Molybdenum-Catalyzed Allylic Substitution. Influence of 1,10-Phenanthroline Ligands on Reactivity and Selectivity

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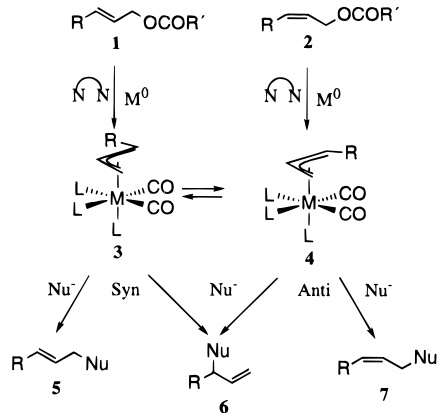
Some new allylmolybdenum complexes containing 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline as ligand have been synthesized and shown to have different geometries by NMR and X-ray diffraction analysis. The geometries of the complexes were elucidated by NMR techniques and confirmed by X-ray diffraction analysis. The catalytic activity and the influence on regio- and stereocontrol in the alkylation of allylic acetates have been investigated. The 2,9-dimethyl-1,10-phenanthroline complex was found to be a very efficient catalyst for selective conversion of (*Z*)-allyl acetates into (*Z*)-products.

Introduction

Metal-catalyzed nucleophilic substitution of allylic acetate has become a standard reaction in organic synthesis.[1] The reaction most probably proceeds via η^3-allyl intermediates, and both formation of these and the ensuing nucleophilic attack are frequently stereospecific. Thus in principle (*E*)-acetates will give (*E*)-products **5** via syn complexes, and (*Z*)-acetates (*Z*)-products **7** via anti complexes. However, as illustrated in Scheme 1, the intermediate (η^3-allyl) complexes can undergo syn-anti isomerization, leading to mixtures of (*E*)- and (*Z*)-products. If the syn/anti distribution can be controlled, the isomerization can be used to advantage, making it possible to prepare selectively (*Z*)-products from (*E*)-acetates and vice versa. We have recently shown that it is possible to convert both 1-(*E*)- and 1-(*Z*)-acetates into (*E*)-products, using (1,10-phenanthroline)palladium complexes as catalysts.[2] A couple of factors evidently contribute to this result: (i) The syn−anti isomerization is fast relative to nucleophilic addition, and (ii) the product between reaction rate and concentration is considerably greater for the syn complex. As a step toward the development of ligands which induce a similar selectivity for (*Z*)-products, we have prepared phenanthroline type ligands which in contrast to the parent phenanthroline (phen) favor an anti configuration in the (η^3-allyl)palladium intermediates.[3] However, in the presence of these ligands, the syn−anti isomerization was slowed down dramatically. In addition, it appeared that even selective conversion of (*Z*)-acetates into (*Z*)-products became difficult. The reason was that the regioselectivity of the nucleophilic attack was decreased and e.g. the anti complex from crotylpalladium gave approximately equal amounts of the two products **6** and **7** (R = CH_3, Scheme 1).

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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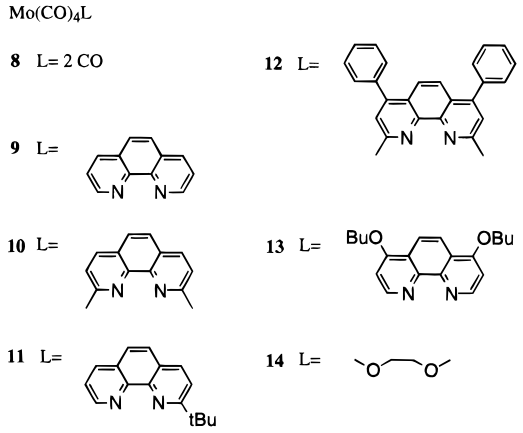
Chart 1

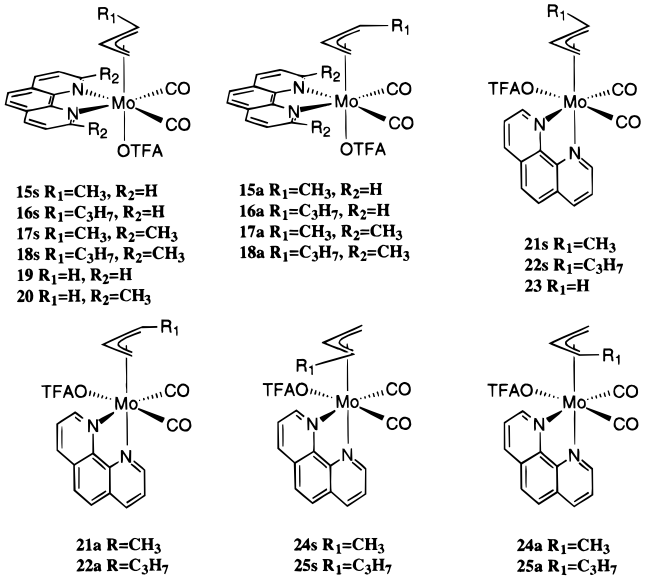


There are relatively few reports on the use of catalysts based on metals other than palladium, but tungsten,[4] iron,[5] and molybdenum[6] have been used. In the pioneering work by Trost *et al.*, it was shown that the activity of molybdenum catalysts was strongly ligand dependent.[6a−c] We have earlier shown that small changes in the structure of phenanthroline type ligands have a profound influence on the activity of catalysts based on palladium[2] and tungsten.[4c] We therefore decided to study the effect of such ligands on molybdenum-catalyzed reactions. Specifically we wanted to find out if (*E*)- or (*Z*)-substrates, e.g. **1** or **2**, could be selectively converted into (*Z*)-products, e.g. **7** (Scheme 1). We have now found that while the transformation of (*E*)-substrates is difficult with the present system due to lack of isomerization of the intermediate η^3-allyl complexes, e.g. **3** and **4**, the conversion of (*Z*)-substrates to (*Z*)-products e.g. **2** → **7** can be quite efficient with molybdenum catalysis.

Preparation of the Precatalysts

Starting from molybdenum hexacarbonyl, which was also used as precatalyst, we have prepared some catalytically active Mo(0) and Mo(II) complexes containing 1,10-phenanthroline (phen) type ligands. The Mo(0) complexes were prepared by reacting molybdenum hexacarbonyl with the appropriate ligand in toluene at reflux temperature.[7] High yields of complexes $Mo(CO)_4L$ (**9**−**13**) (Chart 1) were obtained, where L is phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmphen), 2-*tert*-butyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and 4,7-dibutoxy-1,10-phenanthroline. Also the complex **14**, where L = 1,2-dimethoxy ethane (DME), was prepared by heating molybdenum hexacarbonyl at reflux in DME. All the complexes **9**−**13** are air-stable, orange-red solids. The molybdenum(II) precatalysts were prepared by reacting the molybdenum(0) complexes **9** and **10** with crotyl trifluoroacetate or crotyl chloride in refluxing THF according to a modification of a procedure described earlier. Somewhat unexpectedly, the structures of the two products differed. The dmphen complex **10** gave exclusively the complex **17s** (Chart 2) with the dmphen ligand in the equatorial plane defined by the molybdenum and the two carbonyls. In contrast, the phen complex **9** gave complex **21** with the phen ligand occupying one equatorial and one axial position. The related complexes **15**−**25** were also prepared, sometimes as mixtures between syn and anti forms, and studied by NMR, but only **17** and **21** were used in catalytic reactions.

