Article

Coordination Properties of Non-Rigid Phosphinoyldithioformate Complexes of the $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ Cation in Catalytic Sulfur Transfer Reactions with Thiiranes

Dmitrii Razinkov , Hafdís I. Ingvarsdottir, Ágúst Kvaran , Sigridur Jonsdottir and Sigridur G. Suman *

Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland; dmr2@hi.is (D.R.); hiingvarsdottir@gmail.com (H.I.I.); agust@hi.is (Á.K.); sigga@hi.is (S.J.)

* Correspondence: sgsuman@hi.is

Abstract: Two “ $\text{Mo}_2\text{O}_2\text{S}_2$ ”-based complexes with phosphinoyldithioformate ligands were synthesized from the metathesis reaction of $[\text{R}_2\text{P}(\text{O})\text{CS}_2]^-$ with $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ to give $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2\{\text{R}_2\text{P}(\text{O})\text{CS}_2\}_2]$ (**1**; R = Ph, **2**; R = Bn). The complexes were fully characterized, including the X-ray crystal structure for **1**. Variable temperatures ^{31}P NMR of **1** and **2** exhibit non-rigid behavior in solution where three and two coordination isomers were present, respectively. The organic substituent on the P atom greatly impacts the complex non-rigid properties and behavior. The catalytic activity of **1** and **2** towards sulfur atom transfer (SAT) using propylene sulfide and cyclohexene sulfide was explored, employing homogeneous reaction conditions at an ambient temperature on the NMR scale. The complexes showed distinctly different properties along with high conversions in short reaction times. A catalytic cycle consistent with the results is proposed.

Keywords: molybdenum; sulfur; thiiranes; propylene sulfide; cyclohexene sulfide; catalysis

Citation: Razinkov, D.; Ingvarsdottir, H.I.; Kvaran, Á.; Jonsdottir, S.; Suman, S.G. Coordination Properties of Non-Rigid Phosphinoyldithioformate Complexes of the $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ Cation in Catalytic Sulfur Transfer Reactions with Thiiranes. *Catalysts* **2021**, *11*, 593. <https://doi.org/10.3390/catal11050593>

Academic Editor: Manas Sutradhar

Received: 12 April 2021

Accepted: 1 May 2021

Published: 4 May 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The catalytic transfer of sulfur atoms by transition metal complexes has received extensive attention due to its many industrial applications [1–9]. The polymerization of thiirane to form sulfur-rich polymers is very attractive as a basic material for plastic lenses, prisms, e.g., which could replace inorganic optical materials [10,11]. A few studies have been reported regarding direct metal-mediated SAT using molybdenum [3,12–17], tungsten [18–20], rhenium [21], or rhodium [22–24] complexes. These studies show that certain characteristics can improve catalyst performance in episulfidation reactions such as improved catalyst stability and efficiency.

Sulfur atom transfer from a thiirane to a metal may proceed through either an oxidative addition reaction to the metal or in an insertion reaction into M-S bond accompanied by an internal redox of the ligand (Scheme 1) [5,6,9,25]. Dinuclear molybdenum or rhodium complexes in episulfidation reactions have shown results that indicate that a dinuclear complex may improve sulfur atom transfer [3,21,26–28]. Bulky phosphine ligands can increase the efficiency of catalysts in general by preventing common obstacles like dimerization and subsequent deactivation of the catalyst [3,29].

A general synthesis route of a large variety of thiiranes from olefins is hampered by steric accessibility to the metal center, and oligomerization among other side reactions take place. The sulfur donors in these reactions often compound the number of side reactions and influence the reaction mechanism to give low stereochemical yields [3]. Elemental sulfur is a common sulfur source that has only been successful with a handful of sterically hindered cyclic substrates [3]. Dinuclear molybdenum complexes have a natural ability to coordinate sulfur and add sulfur atoms into the Mo-S bond to form sulfur ligand rings with several sulfur atoms [30]. These sulfur ligand rings undergo internal redox where elemental sulfur is expelled when the ring size becomes sterically crowded [30].

Scheme 1. Metal mediated sulfur atom transfer reactions; (a) oxidative addition of a sulfur atom to a metal center and (b) sulfur atom insertion into a metal-sulfur bond.

It follows that a dinuclear molybdenum complex with accessible coordination sites that could accommodate a growing sulfur ligand ring and adjust to sulfur expulsion would be a desirable catalytic system for thiirane synthesis where deactivation and substrate coordination could be avoided. Ligands with non-rigid behavior [31–33] could accommodate this change in coordination geometry around the metal center and facilitate catalysis, minimizing deactivation reactions based on the unsaturated coordination sphere around the metal center. To test this hypothesis, ambidentate phosphinoyldithioformate ligands showing non-rigid S,O-bidentate, S,S-bidentate, and S-monodentate coordination abilities (Scheme 2) were synthesized [34,35]. One dithioformate sulfur is always coordinated to the metal center and sigma bonded. The second metal-O/S bond may dissociate in solution [34], opening up a vacant coordination site on the metal and possibly facilitating sulfur transfer. In preliminary experiments, a reaction of a dinuclear molybdenum complex with thiirane would be expected to form an olefin and elemental sulfur, as well as a catalyst intermediate possessing an additional sulfur ligand in the reaction shown in Scheme 1b.

Scheme 2. Coordination modes of phosphinoyldithioformate ligands to a metal center; R = Ph, or Bn. L is bridging sulfur and the second Mo center. S,O-bidentate shown is equatorial/axial coordination in III, and equatorial/equatorial in IV.

In this paper, the $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ cation was reacted to form complexes **1** and **2** with the ambidentate ligands (R = Ph, or Bn) shown in Scheme 3. The complexes **1** and **2** were isolated and characterized (Scheme 3). Complex **1** was crystallized and its structure elucidated. The coordination properties of the ligands were studied employing IR and ^{31}P NMR spectra to evaluate the impact of the organic substituent on the catalytic abilities of the complexes. Interestingly, variable temperature ^{31}P NMR showed the compounds to be non-rigid and a clear difference was observed between solution behavior and properties of the complexes. Both complexes proved able to accept sulfur from thiiranes in sulfur transfer reactions with cyclohexene sulfide and propylene sulfide, even showing high conversions in short times without apparent catalyst degradation.

Scheme 3. Synthesis of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2\{\text{R}_2\text{P}(\text{O})\text{CS}_2\}_2]$ (1; $\text{R} = \text{Ph}$; 2; $\text{R} = \text{Bn}$).

2. Results and Discussion

2.1. Syntheses

Complexes **1** and **2** were synthesized in the ligand exchange reactions in air at ambient temperature as shown in Scheme 3. The Et_4N^+ and Me_4N^+ alkylammonium salts of $[\text{R}_2\text{P}(\text{O})\text{CS}_2]^-$ ($\text{R} = \text{Ph}$, Bn) were obtained from a salt metathesis reaction of the potassium salt with the appropriate alkylammonium chloride in air at ambient temperature. The reactions were conducted in stoichiometric ratios. Complex **1** was isolated as a crystalline solid, while complex **2** was isolated as a solid.

2.2. Molecular Structure of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2\{\text{R}_2\text{P}(\text{O})\text{CS}_2\}_2(\text{DMF})_2]$, **1**

X-ray quality single crystals were obtained by diffusion of ethanol into a DMF solution of **1**. Crystallographic analysis and data collection are summarized in Table S1. Selected bond angles and distances are listed in Tables S2 and S3. Analysis of the X-ray diffraction data revealed that the symmetric $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ core with the sulfur atoms of the ligand is a trans orientation and the DMF coordinated in the equatorial plane is also in trans configuration. The molecular structure is shown in Figure 1. The molecule sits on a crystallographic C_2 axis and the positions of half of the molecule were generated by the symmetry operation. The ligand is coordinated as an S,O-bidentate chelate, with sulfur coordinated in the equatorial position and oxygen in the axial position. Each molybdenum atom is in an overall distorted octahedral coordination geometry. The molybdenum atom is located slightly above the plane formed by the bridging sulfur atoms and the equatorial S,O donor atoms and the axial oxygen atoms are leaning away from the sulfur bridges (see also Scheme 3).

Figure 1. Structure and labeling of **1** with ellipsoids at 50% probability. H atoms were omitted for clarity.

The Mo-Mo bond distance is 2.835 Å and the bridging sulfur Mo-S bond distances are 2.3174(7) Å and 2.3241(7) Å with bridging sulfur (S_b) angles (Mo- S_b -Mo) of 75.29° and (S_b -Mo- S_t) of 103.24° (S_t = terminal sulfur). The axial Mo=O bond distance is 1.798(2) Å with an angle (O-Mo- S_b) of 102.01°. The structural parameters for the $[Mo_2O_2(\mu-S)_2]^{2+}$ are very similar to other coordination compounds with this core [28,36,37]. The ligand coordinates to the Mo with Mo-O and Mo-S bond distances of 2.2061(18) and 2.6051(17) Å, respectively, with an angle (O2-Mo1-S2) of 77.84°. DMF coordinates with the Mo-O3 bond distance of 2.2125(17) Å. The trans influence of the molybdenyl group leads to elongation of the Mo-O2 bond and a stronger P=O bond. The coordinating ligand P-O bond shows substantial single bond character with a bond distance of 1.5195(19) Å compared to 1.49 Å for the P=O bond in the free ligand [38], and 1.506 Å in $[Ph_2Pb(L1)_2(H_2O)]$ [34]. The stronger P-O bond observed here is to be expected considering trans influence of the Mo=O group that results in a long Mo-O bond of 2.2061(18) Å compared to 1.95 Å for a single Mo-O2 bond.[39] The dihedral angle of the $[Mo_2O_2(\mu-S)_2]^{2+}$ core was calculated as 159.3° in good agreement with other complexes with the same core that normally fall within the range of 150 to 160° [40].

