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Catalytic Applications of Transition-Metal Complexes with Sulfide Ligands

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Contents

I. Introduction

Sulfur-containing compounds have long been known to act as a poison for noble metal catalysts because of their strong coordinating and adsorptive properties, which cause them to block reactive metal sites.[1] Nevertheless, many transition-metal sulfides (S^{2-}) display intriguing catalytic activity in their own right.[2] For example, several of the nonmolecular metal sulfides provide surfaces that activate molecular hydrogen and catalyze the reductive transformations of organic molecules.[2-4] Hydrogenations of unsaturated and aromatic hydrocarbons and hydrogenolyses of molecules with carbon–sulfur, carbon–oxygen, and carbon–nitrogen bonds have been catalyzed. These catalysts have therefore found extensive use in fuel processing. In the large-scale commercial hydrotreating processes, sulfided molybdenum–cobalt catalysts supported on alumina are generally the systems of choice.[5-7] The polyfunctional character of the sulfide catalysts has been noted. In addition to the reductive chemistry described above, reactions characteristic of acid catalysts, such as isomerizations, dehydrations, and hydrocracking processes, are also catalyzed by the sulfide surfaces during the hydrorefining process.[2,5-8]

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Other catalytic applications of metal sulfides are also known. Those sulfides that display semiconductor properties have been used in the development of photo- and electrocatalytic systems.[9-11] For example, WS_2 has been used both as a photocathode and as a photoanode,[12,13] and zinc and cadmium sulfides have been extensively studied as photocatalysts.[14,15] In the realm of biochemistry, sulfide ligands have been identified in the coordination spheres of the metal centers for several metalloprotein and metalloenzyme systems, including the ferredoxins, the nitrogenases[16,17] and hydrogenases,[18] and some of the molybdenum-containing hydroxylases.[19-22]

A large number of synthetic molecular transition-metal complexes with either terminal or bridging sulfide ligands have been reported. The many possible coordination modes available for sulfide ligands were summarized in an early review;[23] this versatile coordination behavior has been utilized in the development of synthetic routes to metal–sulfur cluster compounds with varied structural features.[24-26] The electronic and structural flexibility provided by one or more sulfide

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atoms ligated to a transition metal might be expected to permit catalytic activity for the synthetic molecular complexes, and it is interesting to explore to what extent this catalytic activity parallels that of the nonmolecular sulfides or that of the biological systems.

In this review the catalytic activity of soluble synthetic transition-metal complexes with sulfide ligands has been surveyed over the period from 1967 through March 1988. Stepwise stoichiometric transformations in which the metal sulfide complex has been regenerated have also been included. The level of understanding of the mechanistic features of these catalytic reactions is, in most cases, not very advanced. A discussion of the mechanisms of the reactions has been included when available, but for many systems the reports of the catalytic processes have been limited to investigations of reaction scope and of relative activities. In most cases, catalytic activities are expressed in turnover numbers (moles of product/moles of catalyst) for a given time period.

II. Sulfide Complexes That Catalyze Reactions with Hydrogen

The ability of sulfide complexes to activate molecular hydrogen and to catalyze substrate reduction by hydrogen is particularly relevant to the chemistry of the hydrotreating catalysts. Sulfide complexes that function primarily as catalysts for hydrogen addition to substrates are discussed in this section.

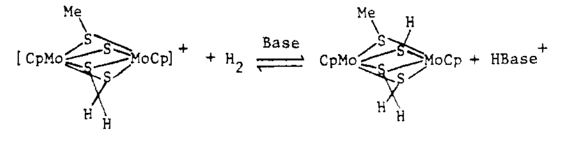
A. Complexes of Group 6 Metals

Dinuclear cyclopentadienyl molybdenum complexes with bridging sulfide ligands have been found to activate molecular hydrogen under mild homogeneous conditions. In the stoichiometric reaction of hydrogen with the Mo(IV) dimer shown in eq 1, the hydrogen–hydrogen bond was cleaved and a product with two hydrosulfido ligands was cleanly formed.[27] Although

$$(\mathrm{CpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2) + \mathrm{H}_2 \rightarrow (\mathrm{CpMo})_2(\mu\text{-S})_2(\mu\text{-SH})_2 \quad (1)$$

this product did not detectably add a second mole of hydrogen to form a stable product, it did serve as a catalyst for the formation of HD from a mixture of hydrogen and deuterium.[28] A structurally related Mo(IV) complex $(\mathrm{CpMo}(\mu\text{-S}))_2\mathrm{S}_2\mathrm{CH}_2$ also catalyzed HD exchange, even though no interaction of this complex with H_2 was detected spectroscopically.[29]

In addition to these neutral complexes, cationic molybdenum(IV) derivatives of the formula $[(\mathrm{CpMo})_2(\mathrm{S}_2\mathrm{CH}_2)(\mu\text{-S})(\mu\text{-SR})]^+$ also reacted under 1–3 atm of molecular hydrogen. Products varied, depending on the nature of R.[30-32] When R = Me, the reaction proceeded to form final products shown in eq 2.[30] The mechanisms of hydrogen interaction with the complexes in eq 1 and 2 have not been established, but the products represent a net homolytic and heterolytic cleavage of hydrogen, respectively. It is apparent that the sulfido ligands play a role in hydrogen coordination, and this ligand reactivity has been a dominant characteristic throughout the study of these dinuclear molybdenum systems.

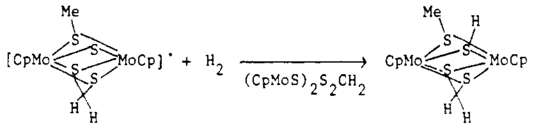


(2)

The activation of hydrogen by the neutral derivatives has been found to be useful in the catalytic hydrogenation of organic molecules. For example, $[\mathrm{CpMo}(\mu\text{-S})(\mu\text{-SH})]_2$ catalyzed the hydrogenation of N=N bonds in azo compounds to produce the corresponding hydrazines under mild conditions (for azobenzene, 10 turnovers in 1 h at room temperature).[27] Similar catalytic activity was observed for $(\mathrm{CpMo}(\mu\text{-S}))_2\mathrm{S}_2\mathrm{CH}_2$. The latter complex also catalyzed the hydrogenation of C=N bonds in imines, isocyanates, and isothiocyanates to form amines, formamides, and thioformamides, respectively. The latter reactions generally proceeded more slowly than the azobenzene reduction. Interactions of these substrates with the sulfido ligands of the catalyst have not been detected spectroscopically. Stoichiometric steps in the cyclic hydrogenation of azobenzene in the presence of $[\mathrm{CpMo}(\mu\text{-S})(\mu\text{-SH})]_2$ have been characterized and found to proceed quantitatively according to eq 1 and 3.