Chart 2



The reactions of (*E*)-allyl trifluoroacetates gave essentially pure syn complexes with both phen and dmphen ligands as shown by the reactions of crotyl trifluoroacetate to give **17s** and **21s**, and (*E*)-2-hexenyl trifluoroacetate to give **18s** and **22s**, respectively. The use of (*Z*)-2-hexenyl trifluoroacetate gave the pure anti complex **22a** with **9**, but with the dmphen complex **10** the corresponding anti complex **18a** was only obtained in ca. 80% isomeric purity. The isomerization appears to take place during formation of the η^3-allyl complex because this was stable when heated in toluene at the reaction temperature. There is thus a distinct difference between the Mo(II) and Pd(II) allyl complexes in that the former are very configurationally stable. Thus, the pure syn and anti complexes **18** and **22** could be heated at reflux for 24 h in benzene or acetonitrile without appreciable isomerization. This can probably be ascribed to the lack of associative pathways for the $\eta^3-\eta^1-\eta^3$ interconversion for the coordinatively saturated molybdenum complexes. The slow syn−anti isomerization of these (η^3-allyl)molybdenum complexes is in accordance with results from studies of such complexes with cyclopentadienyl ligands[8a] but in sharp

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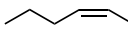
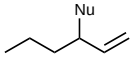
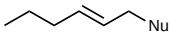
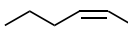
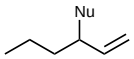
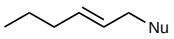
Table 1. Product Distribution with Molybdenum-Catalyzed Alkylation of (*Z*)-1-Acetoxy-2-hexene[g]

entry	precatalyst				yield[a] (%)
1	**8**	52	35	13	57
2	**9**	84	13	3	58
3	**9**	88	10	2	87[b,c]
4	**10**	91	6	3	31
5	**10**	87	11	2	23[d]
6	**11**[g]	50	19	31	76
7	**12**	77	10	13	100
8	**13**	89	3	8	66
9	**14**[h]	45	26	29	100
10	**21**	84	12	4	46
11	**21**	86	11	3	34[b]
12	**17**	85	9	6	100[c]
13	**17**	87	10	3	100[d]
14	**8**	12	88	0	100[e]
15	**9**	88	12	0	58[b,e]
16	**17**	88	12	0	98[e]
17	**9**	100	0	0	48[f]

[a] GC yields after 20 h reaction time. [b] 20 mol % of 1,10-phenanthroline was added. [c] The reaction was finished within 5 h. [d] 20 mol % dmphen was added. [e] Sodium dimethyl malonate was used as nucleophile. [f] Sodium ethyl 2-methylacetoacetate was used as nucleophile. [g] 10 mol % of the free ligand was added together with 10 mol % of $Mo(CO)_6$. [h] The precatalyst, **14**, was prepared by heating $Mo(CO)_6$ in 1,2-dimethoxyethane at reflux temperature for 3 h (under inert atmosphere). The resulting complex (moisture sensitive) was then filtered out, dried under vacuum, and used directly in the catalytic reaction. [i] The standard conditions are 110 °C, 10 mol % of the catalyst using 200 mol % of sodium dimethyl methylmalonate in toluene.

Table 2. Product Distribution with Molybdenum-Catalyzed Alkylation of (*E*)-1-Acetoxy-2-hexene[e]

entry	precatalyst				yield[a] (%)
1	**8**	6	17	77	28
2	**9**	1	10	89	22
3	**10**	0	11	89	42[b]
4	**21**	0	12	88	21
5	**17**	2	12	86	85[c]
6	**8**	0	83	17	100[d]
7	**9**	0	52	48	38[b,d]
8	**17**	0	52	48	46[d]

[a] GC yields after 20 h reaction time. [b] 20 mol % of 1,10-phenanthroline was added. [c] The reaction was finished within 5 h. [d] Sodium dimethyl malonate was used as nucleophile. [e] The standard conditions are 110 °C, 10 mol % of the catalyst using 200 mol % of sodium dimethyl methylmalonate in toluene.

contrast to the behavior of complexes which instead have a ligand of the tris(pyrazolyl)borate type.[8b]

It is likely that the observed isomerization during formation of **18a** is due to some reversibility in the oxidative addition rather than $\eta^3-\eta^1-\eta^3$ interconversion in the intermediate η^3-allyl complex. Finally, while mixtures of syn and anti complexes were obtained by reacting **10** with 3-acetoxy-1-butene and hexene, essentially pure syn complexes were formed in the reaction between **9** and the same allylic trifluoroacetates.

Reactivity and Selectivity

The acetates derived from (*Z*)- and (*E*)-2-hexen-1-ol were used as model substrates in the catalytic nucleophilic substitution. Because the formation of (*Z*)-products was of primary interest, the attention was focused on the (*Z*)-acetate. The main nucleophile was the anion of dimethyl methylmalonate, but a few experiments were performed with sodium ethyl 2-methylacetoacetate, with sodium dimethylmalonate which is less hindered, and with the anion of bis(phenylsulfonyl)methane, which is more hindered than dimethyl methylmalonate. As evident from Tables 1 and 2, the ligands of the precatalysts have a strong influence on yields and rates. In the reactions between 2-hexenyl-1-acetate and dimethyl methylmalonate, using $LMo(CO)_4$ as catalyst, where L is various phenanthrolines, it seems that both electron donation and steric effects are important. The parent phen is a fairly poor donor, and the yield (ca. 50%) and the rate with the precatalyst **9** are about the same as with molybdenum hexacarbonyl (**8**). When phen was replaced by dibutoxyphenanthroline (complex **13**), which should be a better donor, the yield went up by about 10% (Table 1, entries 1, 2, 8). In contrast, a large difference was noted between the dmphen complex **10** and diphenyl dmphen complex **12**, the yield increasing from ca. 30% to 100% with the complex **12** as precatalyst (Table 1, entries 4, 7). The suggested difference in electron density in the complexes **9** and **13** is supported by ^{95}Mo NMR, which shows that molybdenum is more shielded in the complex **13**.[9] Other factors, such as ease of ligand displacement, are probably also important. This is shown by the high reactivity of the complexes **11** and **14** where the ligands could be assumed to coordinate fairly weakly to the metal, in **14** for the steric reasons, due to the bulky *tert*-butyl group on the phen ligand. Addition of excess ligand increased the efficiency of the phen complex **9** but decreased that of the dmphen and diphenyl dmphen complexes **10** and **12**.

(9) The Mo shift is −1173 ppm relative to external reference Na_2MoO_4 at pH 11 for precatalyst **9** and −1196 ppm for **13**; cf. ref 4a.

Because the phen carbonyl complex **9** was more efficient than the dmphen complex **10**, it came as a surprise that among the η^3-allyl complexes, the dmphen ligand was vastly superior. Thus the phen allyl complex **21** gave only ca. 50% of the products from nucleophilic displacement of a acetate from (*Z*)-1-acetoxy-2-hexene in a slow reaction while ca. 100% yield was obtained in the fast reaction catalyzed by the dmphen complex **17** (Table 1). Similar trends were observed in the reactions with (*E*)-substrate (Table 2).

Also the regio- and stereoselectivity of the different precatalysts varies. With molybdenum hexacarbonyl as precatalyst and sodium dimethyl methylmalonate as nucleophile, (*Z*)-1-acetoxy-2-hexene gave a mixture of stereo- and regioisomers. Circa 35% of the product was the result of nucleophilic attack at the more substituted terminus of the presumed intermediate η^3-allyl complex. In contrast, most of the other precatalysts gave mainly the desired (*Z*)-product resulting from reaction at the least substituted η^3-allyl terminus with retention of configuration (Table 1). The exceptions were the two precatalysts **11** and **14**, which gave substantial reaction at the more substituted η^3-allyl terminus and also ca. 30% formation of the (*E*)-product (Table 1, entries 6, 9).

