



Mo Pentachloride in Catalysis

One-Pot Intermolecular C–S Self-Coupling of Dimethyl Sulfoxide Promoted by Molybdenum Pentachloride

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Abstract: The reactions between $MoCl_5$ and 1-2 equiv. of a selection of sulfoxides at room temperature in dichloromethane as solvent were studied. The 1:1 molar reaction between $MoCl_5$ and dimethyl sulfoxide (DMSO) afforded the C–S coupling product $[Me_2SCH_2SMe][MoOCl_4]$ (1), which was isolated in 46 % yield and characterized by analytical and spectroscopic methods and by X-ray diffraction. $MoOCl_3$, SMe_2 and HCl were identified as side products. The reactions between $MoCl_5$ and tetrahy-

Introduction

Molybdenum pentachloride^[1] is a cheap and environmentally acceptable chemical^[2] that has been employed as a catalytic precursor for a large variety of organic reactions.^[3] In particular, MoCl₅ is a powerful reagent for oxidative transformations, especially the dehydrogenative coupling of arenes.[3a,3b,3d] The interesting reactivity exhibited by MoCl₅ in catalytic situations has triggered the exploration of the related coordination chemistry, with consequent advances in knowledge.^[4] A variety of reaction pathways may be viable when MoCl₅ is allowed to come into contact with potential ligands, thus often resulting in low selectivity. In particular, the two main pathways observed in the reactions between MoCl₅ and oxygen donors are: (a) Cl/O interchange between the metal centre and the organic substrate, affording oxidomolybdenum complexes,^[4c-g,5,6] and (b) Mo^V to Mo^{IV} reduction with formation of MoCl₄ adducts.^[4c-4e,5a,5b] As a consequence, simple derivatives with formula MoCl₅L are rare,^[4b,7] and the only cases of crystallographic characterization relate to the complexes with phosphorus oxychloride^[7] and 2,5dihydrothiophene 1,1-dioxide.[8]

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drothiophene 1-oxide, nBu_2SO , MePhSO or $(PhCH_2)_2SO$ yielded the corresponding sulfides and, in the cases of $(PhCH_2)_2SO$ and MePhSO, also C–S activation compounds. According to DFT calculations, the unusual formation of **1** is the consequence of thermodynamically feasible Cl/O interchange between MoCl₅ and DMSO, this being a prerequisite for successive C–H bond activation.

We have recently described the reactions between MoCl₅ and sulfones RR'SO₂,^[8] showing that both Mo^V and Mo^{IV} coordination complexes may be obtained, depending on the R/R' substituents. In contrast, different structural motifs can arise from the reactions between MoCl₅ and molecules containing the $-SO_3$ functionality, through oxygen abstraction by the metal centre.^[9]

With regard to completing this picture, it can be observed that the data available in the literature relating to the chemistry of MoCl₅ with sulfoxides RR'SO are still rather sparse. MoOCl₃(O=SPh₂)₂ was isolated from MoCl₅ and an excess of diphenyl sulfoxide, but no information on the destiny of the organic material possibly involved in the formation of the oxide ligand was supplied.^[10] Similarly, MoOCl₃(DMSO)₂ was believed to form from MoCl₅ and an excess of DMSO, on the basis of insufficient characterization data.^[11]

The scarce knowledge on MoCl₅–RR'SO interactions contrasts with the fact that sulfoxides are an intensively investigated class of organic compounds;^[12] in particular, their deoxygenation to sulfides,^[13] as well as the reverse transformation,^[14,15] are strategic reactions because of industrial and biochemical concerns. In the class of sulfoxides, dimethyl sulfoxide (DMSO), playing various roles as an ancillary ligand, is almost ubiquitous in coordination chemistry.^[16] A large number of complexes of DMSO with transition metals have aroused interest in diverse fields, including catalysis^[17] and medicinal chemistry.^[18]

