# Direct Episulfidation of Alkenes and Allenes with Elemental Sulfur and Thiiranes as Sulfur Sources, Catalyzed by Molybdenum Oxo Complexes

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***Abstract:*** The molybdenum oxo complexes **1a** and **1b** catalyze efficiently the sulfur transfer to a series of alkenes **4** and allenes **6**, for which elemental sulfur, phenylthiirane, or methylthiirane have been employed as sulfur sources to afford the corresponding episulfides **5** and **7**. The most effective catalytic episulfidation system to date is the combination of the dithiophosphate-ligated oxo complex **1b** and phenylthiirane (**I**$\beta$). This metathesis process is efficient enough to convert usually reluctant alkenes (cyclopentene, cycloheptene, *Z*-cyclooctene, *Z*-cyclononene, *E*-cyclodecene, norbornene, and even bicyclopropylidene) to their episulfides in good yields under mild conditions. The direct catalytic sulfuration of allenes (cyclonona-1,2-diene, cyclonona-1,2,5-triene, cyclodeca-1,2-diene, and 2,4-dimethylpenta-2,3-diene) to their labile methylene-thiiranes is unprecedented.

## Introduction

The traditional method to prepare thiiranes is from the corresponding epoxides, by attack with an appropriate sulfur nucleophile and subsequent cyclization, a sequence that is still commonly employed, giving effective access to the episulfides of unstrained acyclic and cyclic alkenes, for example, styrene and cyclohexene.[1] In contrast, the conversion of an alkene to a thiirane[2] by direct sulfur-atom transfer is as yet a scarce transformation and remains a synthetic challenge of timely interest. Like the epoxidation,[3] which for synthetic purposes is one of the best investigated oxidations in organic chemistry, a stereoselective one-step episulfidation of alkenes to thiiranes without oligomerization and polymerization[4] would constitute an attractive but demanding aim. In this context, several electrophilic sulfur-transfer agents have been developed in the

past[5] for the direct episulfidation of alkenes, most recently also by our group.[6] Specifically, Capozzi[5a] used trimethylsilylsulfenyl bromide to episulfidate 1,2-disubstituted *E*-alkenes and Bruice[5b] transferred sulfur from carbon disulfide to 2,3-dimethyl-2-butene. As direct sulfur donors, our group used a thiophene endoperoxide,[6a,b] thermally or photochemically generated oxathiiranes from sulfines[6c] or α-triketones;[6d] a cyclic sulfenate;[6e,f] and 5-aryloxy-1,2,3,4-thiatriazoles[6g] to effect the episulfidation of *E*-cyclodecene, *E*- and *Z*-cyclooctenes, norbornene, cyclo-heptene, and cyclopentene. One of the few uses of elemental sulfur as sulfur source for direct episulfidation is the formation of bis(adamantylidene)episulfide[7a] or 9,9′-bibenzonorborne-nylidene episulfides[7b] by heating in DMF without a catalyst. In all of the above-mentioned episulfidations, the sulfur source is also the sulfur-transferring agent and used necessarily stoichio-metrically.

To date little is known about the catalytic episulfidation of alkenes with metal complexes. Simpkins and co-workers[8] developed the first thiirane metathesis, in which methylthiirane as sulfur source and rhodium acetate as catalyst were used to convert norbornene and norbornadiene to their episulfides. However, it was noted that this metal-catalyzed sulfur transfer was ineffective with *Z*-cyclooctene and dicyclopentadiene. An

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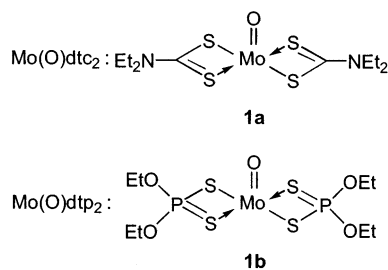(8) (a) Kendall, J. D.; Simpkins, N. S. *Synlett* **1998**, 391−392.