2.3. IR and Raman Spectroscopy

Infrared spectra of **1** and **2** were obtained for the compounds in KBr pellets and for solutions in CH_2Cl_2 . The observed $[Mo_2O_2(\mu-S)_2]^{2+}$ core IR stretches are unexceptional (see Table 1 and Figures S1 and S2) [28,37].

Table 1. Selected vibrational data for **1** and **2**.

Cmpd/Method	IR, KBr, cm^{-1}	IR, CH_2Cl_2 cm^{-1}	Raman, neat, cm^{-1}	Scheme 2
1	$\tilde{\nu}(P=O)$, $\tilde{\nu}(CS_2)$, $\tilde{\nu}(Mo=O)$ 1077 1071 945 1121 915 933 1251 1054	$\tilde{\nu}(P=O)$, $\tilde{\nu}(CS_2)$, $\tilde{\nu}(Mo=O)$ 1079 1050 947 1118 937	$\tilde{\nu}(P=O)$, $\tilde{\nu}(CS_2)$, $\tilde{\nu}(Mo=O)$ 1052 918	II III IV
2	1080 1071 932(br.) 1251 1054	1077 1057 946 932	1073 930	II, III, IV
$[Ph_2P(O)CS_2]^-$	1176 ^a 1032 ^a 915 ^a	1168 ^b 1034 ^b		
$[Bn_2P(O)CS_2]^-$	1200 ^a 1030 ^a 910 ^a			

^a From reference [34]. br.: broad; ^b From reference [38] in $CHCl_3$.

The IR spectra for KBr pellets of **1** and **2** show vibrational stretches in the infrared spectrum for $\tilde{\nu}(Mo=O)$ as strong bands at 945 cm^{-1} and at 932 cm^{-1} , respectively (see Table 1). Additionally, **1** has a shoulder at 933 cm^{-1} . The stretch for the bridging sulfur, $\tilde{\nu}(Mo-S_b-Mo)$, was found at ~ 462 cm^{-1} in both complexes. The characteristic $\tilde{\nu}(C=O)$ stretches from the DMF ligands for **1** and **2** were found at ~ 1640 cm^{-1} . Variation in coordination of the dithioformate ligand gives rise to different bands in the infrared spectrum (Scheme 1) [38]. Coordination of the P=O group to the Mo center appears as a strong shift to lower energy, whereas a singly S-bonded ligand has little effect. S,S-bidentate coordination shifts the P=O band to higher energy [34]. The dithioformate appears as iso bidentate with a single band for S,S-coordination, or as two bands for aniso bidentate as reported for aryl mercury dithiocarbamate complexes [41], or for a singly S-bonded ligand. Three vibrational bands for $\tilde{\nu}(P=O)$ were found for **1**; two are shifted from 1173 cm^{-1} to lower energies at 1121 and 1077 cm^{-1} in **1**, and one is shifted to higher energy of 1251 cm^{-1} . Two bands for $\tilde{\nu}(P=O)$ were observed for **2**; one shifted from 1191 cm^{-1} to lower energy at 1080 cm^{-1} while the second band was found at the higher energy of 1251 cm^{-1} . Bands for the $\tilde{\nu}(CS_2)$ moiety were observed as strong bands at 1054, 1071, and a weak band at 915 cm^{-1} for **1**. In **2** two $\tilde{\nu}(CS_2)$ bands were observed at 1054 cm^{-1} and at 1071 cm^{-1} , with the third expected band obscured by the broadness of the Mo=O stretch at about 932 cm^{-1} .

The infrared spectra suggest the presence of at least two coordination modes of the ligands in the KBr pellet. Scheme 4 shows possible coordination geometries of **1** and **2**. The crystal structure of **1** revealed an S,O-bidentate coordination that gives rise to a $\tilde{\nu}(\text{P}=\text{O})$ band shifted to lower energy, and two bands from the CS_2 moiety (Schemes 4I and 2III). An S,S-bidentate coordinated ligand is expected to show $\tilde{\nu}(\text{P}=\text{O})$ shifted to higher energy, and a single CS_2 band (Scheme 2II). A third coordination mode may be equatorially coordinated P=O oxygen (Scheme 2IV) whereas in the crystal structure, this oxygen is axial to the $\text{Mo}=\text{O}$ group with an elongated Mo-O dative bond imposed by *trans*-influence of the molybdenyl group resulting in a smaller shift in frequency ($\Delta\{\tilde{\nu}(\text{P}=\text{O})\}$). This is not expected to affect the $\tilde{\nu}(\text{CS}_2)$ vibrational frequency. In **2**, only two coordination modes are observed, S,O-bidentate (III or IV; Scheme 2) with comparable shifts of the $\tilde{\nu}(\text{P}=\text{O})$ and $\tilde{\nu}(\text{CS}_2)$ bands noting that the coordination shift $\Delta\{\tilde{\nu}(\text{P}=\text{O})\}$ of the benzyl substituted ligands is normally larger than for the phenyl [35]. The second coordination mode shows the non-coordinated $\tilde{\nu}(\text{P}=\text{O})$ at 1251 cm^{-1} and a second $\tilde{\nu}(\text{CS}_2)$ band indicating the presence of the S,S-bidentate coordination mode in KBr (Scheme 2II). Although the 1121 cm^{-1} band in **1** is assigned to the axially coordinated P=O group, the larger $\Delta\{\tilde{\nu}(\text{P}=\text{O})\}$ in **2** prevents assignment of the band at 1080 cm^{-1} to a specific coordination. Therefore, **2** is most likely the coordination isomer III in Scheme 4 although it is not possible to determine if the P=O group is axial or equatorially coordinated.

Scheme 4. Possible coordination isomers of **1** and **2**. R groups on P were omitted for clarity. (I–III) show possible combination of coordination geometries from Scheme 2 in the binuclear structure of **1** and **2**.

The solution IR spectra were obtained in CH_2Cl_2 to investigate possible non-rigid behavior in solution. However, the solvent obscures the band at about 1250 cm^{-1} . For **1**, a single band from the CS_2 and two bands from the P=O moieties corresponding to the S,O-bidentate coordination (III and IV in Scheme 2) were observed, whereas for **2**, single P=O and CS_2 bands were observed (I or III in Scheme 4). The benzyl substituted ligand therefore appears to have a single identifiable coordination mode in solution at an ambient temperature while the phenyl substituted ligand presents two identifiable coordination modes in solution on the IR timescale. The coordinated DMF does not shift in the solution IR spectra.

Raman spectra (Figure S3) of the bulk solids of **1** and **2** revealed spectra with only three observable bands, at 918 cm^{-1} , 1052 cm^{-1} , and 430 cm^{-1} for **1**, and at 930 , 1073 , and 430 cm^{-1} for **2**, of which only one band is assignable to the $\text{Mo}=\text{O}$ group, consistent with C_1 symmetry where C_2 symmetry results in two Raman active bands for the $\text{Mo}=\text{O}$ group. IR revealed two bands for $\text{Mo}=\text{O}$ groups for **1** consistent with the C_2 symmetry of the isolated crystals. The Raman spectra reveals that the bulk samples are not centrosymmetric and that the coordination of the ligands to the two molybdenum centers may be as shown in Scheme 4III.

2.4. NMR Spectroscopy

^1H , ^{13}C , and ^{31}P NMR spectra were obtained for complex **1** in CD_2Cl_2 (Figure S13), ^1H NMR spectrum for **2** was obtained in CDCl_3 (Figure S14), and ^{13}C NMR spectrum in DMSO-d_6 , ^{31}P NMR spectra were obtained in CD_2Cl_2 . In all spectra recorded, the coordinated DMF ligands were found to dissociate in solution.

The ^1H NMR spectra for **1** and **2** at ambient temperature shows a single set of protons for both ligands at ambient temperature. The ^1H NMR spectrum at ambient temperature

shows four resonances associated with the four phenyl groups: a quartet at 8.12 ppm for the 4 *ortho*-protons, a doublet of doublets at 7.77 ppm for the 4 *ortho*-protons and the 2 *para*-protons, a doublet at 7.62 ppm for the 4 *meta*-protons and 2 *para*-protons, and a multiplet at 7.52 ppm for the 4 *meta*-protons.

The ^1H NMR spectrum for **2** shows a doublet at 7.47 ppm associated with the 2 *ortho*-protons, a multiplet at 7.44 ppm associated with the 6 *ortho*-protons and 2 *para*-protons, a triplet at 7.00 ppm associated with the 4 *meta*-protons and 2 *para*-protons, and a doublet at 6.93 ppm for the 4 *meta*-protons. The coupling pattern for the methylene protons has been described elsewhere [42]. The three signals observed were a quartet at 3.76 (-CH₂ protons), a multiplet at 4.00 ppm (2 CH₂ protons), and at 3.54 ppm (4 CH₂ protons).

