Coupling of η^3-Allyl and Alkyne in Molybdenum Carbonyl Complexes

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The complexes [Mo(η^3-allyl)$(CO)_2(S_2PX_2)$(NCMe)] (X = OEt (**1a**), Ph (**1b**)) react with DMAD (dimethyl acetylenedicarboxylate) to give the tricarbonyl complexes [$Mo(CO)_3(S_2PX_2)${OC(OMe)C(allyl)=CCO_2Me}] (**2a,b**) in a reaction involving the coupling of allyl and alkyne. Subsequent addition of PEt_3 affords crystalline, air-stable dicarbonyl complexes [$Mo(CO)_2(PEt_3)(S_2PX_2)${OC(OMe)C(allyl)=CCO_2Me}] (**3a,b**). An X-ray structural analysis of the dithiophosphinate derivative **3b** reveals that the alkenyl ligand is stabilized through intramolecular coordination of one oxygen of the ester group to the metal, forming a five-membered oxametallacycle. The alkenyl ligand shows unusual trans stereochemistry in contrast to the cis disposition usually found in previous examples of metal-mediated η^3-allyl−alkyne coupling. Demetalation of the organic moiety can be easily afforded by reaction with air or HCl gas to give the corresponding 2-allyl fumarate **4** in high yield. Regioselectivity studies employing 1-methylallyl complexes reveal that the reaction is strongly influenced by the dithio ligand bonded to molybdenum. In all cases reaction at the more substituted carbon of the allyl is favored.

Introduction

Coupling of allyl and alkyne promoted by transition metals has been studied intensively in the last 25 years by several research groups. Synthetically useful methods have been developed in linear as well as in cyclization coupling reactions.[1,2] In most cases η^1-allyl compounds have been employed, whereas η^3-allyls have attracted less attention. Nevertheless, complexes containing η^3-allyl have been frequently used as allyl transfer reagents in organic synthesis.[3] In contrast, there are only a few reported cases in which the resulting organic moiety remained attached to the metal. In two cases such reaction leads to a cyclopentadienyl ring bonded to the metal as a η^5-ligand (**A** in Chart 1),[4] while in other cases an allyl-substituted σ-alkenyl is produced.[5] Recently a new reactivity pattern leading to seven-membered carbocycles by insertion of two alkynes in the allyl−metal bond has been reported (**B** in Chart 1).[6] Usually, the final products contain the allyl group in a position cis to the metals, as it can be expected for a metal-mediated allyl−alkyne coupling. We want to report the coupling of a η^3-allyl with dimethyl acetylenedicarboxylate (DMAD) within the coordination sphere of Mo(II) to give an intramo-

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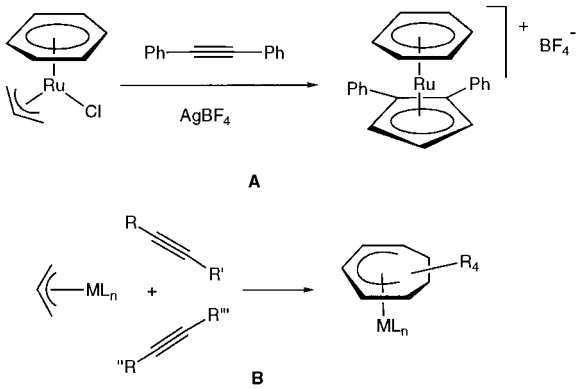
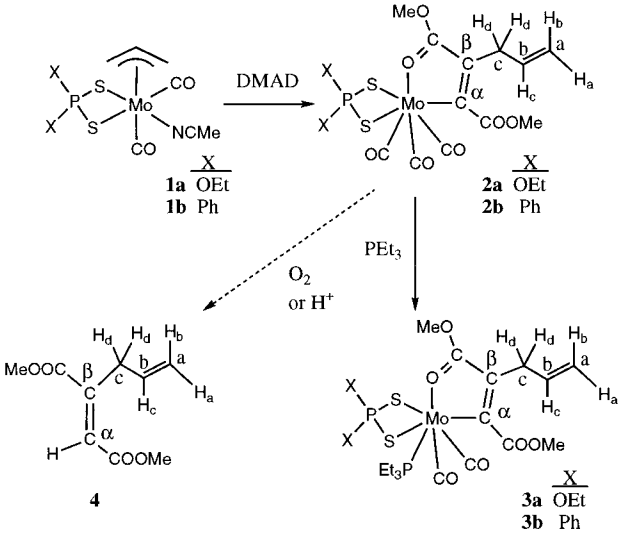
Chart 1



Scheme 1



DMAD = MeOOCC≡CCOOMe

lecularly stabilized σ-alkenyl complex. In contrast to most previously known examples of η^3-allyl/alkyne coupling, the reaction affords an alkenyl displaying trans stereochemistry which, after easy demetalation, produces the corresponding dimethyl 2-allylfumarate in high yield. Additionally we present here the results of a preliminary study of the regiochemistry of the coupling reaction.

Results and Discussion

Compounds with Unsubstituted Allyl Ligands. The reaction of the η^3-allyl acetonitrile dicarbonyl complexes **1a,b**[7] with DMAD in dichloromethane produces a solution which, after chromatography, yields tricarbonyl compounds **2a,b** as orange oils.

The structures proposed for them in Scheme 1 are supported by analytical and spectroscopic data and, indirectly, by the structure determination carried out on the phosphine-substituted derivative **3b** (see below). Thus, the high ν(CO) frequencies observed in the IR spectra of **2a,b** are in accordance with the presence of a "$Mo(CO)_3$" rather than a "$Mo(CO)_2$" fragment which was contained in the parent compounds **1a,b**. The tricarbonyls **2a,b** are probably produced by CO scavenging from an unstable dicarbonyl intermediate in the course of the reaction. This means that the yield of **2a,b** is limited by the amount of CO available, and it cannot be higher than 66% in this case. However, when the reaction with DMAD was carried out under CO atmosphere, with continuous bubbling of CO through the reaction mixture, no significant improvement of the yield was observed. The crude products **2a,b** can be purified by chomatography over silica to give an oil which decomposes rapidly when exposed to air. Due to some decomposition on the column, the isolated yield is low.