In addition, some well-defined coordination complexes of sulfoxides with homoleptic halides of high-valent metals have been reported;^[19] however, it seems that the metal oxophilicity is a condition favouring the deoxygenation of the sulfoxide moiety. Thus, even though coordination adducts of sulfoxides with TiCl₄ can be isolated,^[19b,19c] the same TiCl₄ has been employed as a component of catalytic systems promoting the de-

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oxygenation of sulfoxides to sulfides.^[20] In addition, the reactions between niobium or tantalum pentahalides and DMSO or diphenyl sulfoxide are known to proceed with Cl/O interchange to produce the corresponding halo-substituted sulfides.^[21] This outcome parallels the reactivity shown by sulfoxides when allowed to interact with oxophilic main group chlorides, such as SOCl₂,^[22] BCl₃ and SiCl₄.^[23]

Here we report our study on the reactions between $MoCl_5$ and limited amounts of a selection of sulfoxides; the reaction between $MoCl_5$ and DMSO, leading to the one-pot conversion of DMSO into a mercaptomethylsulfonium salt, has been studied in detail, by means of X-ray crystallography, DFT calculations and spectroscopic and analytical techniques.

Results and Discussion

Molybdenum pentachloride slowly dissolved in dichloromethane in the presence of one equivalent of DMSO at room temperature, under strictly anhydrous conditions. After workup, the crystalline compound $[Me_2SCH_2SMe][MoOCl_4]$ (1) was isolated in 46 % yield and identified by elemental and magnetic analysis, IR spectroscopy, and X-ray diffraction (Scheme 1). The analogous reaction between MoCl₅ and DMSO carried out at a 1:2 molar ratio afforded 1 in lower yield.

$$H_{3C} \xrightarrow{O} H_{3}C \xrightarrow{H_{3}C} H_{3}C \xrightarrow{\Theta} H_{3}C \xrightarrow{\Theta}$$

Scheme 1. One-pot synthesis of a mercaptomethyl sulfonium salt from ${\rm MoCl}_{\rm 5}$ and DMSO.

The magnetic susceptivity value found for 1 is consistent with previous findings for [MoOCl₄]⁻ salts.^[5f,24] The IR spectrum (solid state) displays a strong band at 985 cm⁻¹, diagnostic of the presence of the [Mo=O] moiety.^[4d,4e,5a,25] X-ray-quality crystals could be collected from a dichloromethane/hexane mixture; the crystal structure of 1 is shown in Figure 1, and a selection of interatomic distances and angles is listed in Table 1. The structure is based on ionic packing of [Me₂SCH₂SMe]⁺ cations and [MoOCl₄]⁻ anions; two independent cations and anions are present within the asymmetric unit of the unit cell. The structure of the [Me₂SCH₂SMe]⁺ cation is reported here for the first time. The [MoOCl₄]⁻ anion displays a distorted square-pyramidal structure, as also previously found for other [MoOCl₄]salts.^[5e,24c,26] The Mo(1)–O(1) bond [1.657(2) Å] reveals a strong π character, as expected for a MoV=O unit.^[5e,5f] [MoOCl₄]⁻ anions are usually found in the solid state in different forms: (A) isolated anions, (B) weak intermolecular adducts with a donor atom of the cation or the co-crystallized solvent molecule, (C) dimeric { $[MoOCl_4]^-$ } units, or (D) infinite { $[MoOCl_4]^-$ }. chains.^[26a,26b] In the case of **1**, the $[MoOCI_4]^-$ anions form weak interactions with the mercapto groups of the cations, with Mo(1)...S(3) contacts of 2.97 and 2.98 Å for the two independent molecules. It should be noted that the sums of the covalent and van der Waals radii of Mo and S are 2.56 and 3.80 Å, respectively.[27]





Figure 1. ORTEP drawing of $[Me_2SCH_2SMe][MoOCl_4]$ (1). Displacement ellipsoids are at the 50 % probability level.

Table 1. Selected interatomic distances [Å] and angles (deg) in 1.

