction study revealed an $\eta^3 \Rightarrow \eta^1$ distortion of the allylic moiety of **3f**. The Mo−C(1) bond distance of 2.66 Å was considerably longer than those of Mo−C(3) and Mo−C(2) (2.30 and 2.25 Å, respectively), a phenomenon previously seen in the crystal structures reported for a number of acyclic π-allyl complexes of molybdenum possessing *syn* substituents.[40] It also appears that one of the CO ligands (C(9)−O(3)) assumes a pseudo-axial position, with a N(6)−Mo−C(9) bond angle of 172.0°. The bond angle of N(4)−Mo−C(8) is 159.3°, and this CO ligand assumes a pseudo-equatorial position. The structure of **3f** also revealed preferential alignment of C(2)−C(3) with Mo−C(8) (dihedral angle = 12°).

Conclusions

A convenient method for the preparation of 1-(*tert*-butyldimethylsiloxy)-, 1-acetoxy-, 1-methoxy-, and 1-isopropoxy-substituted allyls based on the $TpMo(CO)_2$ fragment was developed using the *tert*-butyldimethylsilyl chloride promoted oxidative addition of α,β-unsaturated aldehydes and acyclic and cyclic ketones to $(DMF)_3Mo(CO)_3$ followed by ligand metathesis with potassium hydrotris(1-pyrazolyl)borate. α,β-Unsaturated esters and amides failed to react with $Mo(CO)_3(DMF)_3$ under a variety of conditions, as did the vinylogous ester, 3-ethoxy-2-cyclohexenone.

In the case of the acyclic η^3-allyls, coupling constants and ^{1}H nOe experiments confirmed the stereochemistry about the allyl. The crystal structures of **3a** (previously published) and **3f** provided further evidence for these assignments. Synthetic transformations of these novel molybdenum allyls will be described in a future publication.

Experimental Section

General Procedures. All reactions were performed under a positive pressure of dry argon or nitrogen. Dichloromethane was distilled from calcium hydride or dried with 4 Å molecular sieves prior to use. Anhydrous *N*,*N*-dimethylformamide and anhydrous toluene were purchased from Aldrich Chemical Co. and sparged with dry argon or nitrogen for at least 5 min prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone prior to use. All α,β-unsaturated ketones and aldehydes, acetic anhydride, methyl iodide, isopropyl iodide, molybdenum hexacarbonyl, and tetra-*n*-butylammonium fluoride were purchased from Aldrich Chemical Co. and used as received. $(DMF)_3Mo(CO)_3$[45] and KTp[43] were prepared using literature procedures. Analytical TLC was performed on glass plates precoated with Merck F_{254} silica gel 60, and visualization was accomplished using UV. Column chromatography of (π-allyl)molybdenum complexes was performed with mixtures of hexane and ethyl acetate on Merck silica gel 60 under air pressure.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1S,2R)-1-((*tert*-butyldimethylsilyl)oxy)-2-propen-1-yl]-molybdenum, 1a (*syn*-OTBDMS). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.46 g, 3.66 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 2-propenal (206 mg, 3.68 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (606 mg, 4.02 mmol, 1.10 equiv) were added and stirred for 0.5 h. Solid KTp (922 mg, 3.66 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Flash silica gel chromatography (hexanes/EtOAc, 2/1) and recrystallization (hexane) provided pure **1a** (1.32 g, 2.46 mmol, 67%) as an orange solid: Mp = 147−149 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.48 (br s, 1 H), 8.26 (br s, 1 H), 7.78 (br s, 1 H), 7.56 (br s, 2 H), 7.51 (br s, 1 H), 6.26 (br s, 1 H), 6.17 (br s, 1 H), 6.09 (br s, 1 H), 4.57 (d, J = 7.8 Hz, 1 H), 3.77 (dt, J = 7.5, 7.5 Hz, 1 H), 3.24 (dd, J = 7.2, 3.3 Hz, 1 H), 1.22 (dd, J = 9.0, 3.0 Hz, 1 H), 1.01 (s, 9 H), 0.32 (s, 3 H), 0.28 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 231.5, 228.3, 147.2, 144.9, 141.6, 135.5 (app s, 2 C), 134.1, 113.2, 105.6, 105.0, 104.3, 64.9, 46.9, 25.8, 18.6, −4.7, −5.6; IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (m), 1931 (s), 1835 (s). Anal. Calcd for $C_{20}H_{29}BMoN_6O_3Si$: C, 44.79; H, 5.45; N, 15.67. Found: C, 44.95; H, 5.51; N, 15.43.