**Figure 1.** Dithiocarbamate molybdenum complex **1a** and dithiophosphate molybdenum complex **Iβ**.

earlier report by Khan and Siddiqui[9] claimed the ruthenium-catalyzed direct episulfidation of cyclohexene with $S_8$ as the sulfur source. Unquestionably, this would constitute a breakthrough, since cyclohexene is a particularly unreactive sulfur-atom acceptor.[6] Our attempts to reproduce the reported procedure failed, since not even traces of the cyclohexene episulfide were detected by GC analysis, when a stoichiometric amount of the ruthenium complex was employed. In view of the need for an effective metal-catalyzed episulfidation method with elemental sulfur as sulfur source, we reported recently[10] the episulfidation mediated by oxobis(diethyldithiocarbamato-κS,κS′)oxomolybdenum, but this sulfur-transfer method is restricted to the strained *E*-cyclooctene and *E*-cyclononene.

In this study, we demonstrate that metal-catalyzed sulfur transfer, still a relatively unexplored field of sulfur chemistry, offers promising opportunities for the direct sulfuration of organic substrates. Indeed, we divulge the first efficient catalyst system, namely $MoO[S_2P(OEt)_2]_2$/phenylthiirane, for the episulfidation of a variety of alkenes. Moreover, with this novel catalyst system, also allenes are effectively episulfidated to the respective methylenethiiranes, which are valuable intermediates in organosulfur chemistry.[11] Such a catalytic process for the direct synthesis of allene episulfides is to date unprecedented.

## Results

**Catalytic Episulfidation of Alkenes.** The good results obtained in the catalytic episulfidation of the *E*-cycloalkenes with the dithiocarbamate molybdenum oxo complex **1a**[12] as catalyst (Figure 1) and elemental sulfur as donor[10] encouraged us to undertake an intensive catalyst screening for more active molybdenum oxo complexes. For this purpose, *Z*-cyclooctene was used as model substrate, $S_8$ was used as sulfur-atom donor, and a variety of readily accessible known complexes of molybdenum in its oxidation states +4, +5, and +6 with acetylacetonate, oxinate, dithiocarbamate, and dithiophosphate were used as ligands (see Supporting Information). This search revealed that also the dithiophosphate molybdenum oxo complex **1b**[12] displays catalytic activity for sulfur transfer, but only slightly better than the dithiocarbamate complex **1a** (see Table S1 in Supporting Information).

Presumably, a more effective sulfur donor than elemental sulfur was required for catalytic sulfur transfer. Since it is known

**Scheme 1.** Desulfuration of Thiiranes **Iα** and **Iβ** by the Complex **1b**[a]
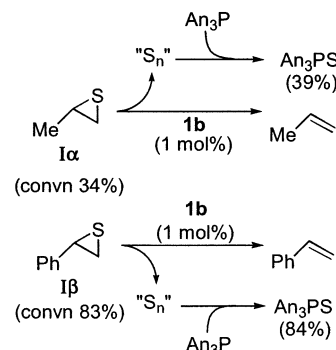


[a] "An" stands for $p$-MeOC_6H_4.

that episulfides are desulfurized by molybdenum oxo complexes,[13] methylthiirane (**Iα**) and phenylthiirane (**Iβ**) were employed as potential sulfur sources. Indeed, when the dithiophosphate complex **1b** was treated with the thiirane **Iα** or **Iβ** in the absence of an alkene substrate as sulfur acceptor, these were desulfurized with formation of elemental sulfur. The amount of extruded sulfur was quantified by addition of an excess (1.15 equiv) of trianisylphosphine (Scheme 1) to a spent solution of methylthiirane (**Iα**) or phenylthiirane (**Iβ**) and the oxo complex **1b** (0.01 equiv). ^{1}H NMR analysis of trianisylphosphine sulfide revealed that the thiirane **Iβ** was more efficiently desulfurized than **Iα**. A time profile of the sulfur extrusion showed that the phenylthiirane is more reactive than methylthiirane (see Supporting Information) by a factor of 12.8. In all subsequent sulfur-transfer reactions with the oxo complex **1b**, the phenylthiirane (**Iβ**) was used as a sulfur donor, and this constitutes to date the most effective catalytic system for the episulfidation of alkenes. For example, the thiiranes of *Z*-cyclooctene (*Z*-**4a**), *E*-cyclononene (*E*-**4b**), *Z*-cyclononene (*Z*-**4b**), *E*-cyclodecene (*E*-**4c**), cyclopentene (**4f**), cycloheptene (**4g**), and even of bicyclopropylidene (**4h**)[14,15] were formed in good yields (Table 1). To date, none of the previous direct stoichiometric episulfidation methods have been successful with bicyclopropylidene (**4h**) as the substrate.[6] For *Z*-cyclononene (*Z*-**4b**), besides the expected *cis*-cyclononene episulfide (*cis*-**5b**), also a significant quantity (12%) of the *trans*-cyclononene episulfide (*trans*-**5b**) was obtained. A control experiment showed that when *Z*-cyclononene (*Z*-**4b**) was added to the reaction mixture, which had been prepared by treating a catalytic amount (1 mol %) of complex **1b** and a stoichiometric quantity of phenylthiirane until complete consumption of the latter and heated to 60 °C for 120 min, no *E*-cyclononene (*E*-**4b**) was formed. Thus, the *trans*-episulfide *trans*-**5b** did not arise through sulfur transfer to the *E*-cyclononene (*E*-**4b**) produced from thermal isomerization of (*Z*)-cyclononene by extruded polymeric sulfur; however, when *Z*-stilbene was heated in the mixture of a catalytic amount (1 mol %) of complex **1b** and a stoichiometric quantity of phenylthiirane at 60 °C for 2 h, about 18% of *E*-stilbene was formed. The isomerized stilbene was not detected when the