	Molecule 1	Molecule 2
Mo(1)-O(1)	1.657(2)	1.660(2)
Mo(1)–Cl(1)	2.3655(9)	2.3750(8)
Mo(1)–Cl(2)	2.3645(8)	2.3575(9)
Mo(1)–CI(3)	2.3598(9)	2.3654(8)
Mo(1)-Cl(4)	2.3674(8)	2.3560(10)
C(5)–S(3)	1.806(3)	1.804(4)
S(3)–C(6)	1.796(3)	1.799(3)
C(6)–S(4)	1.813(3)	1.812(3)
S(4)-C(8)	1.789(3)	1.784(3)
S(4)–C(7)	1.789(3)	1.778(4)
Cl(1)-Mo(1)-Cl(3)	157.51(3)	158.28(3)
Cl(2)-Mo(1)-Cl(4)	159.97(3)	159.17(3)
C(5)-S(3)-C(6)	99.08(16)	99.85(17)
S(3)-C(6)-S(4)	110.59(17)	110.39(17)
C(6)-S(4)-C(7)	101.08(16)	101.16(18)
C(6)-S(4)-C(8)	99.50(15)	99.88(15)
C(7)-S(4)-C(8)	103.21(16)	100.60(19)

The formation of **1** appears to be the result of multiple activation of DMSO, consisting of oxygen transfer to the metal centre, C–H cleavage and intermolecular C–S bond formation. Molybdenum pentachloride behaves in a previously unobserved way, directing the overall sequence in a one-pot process.

The cation $[Me_2SCH_2SMe]^+$ had previously been obtained by the combination of the preliminarily generated MeSCH₂Cl with Me_2S , variously as chloride,^[28] $[SbCI_6]^-$ or $[BF_4]^-$ salts.^[29] Alternative routes to mercapto-substituted sulfonium cations analogous to **1** involve reactions between (1) sulfoxides and trifluoroacetic anhydride, followed by treatment with sulfides,^[30] or (2) alkyl chlorosulfinates and DMSO in the presence of $SbCI_5$.^[31] All of these syntheses are believed to proceed through the formation of ionic intermediates $[R_2SC(H)(R)]^+$ or neutral intermediates $R_2SC(H)(R)CI$, depending on the procedure.

We carried out a DFT study in order to determine a possible pathway for the synthesis of **1**. The hypothesized metal intermediates are summarized in Scheme 2 (black path), with relative Gibbs energy values.

The reaction between Mo_2CI_{10} and DMSO should initially afford the complex $MoCI_5$ (DMSO) [Figure 2, Equation (1)]. A possible following step may involve Cl/O interchange between molybdenum and sulfur (Scheme 2, black path), resulting in the formation of the sulfonium salt [S(Cl)Me₂][MoOCl₄] [Figure S1 in







Scheme 2. Possible intermediates involved in the reaction between Mo_2CI_{10} and DMSO, together with relative Gibbs energy values (kcal mol⁻¹, Mo_2CI_{10} and DMSO taken as zero).

the Supporting Information, Equation (2)]. Hence, HCl release from $[S(Cl)Me_2][MoOCl_4]$ might afford an ylide species [Figure S2 in the Supporting Information, Equation (3)]. Indeed, HCl [see Equation (3)] is one of the experimentally detected byproducts in the synthesis of **1** (see the Experimental Section). All attempts to optimize the ylide CH₂=S(Cl)Me in non-metal-coordinated form afforded MeSCH₂Cl as a stationary point.

$$Mo_2CI_{10} + DMSO \rightarrow 2 MoCI_5(DMSO)$$
 (1)

 $\Delta G = -47.9 \text{ kcal mol}^{-1}$

 $MoCl_5(DMSO) \rightarrow [S(CI)Me_2][MoOCl_4]$ (2)

 $\Delta G = -22.3 \text{ kcal mol}^{-1}$

$$[S(CI)Me_2][MoOCI_4] \rightarrow MoOCI_3\{CH_2=S(CI)Me\} + HCI$$
(3)

$$\Delta G = +11.1 \text{ kcal mol}^{-1}$$

Despite the fact that the hypothetical formation of $MoOCl_3$ {CH₂=S(Cl)Me} is an endoergonic step, this might be followed by the favourable nucleophilic attack of the coordinated ylide onto another sulfonium cation, resulting in C–S bond formation [Equation (4)].^[32] According to the computational results, transfer of one chloride from the sulfonium to the MoOCl₃ moiety should take place at this stage. The optimized structure of [Me₂SCH₂S(Cl)Me][MoOCl₄]₂ is reported in Figure S3 in the Supporting Information. The subsequent rearrangement of this salt would lead to **1** and MoOCl₃ through Cl₂ release [Equation (5)].