Dicarbonyl[[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*,3*R*)-1-((*tert*-butyldimethylsilyl)oxy)-2-buten-1-yl]molybdenum, 1b (*anti*-Me/*syn*-OTBDMS). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.15 g, 2.88 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, *E*-2-butenal (239 μL, 2.88 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (477 mg, 3.16 mmol, 1.10 equiv) were combined and stirred for 0.5 h. Solid KTp (726 mg, 2.88 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexane) provided pure **1b** (1.32 g, 2.36 mmol, 82%) as a yellow solid: Mp = 181−182 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.47 (d, *J* = 1.4 Hz, 1 H), 8.12 (d, *J* = 1.4 Hz, 1 H), 7.70 (d, *J* = 1.4 Hz, 1 H), 7.56 (d, *J* = 2.2 Hz, 1 H), 7.55 (d, *J* = 2.2 Hz, 1 H), 7.49 (d, *J* = 2.2 Hz, 1 H), 6.24 (app t, *J* = 1.8 Hz, 1 H), 6.16 (app t, *J* = 1.6 Hz, 1 H), 6.10 (app t, *J* = 2.0 Hz, 1 H), 5.29 (d, *J* = 6.8 Hz, 1 H), 3.90−3.83 (m, 2 H), 1.32 (d, *J* = 6.0 Hz, 3 H), 1.01 (s, 9 H), 0.29 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 231.3, 230.1, 147.1, 145.2, 141.0, 135.5 (2 C), 134.1, 112.4, 105.6, 105.0, 104.3, 69.6, 56.9, 25.9, 18.7, 17.5, −4.7, −5.6; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (w), 1926 (s), 1830 (s). Anal. Calcd for $C_{21}H_{31}BMoN_6O_3Si$: C, 45.83; H, 5.68; N, 15.27. Found: C, 45.75; H, 5.65; N, 15.19.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*,3*R*)-1-((*tert*-butyldimethylsilyl)oxy)-2-penten-1-yl]-molybdenum, 1c (*anti*-Ethyl/*syn*-OTBDMS). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.09 g, 2.73 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, *E*-2-pentenal (267 μL, 2.73 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (452 mg, 3.00 mmol, 1.10 equiv) were combined and stirred for 0.5 h. Solid KTp (687 mg, 2.73 mmol, 1.00 equiv) was added, and the solution stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexanes) provided pure **1c** (1.34 g, 2.37 mmol, 87%) as a yellow solid: Mp = 125−126 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.46 (d, *J* = 1.4 Hz, 1 H), 8.13 (d, *J* = 1.8 Hz, 1 H), 7.74 (d, *J* = 1.4 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.55 (d, *J* = 1.8 Hz, 1 H), 7.48 (d, *J* = 1.8 Hz, 1 H), 6.23 (app t, *J* = 2.2 Hz, 1 H), 6.17 (app t, *J* = 1.8 Hz, 1 H), 6.10 (app t, *J* = 1.8 Hz, 1 H), 5.23 (d, *J* = 8.3 Hz, 1 H), 8.87 (m, 1 H), 3.78 (app t, *J* = 8.3 Hz, 1 H), 2.15 (ddq, *J* = 13.6, 6.8, 4.3 Hz, 1 H), 1.14 (app t, *J* = 7.2 Hz, 3 H), 1.01 (s, 9 H), 0.52 (ddq, *J* = 13.6, 10.8, 6.8 Hz, 1 H), 0.27 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 231.5, 230.0, 147.0, 145.3, 141.3, 135.6, 135.5, 134.1, 111.8, 105.6, 105.0, 104.3, 68.1, 65.5, 26.4, 25.9, 19.4, 18.7, −4.8, −5.5; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (m), 1927 (s), 1823 (s). Anal. Calcd for $C_{22}H_{33}BMoN_6O_3Si$: C, 46.82; H, 5.89; N, 14.89. Found: C, 46.97; H, 5.89; N, 14.95.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1R,2S,3R)-1-((*tert*-butyldimethylsilyl)oxy)-3-phenyl-2-propen-1-yl]molybdenum, 1d (*syn*-Phenyl/*syn*-OTBDMS). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (880 mg, 2.20 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, *E*-3-phenyl-2-propenal (291 mg, 2.20 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (365 mg, 2.42 mmol, 1.10 equiv) were combined and stirred for 1 h. Solid KTp (715 mg, 2.84 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 4/1), and recrystallization (hexanes) provided a mixture of **1d/1d′** (10:1) (1.05 g, 1.71 mmol, 78%) as an orange solid: Mp = 169−171 °C; ^{1}H NMR for **1d** ($CDCl_3$, 360 MHz) δ 8.62 (br s, 1 H), 8.44 (br s, 1 H), 7.61 (br s, 1 H), 7.43 (br s, 2 H), 7.08 (m, 3 H), 6.92 (br s, 2 H), 6.19 (br s, 3 H), 5.61 (br s, 1 H), 4.63 (d, *J* = 6.8 Hz, 1 H), 4.54 (dd, *J* = 10.1, 6.8 Hz, 1 H), 2.90 (d, *J* = 9.7 Hz, 1 H), 1.05 (s, 9 H), 0.38 (s, 3 H), 0.27 (s, 3 H); ^{1}H NMR for **1d′** ($CDCl_3$, 360 MHz) δ 7.37 (d, *J* = 2.5 Hz, 1H), 7.14 (d, *J* = 5.4 Hz, 1H), 6.98 (d, *J* = 5.4 Hz, 1H), 4.45 (d, *J* = 13.0 Hz, 1H), 4.32 (dd, *J* = 13.0, 5.8 Hz, 1H), 0.92 (s, 9H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 227.7, 146.9, 146.5 (br s), 145.8, 145.3 (br s), 140.4, 140.2, 139.0, 135.8, 135.6, 135.4, 134.1, 128.5, 128.4, 128.3, 127.9, 127.0, 126.3, 105.5, 104.5, 102.5, 96.3, 80.1, 74.0, 72.8, 70.2, 25.9, 25.7, 18.6, 18.5, −4.7, −5.1, −5.5, −5.7; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (m), 1924 (s), 1835 (s). Anal. Calcd for $C_{26}H_{33}BMoN_6O_3Si$: C, 50.99; H, 5.43; N, 13.72. Found: C, 51.08; H, 5.47; N, 13.67.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(2,3,4)-(±)-(1*S*,2*R*)-2-((*tert*-butyldimethylsilyl)oxy)-3-buten-2-yl]molybdenum, 1e (*syn*-OTBDMS). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (792 mg, 1.98 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 3-buten-2-one (161 μL, 1.985 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (329 mg, 2.18 mmol, 1.10 equiv) were combined and stirred for 2.5 h. Solid KTp (500 mg, 1.98 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexanes) provided pure **1e** (715 mg, 1.30 mmol, 66%) as an orange solid: Mp = 180−182 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.34 (d, *J* = 1.4 Hz, 1 H), 7.80 (d, *J* = 1.4 Hz, 1 H), 7.60 (d, *J* = 1.4 Hz, 1 H), 7.58 (app d, *J* = 1.8 Hz, 2 H), 7.50 (d, *J* = 2.2 Hz, 1 H), 6.20 (app t, *J* = 2.2 Hz, 1 H), 6.19 (app t, *J* = 2.2 Hz, 1 H), 6.13 (app t, *J* = 2.2 Hz, 1 H), 3.46−3.39 (m, 2 H), 1.75 (s, 3 H), 1.48 (dd, *J* = 14.0, 9.0 Hz, 1 H), 0.87 (s, 9 H), −0.40 (s, 3 H), −0.64 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 232.8, 229.8, 146.8, 145.9, 139.6, 138.8, 135.4, 134.5, 105.5, 105.1, 104.9, 70.5, 42.4, 25.8, 23.5, 18.3, −4.9, −5.5; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (w), 1923 (s), 1818 (s). Anal. Calcd for $C_{21}H_{31}BMoN_6O_3Si$: C, 45.83; H, 5.68: N, 15.27. Found: C, 45.72; H, 5.70; N, 15.36.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-((*tert*-butyldimethylsilyl)oxy)-2-cyclohexen-1-yl]molybdenum, 1f. In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.16 g, 2.91 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 2-cyclohexenone (281 μL, 2.90 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (482 mg, 3.20 mmol, 1.10 equiv) were combined and stirred for 2.5 h. Solid KTp (732 mg, 2.91 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexanes) provided pure **1f** (1.02 g, 1.77 mmol, 61%) as an orange solid: Mp = 175−176 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.40 (d, *J* = 1.8 Hz, 1 H), 7.81 (d, *J* = 1.5 Hz, 1 H), 7.59 (d, *J* = 2.1 Hz, 2 H), 7.55 (d, *J* = 2.1 Hz, 1 H), 7.46 (d, *J* = 2.4 Hz, 1 H), 6.19 (app t, *J* = 2.1 Hz, 1 H), 6.17 (app t, *J* = 2.1 Hz, 1 H), 6.07 (app t, *J* = 2.1 Hz, 1 H), 3.89 (br d, *J* = 7.5 Hz, 1 H), 3.48 (d, *J* = 7.8 Hz, 1 H), 2.41−2.19 (m, 2 H), 2.06 (m, 1 H), 1.91 (br m, 1 H), 1.23 (m, 1 H), 0.90 (s, 9 H), 0.92−0.88 (m, 1 H), 0.04 (s, 3 H), −0.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 230.2, 229.9, 146.6, 146.2, 139.0, 135.7, 135.6, 134.7, 134.2, 105.4, 105.1, 104.7, 64.3, 55.6, 31.7, 25.9, 23.0, 19.5, 18.5, −4.0, −5.7; IR (CH_2Cl_2, KCl, cm^{-1}) 2483 (w), 1916 (s), 1821 (s). Anal. Calcd for $C_{23}H_{33}BMoN_6O_3Si$: C, 47.93; H, 5.77; N, 14.58. Found: C, 47.89; H, 5.84; N, 14.60.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-(*tert*-butyldimethylsilyl)oxy-2-cyclopenten-1-yl]molybdenum, 1g. In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.13 g, 2.83 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 2-cyclopentenone (237 μL, 2.83 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (470 mg, 3.12 mmol, 1.10 equiv) were combined and stirred for 2 h. Solid KTp (715 mg, 2.84 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexanes) provided pure **1g** (996 mg, 1.77 mmol, 63%) as an orange solid: Mp = 158−161 °C (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33 (br s, 1 H), 8.18 (d, *J* = 1.5 Hz, 1 H), 7.61 (br s, 1 H), 7.65 (app t, *J* = 2.4 Hz, 2 H), 7.49 (d, *J* = 1.8 Hz, 1 H), 6.21 (app t, *J* = 2.1 Hz, 1 H), 6.15 (app t, *J* = 2.1 Hz, 1 H), 6.07 (app t, *J* = 2.0 Hz, 1 H), 3.92 (app t, *J* = 3.9 Hz, 1 H), 3.46 (d, *J* = 4.2 Hz, 1 H), 2.51−2.20 (m, 3 H), 1.88 (ddd, *J* = 13.8, 7.2, 2.1 Hz, 1 H), 0.99 (s, 9 H), 0.24 (s, 3 H), 0.21 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 229.2, 229.0, 146.6, 144.6,