The ^{13}C NMR spectrum for **1** exhibit coupling of the carbon atoms to the ^{31}P where the C_{ipso} of the aromatic ring reveals the largest coupling constant $^1J(^{31}\text{P}-^{13}\text{C})$ of 126.2 Hz, and successively smaller coupling constants for C_{ortho} , C_{meta} , and C_{para} . These values are in good agreement with organometallic $[\text{Sn}(\text{IV})\text{R}_2\{\text{Ph}_2\text{P}(\text{O})\text{CS}_2\}_2]$ compounds with same dithioformate ligands [35]. The signal for the CS₂ carbon was not observed in **1** because of an insufficient signal-to-noise ratio (expected at ~240 ppm). **2** shows a single CS₂ carbon atom at δ 240.5 ppm with $J(^{31}\text{P}-^{13}\text{C})$ of 59.4 Hz. Both **1** and **2** show two sets of carbon atoms for the aromatic rings although they also show distinct differences. The two sets of carbon atoms in the spectrum of **1** show the same $^nJ(^{31}\text{P}-^{13}\text{C})$ coupling constants for respective carbon atoms and chemical shifts that are very similar, whereas **2** shows a larger difference for the chemical shifts and slightly different coupling constants for the two respective carbon atoms, as well as two clearly different methylene carbon atoms. The data are given in the experimental section. The ^{13}C NMR of **2** therefore supports the presence of both S,S and S,O coordination of the ligands that may be as shown in Scheme 2II or in Scheme 2III,IV. The carbon spectra in S,O-bidentate, S-monodentate, and S,S-bidentate coordination modes have been described in detail elsewhere [35].

The ^{31}P spectrum for **1** and **2** at ambient temperature shows two broad resonances centered at 48.8 ppm for **1**, and a single resonance with a shoulder at 73.7 ppm for **2**. The ligands show a signal for ^{31}P at δ = 15.1 ppm for R = Ph and at δ = 30.3 ppm for R = Bn in CD₂Cl₂ [38]. The reported ranges for coordination shifts of the ^{31}P signal for a series of Sn compounds show the largest shift to occur in the S,O-bonded ligands [35], and the singly S-bonded ligand showed coordination shifts as small as 7.6 ppm [35]. In the ambient temperature NMR and IR data, no evidence was found to support singly S-bonded ligands.

2.5. Variable ^{31}P NMR study of **1** and **2**; Non Rigid Behavior

The IR and ^{31}P -NMR spectra recorded confirmed the presence of S,O and S,S coordination modes in the solid state and in solution at an ambient temperature. The ^{31}P NMR spectra show a split signal for **1**, and a broad resonance with a shoulder for **2**. Variable temperature ^{31}P NMR spectra were recorded from room temperature down to 201 K for **1** (Figure 2, Figure S4) and to 190 K (Figure 2, Figure S5) for **2** in CD₂Cl₂. As the temperature was lowered, the resonances separated and split into a number of sharp resonances; a total of five for **1** and four resonances for **2**. This clearly indicates a non-rigid behavior of the complexes. Closer inspection of the resonance intensities and line widths (S6 and S7: Spectra for lowest temperatures showing relative intensities of resonances) revealed the following.

Figure 2. Variable ^{31}P NMR data for **1** (top) and **2** (bottom) showing three coordination isomers for **1** and two for **2** emerging upon cooling.

Three coordination isomers were observed in the ^{31}P NMR of **1**, one centrosymmetric giving rise to a single signal, and two non-centrosymmetric giving rise to two signals each. In comparison, **2** only exhibits two non-centrosymmetric coordination isomers in its spectrum. Thus, a non-centrosymmetric isomer is shown in Scheme 4III and possible centrosymmetric isomers are shown in Scheme 4I,II. The ^{31}P NMR signals show large coordination shifts ($\Delta(\delta\text{P})$) for both compounds accompanied with more moderate shift. The non-rigid behavior presumably goes through dissociation and coordination of the ligand to the metal and a singly S-bonded ligand may be present as shown in Scheme 2I revealing two non-centrosymmetric isomers at a low temperature.

The ambient temperature IR and NMR data revealed room temperature S,O and S,S bidentate coordination modes. Assuming the chemical shifts of the ^{31}P signal in the axial versus the equatorial coordination modes shown in Scheme 2III,IV are indistinguishable, the low-temperature ^{31}P NMR data reveal the presence of the singly S-bonded ligand. The spectroscopic data show that complex **1** presents three coordination isomers overall while complex **2** presents two isomers. A summary of the results from the spectroscopic data is shown in Figure 3.

Figure 3. Summary of coordination mode analysis from spectroscopic data.

3. Catalytic Experiments on the NMR Scale

The complexes **1** and **2** were tentatively able to accept sulfur atoms in a unidirectional SAT reaction. Sulfur coordination may take place as a terminal ligand addition to the Mo center or as a bridging sulfur atom to both Mo centers [1,9,25]. Catalytic activity studies of SAT employing **1** and **2** as catalysts were performed at using cyclohexene sulfide and propylene sulfide as sulfur source. Catalytic activity towards cyclohexene sulfide was also tested with the starting complex: $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$, [43] in deuterated acetonitrile due to its low solubility in non-coordinating solvents (Figure S8). The reactions were monitored using ^1H NMR spectroscopy at homogeneous reaction conditions at ambient conditions. Reaction yields were evaluated by integration of the cyclohexene or propylene sulfide resonances and using integration of the solvent resonance as an internal standard (Figure S15). Blank reactions were run to evaluate the spontaneous conversion of cyclohexene sulfide to cyclohexene and propylene sulfide to propylene in deuterated dichloromethane and deuterated chloroform, respectively. The blank reactions did not result in detectable cyclohexene or propylene formation after 46 h and 45 h, respectively.

3.1. SAT Reaction of Cyclohexene Sulfide

The results from the catalytic SAT reaction employing $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$, **1**, and **2** as catalysts in reactions with cyclohexene sulfide are shown in Scheme 5. Calculated TON (turnover number) and TOF (turnover frequency) of **1** and **2** at different catalyst concentrations and 50 % conversion are given in Table 2. The reaction progress as a function of time is shown in Figure 4.

Scheme 5. The catalyzed SAT reaction of cyclohexene sulfide.

Table 2. TON and TOF for catalytic desulfurization of cyclohexene sulfide for **1** in CD_2Cl_2 and **2** in CDCl_3 and for $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ in CD_3CN at 50 % conversion.

Complex	Mol%, Catalyst	TON	TOF, h^{-1}	$t_{50\%}$, hr. (a)
1	0.1	500	140	3.58
	0.3	167	102	1.63
	0.5	100	93	1.07
	1.0	50	58	0.87
2	0.1	500	698	0.72
	0.3	167	435	0.38
	0.5	100	286	0.35
	1.0	50	194	0.26
$(\text{Me}_4\text{N})_2$ $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$	0.1	500	48	10.5
	0.3	167	25	6.6
	0.5	100	24	4.2
	1.0	50	24	2.1

TON: Molecules of product converted by molecules of cat: $\text{mol}_{\text{prod}}/\text{mol}_{\text{cat}}$. TOF: TON/h (TON and TOF were calculated for 50% conversion). (a) time at 50% conversion in hours.

Figure 4. Conversion of cyclohexene sulfide to cyclohexene as a function of time; (a) **1**, (b) **2**.

Catalytic activity of **1** and **2** with cyclohexene sulfide were performed employing different mol percentages (%) of catalyst loading. Figure 4 shows that employing higher than 0.5 mol% catalyst loading did not improve the turnover rates for **1**. Furthermore, 0.1 mol% for **1** shows linear conversion leading to 90% reaction yield in ~ 8 h. Complex **2** shows more rapid turnover rates with 100% reaction yields for all catalyst concentrations. A low catalyst loading of 0.1 mol% of **2** achieved 100% reaction yield in ~ 4 h. The saturation curve obtained for the 0.1 mol% reaction progress also reveals that it is possible to lower the catalyst loading further for **2**. The data show that **2** is clearly a better catalyst. Table 2 shows that 50% conversion is achieved with a catalyst concentration of 0.1% mol of **2** compared to 0.5% mol of **1** in about one hour.

Assuming that the catalytic rates depend on the complex non-rigid behavior, **2** must have more movement in solution. The starting complex with four terminal chloro ligands has two open coordination sites and could therefore also potentially accept a sulfur atom. Furthermore, it was previously shown that its chloro ligands are labile in coordinating solvents [43], suggesting additional ability to accept sulfur in ligand exchange reactions, thereby serving as a suitable comparison. Its poorer solubility properties in non-coordinating solvents and the competition of a coordinating solvent with the substrate in the SAT reaction may lead to a slower catalytic reaction. It performs only slightly worse than **1** when reaction yields per mol of catalyst are compared at one-hour reaction time as shown in Figure 5. The highest turnover frequency for $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ was

observed for 0.1 mol % of with value 48 h^{-1} compared to 140 h^{-1} and 698 h^{-1} for **1** and **2**, respectively (Table 2 and Figure S8). Coordinating solvents negatively impact the reaction rates confirming importance of accessible coordination in this reaction.

Figure 5. Catalytic conversion of cyclohexene sulfide at one hour employing **1** (CD_2Cl_2), **2** (CDCl_3), and $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ (CD_3CN) as a function of catalyst mol%.