$$(\mathrm{CpMo})_2(\mu\text{-S})_2(\mu\text{-SH})_2 + \mathrm{PhN{=}Ph} \rightarrow (\mathrm{CpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2) + \mathrm{PhNH{-}NHPh} \quad (3)$$

Studies of stoichiometric reactions of additional related complexes with SH ligands suggested that the catalytic role of $(\mathrm{CpMo}(\mu\text{-S}))_2\mathrm{S}_2\mathrm{CH}_2$ in the azobenzene reduction involved facile hydrogen atom transfer from S-H ligands generated during the catalytic cycle.[27] The activation of hydrogen and transfer of hydrogen atoms by $(\mathrm{CpMo}(\mu\text{-S}))_2\mathrm{S}_2\mathrm{CH}_2$ was further demonstrated by the catalytic role of this complex in eq 4, which involved the reduction of a paramagnetic mixed-valence dinuclear complex.[33]



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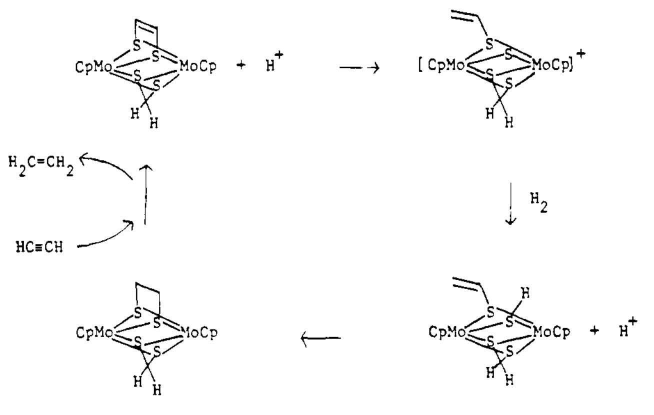
Relatively few examples of catalytic hydrogenolysis reactions have been reported for homogeneous systems containing sulfide ligands. However, the dinuclear cyclopentadienyl molybdenum complexes provide examples of the catalytic hydrogenolysis of several bond types. $[\mathrm{Me}_n\mathrm{CpMo}(\mu\text{-S})(\mu\text{-SH})]_2$ (n = 0, 1, 5) catalyzed the hydrogenolysis of elemental sulfur to hydrogen sulfide under 2–3 atm of hydrogen. For $[\mathrm{MeCpMo}(\mu\text{-S})(\mu\text{-SH})]_2$, the turnover number = 10 in 24 h at 25 °C in CHCl_3, and 800 in 24 h at 100 °C in CHCl_3/toluene.[28]

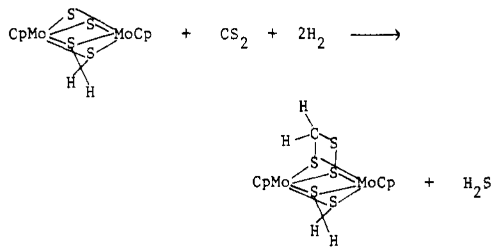
$[(\mathrm{Me}_5\mathrm{Cp})\mathrm{Mo}(\mu\text{-S})(\mu\text{-SH})]_2$ has also been reported to catalyze the reduction of sulfur dioxide in CHCl_3 at 75 °C under 2.8 atm of H_2.[34] The initial product was found to be $\mathrm{H}_2\mathrm{S}$, which rapidly reacted with excess SO_2 to yield the final observed products, S_8 and $\mathrm{H}_2\mathrm{O}$. If excess hydrogen was present, sulfur was further reduced to $\mathrm{H}_2\mathrm{S}$, and this source of $\mathrm{H}_2\mathrm{S}$ provided a second simultaneous cycle for SO_2 reduction. $\mathrm{H}_2\mathrm{S}$ production from S_8 was probably not dominant in this system since catalytic activity decreased with time. The use of a weakly basic solvent, such as an alcohol, or addition of catalytic amounts of Brønsted bases, such as amines, promoted the reaction (e.g., 355 turnovers/h). The base

Scheme I



promotion suggested that deprotonation of the SH complex followed by electrophilic attack of SO_2 on a sulfide ligand of the complex may be an initial step in the reduction.

The complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ catalyzed the reduction of carbon disulfide to hydrogen sulfide and thioformaldehyde under 1–2 atm of H_2 at 70 °C.[35] The latter product was stabilized by interaction with the sulfido ligands in the catalyst (eq 5). At 70 °C the



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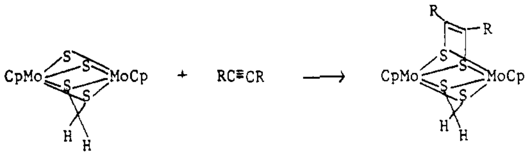
thioformaldehyde adduct slowly dissociated to form trithiane and regenerate the original catalyst. An additional reaction of the thioformaldehyde adduct with hydrogen, which generated the original molybdenum complex and uncharacterized organic products, was also observed at this temperature.

The hydrogenolysis of N–O bonds has also been catalyzed by $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ and $(CpMo(\mu\text{-}S))_2S_2CH_2$.[27] Nitrobenzenes were converted to anilines (22 turnovers/day, room temperature); phenylhydroxylamine was observed as an intermediate in the process. The catalytic reduction of nitrosobenzene in the presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$ led to the formation of azoxybenzene through the initial formation of phenylhydroxylamine and its coupling with excess nitrosobenzene. Azoxybenzene was further reduced to diphenylhydrazine under these conditions (8 turnovers in 1 h at room temperature). The reduction of *o*-nitrobenzaldehyde resulted in the clean formation of anthranil (6 turnovers in 1 h at room temperature).