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**Table 1.** Episulfidation of Cycloalkenes, Catalyzed by the Molybdenum Oxo Complex 1b with Styrene Sulfide (I$\beta$) as Sulfur Source



| entry | olefin 4 | equiv I$\beta$ | convn (%)[a] | | rel. yield of 5 (%)[a,b] |
|---|---|---|---|---|---|
| | | | 4 | I$\beta$ | |
| 1 | (Z)-4a | 1.5 | 74 | 82 | 85 |
| 2 | (E)-4b | 1.0 | >95 | >95 | >95 |
| 3 | (Z)-4b | 1.6 | 71 | >95 | >95[c,d] |
| 4 | (E)-4c | 1.3 | 83 | >95 | 81 |
| 5 | 4d | 1.6 | 12 | 24 | 100 |
| 6 | 4f | 1.0 | 48 | 77 | 90 |
| 7 | 4g | 1.0 | 50 | 79 | 90 |
| 8 | 4h | 1.0 | 66 | 85 | 88[c] |

*a* Determined by ^{1}H NMR analysis of the crude products with dimethyl isophthalate as internal standard (error ± 5% of the stated values); the yield is based on converted olefin by normalizing it to 100%. *b* Material balance > 80%. *b* $C_6D_6$, 60 °C, 2 h. *c* 12% of *trans*-5b were formed.

*Z*-stilbene was heated in a spent reaction mixture (1 mol %) of the complex **1b** and phenylthiirane. These experiments indicate that *Z*-cyclononene is isomerized to its *E* isomer during the sulfur-transfer process. The reason the *E*-stilbene accumulated during the isomerization but the *E*-cyclononene did not is the fact that *E*-stilbene is inert toward episulfidation, whereas *E*-cyclononene reacts faster with the sulfur-transferring agent than its precursor *Z*-cyclononene. This was confirmed by means of a competition experiment, in which a mixture of both olefins was allowed to react with the oxo complex **1b** (1 mol %) and phenylthiirane at 20−25 °C (cf. Supporting Information).

Norbornene (**4d**), although known as a relatively good sulfur-atom acceptor,[6g] exhibited only a low reactivity in the present sulfur-transfer reaction. Possibly, the steric interference between the dithiophosphate ligands of the complex **1b** and the methylene bridge in norbornene is responsible for the low reactivity of the latter. Also tetramethylethylene and cyclohexene were resistant toward episulfidation under the catalytic conditions of Table 1 (data not shown), since only traces of their thiiranes were detected. The low reactivity of cyclohexene toward episulfidation is analogous to its reduced reactivity toward epoxidation of this cycloalkene. This finding has been attributed to the steric hindrance caused by the quite rigid transoid conformation of cyclohexene.[3a]

The results of Table 1 suggest that the dithiophosphate complex **1b** is more reactive as catalyst than the dithiocarbamate complex **1a**. To confirm this, a comparative experiment was conducted with *E*-cyclononene (*E*-**4b**) as substrate and complexes **1a** or **1b** as catalysts under identical conditions. Whereas catalyst **1b** converted the olefin *E*-**4b** quantitatively to its episulfide *trans*-**5b** without isomerization, for catalyst **1a** the conversion was only 20%, as shown in Table 2. The superior performance of the new catalytic sulfur-transfer system **1b**/I$\beta$ is therewith demonstrated.