Comparable methods of desulfurization of thiiranes have been reported. A well-known reaction is desulfurization of thiiranes in a direct reaction with phosphorus compounds such as Ph_3P , although the reactions tend to be slow [44]. Other reported methods include stoichiometric reactions, radical, and metal mediated reactions, often with phosphine that forms $\text{R}_3\text{P}=\text{S}$ in the reaction.

Molybdenum hexacarbonyl $[\text{Mo}(\text{CO})_6]$ was reported as an efficient stoichiometric reagent for desulfurization of a range of structurally diverse activated thiiranes to the corresponding alkenes in high yields at reflux in toluene [45]. In other solvents, the products were obtained in moderate to low yields and the energy favorable $\text{Mo}=\text{S}$ bond formation was credited for high reaction yields. The formation of 1-dodecene as the only aliphatic product was completed in stoichiometric reaction in 3 h and 85% yield. In comparison, catalytic desulfuration of cyclohexene sulfide employing **2** was completed in 3 h employing 0.1% catalyst loading (Figure 3) and significantly faster with higher catalyst loading.

Desulfurization of allyl-thiiranes has been reported in radical catalyzed reactions with aminium antimonate salts $[(4\text{-C}_6\text{H}_4\text{Br})_3\text{N}^+]\text{SbCl}_6^-$ (magic blue) and $[(2,4\text{-C}_6\text{H}_3\text{Br}_2)_3\text{N}^+]\text{SbCl}_6^-$ (10 mol%) in freshly distilled dichloromethane in good yield (80%) within a few minutes [46]. Presumably, the mechanism proceeds through the ring opening of the thiirane by electron transfer from the radical. Complex **2** (1 mol%) showed 100% conversion in 60 min (Figure 3), but higher catalyst concentrations were not tested.

Rhenium complexes are useful reagents for catalytic sulfur transfer reactions from thiiranes to phosphorus(III) compounds [47]. $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)_2$ (5mol%) showed 95% conversion of thiirane to alkene after 5 min in presence of PPh_3 for substrates like cyclohexene sulfide and propylene sulfide in dichloromethane. Calculation of the TOF values at 50% conversion based on the reported data at 3 min were $\text{TON} = 10$ and $\text{TOF} = 227\text{ h}^{-1}$ respectively.

Catalytic desulfuration of thiiranes was reported employing the mononuclear $\text{MoO}(\text{S}_2\text{CP}(\text{OEt})_2)_2$ complex where $(p\text{-MeOPh})_3\text{P}$ was employed to trap the sulfur in the reaction [14]. Efficient catalyst loading was determined at 1 mol% leading to 34% reaction yield for aliphatic substrates and 84% for aromatic substituted thiiranes. Sulfidation reactions were also performed where phenylthiirane was employed as a sulfur source with 1 mol% catalyst leading to 80 to 100% yields in 2 h at 60°C . Employing elemental sulfur as the sulfur source led to sulfur addition to the Mo center and deactivation through dimerization

of the catalyst. The catalyst deactivation reaction competed with the thiirane formation leading to successful sulfuration of the more reactive substrates.

Comparison of the calculated TOF values to the reported values is limited due to the lack of directly comparable data. As a comparison, a very high TON value for epoxidation of 2-cyclooctene of 10,000 with 0.008%mol zeolite catalyst converts to a moderate TOF value of 26 h^{-1} [48]. The reactions of **1** and **2** were performed with higher TOF values in comparison with lower TON values and shorter reaction times where 100% reaction yield was observed within the reaction run time.

3.2. SAT Reaction of Propylene Sulfide

The results obtained suggest that optimizing ligand properties, specifically the substituent on the P atom, may increase turnover frequency to improve performance.

Catalytic activities of **1** and **2** with propylene sulfide in dichloromethane was studied employing NMR to monitor the reaction progress. The overall reaction is shown in Scheme 6. Conversion to propylene for different mol % of catalyst is shown in Figure 6. Calculated TONs and TOFs of **1** and **2** at different catalyst concentrations and 50 % conversion are shown in Table 3.

The calculated TOF for 1 mol % of **1** is very low. These results did not justify further decrease in the catalyst loading of **1**. Catalytic SAT reactions with cyclohexene sulfide were performed employing different mol % of **2**. The results are presented in Figure 6. Conversion was observed immediately and reaction time to 100% conversion were shorter than for **1** but modest overall. Conversion increased with catalyst concentration. The calculated TON and TOF values at different catalyst concentrations and at 50% conversion are given in Table 3.

Scheme 6. The catalyzed SAT reaction of propylene sulfide.

Figure 6. Catalytic conversion of propylene sulfide as a function of time for **2** in CD_2Cl_2 at 5 different catalyst concentrations.

Table 3. TON and TOF for catalytic desulfurization of propylene sulfide for **1** in CD₂Cl₂ and **2** in CDCl₃ at 50 % conversion.

Complex	Mol%, Catalyst	TON	TOF, h ^{−1}	t _{50%} , hr. ^(a)
1	1.0	50	0.50	100
	3.0	16.7	0.36	47
2	0.1	500	12.91	39
	0.5	100	4.56	22
	1.0	50	2.46	20
	2.0	25	5.85	4.3
	3.0	16.7	4.56	3.7

TON: Molecules of product converted by molecules of cat: mol_{prod}/mol_{cat}. TOF: TON/h (TON and TOF were calculated for 50% conversion). ^(a) time at 50% conversion.

1 and **2** are able to catalyze the desulfuration reaction of propylene sulfide to propylene. The best results were observed for **2** (0.1 mol % of catalyst) with a value of 12.91 h^{−1}, or on the same order of magnitude as the lowest satisfactory turnover for industrial application. The comparable catalytic SAT reaction of propylene sulfide with [W₂S₃{S₂CN(Bn)₂]₂{S₂C₂(Ph)₂}] exhibited TOF of 17.1 at 100% conversion [18]. The expectation was that propylene sulfide could react faster than the cyclohexene sulfide and exhibit more rapid sulfur transfer. Likely explanations for this are steric hindrance in the catalytic rate-limiting step in the interaction of propylene sulfide with **1** and **2**, although other factors such as reversibility of the reaction may play a role.

The reaction of propylene sulfide with PPh₃ in presence of catalytic amount of MeReO₃ formed propylene, albeit slowly. Treatment of thiiranes with a catalytic amount of the Re complex in the presence of H₂S showed increased catalytic activity compared to PPh₃ [49], where complete conversion of cyclohexene sulfide to cyclohexene was observed after 5 min, and 100% conversion of propylene sulfide to propylene was achieved after 3 h. This sluggish behavior of propylene sulfide in sulfur transfer reactions has been suggested as potentially caused by reversibility of the reaction [50].

3.3. Proposed Mechanism of the Catalytic SAT Reaction

The samples from the catalytic reactions were examined post-reaction. All of the NMR tubes contained elemental sulfur that formed a yellow precipitate, which was isolated. Mass spectra of the crude post-catalysis solution after conversion of cyclohexene sulfide to cyclohexene with **2** was obtained in the negative scan mode (Figures S9–S12). The mass spectra of **2** exhibits a peak at *m/z* = 900.7967 (Figure S9) that gives an excellent isotope match for the parent anion (Figure S10) and a minor peak corresponding to a sulfur added to the molecule at *m/z* ~932 in the negative ion scan. The crude post-reaction mixture shows these two peaks where the peak at *m/z* ~ 932 representing [Mo₂O₂(μ-S)₂{S₂CP(O)Bn₂}]₂ + “S”[−] has now become equally intense as the main molecular ion peak (Figure S11), confirming that sulfur coordinated to the catalyst and that the catalyst was otherwise intact after the reaction. The measured and simulated isotope pattern for this composition gave a match with good confidence (Figure S12). The NMR spectra did not show any evidence of coordinated cyclohexene. The complex color did not change drastically, indicating absence of redox processes.

A few mechanisms have been proposed for sulfur transfer reactions [5,18,24,51,52]. Complexes **1** and **2** have two open coordination sites; one on each molybdenum center. The S,O-bidentate phosphinoyldithioformate ligands are non-rigid where the “P=O” oxygen or a “CS₂” sulfur dissociates in the solution leaving a second open coordination site [34]. Scheme 7 shows a possible mechanism where the dithioformate is shown as singly S-bonded ligand for clarity, although the assumption is that the ligands do not dissociate simultaneously based on the ³¹P NMR data. In the proposed mechanism, initiation takes place upon dissociation of the Mo-O dative bond in solution followed by a nucleophilic attack by sulfur on the Mo center with a concomitant ring opening of the episulfide. The

sulfur releases the alkene and inserts into a sulfur bridge to form a bridging disulfide. In the absence of a sulfur acceptor, further reaction with episulfide leads to the expulsion of elemental sulfur [28,53]. This mechanism may explain the slower conversion of the propylene sulfide where the smaller reagent may persist as a bridging propylene disulfide ligand. Such coordination modes have been reported for both tungsten and molybdenum with propylene sulfide [18,52,54], where it serves as a deactivation reaction in the catalytic SAT reaction or in addition to alkynes to dinuclear Mo complexes to form olefin complexes [55,56].

Scheme 7. Proposed mechanism of the catalytic SAT reaction.