Figure 2. DFT-optimized geometry of MoCl₅(DMSO). wB97X DFT functional, C-PCM solvation model for dichloromethane. Selected computed bond lengths [Å]: Mo-Cl (*trans O*) 2.308; Mo-Cl (*cis O*) 2.318, 2.318, 2.335, 2.356; Mo-O 2.027; O-S 1.584; S-C 1.787, 1.787. Selected computed interatomic angles [°]: O-Mo-Cl 86.9, 86.9, 86.7, 90.2, 178.1; Mo-O-S 130.9; O-S-C 101.1, 101.1.

$$\begin{split} &\text{MoOCl}_3\text{[CH}_2=\text{S}(\text{Cl})\text{Me}\} + \\ & [\text{SCIMe}_2][\text{MoOCl}_4] \rightarrow [\text{Me}_2\text{S}\text{CH}_2\text{S}(\text{Cl})\text{Me}][\text{MoOCl}_4]_2 \quad (4) \\ &\Delta G = -11.0 \text{ kcal mol}^{-1} \\ & [\text{Me}_2\text{S}\text{CH}_2\text{S}(\text{Cl})\text{Me}][\text{MoOCl}_4]_2 \rightarrow [\text{Me}_2\text{S}\text{CH}_2\text{S}\text{Me}][\text{MoOCl}_4] + \\ & \text{MoOCl}_3 + \text{Cl}\text{-Cl} \quad (5) \\ &\Delta G = -4.0 \text{ kcal mol}^{-1} \end{split}$$



Importantly, MoOCl₃ was detected by IR spectroscopy on analysis of the solid residue obtained from the reaction mixture (band at $\nu = 983 \text{ cm}^{-1}$).^[33] On the other hand, our attempts to detect elemental chlorine were unsuccessful, this compound possibly being consumed in the medium during the reaction time (18 h).

Because the formation of dimethyl sulfide from MoCl₅/DMSO was detected (GC–MS and ¹H NMR; see Experimental), it seems plausible that reaction pathways alternative to that described above (Equation 1–5) are also working. In principle, dimethyl sulfide might be produced by decomposition of the presumable initial adduct MoCl₅(DMSO) [Equation (6) and Scheme 2, path printed in red].

$$MoCl_5(DMSO) \rightarrow MoOCl_3 + Cl_2 + SMe_2$$
 (6)

 $\Delta G = -4.0 \text{ kcal mol}^{-1}$

Subsequent coordination of SMe_2 to still unreacted $MoCl_5$ (Figure S4 in the Supporting Information) could represent the preliminary step of another route affording **1** [see Equations (7), (8), (9)]. Molybdenum pentachloride would behave as a catalyst along this route (Scheme 2, catalytic Mo_2Cl_{10} is highlighted in blue).

 $Mo_2Cl_{10} + 2 SMe_2 \rightarrow 2 MoCl_5(SMe_2)$ $\Delta G = -18.7 \text{ kcal mol}^{-1}$ (7)

$$MoCl_5(SMe_2) \rightarrow MoCl_4(CH_2SMe) + HCl$$
 (8)

 $\Delta G = 2.4 \text{ kcal mol}^{-1}$

$$\begin{array}{l} \mathsf{MoCl}_4(\mathsf{CH}_2\mathsf{SMe}) + [\mathsf{SCIMe}_2][\mathsf{MoOCl}_4] \rightarrow \\ & [\mathsf{Me}_2\mathsf{SCH}_2\mathsf{SMe}][\mathsf{MoOCl}_4] + 1/2 \ \mathsf{Mo}_2\mathsf{Cl}_{10} \end{array} \tag{9}$$