In regard to the efficacy of the catalytic episulfidation with thiiranes as sulfur source, it was of relevance to test for

**Table 2.** Episulfidation of *E*-Cyclononene (*E*-4b) with Styrene Episulfide (I$\beta$), Catalyzed by the Molybdenum Oxo Complexes 1a,b



| entry | complex | convn (%)[a] | | rel yield of *trans*-5b (%)[a,b] |
|---|---|---|---|---|
| | | (E)-4b | I$\beta$ | |
| 1 | 1a | 22 | 20 | >95 |
| 2 | 1b | >95 | 86 | >95 |

*a* Determined by ^{1}H NMR analysis of the crude products with dimethyl isophthalate as internal standard (error ± 5% of the stated values); the yield is based on converted olefin *E*-**4b**. *b* Material balance > 80%.

competitive desulfuration of the thiirane versus sulfur transfer. Such competitive desulfuration of the sulfur source I$\beta$ should be particularly prone to occur in the episulfidation of sluggishly reactive substrates. In this context, a control experiment was conducted for the catalytic system **1b**/I$\beta$ with *Z*-**4a** as substrate. Variation of the initial amount of the sulfur source phenylthiirane (I$\beta$) at a constant quantity of substrate *Z*-**4a** disclosed that the yield of *cis*-cyclooctene episulfide (cis-**5a**) was maximal (85%) when only one-seventh of the thiirane I$\beta$ was used (see Table S2, Supporting Information). Consequently, at a higher alkene *Z*-**4a**/thiirane I$\beta$ ratio, episulfidation of the substrate *Z*-**4a** competes more effectively with sulfur extrusion from the sulfur-activated molybdenum intermediate, since the episulfidation process depends on the alkene concentration. Evidently, the *Z*-**4a**/thiirane I$\beta$ ratio is decisive for the efficiency of episulfidation.

**Catalytic Episulfidation of Allenes.** In view of the successful catalytic episulfidation of the alkenes in Table 1, it was of synthetic interest to examine allenes as substrates. So far, the presently available stoichiometric sulfur-transfer agents had failed to produce directly allene episulfides.[16] The results in Table 3 demonstrate that such sulfur transfer may be achieved with the catalytic molybdenum-based systems developed herein. In fact, for the first time allene episulfides have been synthesized by direct sulfur transfer to allenes under *catalytic* conditions.

For the dithiocarbamate molybdenum catalyst **1a**, three different sulfur sources, namely, the sodium tetrasulfide ($Na_2S_4$), elemental sulfur ($S_8$), and methylthiirane (I$\alpha$), were examined under similar conditions with cyclononadiene (**6a**) as the substrate. In contrast to the catalytic sulfur transfer to *Z*-cycloalkenes (Table 1), the most reactive allene **6a** (Table 3) was also episulfidated by $Na_2S_4$ (entry 1) and even $S_8$, but an elevated temperature (60 °C) was necessary (entries 2 and 3) for the latter. Of the employed sulfur sources, the best performance is displayed by methylthiirane (entry 4), which afforded the episulfide **7a** in high yield (95%). The latter combination **1a**/I$\alpha$ also worked well for the episulfidation of the allenes **6b,c** (entries 5 and 6). Clearly, the acyclic tetramethylallene (**6b**) is more receptive to accept a sulfur atom than the corresponding tetramethylethylene, which is reluctant toward direct episulfidation with currently known sulfur-transfer agents.[6,10]

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**Table 3.** Episulfidation of Allenes **6** with Various Sulfur Donors, Catalyzed by the Molybdenum Oxo Complexes **1a,b**
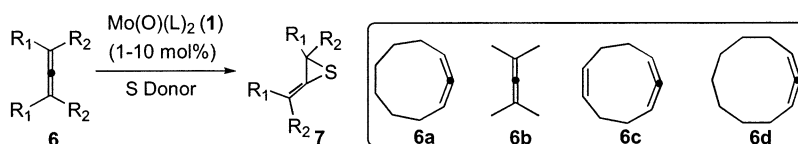