4. Materials and Methods

4.1. General Consideration

Infrared spectra were obtained with Nicolet Avatar FT-IR spectrophotometer in the mid IR range. Raman spectra were recorded with LabRAM HR *Evolution*[®]—High Resolution MicroRaman Spectrometer from Horiba. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 400, 101, and 63 MHz for ¹H, ¹³C, and ³¹P, respectively. The deuterated solvents served as a lock in the ¹H and ¹³C measurements. UV-visible spectra were recorded on Perkin-Elmer Lambda 25 spectrometer. Mass spectra were recorded on a microTOF-Q spectrometer, equipped with E-spray atmospheric pressure ionization chamber (ESI). Elemental analyses were obtained from Midwest Microlab, IN, United States.

Reagents and solvents were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Deuterated solvents were used as obtained from Sigma-Aldrich (Hafnarfjörður, Iceland, Medor ehf). (Me₄N)₂[Mo₂O₂(μ-S)₂(Cl)₄] [43], K[Ph₂P(O)CS₂]·C₄H₈O₂, and K[Bn₂P(O)CS₂] were prepared by published methods [42].

4.2. Syntheses

[Et₄N][Ph₂P(O)CS₂]; Tetraethylammonium chloride monohydrate (0.377 g, 2.05 mmol) was added to a stirred suspension of K[Ph₂P(O)CS₂]·C₄H₈O₂ (0.831 g, 2.05 mmol) in CH₂Cl₂ (10 mL). The solution changed instantaneously from a red to a dark red solution, and a white precipitate (KCl) formed. After filtration, the solvent was removed under reduced pressure. The dark red oil was dissolved in acetonitrile (10 mL) and diethyl ether added to the solution until turbid, then allowed to sit at 4 °C for 20 h. The resulting purple

pink powder was filtered off in air, washed with diethyl ether, and dried in vacuo. Yield: 0.433 g, 52%. FT-IR (KBr, cm^{-1}): $\nu(\text{P}=\text{O})$, 1173(vs); $\nu(\text{CS}_2)_{\text{asym}}$, 1030(vs); $\nu(\text{CS}_2)_{\text{sym}}$, 890(w). ^1H NMR (D_2O) δ , ppm: 7.83 (dddd, $J = 11.4, 6.7, 2.7, 1.5$ Hz, 4H, C-H_o), 7.67 (tq, $J = 6.7, 1.6$ Hz, 2H, C-H_p), 7.61–7.48 (m, 4H, C-H_m), 3.23 (qd, $J = 7.3, 1.7$ Hz, 8H, C-H₂), 1.25 (ddq, $J = 7.3, 5.7, 1.9$ Hz, 12H, C-H₃). ^{31}P NMR (CD_2Cl_2) δ , ppm: 16.52 (s). ^{13}C NMR (D_2O) δ , ppm: 256.3 (d, $^1\text{J}(\text{P}-\text{CS}_2)$ 71.71 Hz), 132.29 (d, $^4\text{J}(\text{P}-\text{C}_p)$ 3.03 Hz), 131.92 (d, $^2\text{J}(\text{P}-\text{C}_o)$ 9.09 Hz), 131.62 (d, $^1\text{J}(\text{P}-\text{C}_i)$ 102.1 Hz), 131.62 (d, $^3\text{J}(\text{P}-\text{C}_m)$ 11.11 Hz), 51.85 (t, C-H₂); 8.1 (s, C-H₃). UV/Vis (CH_2Cl_2 , $9.2 \cdot 10^{-5}\text{M}$), nm: 270 ($6318\text{ M}^{-1}\text{cm}^{-1}$), 292(sh), 368 ($11,819\text{ M}^{-1}\text{cm}^{-1}$). Elemental anal. Calc. for $\text{C}_{21}\text{H}_{30}\text{NOP}_2\text{S}_2$: C, 61.89; H, 7.42; N, 3.44. Found: C, 61.65; H, 7.27; N, 3.52%.

$[\text{Me}_4\text{N}][\text{Bn}_2\text{P}(\text{O})\text{CS}_2]$; This compound was prepared in a similar way as described above. $\text{K}[\text{Bn}_2\text{P}(\text{O})\text{CS}_2]$ (0.706 g, 2.05 mmol) was mixed with tetramethylammonium chloride (0.274 g, 2.05 mmol) in CH_2Cl_2 (10 mL). After solvent removal, the resulting purple solid was filtered off in air, washed with diethyl ether, and dried in vacuo. Yield: 0.57 g, 73%. FT-IR (cm^{-1}): $\nu(\text{P}=\text{O})$, 1191 (vs); $\nu(\text{CS}_2)_{\text{asym}}$, 1031 (vs); $\nu(\text{CS}_2)_{\text{sym}}$, 920 (w). ^1H NMR (D_2O) δ , ppm: δ 7.36–7.13 (m, 10H, C-H), 3.68 (dd, $J = 14.4, 12.3$ Hz, 2H, C-H₂), 3.43 (t, $J = 13.9$ Hz, 2H, C-H₂), 3.05 (d, $J = 1.3$ Hz, 12H, C-H₃). ^{31}P NMR (D_2O) δ , ppm: 37.46 (s). ^{13}C NMR (D_2O) δ , ppm: 255.05 (d, $^1\text{J}(\text{P}-\text{CS}_2)$ 61.61 Hz), 131.86 (d, $^2\text{J}(\text{P}-\text{C}_i)$ 8.08 Hz), 130.07 (d, $^3\text{J}(\text{P}-\text{C}_o)$ 5.05 Hz), 128.63 (d, $^5\text{J}(\text{P}-\text{C}_p)$ 3.03 Hz), 126.94 (d, $^4\text{J}(\text{P}-\text{C}_m)$ 3.03 Hz), 55.22 (t, C-H₃), 35.53 (d, $^1\text{J}(\text{P}-\text{CH}_2)$ 61.61 Hz). UV/Vis (DMF, $4.6 \cdot 10^{-5}\text{M}$), nm: 285 ($6043\text{ M}^{-1}\text{cm}^{-1}$), 383 ($18,734\text{ M}^{-1}\text{cm}^{-1}$).

$[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Ph}_2\text{P}(\text{O})\text{CS}_2)_2(\text{C}_3\text{H}_7\text{NO})_2]$, 1. $[\text{Et}_4\text{N}][\text{Ph}_2\text{P}(\text{O})\text{CS}_2]$ (0.262 g, 0.643 mmol) was dissolved in DMF (3 mL) and added dropwise to a solution of $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ (0.186 g, 0.321 mmol) in DMF (7 mL) over 3 min and stirred for 30 min. Diethyl ether (20 mL) was then added to the dark red solution and the suspension was allowed to stand for 10 min. After filtration the diethyl ether was removed under reduced pressure. Then EtOH (8 mL) was added to the solution at 4°C for 48 h. The resulting dark red microcrystalline solid was filtered off in air and dried in vacuo. Yield: 0.183 g, (58%). FT-IR (cm^{-1}): (Mo=O), 945(vs), 933(s); (P=O), 1251(w), 1121 (vs), 1077 (s); $\nu(\text{CS}_2)$, 1071(s), 1054(vs), 857(w), 915 (w); $\nu(\text{Mo-S})_b$, 462 (s); $\nu(\text{C=O})$, 1637(vs). ^1H NMR (CD_2Cl_2) δ , ppm: δ 8.12 (q, $J = 9.68$ Hz, 4H, C-H_o), 7.98 (s, 2H, C-H), 7.77 (dd, $J = 7.82, 12.35$ Hz, 4 H, C-H_o, 2 H, C-H_p), 7.62 (d, $J = 8.53$ Hz, 4 H, C-H_m, 2 H, C-H_p), 7.50–7.36 (m, 4H, C-H_m), 2.88 (s, 6H, CH₃), 2.73 (s, 6H, CH₃). ^{31}P NMR (CD_2Cl_2) δ , ppm: 48.8 (s, split). ^{13}C NMR (CD_2Cl_2) δ , ppm: 163.6 (s, C(O)H), 135.0, 134.7 (d, d, $^4\text{J}(\text{P}-\text{C}_p)$ 3.0 Hz, 3.0 Hz), 133.3, 133.1, (d, d, $^2\text{J}(\text{P}-\text{C}_o)$ 10.1 Hz, 10.1 Hz), 129.9, 129.5, (d, d, $^3\text{J}(\text{P}-\text{C}_m)$ 13.1 Hz, 13.1 Hz), 126.1 (d, $^1\text{J}(\text{P}-\text{C}_i)$ 126.2 Hz), 37.0 (s, C-H₃); 31.9 (s, C-H₃). UV/Vis (CH_2Cl_2 solution, $1.82 \cdot 10^{-5}\text{M}$), nm: 270 ($32,292\text{ M}^{-1}\text{cm}^{-1}$), 292(sh), 328(sh), 376 ($42,215\text{ M}^{-1}\text{cm}^{-1}$). Anal. Calc. for $\text{C}_{32}\text{H}_{34}\text{Mo}_2\text{N}_2\text{O}_6\text{P}_2\text{S}_6$: C, 38.87; H, 3.47; N, 2.83. Found: C, 39.15; H, 3.61; N, 2.95%.