141.2, 137.2, 135.5 (2 C), 134.1, 105.5, 105.0, 104.2, 63.4, 63.2, 35.8, 29.7, 25.9, 18.8, −3.0, −3.9; IR (CH_2Cl_2, KCl, cm^{-1}) 1923 (s), 1829 (s). Anal. Calcd for $C_{22}H_{31}BMoN_6O_3$: C, 46.99; H, 5.56; N, 14.94. Found: C, 47.09; H, 5.59; N, 14.98.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-((*tert*-butyldimethylsilyl)oxy)-3-methyl-2-cyclopenten-1-yl]molybdenum, 1h. In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (822 mg, 2.06 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 3-methyl-2-cyclopenten-1-one (204 μL, 2.06 mmol, 1.00 equiv) and *tert*-butyldimethylsilyl chloride (341 mg, 2.26 mmol, 1.10 equiv) were combined and stirred for 0.5 h. Solid KTp (519 mg, 2.06 mmol, 1.00 equiv) was added, and the solution was stirred for 30 min. Concentration, flash silica gel chromatography (hexanes/EtOAc, 2/1), and recrystallization (hexanes) provided pure **1h** (435 mg, 0.76 mmol, 37%) as an orange solid: Mp = 165 °C with decompostion; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.35 (d, *J* = 1.8 Hz, 1 H), 8.14 (d, *J* = 1.8 Hz, 1 H), 7.73 (d, *J* = 1.4 Hz, 1 H), 7.62 (d, *J* = 2.2 Hz, 1 H), 7.60 (d, *J* = 1.8 Hz, 1 H), 7.50 (d, *J* = 2.2 Hz, 1 H), 6.21 (app t, *J* = 2.2 Hz, 1 H), 6.16 (app t, *J* = 2.2 Hz, 1 H), 6.13 (app t, *J* = 2.2 Hz, 1 H), 3.70 (s, 1 H), 2.51 (ddd, *J* = 15.1, 9.4, 3.2 Hz, 1 H), 2.42 (ddd, *J* = 15.1, 7.6, 3.2 Hz, 1 H), 2.21 (s, 3 H), 2.15 (ddd, *J* = 14.8, 9.0, 3.6 Hz, 1 H), 1.93 (ddd, *J* = 14.4, 7.6, 3.2 Hz, 1 H), 0.97 (s, 9 H), 0.03 (s, 3 H), −0.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 231.0, 230.8, 146.1, 145.2, 143.4, 136.0, 135.4, 134.1, 128.5, 105.3, 104.9, 104.6, 77.9, 70.4, 37.8, 37.0, 26.0, 22.4, 18.7, −3.9, −4.5; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (w), 1912 (s), 1822 (s). Anal. Calcd for $C_{23}H_{33}BMoN_6O_3Si$: C, 47.93; H, 5.77; N, 14.58. Found: C, 47.83; H, 5.78; N, 14.62.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*)-1-acetoxy-2-propen-1-yl]molybdenum, 2a (*syn*-Acetoxy). Method B. A Schlenk flask equipped with a magnetic stirring bar was charged with $(DMF)_3Mo(CO)_3$ (780 mg, 1.95 mmol, 1.00 equiv) and 12 mL of dry deoxygenated CH_2Cl_2 to give a green solution. 2-Propenal (0.131 mL, 1.95 mmol, 1.00 equiv) was added producing a dark red solution to which acetic anhydride (0.203 mL, 2.15 mmol, 1.1 equiv) was added, and the reaction mixture was stirred at ambient temperature for 1 h during which time the color slowly lightened to dark yellow-orange. Solid KTp (493 mg, 1.95 mmol, 1.00 equiv) was added, and the reaction mixture was stirred an additional 15 min. The solution was concentrated to a yellow paste that was flash chromatographed on silica gel (hexanes/EtOAc, 15/10) and recrystallized (hexanes/CH_2Cl_2, 7/1) to give the *syn*-acetoxy complex **2a** (605 mg, 1.30 mmol, 67%): Mp 170−171 °C (hexanes/CH_2Cl_2, 7/1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.70−8.10 (br s, 1 H), 8.30−7.70 (br s, 2 H), 7.57 (br s, 3 H), 6.22 (br s, 3 H), 5.42 (d, *J* = 7.2 Hz, 1 H), 4.05 (ddd, *J* = 9.0, 7.4, 7.4 Hz, 1 H), 3.38 (dd, *J* = 7.2, 2.5 Hz, 1 H), 2.23 (s, 3 H), 1.49 (dd, *J* = 9.4, 2.3 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 228.7, 227.5, 169.0, 147−143 (br s, 3 C), 136−135 (br s, 3 C), 105.4 (br s, 3 C), 97.9, 66.6, 48.2, 21.2; IR (CH_2Cl_2, KCl, cm^{-1}) 2486 (w), 1949 (s), 1859 (s), 1753 (s). Anal. Calcd for $C_{16}H_{17}BMoN_6O_4$: C, 41.41; H, 3.69. Found: C, 41.34; H, 3.68.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*)-1-methoxy-2-propen-1-yl]molybdenum, 3a (*syn*-Methoxy). Method A. In a Schlenk tube equipped with a magnetic stirring bar, $(DMF)_3Mo(CO)_3$ (1.46 g, 3.65 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 2-propenal (225 mg, 4.01 mmol, 1.10 equiv) and *tert*-butyldimethylsilyl chloride (660 mg, 4.38 mmol, 1.20 equiv) were added, and the resulting dark red solution was stirred at ambient temperature for 1 h during which time the color slowly lightened to orange. Solid KTp (1.01 g, 4.01 mmol, 1.10 equiv) was added in one portion and stirred for 15 min. A THF solution of tetra-*n*-butylammonium fluoride (9.13 mL, 1.00 M, 4.01 mmol, 2.50 equiv) was added, and after 15 min, methyl iodide (10.4 g, 73.01 mmol, 20.00 equiv) was added. After being stirred for 48 h, the reaction mixture was concentrated to a dark red oil which was flash chromatographed on silica gel (hexanes/EtOAc, 1/1) to give an orange-red solid that was recrystallized (hexanes/CH_2Cl_2, 4/1) to yield pure *syn*-MeO complex **3a** (1.01 g, 2.32 mmol, 64%) as a high-melting yellow solid: Mp 161−163 °C with decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (br s, 1 H), 8.11 (br s, 1 H), 7.81 (br s, 1 H), 7.58 (br s, 2 H), 7.54 (br s, 1 H), 6.27 (br s, 1 H), 6.17 (br s, 2 H), 4.59 (d, *J* = 8.0 Hz, 1 H),), 3.81 (m, 1 H), 3.85 (s, 3 H), 3.31 (dd, *J* = 7.0, 4.0 Hz, 1 H), 1.26 (dd, *J* = 9.0, 3.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 232.6, 227.8, 147.1, 144.4, 141.8, 135.7 (2C), 134.2, 120.4, 105.1, 104.9 (2 C), 61.7, 59.8, 47.5; IR (CH_2Cl_2, KCl, cm^{-1}) 1930 (s), 1832 (s). Anal. Calcd for $C_{15}H_{17}BMoN_6O_3$: C, 41.31; H, 3.93; N, 19.27. Found: C, 41.27; H, 3.97; N, 19.19.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*)-1-((1-methylethyl)oxy)-2-propen-1-yl]molybdenum, 4a (*syn*-Isopropoxy). In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (631 mg, 1.58 mmol, 1.00 equiv) was dissolved in 15 mL of dry, degassed CH_2Cl_2. To this solution, 2-propenal (97 mg, 1.73 mmol, 1.09 equiv), *tert*-butyldimethylsilyl chloride (286 mg, 1.90 mmol, 1.20 equiv), and KTp (439 mg, 1.74 mmol, 1.10 equiv) were combined in the manner described above for the preparation of complex **3a**. A THF solution of TBAF (3.95 mL, 1.00 M, 1.74 mmol, 2.50 equiv) was added to the crude dichloromethane solution of **1a**. After the solution was stirred for 5 min, isopropyl iodide (5.37 g, 31.59 mmol, 19.99 equiv) was added and stirring was continued for 24 h. Flash silica gel chromatography (hexanes/EtOAc, 4/1) and recrystallization (CH_2Cl_2/hexanes, 1/3) provided pure **4a** (410 mg, 0.88 mmol, 56%) as an orange high melting solid: Mp 195−197 °C with decomposition; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.48 (br s, 1 H), 8.35 (br s, 1 H), 7.81 (br s, 1 H), 7.56 (br s, 2 H), 7.53 (br s, 1 H), 6.27 (br s, 2 H), 6.13 (br s, 1 H), 4.67 (d, *J* = 8.0 Hz, 1 H), 4.54 (m, 1 H), 3.75 (m, 1 H), 3.27 (dd, *J* = 7.0, 3.0 Hz, 1 H), 1.42 (d, *J* = 4.0 Hz, 3 H), 1.41 (d, *J* = 4.0 Hz, 3 H), 1.30 (dd, *J* = 9.0, 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 233.6, 227.9, 147.1, 144.6, 142.0, 135.6, 134.2, 119.3, 105.7, 105.0, 104.6, 76.5, 61.5, 45.0, 22.4; IR (CH_2Cl_2, KCl, cm^{-1}) 1928 (s), 1826 (s). Anal. Calcd for $C_{17}H_{21}BMoN_6O_3$: C, 43.99; H, 4.56; N, 18.11. Found: C, 43.75; H, 4.56; N, 18.00.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-1-(1-methoxy)-2-buten-1-yl]molybdenum, 2b and 2b′. Method A. The *tert*-butyldimethylsilyloxy allyl complex **1b** (1.32 g, 2.400 mmol, 1.00 equiv) was dissolved in 10 mL of CH_2Cl_2, then acetic anhydride (270 mg, 2.645 mmol, 1.10 equiv) was added via syringe. A THF solution of TBAF (6.00 mL, 1.00 M, 6.00 mmol, 2.50 equiv) was added, and the solution was stirred for 5 min at room temperature. The solution was concentrated, and the orange oil was chromatographed on silica gel (1:4 EtOAc/hexane). The orange solution was concentrated, yielding an orange solid (820 mg, 1.72 mmol, 71%). ^{1}H NMR revealed a mixture of **2b′**, **2b**, and **2b‴** (3.6/3.0/1.0). ^{1}H NMR for **2b′** ($CDCl_3$, 300 MHz) δ 8.49 (br s, 1 H), 7.81 (br s, 1 H), 7.66 (br s, 1 H), 7.59 (br s, 2 H), 7.48 (br s, 1 H), 6.24 (br s, 1 H), 6.20 (br s, 1 H), 6.17 (br s, 1 H), 6.14 (d, *J* = 7.3 Hz, 1 H), 4.13 (m, 2 H), 2.19 (s, 3 H), 1.34 (d, *J* = 7.2 Hz, 3 H).