| entry | allene 6 | catalytic system | | | | solvent | temp (°C) | time (h) | convn of 6 (%)[b] | rel yield of 7 (%)[a−c] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | complex | mol % | S donor | equiv | | | | | |
| 1 | 6a | 1a | 10 | Na$_2$S$_4$ | 1.5 | CD$_3$COCD$_3$ | 20 | 96 | 36 | 56 |
| 2 | 6a | 1a | 10 | S$_8$ | 0.25 | CD$_3$COCD$_3$ | 20 | 96 | <5 | <5 |
| 3 | 6a | 1a | 10 | S$_8$ | 0.25 | CD$_3$COCD$_3$ | 60 | 12 | >95 | 36 |
| 4 | 6a | 1a | 10 | Iα | 2.0 | CDCl$_3$ | 65 | 4 | >95 | 83 |
| 5 | 6b | 1a | 10 | Iα | 2.0 | CDCl$_3$ | 65 | 4 | >95 | 95 |
| 6 | 6c | 1a | 10 | Iα | 2.0 | CDCl$_3$ | 65 | 4 | 86 | 67 |
| 7 | 6d | 1a | 10 | Iα | 2.0 | CDCl$_3$ | 65 | 4 | <5 | <5 |
| 8 | 6a | 1b | 1 | Iβ | 1.0 | C$_6$D$_6$ | 80 | 0.5 | 74 | 70 |
| 9 | 6b | 1b | 1 | Iβ | 1.0 | C$_6$D$_6$ | 80 | 0.5 | 87 | >95 |
| 10 | 6c | 1b | 1 | Iβ | 1.0 | C$_6$D$_6$ | 80 | 0.5 | >95 | 65 |
| 11 | 6d | 1b | 1 | Iβ | 1.0 | C$_6$D$_6$ | 80 | 0.5 | 32 | 53 |

[a] NMR-scale experiments. [b] Determined by $^1$H NMR analysis of the crude product mixture with dimethyl isophthalate as internal standard (error ± 5% of the stated values); the yield is based on converted allene **6**. [c] Material balance > 80%.

This unusual reactivity of tetramethylallene compared to tetramethylethylene has been already observed in methoxymercuration.[17]

The allene **6d** (entry 7) gave the thiirane **7d** only in trace amounts with the **1a**/**Iα** catalyst system. When, however, the combination of the phenylthiirane (**Iβ**) sulfur donor and the dithiophosphate molybdenum catalyst **1b** was employed, the cyclodecadiene gave the episulfide **7d** in a moderate yield (entry 11). Thus, also for the episulfidation of allenes, the superiority of the combination **1b**/**Iβ** versus **1a**/**Iα** as catalytic sulfur-transfer agent should be evident. The allenes **6a**−**c** were efficiently converted to their episulfides in good yields, even at $^1/_{10}$ of the amount of the dithiophosphate molybdenum catalyst **1b**, a stoichiometric quantity of the sulfur source **Iβ**, and a much shorter reaction time, but at elevated temperature (entries 8−10).

All allene episulfides have been isolated in pure form and fully characterized. The monomeric structure of the cyclononadiene episulfide (**7a**) was established by its spectral data and an ebullioscopic molecular weight determination. Moreover, desulfuration of the episulfide **7a** with methyloxothiorhenium regenerated the allene **6a** (see Supporting Information). The reversibility of the sulfur transfer was demonstrated by treatment of a mixture of allene episulfide **7a** and allene **6b** with 0.10 equiv of the dithiocarbamate complex **1a** at 65 °C for 5 h in deuteriochloroform (see Supporting Information). About 36% of the allene episulfide **7a** was desulfurized to the allene **6a** and about 30% of sulfur transferred to the allene **6b** in the form of its episulfide.