Apart from the presence of the tricarbonyl grouping, the most important feature of the spectra of complexes **2a,b** is the presence of a terminal allyl. Since on the basis of spectroscopic data alone it was not possible to ascertain the structural details of these tricarbonyls, and we were unable, despite repeated attempts, to grow crystals of these compounds which could be suitable for a crystallographic study, we decided to attempt the preparation of crystalline derivatives.

It was found soon that reactions of tricarbonyls **2a,b** with triethylphosphine gave red microcrystalline dicarbonyl complexes **3a,b**. An X-ray determination was carried out on a crystal of the diphenyldithiophosphinate derivative **3b**. Crystal and refinement data are collected in Table 1, atomic parameters are found in the Supporting Information, and selected bond distances and angles are in Table 2.

As it can be seen in Figure 1, the most salient feature of the molecule is the presence of a 2-allyl-substituted alkenyl ligand, which originates from the coupling of the allyl group of the parent **1b** to DMAD.

This alkenyl is stabilized by intramolecular coordination of the oxygen atom of the ester group on the β carbon, thus producing a five-member oxametallacycle

Table 1. Crystal Data and Refinement Details for $[Mo(CO)_2(PEt_3)(S_2PPh_2)\{OC(OMe)C(C_3H_5)=CCO_2Me\}]$ (3b)

formula	$C_{29}H_{36}MoO_6P_2S_2$
fw	702.61
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.999(1)
b, Å	19.556(4)
c, Å	18.558(4)
β, deg	91.18(1)
V, Å^3	3265(1)
Z	4
T, K	200(2)
ρ_{calc}, g cm^{-3}	1.43
$F(000)$	1448
λ(Mo Kα), Å	0.710 73
cryst size, mm; color	0.14 × 0.13 × 0.13, orange
μ, cm^{-1}	6.48
method of collcn	$\omega/2\theta$ scan
scan range, deg	$0 \le \theta \le 25$
abs corr	empirical (ψ-scan)
corr factors (min, max)	0.910, 0.994
no. of reflcns measd	5926
no of reflcns obsd, $I \ge 3\sigma(I)$	2939
no. of params	364
data-to-param ratio	8.07
weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
g	0.0003
goodness of fit	1.3252
residuals R, R_w[a]	0.041, 0.040

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = \{\Sigma(w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2\}^{1/2}$.

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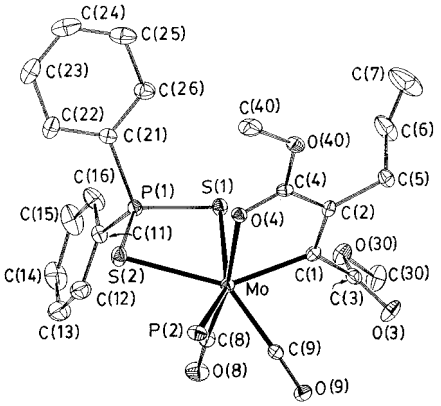
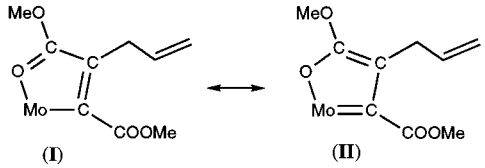


Figure 1. Perspective view (EUCLID Package)[21] of [Mo(CO)$_2$(PEt$_3$)(S$_2$PPh$_2$){OC(OMe)C(C$_3$H$_5$)=C(CO$_2$Me)}] (**3b**), showing the atom numbering. Ethyl groups of the PEt$_3$ ligand have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Mo(CO)$_2$(S$_2$PPh$_2$)(PEt$_3$){OC(OMe)C(C$_3$H$_5$)=CCOOMe}] (3b)

Mo−S(1)	2.594(2)	Mo−S(2)	2.624(2)
Mo−P(2)	2.503(2)	Mo−C(8)	1.935(7)
Mo−C(9)	1.935(7)	Mo−C(1)	2.181(7)
Mo−O(4)	2.201(4)	C(1)−C(2)	1.353(9)
C(1)−C(3)	1.481(9)	C(2)−C(4)	1.443(9)
C(2)−C(5)	1.522(9)	C(3)−O(30)	1.341(8)
C(4)−O(4)	1.234(7)	O(40)−C(40)	1.460(8)
C(5)−C(6)	1.50(1)	C(6)−C(7)	1.18(1)
S(2)−Mo−S(1)	77.0(1)	O(4)−Mo−C(1)	73.2(2)
C(2)−C(1)−Mo	116.7(5)	C(3)−C(1)−Mo	124.1(5)
C(4)−C(2)−C(1)	112.7(6)	C(5)−C(2)−C(1)	125.7(6)
C(5)−C(2)−C(4)	121.6(6)	O(3)−C(3)−C(1)	125.4(7)
O(30)−C(3)−C(1)	111.2(6)	O(30)−C(3)−O(3)	123.4(6)
C(30)−O(30)−C(3)	115.1(6)	O(4)−C(4)−C(2)	121.4(6)
C(4)−O(4)−Mo	115.8(4)	C(40)−O(40)−C(4)	115.7(5)
C(6)−C(5)−C(2)	113.4(6)	C(7)−C(6)−C(5)	131.(1)