Method B. In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (1.10 g, 2.75 mmol, 1.00 equiv) was dissolved in 10 mL of CH_2Cl_2 under nitrogen atmosphere. To this solution was added *E*-2-butenal (212 mg, 3.03 mmol, 1.10 equiv). The solution was stirred for 5 min, and then acetic anhydride (309 mg, 3.03 mmol, 1.10 equiv) was added via syringe. After being stirred for 30 min, solid KTp (764 mg, 3.03 mmol, 1.10 equiv) was added, and the solution was stirred for an additional 30 min. The orange-brown solution was filtered through a pad of silica gel on a glass frit with 1/4 EtOAc/hexane. The solution was concentrated, and the ^{1}H NMR spectrum of the yellow solid revealed a mixture of **2b**, **2b′**, and **2b‴** (1.15 g, 2.41 mmol, 88%). Upon standing for four days, **2b** equilibrated to a mixture of **2b**/**2b′**/**2b″**/**2b‴** (9.3:6.0:4.1:1.0) Complex **2b** was isolated exclusively by column chromatography (1/4 EtOAc/hexane): TLC (silica gel, 1/4 EtOAc/hexane, R_f = 0.68); Mp 175−177 °C with

decomposition (CH_2Cl_2/hexane, 1/4); IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (w), 1942 (s), 1853 (s), 1734 (s); ^1H NMR for **2b** ($CDCl_3$, 300 MHz) δ 8.64 (br s, 1 H), 8.50 (br s, 1 H), 7.76 (br s, 1 H), 7.63 (d, J = 5.1 Hz, 1 H), 7.57 (br s, 2 H), 7.50 (br s, 1 H), 6.25 (br s, 2 H), 6.16 (br s, 1 H), 3.88 (dd, J = 10.8, 5.4 Hz, 1 H), 3.15 (dq, J = 10.8, 6.6 Hz, 1 H), 2.31 (d, J = 6.6 Hz, 3 H), 2.06 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 232.3, 225.2, 171.0, 147.3, 144.9, 135.9 (br s), 105.5 (br s), 104.1 (br s), 71.6, 71.2, 70.7, 21.0, 17.4. Anal. Calcd for $C_{17}H_{19}BMoN_6O_4$: C, 42.71; H, 4.01; N, 17.50. Found: C, 42.80; H, 3.97; N, 17.50.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*,3*R*)-1-methoxy-2-buten-1-yl]molybdenum, 3b (*anti*-Methyl/*Syn*-Methoxy). Method A. $(DMF)_3Mo(CO)_3$ (1.09 g, 2.73 mmol, 1.00 equiv), 2-butenal (210 mg, 3.00 mmol, 1.10 equiv), *tert*-butyldimethylsilyl chloride (494 mg, 3.28 mmol, 1.20 equiv), and KTp (827 mg, 3.28 mmol, 1.20 equiv) were combined in the manner described above for the preparation of complex **1b**. A THF solution of TBAF (8.20 mL, 1.00 M, 3.28 mmol, 3.00 equiv) was added to the crude dichloromethane solution of **1b**. After the solution was stirred for 5 min, methyl iodide (7.75 g, 54.6 mmol, 20.01 equiv) was added and stirring was continued for 24 h. Flash silica gel chromatography (hexanes/EtOAc, 4/1) and recrystallization (CH_2Cl_2/hexanes, 1/3) provided pure **3b** (786 mg, 1.746 mmol, 64%) as a yellow high melting solid: Mp 168−170 °C with decomposition; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.48 (d, J = 2.0 Hz, 1 H), 8.06 (d, J = 2.0 Hz, 1 H), 7.72 (d, J = 2.0 Hz, 1 H), 7.56 (m, 2 H), 7.51 (d, J = 2.0 Hz, 1 H), 6.25 (app t, J = 2.0 Hz, 1 H), 6.17 (m, 2 H), 5.30 (d, J = 9.0 Hz, 1 H), 3.89 (m, 2 H), 3.67 (s, 3 H), 1.35 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 232.3, 229.7, 147.0, 144.7, 141.4, 135.8, 135.6, 134.3, 119.5, 105.7, 105.2, 105.0, 65.9, 58.8, 57.6, 17.8; IR (CH_2Cl_2, KCl, cm^{-1}) 1925 (s), 1826 (s). Anal. Calcd for $C_{16}H_{19}BMoN_6O_3$: C, 42.69; H, 4.25; N, 18.67. Found: C, 42.78; H, 4.34; N, 18.67.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*,3*R*)-1-((1-methylethyl)oxy)-2-buten-1-yl]molybdenum, 4b (*anti*-Methyl/*syn*-Isopropoxy). Method A. $(DMF)_3Mo(CO)_3$ (1.02 g, 2.55 mmol, 1.00 equiv), 2-butenal (197 mg, 2.81 mmol, 1.10 equiv), TBDMSCl (461 mg, 3.06 mmol, 1.20 equiv), and KTp (772 mg, 3.062 mmol, 1.20 equiv) were combined in the manner described above for the preparation of complex **1b**. A THF solution of TBAF (6.38 mL, 1.00 M, 3.06 mmol, 2.50 equiv) was added to the crude dichloromethane solution of **1b**. After the solution was stirred for 5 min, isopropyl iodide (8.70 g, 51.2 mmol, 20.07 equiv) was added and stirring was continued for 24 h. Flash silica gel chromatography (hexanes/EtOAc, 4/1) and recrystallization (CH_2Cl_2/hexanes, 1/2) provided pure **4b** (281 mg, 0.588 mmol, 23%) as a yellow high melting solid: Mp 190−193 °C with decomposition; ^1H ($CDCl_3$, 300 MHz) δ 8.48 (d, J = 1.8 Hz, 1 H), 8.25 (d, J = 1.5 Hz, 1 H), 7.74 (d, J = 1.5 Hz, 1 H), 7.55 (m, 2 H), 7.50 (d, J = 2.1 Hz, 1 H), 6.25 (app t, J = 2.1 Hz, 1 H), 6.15 (app t, J = 2.1 Hz, 1 H), 6.13 (app t, J = 2.1 Hz), 5.27 (d, J = 7.8 Hz, 1 H), 4.50 (sept, J = 6.3 Hz, 1 H), 3.92−3.79 (m, 2 H), 1.42 (d, J = 6.3 Hz, 3 H), 1.41 (d, J = 6.3 Hz, 3 H), 1.37 (d, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 233.7, 229.3, 147.7, 144.9, 141.7, 135.6, 135.5, 134.2, 117.9, 105.6, 105.1, 104.5, 76.2, 65.5, 58.4, 22.3, 22.2, 17.8; IR (CH_2Cl_2, KCl, cm^{-1}) 1922 (s), 1817 (s). Anal. Calcd for $C_{18}H_{23}BMoN_6O_3$: C, 45.21; H, 4.85; N, 17.58. Found: C, 45.07; H, 4.84; N, 17.66.