 $\Delta G = -15.3 \text{ kcal mol}^{-1}$

We extended our investigation to reactions between $MoCl_5$ and a selection of commercial sulfoxides. We could not cleanly isolate and characterize any metal compound from these reactions; however, most of the organic products were identified by means of GC–MS and NMR spectroscopy after hydrolysis of the reaction mixtures.^[34]

The reaction between cyclic tetrahydrothiophene 1-oxide (THTO) and $MoCl_5$ was selective, and the former component was almost quantitatively converted into tetrahydrothiophene when combined with $MoCl_5$ in 2:1 molar ratio (Scheme 3). The observed process is presumably accompanied by oxygen transfer from the organic reactant to the metal centre (IR spectrum of the reaction solid residue: Mo=O band at 983 cm⁻¹, disappearance of S=O band around 1010 cm⁻¹).

On the other hand, the reactions between $MoCl_5$ and $(PhCH_2)_2SO$, MePhSO or nBu_2SO , performed with use of a 1:2 molar ratio, proved to be nonselective (Scheme 3). The IR spectra of the reaction mixtures in every case suggested the occurrence of oxygen abstraction by the Mo centre, whereas DEPT NMR experiments on the same mixtures treated with water ruled out the presence of C–H activation products, in contrast with what had been shown by the MoCl₅/DMSO system.

The prevalent compound originating from $MoCl_5/(PhCH_2)_2SO$ was benzyl chloride,^[35] thus indicating that preferential α -chlorination of the sulfoxide moiety took place, accompanied by C–S cleavage. In addition, significant amounts of benzalde-





Scheme 3. Organic compounds identified in the ${\rm MoCl}_{\rm 5}/{\rm sulfoxide}$ mixtures after treatment with water.

hyde and benzyl-thiol were found, besides traces of dibenzyl sulfide. $^{\rm [22,35a,36]}$

MeSPh and traces of MeCl were formed from MoCl₅/MePhSO (Scheme 3). The sulfide nBu_2S (major) and the disulfide nBu_2S_2 (minor) are the two organic compounds that could be detected from MoCl₅/ nBu_2SO .

We investigated the reactions between MoCl₅ and THTO and between MoCl₅ and MePhSO by DFT calculations, in order to provide an explanation for the different outcomes observed with respect to MoCl₅/DMSO. According to the calculations, the preliminary *O*-coordination of the sulfoxide to Mo^V chloride is a largely favourable process [Equation (10), to be compared with Equation (1)]. The calculated structure of MoCl₅(THTO) is shown in Figure 3, whereas that of MoCl₅(MePhSO) is included in Figure S6 in the Supporting Information.

$$Mo_2CI_{10} + L=O \rightarrow 2 MoCI_5(L=O)$$
(10)

L=O: THTO, $\Delta G = -75.9 \text{ kcal mol}^{-1}$ L=O: MePhSO, $\Delta G = -48.4 \text{ kcal mol}^{-1}$



Figure 3. DFT-optimized geometry of $MoCl_5$ (THTO). wB97X DFT functional, C-PCM solvation model for dichloromethane. Selected computed bond lengths [Å]: Mo-Cl (*trans O*) 2.280; Mo-Cl (*cis O*) 2.339, 2.344, 2.376, 2.390; Mo-O 1.916; O-S 1.580; S-C 1.814, 1.832. Selected computed interatomic angles [°]: O-Mo-Cl 87.4, 87.9, 89.5, 91.3; Mo-O-S 166.4; O-S-C 102.6, 103.2.

In agreement with the experimental observations, the conversion of $MoCl_5(L=O)$ [Equation (10)] into the corresponding sulfonium salts through Cl/O interchange are nonspontaneous reactions [Equations (11) and (12), to be compared with Equation (2)]. In other words, the uncommon behaviour exhibited by DMSO in the reaction with $MoCl_5$ should be related to the specific nature of the former, making the Cl/O interchange with the metal complex thermodynamically acceptable.