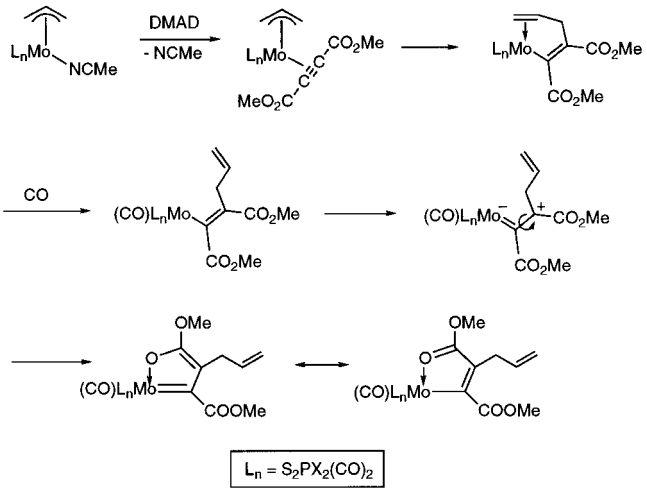
Scheme 2



Mo−O=C−C=C, similar to that found in [Mo{C(Me)=C(Me)C(O)C(Me)=CHMe}(CO)$_2$(η^5-C$_5$H$_5$)],[8] which, however, was produced by a very different route, through the addition of two acetylenes and subsequent CO insertion. The distance Mo−C(1) of 2.181(7) Å is shorter than the Mo−C(alkenyl) of 2.243(3) Å found in [Mo{P(OMe)$_3$}$_3${σ-(*E*)-CH=CHBu^t}(η-C$_5$H$_5$)].[9] As for the cyclopentadienyl compound mentioned above, the ^{13}C{^{1}H}NMR spectrum of the more soluble **3a** shows the signal attributable to C$^\alpha$ in the region of δ 250 ppm. The same feature has been found in some alkenyl complexes, and it has been ascribed to some carbenic character in this carbon C$^\alpha$, arising from the contribution of the canonic form II in Scheme 2.[10]

Accordingly, the distances C(1)−C(2) of 1.353(9) Å and C(4)−O(4) of 1.234(7) Å are somewhat longer for C=C and C=O bonds, while the distance C(2)−C(4) of 1.443(9) Å is slightly shorter than that expected for a C−C bond. All this indicates some degree of electron delocalization around the ring. The atoms forming the oxametallacycle in **3b** and the atoms directly bonded to them, i.e. C(3), C(5), and O(40), display a planar arrangement, from which the maximum deviation of 0.057(4) Å is found for O(4). The ester group not involved in the bonding with the metal is nearly pependicular to the oxametallacycle, a fact which precludes electron delocalization over the alkenyl−ester−metal ring. As it can be seen in Figure 1, the allyl group in **3b** is attached to the β-carbon of the alkenyl and, quite remarkably, is placed in a trans position relative to the metal. If the coupling of the allyl and the alkyne is produced within the coordination sphere of the metal, there should be expected a cis disposition of the metal with respect to the allyl group in the resulting alkenyl. As far as we know there is only one other example of allyl/alkyne coupling resulting in a trans alkenyl. Thus, the reaction of CpMo(CO)$_3$(η^1-allyl) with excess hexafluoro-2-butyne, under UV irradiation for 3 days, gives CpMo(CO){C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)CH$_2$CH=CH$_2$} through a double insertion of the alkyne into the Mo−C(allyl) bond.[2e] The structure of the resulting molybdenum alkenyl complex was proposed, on the basis of spectroscopic data, to have a trans disposition around the double bond in position 3.

Scheme 3



Although the available experimental data do not permit us to propose an unambiguous mechanism, we can offer here a rationalization for the formation of the final product, as shown in Scheme 3.

The first step may consist in a subsitution of acetontrile by DMAD followed by the coupling of the allyl and the alkyne. Precoordination of the alkyne is likely as the reaction did not take place when acetonitrile was employed as a solvent. Since a complete dissociation of the allyl from the metal *before* the carbon−carbon bond formation seems unlikely, it appears that the addition of the metal and the allyl group to the alkyne should proceed from the same side to produce initially a cis alkenyl which would isomerize afterward to the trans geometry observed in the final product. In the present case, the resulting intramolecular stabilization due to the Mo−O(ester) bond could be the driving force for this isomerization which would be aided by the

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contribution of the canonic form of the type II displayed in Scheme 2.

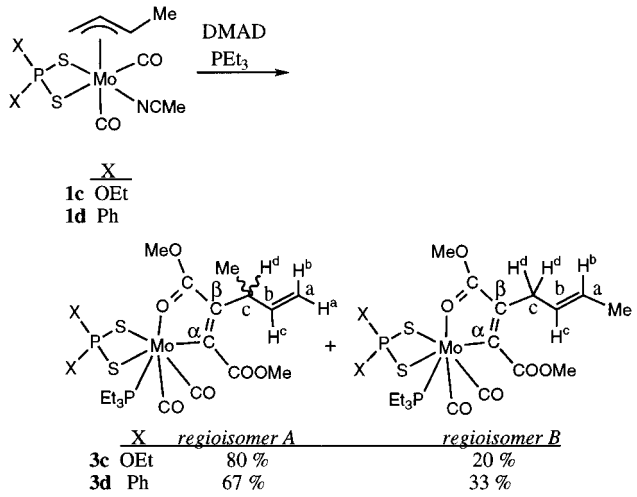
Alternatively, it could be considered that the trans stereochemistry could be originated by the external attack of the allyl to the activated acetylene, as proposed to account for the reactivity of η^3-allyls toward aldehydes found by Faller and co-workers.[11] In such cases, the attack of the allyl on the carbonyl group of the aldehyde is favored by the easy conversion of the allyl from η^3 to η^1, which is easily observed by ^{1}H NMR spectroscopy. However, no indication of η^3 to η^1-transformation of the allyl is observed for complexes **1a,b**, even when treated with good donors such as pyridine.[7]

Demetalation. After we elaborated the structure of compounds **3a,b**, it seemed interesting to us to find methods for the clean hydrolysis of the organic moiety. When the crude product from the reaction of DMAD and Mo−allyls **1** is redissolved in dichloromethane, and oxygen is bubbled through the solution for several hours or the solution left for several days at air, the ^{1}H NMR spectra showed the formation of only one product. After chromatography, the corresponding dimethyl 2-allylfumarate **4** (see Scheme 1) was obtained in high yield. Experiments carried out by bubbling HCl gas through the solution for several minutes led also to clean demetalation without isomerization of the alkene.