$[\text{Mo}_2\text{O}_2(\mu\text{-S})_2[\text{Bn}_2\text{P}(\text{O})\text{CS}_2]_2(\text{C}_3\text{H}_7\text{NO})_2]$, 2. $[\text{Me}_4\text{N}][\text{Bn}_2\text{P}(\text{O})\text{CS}_2]$ (0.22 g, 0.64 mmol) was dissolved in DMF (5 mL) and added dropwise to a stirred solution of $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]$ (0.185 g, 0.32 mmol) in DMF (5 mL) and stirred for 1 h. After filtration, diethyl ether (25 mL) was added to precipitate Me_4NCl and the suspension was allowed to stand for 10 min. After filtration, DMF and diethyl ether were removed under reduced pressure. The dark red oil was dissolved in acetonitrile (5 mL) and diethyl ether (30 mL) was added. The resulting dark red solid was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.2 g (69%). FT-IR (cm^{-1}): $\nu(\text{P}=\text{O})$, 1251(w), 1080(vs); $\nu(\text{CS}_2)$, 1071(vs), 1054(vs); $\nu(\text{Mo=O})$, 932(s); $\nu(\text{Mo-S})_b$, 463; $\nu(\text{C=O})$, 1640(vs). ^1H NMR (CDCl_3) δ , ppm: 7.99 (s, 2H, C-H), 7.47 (d, $J = 6.31$ Hz, 2H, C-H_o), 7.44–7.29 (m, 6H, C-H_o, 2H, C-H_p), 7.00 (t, $J = 7.81$ Hz, 4H, C-H_m, 2H, C-H_p), 6.93 (d, $J = 4.77$ Hz, 4H, C-H_m), 4.00–3.85 (m, 2H, C-H₂), 3.76 (q, $J = 13.95$ Hz, 2H, C-H₂), 3.54–3.41 (m, 4H, C-H₂), 2.94 (s, 6H, C-H₃), 2.86 (s, 6H, C-H₃). ^{31}P NMR (CD_2Cl_2): δ 73.71 (s, split). ^{13}C NMR (D_2O) δ , ppm: 240.5 (d, $^1\text{J}(\text{P}-\text{CS}_2)$ 59.42 Hz), 162.29 (s, C(O)H), 130.55, 130.36 (d, d, $^3\text{J}(\text{P}-\text{C}_o)$ 6.17 Hz, 4.93 Hz), 129.5, 128.01 (d, d, $^2\text{J}(\text{P}-\text{C}_i)$ 8.83 Hz, 9.24 Hz), 128.38 (s, C_m, br), 128.19 (s, C_m, br), 127.07 (d, $^5\text{J}(\text{P}-\text{C}_p)$ 2.13Hz), 126.94 (s, C_p, br), 34.82 (d, $^1\text{J}(\text{P}-\text{CH}_2)$ 60.49 Hz), 35.79 (s, C-H₃), 33.6 (d, $^1\text{J}(\text{P}-\text{CH}_2)$

63.59 Hz), 30.79 (s, C–H₃). UV/Vis (DMF, 5·10^{−5} M): 271 (13,814 M^{−1}cm^{−1}), 310(sh), 364 (12,562 M^{−1}cm^{−1}). ESI-MS: [M + H]⁺ = C₃₀H₂₈Mo₂O₄P₂S₆ (m/z = 902.7979); found m/z = 902.7846. Anal. Calc. for C₃₀H₂₈Mo₂O₄P₂S₆: C 41.37, H 4.05, N 2.68. Found: C 41.65, H 4.07, N 2.31.

4.3. Catalytic Experiments

The progress of the catalytic sulfur atom transfer reactions was monitored by ¹H NMR spectroscopy, recorded on a Bruker AVANCE 400 MHz spectrometer. Samples were prepared aerobically by mixing together thiirane and deuterated solvent in a screw cap NMR tube. Initial ¹H NMR spectrum was recorded at ambient temperature and pressure to obtain a blank spectrum. A pre-weighed amount of solid catalyst (0.01 mmol) was added to the NMR tube and ¹H NMR spectrum was recorded. The progress of the reaction was monitored for the first few hours to determine conversion of thiirane to alkene. Control reactions, under the same conditions but in the absence of catalyst, showed no identifiable alkene formation over the time period of the catalytic runs. Reagent concentration was obtained and related to solvent by integration as an internal standard in the beginning of the reaction, without catalyst. Conversion was determined as a decrease in the concentration of thiirane by integration of NMR resonances.

Example catalyst runs: (a) **1** + C₆H₁₀S in CD₂Cl₂. Deuterated dichloromethane (0.75 mL) and cyclohexene sulfide (0.010 mol, 0.0050 mol, 0.0033 mol, or 0.0010 mol). (b) **2** + C₆H₁₀S in CDCl₃. Deuterated chloroform (0.75 mL) and cyclohexene sulfide (0.010 mol, 0.0050 mol, 0.0033 mol or 0.0010 mol). Example SAT reaction progress is shown in S15. (c) (Me₄N)₂[Mo₂O₂(μ-S)₂(Cl)₄] + C₆H₁₀S in CD₃CN. Deuterated acetonitrile (0.75 mL) and cyclohexene sulfide (0.010 mol, 0.0050 mol, 0.0033 mol, or 0.0010 mol). (d) **1** + C₃H₆S in CD₂Cl₂. Deuterated dichloromethane (0.75 mL) and propylene sulfide (0.010 mol or 0.033 mol). (e) **2** + C₃H₆S in CDCl₃. Deuterated chloroform (0.75 mL) and propylene sulfide (0.033 mol, 0.020 mol, 0.010 mol, 0.0050 mol, or 0.0010 mol).

4.4. X-ray Crystallography

X-ray-quality single crystals were obtained by liquid–liquid diffusion of ethanol into a DMF solution of **1**. The crystals were isolated from their mother liquor, immediately immersed in cryogenic oil and mounted. The X-ray single-crystal data were collected using MoKα radiation (λ = 0.71073 Å) on a Bruker D8Venture (Photon100 CMOS detector) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at a temperature of 150(2) K. The unit cell determination, data collection, data reduction, structure solution/refinement, and empirical absorption correction (SADABS) were carried out using Apex-III [57]. The structure was solved by direct method and refined by full-matrix least squares in F₂ for all data using SHELXTL [58] and Olex2 [59] software. All non-disordered non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in the calculated positions and refined in riding model.

5. Conclusions

Two phosphinoyldithioformate molybdenum complexes with different organic substituents on the phosphorous were synthesized and characterized. X-ray crystallography of **1** confirmed S,O-bidentate coordination and coordinated DMF ligands to complete octahedral geometry. Spectroscopic data confirmed that **1** and **2** are very flexible, non-rigid molecules, and an indication of S,O-bidentate, S,S-bidentate, and S-singly bonded coordination of the ligand to molybdenum was confirmed by IR and multinuclear NMR spectroscopy. Variable ³¹P NMR study revealed three coordination isomers for **1** and two for **2**.

The efficiency of **1** and **2** in catalytic SAT reactions was studied under homogeneous reaction conditions for various catalyst loadings, confirming that they are efficient unidirectional SAT catalysts. The lower catalytic activity of **1** is presumably caused by increased stability of a symmetric coordination of the ligand that is present for **1** and not for **2** in solu-

tion. The catalytic abilities of the complexes appear closely tied to the non-rigid behavior of the ligands controlled by the organic substituent on the phosphorous. The differences in the observed catalytic activity for cyclohexene sulfide and propylene sulfide with **2** are considered to be caused by one of two things: A reversible sulfur transfer reaction or substrate coordination. The slower reaction for propylene sulfide suggests reversibility of this reaction since no evidence was found for propylene sulfide coordination in NMR or mass spectra.

The reversibility of this reaction is under further study with additional substrates and organic substituents on the phosphorous. In the presented study, the complexes were found to transfer sulfur and elemental sulfur was formed. The intermediate complex with the extra sulfur atom was identified in the mass spectrum and the complexes were found intact post-reaction. In this regard, a promising system for further studies was established.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050593/s1>, Tables S1–3 of crystallographic data collection, bond distances and angles for **1**, and Figures S1 and S2 of IR spectra, Figure S3 of Raman spectra of **1** and **2**, Figures S4–S7 of variable temperature ^1H NMR spectra of **1** and **2**, Figures S4–S8 of variable temperature ^{31}P NMR spectra and analysis. Figure S8 of catalytic reaction data for $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cl})_4]^{2-}$, Figures S9–S12 of mass spec data, Figures S13 and S14 of NMR data, Figure S15 of SAT reaction progress. CheckCIF file for **1**. CCDC depository number for crystal data of **1** is 2051629.

Author Contributions: Conceptualization, D.R., H.I.I., and S.G.S.; data curation, D.R., H.I.I., Á.K., and S.J.; formal analysis, D.R. and H.I.I.; funding acquisition, S.G.S.; investigation, D.R., H.I.I., Á.K., S.J., and S.G.S.; methodology, D.R. and H.I.I.; project administration, S.G.S.; resources, Á.K., S.J., and S.G.S.; software, Á.K. and S.J.; supervision, S.G.S.; validation, D.R. and S.G.S.; visualization, Á.K. and S.G.S.; writing—original draft, D.R. and S.G.S.; writing—review and editing, D.R., Á.K., and S.G.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Icelandic Centre of Research, grant number 173667 and by University of Iceland Research Fund. The Icelandic Centre of Research infrastructure grant number (X-ray diffractometer; 150998-0031).