**NMR−Spectral Studies for the Detection of Intermediary Molybdenum Complexes.** $^{31}$P NMR spectra of CD$_2$Cl$_2$ solutions of the dithiophosphate molybdenum oxo complex **1b** and of mixtures with methylthiirane (**Iα**), phenylthiirane (**Iβ**), and the unsubstituted thietane were measured at low temperature (−50 °C) (see Figures S2−S5, Supporting Information). The $^{31}$P NMR spectrum of the dithiophosphate complex **1b** alone exhibits one single absorption at δ 138 ppm, whereas mixtures with the sulfur sources thiirane **Iα** or **Iβ** show an additional
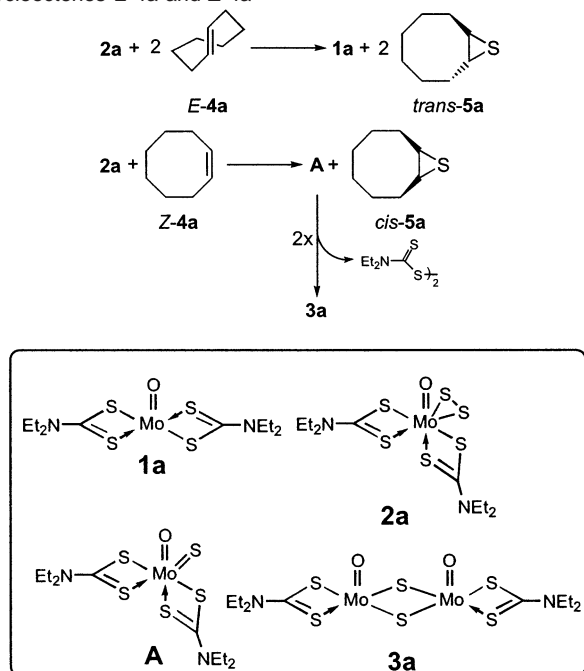
major signal at δ 108 ppm (minor signals were also observed, but they could not be assigned to definitive molybdenum intermediates). With the unsubstituted thietane, which does not serve as sulfur source, a new signal was observed at δ 93 ppm. The $^{31}$P NMR absorption of the thietane adduct for complex **1b** has served as reference spectral data for the presumed thiirane adduct.

The fact that for both thiiranes **Iα** and **Iβ** the same new signal was observed indicates a common intermediate. The single phosphorus resonance of the **1b**/**Iα**, **Iβ** mixtures at δ 108 ppm indicates that both phosphorus atoms are magnetically equivalent, which suggests that the new molybdenum intermediate bears a thio or a thiirane ligand trans to the oxo group in the complex **1b**. A molybdenum oxo−disulfur complex **2b** similar to **2a**[18] may be ruled out, since it should have two phosphorus absorptions in the $^{31}$P NMR spectrum. In this context, it is relevant to mention that the dithiocarbamate carbon atoms in the oxo-disulfur complex **2a** displays two absorptions in the $^{13}$C NMR spectrum (see Supporting Information). A simple adduct between the thiiranes **Iα** and **Iβ** and the oxo complex **1b** may also be ruled out, since the signals for the phenylthiirane versus the methylthiirane adducts should be different. Moreover, the fact that the unsubstituted thietane exhibits a signal significantly different from that of the two thiiranes **Iα** and **Iβ** with the complex **1b** implies that distinct molybdenum species are involved. Thietanes are not readily desulfurized and thus do not serve as effective sulfur donors, as manifested by the finding that high-valent metal halides desulfurize methylthiirane; in contrast, with thietane they form adducts.[19] Consequently, we propose that the new phosphorus resonance in the complex **1b**/thietane mixture corresponds to adduct formation, whereas with the thiiranes **Iα** and **Iβ** a molybdenum intermediate structurally similar to the oxo−thio complex **A** operates as the active sulfur-transfer catalyst.
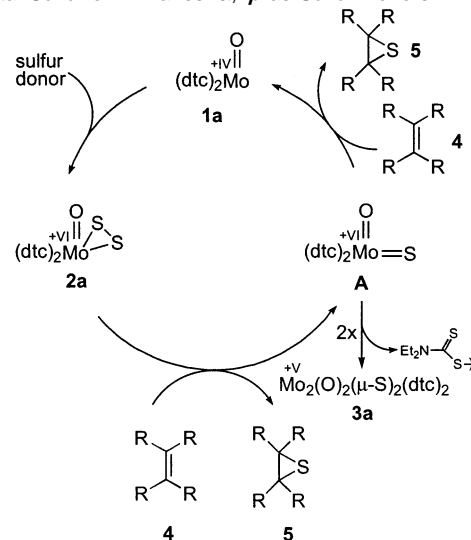
**Stoichiometric Episulfidation of the Cyclooctenes.** In the catalytic mode, the Z-cyclooctene (Z-**4a**) was unreactive toward the sulfur-transfer system **1a**/S$_8$, whereas the E-**4a** diastereomer

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**Scheme 2.** Stoichiometric Episulfidation of the Diastereomeric Cyclooctenes E-4a and Z-4a