The compound surprisingly turned out to be a liquid at room temperature, in contrast to the well-known dimethyl fumarate. The ^{1}H NMR spectrum displays a singlet at 6.8 ppm which is assigned to the alkenylic proton H^e. Two singlets at 3.8 and 3.7 ppm are attributed to the methyl groups of the diester. A DEPT experiment gave unambiguous assignment of the alkenyl carbons C$^\alpha$ and C$^\beta$. C$^\alpha$ showed an upfield shift of more than 100 ppm to $\delta = 127.5$ ppm whereas C$^\beta$ shifted down *ca.* 15 ppm to $\delta = 145.9$ ppm.

Complexes with Substituted Allyls. With the aim of obtaining some information about the regiochemistry of the reaction, the crotyl (1-methylallyl) derivatives **1c,d** were prepared in two steps by reacting [Mo(CO)$_3$(NCMe)$_3$] with *trans*-1-chloro-2-butene (crotyl chloride) and subsequent addition of $NH_4[S_2P(OEt)_2]$ or $Na_2[S_2PPh_2]$. Crotyl derivatives **1c,d** were obtained as oily substances which decompose rapidly in air, being considerably less stable than the corresponding allyl complexes **1a,b**. Since the oily, air-sensitive samples of **1c,d** were not suitable for microanalysis, they were characterized by high-resolution mass spectra of samples drawn from acetonitrile solutions. Due to rapid loss of the nitrile, M^+ could not be detected. The compounds were identified by the $(M - MeCN)^+$ peaks, which showed the typical isotopic pattern of molybdenum. The spectroscopic features of **1c,d** are similar to those found for the complexes containing unsubstituted allyls **1a,b**, and accordingly, it has been assumed for them the same structure, which was supported by the structural determination of the hydrazine derivative [{Mo(η^3-C$_3$H$_5$)(CO)$_2${S$_2$P(OEt)$_2$}}$_2$(μ-NH$_2$NH$_2$)].[7] According to their ^{1}H NMR spectra, complexes **1c,d** consist mainly of the syn isomers, as expected from the trans geometry of the starting crotyl chloride. We have not observed any indication of equilibration of the syn and anti isomers either in the substituted **1c,d** or in their homologues **1a,b**, containing unsubstituted allyls. The ^{13}C{^{1}H} NMR spectra of the crotyl complexes **1c,d** display two signals for the CO ligands, reflecting their inequivalency. In contrast, complexes **1a,b**, bearing unsubstituted allyl, exhibit only one signal for the two carbonyls. The same occurs with other related complexes although, according to X-ray crystallography, they contain two inequivalent carbonyl ligands in the solid.[7,12] A trigonal-twist process has been invoked to account for the equilibration of the two inequivalent CO groups in the NMR time scale. This process consists of the rotation of the triangular face formed by two CO's and one allyl ligand, this being a structural feature commonly found in η^3-allyl dicarbonyl complexes.[13] The inequivalency of the two CO's in solution for compounds **1c,d** may be due to the presence of the methyl substituent on the allyl, which makes the carbonyl groups diastereotopic.

Scheme 4



Regiochemistry. When crotyl complexes **1c,d** are reacted with DMAD, two regioisomers A and B can be expected depending on which of the two allyl termini is attacked by the alkyne (see Scheme 4). The complex bearing diethyldithiophosphate **1c** leads to complex **3c**, showing an 8/2 (A/B) mixture of the regioisomers, whereas for the complex **3d** containing diphenyldithiophosphinate a selectivity of 2/1 (A/B) was observed.

The signals for methyl group of the allyl of the two isomers were well separated (**3c**: A, 1.12 ppm; B, 1.51 ppm. **3d**: A, 1.21 ppm; B, 1.63 ppm) and did not overlap with other signals. This permitted an easy evaluation of the proportion of the regioisomers in the mixture.

The ^{31}P spectrum of **3d** shows a well-resolved pattern with the expected four signals reflecting the isomer distribution found in the ^{1}H NMR spectrum. Thus, two doublets appear for the signal of S_2PPh_2. One of them,

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centered at 85.4 ppm, is of double intensity than the other, being therefore assigned to isomer A. The one at higher field (84.9 ppm) is of half intensity and is assigned to isomer B. Interestingly, the signals due to PEt_3, at ca. 40 ppm, show reverse order. The signals in the ^{31}P NMR spectrum of **3c** are not so well separated. The two doublets corresponding to $S_2P(OEt)_2$ appear overlapped in the same position (103.4 ppm) while the signals of PEt_3 appear very close to each other (40.7 ppm for isomer A, 40.6 for isomer B).

Although unambiguous signal assignment was not possible in the ^{13}C NMR of **3d**, the easily identified signals which are due to the carbonyl ligands, the ester groups, and the methylene groups of triethylphosphine resolve well for the isomers and show in all cases the 2/1 intensity ratio for the isomers A/B.

For compound **3c** the signals observed in the $^{31}C\{^1H\}$ NMR are assigned to the major isomer (A). The signals of the minor isomer B may be obscured by those of the major isomer A or may be lost under the noise.

