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Carbon–chalcogen bond cleavage reactions characterized for dinuclear sulfur-bridged cyclopentadienyl molybdenum complexes

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Abstract—The types of carbon–chalcogen bond cleavage reactions which have been characterized for dinuclear cyclopentadienylmolybdenum complexes are reviewed. The reactions include both the homolytic cleavage and the protonolysis of carbon–chalcogen bonds in neutral μ-thiolate derivatives of Mo^{III}, nucleophilic cleavage of carbon–chalcogen bonds in certain cationic derivatives of Mo^{III} or Mo^{IV}, and the reactions of certain dinuclear complexes with molecular hydrogen. Unique features of the sulfur-bridged complexes which contribute to this versatile reaction chemistry are discussed. © 1997 Elsevier Science Ltd

Keywords: molybdenum; sulfur; dinuclear; hydrogenolysis; protonolysis; C–S bond cleavage.

The removal of organosulfur impurities from crude petroleum is accomplished by means of heterogeneous molybdenum sulfide catalysts which incorporate small amounts of sulfided cobalt or nickel species as promoters. The complex nature of the surface catalysts is one factor that limits the mechanistic investigations of these reactions. Nevertheless, kinetic studies of the heterogeneous reaction systems as well as model studies of homogeneous organometallic systems have led to the proposal of several related mechanisms for the hydrodesulfurization of thiophene [1–10]. The key reaction in this transformation is the net hydrogenolysis of the carbon–sulfur bonds of the substrate to produce hydrocarbon products and hydrogen sulfide. The proposed mechanisms have suggested possible pathways for the activation of molecular hydrogen and of thiophene by interaction with the catalyst surface, but the mechanism for carbon–sulfur bond cleavage and the pathways for hydrogen transfer on the surface catalysts are still quite speculative.

Dinuclear cyclopentadienyl molybdenum complexes with bridging sulfido ligands have been extensively studied, and their potential to undergo reactions similar to those proposed for the heterogeneous catalysts have been investigated. One of the earliest reactions identified for these structures was the reversible binding of alkenes to sulfido ligands to form dimers with μ-alkanedithiolate ligands [11a]. The reverse dissociation of the alkene under very mild conditions provided one of the first examples of facile carbon–sulfur bond cleavage in a synthetic molybdenum sulfide complex [11b]. In later reactivity studies of the dinuclear systems, several other examples of carbon–chalcogen bond cleavage were identified, and these were found to proceed by diverse mechanisms. In this paper we present a review of the types of reactions of the dinuclear systems which involve carbon–chalcogen bond cleavage. The reactions permit us to probe the complex interactions between metal ion and sulfido sites which provide electronic characteristics crucial to the bond cleavage mechanisms, and the systems provide a basis for a better understanding of reactions of the heterogeneous metal sulfides.

Other aspects of the reactivity of the μ-sulfido molybdenum dimers which are relevant to the HDS process have been reviewed recently. These include the chemistry involving hydrogen activation and addition [12], the catalytic activity [13,14], and the reactions of a specific class of cationic dimers containing a μ-sulfido ligand [15].

DISCUSSION

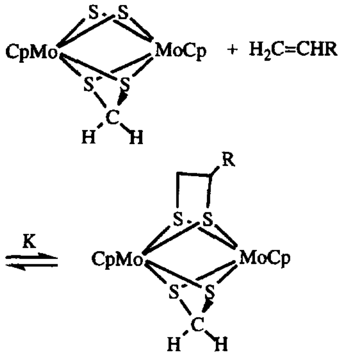
Homolytic carbon–sulfur bond cleavage

Olefin dissociation from alkanedithiolate ligands. The reversible reactions of $(CpMo\mu\text{-}S)_2S_2CH_2$ with alkenes, eq. (1), can be readily monitored by NMR

Table 1. Kinetic data for olefin dissociation reactions

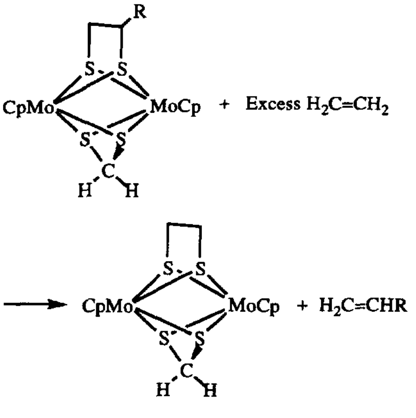
Starting complex	Reactant	Solvent	Temperature, (°C)	k (sec^{-1} × 10^4)	ΔH* (kJ/mol)	ΔS* (J/mole-K)
$[CpMoSC_2H_4S]_2$	$PhCH_2NC$	$CDCl_3$	20	0.22	102	46
$[CpMoSC_3H_6S]_2$	C_2H_4	$CHCl_3$	38	1.0		
Propene adduct of 1[a]	C_2H_4	C_6D_6	18	1.6		
	C_2H_2	$CDCl_3$	18	1.4		
1-Butene adduct of 1	C_2H_4	C_6D_6	18	1.5		
t-2-Butene adduct of 1	C_2H_4	C_6D_6	18	0.98		
	C_2H_2	$CDCl_3$	18	0.92		
c-2-Butene adduct of 1	C_2H_4	C_6D_6	18	28		
Propene adduct of 2[b]	$H_2C{=}CHSO_3^-$	D_2O	25	0.53	110	43

[a] Complex 1 is $(CpMo\mu\text{-}S)_2S_2CH_2$ (see structure in eq. (1)).
[b] Complex 2 is $(NaO_2C\text{-}CpMo\mu\text{-}S)_2S_2CH\text{-}CO_2Na$.