The same general trends were observed in the reactions with (*E*)-1-acetoxy-2-hexene, although the (*E*)-substrate gave distinctly lower yields than the (*Z*)-substrate (Table 2, entries 1−5).

The uniqueness of molybdenum hexacarbonyl as precatalyst was nicely demonstrated with sodium dimethyl malonate as nucleophile. More than 80% preference for reaction at the more substituted η^3-allyl terminus (cf. ref 6e) was observed with both (*Z*)- and (*E*)-substrates. In addition, essentially quantitative yields were obtained. For the (*Z*)-substrate the selectivity was changed to 88% for the least substituted position when **9** was used as precatalyst. In contrast, the (*E*)-substrate reacted equally readily at the two η^3-allyl termini (Table 1, entries 14 and 15; Table 2, entries 6 and 7). An interesting result was the extraordinary selectivity with (*Z*)-substrate, **9** as catalyst, and sodium ethyl 2-methylacetoacetate as nucleophile. The product yield was moderate (ca. 50%), but the (*Z*)-product was formed exclusively (Table 1, entry 17). The more hindered nucleophile, bis(phenylsulfonyl)methane, finally, was evidently too sterically demanding because no reaction was observed when **9** was used as catalyst.

A lower reactivity for the (*E*)-substrate was observed also with the η^3-allyl catalysts **17** and **21** (Table 2, entries 4, 5). With both, high selectivity (>85%) was observed for reaction with retention of configuration and reaction at the least substituted (η^3-allyl) terminus. As with the (*Z*)-substrate, the dmphen complex **17** was more efficient. In an attempt to shed some light on the surprising difference between the precatalysts **21** and **17**, a series of (η^3-allyl)molybdenum complexes were prepared and studied by NMR, molecular mechanics, and, for **21** and **23**, X-ray diffraction analysis.

Structure and Stereochemistry of the η^3-Allyl Precatalysts

One possible explanation for the different reactivities of the complexes **21** and **17** is that the active catalysts have different structures. An extensive NMR investigation was therefore done, including the determination of crucial NOEs. The ^{1}H NMR spectrum of the complex **21s** at 298 K showed that the two halves of the phen ligand are in different environments since there was a shift difference of 1.32 ppm between the H_{P2} and H_{P9} protons (the 2,9 protons of the phenanthroline ligand). Irradiation of H_{P2} gave NOE to the allyl protons H_2 (16%) and H_{1s} (11%), indicating a close proximity in space between H_{P2} and these protons. By contrast, irradiation of H_{P9} gave no NOE to the allyl protons. These results strongly suggest that the structure in solution is in fact **21s**, mainly or exclusively, where one of the phen nitrogens, N_1, occupies an equatorial position and the other, N_{10}, an axial position (the equatorial plane is defined by the two carbonyl groups and the molybdenum atom). None of the isomer **24s** could be detected, suggesting that steric interaction between H_{P2} and the syn methyl group of the allyl is important. The trifluoroacetate is coordinated[10] and occupies an equatorial position. It seems reasonable to exclude the possibility that the signals observed for **21s** are due to a dynamic average of different structures because no changes in the NMR spectrum were detected down to 188 K.

For **17s**, the two methyl groups of the dmphen ligand appeared at nearly equal shifts in NMR. In addition, a small NOE (2%) was observed between one of the methyl groups and H_{1s}, but none was observed with H_{1a} of the allyl group. These data suggest that the complex has the structure **17s** where the dmphen ligand is in the equatorial plane. The different structures of **21s** and **17s** were unexpected because the X-ray diffraction studies of three related complexes showed that the N,N-ligand occupied the equatorial position exclusively.[11] An X-ray diffraction structure determination confirmed the assignment of the structure of **21s** (Figure 1).

In order to eliminate the asymmetry introduced by the crotyl methyl group, the η^3-propenyl complexes with phen and dmphen ligands were also prepared and studied by NMR. For the dmphen complex a symmetric structure **20** with the dmphen ligand in the equatorial plane could be inferred from the identical shifts of corresponding phen protons and the NOE between syn allyl protons H_s and phen methyl groups. This also shows that the η^3-allyl group is oriented with the open face toward the carbonyls, in agreement with the results of theoretical studies.[12]

In contrast to the η^3-butenyl complex **21s**, the η^3-propenyl complex in solution at 298 K turned out to consist of a mixture of the axial (**23**) and equatorial (**19**) isomers in a ratio of 2:1. A slight broadening of the peaks suggested a dynamic system, and on warming of the sample in $CDCl_2CDCl_2$ coalescence of signals was observed. In order to characterize the two structures, NOE experiments were performed at 213 K, where interconversion between **19** and **23** is slow. Irradiation of H_2 and H_9 of the minor isomer gave a fair NOE (6%)

(10) Measurements on complexes **17s** and **21s** in CH_2Cl_2 showed very low conductivity, indicating little ionization.

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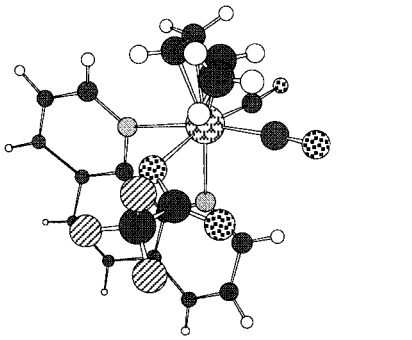

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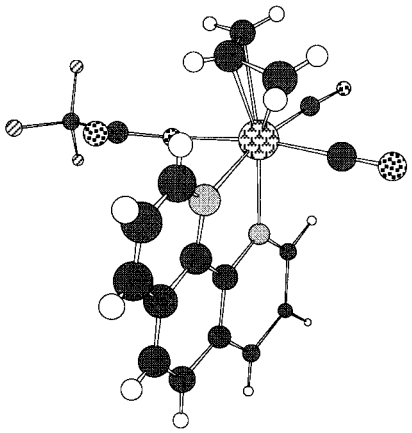
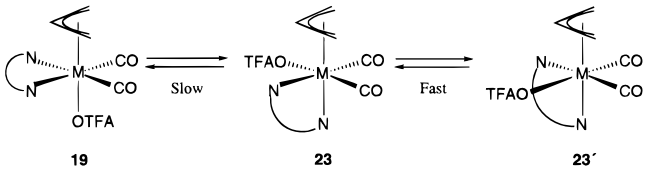


23

Figure 1. X-ray diffraction structures. Hydrogens have been added at appropriate positions using the Chem3D plus program.

Scheme 2. Dynamic Processes of (1,10-phenanthroline)Mo(η^3-allyl)$(CO)_2$OTFA

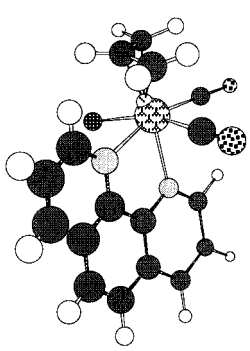


19 **23** **23′**

to H_{1s} but none to H_{1a} of the allyl. In addition the spectrum was symmetric, showing that the structure of this isomer is **19**. The major isomer showed a dynamic behavior even at 213 K, but at 193 K, H_{p2} and H_{p9} on the phenanthroline gave rise to two signals with a shift difference of 1.34 ppm, close to that of the butenyl complex **21s**. A structure **23** seemed highly probable and could be confirmed by X-ray crystallography (Figure 1).