The reactions of cationic dinuclear molybdenum complexes with hydrogen have also led to substrate reduction. For example, the stepwise reductions of alkynes to the corresponding *cis*-alkenes, which have been carried out in the presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$,[36] involve cationic intermediates. In these cases the substrates formed stable adducts with the bridging sulfide ligands of the complex (eq 6). Catalytic amounts of protic acid were required for further reaction of the adducts with molecular hydrogen. The role of acid appeared to be to cleave a carbon–sulfur bond of the alkenedithiolate ligand. Such a protonation reaction to form the alkenylthiolate-bridged cation has been characterized in detail with the phenylacetylene adduct (eq 7).[30] The cationic complexes reacted with molecular hydrogen, as discussed above. Note that the acid catalyst was also regenerated in this step. Although a hydrosulfido-bridged product was not detected in the hydrogenation of the alkenylthiolate-bridged cations, it was proposed as a likely intermediate, which reacted further to form, in some cases, the alkene adduct (Scheme I). Facile displacement of alkene by alkyne re-formed the original alkenedithiolate complex. Allene and ketene adducts also reacted with hydrogen in chloroform solution to form alkenes and aldehydes, respectively.[36] A similar mechanism is presumed in these reactions.



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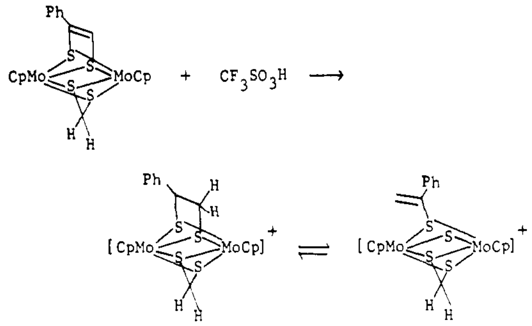

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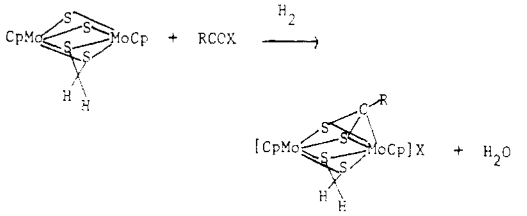
The hydrogenolysis of carbon–halogen bonds in the presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$ has also been shown to proceed through the intermediacy of cationic derivatives. β-Bromostyrene and bromoethylbenzene were catalytically converted to ethylbenzene in the presence of $(CpMo(\mu\text{-}S))_2S_2CH_2$ under hydrogen pressures of 2–3 atm.[31] Intermediate steps were shown to involve alkylation of a bridging sulfide ligand by the organic halide to form $[(CpMo)_2S_2CH_2(\mu\text{-}S)(\mu\text{-}SR)]^+$ (R = $CH{=}CHPh$ or CHPhMe). The cationic derivatives were found to react with hydrogen to form the final products. A similar sulfide alkylation of the dinuclear complex by methyl bromoacetate or 2-bromobutanone led to the cations $[(CpMo)_2S_2CH_2(\mu\text{-}S)(\mu\text{-}SCH_2COR)]^+$ (R = OMe, Et). Under an atmosphere of hydrogen at room temperature these cations reacted slowly to form methyl acetate or 2-butanone, respectively, $(CpMo(\mu\text{-}S))_2S_2CH_2$, and protons.[32] In the attempted continuous catalytic reduction of methyl bromoacetate in chloroform, turnover numbers were low (2.5–5/day) because of a competing protonation of the catalyst that resulted in a product of limited solubility. In the reaction of excess methyl chloroformate with $(CpMo(\mu\text{-}S))_2S_2CH_2$ under hydrogen, no cationic intermediate with an alkylated sulfide ligand was detected.[32] However, slow catalytic hydrogenolysis of the methyl chloroformate to methyl formate was observed (17 turnovers in 24 h, 70 °C).

The catalytic reductions of acetyl chloride, benzoyl chloride, and phenylacetyl chloride under 2–3 atm of hydrogen to form the corresponding aldehydes were also carried out with $(CpMo(\mu\text{-}S))_2S_2CH_2$ as a catalyst.[32] In the acyl halide reactions, catalytic turnovers were limited by a competing stoichiometric process that involved hydrogenolysis of the carbon–oxygen bond of the acyl group and formation of a catalytically inactive complex of the formula $[CpMo(S_2CH_2)(S_2\overline{CR)M}oCp]^+$ (eq 8).[32]



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Catalytic activity for a mononuclear tungsten sulfide complex has been observed. The seven-coordinate complex $W(S_2CNR_2)_2(S)(\eta^2\text{-}S_2)$ (R = Et) was reported to be a catalyst or catalyst precursor for the removal of sulfur from dibenzothiophene in decalin solution at 350 °C under a flow of hydrogen.[37]

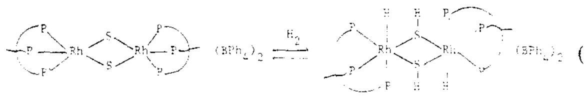
B. Complexes of Groups 8–10

Complexes of the noble metals have been extensively developed as hydrogenation catalysts, and several examples of sulfide clusters and complexes with these metal ions have been found to show catalytic activity under hydrogen.

The largest sulfide-containing cluster to be studied for its catalytic applications is $[Rh_{17}S_2(CO)_{32}]^{3-}$, which contains an antiprismatic arrangement of rhodium atoms with two sulfide atoms located in an interlayer cavity. This cluster was found to catalyze the reduction of phenylglyoxal to (2-hydroxyethyl)benzene in the presence of hydrogen (1 atm) at 25 °C in THF (59 turnovers in 150 h).[38] Under much more rigorous conditions, the catalytic conversion of CO/H_2 (1:1) to ethylene glycol and methanol was achieved in the presence of the cluster catalyst and base promoters.[39,40] For example, rates of product formation at 280 °C under 15 000 psi H_2/CO in 18-crown-6 with 1.5 mmol of rhodium (as the sulfide cluster), 7.0 mmol of *N*-methylmorpholine, and 0.125 mmol of cesium benzoate were 1.34 M/h for ethylene glycol and 0.89 M/h for methanol. Spectroscopic studies indicated that the cluster may in fact serve as the catalytically active species. The anion was found by FT-IR studies to be stable under catalytic conditions, and high recoveries (>90%) of the cluster were achieved after catalytic runs. Fourier subtraction of IR spectra taken before and after a catalytic run showed very weak absorptions attributed to $[Rh_{17}S_2(CO)_{32}H_m]^{3-m}$.[41]

The complex $Ir_2H_2(\mu\text{-}S)(CO)_2(dpm)_2$ (dpm = bis(diphenylphosphino)methane) was prepared by the oxidative addition of H_2 to the A-frame complex $Ir_2(\mu\text{-}S)(CO)_2(dpm)_2$.[42] Product isomers with both bridging and terminal hydride ligands were characterized. The hydride complex served as a catalyst for acetylene and olefin hydrogenation in toluene solutions at 80 °C. Under a pressure of 300 Torr of H_2 and 300 Torr of acetylene, ethylene, or propylene, the rates of ethane or propane formation were 1.2, 6.7, and 2.9 mol of product (mol of catalyst)$^{-1}$ h^{-1}, respectively. The hydride complex could be recovered quantitatively after the hydrogenation reactions.