(1)

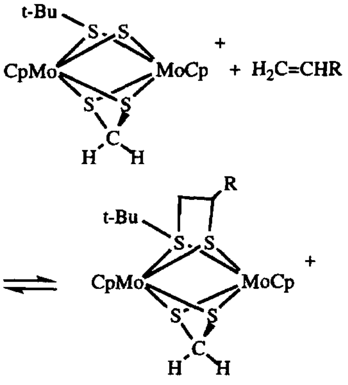
spectroscopy and equilibrium constants have been estimated from these data [16]. The constants were found to vary over a range of 0 to $>10^4$ M^{-1}. The nature of the olefin is a primary factor which influences the magnitude of K, with ethylene showing one of the largest binding constants and tetrasubstituted olefins the smallest. In addition to these steric factors, electronic effects of the olefin substituents are also important, with electron withdrawing groups on the olefin enhancing the binding properties. In order to determine kinetic and mechanistic information for the loss of alkene from the ligands under irreversible conditions, the olefin dissociation reactions were carried out in the presence of a large excess of a second binding reagent, e.g. eq. (2). Rate constants for this type of reaction have been determined for a series of complexes in which the nature of the displaced olefin, the substituting reagent, the solvent and substituents on other ligands in the dimer have been varied [16]. Representative data are summarized in Table 1.



(2)

In all cases the rates of the reactions were found to be independent of the concentration of the substituting reagent, and no evidence for isomerization of the released olefin was observed. The data are consistent with a concerted dissociative mechanism for the cleavage of the C—S bonds in these systems. In almost all cases the first order rate constants at 20°C are found to be in the range from 0.5×10^{-4} to 5.0×10^{-4} sec^{-1}. The rates for the dissociation of *cis*-olefins were consistently found to be approximately an order of magnitude faster. Unfavorable steric interactions between adjacent substituents on the sp^3 hybridized carbon atoms of the *cis*-alkanedithiolate ligand may contribute to the observed lability for the *cis*-alkenes. The activation parameters determined for two of the reaction systems are also included in the table. The data show very little variation over a wide range of solvent polarities and reactant molecules.

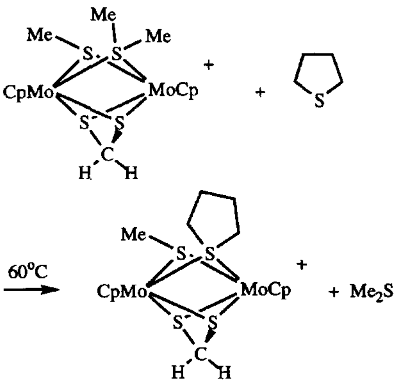
Similar reversible olefin interactions have been observed for cationic dinuclear complexes that contain bridging *t*-Bu-thiolate and sulfido ligands, eq. (3) [17]. The equilibrium constants for these reactions were found to be about two orders of magnitude smal-



(3)

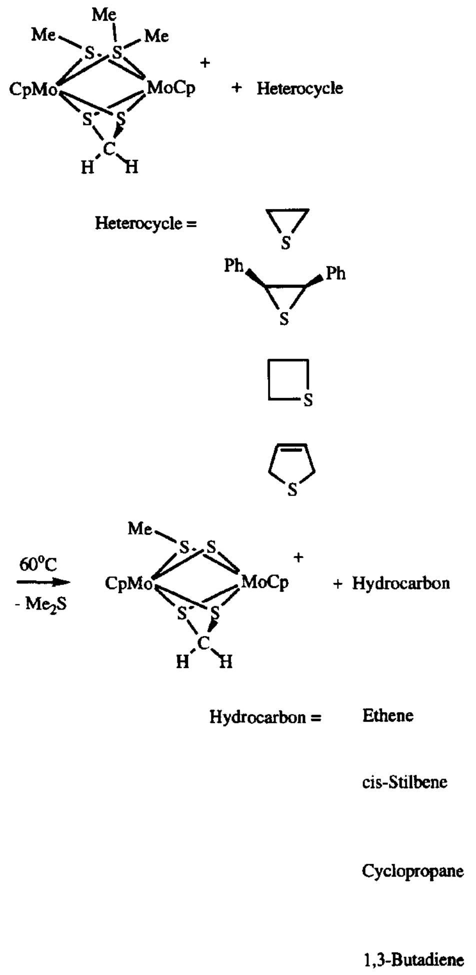
ler than those for the neutral bis(sulfido) bridged dimers, but relative contributions of k_{on} and k_{off} have not been determined for these systems. The reactions have been found to be very sensitive to the nature of the thiolate substituent; for example, similar olefin adducts have not been detected for the related dimer where μ-SR = SMe [17]. Our observations suggest that the bridging thioether ligand is relatively unstable in these dimers, and this is supported by additional studies described below.

Desulfurization of heterocycles. Sulfur abstraction from heterocyclic substrates has been achieved with coordinatively unsaturated molybdenum dimers [18]. Cationic thioether complexes, which undergo thermal dissociation of the thioether ligand, serve as precursors to the coordinatively unsaturated intermediate. A thioether substitution reaction has been demonstrated in the reaction of the dimethylsulfide complex with tetrahydrothiophene, eq. (4). The product complex with a μ-tetrahydrothiophene ligand was stable and was readily isolated and characterized by spectroscopic methods. Similar reactions of the dimethylsulfide complex with thiiranes, thietane and 2,5-dihydrothiophene are also presumed to proceed initially by thioether substitution, but the intermediate complexes with μ-heterocyclic ligands were not detected in these reactions. Intramolecular hydrocarbon elimination was observed to form the μ-sulfido bridged cation and the corresponding organic product shown in eq. (5).