In addition to the interconversion between **19** and **23** the complex **23** undergoes fast epimerization (cf. ref 13). The whole process can be viewed as a turnstile rotation where the interconversion of **19** and **23** is fairly slow at 298 K ($\approx$1.5 s^{-1}) and the epimerization (**23** to **23′**) is fast ($\approx 8 \times 10^4$ s^{-1}) (Scheme 2). The activation parameters (Table 3) were determined by NMR measurements of coalescence temperatures and saturation transfer[14] (see Experimental Section). The syn η^3-hexenyl complex **22s** behaved similary to the η^3-butenyl complex **21s**. For the hexenyl complex, also the anti isomer could be prepared. In contrast to the syn complex, the anti complex gave a mixture of the all equatorial and the equatorial−axial isomers (**22a** + **25a** ⇌ **16a**).

(14) Sjögren, M. P. T. Dissertation. Selectivity Control in Transition Metal-Catalyzed Nucleophilic Substitution of Allylic Leaving Groups. The Royal Institute of Technology, Stockholm, 1993.



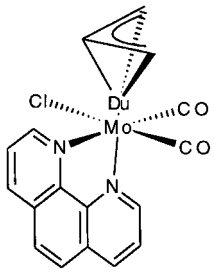


Figure 2. Geometry-optimized structure from MM3(92) calculations.

Table 3. Kinetic Constants and Activation Parameters for the Dynamic Processes of Mo(η^3-propenyl)$(CO)_2$OTFA

exchange process	$k^{\ddagger}$ (s^{-1})	$\Delta G^{\ddagger}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/K mol)
19 to **23**	1.49 ± 0.13	72.0 ± 0.2	74.9 ± 2.2	10 ± 7
23 to **23′**	$7.9 \times 10^4 \pm 1.2 \times 10^4$	45.1 ± 0.4	56.0 ± 0.9	36.9 ± 4.4

Table 4. MM3 Calculation on (Phenanthroline)molybdenum(II) Complexes

entry	complex	steric energy E (kcal/mol)	rel steric energy diff ΔE (kcal/mol)
1	**19**	−1781.31	0.14
2	**23**	−1781.45	0
3	**15s**	−1777.74	0.46
4	**15a**	−1775.71	2.49
5	**21s**	−1778.20	0
6	**21a**	−1775.04	3.16
7	**24s**	−1777.24	0.96
8	**24a**	−1775.70	2.50
9	**17s**	−1768.72	0
10	**17a**	−1767.39	1.33

Molecular Modeling

In an attempt to understand the dynamic properties of the η^3-allyl complexes with phen and dmphen ligands, molecular mechanics calculations were performed on complexes **15**, **19**, **21**, and **24** (Table 4). The bonding model for the molecular mechanics treatment of the η^3-allyl moiety, coordinated to an octahedral transition metal, was constructed in the following way: one dummy atom was placed at a distance of 0.500 Å from the molybdenum atom and connected to the three η^3-allyl carbon atoms, making this substructure "umbrella shaped" (see Figure 2). The dummy atom was used to control all molybdenum−allyl bond lengths, bond angles, and dihedral angles. The MM3(92)[15] force field was used for the parametrization procedure, and parameters are given in the Supporting Information. This bonding model can be referred to as a valence force field (VFF) approach and is by far the most common way for handling metal−ligand and ligand−ligand interactions in molecular mechanics calculations.[16]

(15) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(16) Comba, P. *Coord. Chem. Rev.* **1993**, *123*, 1. Hay, B. P. *Coord. Chem. Rev.* **1993**, *126*, 177. Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187. Boyd, R. H. *J. Chem. ys.* **1968**, *49*, 2574.

The MM3(92) force field uses a special 1,3-electron pair repulsion energy term, which improves the modeling of ligand−ligand interactions. Ideal bond lengths (L−M) and angles (L−M−L), with corresponding force constants, were assigned using X-ray diffraction structures and experimentally obtained vibrational levels. All force constants involving dihedral angles with the molybdenum atom as one of the atoms in the central bond have been set to 0, which is common practice when applying the VFF approach to calculate coordination compounds.

In our MM3(92) calculations of the molybdenum complexes **15**−**24**, the trifluoroacetate group was replaced with a chloride, but this should only have a minor effect on the relative energies of the different isomeric structures.

Although calculations were done on the η^3-propenyl and η^3-butenyl complexes, the η^3-hexenyl complexes should be sufficiently similar to permit qualitative extrapolations.

For the η^3-propenyl phen complex the calculations suggest that the isomer **23** with the ligand in an equatorial−axial position is slightly more stable than **19**, which has an all equatorial ligand (by 0.14 kcal/mol, Table 4). This corresponds to a ratio of **23**/**19** of ca. 2/1, in excellent agreement with the measured value. When the η^3-propenyl was replaced by syn-η^3-2-butenyl, the energy difference was increased to 0.46 kcal/mol (Table 4). This is in qualitative agreement with the fact that only **21s** could be detected by NMR in the potential equilibrium with **15s**. The trend is clear; that is, the equatorial−axial arrangement of the ligand becomes more favored on introduction of a syn substituent on the η^3-allyl group. By contrast, on anti-substitution the isomers **15a** and **24a** get about the same energy, both lower than **21a**. In agreement, NMR shows that, in solution, the anti hexenyl complexes (the anti-η^3-butenyl complexes could not be prepared in pure form) form an equilibrium mixture of **25a** and 17−50% of **16a**, depending on the solvent. The calculations also suggest that, with the dmphen ligand, the all equatorial isomer will be favored by at least 5 kcal/mol. This is in accordance with the exclusive observation (by NMR) of the equatorial isomers, **17s** and **17a**, respectively, in solution. Finally, the calculations suggest that the syn complexes generally have lower energies than the anti complexes, independent of ligand arrangement. This is contrary to the results with tris(pyrazolyl)borate complexes,[8b] and it clearly represents a problem in attempts to turn *Z*- and *E*-substrates both into anti products.

Discussion

It is evident from the experimental results that the ligands strongly affect both reactivity and selectivity in molybdenum-catalyzed substitution of allylic acetate. The examination of the results presented in Tables 1 and 2 shows that even with very simple substrates, small changes in precatalyst have a profound influence on yield and selectivity. Our results also show that very active precatalysts, such as the dmphen η^3-allyl complex **17**, can be obtained by fairly minor modifications of phen type ligands.

When the dimethyl methylmalonate anion was used as nucleophile, electron-releasing substituents have beneficial influence on the yields, as shown by a comparison between complexes **9** and **13** and between **10** and **12** (Table 1). This could perhaps reflect a higher activity in the oxidative addition, e.g. **1** to **2** in Scheme 1. Also two complexes with ligands which should be readily displaced, **11** and **14**, gave high yields, but with these complexes, the regio control was low, close to that observed for molybdenum hexacarbonyl (**8**, Table 1). An interesting observation is that addition of excess ligand increased the efficiency of the phen complex **9** but not the dmphen complex **10** (Table 1, entries 2−5). A tentative explanation is that the phen ligand is sufficiently small to generate cationic $(phen)_2$ type intermediates (cf. ref 17). However, so far we have not been able to detect such species, and even in dichloromethane solution, the lack of conductivity contradicts facile formation of cationic species. An alternative explanation is that a favorable effect of added ligand could be stabilization of the catalyst.