Acknowledgments: Gissur Örlygsson at the Innovation Center of Iceland is thanked for help with Raman data collection. Krishna K. Damodaran, the Department of Chemistry, University of Iceland, is acknowledged for the single crystal X-ray analysis of **1**.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Rakowski Dubois, M. Catalytic Applications of Transition-Metal Complexes with Sulfide Ligands. *Chem. Rev.* **1989**, *89*, 1–9. [CrossRef]
2. Topsøe, H.; Clausen, B.S. Importance of Co-Mo-S Type Structures in Hydrodesulfurization. *Catal. Rev.* **2007**, *26*, 395–420. [CrossRef]
3. Adam, W.; Bargon, R.M. Synthesis of Thiiranes by Direct Sulfur Transfer: The Challenge of Developing Effective Sulfur Donors and Metal Catalysts. *Chem. Rev.* **2004**, *104*, 251–262. [CrossRef]
4. Garrett, B.R.; Click, K.A.; Durr, C.B.; Hadad, C.M.; Wu, Y. $[\text{MoO}(\text{S}_2)_2\text{L}]$ (L = picolinate or pyrimidine-2-carboxylate) Complexes as MoS_x Inspired Electrocatalysts for Hydrogen Production in Aqueous Solution. *J. Am. Chem. Soc.* **2016**, *138*, 13726–13731. [CrossRef] [PubMed]
5. Young, C.G. Facets of early transition metal-sulfur chemistry: Metal-sulfur ligand redox, induced internal electron transfer, and the reactions of metal-sulfur complexes with alkynes. *J. Inorg. Biochem.* **2007**, *101*, 1562–1585. [CrossRef]
6. Donahue, J.P. Thermodynamic Scales for Sulfur Atom Transfer and Oxo-for-Sulfido Exchange Reactions. *Chem. Rev.* **2006**, *106*, 4747–4783. [CrossRef] [PubMed]
7. Kuwata, S.; Hidai, M. Hydrosulfido complexes of transition metals. *Coord. Chem. Rev.* **2001**, *213*, 211–305. [CrossRef]
8. Stiefel, E.I. Transition Metal Sulfur Chemistry: Biological and Industrial Significance and Key Trends. In *Transition Metal Sulfur Chemistry*; ACS Symposium Series; American Chemical Society: Washington, WA, USA, 1996; pp. 2–38.
9. Liu, H.; Jiang, X. Transfer of Sulfur: From Simple to Diverse. *Chem.—Asian J.* **2013**, *8*, 2546–2563. [CrossRef]

10. Nakano, K.; Tatsumi, G.; Nozaki, K. Synthesis of Sulfur-Rich Polymers: Copolymerization of Episulfide with Carbon Disulfide by Using [PPN]Cl/(salph)Cr(III)Cl System. *J. Am. Chem. Soc.* **2007**, *129*, 15116–15117. [\[CrossRef\]](#)
11. Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. Optical material of high refractive index resin composed of sulfur-containing aliphatic and alicyclic methacrylates. *J. Appl. Polym. Sci.* **2000**, *76*, 45–49. [\[CrossRef\]](#)
12. Rys, A.Z.; Harpp, D.N. Catalytic sulfuration of dienes with metallocene polysulfides. *Tetrahedron Lett.* **1998**, *39*, 9139–9142. [\[CrossRef\]](#)
13. Farrell, W.S.; Zavalij, P.Y.; Sita, L.R. Catalytic Production of Isothiocyanates via a Mo(II)/Mo(IV) Cycle for the “Soft” Sulfur Oxidation of Isonitriles. *Organometallics* **2016**, *35*, 2361–2366. [\[CrossRef\]](#)
14. Adam, W.; Bargon, R.M.; Schenk, W.A. Direct Episulfidation of Alkenes and Allenes with Elemental Sulfur and Thiiranes as Sulfur Sources, Catalyzed by Molybdenum Oxo Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 3871–3876. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Adam, W.; Bargon, R.M.; Bosio, S.G.; Schenk, W.A.; Stalke, D. Direct Synthesis of Isothiocyanates from Isonitriles by Molybdenum-Catalyzed Sulfur Transfer with Elemental Sulfur. *J. Org. Chem.* **2002**, *67*, 7037–7041. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Ooi, M.L.; Lim, C.E.; Wong, R.C.S.; Ng, S.W. Isolation and characterization of thiolato complexes of [CpCr(SBz)]₂S, isomeric trans [CpMo(CO)(SBz)]₂ and [CpMo(SBz)]₂ (Cp = (η⁵-C₅H₅), Bz = PhCH₂) from the reactivity of bibenzyl disulfide towards [CpM(CO)₃]₂ (M = Cr, Mo). *Inorg. Chim. Acta* **2017**, *467*, 364–371. [\[CrossRef\]](#)
17. Pétilion, F.Y.; Schollhammer, P.; Talarmin, J. Recent advances in the chemistry of tris(thiolato) bridged cyclopentadienyl dimolybdenum complexes. *Coord. Chem. Rev.* **2017**, *331*, 73–92. [\[CrossRef\]](#)
18. Ward, J.P.; Lim, P.J.; Evans, D.J.; White, J.M.; Young, C.G. Tungsten Ligand-Based Sulfur-Atom-Transfer Catalysts: Synthesis, Characterization, Sustained Anaerobic Catalysis, and Mode of Aerial Deactivation. *Inorg. Chem.* **2020**, *59*, 16824–16828. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Sugimoto, H.; Tajima, R.; Sakurai, T.; Ohi, H.; Miyake, H.; Itoh, S.; Tsukube, H. Reversible Sulfurization–Desulfurization of Tungsten Bis(dithiolene) Complexes. *Angew. Chem. Int. Ed.* **2006**, *45*, 3520–3522. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Eagle, A.A.; Gable, R.W.; Thomas, S.; Sproules, S.A.; Young, C.G. Sulfur atom transfer reactions of tungsten(VI) and tungsten(IV) chalcogenide complexes. *Polyhedron* **2004**, *23*, 385–394. [\[CrossRef\]](#)
21. Ibdah, A.; Jenks, W.S.; Espenson, J.H. Kinetics, Mechanism, and Computational Studies of Rhenium-Catalyzed Desulfurization Reactions of Thiiranes (Thioepoxides). *Inorg. Chem.* **2006**, *45*, 5351–5357. [\[CrossRef\]](#)
22. Arisawa, M.; Ichikawa, T.; Yamaguchi, M. Synthesis of thiiranes by rhodium-catalyzed sulfur addition reaction to reactive alkenes. *Chem. Commun.* **2015**, *51*, 8821–8824. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Arisawa, M.; Tanaka, K.; Yamaguchi, M. Rhodium-catalyzed sulfur atom exchange reaction between organic polysulfides and sulfur. *Tetrahedron Lett.* **2005**, *46*, 4797–4800. [\[CrossRef\]](#)
24. Moon, S.; Kato, M.; Nishii, Y.; Miura, M. Synthesis of Benzo[b]thiophenes through Rhodium-Catalyzed Three-Component Reaction using Elemental Sulfur. *Adv. Synth. Catal.* **2020**, *362*, 1669–1673. [\[CrossRef\]](#)
25. Huang, C.Y.; Doyle, A.G. The chemistry of transition metals with three-membered ring heterocycles. *Chem. Rev.* **2014**, *114*, 8153–8198. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Li, M.; Ellern, A.; Espenson, J.H. Rhenium(V) Complexes with Thiolato and Dithiolato Ligands: Synthesis, Structures, and Monomerization Reactions. *Inorg. Chem.* **2005**, *44*, 3690–3699. [\[CrossRef\]](#)
27. Koshino, N.; Espenson, J.H. Kinetics and Mechanism of Oxygen Atom Transfer from Methyl Phenyl Sulfoxide to Triarylphosphines Catalyzed by an Oxorhenium(V) Dimer. *Inorg. Chem.* **2003**, *42*, 5735–5742. [\[CrossRef\]](#)
28. Birgisson, B.O.; Monger, L.J.; Damodaran, K.K.; Suman, S.G. Synthesis and characterization of asymmetric [Mo₂O₂(μ-S)₂(S₂)(L)] complexes (L = bipy, en, dien) and their heterogeneous reaction with propylene sulfide. *Inorg. Chim. Acta* **2020**, *119272*. [\[CrossRef\]](#)
29. Dave, M.; Rajagopal, A.; Damm-Rüttensperger, M.; Schwarz, B.; Nägele, F.; Daccache, L.; Fantauzzi, D.; Jacob, T.; Streb, C. Understanding homogeneous hydrogen evolution reactivity and deactivation pathways of molecular molybdenum sulfide catalysts. *Sustain. Energy Fuels* **2018**, *2*, 1020–1026. [\[CrossRef\]](#)
30. Coucouvanis, D. Syntheses, Structures, and Reactions of Binary and Tertiary Thiomolybdate Complexes Containing the (O)Mo(S_x) AND (S)Mo(S_x) Functional Groups (x = 1, 2, 4). In *Advances in Inorganic Chemistry*; Sykes, A.G., Ed.; Academic Press: Cambridge, MA, USA, 1998; Volume 45, pp. 1–73.
31. McKee, M.L. Fluxional Molecules. *Wires Comput. Mol. Sci.* **2011**, *1*, 943–951. [\[CrossRef\]](#)
32. Faller, J.W. Fluxional and Nonrigid Behavior of Transition Metal Organometallic π-Complexes. In *Advances in Organometallic Chemistry*; Stone, F.G.A., West, R., Eds.; Academic Press: Cambridge, MA, USA, 1977; Volume 16, pp. 211–239.
33. Scorzelli, A.G.; Macalush, B.E.; Naik, D.V.; Moehring, G.A. Comparative study of fluxional processes at two different classes of eight-coordinate rhenium(V) polyhydride complexes. *Inorg. Chim. Acta* **2021**, *516*, 120120. [\[CrossRef\]](#)
34. Ólafsson, S.N.; Kvaran, Á.; Jonsdóttir, S.; Suman, S.G. Non-rigid coordination behavior of the ambidentate phosphinoyldithioformate ligands, [S₂CP(O)R₂][−], (R = Ph, CH₂Ph) in organometallic Lead(IV) and Mercury(II) compounds. *J. Organomet. Chem.* **2018**, *854*, 38–48. [\[CrossRef\]](#)
35. Ólafsson, S.N.; Björnsson, R.; Helgason, Ö.; Jonsdóttir, S.; Suman, S.G. Coordination geometry determination of stannane compounds with phosphinoyldithioformate ligands using multinuclear NMR, Sn Mössbauer and DFT methods. *J. Organomet. Chem.* **2016**, *825–826*, 125–138. [\[CrossRef\]](#)