Attempted Reactions with Less Activated Alkynes. Unfortunately, all attempts to extend this reactions to less activated alkynes, such as methyl 2-butynoate, phenyl 2-propynoate, 2-butyne, and bis(trimethylsilyl)acetylene, have been fruitless so far. Heating of reaction mixtures led only to extensive decomposition. This may be due to the thermal lability of the alkyne complexes, which dissociate upon heating, rather than undergoing coupling with the allyl.

Conclusion

We have described in this paper the reaction of labile ligand allyl complexes with the activated alkyne DMAD. The coupling between allyl and alkyne leads to an alkenyl ligand which is stabilized through intramolecular coordination of one oxygen of the ester group to the metal, forming a five-membered oxometallacycle. It shows unusual trans stereochemistry in contrast to all previously known examples of metal-mediated η^3-allyl−alkyne coupling. Demetalation of the organic moiety can be easily effected by air or gaseous HCl to give the corresponding 2-allylfumarate in good yield.

Regioselectivity studies employing 1-methylallyl complexes reveal that the reaction is strongly influenced by the dithio ligand bonded to molybdenum. In both cases reaction at the more substituted carbon of the allyl is favored.

Currently, investigations are under way to extend the reactivity of the complexes to less activated alkynes by proper choice of the appropriate dithio and allyl ligands. This would give the reaction a potential use in organic synthesis.

Experimental Section

General Methods. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or under nitrogen in a glovebox. Methylene chloride and acetonitrile were distilled from CaH_2. Methylene chloride was degassed by one freeze−pump−thaw cycle prior to use. THF and diethyl ether were distilled from Na/benzophenone. Hexane was distilled from Na. All NMR solvents were stored over 3 Å molecular sieves (Aldrich) and degassed by three freeze−pump−thaw cycles. $NH_4S_2P(OEt)_2$ was recrystallized from THF and kept under argon. NaS_2PPh_2[15] and [Mo(η^3-R-C_3H_4)$(CO)_2(NCMe)_2X$] (R = H, Me; X = Cl, Br)[16] complexes were synthesized according to published methods. Crotyl chloride (95% predominantly trans) was purchased from Aldrich. All other reagents were used without further purification. Column chromatography was carried out employing silica gel (60, 230−400 mesh, Merck) or neutral alumina (activity I). Filtering was performed using kieselgur (Merck).

^1H, ^{31}P, and ^{13}C NMR spectra were measured on 300 and 200 MHz spectrometers. Shift values are given in ppm. ^1H NMR and ^{13}C shifts are referenced to solvents. In $^{31}P\{^1H\}$ spectra 85% H_3PO_4 is used as an external reference. High-resolution mass spectra were recorded in the EI mode. Compounds **2c,d** were obtained as oils which were not suitable for elemental analysis due to rapid decomposition when exposed to air.

[Mo{η^3-C_3H_4(Me-1)}$(CO)_2${$S_2P(OEt)_2$}(NCMe)] (1c). To a solution of $Mo(CO)_3(CH_3CN)$ (0.1 g, 0.33 mmol) in acetonitrile (20 mL) was added crotyl chloride (50 μL, 0.5 mmol). The mixture was heated at 60 °C for 1 h, and then $NH_4[S_2P(OEt)_2]$ was added (0.066 g, 0.33 mmol). After the mixture was stirred for 15 min, the precipitate of NH_4Cl was removed by filtering over kieselguhr. The filtrate was evaporated in vacuo to to give **1c** as an orange oil. Yield: 0.123 g, 76%. Anal. Calc for $C_{12}H_{20}MoNO_4PS_2$: C, 33.26; H, 4.65; N, 3.23. Found: C, 32.89; H, 5.73; N, 2.76. IR (CH_2Cl_2; cm^{-1}): ν(CN) 2285 w; ν(CO) 1941 s, 1850 s. ^1H NMR (acetone-d_6): δ 4.1 (m, 5H, C$H_{central}$ of crotyl and POCH_2), 3.05 [d (6 Hz), 1H, H_{syn}], 2.24 (s, 3H, NCCH_3), 1.91 (m, 4H, CH_3 and CH_3CH_{anti} of crotyl), 1.26 [t (7 Hz), 6 H, $POCH_2CH_3$], 1.15 [d (7 Hz), 1H, H_{anti}]. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 103.8. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 227.8, 227.0, 226.9 (2CO), 120.1 (NCCH$_3$), 74.7, 74.6 [$C_{central}$ of crotyl and CCH$_3$], 62.9, 62.8 (POCH$_2$), 52.2 (CH$_2$ of crotyl), 18.7 (CH$_3$ of crotyl), 15.8 and 15.7 ($POCH_2CH_3$), 1.9 (NCCH$_3$). MS (EI): *m*/*z* 393.94 (M^+ − MeCN).

[Mo{η^3-C_3H_4(Me-1)}$(CO)_2$(S_2PPh_2)(NCMe)] (1d). The compound was obtained as described above for **1c**, from [Mo$(CO)_3(CH_3CN)$] (0.1 g, 0.33 mmol), crotyl chloride (50 μL, 0.5 mmol), and NaS_2PPh_2[15] (0.09 g, 0.33 mmol), to give **1d** as an orange oil. Yield: 0.137 g, 79%. Anal. Calc for $C_{20}H_{20}MoNO_2PS_2$: C, 48.29; H, 4.05; N, 2.82. Found: C, 47.68; H, 4.71; N, 2.34. IR (CH_2Cl_2; cm^{-1}): ν(CN) 2285 w; ν(CO) 1941 s, 1848 s. ^1H NMR (C_6D_6): δ 7.85 (m, 4H, Ph), 7.0 (m, 6H, Ph), 3.95 (m, 1H, $H_{central}$ of crotyl), 3.29 [d (5 Hz), 1H, H_{syn}], 2.01 [d (6 Hz), 3H, CH_3 of crotyl), 1.85 (m, 1H, H_{anti}), 1.26 [d (9 Hz), 1H, H_{anti}], 0.3 (s, 3H, NCCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 86.3. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 228.9, 227.9 (2s, CO) 141.8−129.0 (m, Ph), 123.3 (s, NCCH$_3$), 77.5 (s, $C_{central}$ of crotyl), 75.9 (s, CCH$_3$ of crotyl), 53.5 (CH$_2$ of crotyl), 19.7 (CH$_3$ of crotyl), 1.2 (CH$_3$CN). MS (EI): *m*/*z* 457.95 (M^+ − MeCN).