Hydrogen activation by a dinuclear rhodium complex with bridging sulfide ligands has been observed at 25 °C (eq 9).[43] The reaction provides another example of hydrogen coordination by a sulfide ligand during or following the process of hydrogen activation. However, catalytic hydrogenations based on this system have not been reported to date.



(9)

The chelating phosphine ligand = $MeC(CH_2PPh_2)_3$

A tetranuclear palladium cluster with sulfide ligands, $(\eta^3\text{-}2\text{-}CH_3C_3H_4Pd)_4S_2$, has been synthesized from the reaction of $(\eta^3\text{-}2\text{-}CH_3C_3H_4)_2Pd$ and H_2S.[44] The structure was postulated to involve a square-planar or tetrahedral array of metal ions capped by μ_4- or μ_3-sulfide ligands, respectively. The cluster served as a homogeneous catalyst, or catalyst precursor, for the hydrogenation of 3-hexyne at ambient pressure and temperature (50 turnovers/<20 h).[45] The initial product was *cis*-3-hexene, which isomerized under reaction conditions. Related mixed-metal palladium–nickel and palladium–platinum clusters with sulfide ligands were insoluble in the reaction medium and showed lower catalytic activity.

The trinuclear complex $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(C_2H_4)_2]PF_6$ was prepared from the reaction of $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ with $[Rh(C_2H_4)_2Cl]_2$.[46] X-ray diffraction studies of related complexes indicated that the metal–metal distances of 3.0–3.3 Å were longer than those associated with single Pt–Rh bonds. The complex was therefore described as an aggregate rather than a cluster. The catalytic activity of the aggregate for cyclohexene hydrogenation under 1 atm of H_2 at 25 °C was approximately 1/500 the rate of $Rh(PPh_3)_3Cl$. No evidence was observed for cooperative effects resulting from the aggregation of the three metal ions.

The iron–sulfide cluster $[Fe_4S_4Cl_4]^{2-}$ which has been treated with excess phenyllithium has been found to react with molecular hydrogen at room temperature.[47] When 12 equiv of phenyllithium/iron cluster was used, the uptake of 2.3 mol of hydrogen/cluster was observed. Lower ratios of phenyllithium led to lower hydrogen uptake numbers. No characterization data have been reported for the hydrogen-rich cluster, but the system has been used as a hydrogenation catalyst. For example, under 1 atm of H_2 at 0 °C with 10–16 equiv of PhLi, the cluster catalyzed the hydrogenation of diphenylacetylene and *cis*- and *trans*-stilbene to the corresponding alkane (e.g., 15 turnovers of *cis*-stilbene/30 min).[48] The lability of the chloride ligands was believed to be important in this system since related clusters with thiolate ligands, e.g., $[Fe_4S_4(SPh)_4]^{2-}$, were not catalytically active under similar reducing conditions. In further studies the $[Fe_4S_4Cl_4]^{2-}$/PhLi system was found to catalyze the reduction of octenes to octanes and under certain conditions to selectively promote the hydrogenation of terminal double bonds in systems of monoenes and dienes.[49] Selectivity was controlled by adjusting the PhLi/cluster ratio.

The reaction of the iron cubane cluster $[Fe_4S_4(SPh)_4]^{2-}$ with 2 mol of H_2 in DMF has been reported,[50] but this result could not be confirmed by another laboratory.[51] The reduced form of the cluster, $[Fe_4S_4$-

$(SPh)_4]^{4-}$, produced from a reaction with excess acenaphthylide, catalyzed the formation of HD from H_2 and D_2 in hexamethylphosphoramide.[50] Equilibrium ratios were reached in 2 days. Similar H/D exchange activity was observed for a reduced form of a mixed-metal sulfide cluster that contained two $MoFe_3$ cubane units, $[Mo_2Fe_6S_8(SPh)_9]^{5-}$.

III. Sulfide Complexes That Catalyze Hydride Additions or Electron Transfers

A. Iron–Sulfide Clusters

Iron–sulfur cubane clusters of the general formula $[Fe_4S_4(SR)_4]^{n-}$[52] have been widely investigated as catalysts for reductions of a variety of substrates by hydride or electron donors. The presence of these cluster types in the ferrodoxin proteins, which function in many biological electron-transfer processes, has provided much of the impetus for these studies.

1. Chemical Reductions

$[Fe_4S_4(SR)_4]^{2-}$ (R = Ph, C_6H_4Me) catalyzed the reduction of diphenylacetylene to *cis*-stilbene by excess sodium borohydride in $CH_3CN/MeOH$ (10 turnovers in 0.25 h).[53] Deuterium labeling studies indicated that one hydrogen of the stilbene product originated from $NaBH_4$ and the other from MeOH.

$[Fe_4S_4(SPh)_4]^{2-}$ mediated the transfer of electrons from *n*-butyllithium to aromatic ketones and aldehydes at 0 °C in hexane/diethyl ether.[54,55] Upon workup with water, both the alcohols and coupled diols (pinacols) were observed as products, and their relative ratios depended on the ratios of *n*-BuLi to iron–sulfur cluster. The cluster could be regenerated in over 97% purity by addition of benzenethiol instead of water at the end of the electron-transfer reactions. When $[Fe_4S_4(SPh)_4]^{2-}$ was treated with excess PhLi (up to 12:1 molar ratio) in ether/hexamethylphosphorous triamide in the presence of excess benzenethiol or acetic acid, the complex served as a homogeneous electron-transfer catalyst between phenyllithium and protons to give biphenyl and hydrogen (2.2 turnovers at a 10:1 PhLi/cluster ratio, 0 °C, 3 h).[56]

Hydrogen evolution from the reduction of water by dithionite was found to be promoted by Fe_4S_4-type clusters that incorporated bovine serum albumin or that contained cleaved serum albumin as ligands.[57,58] The clusters were not characterized in detail, but, for example, the former system catalyzed the evolution of 18 mol of H_2/mol of cluster in 44 h in an aqueous $Na_2S_2O_4$ solution, pH 7, in the presence of reduced methylviologen.