**Scheme 3.** Catalytic Cycle for the Generation of the Molybdenum Oxo-Disulfur Complex 2a and the Sulfuration of the Alkenes 4 by Elemental Sulfur or Thiiranes Iα, Iβ as Sulfur Donors



was quantitatively converted to its *trans*-**5a** episulfide.[10] To understand this difference in reactivity mechanistically, the episulfidation of this pair of diastereomers was carried out under stoichiometric conditions. It was suspected that with reluctant substrates such as the *Z*-cyclooctene diastereomer the molybdenum oxo−disulfur complex **2a** was consumed in competition reactions rather than for sulfur transfer. Fortunately, the disulfur complex **2a** is sufficiently persistent to be isolated, which enables its direct use for stoichiometric episulfidation. The comparative results for the diastereomeric pair of cyclooctenes **4a** are displayed in Scheme 2. As in the catalytic mode with the **1a**/S$_8$ system, also for the stoichiometric process with the complex **2a**,[18] the *E* Isomer was quantitatively converted to its *trans*-**5a** episulfide. In contrast, when the diastereomer *Z*-**4a** was treated with the disulfur complex **2a**, only one sulfur atom was abstracted from the disulfur bridge to afford the *cis*-**5a** episulfide in 20% yield (see Table S4, Supporting Information); however, the dimeric molybdenum complex **3a** was isolated as main product (80% yield), characterized by its IR, UV, and NMR spectra. To exclude the possibility that the in-situ-generated oxo complex **1a** may have reacted with the *cis*-**5a** episulfide to afford the dimer complex **3a**, a control experiment (see Supporting Information) was conducted, in which the authentic oxo complex **1a** was treated with the episulfide *cis*-**5a** as sulfur donor. Instead of the dimer complex **3a**, the disulfur complex **2a** was formed quantitatively, as confirmed by the characteristic IR vibration for the sulfur−sulfur bond in the disulfur functionality of **2a** at $\tilde{\nu}$ 550 cm$^{-1}$, which is not observed for the dimer complex **3a**. Consequently, it is unlikely that the oxo complex **1a** is generated in the *Z*-cyclooctene reaction; instead, the intermediary molybdenum oxo−thio complex **A** mainly dimerizes with elimination of tetraethylthiuram disulfide. Thus, for the **1a**/S$_8$ combination, the catalytic process failed with the relatively unreactive substrate such as the cyclooctene *Z*-**4a**, because the essential molybdenum oxo complex **1a** is not regenerated to sustain catalysis.

## Mechanistic Discussion

On the basis of the results of the stoichiometric episulfidation (Scheme 2), in particular, the fact that the oxo−disulfur complex **2a** functions as effective sulfur-transfer agent and that the oxo−sulfido species **A** presumably intervenes, we propose the catalytic cycle in Scheme 3. This catalysis accounts adequately for the sulfur transfer to the alkenes **4** by elemental sulfur or the thiiranes **Iα**, **Iβ** as sulfur donors and the dithiocarbamate molybdenum oxo complex **1a** as catalyst.[10] A similar cycle operates also for the transformation of the allenes **6** to the methylenethiiranes **7**. Moreover, this catalytic sulfur-transfer process is analogous to the conversion of isonitriles to the corresponding isothiocyanates.[20] First, the molybdenum oxo complex **1a** reacts with the sulfur source (S$_8$ or thiirane **Iα**, **Iβ**) to generate the disulfur complex **2a**, the active sulfur-transferring species in the catalytic episulfidation of the alkenes **4**. A stepwise mechanism for the sulfur abstraction by substrate **1a** from two molecules of thiiranes, with the oxo−thio molybdenum complex **A** as intervening intermediate, has been documented.[13] The disulfur complex **2a** the transfers successively both sulfur atoms of the disulfur functionality to two alkene molecules, provided that the substrate is sufficiently reactive, e.g. the *E*-configured cycloalkenes **4a,b**. During the sulfur transfer, the oxo complex **1a** is regenerated and the catalytic cycle is sustained through the sulfuration of the oxo complex **1a**. Presumably, the oxo−sulfido species **A** intervenes as intermediate, as previously suggested for the disulfur complex **2a** in its reaction with isonitriles[20] or triphenylphosphine.[21] Related molybdenum oxo−sulfido complexes with sterically demanding ligands have been isolated.[22]