[Mo$(CO)_3${$S_2P(OEt)_2$}{OC(OMe)C(C_3H_5)C=CCO_2Me}] (2a). To a solution of **1a** (0.2 g, 0.48 mmol) in CH_2Cl_2 (10 mL) was added DMAD (58 μL, 0.48 mmol). The color of the solution changed immediately to green and then to brown. After 15 min the solvent was removed in vacuo. The residue was dissolved in a mixture of CH_2Cl_2/hexane (3:1) and chromatographed over silica. The first fraction was collected. After removal of the solvent, an orange yellow oil remained. Yield: 0.034 g (12%). Anal. Calc for $C_{17}H_{21}MoO_9PS_2$: C, 36.44; H, 3.78. Found: C, 36.18; H, 3.93. IR (CH_2Cl_2; cm^{-1}): ν(CO) 2036 s, 1957 s, 1713 w, 1598 w. ^1H NMR ($CDCl_3$): δ 5.78 [ddt (17, 10, and 6 Hz), 1H, H^c], 5.03 [dd (17 and 2 Hz, 1H, H^b], 5.01 [dd (10 and 2 Hz), 1H, H^a], 4.19 (m, 2H, POCH_2), 4.11 (m, 2H, POCH_2), 3.95 and 3.80 (s, 3H, OCH_3), 3.12 [d (5 Hz), 2H, H^d],

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1.36 [t (7 Hz), 6H, $POCH_2CH_3$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 102.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 229.3, 229.2, and 197.6 (s, 3CO), 177.7 and 174.0 (s, 2 CO_2Me), 134.8 (s, C^b), 130.5 (s, C^β), 116.0 (s, C^a), 63.8 and 63.6 (s, $2POCH_2$), 54.4 and 51.8 (s, $2CO_2CH_3$), 34.5 (s, C^c), 15.9 (s, $POCH_2CH_3$).

$[Mo(CO)_3(S_2PPh_2)\{OC(OMe)C(C_3H_5)=CCO_2Me\}]$ (2b). The compound was prepared from **1b** (0.2 g, 0.41 mmol) and DMAD (51 μL, 0.41 mmol) by following the procedure for **2a**. The first orange fraction which was eluted with a mixture of CH_2Cl_2/hexane (5/3) contained the desired product. After evaporation remained 0.037 g (20%) of an orange oil, which converted into a solid after drying for several days at 40 °C. Anal. Calc for $C_{25}H_{21}MoO_7PS_2$: C, 48.08; H, 3.39. Found: C, 47.46; H, 3.94. IR (CH_2Cl_2; cm^{-1}): ν(CO) 2034 s, 1954 s, 1710 w, 1597 w. ^1H NMR ($CDCl_3$): δ 7.90−7.39 (m, 10H, Ph), 5.68 [ddt (17, 10, and 6 Hz), 1 H, H^c], 4.94 [dd (17 and 2 Hz), 1 H, H^b], 4.89 [dd (10 and 2 Hz), 1 H, H^a], 3.68 and 3.25 (s, 2 × 3H, OCH_3], 3.00 [d (6 Hz), 2H, H^d]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 97.3. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 228.9 (s, 2 CO), 197.4 (s, CO), 176.8 and 173.2 (s, 2 $COOMe$), 138.8−127.2 (m, C_6H_5), 134.0 (s, C^b), 129.1 (s, C^β), 114.9 (s, C^a), 52.8 and 50.7 (s, 2 x $COOCH_3$), 33.5 (s, C^c).

$[Mo(CO)_2(PEt_3)\{S_2P(OEt)_2\}\{OC(OMe)C(C_3H_5)=CCO_2Me\}]$ (3a). To a solution of **1a** (0.200 g, 0.48 mmol) in CH_2Cl_2 (10 mL) was added DMAD (59 μL, 0.48 mmol). The reaction mixture was stirred for 15 min. Addition of PEt_3 (71 μL, 0.48 mmol) changed the color of the solution immediately to red. Stirring for another 15 min was followed by evaporation of the solvent. The crude product was redissolved in CH_2Cl_2 and chromatographed over silica. The second orange-red fraction contained the desired product **3a**. The solvent was removed in vacuo affording a red air-stable powder. Yield: 0.216 g (45%). Anal. Calc for $C_{21}H_{36}MoO_8P_2S_2$: C, 39.50; H, 5.69. Found: C, 39.34; H, 5.41. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1935 s, 1851 s, 1704 w, 1589 w. ^1H NMR ($CDCl_3$): δ 5.74 [ddt (17, 10, and 6 Hz), 1H, H^c], 5.02 [ddt (17, 2, and 1 Hz, 1H, H^b], 4.91 [ddt (10, 2, and 1 Hz), 1H, H^a], 4.29 (m, 2H, $POCH_2$), 4.01 (m, 2H, $POCH_2$), 3.89 and 3.76 (s, 3H, OCH_3), 3.01 [ddd (6, 1, and 1 Hz), 2H, H^d], 1.87 [m, 6 H, PCH_2], 1.39 [t (7 Hz), 3H, $POCH_2CH_3$], 1.33 [t (7 Hz), 3H, $POCH_2CH_3$], 0.97 [m, 9H, PCH_2CH_3]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 102.9 [d (39 Hz), $S_2P(OEt)_2$], 40.4 [d (39 Hz), PEt_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 253.0 (s, C^α), 217.2 [d (4 Hz), CO], 217.0 [d (7 Hz), CO], 178.3 and 175.6 (s, 2 × CO_2Me), 136.0 (s, C^b), 127.1 (s, C^β), 115.2 (s, C^a), 63.7 [d (5 Hz), $POCH_2$], 53.6 and 51.2 (s, 2 × CO_2CH_3), 34.2 (s, C^c), 15.9 [d (25 Hz), PCH_2], 14.9 [d (8 Hz), $POCH_2CH_3$], 6.6 (s, PCH_2CH_3).