The cluster $[Fe_4S_4(SPh)_4]^{2-}$ was also found to catalyze the reduction of nitroarenes to anilines, quinones to hydroquinones, and *N*-oxide compounds to the deoxygenated compounds.[59] Benzenethiol was generally used as the reductant. The following turnover numbers were obtained: p-$(NO_2)_2C_6H_4$, 8.5/20 h; *p*-quinone, 9/20 h; pyridine *N*-oxide, 5.5/20 h. In contrast to the systems discussed above, which involved reduced forms of $[Fe_4S_4(SR)_4]^{2-}$, the 2–/1– redox couple of the cluster was proposed to be involved in the catalytic cycle with quinones. The reaction of *p*-benzoquinone with $[Fe_4S_4(SPh)_4]^{2-}$ in CH_3CN at 297 K generated an EPR spectrum of the semiquinone anion radical. At 20 K the same reaction solution showed a different EPR signal, which was tentatively assigned to $[Fe_4S_4(SPh)_4]^{-}$. The one-electron reduction of this intermediate by the thiol was proposed to regenerate the original 2– cluster. No discrete 2–/1– oxidation wave was observed for this cluster when its polarography was studied in DMF.[60] However, the presence of excess PhSH may help to stabilize the oxidized species in this system. A review of the chemical reduction reactions catalyzed by the iron–sulfur clusters has been published.[61]

The first report of a nonenzymic reaction catalyzed by an iron–sulfur cubane, $[Fe_4S_4(SEt)_4]^{n-}$, involved the addition of ethanethiol to *p*-chlorophenyl isocyanide to form *N*-(*p*-chlorophenyl)ethyl thioformididate, which could be hydrolyzed to *p*-chloroaniline.[62] Turnover numbers at 22 °C were 37/h for $n = 2$ and 73/h for $n = 4$. Electrochemical evidence for formation of an isocyanide adduct with the $n = 4$ cluster was presented. The proposed mechanism postulated initial isocyanide coordination to an iron center followed by carbon insertion into an iron–thiolate bond. The α,α-addition of other reagents, such as R_2NH, was not achieved with this system, suggesting that the thiol was also necessary for regenerating the cluster catalyst.

2. Electrochemical Reductions

Electrochemically reduced forms of $[Fe_4S_4(SPh)_4]^{2-}$ have served as catalysts for the electrochemical reduction of many molecules, with a special focus on nitrogenase-related substrates. The mixed-metal cluster $[Mo_2Fe_6S_8(SR)_9]^{n-}$[63] and related Mo–Fe–S clusters, which have been synthesized as potential models for the cofactor of the nitrogenase enzymes, have been compared with the iron–sulfur cubanes in these studies. The homogeneous systems generally involved the formation of the reduced clusters $[Fe_4S_4(SPh)_4]^{3-}$ (formed at −1.25 V vs SCE), $[Fe_4S_4(SPh)_4]^{4-}$ (−1.65 V vs SCE), and $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ (−1.25 V) at a mercury electrode in THF/MeOH solution. For example, the reduced clusters were found to be active in promoting the reduction of acetylene to primarily ethylene.[64] Turnover rates for ethylene formation, monitored over a period of 150 min, were 0.012/min for $[Fe_4S_4(SPh)_4]^{3-}$, 0.069/min for $[Fe_4S_4(SPh)_4]^{4-}$, and 0.011/min for $[Mo_2Fe_6S_8(SPh)_9]^{5-}$. For the 3– and 5– clusters, hydrogen evolution was suppressed in the presence of acetylene. Labeling studies demonstrated that primarily *cis*-ethylene-d_2 was formed under conditions where H–D exchange between CH_3OD and $HC{\equiv}CH$ was minimized. A plot of the rate of ethylene formation vs initial concentration of $[Fe_4S_4(SPh)_4]^{2-}$ in MeOH/THF showed a first-order dependence on the cluster.[65] The reaction was therefore proposed to proceed via stepwise one-electron transfer from the reduced cluster to acetylene. The electrochemical reduction of acetylene could be catalyzed in aqueous solution, pH 7.0–12.0, at −1.2 V by a reduced form of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$.[65]

The controlled-potential electrolysis of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ at −1.25 V vs SCE at a glassy carbon electrode in DMF containing excess PhSH led to the formation of hydrogen with a current efficiency near 100%.[66] The turnover number was 3.6 in 6 h. Hydrogen evolution was a competing reaction in many of the substrate reductions described below that were carried out in hydroxylic solvents.

The electrochemical reduction of hydrazine to ammonia in the presence of $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ or $[Fe_4S_4(SPh)_4]^{3-}$ (-1.25 V vs SCE) in MeOH was carried out with current efficiencies near 100%.[67] For the former system the ratio of NH_3 to H_2 produced was ca. 60 (for NH_3, 90 turnovers in 4 h). The water-soluble clusters $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{5-}$, $[Fe_4S_4(SCH_2CH_2OH)_4]^{3-}$, and $[Fe_4S_4(SCH_2CH_2OH)_4]^{4-}$ served as electrocatalysts for the hydrazine reduction in aqueous solution at pH 12. Total current efficiencies were 92% and 96% respectively, but ammonia turnover numbers (12 and 7, respectively, in 4 h) and ammonia/hydrogen ratios (3.2 and 0.29, respectively) were considerably lower than those observed in MeOH. Attempts to reduce N_2 to ammonia with the nonaqueous systems described above formed less than stoichiometric amounts of NH_3 with current efficiencies of <0.1%.[68]

The same clusters have been used in the catalysis of more than two electron reductions of other nitrogen-containing substrates with greater success. For example, the reduced forms of the clusters $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ have served as soluble electrocatalysts for the reduction of MeNC in MeOH/THF at a mercury electrode.[69] Major products were H_2, CH_4, and CH_3NH_2 when $[Fe_4S_4(SPh)_4]^{4-}$ was the catalyst (180 turnovers of H_2, 1.3 turnovers of CH_4 in 24 h). The methylamine formed under these electrolytic conditions underwent further reactions with solvent oxidation products. When $[Fe_4S_4(SPh)_4]^{3-}$ was the catalyst, C_2H_6 was the major hydrocarbon product ($C_2H_6/CH_4 = 2.7$). The proposed mechanisms involved isonitrile coordination to the cluster followed by proton and electron transfer to form methylamine and a methyl-ligated cluster. Proton and electron transfer to this ligand would form methane, while a competitive process involving isonitrile insertion into the cluster–methyl bond could ultimately lead to ethane formation.