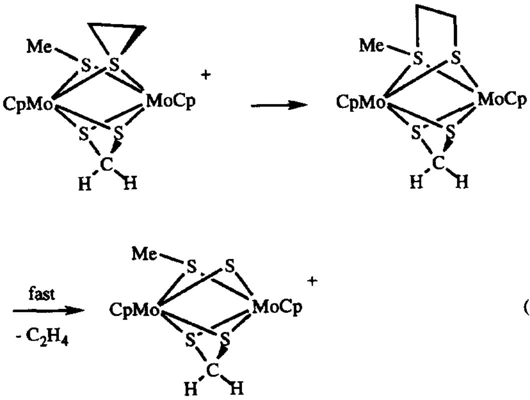
(4)

Mechanistic aspects of reactions of episulfides with metal surfaces [19,20], metal clusters [21–23], and discrete metal complexes [24–26] have been studied previously. Examples of ring opening of the episulfide ligand through nucleophilic attack have been observed, and mechanisms for the olefin elimination involving either a concerted pathway, or a stepwise opening of the coordinated episulfide to give a diradical intermediate have been proposed for the different systems. In the reaction of the molybdenum dimer with *cis*-stilbene sulfide, only the *cis* isomer of stilbene was formed [18]. Since inversion of a radical carbon center should be very facile, this stereoselectivity suggests that a stepwise homolytic cleavage of C—S bonds in the thiirane is unlikely here, and favors the concerted elimination of hydrocarbon from a μ-episulfide ligand. A similar concerted pathway might be considered for the hydrocarbon elimination reactions from coordinated thietane and dihydrothiophene as well, but mechanistic aspects of these reactions have not been studied.



(5)

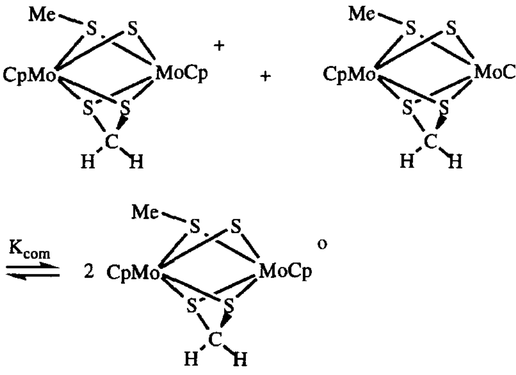
An alternate stepwise mechanism for the elimination of olefin from the episulfide complex may also be considered. The first step could involve a ring opening induced by (stereospecific) nucleophilic attack of the adjacent thiolate ligand, eq. (6). The resulting



(6)

intermediate is known to undergo facile olefin dissociation [17]. However there currently is no basis for extending a similar mechanistic proposal to the reactions with the other ring sizes. Eliminations of cyclopropane from 1,3-propanedithiolate ligands or of butadiene from 1,4-butenedithiolate ligands have not been characterized independently.

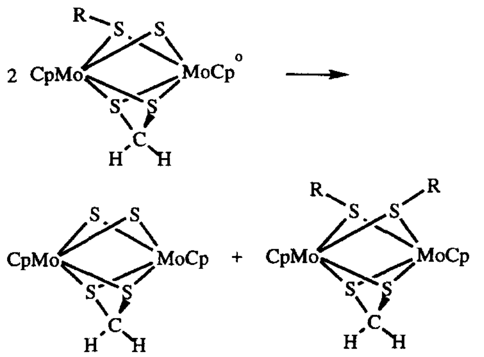
Alkyl transfer reactions. The one electron reduction of stable μ-thiolate cations produces mixed valence $\mathrm{Mo^{III}/Mo^{IV}}$ derivatives of the formula $[\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-SR})]$ [27]. The product can also be prepared by the reaction of equimolar amounts of the $\mathrm{Mo^{IV}}$ cation and the anionic $\mathrm{Mo_{III}}$ derivative, eq. (7).



(7)

The comproportionation equilibrium constant for this reaction, which can be determined from the cyclic voltammetric data, has been found to be very large for these systems, e.g. for R = Me, $K_{\mathrm{com}} = 10^{15}$ [28]. The value is consistent with a completely delocalized distribution of the unpaired electron between the two metal ions in the mixed valence product. Other spectroscopic and reactivity studies of these complexes suggest that the unpaired electron occupies a molecular orbital of primarily metal character with little contribution from the sulfido ligand. The complexes generally do not show reactivity at the μ-sulfido ligand characteristic of thiyl radicals [27].

Despite the large value for K_{com}, the mixed valence derivatives are kinetically labile. A primary pathway for their decomposition is through an alkyl transfer reaction that results in valence disproportionation to $\mathrm{Mo^{III/III}}$ and $\mathrm{Mo^{IV/IV}}$ products, eq. (8) [29]. The reaction involves a net homolytic cleavage of the thiolate carbon–sulfur bonds. The disproportionation was very slow at room temperature and was carried out at 60°C in THF when R was Me [29], but the reaction occurred readily at room temperature when R was an electron withdrawing substituent [30, 31].