**In contrast to the more strained *E* cycloalkenes, the less reactive *Z*-cycloalkenes, e.g. *Z*-cyclooctene (*Z*-4a), only** abstract one sulfur atom from the disulfur functionality in the complex **2a** (Scheme 2), to release the intermediary oxo−sulfido

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**Scheme 4.** Internal Ligand Redox Reaction of Intermediate A
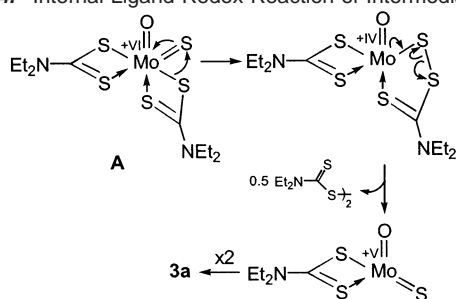


complex **A**. The less reactive Z-cycloalkenes do not manage to abstract the second available sulfur atom and, rather than regenerate the molybdenum oxo complex **1a** to sustain the catalytic cycle for the sulfur transfer in Scheme 3, complex **A** dimerizes irreversibly to the inactive **3a** by elimination of tetraethylthiuram disulfide.

For the formation of the dimer **3a**, analogous to the redox reaction between $S^{2-}$ ligands and its Mo(VI) center proposed for the nitrogenase enzyme[23] (Scheme 4), we speculate that such internal electron transfer takes place in intermediate **A**, in which Mo(VI) is reduced to Mo(IV) and the sulfido ligand is oxidized by insertion of the thio group into the dithiocarbamate ligand. After back-transfer of an electron from the Mo(IV) and homolysis of the sulfur–sulfur bond, with subsequent formation of the tetraethylthiuram disulfide, the resulting Mo(V) fragment dimerizes to complex **3a**.[24] This dimer **3a** is reluctant toward desulfuration and, therefore, with less reactive Z-cycloalkenes only stoichiometric sulfur transfer operates for the disulfur complex **2a** (Scheme 2).

The best metal-catalyzed sulfur-transfer system achieved in the present work consists of the combination phenylthiirane as sulfur donor and the molybdenum oxo complex **1b** as metal catalyst for alkenes (Table 1) and for allenes (Table 3). This new episulfidation catalyst effects sulfur transfer to the less reactive Z-cycloalkenes even more efficiently than when stoichiometric amounts of the molybdenum oxo complex **1a** are utilized. We suggest that the catalytic cycle in Scheme 3, proposed for catalyst **1a**, also operates for **1b**, with the corresponding oxo–disulfur complex as the electrophilic sulfur-transfer agent. The following differences between these two catalyst systems should, however, be noted: Whereas the oxo–disulfur complex **2a** is an isolable substance that may be employed for stoichiometric episulfidation (Table S4, Supporting Information), a similar species **2b** could not be detected by IR and NMR spectral methods; furthermore, a dimeric structure like **3a**, as produced from the oxo–thio complex **A**, was not observed. Therefore, we propose that the dithiophosphate molybdenum complex **1b** is converted to an oxo–thio complex, structurally similar to **A**, which instead of being further sulfurated to complex **2b**, transfers the sulfur atom to the sulfur acceptor to regenerate complex **1b**. Presumably, the oxo–thio intermediate of the complex **1b** is considerably more reactive than the corresponding species derived from catalyst **1a** and, thus, does not accumulate nor engage in competitive reactions. This would reconcile the higher efficiency of catalyst **1b** versus **1a** for sulfur transfer to alkenes.

In closing, we emphasize that the metal-catalyzed direct synthesis of a variety of alkene and allene episulfides has been achieved in the present work, of particular note are the dispirocyclic and exomethylenic thiiranes derived from bicyclopropylidene and tetramethylallene. A catalytic cycle is proposed in which the molybdenum oxo–disulfur complex figures as electrophilic sulfur-transferring agent.

**Supporting Information Available:** Experimental procedures and full characterization of the new episulfides **5h**, *cis*-**5b**, and **7a**–**d**, and the low-temperature $^{31}$P NMR and $^{13}$C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) In principle, also a dimerization–elimination mechanism may apply; however, it would be expected that the dimerization of the intermediate **A** would first yield a corresponding *μ*-(S₂) disulfido complex, which should not fragment into the dimer **3a**. The dimerization of an oxo–thio complex has been reported, see: Smith, P. D.; Slizys, D. A.; George, G. N.; Young, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 2946–2947.