Electrochemically reduced forms of $[Fe_4S_4L_4]^{2-}$, $[Mo_2Fe_6S_8L_9]^{3-}$ (L = SCH_2CH_2OH), and $[Fe_4S_4(SPh)_4]^{2-}$ catalyzed the reduction of NaN_3 to NH_3 and N_2 in an aqueous solution buffered at pH 7 (for the complexes with L) or in MeOH/THF at -1.25 V vs SCE at a mercury electrode.[70] N_2H_4 was detected as an intermediate in the ammonia formation. The intermediacy of N_2H_2 was implied by the conversion of stilbene to dibenzyl during the course of the electrolysis in MeOH/THF and by the overall N_2/NH_3 ratios observed. For $[Mo_2Fe_6S_8L_9]^{3-}$, the turnover number for NH_3 was 5 in 1 h, and the ratios of other products were 15 (H_2/NH_3), 1.9 (N_2/NH_3), and 0.08 (N_2H_4/NH_3).

Azides, RN_3 (R = C_2H_4OH or CH_3), were electrochemically reduced to amines and N_2 at -1.25 V vs SCE in MeOH/THF or H_2O in the presence of $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ or $[Mo_2Fe_6S_8(\mu\text{-}SEt_3)(\mu\text{-}SCH_2CH_2OH)_6]^{5-}$, respectively.[70,71] At azide concentrations $<1 \times 10^{-2}$ mol/dm^3, N_2H_4, NH_3, and H_2 were also produced in six- and eight-electron reduction processes. For the aqueous system at pH 9 turnover numbers were 14 for H_2, 7.8 for N_2, 9.1 for RNH_2, 3.5 for NH_3, and 0.05 for N_2H_4 after 80 min. When the clusters were attached to a modified glassy carbon electrode, turnover numbers increased dramatically by 3–4 orders of magnitude. This was attributed to an improved efficiency for multielectron transfers relative to that displayed by dissolved species. Spectroscopic data suggested that substitution of a thiolate ligand by azide occurred after an initial one-electron reduction of the cluster.

Related iron–sulfur and molybdenum–iron–sulfur clusters have also been studied as catalysts in the electrochemical reduction of carbon dioxide.[72,73] $[Fe_4S_4(SR)_4]^{2-}$ (R = $PhCH_2$) and $[M_2Fe_2S_8(SEt)_9]^{3-}$ (M = Mo or W) served as catalyst precursors for the electrochemical reduction of CO_2 at a mercury pool electrode at -2.0 V vs SCE in DMF. Phenyl acetate (0.88 mol/cluster) and phenyl formate (11 mol/cluster) were observed products. At this potential the clusters decomposed rapidly. The yield of phenyl acetate suggested it was produced from one thiolate ligand of the Fe_4 cluster, and this probably initiated cluster degradation. In the presence of excess $PhCH_2SH$, the Fe_4 cluster remained intact and the phenyl acetate yield approximately tripled while the formate formation was suppressed. Current efficiencies were in the range of 4–12%.

3. *Oxidations*

$[Fe_4S_4(SR)_4]^{2-}$ served as a catalyst for the oxidation of thiols to disulfides by oxygen.[74] Turnover numbers for the thiols PhSH, $PhCH_2SH$, and C_2H_5SH were ~ 20/min. Although well-defined 2–/1– oxidation waves were not observed in electrochemical studies of these complexes, the turnover numbers were found to increase as the 2–/3– reduction potentials of the cluster became more negative. The potentials were varied by changing the ligand substituent R from C_6H_5 to p-C_6H_4Cl and p-$C_6H_4NO_2$. This correlation led the authors to propose that electron transfer from cluster to oxygen was the rate-determining step, followed by rapid oxidation of thiol by O_2^-. Possible decomposition of the clusters by oxygen was not discussed in this report.

Iron–sulfur cubane clusters $[Fe_4S_4L_4]^{2-}$ with bulky and hydrophobic terminal ligands such as L = triisopropylbenzenethiolate (A) or Z-Cys-Ile-Ala-OMe (B) (Z = benzyloxycarbonyl) have been found to undergo quasi-reversible one-electron oxidations in DMF (-0.03 V vs SCE for A and +0.12 V for B).[75] The relatively stable 2–/1– redox couple permitted the use of these clusters as catalysts in the oxidation of benzoin to benzil by 1,4-benzoquinone.[76] (The average turnover number for B at 25 °C was 0.93/min for a total yield of 16800%/3 h.) Electron transfer from the 2– cluster to benzoquinone was observed at room temperature in DMF. Benzoin was proposed to reduce the 1– cluster to generate benzil and the original catalyst.

B. Iron–Molybdenum–Sulfide Clusters

The ability of $[Mo_2Fe_6S_8(SR)_9]^{n-}$ to function as a catalyst in electrochemical reductions was discussed in section IIIA2. A number of additional types of molybdenum–iron–sulfide clusters have been prepared recently and found to show catalytic activity for acetylene reduction by a hydride donor. Clusters that have been characterized by X-ray diffraction are shown in Figure 1.[77] Additional mixed-metal clusters were synthesized and formulated on the basis of elemental analyses and spectroscopic studies. These include $[(SCN)_2(OCH_3)Fe(\mu\text{-}S)_2Mo(OCH_3)(\eta^2\text{-}S_2)]^{3-}$,[78] $[S_2Mo(\mu\text{-}S)_2Fe(OCH_3)_2(\mu\text{-}S)_2MoO(\eta^2\text{-}S_2)]^{3-}$,[77] $[Mo_2Fe_7S_{12}(SC_6H_5)_6]^{4-}$,[79] $[MoFe_6S_8(PhCH_2SH)(OCH_3)_6]^{2-}$,[80] and a