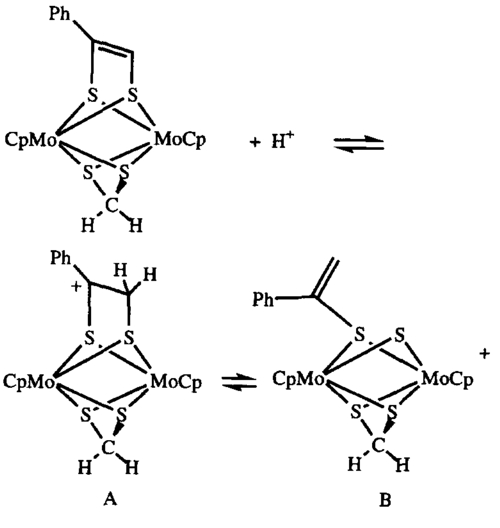


(8)

The reaction of $[\mathrm{Cp}^{\ddagger}_2\mathrm{Mo_2(CO)_4}]$ with $\mathrm{Me_2S_2}$ in toluene at 80°C led to the formation of a sulfido bridged derivative $[\mathrm{Cp}^{\ddagger}_2\mathrm{Mo_2(CO)_2}(\mu\text{-SMe})_2(\mu\text{-S})]$, which was characterized by an X-ray diffraction study [32]. Possible intermediates in the formation of this product have been discussed.

Cleavage of carbon–chalcogenide bonds by electrophilic attack

Reactions of dithiolate complexes with protic acid. Dinuclear molybdenum complexes with bridging alkenedithiolate ligands reacted with protic acid to give an equilibrium mixture of isomers shown in eq. (9) [33]. The major isomer, B, which results from carbon–sulfur bond cleavage, has been characterized by an X-ray diffraction study, Fig. 1. The α-phenylvinyl substituent is directed away from the sulfido bridge in an equatorial configuration, indicating that inversion at the thiolate sulfur atom has occurred subsequent to protonolysis. No evidence was observed in this system for the product resulting from protonolysis of the sulfur–carbon bond containing the phenyl substituent. However cleavage of a substituted alkenedithiolate bond has been observed in the related protonolysis of the complex containing the 2-butenedithiolate ligand.



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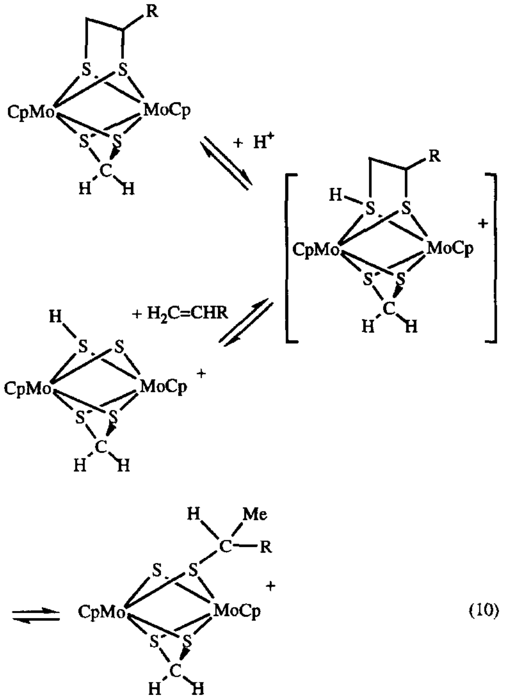
A similar room temperature protonolysis reaction has been observed for the dinuclear complexes containing alkanedithiolate ligands, eq. (10). The result-



(10)

ing cations with μ-thiolate ligands have also been prepared by addition of alkene to the hydrosulfido bridged cation, and a common intermediate with a μ-thiolate-thiol ligand has been proposed, but not detected spectroscopically [34]. The olefin insertion into the hydrosulfido ligand occurred regioselectively, and Markovnikov addition products were found to be the kinetic products of addition. In reactions with several substituted olefins, rearrangements of the kinetic products to the anti-Markovnikov structures were observed at room temperature, providing evidence for the reversibility of the olefin insertion.

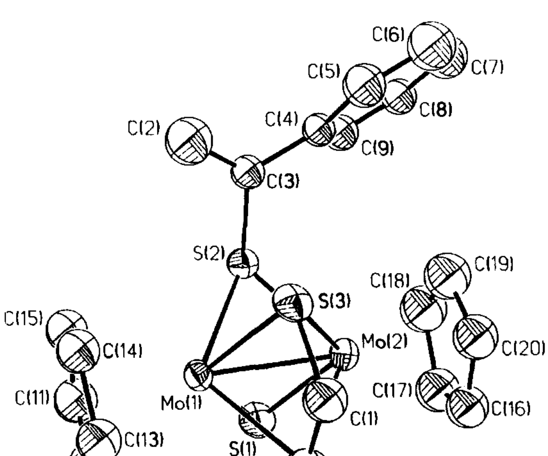
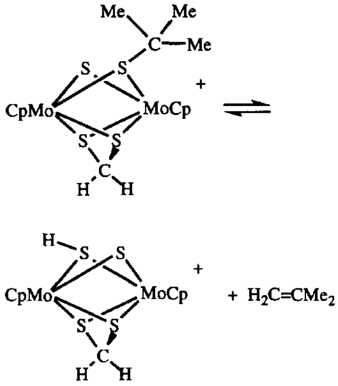


Fig. 1. Thermal ellipsoid plot of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph){=}CH_2)]^+$. Reprinted with permission from [33]. Copyright © 1986, American Chemical Society.