36. Suman, S.G.; Gretarsdottir, J.M.; Penwell, P.E.; Gunnarsson, J.P.; Frostason, S.; Jonsdottir, S.; Damodaran, K.K.; Hirschon, A. Reaction Chemistry of the syn-Mo₂O₂(μ-S)₂(S₂)(DMF)₃ Complex with Cyanide and Catalytic Thiocyanate Formation. *Inorg. Chem.* **2020**. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Coucouvanis, D.; Toupadakis, A.; Lane, J.D.; Koo, S.M.; Kim, C.G.; Hadjikyriacou, A. Reactivity of the Mo(O)(S) functional group in the [(L)Mo(O)(μ-S)₂Mo(O)(S)]_n- dimeric thiomolybdate complexes, (L = C₅H₅—, *n* = 1; S₄2-, *n* = 2) and implications regarding the function of xanthine oxidase. Synthesis and structural characterization of [(DMF)₃Mo(O)(μ-S)₂Mo(O)(S₂)], [Ph₄P][[(C₅H₅)Mo(O)(μ-S)₂Mo(O)(S₂)], [Ph₄P]₂[(S₄)Mo(O)(μ-S)₂Mo(O)(S)] and (Et₄N)₄[[[(S₄)Mo(O)(μ-S)₂Mo(O)(S)]₂]. *J. Am. Chem. Soc.* **1991**, *113*, 5271–5282. [\[CrossRef\]](#)
38. Ólafsson, S.N.; Flensburg, C.; Andersen, P. Lead(IV) complexes with phosphinoyldithioformates, R₂P(O)CS₂~ (R = Ph or PhCH₂). Syntheses and characterization. Crystal structures of PPh₂[S₂CP(O)Ph₂]-0.5H₂O, [PbPh₂[S₂CP(O)Ph₂]₂] and [PbPh₂Cl[S₂CP(O)Ph₂]]. *J. Chem. Soc. Dalton Trans.* **2000**, 4360–4368. [\[CrossRef\]](#)
39. Djordjevic, C.; Vuletic, N.; Jacobs, B.A.; Lee-Renslo, M.; Sinn, E. Molybdenum(VI) Peroxo α-Amino Acid Complexes: Synthesis, Spectra, and Properties of MoO(O₂)₂(α-aa)(H₂O) for α-aa = Glycine, Alanine, Proline, Valine, Leucine, Serine, Asparagine, Glutamine, and Glutamic Acid. X-ray Crystal Structures of the Glycine, Alanine, and Proline Compounds. *Inorg. Chem.* **1997**, *36*, 1798–1805. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Clegg, W.; Mohan, N.; Mueller, A.; Neumann, A.; Rittner, W.; Sheldrick, G.M. Crystal and molecular structure of [N(CH₃)₄]₂[Mo₂O₂S₂(S₂)₂]: A compound with two S₂²⁻ ligands. *Inorg. Chem.* **1980**, *19*, 2066–2069. [\[CrossRef\]](#)
41. Singh, V.; Kumar, A.; Prasad, R.; Rajput, G.; Drew, M.G.B.; Singh, N. The interplay of secondary Hg···S, Hg···N and Hg···π bonding interactions in supramolecular structures of phenylmercury(II) dithiocarbamates. *CrystEngComm* **2011**, *13*, 6817–6826. [\[CrossRef\]](#)
42. Ólafsson, S.N.; Petersen, T.N.; Andersen, P. Crystal structure of diphenylbis(diphenyldithio-phosphinato)lead(IV), PbPh₂(S₂PPh₂)₂. *Acta Chem. Scand.* **1996**, *50*, 745–748. [\[CrossRef\]](#)
43. Ogienko, D.S.; Smolentsev, A.I.; Bashirov, D.A.; Afonin, M.Y.; Petrov, P.A.; Konchenko, S.N. Syntheses and structures of complexes {Mo₂S₂O₂}₂⁺ with labile Cl[−] and DMF ligands. *Russ. J. Coord. Chem.* **2015**, *41*, 759–764. [\[CrossRef\]](#)
44. Denney, D.B.; Boskin, M.J. Concerning the Mechanism of the Reaction of Trisubstituted Phosphines with Episulfides. *J. Am. Chem. Soc.* **1960**, *82*, 4736–4738. [\[CrossRef\]](#)
45. Yoo, B.W.; Kim, J.Y. Selective and efficient desulfurization of thiiranes with Mo(CO)₆. *J. Sulfur Chem.* **2020**, *41*, 13–18. [\[CrossRef\]](#)
46. Caló, V.; Lopez, L.; Nacci, A.; Mele, G. Aminium Salts Induced Desulphurization of Allyl and Diallyl Thiiranes. Synthesis of Dienes and Trienes. *Tetrahedron* **1995**, *51*, 8935–8940. [\[CrossRef\]](#)
47. Arterburn, J.B.; Perry, M.C. Rhenium catalyzed sulfurization of phosphorus(III) compounds with thiiranes: New reagents for phosphorothioate ester synthesis. *Tetrahedron Lett.* **1997**, *38*, 7701–7704. [\[CrossRef\]](#)
48. Nishiyama, Y.; Nakagawa, Y.; Mizuno, N. High Turnover Numbers for the Catalytic Selective Epoxidation of Alkenes with 1 atm of Molecular Oxygen. *Angew. Chem. Int. Ed.* **2001**, *40*, 3639–3641. [\[CrossRef\]](#)
49. Jacob, J.; Espenson, J.H. Stereospecific rhenium catalyzed desulfurization of thiiranes. *Chem. Commun.* **1999**, 1003–1004. [\[CrossRef\]](#)
50. Nguyen, T.B. Recent Advances in Organic Reactions Involving Elemental Sulfur. *Adv. Synth. Catal.* **2017**, *359*, 1066–1130. [\[CrossRef\]](#)
51. Wang, J.-J.; Kryatova, O.P.; Rybak-Akimova, E.V.; Holm, R.H. Comparative Kinetics and Mechanism of Oxygen and Sulfur Atom Transfer Reactions Mediated by Bis(dithiolene) Complexes of Molybdenum and Tungsten. *Inorg. Chem.* **2004**, *43*, 8092–8101. [\[CrossRef\]](#)
52. Dubois, M.R. Carbon-chalcogen bond cleavage reactions characterized for dinuclear sulfur-bridged cyclopentadienyl molybdenum complexes. *Polyhedron* **1997**, *16*, 3089–3098. [\[CrossRef\]](#)
53. Romano, F.; Linden, A.; Mba, M.; Zonta, C.; Licini, G. Molybdenum(VI) Amino Triphenolate Complexes as Catalysts for Sulfoxidation, Epoxidation and Haloperoxidation. *Adv. Synth. Catal.* **2010**, *352*, 2937–2942. [\[CrossRef\]](#)
54. Gabay, J.; Dietz, S.; Bernatis, P.; DuBois, M.R. Dinuclear cyclopentadienylmolybdenum complexes containing thioether ligands. Ligand substitution and desulfurization reactions. *Organometallics* **1993**, *12*, 3630–3635. [\[CrossRef\]](#)
55. Cabon, N.; Le Goff, A.; Le Roy, C.; Pétillon, F.Y.; Schollhammer, P.; Talarmin, J.; McGrady, J.E.; Muir, K.W. Transformations and Agostic Interactions of Hydrocarbyl Ligands Bonded to the Sulfur-Rich Dimolybdenum Site {Mo₂Cp₂(μ-SMe)₃}: Chemical and Electrochemical Formation of μ-Alkyl and μ-Vinyl Compounds from a μ-Alkylidene Derivative. *Organometallics* **2005**, *24*, 6268–6278. [\[CrossRef\]](#)
56. Cabon, N.; Pétillon, F.Y.; Orain, P.-Y.; Schollhammer, P.; Talarmin, J.; Muir, K.W. Controlled nucleophilic activation of different sites in [Mo₂Cp₂L₂(μ-SMe)₂(μ-L')]⁺ cations (L = ButNC, xyINC, CO; L' = SMe or PPh₂). *J. Organomet. Chem.* **2005**, *690*, 4583–4601. [\[CrossRef\]](#)
57. Bruker. *Apex III*; Bruker AXS Inc.: Madison, WI, USA, 2015.
58. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [\[CrossRef\]](#)
59. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [\[CrossRef\]](#)