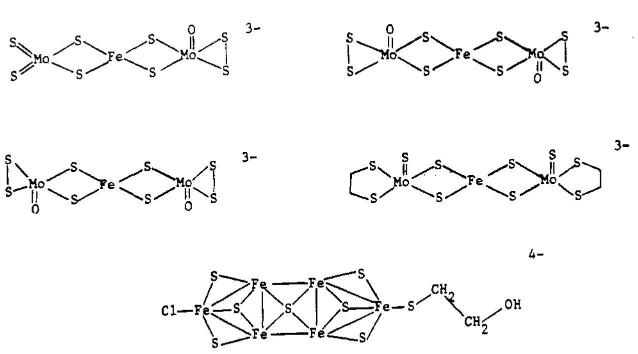


Figure 1. Examples of molybdenum–iron–sulfide clusters that have been characterized by X-ray diffraction and studied as catalysts for the reduction of acetylene by KBH_4.

series of complexes of the general formula $[MoFe_2S_4L_{0-2}X_4]^{n-}$, where X = Cl or OCH_3 and L = PhS, $PhCH_2S$, or PhSH.[80] The KBH_4 reduction of acetylene to ethylene was catalyzed at 25–30 °C by each of these clusters in DMF/H_2O. Turnovers for ethylene ranged from 2 to 17 mol (nmol of Mo)$^{-1}$ min^{-1}, with $[MoFe_6S_8(PhCH_2SH)(OCH_3)_6]^{2-}$ showing the highest activity. Small amounts of ethane were also formed, but the systems showed selectivity for ethylene formation which was generally in the range of 80–90%.

The reduction of $^{15}N_2$ to $^{15}NH_3$ by KBH_4 was carried out in the presence of $[MoFe_2S_4(PhSH)_2(OCH_3)_4]^-$ or $[MoFe_6S_8(PhCH_2SH)(OCH_3)_6]^{2-}$ in DMF/H_2O (borate buffer) at 30 °C. Yields were much less than stoichiometric (e.g., for the former complex, 4 nmol of NH_3/2192 nmol of Mo in 2 h). The same clusters were used in the reconstitution of an inactive MoFe protein from the mutant strain of nitrogenase UW45. The reconstitution activity for acetylene reduction was 6–9% of that of the original MoFe cofactor.[80]

The cluster $[(t\text{-BuS})MoFe_3S_4(SPh)_3]^{2-}$, which was proposed to have a distorted cubane structure, catalyzed, alone and with $[Fe_4S_4(SPh)_4]^{2-}$, the reductions of acetylene to ethylene by dithionite or by $NaBH_4$ in DMF/H_2O.[81] Turnover numbers were low (2–4 in 5 h) in this system.

A recent study has compared the catalytic activity of $[Fe_4S_4(SR)_4]^{2-}$ with a related molybdenum-substituted single cubane of the formula $[MoFe_3S_4(SR)_3(O_2C_6Cl_4)(L)]^{2-}$ (R = p-n-$C_8H_{17}C_6H_4$ and L = Me_2CO or DMF).[82] The clusters were solubilized in aqueous Triton X-100 micellar solutions containing sodium dithionite and methylviologen dibromide at 30 °C. Under these conditions n-$C_5H_{11}N_3$ was catalytically reduced in the presence of the iron–sulfur cluster to form n-$C_5H_{11}NH_2$ and N_2 (16.1 and 16.8 turnovers, respectively, in 1 h). The molybdenum-containing cluster was more effective at catalyzing the formation of RNH_2 and N_2 (75 and 90 turnovers, respectively, in 1 h), and this cluster also promoted the formation of N_2H_4 and NH_3 in multielectron processes (0.5 and 20 turnovers, respectively). The multielectron reduction products were not detected with the Fe_4 system. Electrochemical characterizations of the clusters were reported which indicated that the azide molecule formed an adduct with the $MoFe_3$ cluster by replacing a DMF or acetone molecule. The 2–/3– couple was shifted anodically by 300 mV. In contrast, excess azide appeared to interact only with the 3– oxidation state of the iron cluster; the azide-substituted cluster showed a 2–/3– couple shifted cathodically by ca. 100 mV relative to the original complex.

C. Ruthenium–Molybdenum–Sulfide Clusters

The molybdenum–ruthenium complexes $(bpy)_2Ru(\mu\text{-}S)_2MoS_2$ and $[(bpy)_2Ru(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Ru(bpy)_2]^{2+}$ were synthesized from MoS_4^{2-} and $Ru(bpy)_2Cl_2$ (bpy = 2,2′-bipyridine) and characterized by spectroscopic techniques.[83] The electrolysis of the latter cluster under an acetylene atmosphere at −1.70 V vs SCE at a mercury electrode in MeOH/DMF led to the formation of 1.4 mol of C_2H_4, 0.4 mol of C_2H_6, and 19 mol of H_2 per mol of catalyst in 400 min. The catalyst generated at this potential was proposed on the basis of cyclic voltammetric characterization to be a dianionic cluster.

An organometallic Mo–Ru cluster of the formula $[CpMo(CO)_2]_2SRu(CO)_3$, which contained a μ_3-sulfide ligand capping the trigonal plane of the metal ions, was found to promote a nonreductive coupling of alkynes.[84] The cluster reacted with 3 equiv of phenylacetylene. The isolated product, characterized by an X-ray diffraction study, contained a π-bonded linear hydrocarbon ligand resulting from the head-to-tail coupling of three alkyne molecules. When this product, $(CpMo)_2Ru(CO)_2(\mu_3\text{-}S)[\mu_3\text{-}\eta^6\text{-}HC_2(Ph)CHC(Ph)CHC(Ph)]$, was heated under 25 atm of CO at 100 °C, it eliminated 1,3,5-triphenylbenzene and formed the original cluster in 80% yield. The recycling involved a sequence of stoichiometric reactions that permitted detailed characterization of an intermediate species involved.