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*S*,2*R*,3*R*)-1-methoxy-2-penten-1-yl]molybdenum, 3c (*anti*-Ethyl/*syn*-Methoxy). Method A. A Schlenk flask under argon was charged with $(DMF)_3Mo(CO)_3$ (1.40 g, 3.51 mmol, 1.00 equiv) and 15 mL of dry, deoxygenated CH_2Cl_2 to give a dark green solution. *E*-2-pentenal (376 μL, 3.84 mmol, 1.10 equiv) was added via syringe to give a dark red solution. *tert*-Butyldimethylsilyl chloride (533 μL, 4.20 mmol, 1.20 equiv) was added, and the reaction mixture was stirred at room temperature for 10 min during which time the color lightened to orange. Solid KTp (926 mg, 3.67 mmol, 1.05 equiv) was added, and the reaction mixture was stirred for an additional 10 min. Solid TBAF trihydrate (2.76 g, 8.75 mmol, 2.49 equiv) was added followed 5 min later by methyl iodide (4.40 mL, 70.7 mmol, 20.1 equiv). The resulting solution was stirred at ambient temperature for 12 h at which time the solution was concentrated to a dark red paste which was subjected to flash silica gel chromatography (hexanes/EtOAc, 4/1) and recrystallization (hexanes/CH_2Cl_2, 10/1) to yield **3c** (490 mg, 1.06 mmol, 30%) as a yellow solid: Mp 149−151 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.47 (d, J = 1.8 Hz, 1 H), 8.07 (d, J = 1.8 Hz, 1 H), 7.76 (d, J = 1.4 Hz, 1 H), 7.57 (app t, J = 2.5 Hz, 2 H), 7.50 (d, J = 2.2 Hz, 1 H), 6.25 (app t, J = 2.2 Hz, 1 H), 6.17 (app t, J = 2.2 Hz, 1 H), 6.15 (app t, J = 2.2 Hz, 1 H), 5.22 (d, J = 8.6 Hz, 1 H), 3.90 (ddd, J = 11.2, 8.6, 4.3 Hz, 1 H), 3.79 (app t, J = 8.6 Hz, 1 H), 3.68 (s, 3 H), 2.17 (ddq, J = 14.4, 7.2, 4.3 Hz, 1 H), 1.15 (app t, J = 7.2 Hz, 3 H), 0.52 (ddq, J = 14.4, 10.8, 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 232.7, 229.3, 146.9, 144.6, 141.6, 135.7, 135.5, 134.2, 118.7, 105.6, 105.0, 104.9, 66.3, 64.2, 58.9, 26.5, 19.4; IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (w), 1926 (s), 1827 (s). Anal. Calcd for $C_{17}H_{21}BMoN_6O_3$: C, 43.99; H, 4.56; N, 18.11. Found: C, 44.11; H, 4.60; N, 17.97.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(2−4)-(±)-(2*S*,3*R*)-2-methoxy-3-buten-2-yl]molybdenum, 3e (*syn*-Methoxy/*anti*-Methyl). Method A. In a Schlenk tube equipped with a magnetic stirring bar, $(DMF)_3Mo(CO)_3$ (1.04 g, 2.60 mmol, 1.00 equiv) was dissolved in dry, degassed CH_2Cl_2 (20 mL). To this solution, 3-buten-2-one (201 mg, 2.87 mmol, 1.10 equiv) and *tert*-butyldimethylsilyl chloride (471 mg, 3.12 mmol, 1.20 equiv) were added, and the resulting dark red solution was stirred at ambient temperature for 1 h during which time the color slowly lightened to orange. Solid KTp (657 mg, 2.61 mmol, 1.00 equiv) was added in one portion, and the solution was stirred for 15 min. A THF solution of tetra-*n*-butylammonium fluoride (6.51 mL, 1.00 M, 2.61 mmol, 2.50 equiv) was added, and after 15 min, methyl iodide (3.24 mL, 52.06 mmol, 20.00 equiv) was added. After being stirred for 48 h, the reaction mixture was concentrated to a dark red oil which was flash chromatographed on silica gel (hexanes/EtOAc, 1/1) to give an orange-red solid that was recrystallized (hexanes/CH_3Cl, 2/1) to yield pure *syn*-MeO complex **3e** (759 mg, 1.69 mmol, 65%) as a high-melting red solid: ^1H NMR ($CDCl_3$, 360 MHz) δ 8.32 (app s, 1 H), 7.82 (app s, 1 H), 7.63 (app s, 2 H), 7.59 (d, J = 1.8 Hz, 1 H), 7.50 (d, J = 1.4 Hz, 1 H), 6.19 (m, 3 H), 3.49−3.43 (m, 2 H), 2.89 (s, 3 H), 1.83 (s, 3 H), 1.63 (dd, J = 13.3, 8.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 Mhz) δ 232.6, 227.8, 147.1, 144.4, 141.8, 135.7, (s, 2C), 134.2, 120.4, 105.1, 104.9 (2C), 61.7, 59.8, 47.5; IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (m), 1922 (s), 1815 (s). Anal. Calcd for $C_{16}H_{19}BMoN_6O_3$: C, 42.69; H, 4.25; N, 18.67. Found: C, 42.78; H, 4.28; N, 18.74.