The reverse reaction of olefin deinsertion involves an additional example of a C—S bond cleavage which was studied in more detail using the complex with the *t*-butylthiolate ligand [17]. In this system, the equilibrium between the μ-thiolate cation and the hydrosulfido complex, eq. (11), could be monitored by

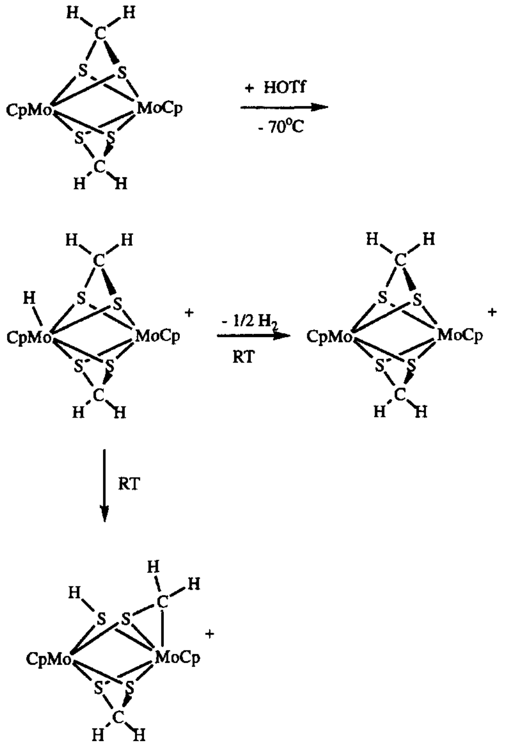


(11)

NMR spectroscopy. Thermodynamic information on the carbon–sulfur bond cleavage reaction has been obtained by the determination of equilibrium constants over a temperature range of 20–70°C. The value of K_{eq} at 20°C was found to be $(3.2 \pm 0.5) \times 10^{-4}$ M, and the values for ΔH and ΔS were estimated to be 47 kJ/mol and 95 J/mole-K, respectively. The reaction, which involves a β-hydrogen transfer from thiolate to adjacent sulfido ligand, provides a facile mechanism for the cleavage of C—S bonds in sulfur rich complexes, which may be applicable to reactions on metal sulfide surfaces as well.

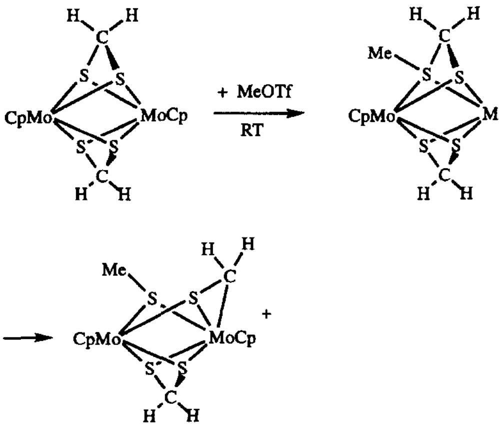
In the reactions of dithiolate bridged dimers with acid, selective protonation of the 1,2-dithiolate ligand has been observed in preference to reaction with the methanedithiolate bridge also present in the complexes. The selectivity could reflect a greater degree of reversibility for protonation of the methanedithiolate sulfur, or a lower basicity for this ligand. Reversibility seems unlikely in view of the strain imposed by the small S—C—S angle of this ligand. Perhaps a lower basicity of the 1,1-dithiolate ligand is related to this small angle and the potential for intraligand sulfur–sulfur bonding interactions. The S···S distance in this ligand has been found to be in the range 2.67–2.72 Å [27,30,33,35].

Reactions of protic acid with dinuclear Mo^{III} complexes which contain only 1,1-dithiolate ligands have also been studied. For example, when $[CpMoS_2CH_2]_2$ was reacted with triflic acid at −70°C, NMR data suggested the formation of a new Mo—H intermediate [36]. Upon warming to room temperature, a one electron oxidation of the complex was observed along with the formation of H_2, eq. (12). In addition



(12)

to the products of the redox reaction, a second minor product was formed as a result of a rearrangement when the solution was warmed to room temperature. Spectroscopic data for this isomeric complex suggested a new structure with a hydrosulfido ligand and a η^2-thioformaldehyde ligand. Although this complex was not successfully isolated and characterized further, an analogous product was formed in high yield in the reaction of $[CpMoS_2CH_2]_2$ with methyl triflate, eq. (13). An X-ray diffraction study of the



(13)

methylated product confirmed that the carbon–sulfur bond cleavage reaction resulted in the formation of a thioformaldehyde ligand, Fig. 2. A new molybdenum–carbon bond was formed with the ligand, which was

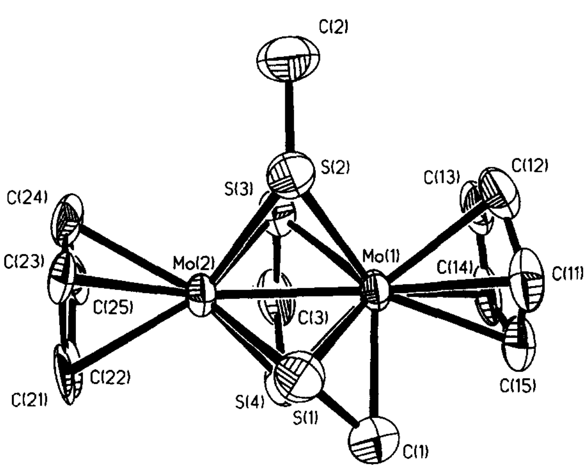
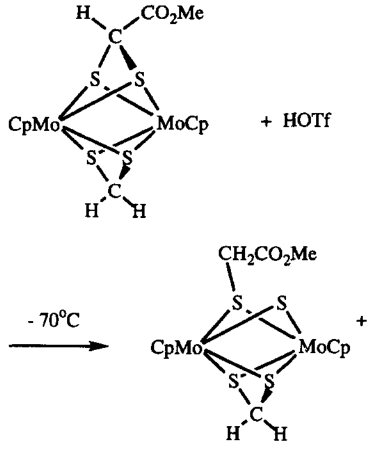


Fig. 2. Thermal ellipsoid plot of $[(CpMo)_2(S_2CH_2)(\mu\text{-SMe})(\mu\text{-}\eta^1,\eta^2\text{-SCH}_2)]^+$. Reprinted with permission from [36]. Copyright © 1992, American Chemical Society.