A change in precatalyst from molybdenum hexacarbonyl (**8**) to $(phen)Mo(CO)_4$ resulted in a dramatic decrease in efficiency when dimethyl malonate anion was used as nucleophile. Also a change in selectivity from addition at the more substituted η^3-allyl terminus with **8** to addition at the less substituted with **9** as catalyst was observed (Table 1). It was shown earlier that more efficients catalysts were obtained by replacing one carbon monoxide with acetonitrile in the $LMo(CO)_4$ precatalyst, where L is phenanthroline or bipyridine.[6a] Such complexes would presumably give η^3-allyl intermediates similar to **17** and **21**, containing only two carbonyls. However, only the dmphen complex **17** was an efficient catalyst, while the phen complex **21** gave the same low yields as the $Mo(CO)_4(phen)$ complex (Table 1, entries 10−13; Table 2, entries 4, 5). The difference in efficiency between the η^3-allyl catalysts **17** and **21** is hard to understand. One explanation is that this is related to different structures in solution. Both NMR and calculations clearly show the dmphen complex should have the exclusive structure **17**, with an all equatorial ligand, while the phen complex should have a preference for structure **21**, with an axial−equatorial ligand. A higher reactivity of the complex with an all equatorial ligand would then explain the result.[18] The decrease in reactivity on going from allyl to crotyl acetate is also explainable in these terms because syn substitution on the allyl leads to preference for equatorial−axial structures, such as **21s** and **22s**.

Finally, the possibility to achieve the desired conversion of an *E*-acetate to a *Z*-product requires some comment. First, a qualitative rate experiment shows that the rates of nucleophilic attack and oxidative addition may be comparable. Thus the catalytic alkylation of butenyl acetate with the anion of dimethyl malonate with **17** as catalyst has about the same rate as the stoichiometric addition of the malonate anion to the complex **17**. Second, the syn−anti isomerization is

(17) Chisholm, M. H.; Connor, J. A.; Huffman, J. C.; Kober, E. M.; Overton, C. *Inorg. Chem.* **1984**, *23*, 2298.

(18) It is interesting to note two pairs of the ^{13}C-shifts of the η^3-propenyl group are found for the phen complex, corresponding to the two isomeric structures **19** and **23** (55, 68 ppm; 63, 72 ppm). As expected, the dmphen ligand gave only the all equatorial structure **23** (58 and 76 ppm for the allyl group). If a low-field shift is an indication of higher reactivity, as suggested for (η^3-allyl)palladium compounds, the diequatorial structure should be more reactive; cf. ref 19.

(19) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

very slow under the conditions for the catalytic reaction. It therefore seems very likely that the catalytic conversion of (*E*)-substrates into (*Z*)-products, using phenanthroline type auxilliary ligands, is not going to be successful. However, it is interesting to note that the dmphen catalyst is one of the most active molybdenum catalysts developed so far. It also complements the palladium-based catalysts[3] in that it can convert (*Z*)-substrates very selectively into (*Z*)-products with a nucleophile such as the anion of dimethyl methylmalonate.

Experimental Section

All reactions were performed in oven-dried glassware. Melting points (uncorrected) were determined by using a Büchi SMP-20 melting point apparatus. ^{1}H and ^{13}C NMR were recorded on 400 MHz (Bruker Model AM400) and a 250 MHz (Bruker Model AC250) instruments at 298 K in $CDCl_3$ (unless otherwise indicated), using $CHCl_3$ (δ 7.26 ppm) and $CDCl_3$ (δ 77.0 ppm) as internal references for ^{1}H and ^{13}C, respectively. The following abbreviations are used in descriptions of NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened, and J = coupling constant. These subscripts are used:[20] P = phenanthroline protons, s = proton in syn position, and a = proton in anti position relative to H_2. IR spectra (cm^{-1}) were recorded on a Perkin-Elmer 1725X FTIR instrument. Gas chromatographic determinations of yields and product patterns were performed using a Varian Model 3700 chromatograph equipped with a 15 m × 0.15 mm dimethylpolysiloxane (100%) capillary column and a Varian 4290 integrator. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany. All solvents and reagents were purchased from commercial sources and dried and purified by standard techniques.[21,22] 2-*tert*-Butyl-1,10-phenanthroline, 1-butenyl-3-trifluoroacetate, (*E*)-2-butenyl-1-trifluoroacetate, (*Z*)-1-acetoxy-2-hexene, and (*E*)-1-acetoxy-2-hexene were prepared according to literature procedures.[23]

Computational Details. The MM3(92) calculations were performed using the Mac Mimic 2[24] program package on a Macintosh Quadra 800 computer. The parameter set for molybdenum complexes used in this paper can be ordered from Håkan Frisell, Royal Institute of Technology (e-mail: haak@kth.se). Graphical presentations of the X-ray diffraction and the MM3(92) geometry-optimized structures (Figures 1 and 2) were produced using the Chem3D plus program.[25]

Anti−Syn Equilibrium of the Complexes. The anti-syn isomerization was followed by integration in ^{1}H NMR of the corresponding protons in the two isomers at regular time intervals.

General Procedure for Molybdenum-Catalyzed Alkylation. Toluene (10 mL) was added to a flask containing sodium hydride (48 mg, 2 mmol) under N_2. Dimethyl methylmalonate (321 mg, 2.2 mmol) was added with a syringe. After stirring of the solution for 45 min at ambient temperature, a mixture of hexenylacetate (142 mg, 1 mmol) and the internal standard dodecane (70 mg) was added followed by the catalyst (0.1 mmol). The content of the flask was heated to reflux. The reaction was monitored by GC at regular time intervals (1, 2, 5, and 20 h).

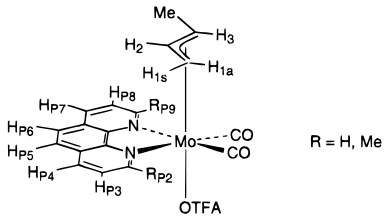
Kinetic Measurements. The dynamic processes of complex **23** were investigated by ^{1}H NMR spectroscopy with a sample of concentration 0.028 mol/dm^3. CD_2Cl_2 was used as solvent at a temperature below or equal to 303 K. In the high temperature range $CDCl_2CDCl_2$ was used. The isomerization rates were determined with the aid of the following techniques: (i) Measurements of the *coalescence temperature* of a pair of exchanging nuclei. The rate was simply calculated from the equation $k = \pi\Delta\nu 2^{-1/2}$. No line shape analysis was performed. (ii) *Saturation transfer experiments*. These were performed under steady-state conditions, using a standard program for NOE difference spectroscopy, with a pre-irradiation time of 4 s. The fractional change of the observed magnetization of nucleus b (f^b) was evaluated in the difference spectrum by integration of the residual signals due to nuclei b and a. A change of ±2 s in the pre-irradiation time did not cause any appreciable change in f^b. The exchange rate for the process a ⇌ b was evaluated by equation $k_1 = R_a(-f^b + \eta)/(K + f^b)$, where K is the equilibrium ratio a/b, R_a is the apparent relaxation rate of nucleus a, and η is the NOE enhancement factor due to cross-relaxation between b and a estimated to 8%. R_a was independently estimated through linear interpolation of the values obtained by standard inversion-recovery experiments, run at the extremes of the temperature interval of interest.

Tetracarbonyl(1,10-phenanthroline)molybdenum(0) (9). Hexacarbonylmolybdenum (2.64 g, 10 mmol) and 1,10-phenanthroline (10 mmol) were dissolved and refluxed in dry toluene (100 mL) for 2 h under nitrogen. The deep red crystals which were formed upon cooling were washed with toluene and dried in vacuo. Yield: 3.66 g (94%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.45 (d, $J_{P2,3} = J_{P9,8} = 5.0$ Hz, 2 H, $H_{P2,9}$), 8.47 (d, $J_{P4,3} = J_{P7,8} = 8.2$ Hz, 2 H, $H_{P4,7}$), 7.99 (s, 2 H, $H_{P5,6}$), 7.99 (dd, 2 H, $H_{P3,8}$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 223.0, 205.3, 153.0, 146.4, 136.8, 130.2, 127.2, 124.5. IR: 2007, 1866 br, 1827.