Dicarbonyl[η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-(ethanoyloxy)-2-cyclohexen-1-yl][hydrotris(1-pyrazolyl)borato]molybdenum, 2f. Method A. A solution of (*tert*-butyldimethylsilyl)-oxy complex **1f** (1.13 g, 1.96 mmol, 1.00 equiv) and acetic anhydride (3.70 mL, 39.2 mmol, 20.0 equiv) was prepared in dry THF (10 mL) under argon. Solid tetra-*n*-butylammonium fluoride trihydrate (1.86 g, 5.90 mmol, 3.0 equiv) was rapidly added. The solution warmed noticeably and the color changed from orange to a brighter yellow. After being stirred at room temperature for 20 min, the reaction mixture was concentrated and the product was purified via flash silica gel chromatography (hexanes/EtOAc, 3/1) and recrystallization (CH_2Cl_2/hexanes, 1/10) to yield pure acetoxy complex **2f** as a microcrystalline yellow solid: Mp = 208−209 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 8.55 (d, J = 2.2 Hz, 1 H), 8.08 (d, J = 1.8 Hz, 1 H), 7.65 (d, J = 1.8 Hz, 1 H), 7.60 (d, J = 2.2 Hz, 1 H), 7.56 (d, J = 2.2 Hz, 1 H), 7.50 (d, J = 2.5 Hz, 1 H), 6.27 (app t, J = 2.2 Hz, 1 H), 6.20 (app t, J = 2.2 Hz, 1 H), 6.13 (app t, J = 2.2 Hz, 1 H), 4.07 (dt, J = 7.2, 2.2 Hz, 1 H), 4.00 (d, J = 7.6 Hz, 1 H), 2.51 (m, 1 H), 2.21 (m, 1 H), 2.06 (m, 1 H), 2.05 (s, 3 H), 1.91 (m, 1 H), 1.25 (ddd, J = 13.0, 5.8, 5.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 228.8, 226.5, 169.3, 146.8, 146.1, 139.3,