 $MoCl_{5}(THTO) \rightarrow [S(CI)C_{4}H_{8}][MoOCl_{4}]$ (11)

 $\Delta G = +4.2 \text{ kcal mol}^{-1}$

 $MoCl_5(MePhSO) \rightarrow [S(Cl)(Me)(Ph)][MoOCl_4]$ (12)

 $\Delta G = +12.0 \text{ kcal mol}^{-1}$

In order to allow the formation of the corresponding sulfides from THTO and MePhSO, the oxygen transfer to the metal centre should not be accompanied by Cl transfer to the organic moiety [Equations (11) and (12)]. DFT analyses suggest the possibility of Cl₂ release [Equation (13)]. This process is slightly endoergonic in the case of THTO; nevertheless, it could be driven by the subsequent reactions of the products, including the possible coordination of THT to the metal species.^[37]

$$\begin{split} &\text{MoCl}_5(\text{L=O}) \rightarrow \text{MoOCl}_3 + \text{Cl}_2 + \text{L} \end{split} \tag{13} \\ &\text{L: THT, } \Delta G = 5.0 \text{ kcal mol}^{-1} \\ &\text{L: MePhS, } \Delta G = -3.6 \text{ kcal mol}^{-1} \end{split}$$

Interestingly, evolution of HCl from the reaction mixtures (Scheme 2) was detected in every case (see the Experimental Section for details). In the absence of C–H activation processes (see above), this may constitute indirect confirmation of the formation of elemental chlorine.^[38,39]

Conclusions

Despite the interest that sulfoxides have attracted in organic synthesis, and their wide use in coordination chemistry, the reactivity of this class of compounds with molybdenum pentachloride has previously been scarcely elucidated. In general, chlorination of alkyl sulfoxides by oxophilic metal chlorides is well known; nevertheless, it typically stops at the formation of halogen-substituted sulfides. Here we have described the 1:1 reaction between MoCl₅ and DMSO, providing an example of one-pot sulfoxide conversion into a mercapto-substituted sulfonium compound. This unusual result seems to be directed by specific electronic and steric properties of the sulfur substituents; different outcomes have thus been found in the reactions between MoCl₅ and other sulfoxides.

Experimental Section

General Considerations: Warning. The metal products reported in this paper are highly moisture-sensitive, so rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven-dried at 140 °C prior to use, evacuated (10⁻² mmHg) and then filled with argon. MoCl₅ was purchased from Strem (99.6 % purity) and stored under argon as received. The organic reactants were purchased from Alfa Aesar. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma–Aldrich) were distilled over CaH₂ under argon before use. IR spectra were recorded at 298 K with a Perkin–Elmer FTIR spectrometer equipped with a UATR sampling accessory. Magnetic susceptibility (reported per Mo atom) was measured on a solid sample at 298 K with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd). Diamagnetic corrections were introduced according to König.^[40] NMR spectra were recorded with a Bruker Avance II DRX400 instrument



equipped with a BBFO broadband probe at 298 K. GC/MS analysis was performed with a HP6890 instrument interfaced with MSD-HP5973 detector and equipped with a Phenonex Zebron column. Carbon and hydrogen analyses were performed with a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method^[41] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO₃ to neutralization. The molybd-enum content was determined by the spectrophotometric method proposed by Crouthamel and Johnson,^[42] after dissolution of a weighed amount of sample (30–60 mg) in HCl (4 m, 100 mL). A calibration curve was obtained with (NH₄)₆Mo₇O₂₄·4 H₂O as standard ($R^2 = 0.999$), whereas MoO₂(acac)₂ was used as a reference compound (anal. found: Mo 30.2 %; C₁₀H₁₄MoO₄ requires Mo 29.8 %).