$[Mo(CO)_2(PEt_3)(S_2PPh_2)\{OC(OMe)C(C_3H_5)=CCO_2Me\}]$ (3b). Compound **3b** was obtained as described above for **3a**, starting from **1b** (0.183 g, 0.38 mmol), DMAD (47 μL, 0.38 mmol), and PEt_3 (56 μL, 0.38 mmol). Similar workup gave **3b** as orange microcrystals. Yield: 0.163 g, 61%. Anal. Calc for $C_{29}H_{36}MoO_6P_2S_2$: C, 49.58; H, 5.16. Found: C, 49.41; H, 4.89. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1934 s, 1849 s, 1701 w, 1590 w. ^1H NMR ($CDCl_3$): δ 7.96−7.43 (m, 10H, Ph), 5.75 [ddt (17, 10, and 6 Hz), 1 H, H^c], 5.03 [dd (17 and 2 Hz), 1 H, H^b], 4.92 [dd (10 and 2 Hz), 1 H, H^a], 3.75 and 3.63 (s, 2 × 3 H, OCH_3], 3.00 [d (6 Hz), 2H, H^d], 1.85 (m, 6 H, PCH_2), 0.95 (m, 9 H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 85.6 [d (20 Hz), S_2PPh_2], 40.5 [d (20 Hz), PEt_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.0 [d (7 Hz), CO], 217.9 [d (7 Hz), CO], 178.3 and 175.7 (s, 2 $COOMe$), 138.9−128.1 (m, C_6H_5), 136.1 (s, C^b), 126.8 (s, C^β), 115.1 (s, C^a), 53.5 and 51.1 (s, 2 × $COOCH_3$), 34.1 (s, C^c), 16.6 [d (25 Hz), PCH_2], 7.6 (s, PCH_2CH_3).

X-ray Diffraction Study of 3b. Crystals were grown by slow diffusion of hexane into a concentrated solution of **3b** in diethyl ether at −20 °C. Relevant crystallographic details are given in Table 1. The experimental temperature was 200 K.[17] Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections in the range $15 < \theta < 19°$. Three reflections were measured every 1 h as orientation and intensity controls. Significant decay was not observed. The structure was solved by Patterson methods, phase expansion, and subsequent Fourier maps with DIRDIF.[18] Full-matrix least-squares refinement was made with SHELX-76.[19] After isotropic refinement, an absorption correction was applied with DIFABS.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned, with a common isotropic temperature factor which was refined.

$[Mo(CO)_2(PEt_3)\{S_2P(OEt)_2\}\{OC(OMe)(C_3H_4\text{-}Me\text{-}1)=CCO_2Me\}]$ (3c). To a suspension of $[Mo(CO)_6]$ (0.1 g, 0.38 mmol) in acetonitrile (20 mL) was added crotyl chloride (50 μL, 0.51 mmol), and the reaction mixture was refluxed for 5 h. Subsequent addition of $NH_4S_2P(OEt)_2$ (0.077 g, 0.38 mmol) was followed by filtration over kieselguhr. The solvent was removed, and the orange residue of **1c** was redissolved in CH_2Cl_2. To the solution were successively added DMAD (47 μL, 0.38 mmol) and, after stirring for 15 min, PEt_3 (56 μL, 0.38 mmol). The mixture was stirred for 15 min, and the solvent was evaporated in vacuo to give a brown red powder. This was purified by chromatography over silicagel (2.5 × 15 cm column). The red band eluted with CH_2Cl_2 as the second fraction was identified as the desired product. Vacuum concentration and addition of hexane gave **3c** as a microcrystalline powder containing a mixture of isomers. Yield: 0.106 g, 43%. Anal. Calc for $C_{22}H_{38}MoO_8P_2S_2$: C, 40.49; H 5.87. Found: C, 40.18; H 5.67. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1935 s, 1851 s, 1699 w, 1585 w. ^1H NMR ($CDCl_3$): isomer A, δ 5.82 [ddd (17, 10, and 7 Hz), 1H, H^c), 4.93 [d (17 Hz, 1H, H^b], 4.85 [d (10 Hz), 1H, H^a], 4.20 and 3.94 (m, 4H, 2 × $POCH_2$), 3.82 and 3.66 (s, 2 × 3H, OCH_3), 3.23 [qd (7 and 7 Hz),1H, H^d], 1.80 [m, 6 H, PCH_2], 1.31−1.26 [m, 6H, $POCH_2CH_3$], 1.12 [d (7 Hz), CCH_3], 0.89 [m, 9H, PCH_2CH_3]; isomer B, δ 5.32 [m, 2H, $H^b + H^c$], 4.20 and 3.94 [m, 4 H, 2 × $POCH_2$], 3.82 and 3.68 (s, 2 × 3H, OCH_3), 2.85 [d (5 Hz), 2H, H^d], 1.80 [m, 6H, PCH_2], 1.51 [d (5 Hz), CCH_3) 1.31−1.26 [m, 6H, $POCH_2CH_3$], 0.89 [m, PCH_2CH_3]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 103.4 [d (39 Hz), $S_2P(OEt)_2$ (isomer A + B)], 40.7 [d (39 Hz), PEt_3 (isomer A)], 40.6 [d (39 Hz), PEt_3 (isomer B)]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): isomer A, δ 251.5 (s, C^α), 215.6 [d (6 Hz), CO], 215.4 [d (6 Hz), CO], 177.3 and 174.6 (s, 2 × CO_2Me), 140.0 (s, C^b), 130.9 (s, C^β), 112.5 (s, C^a), 62.7 [d (5 Hz), $POCH_2$], 61.9 [d (5 Hz), $POCH_2$], 52.4 and 49.9 (s, 2 × CO_2CH_3), 38.7 (s, C^c), 15.9 [d (25 Hz), PCH_2], 14.9 [d (6 Hz), $POCH_2CH_3$), 14.3 [s, C^bCH_3], 6.6 (s, PCH_2CH_3).