136.0, 135.9, 134.1, 111.8, 105.7, 105.3, 104.5, 67.0, 58.8, 27.9, 22.4, 21.5, 19.8; IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (w), 1936 (s), 1850 (s). Anal. Calcd for $C_{19}H_{21}BMoN_6O_4$: C, 45.27; H, 4.20; N, 16.74. Found: C, 45.15; H, 4.18;, N, 16.74.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclohexen-1-yl]molybdenum, 3f. The crude (*tert*-butyldimethyl)silyloxy complex **1f** was prepared in 30 mL of dry CH_2Cl_2 from $(DMF)_3Mo(CO)_3$ (2.25 g, 5.63 mmol, 1.00 equiv), 2-cyclohexenone (545 μL, 5.63 mmol, 1.00 equiv), *tert*-butyldimethylsilyl chloride (858 μL, 6.76 mmol, 1.20 equiv), and KTp (1.42 g, 5.63 mmol, 1.00 equiv) according to the procedure given above except that stirring before KTp addition was continued for only 0.5 h. To the crude material is added solid tetra-*n*-butylammonium fluoride trihydrate (4.40 g, 5.63 mmol, 2.48 equiv). Stirring was continued for 5 min, and then methyl iodide (7.00 mL, 112.5 mmol, 20.0 equiv) was added and stirring was continued for an additional 36 h. Concentration, flash silica gel chromatography (hexanes/EtOAc, 3/1), and recrystallization (CH_2Cl_2/hexanes, 1/10) provided pure methoxyallyl **3f** (2.10 g, 4.41 mmol, 78%) as a microcrystalline orange solid: Mp = 189−192 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.41 (d, J = 1.5 Hz, 1 H), 7.84 (d, J = 1.8 Hz, 1 H), 7.65 (d, J = 1.2 Hz, 1 H), 7.62 (app d, J = 1.8 Hz, 2 H), 7.49 (d, J = 2.1 Hz, 1 H), 6.22 (app t, J = 2.1 Hz, 1 H), 6.20 (app t, J = 2.1 Hz, 1 H), 6.15 (app t, J = 2.1 Hz, 1 H), 3.93 (br d, J = 8.1 Hz, 1 H), 3.63 (d, J = 8.1 Hz, 1 H), 3.14 (s, 3 H), 2.51 (dd, J = 16.5, 6.9 Hz, 1 H), 2.36 (ddd, J = 17.4, 10.8, 6.9 Hz, 1 H), 2.12 (m, 1 H), 1.99 (m, 1 H), 1.29 (m, 1 H), 0.93 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 230.3, 230.0, 146.5, 144.3, 140.4, 139.6, 136.0, 135.7, 134.3, 105.4, 105.2, 105.1, 58.1, 56.2, 54.7, 28.5, 23.3, 19.0; IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (w), 1915 (s), 1819 (s). Anal. Calcd for $C_{18}H_{21}BMoN_6O_3$: C, 45.41; H, 4.45; N, 17.65. Found: C, 45.30; H, 4.37; 17.74.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-(1-methylethyl)-1-oxy-2-cyclohexen-1-yl]molybdenum, 4f. In a Schlenk tube, $(DMF)_3Mo(CO)_3$ (629 mg, 1.575 mmol, 1.00 equiv) was dissolved in 30 mL of CH_2Cl_2 under nitrogen. To this solution, 2-cyclohexen-1-one (166 mg, 1.73 mmol, 1.10 equiv) was added via syringe. *tert*-Butyldimethylsilyl chloride (286 mg, 1.89 mmol, 1.20 equiv) was added 10 min later, and the solution was stirred for 2 h at room temperature. Solid KTp (436 mg, 1.73 mmol, 1.10 equiv) was added. After the mixture was stirred for 1 h, TBAF (3.95 mL, 1.00 M, 1.73 mmol, 2.51 equiv) and 2-iodopropane (537 mg, 3.16 mmol, 2.01 equiv) were added, and the solution was stirred for 24 h. Solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography (1/4 EtOAc/hexane as eluant). Removal of solvent under reduced pressure afforded **4f** as a dark red solid (149 mg, 0.23 mmol, 19%): Mp 93−95 °C with decomposition (CH_2Cl_2/hexane, 1/3); IR (CH_2Cl_2, KCl, cm^{-1}) 1912 (s), 1815 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, J = 6.0 Hz, 3 H), 1.26 (d, J = 6.0 Hz, 3 H), 1.27 (m, 2 H), 2.09 (m, 1 H), 2.22 (m, 2 H), 2.46 (dd, J = 17.0, 7.0 Hz, 1 H), 3.58 (d, J = 8.0 Hz, 1 H), 3.66 (m, 1 H), 3.98 (br d, J = 8.0 Hz, 1 H), 6.14 (t, J = 2.0 Hz, 1 H), 6.20 (m, 2 H), 7.48 (d, J = 2.0 Hz, 1 H), 7.60 (d, J = 2.0 Hz, 1 H), 7.62 (d, J = 2.0 Hz, 1 H), 7.65 (d, J = 2.0 Hz, 1 H), 7.88 (d, J = 2.0 Hz, 1 H), 8.38 (d, J = 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 230.7, 230.4, 146.6, 145.4, 144.3, 139.4, 135.9, 135.8, 134.2, 105.4, 105.1, 104.7, 69.1, 60.2, 55.7, 31.0, 23.5, 22.3, 20.1, 19.1. Anal. Calcd for $C_{20}H_{25}BN_6O_3Mo$: C, 47.64; H, 5.00; N, 16.67. Found: C, 47.71; H, 5.08; N, 16.61.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-(ethanoyloxy)-2-cyclopenten-1-yl]molybdenum, 2g. The (*tert*-butyldimethylsilyl)oxy allyl complex **1g** (928 mg, 1.65 mmol, 1.00 equiv) was dissolved in 50 mL of THF under nitrogen. Acetic anhydride (3.37 g, 33.01 mmol, 20.01 equiv) and TBAF·$3H_2O$ (1.56 g, 4.94 mmol, 3.00 equiv) were added, and the solution was stirred for 1 h at room temperature. Solvent was removed under reduced pressure, and the resulting residue was purified using column chromatography (1/1 EtOAc/hexane as eluant). Removal of solvent under reduced pressure afforded **2g** as a yellow solid (403 mg, 0.82 mmol, 50%): Mp 178−180 °C with decomposition (CH_2Cl_2/hexane, 1/1); IR (CH_2Cl_2, KCl, cm^{-1}) 2485 (w), 1946 (s), 1851 (s), 1749 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.82 (m, 1 H), 1.95 (m, 1 H), 2.25 (s, 3 H), 2.50 (br d, J = Hz, 2 H), 3.89 (d, J = 4.4 Hz, 1 H), 4.13 (t, J = 4.4 Hz, 1 H), 6.15 (t, J = 2.2 Hz, 1 H), 6.20 (t, J = 2.2 Hz, 1 H), 6.26 (t, J = 2.2 Hz, 1 H), 7.51 (d, J = 2.2 Hz, 1 H), 7.59 (br s, 2 H), 7.64 (d, J = 2.9 Hz, 1 H), 8.04 (d, J = 1.4 Hz, 1 H), 8.40 (d, J = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 227.5, 225.5, 169.5, 146.4, 144.4, 141.2, 136.2, 135.8, 134.3, 114.8, 105.7, 105.4, 104.8, 66.3, 65.4, 33.4, 29.7, 21.6. Anal. Calcd for $C_{18}H_{19}BN_6O_4Mo$: C, 44.11; H, 3.91; N, 17.15. Found: C, 44.24; H, 3.89; N, 17.17.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclopenten-1-yl]molybdenum, 3g. The crude *tert*-butyldimethylsiloxy complex **1g** was prepared in 30 mL of dry CH_2Cl_2 from $(DMF)_3Mo(CO)_3$ (2.02 g, 5.06 mmol, 1.00 equiv), 2-cyclopentenone (416 mg, 5.07 mmol, 1.00 equiv), *tert*-butyldimethylsilyl chloride (917 mg, 6.08 mmol, 1.20 equiv), and KTp (1.28 g, 5.08 mmol, 1.00 equiv) according to the procedure described above. To the crude material was added TBAF (12.70 mL, 1.00 M, 5.08 mmol, 2.51 equiv) via syringe. Stirring was continued for 5 min, and then MeI (2.34 g, 16.49 mmol, 3.26 equiv) was added. The solution was stirred for 24 h at room temperature. Concentration and flash silica gel chromatography (hexanes/EtOAc, 2/1) provided pure methoxy allyl **3g** (1.41 g, 3.05 mmol, 60%) as a microcrystalline orange solid: Mp 181−183 °C with decomposition (CH_2Cl_2/hexane, 1:10); IR (CH_2Cl_2, KCl, cm^{-1}) 2484 (w), 1920 (s), 1820 (s). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35 (d, J = 1.5 Hz, 1 H), 8.02 (d, J = 1.5 Hz, 1 H), 7.60 (d, J = 1.5 Hz, 1 H), 7.59 (d, J = 1.8 Hz, 1 H), 7.57 (d, J = 1.8 Hz, 1 H), 7.54 (d, J = 1.8 Hz, 1 H), 6.26 (app t, J = 2.0 Hz, 1 H), 6.16 (m, 2 H), 3.96 (app t, J = 2.7 Hz, 1 H), 3.91 (s, 3 H), 3.55 (d, J = 3.6 Hz, 1 H), 2.53 (m, 3 H), 1.92 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 229.6, 228.5, 146.4, 143.8, 141.1, 140.1, 135.6, 135.5, 134.2, 105.6, 105.0, 64.1, 61.2, 56.8, 31.6, 29.6. Anal. Calcd for $C_{17}H_{19}BN_6O_3Mo$: C, 44.18; H, 4.14; N, 18.19. Found: C, 44.02; H, 4.12; N, 18.44.