Reaction between MoCl₅ and Dimethyl sulfoxide (DMSO)

(1) Synthesis and Isolation of [Me₂SCH₂SMe][MoOCl₄] (1): A suspension of MoCl₅ (326 mg, 1.19 mmol) in CH₂Cl₂ (30 mL) was treated with DMSO (0.086 mL, 1.20 mmol). The mixture was stirred for 18 h at room temperature. The resulting green solution was filtered in order to remove a minor amount of a dark green solid, concentrated to ca. 10 mL, layered with hexane and set aside at –30 °C. Light green crystals of **1** were collected after one week, yield 208 mg, 46 %. IR (solid state): $\tilde{v} = 3003$ (m), 2917 (m), 1693 (w), 1594 (m), 1407 (m), 1319 (m), 1201 (w), 1095 (w), 1033 (m), 985 (s, Mo=O) , 927 (vs), 892 (vs), 807 (m), 746 (w), 721 (w), 685 (w) cm⁻¹. Magnetic measurement: $\chi_{M}^{corr} = 9.58 \times 10^{-4}$ cgsu, $\mu_{eff} = 1.52$ BM cm⁻¹. C₄H₁₁Cl₄MoOS₂ (377.00): calcd. C 12.74, H 2.94, Cl 37.61, Mo 25.45; found C 12.65, H 3.00, Cl 37.48, Mo 25.58.

(2) Detection of HCl and SMe₂: $MoCl_5$ (0.300 mmol) and DMSO (0.300 mmol) were allowed to react in CH_2Cl_2 (8 mL) in a Schlenk tube closed with a silicon stopper. After 72 h, an aliquot of gas was withdrawn from the Schlenk and analyzed by GC–MS. The analysis revealed the presence of SMe₂. Another aliquot of gas was transferred into an aqueous solution of AgNO₃, resulting in the precipitation of a white solid (AgCl).

In a different experiment, $MoCl_5$ (0.300 mmol), CD_2Cl_2 (0.5 mL), CHCl_3 (0.300 mmol) and DMSO (0.300 mmol) were transferred into a NMR tube. The tube was sealed, shaken in order to homogenize the content, and maintained at room temperature. NMR analysis after 72 h indicated the presence of **1**, SMe₂ and other unidentified products (SMe₂/CHCl₃ ratio = 45 %).

Reactions between $MoCl_5$ and Tetrahydrothiophene 1-Oxide, nBu_2SO , MePhSO or $(PhCH_2)_2SO$

(1) Identification of Organic Products. General Procedure: The appropriate sulfoxide (1.60 mmol) was added to a suspension of $MoCl_5$ (0.800 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 18 h at room temperature, and the volatile materials were then removed in vacuo. The residue was analyzed by IR and NMR spectroscopy. Afterwards, a portion of the residue was treated with CDCl₃ (ca. 2 mL), followed by an excess of H_2O (ca. 0.2 mL). The resulting solution was analyzed by GC–MS and NMR spectroscopy.

(A) From MoCl₅/tetrahydrothiophene 1-oxide, green solid. IR (solid state): $\tilde{v} = 2495$ (m), 1598 (m), 1441 (m), 1412 (m), 1307 (w), 1204 (vw), 1175 (vw), 1134 (vw), 1101 (w), 983 (vs), (Mo=O), 875 (w), 800 (m), 731 (m) cm⁻¹. ¹H NMR: tetrahydrothiophene.^[43] NMR/GC-MS (after hydrolysis): tetrahydrothiophene.





(B) From MoCl₅/nBu₂SO, green solid. IR (solid state): $\tilde{v} = 2960$ (s), 2932 (m), 2873 (m), 1599 (m), 1463 (m), 1409 (m), 1381 (w), 1276 (w), 1228 (w), 1191 (vw), 1099 (w), 990 (vs., Mo=O) , 938 (s), 781 (w), 732 (m) cm⁻¹. ¹H NMR: nBu₂S.^[43] NMR/GC–MS (after hydrolysis): nBu₂S and nBu₂S₂ (ratio ca. 3:1).