η^2-bonded to one molybdenum ion and η^1-bonded to the second.

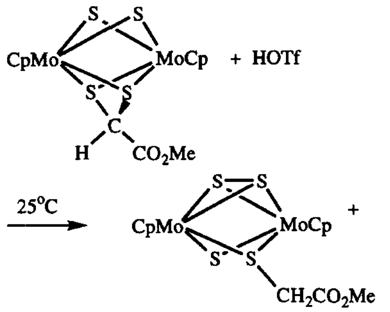
When the methanedithiolate ligand in these dimers is substituted with an electron withdrawing group, it becomes more susceptible to electrophilic cleavage of a C—S bond. Similar electronic effects were observed for monothiolate ligands (see below). For example, the Mo^{III} complex with an ester substituted dithiolate ligand reacted regioselectively with triflic acid to form the thiolate bridged cation, as shown in eq. (14) [36].



(14)

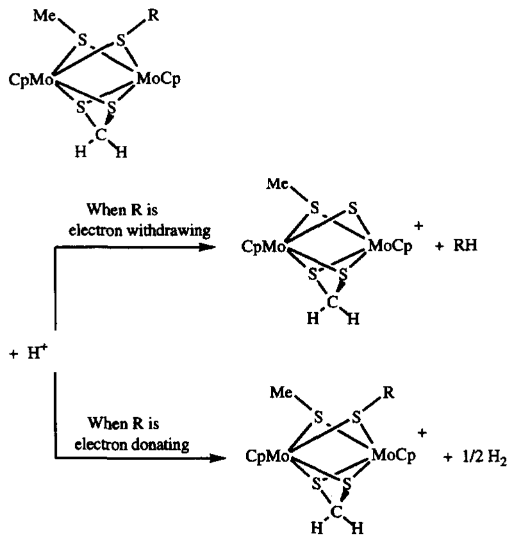
No evidence for metal ion protonation and oxidation was observed in this system. This is consistent with our observation that the electron withdrawing substituent increases the oxidation potential of the complex by *ca* 110 mV, relative to that of the parent complex in eq. (12).

An unusual example of a protonolysis of a carbon–sulfur bond in a Mo^{IV} dimer has also been characterized for the ester substituted 1,1-dithiolate ligand, eq. (15) [37]. An X-ray diffraction study of the product


(15)

cation has confirmed the presence of the μ-η^2-disulfide ligand. In contrast, the methanedithiolate ligand in the parent complex is quite stable under acidic conditions. Protonation of the latter derivative occurs at a sulfido ligand; the resulting cationic μ-SH complex has a pK_a of 7.4 in acetonitrile [38].

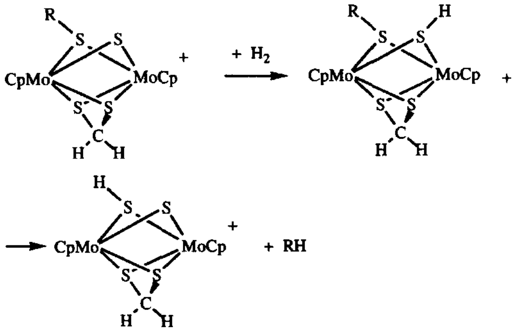
Reactions of protic acid with monothiolate bridged complexes. Protonolysis reactions have also been extended to dinuclear Mo^{III} complexes with bridging monothiolate ligands, eq. (16) [39]. The reactions were favored for thiolate substituents with electron withdrawing character; these can be proposed to shift electron density from metal and sulfur to stabilize carbanionic character in the thiolate carbon. Initial protonation at a thiolate sulfur is tentatively proposed on the basis of the reactions described in the preceding paragraphs, but these intermediates have not been detected spectroscopically.



(16)

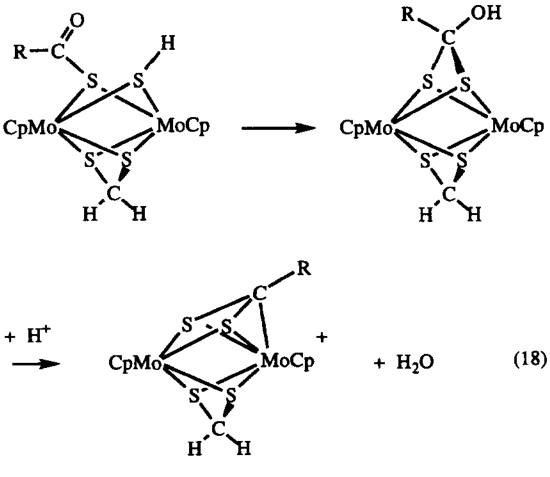
In contrast, the reactions of protic acid with bis(thiolate) derivatives that contained more electron donating substituents, (e.g. R = Me, Et) resulted in a one-electron oxidation of the dimer to form mixed valence Mo^{III} Mo^{IV} derivatives. The latter oxidation reactions are believed to involve initial protonation at a metal ion site by analogy to the observed intermediate in eq. (12).

Several thiolate bridged cations with electron withdrawing substituents, R, react with hydrogen to give carbon–sulfur bond hydrogenolysis products, as shown in eq. (17) [39]. The actual carbon–sulfur bond cleavage in the Mo^{III} intermediate is proposed to proceed by protonolysis, with the reactive proton being produced by heterolytic cleavage of hydrogen by the cation. Indeed when the hydrogen activation reaction is carried out in the presence of a base to serve as proton acceptor, the C—S bond of the thiolate ligand remains intact, and the hydrosulfido derivative proposed as an intermediate in eq. (17) is observed as a final product in some systems.