Tetracarbonyl(2,9-dimethyl-1,10-phenanthroline)molybdenum(0) (10). Hexacarbonylmolybdenum (2.64 g, 10 mmol) and 2,9-dimethyl-1,10-phenanthroline (10 mmol) were dissolved and refluxed in dry toluene (100 mL) for 2 h under nitrogen. The deep red crystals which were formed upon cooling were washed with toluene and dried in vacuo. Yield: 3.81 g (92%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.28 (d, $J_{P4,3} = J_{P7,8} = 8.5$ Hz, 2 H, $H_{P4,7}$), 7.85 (s, 2 H, $H_{P5,6}$), 7.70 (d, 2 H, $H_{P3,8}$), 3.26 (s, 6 H, Me_P). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 223.2, 203.7, 164.1, 147.4, 137.4, 128.4, 126.5, 125.9, 30.9. IR: 2011, 1866 br, 1814.

Tetracarbonyl(4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline)molybdenum(0) (12). Hexacarbonylmolybdenum (0.25 g, 0.95 mmol) and 4,7-dibutoxy-1,10-phenanthroline (0.34 g, 0.95 mmol) were dissolved and refluxed in dry toluene (20 mL) for 2 h under nitrogen atmosphere. The deep red crystals which were formed upon cooling were washed with toluene and dried in vacuo, giving 0.34 g of product. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.84 (s, 2 H), 7.63 (s, 2 H), 7.52−7.56 (m, 10H), 3.33 (s, 6 H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 223.0, 203.4, 162.8, 149.1, 147.9, 136.9, 129.5, 129.1, 128.9, 128.5, 128.3, 126.1, 125.8, 123.8, 30.9. IR: 2003, 1880, 1826.

(20)



(21) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(22) Neocuproine and phenanthroline were dehydrated by the following procedure: In an Erlenmeyer flask 5 g of the ligandwas dissolved in 100 mL of methylene chloride and anhydrous $MgSO_4$ was added. After being stirred overnight, the suspension was filtered and the solution was evaporated *in vacuo*.

(23) Sjögren, M.; Hansson, S.; Norrby, P.-O.; Åkermark, B.; Cucciolito, M. E.;Vitagliano, A. *Organometallics* **1992**, *11*, 3954.

(24) The version of MM3 used is the MM3(92) program, implemented for Macintosh computers in a program called Mac Mimic 2, by InStar Software AB, IDEON Research Park, S-223 70 Lund, Sweden. MM3 versions for platforms other than Macintosh are available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405.

(25) Chem3D Plus 3.0 for Macintosh, Cambridge Scientific Computing Inc., 875 Massachusetts Av., Suite 61, Cambridge, MA 02139.

Tetracarbonyl(4,7-dibutoxy-1,10-phenanthroline)molybdenum(0) (13). Hexacarbonylmolybdenum (0.164 g, 0.62 mmol) and 4,7-dibutoxy-1,10-phenanthroline[4c] (0.20 g, 0.62 mmol) were dissolved and refluxed in dry toluene (20 mL) for 2 h under nitrogen atmosphere. The deep red crystals which were formed upon cooling were washed with toluene and dried in vacuo, giving red-brown crystals, 0.208 g (63%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.99 (d, J = 5.3 Hz, 2 H), 8.17 (s, 2 H), 6.97 (d, J = 5.3 Hz, 2 H), 4.23 (t, J = 6.4 Hz, 4 H), 1.97 (m, 4 H), 1.61 (m, 4 H), 1.04 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 223.1, 205.6, 162.2, 154.0, 147.0, 122.4, 119.7, 104.8, 69.4, 30.8, 19.3, 13.8. IR: 2010, 1869, 1815.

General Procedures to Prepare Complexes of the Type Mo(phenanthroline)(η^3-alkenyl)$(CO)_2$OTFA. Method A. The tetracarbonyl complex Mo(phenanthroline)$(CO)_4$ (1 mmol) and 3-(trifluoroacetyl)-1-butene (336 mg, 2 mmol) were added and refluxed in dry THF (10 mL) for 3 h under nitrogen. The reaction mixture was evaporated *in vacuo* to dryness. The crude solid was dissolved in a small amount of CH_2Cl_2. Deep red crystals were formed upon slow addition of pentane.

Method B. Tetracarbonyl complex Mo(phenanthroline)$(CO)_4$ (3 mmol) and a 5-fold excess of crotyl chloride (1.57 g) were mixed together in THF (30 mL). The mixture was refluxed under nitrogen for 3 h. After cooling to ambient temperature, the reaction was stored overnight in a refrigerator. The crystals formed were filtered off and dried *in vacuo*. NMR data could not be obtained due to the insolubility of the chloride complex. Dicarbonyl(1,10-phenanthroline)(1−3-η-2-butenyl)molybdenum chloride (1 mmol) was suspended in THF (25 mL) followed by addition of AgOTFAc (221 mg, 1 mmol) at ambient temperature for 2 h. The solution was filtered, and the precipitate washed with acetone. Water was slowly added to the filtrate, and a cloudy precipitate was formed. The deep red crystals were filtered off and dried *in vacuo*. Methods A and B are both modifications of a procedure described earlier[26].

Dicarbonyl(1,10-phenanthroline)[(1−3-η)-2-butenyl]-molybdenum Chloride. Yield, method B: 1.22 g (96%). IR: 1924 br, 1836 br.

Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[(1−3-η)-2-butenyl]molybdenum Chloride. Yield, method B: 1.23 g (91%). IR: 1918, 1836.

Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[*anti*-(1−3-η)-2-butenyl]molybdenum Trifluoroacetate (17a) and Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[*syn*-(1−3-η)-2-butenyl](trifluoroacetato)molybdenum (17s). Yield, method A: 345 mg (65%). Decomp pt: 233 °C. **17a**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.34 (d, J = 8.3 Hz, 1 H), 8.31 (d, J = 8.3 Hz, 1 H), 7.84 (br s, 2 H, $H_{P5,6}$), 7.69 (d, J = 8.3 Hz, 1 H), 7.66 (d, J = 8.3 Hz, 1 H), 3.35 (m, $J_{3a,2}$ = 6.9 Hz, 1 H, H_{3a}), 3.31 (s, 3 H, Me_P), 3.26 (s, 3 H, Me_P), 2.64 (ddd (d app t), $J_{1s,2}$ = 6.5 Hz, $J_{1s,1a}$ = 1.8 Hz, $J_{1s,3s}$ = 1.8 Hz, 1 H, H_{1s}), 2.39 (ddd (d app t), 1 H, H_2), 1.71 (dd, $J_{1a,2}$ = 10.0 Hz, 1 H, H_{1a}), 0.98 (d, $J_{Me,3s}$ = 6.6 Hz, 3 H, Me); NOE (400 MHz, CD_2Cl_2) irr.H_{P2} => (2%, H_{1s}). **17s**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.34 (d, J = 8.3 Hz, 1 H), 8.32 (d, J = 8.3 Hz, 1 H), 7.85 (br s, 2 H, $H_{P5,6}$), 7.72 (d, J = 8.3 Hz, 1 H), 7.70 (d, J = 8.3 Hz, 1 H), 3.24 (s, 3 H, Me_P), 3.22 (s, 3 H, Me_P), 2.41 (dd, $J_{1s,2}$ = 6.5 Hz, $J_{1s,1a}$ = 1.8 Hz, 1 H, H_{1s}), 2.17 (ddd, 1 H, H_2), 1.71 (m, $J_{3a,2}$ = 9.8 Hz, 1 H, H_{3a}), 1.15 (d, $J_{Me,3s}$ = 6.5 Hz, 3 H, Me), 0.94 (d, $J_{1a,2}$ = 8.6 Hz, 1 H, H_{1a}); NOE (400 MHz, CD_2Cl_2) irr. H_{P2} => (2%, H_{1s}); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 229.5, 228.7, 228.7, 228.1, 164.3, 164.2, 164.1, 164.1, 146.3, 146.0, 146.0, 145.8, 139.0, 139.0, 138.8, 138.5, 128.8, 128.6, 128.4, 128.3, 126.8, 126.8, 126.7, 126.6, 126.6, 126.4, 126.3, 126.3, 78.3, 77.4, 76.2, 69.5, 55.3, 54.3, 29.1, 28.4, 16.8, 14.9; IR 1931, 1903, 1863 br, 1743, 1694; conductivity (CD_2Cl_2) 2.1 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{22}H_{19}F_3MoN_2O_4$: C, 50.01; H, 3.62. Found: C, 50.09; H, 3.75.