(C) From MoCl₅/MePhSO, green-blue solid. IR (solid state): $\tilde{v} = 3007$ (w), 2921 (w), 1601 (m), 1475 (m), 1445 (m), 1409 (m), 1305 (w-m), 1259 (w), 1142 (m), 1082 (m), 978 (vs., Mo=O) , 955 (vs), 811 (s), 747 (vs), 716 (m), 684 (vs) cm⁻¹. ¹H NMR: MeSPh.^[43] NMR/GC–MS (after hydrolysis): MeSPh and MeCl (ratio ca. 10:1).

(D) From MoCl₅/(PhCH₂)₂SO, purple solid. IR (solid state): $\tilde{v} = 3062$ (w), 3031 (w), 2968 (w), 2910 (w), 1681 (w–m), 1644 (m), 1595 (m), 1579 (m), 1495 (m), 1454 (a), 1399 (w), 1315 (w), 1293 (w), 1218 (w), 1169 (w), 1074 (w), 1028 (w), 990 (s, Mo=O) , 947 (s), 908 (s), 839 (w), 814 (w), 764 (s), 695 (vs) cm⁻¹. ¹H NMR: PhCH₂CI. NMR/GC-MS (after hydrolysis): PhCH₂CI, PhCHO and PhCH₂SH (ratio 7:4:1).^[43]

(2) Detection of HCI: $MoCl_5$ (0.300 mmol) and the sulfoxide (0.300 mmol) were allowed to react in CH_2Cl_2 (8 mL) in a Schlenk tube closed with a silicon stopper. After 72 h, an aliquot of gas was withdrawn from the Schlenk and into an aqueous solution of Ag-NO₃. Precipitation of a white solid (AgCl) was observed in every case.

X-ray Crystallographic Study: Crystal data and collection details for **1** are listed in Table 2. The diffraction experiment was carried out with a Bruker APEX II diffractometer equipped with a CCD detector and with use of Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). The structure was solved by direct methods and refined by full-matrix, least-squares based on all data with use of F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by use of a riding model.

Computational Studies: The computational geometry optimizations were carried out without symmetry constrains and with use of the range-separated DFT functional ω B97XD, including semiempirical dispersion corrections.^[44] This functional was combined with

Table 2. Crystal data and experimental details for 1.

Formula	$C_4H_{11}CI_4MoOS_2$
Formula weight	376.99
<i>T</i> [K]	100(2)
λ [Å]	0.71073
Crystal system	monoclinic
Space group	P2 ₁ /c
a [Å]	11.4970(8)
b [Å]	20.0019(14)
c [Å]	11.3443(8)
β [°]	100.9540(10)
Cell volume [Å ³]	2561.2(3)
Z	8
D _c [g cm ⁻³]	1.955
μ [mm ⁻¹]	2.143
F(000)	1480
Crystal size [mm]	$0.16 \times 0.12 \times 0.11$
heta range [°]	1.80-28.00
Reflections collected	23554
Independent reflections	6069 [$R_{int} = 0.0436$]
Data/restraints/parameters	6069/0/217
Goodness on fit on F^2	1.040
$R_1 \left[l > 2\sigma(l) \right]$	0.0350
wR ₂ (all data)	0.0637
Largest diff. peak/hole [e Å ⁻³]	0.605/-0.6904

the split-valence polarized basis set of Ahlrichs and Weigend, with relativistic ECP on the metal centre.^[45] The "unrestricted" formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed $\langle S^2 \rangle$ values with the theoretical ones. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (*T* = 298.15 K) were obtained. The C-PCM implicit solvation model (ε = 9.08) was added to ω B97XD calculations.^[46] Gaussian 09 was used as software,^[47] running on x86–64 workstations.

Supporting Information: Selected DFT-optimized structures are reported in the Supporting Information, Figures S1–S10, with relevant bonding parameters. Cartesian coordinates of the computed geometries are collected in a separated *xyz* file.

CCDC 1474430 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Molybdenum · Molybdenum pentachloride · S– O activation · Sulfoxides · Density functional calculations

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