(17)

R = C_4H_3S, CH(Me)Ph, CH_2Ph, CH_2CO_2Me, C(O)CH_3, C(O)Ph

Cleavage of carbon–oxygen bonds by electrophilic attack. Because the reactions of cationic dinuclear complexes with molecular hydrogen result in the heterolytic activation of dihydrogen and formation of H^+, further applications of the protonolysis reaction have been observed for reactions under a hydrogen atmosphere. For example, $(CpMo\mu\text{-}S)_2S_2CH_2$ reacts reversibly with acyl halides to form acylthiolate derivatives [31]. These products are in equilibrium with the starting reagents and have not been isolated. However under a hydrogen atmosphere the acylthiolate cations react at room temperature according to the pathway proposed above, eq. (17), to produce the aldehyde product. A second competing reaction is also observed, which results in the formation of H_2O and a molybdenum complex containing a dithioacetate ligand, eq. (18). The competing mechanism is proposed to involve intramolecular insertion of the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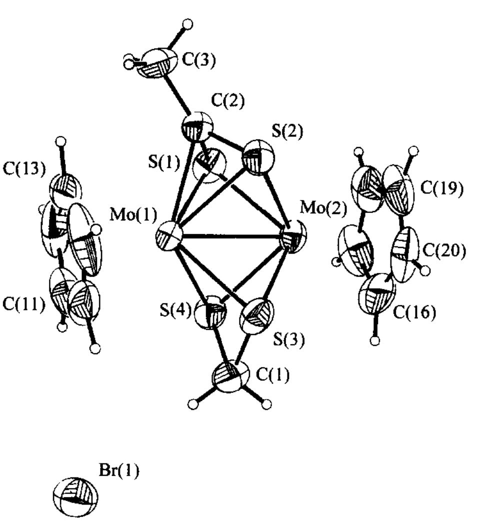
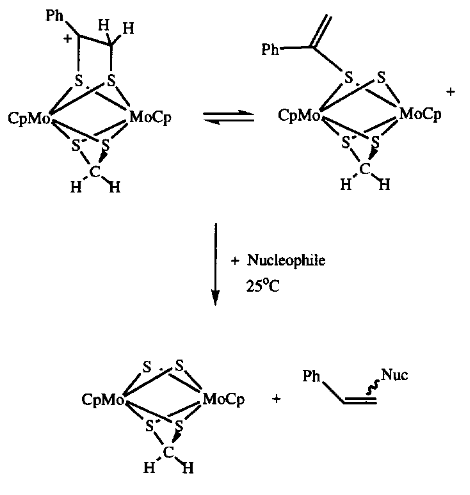


Fig. 3. Thermal ellipsoid plot of $[(CpMo)_2(S_2CH_2)(\mu\text{-}\eta^2, \eta^3\text{-}S_2CCH_3)]^+$. Reprinted with permission from [31]. Copyright © 1987, American Chemical Society.

C=O bond into the S—H ligand of the initial hydrogen activation product. Protonolysis of the resulting hydroxy-dithiolate ligand leads to the formation of the observed products. The crystal structure of the molybdenum product is shown in Fig. 3.

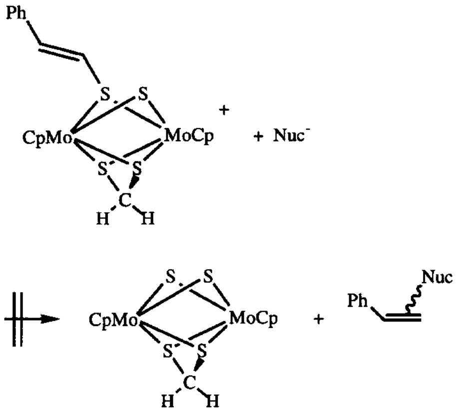
Carbon–chalcogen bond cleavage promoted by nucleophiles

Nucleophilic cleavage of carbon–sulfur bonds in thiolate and thioether ligands. Although much of the chemistry of the dinuclear molydenum(III) complexes is dominated by electrophilic reactions, a few examples of carbon–chalcogen bond cleavage promoted by nucleophilic attack have also been identified. The most notable examples involve the nucleophilic cleavage of protonated alkenedithiolate ligands, as shown in eq. (19) [33]. The reaction was limited to relatively non-basic nucleophiles, such as alcohols, chloride, and nitrite ions, and the regiochemistry of the nucleophilic attack was found to vary with the nucleophile. More basic nucleophiles cannot be used in these reactions because they deprotonate the cationic derivatives to regenerate the neutral alkenedithiolate complex. Similar nucleophilic displacements were found to occur with the analogous mixture of isomers containing the protonated 2-butenedithiolate ligand. The mechanisms of these reactions have not been established.



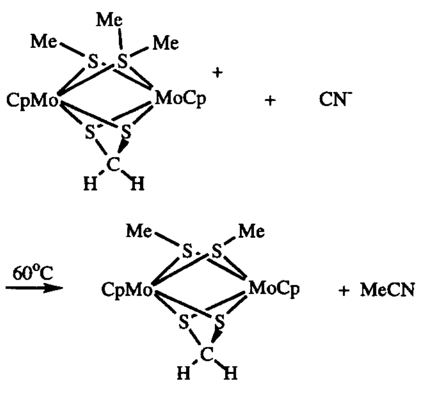
(19)

The isomeric cation with the 2-phenylethenethiolate ligand was prepared by the reaction of β-bromostyrene with the sulfido bridged dimer $(CpMo\mu\text{-}S)_2S_2CH_2$ [30]. It is interesting that this cation does not undergo similar nucleophilic substitution reactions to produce a free substituted alkene, eq. (20). No reactions were observed with non-basic nucleophiles such as chloride ion or methanol, while reaction with methoxide or hydride led to the one electron reduction of the cation. The absence of a substituent on the α carbon atom in the ligand may contribute to the differences in the chemistry. For example, NMR studies of this cation over a temperature range of −50 to +75°C showed no evidence for an equilibrium with a second isomer such as that shown in eq. (19). This is probably a result of the lower potential stabilization of the carbonium ion at an unsubstituted carbon site.