D. Molybdenum–Sulfide Complexes

Studies have been carried out on dinuclear sulfide-bridged complexes of the formula $Mo_2O_2(\mu\text{-}S)_2L_2$, where L = disulfide or a 1,1-dithioacid anion. $[(C_4H_9)_4N]_2[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(\eta^2\text{-}S_2)]$ catalyzed the reduction of acetylene by KBH_4 in DMF/H_2O solution at 30 °C. Ethylene was produced at a rate of 1.93 nmol (nmol of Mo)$^{-1}$ min^{-1}.[76] The sulfide-bridged complexes with dithioacid ligands served as catalysts or catalyst precursors for the reduction of azobenzene by $NaBH_4$ in THF/EtOH at room temperature.[85] For example, in the presence of $Mo_2O_2(\mu\text{-}S)_2(S_2COPr)_2$, 100 equiv of azobenzene was converted to hydrazobenzene (81%) and aniline (19%) after 20 h. Phenylacetylene was reduced to primarily styrene under similar conditions. This report also included studies of mixed catalyst systems in nonaqueous solutions and as micellar reagents in aqueous solution. For example, the mixture of $[Fe_4S_4(SPh)_4]^{2-}$ and $Mo_2O_2(\mu\text{-}S)_2(S_2COR)_2$ in an 8:1 ratio resulted in somewhat higher catalytic activity for azobenzene reduction than was observed for the individual complexes, and selectivity for aniline formation was observed.

A related complex $Mo_2O_2(\mu\text{-}S)_2(\text{L-Cys-NH-}n\text{-Oct})_2$, in which the cysteine derivative formed a five-membered chelate ring with N and S donors, also served as a soluble catalyst for the reduction of azobenzene to hydrazobenzene by $NaBH_4$ (35 turnovers after ca. 2 h).[86] Similar complexes with other cysteine-containing peptide anions that formed five- or seven-membered chelate rings showed catalytic activity under heterogeneous conditions. Similar catalytic activity has also been studied for thioxanthine molybdenum complexes sup-

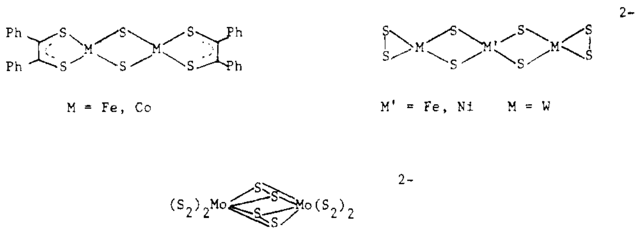


Figure 2. Metal complexes with sulfide and disulfide ligands that have been studied as catalysts for the photolytic reduction of water by tetrahydrofuran.

ported on copolypeptides containing L-cysteine and γ-benzyl L-glutamate.[87]

E. Miscellaneous Systems and Reactions

A group of metal complexes have been tested for their ability to catalyze the photolytic reduction of water by tetrahydrofuran.[88] Hydrogen evolution was monitored, and oxidation products of THF were identified. Complexes with sulfide ligands that were studied are shown in Figure 2. The dinuclear iron and cobalt dithiolenes were among the more active complexes studied for hydrogen evolution. Average turnover numbers of 2/h and 8/h, respectively, were observed compared to <0.5/h for the disulfide complexes. Photodegradation of the complexes occurred upon irradiation, and in most cases solids were formed. The identities of the actual catalysts in these reactions were not determined.

An aqueous CuCl solution with excess Cl^- ion was studied for its catalytic properties in the hydration of acetylene to acetaldehyde.[89] The rate of hydration was found to be promoted by the addition of small amounts of Na_2S, H_2S, or Cu_2S, and this was attributed to the formation of catalytically active anions of the type $[Cu_4Cl_3S]^-$ and $[Cu_5Cl_4S]^-$. It was proposed that the sulfide clusters underwent more facile insertion of acetylene into a Cu–OH_2 bond than the related chloride complex anions, and electronic effects of the sulfide ligands favored the acidolysis of the Cu–C σ bond in the intermediate insertion product.

An example of an oxidation that might be occurring in the presence of a copper–sulfide complex involves the reaction of the distorted cubane cluster $[MoOS_3(CuCl)_3]^{2-}$ with 3 equivalents of PhS^- to form $[Mo_2O_5(SC_6H_4O)_2]^{2-}$.[90] The formation of the 2-sulfidophenolate ligand appeared to involve the aerial oxidation of PhS^- assisted by an unidentified copper-containing species.

The addition of sodium sulfide to a mixture of ferric or nickel(II) chloride and excess dithiothreitol (DTT) in aqueous solution at pH 9 led to the formation of complexes that were formulated as DTT–Fe–S or DTT–Ni–S, respectively.[91] The complexes, which were minimally characterized by visible and EPR (for iron) spectroscopy, served as catalysts for the hydroxylation of acetanilide to form *p*- and *o*-acetaminophenols at 20 °C in a 50% water (pH 9)/acetone solution.[92] For DTT–Fe–S the rate of acetanilide hydroxylation was 3.9×10^{-2} mol (mol of catalyst)$^{-1}$ min^{-1}.

IV. Summary

Sulfide ligands form relatively strong bonds with many transition metals, and the ligands can play an important role in stabilizing di- and polynuclear complexes against fragmentation processes. Many of the catalytic systems that have been covered in this review have taken advantage of this stabilizing effect. Indeed the active catalysts in almost all of the sulfide systems discussed above were presumed to be di- or polynuclear.

As a result of the ability of metal–sulfide complexes to retain their structural integrity, the electron-transfer processes for these complexes often show some degree of reversible character. The extensive development of the iron–sulfide and molybdenum–iron–sulfide clusters as electrocatalysts has taken advantage of their reversible electron-transfer properties. The sulfur donor ligands tend to favor lower oxidation states of metal ions, and the relatively positive reduction potentials of the sulfide complexes, for example, when compared to related oxygen or nitrogen donor systems, provide a favorable situation for the many catalytic reduction reactions that have been characterized. As implied above, the redox changes of the sulfide complexes can be attributed to changes in the formal oxidation states of the metal ions. However, the ability of coordinated sulfide ligands to participate in redox chemistry, e.g.,

$$2S^{2-} \xrightarrow{-2e^-} S\text{–}S^{2-}$$

has also been demonstrated.[93] Although such ligand-based redox reactions have not been directly identified in the catalytic systems surveyed here, they may play a role, for example, in the chemistry of the dinuclear quadruply bridged molybdenum–sulfide complexes.

The mechanisms for many of the molecular sulfide catalysts proposed or implied substrate coordination only to a metal center, and the dissociation of an ancillary ligand from the complex was often cited as a first step in the catalytic reaction. A few examples of the interaction of hydrogen or of unsaturated molecules with sulfide ligands have also been identified. Such interactions may or may not be preceded by a substrate interaction with the metal ion. These systems provide a possible link between the extensive catalytic chemistry of the heterogeneous nonmolecular sulfides, for which active sulfide sites have been proposed,[6–8] and that of the homogeneous systems.

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