(26) Dawens, F.; Dewailly, J.; Mennier-Piret, J.; Piret, J. *J. Organomet. Chem.* **1974**, *76*, 53.

Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[*syn*-(1−3-η)-2-hexenyl](trifluoroacetato)molybdenum (18s). Yield, method A, 450 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, $J_{p3,4}$ = 8 Hz, 1 H, H_{p4}), 8.26 (d, $J_{p7,8}$ = 8 Hz, 1 H, H_{p7}),7.81 (s, 2 H, $H_{p5,6}$), 7.66 (d, 1 H, H_{p3}), 7.63 (d, 1 H, H_{p8}), 3.29 (s, 3H, Me_p), 3.28 (s, 3H, Me_p), 2.39 (dd, $J_{1s,1a}$ = 1.0 Hz, $J_{1s,2}$ = 6.4 Hz, 1 H, H_{1s}), 2.09 (d app t, 1 H, H_2), 2.01 (m, 1 H, H_4), 1.61 (ddd, $J_{2,3a}$ = 9.5 Hz, $J_{3a,4}$ = 3.4 Hz, $J_{3a,4'}$ = 11.2 Hz, 1 H, H_{3a}), 1.37 (m, 1 H, H_5), 1.21 (m, 1 H, $H_{5'}$), 0.97 (dd, $J_{1a,2}$ = 9.0 Hz, 1 H, H_{1a}), 0.71 (t, 3H, Me), 0.18 (m, 1 H, $H_{4'}$). Anal. Calcd for $C_{24}H_{23}F_3MoN_2O_4$: C, 51.81; H, 4.17; N, 5.03. Found: C, 52.03; H, 4.27; N, 4.92.

Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[*anti*-(1−3-η)-2-hexenyl](trifluoroacetato)molybdenum (18a). Yield, method A: 455 mg (82%). Using the *Z*-2-hexen-1-yl trifluoroacetate in the oxidative addition, a mixture of the syn−anti isomers **18s** and **18a** was generally obtained. The relative proportion of the isomers ranged from ca. 50:50 under the conditions of method A to ca. 25:75 in a more diluted solution (1 mmol of complex in 50 mL of THF). Monitoring the reaction by ^{1}H NMR showed isomerization of the excess allylic substrate during the reaction time. No further isomerization of the complex and of the substrate occurred after the reaction was complete.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, $J_{p3,4}$ = 8 Hz, 2 H, H_{p4}), 8.29 (d, $J_{p7,8}$ = 8 Hz, 1 H, H_{p7}), 7.80 (s, 2 H, $H_{p5,6}$), 7.66 (d, 1 H, H_{p3}), 7.64 (d, 1 H, H_{p8}), 3.36 (s, 3H, Me_p), 3.31 (s, 3H, Me_p), 3.25 (m, 1 H, H_{3s}), 2.60 (d app t, $J_{1s,1a}$ = $J_{1s,3s}$ = 2.0 Hz, $J_{1s,2}$ = 7 Hz, 1 H, H_{1s}), 2.29 (d app t, 1 H, H_2), 1.92 (m, 1 H, H_4), 1.65 (dd, $J_{1a,2}$ = 9.4 Hz, 1 H, H_{1a}), 1.29 (m, 1 H, H_5), 1.04 (m, 1 H, $H_{5'}$), 0.74 (t, 3H, Me), 0.03 (m, 1 H, $H_{4'}$).

Dicarbonyl(1,10-phenanthroline)[(1−3-η)-2-propenyl](trifluoroacetato)molybdenum (19). Yield, method A: 379 mg (78%). Mp 217 °C (dec). **7a**: ^{1}H NMR (400 MHz, 193 K, CD_2Cl_2) δ 9.29 (dd, $J_{P2,3}$ = $J_{P9,8}$ = 5.0 Hz, $J_{P2,4}$ = $J_{P9,7}$ = 1.5 Hz, 2 H, $H_{P2,9}$), 8.63 (dd, 2 H, $H_{P4,7}$), 8.06 (s, 2 H, $H_{P5,6}$), 7.92 (dd, $J_{P3,4}$ = $J_{P8,7}$ = 5.0 Hz, 2 H, $H_{P3,8}$), 3.39 (d, $J_{1s,2}$ = 6.2 Hz, 2 H, H_{1s}), 3.00 (m, 1 H, H_2), 1.45 (d, $J_{1a,2}$ = 9.2 Hz, 2 H, H_{1a}); NOE (400 MHz, 213 K, CD_2Cl_2) irr. $H_{P2,9}$ => (6%, H_{1s}), irr. $H_{1s,3s}$ => (26%, $H_{1a,3a}$), (13%, $H_{p2,9}$), (11%, H_2). **7b**: ^{1}H NMR (400 MHz, 193 K, CD_2Cl_2) δ 10.28 (dd, $J_{P2,3}$ = 5.2 Hz, $J_{P2,4}$ = 1.5 Hz, 1 H, H_{P2}), 8.94 (d, $J_{P9,8}$ = 5.2 Hz, 2 H, H_{P9}), 8.72 (dd, $J_{P4,3}$ = 8.2 Hz, 1 H, H_{P4}), 8.61 (d, 1 H, H_{P7}), 8.11 (dd, 1 H, H_{P3}), 8.10 (m, 2 H, $H_{P5,6}$), 8.00 (dd, $J_{P8,7}$ = 8.1 Hz, $J_{P8,9}$ = 5.1 Hz, 1 H, H_{P8}), 4.05 (m, 1 H, H_2), 3.64 (m, $J_{P3s,2}$ = 6.3 Hz, 1 H, H_{3s}), 3.56 (m, $J_{P1s,2}$ = 6.2 Hz, 1 H, H_{1s}), 1.85 (d, $J_{P1a,2}$ = 9.4 Hz, 1 H, H_{1a}), 1.40 (dd, $J_{P3a,2}$ = 9.7 Hz, $J_{P3a,1a}$ = 3.0 Hz, 1 H, H_{3a}); ^{13}C NMR (100 MHz, 213 K, CD_2Cl_2) δ 225.9, 225.2, 225.0,155.0, 154.8, 151.6, 151.6, 148.7, 144.0, 143.5, 141.8, 138.1, 137.7, 137.3, 128.8, 128.7, 126.5, 126.3, 126.3, 124.1, 123.9, 71.6, 68.0, 63.4, 54.8; IR 1938 br, 1856 br, 1687. Anal. Calcd for $C_{19}H_{13}F_3MoN_2O_4$: C, 46.93; H, 2.69. Found: C, 46.94; H, 2.84.