(20)

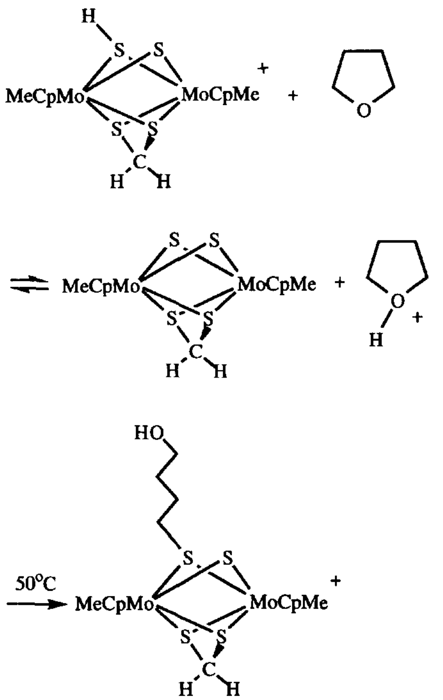
In previous work with other metal complexes and clusters, thioether ligands in bridging bonding modes have been found to be susceptible to nucleophilic cleavage [40,41]. Similar reactions have been identified for the dinuclear molybdenum complexes with both the cyclic tetrahydrothiophene and acyclic dialkyl-



(21)

sulfide ligands, e.g., eq. (21) [18]. The nucleophilic attack appears to be a fairly general reaction for bridging thioether ligands and a facile example of C—S bond cleavage.

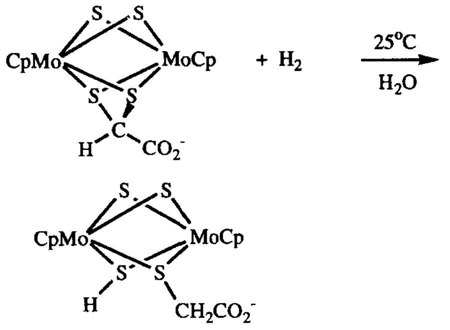
Nucleophilic cleavage of carbon–oxygen bonds. Facile cleavage of carbon–oxygen bonds in certain ethers has also been characterized for reactions with the cationic derivative $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$ [42]. The reactions occur as a result of the strongly acidic character of this complex coupled with the nucleophilic properties of its conjugate base. The initial protonation of the ether by the hydrosulfido ligand has been monitored by visible spectroscopy. Nucleophilic attack by the sulfido ligand in the neutral complex on the protonated cyclic ether, such as tetrahydrofuran, leads to ring opening and formation of a new complex with a μ-hydroxythiolate ligand, eq. (22). Similar pathways have been identified for reactions with epoxides, trimethylene oxide, and certain acyclic ethers.



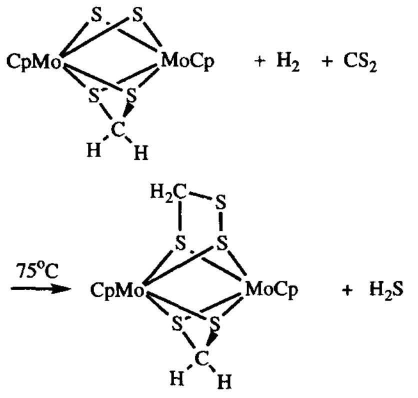
(22)

Hydrogenolysis of carbon–sulfur bonds

In a preceding section the heterolytic activation of hydrogen by *cationic* dinuclear complexes was discussed, and the formation of a proton in this reaction was found to be important in a number of carbon-chalcogen bond cleavage reactions. Other examples of the cleavage of carbon–sulfur bonds in reactions with molecular hydrogen have been observed with neutral and anionic dinuclear molybdenum complexes, eqs (23) and (24) [37,43]. In these cases the nature of the hydrogen activation reaction has not been established. The transformations serve to demonstrate the versatility of the dinuclear complexes in their reactions with molecular hydrogen.



(23)



(24)

CONCLUSIONS

The dinuclear cyclopentadienyl molybdenum complexes with μ-sulfido ligands are characterized by a high structural stability and reversible electron transfer processes which provide access to multiple metal ion oxidation states. As a result of these properties, a wide range of reactions that vary in their electronic characteristics have been identified for these systems. Most of the carbon–chalcogen bond cleavage reactions of coordinated ligands reported for these derivatives occur in dimers with formal metal oxidation state of +III. The relatively low oxidation level appears to promote protonolysis reactions of coordinated ligands and homolytic S—C bond cleavage. Intramolecular M–L electron transfer in the latter pathways produces stable products with formal oxidation states at molybdenum of +IV. The ability to cycle between formal metal ion oxidation states appears to be an important characteristic for promoting ligand based reactions at the sulfido sites. Accessibility to multiple metal oxidation levels is a feature common to the heterogeneous metal sulfide catalysts. The reactions of the molecular complexes reviewed here provide important models for ways in which several different mechanisms for carbon–chalcogen bond cleavage may be achieved on the heterogeneous catalysts.

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