Dicarbonyl[hydrotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-4,4-dimethyl-1-methoxy-2-cyclohexen-1-yl]molybdenum, 3i. $(DMF)_3Mo(CO)_3$ (984 mg, 2.46 mmol, 1.00 equiv), 4,4-dimethyl-2-cyclohexenone (336 mg, 2.71 mmol, 1.10 equiv), *tert*-butyldimethylsilyl chloride (445 mg, 2.95 mmol, 1.20 equiv), and KTp (681 mg, 2.70 mmol, 1.10 equiv) were combined in the manner described above for the preparation of complex **1f**. A THF solution of TBAF (6.15 mL, 1.00 M, 2.70 mmol, 2.50 equiv) was added to the crude dichloromethane solution of the silyl ether. After the solution was stirred for 5 min, methyl iodide (6.98 g, 49.19 mmol, 19.96 equiv) was added and stirring was continued for 24 h. Flash silica gel chromatography (hexanes/EtOAc, 4/1) and recrystallization (CH_2Cl_2/hexanes, 1/2) provided pure **3i** (471 mg, 0.934 mmol, 38%) as an orange high melting solid: Mp 155 °C with decomposition; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.44 (br s, 1 H), 8.05 (br s, 1 H), 7.82 (br s, 1 H), 7.60 (br s, 2 H), 7.49 (br s, 1 H), 6.22 (br t, J = 2.0 Hz, 1 H), 6.20 (br t, J = 2.0 Hz, 1 H), 6.15 (br t, J = 2.0 Hz, 1 H), 3.92 (d, J = 8.0 Hz, 1 H), 3.82 (d, J = 8.0 Hz, 1 H), 3.36 (s, 3 H), 2.61 (dd, J = 16.0, 6.0 Hz, 1 H), 2.49 (m, 1 H), 1.30 (s, 3 H), 1.24 (s, 3 H), 1.06 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 234.2, 232.5, 146.4, 144.3, 142.1, 141.8, 135.9, 135.6, 134.2, 105.5, 105.2, 105.1, 75.0, 63.4, 54.2, 35.0, 34.0, 33.0, 27.9, 26.9; IR (CH_2Cl_2, KCl, cm^{-1}) 1919 (s), 1813 (s). Anal. Calcd for $C_{20}H_{25}BMoN_6O_3$: C, 47.64; H, 5.00; N, 16.67. Found: C, 47.53; H, 5.03; N, 16.57.

X-ray Crystal Structure Determination of [TpMo(CO)$_2$[η-(1,2,3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclohexen-1-yl], 3f. Orange/red crystals were grown by slow evaporation of a methylene chloride solution of **3f**. A suitable crystal (0.30 × 0.36 × 0.41 mm) was selected and mounted on a glass fiber with superglue. Following manual optical alignment, intensity data were collected using the $\omega-2\theta$ scan mode with $1.54 < 2\theta$

Table 5. Summary of X-ray Crystal Data, Intensity Collection, and Structure Refinement for [TpMo(CO)$_2$[η-(1−3)-(±)-(1*R*,2*S*,3*S*)-1-methoxy-2-cyclohexen-1-yl], 3f

formula	$C_{18}H_{21}BMoN_6O_3$
mol wt	476.16
a, Å	10.9310(10)
b, Å	14.644(2)
c, Å	14.6720(10)
α, deg	65.25
β, deg	68.86
γ, deg	77.31
V, Å^3	1982.8(4)
cryst system	triclinic
space group	$P\bar{1}$
$D_{calcd,\ g/cm^3}$	1.594
Z	2
temp, °C	23
F(000)	968
abs coeff (μ), mm^{-1}	0.694
cryst size, mm	0.30 × 0.36 × 0.41
θ range for data, deg	1.54−29.58
index ranges	$-1 \le h \le 11$, $-18 \le k \le 14$, $-15 \le l \le 15$
reflcns collcd	6046
indepdt reflcns	5076 [R(int) = 0.0218]
refinement	Siemens SHELXL-93, full-matrix least-squares on F^2
data/restraints/params	5076/0/523
goodness of fit on F^2	0.687
final R indices [$I > 2\ \sigma(I)$]	$R1 = 0.0277$, w$R2 = 0.0739$
R indices (all data)	$R1 = 0.0339$, w$R2 = 0.0821$
max and min diff peaks, e/Å^3	0.333 and −0.333

< 29.58°, *hkl* range = −1/11, −18/14, and −15/15, on a P4 four-circle automated diffractometer (Siemans) at 23 °C using a monochrometer containing a highly ordered graphite crystal and Mo Kα radiation (0.710 73 Å). The XSCANS software package (Siemens, 1994) was employed in automatic mode for data collection. The primitive unit cell was determined to be triclinic by least squares fit and consisted of two molecules (Figure 5 in the Supporting Information). Three check reflections were measured every 100 reflections with intensities remaining constant to within 3% over the data collection period. Of the 6046 data collected, 5076 were considered observed ($F > 4.0\sigma(F)$). The structure was solved by the Patterson method and refinement carried out using SHELXTL. The hydrogen atom attached to boron was located in the difference fourier map and refined isotropically. All other hydrogen atoms were refined isotropically in calculated positions with isotropic thermal parameters set at 0.05. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied to give a minimum and maximum transmission of 0.594 and 0.700, respectively. Full-matrix least-squares refinement on F^2 resulted in a final R_{index} (observed data) of 2.77%, a goodness of fit of 0.687, and a data-to-parameter ratio of 10:1. Table 5 provides crystal and refinement data, and selected bond lengths and angles were given above in Table 4. Supporting Information contains Tables S-I (atomic coordinates), S-II (complete bond lengths and angles), S-III (hydrogen fixed positional parameters and temperature factors), and S-IV (thermal parameters).

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Supporting Information Available: An ORTEP represention of the two molecules of **3f** in the unit cell (Figure 5) and Tables S-I (atomic coordinates), S-II (complete bond lengths and angles), S-III (hydrogen fixed positional parameters and temperature factors), and S-IV (thermal parameters) for **3f** (10 pages). Ordering information is given on any current masthead page.

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