$[Mo(CO)_2(PEt_3)(S_2PPh_2)\{OC(OMe)(C_3H_4\text{-}Me\text{-}1)=CCO_2Me\}]$ (3d). Compound **3d** was obtained as described above for **3c**, from $[Mo(CO)_6]$ (0.2 g, 0.76 mmol), crotyl chloride (100 μL, 1.02 mmol), $Na[S_2PPh_2]$ (0.206 g, 0.76 mmol), DMAD (94 μL, 0.76 mmol), and PEt_3 (112 μL, 0.76 mmol). Similar workup gave **3d** as red microcrystals. Yield: 0.22 g, 41%. Anal. Calc for $C_{30}H_{38}MoO_6P_2S_2$: C, 50.28; H, 5.34. Found: C, 50.05; H, 5.19. IR (CH_2Cl_2; cm^{-1}) ν(CO) 1934 s, 1851 s, 1698 w, 1586 w. ^1H NMR ($CDCl_3$): isomer A, δ 7.98−7.44 (m, 10H, Ph), 5.92 [ddt (17, 10, and 6 Hz), 1 H, H^c], 5.01 [d (17 Hz), 1 H, H^b], 4.93 [d (10 Hz), 1 H, H^a], 3.75 and 3.62 (s, 2 × 3 H, OCH_3], 3.32 [m, 2H, H^d], 1.85 (m, 6 H, PCH_2), 1.21 [d (7 Hz),

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3 H, CCH_3], 0.94 (m, 9 H, PCH$_2$CH_3); isomer B, δ 7.98−7.44 (m, 10H, Ph), 5.40 [m, 2H, H^a, H^c],], 3.73 and 3.61 (s, 2 × 3 H, OCH_3], 2.92 [d (5 Hz), 2H, H^d], 1.85 (m, 6 H, PCH_2), 1.63 [d (8 Hz), 3H, CCH_3], 0.94 (m, 9 H, PCH$_2$CH_3). ^{31}P{^{1}H} NMR (CDCl$_3$): isomer A, δ 85.4 [d (20 Hz), S$_2$*P*Ph$_2$], 40.7 [d (20 Hz), *P*Et$_3$]; isomer B, δ 84.9 [d (20 Hz), S$_2$*P*Ph$_2$], 40.5 [d (20 Hz), *P*Et$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 255 (broad, C^α), 220.4 (m, 2 × *C*O, isomer A), 219.9 (m, 2 × *C*O, isomer B), 179.1 (s, *C*OOMe, isomer B), 178.9 (s, *C*OOMe, isomer A), and 175.4 (s, 2 × *C*OOMe, isomers A + B), 141.7 (s, C^b), 141.1−128.1 (m, C_6H_5), 125.9 (s, C^β), 113.8 (s, C^a), 53.2 and 51.0 (s, 2 × COOCH$_3$, isomer B), 53.0 and 50.8 [s, 2 × COOCH$_3$, isomer A], 40.2 (s, C^c, isomer A), 33.6 (s, C^c, isomer B), 17.0 [d (25 Hz), PCH$_2$, isomer B], 16.9 [d (25 Hz), PCH$_2$, isomer A], 7.7 [s, PCH$_2$$CH_3$].

Dimethyl 2-Allylfumarate (4). Complex **1b** (1 g, 2.05 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL), and DMAD (255 μL, 2.05 mmol) was added. The mixture was stirred until the IR spectra showed the formation of the tricarbonyl complex **2b** (about 15 min). The solvent was then evaporated in vacuo, and the residue was redissolved in CH$_2$Cl$_2$. The solution was left open in air for several days. A ^{1}H NMR of the crude product showed that the cleavage had taken place quantitatively. The purple solution was chromatographed over silica with CH$_2$Cl$_2$ as eluent. The solvent was removed by distillation. The remaining liquid was found to be nearly pure dimethyl 2-allylfumarate. Yield: 0.203 g, 81% (calculated from the maximum yield (66%) of **2b**). Anal. Calc for C$_9$H$_{12}$O$_4$: C, 39.50; H, 5.69. Found: C, 39.34; H, 5.41. MS (EI): *m*/*z* 184.32 (M$^+$). ^{1}H NMR (CDCl$_3$): δ 6.81 (s, 1H, C═CH^e), 5.83 [ddt (17, 10, and 6 Hz), 1H, H^c], 5.10 [ddt (17, 2 and 1 Hz), 1 H, H^b], 5.03 [ddt (10, 2 and 1 Hz), 1H, H^a], 3.80 (s, 3H, COOCH_3), 3.77 (s, 3H, COOCH_3), 3.58 [d (17 Hz), 2H, H^d]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 167.6 and 166.5 (s, 2 × CO$_2$Me), 145.9 (s, C^β), 134.7 (s, C^b), 127.5 (s, C^α), 117.3 (s, C^a), 53.2 and 52.4 (s, 2 × CO$_2$$CH_3$), 32.3 (s, C^c).

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Supporting Information Available: Complete tables of bond length and angles, anisotropic thermal parameters, atom parameters for all atoms, and weighted least-squares planes for **3b** (9 pages). Ordering information is given on any current masthead page.

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