Dicarbonyl(2,9-dimethyl-1,10-phenanthroline)[(1−3-η)-2-propenyl](trifluoroacetato)molybdenum (20). Yield, method A: 514 mg (84%). Mp: 238 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.33 (d, $J_{P4,3}$ = $J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.84 (s, 2 H, $H_{P5,6}$), 7.72 (d, 2 H, $H_{P3,8}$), 3.31 (s, 6 H, Me_P), 2.41 (d, $J_{1s,2}$ = 6.5 Hz, 2 H, H_{1s}), 2.37 (tt, 1 H, H_2), 1.16 (d, $J_{1a,2}$ = 9.4 Hz, 2 H, H_{1a}). NOE (400 MHz, CD_2Cl_2): irr. H_{1s} => (30%, H_{1a}), (8%, H_2), (6%, Me_P), irr. H_{1a} => (34%, H_{1a}), (2%, H_2). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 227.8, 163.1, 145.9, 138.9, 128.6, 126.9, 126.6, 75.7, 57.9, 29.0. IR: 1935 br, 1873 br, 1698.

Dicarbonyl(1,10-phenanthroline)[*syn*-(1−3-η)-2-butenyl](trifluoroacetato)molybdenum (21s). Yield, method A: 422 mg (80%). Mp: 194 °C. Total yield, method B: 460 mg (87%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.21 (dd, $J_{P2,3}$ = 5.0 Hz, $J_{P2,4}$ = 1.3 Hz, 1 H, H_{P2}), 8.89 (dd, $J_{P9,8}$ = 5.1 Hz, $J_{P9,7}$ = 1.2 Hz, 1 H, H_{P9}), 8.59 (dd, $J_{P4,3}$ = 8.2 Hz, 1 H, H_{P4}), 8.49 (dd, $J_{P7,8}$ = 8.1 Hz, 1 H, H_{P7}), 8.02 (dd, 1 H, H_{P3}), 7.99 (m, 2 H, $H_{P5,6}$), 7.88 (dd, 1 H, H_{P8}), 4.08 (ddd, 1 H, H_2), 3.37 (dd, $J_{1s,2}$ = 6.4 Hz, $J_{1s,1a}$ = 3.4 Hz, 1 H, H_{1s}), 2.47 (dq, $J_{3a,2}$ = 9.3 Hz, 1 H,

H_{3a}), 1.98 (d, $J_{Me,3a}$ = 6.4 Hz, 3 H, Me), 1.26 (dd, $J_{1a,2}$ = 9.2 Hz, 1 H, H_{1a}). NOE (400 MHz, CD_2Cl_2): irr. H_{P2} => (16%, H2), (11%, H_{1s}), (−2%, H_{1a}), irr. H2 => (16%, H_{P2}), (3%, H_{Me}), (2%, H_{1s}), irr. H_{1s} => (35%, H_{1s}), (17%, H_{P2}), (5%, H_2), (-5% ,H_{3a}). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 228.7, 227.7, 150.1, 145.8, 144.0, 138.8, 138.1, 130.1, 127.4, 125.0, 84.7, 75.5, 50.8, 16.5. IR: 1924, 1833 br, 1691. Conductivity (CD_2Cl_2) = 0.83 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{20}H_{15}F_3MoN_2O_4$: C, 48.02; H, 3.02. Found: C, 47.84; H, 3.14.

Dicarbonyl(1,10-phenanthroline)[*syn*-(1−3-η)-2-hexenyl](trifluoroacetato)molybdenum (25s). Yield, method A: 460 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.26 (dd, $J_{p2,3}$ = 5.0 Hz, $J_{p2,4}$ = 1.2 Hz, 1 H, H_{p2}), 8.88 (dd, $J_{p9,8}$ = 5.0 Hz, $J_{p9,7}$ = 1.1 Hz, 1 H, H_{p9}), 8.54 (dd, $J_{p4,3}$ = 8.2 Hz, 1 H, H_{p4}), 8.43 (dd, $J_{p8,7}$ = 8.1 Hz, 1 H, H_{p7}), 8.00 (dd, 1 H, H_{p3}), 7.89 (AB_q, $J_{p5,6}$ = 8.0 Hz, 2 H, $H_{p5,6}$), 7.83 (dd, 1 H, H_{p8}), 4.11 (d app t, 1 H, H_2), 3.34 (dd, $J_{1s,2}$ = 6.7 Hz, $J_{1s,1a}$ = 3.5 Hz, 1 H, H_{1s}), 2.45 (m, 1 H, H_{3a}), 2.36 (m, 1 H, H_4), 2.15 (m, 1 H, $H_{4'}$), 1.72 (m, 2 H, $H_{5,5'}$), 1.29 (dd, $J_{1a,2}$ = 10 Hz, 1 H, H_{1a}), 1.04 (t, 3 H, Me). Anal. Calcd for $C_{22}H_{19}F_3MoN_2O_4$: C, 50.01; H, 3.62; N, 5.30. Found: C, 50.35; H, 3.80; N, 5.24.

Dicarbonyl(1,10-phenanthroline)[*anti*-(1−3-η)-2-hexenyl](trifluoroacetato)molybdenum (22a, 25a, and 16a). Yield, method A: 445 mg (84%). The compound exists in solution as an equilibrium mixture of three isomers (**22a**, **25a**, and **16a**). The former two interconvert rapidly at 25 °C, so that averaged signals are seen in the ^{1}H NMR spectrum.

22a, 25a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.6 (br, 2 H, $H_{p2,9}$), 8.48 (d, $J_{p3,4}$ = $J_{p7,8}$ = 6 Hz, 2 H, $H_{p4,7}$), 7.98 (s, 2 H, $H_{p5,6}$), 7.9 (m, 2 H, $H_{p3,8}$), 4.35 (br, 1 H, H_{3s}), 4.15 (d app t, 1 H, H_2), 3.66 (d, $J_{1s,2}$ = 7 Hz, 1 H, H_{1s}), 2.18 (d, $J_{1a,2}$ = 10 Hz, 1 H, H_{1a}), 2.02 (m, 1 H, H_4), 1.62 (m, 1 H, H_5), 1.45 (m, 1 H, $H_{5'}$), 0.95 (t, 3 H, Me), 0.37 (m, 1 H, $H_{4'}$).

16a : ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, $J_{p2,3}$ = 5 Hz, $J_{p2,4}$ = 1 Hz, 1 H, H_{p2}), 9.30 (dd, $J_{p9,8}$ = 5 Hz, $J_{p9,7}$ = 1 Hz, 1 H, H_{p9}), 8.46 (m, 2 H, $H_{p4,7}$), 7.90 (s, 2 H, $H_{p5,6}$), 7.80 (m, 2 H, $H_{p3,8}$), 3.94 (m, 1 H, H_{3s}), 3.25 (d app t, $J_{1s,2}$ = 7 Hz, $J_{1s,1a}$ = 2 Hz, 1 H, H_{1s}), 2.89 (d app t, $J_{2,1a}$ = 10 Hz, 1 H, H_2), 1.95 (dd, $J_{1a,2}$ = 10 Hz, 1 H, H_{1a}), 0.89 (t, 3 H, Me), 0.29 (m, 1 H, $H_{4'}$).

Anal. Calcd for $C_{22}H_{19}F_3MoN_2O_4$: C, 50.01; H, 3.62; N, 5.30. Found: C, 50.39; H, 3.87; N, 5.22.

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Supporting Information Available: Tables of atomic, torsional, bending, van der Waals, and bond angle parameters (5 pages). Ordering information is given on any current masthead page.

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