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Research on Soluble Metal Sulfides: From Polysulfido Complexes to Functional Models for the Hydrogenases

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Results from this laboratory are surveyed, emphasizing the synthesis of metal sulfides. Four themes are described. Continuing studies exploit the exothermic desulfurization of polysulfido complexes as a means to generate new clusters and rings. Illustrative inorganic rings prepared in this way include 1,5-$[L_2M]_2(S_3)_2$ and 1,4-$[L_2M]_2(S_2)_2$, where $L_2M = CpRu(PPh_3)$ and Cp_2Ti. Fundamentally new clusters prepared in this project included the cubanes $[(C_5R_5)MS]_4$ for M = Ti, V, Ru, Ir. Associated redox studies led to the discovery of the phenomenon of mobile metal–metal bonds, as manifested in $[Cp^*_4Ir_4S_4]^{2+}$ wherein the localized Ir–Ir bond migrates over the six Ir- - -Ir edges of the cluster. Other desulfurization experiments led to the preparation of the reactive species $Ir^{II}_2S_2(PPh_3)_4$ from $[IrS_{16}]^{3-}$ and the synthesis of the first high polymers of ferrocene, $[(RC_5H_3S)_2Fe]_n$ ($n \sim 500$). A second theme uncovered the useful role of donor solvents on the reaction of metals with sulfur. It was found that pyridine accelerates the low temperature conversion of Cu to crystalline CuS via the intermediacy of the cluster $Cu_4(S_5)_2L_4$. Related synthetic methodology led to a family of amine-stabilized zinc polysulfides, e.g. ZnS_6(tmeda), an efficient sulfur-transfer agent. A third theme explored the organic and organometallic chemistry of the tetrathiometalates. The sulfido analogue of OsO_4, ReS_4^- was shown to be broadly reactive toward unsaturated organic substrates such as alkenes, alkynes, nitriles, and isocyanides. The final and still emerging theme focuses on the preparation of functional and structural models for bio-organometallic reaction centers. Studies on models for the Fe-only hydrogenases began with the synthesis of the highly reducing species $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$ where $(SR)_2$ also includes the proposed azadithiolate cofactor $HN(CH_2S^-)_2$. Systematic studies on the cyanide substitution process led to the preparation of $[HFe_2(SR)_2(CN)(CO)_4(PMe_3)]$, which efficiently catalyzes the reduction of protons to H_2. Work on the hydrogenases was expanded to include modeling of acetyl Co-A synthase, leading to the preparation of mixed valence Ni_2 models containing bound CO substrate.

Metal sulfides are key to many topical challenges in inorganic chemistry: catalysis, energy, the environment, and materials. The centrality of metal sulfides is especially evident in the bio-catalysis of small molecule substrates,[1] including CO (the water gas shift reaction, or CO “dehydrogenation”),[2] N_2 (reduction to ammonia),[3] and H_2 (dihydrogen oxidation or proton reduction).[4] The catalytic mechanisms underpinning these and related small molecule transformations[5] promise to inspire new, greener approaches to industrial catalysis. Furthermore, from the synthetic perspective, many metal sulfido enzymes provide existence proofs for unanticipated structures that challenge synthetic chemists.[6−8]

The dominant industrial role for catalysis by metal sulfides is the hydrodesulfurization (HDS) of fossil fuels. This particularly large-scale operation entails the hydrogenolysis of C−S bonds to generate H_2S and more readily processed and more cleanly combusted hydrocarbon product. A range of feedstock and environmental considerations continue to

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drive improvements in HDS, which one can anticipate will ultimately rely on molecular level insights. HDS embraces important contemporary themes in catalysis, including scission of strong bonds and the heterolytic activation of H_2. In biology, C–S bond-forming and -breaking reactions pose unsolved mechanistic challenges related to the syntheses of biological cofactors associated with the biosynthesis of acetyl coenzyme A,[9,10] lipoic acid and biotin,[11,12] and methane.[13]

Understanding catalysis by metal sulfides has been the aim of our research for the past several years. Our approach has focused on the synthesis and reactivity of soluble metal sulfides, with an emphasis on reactions at inorganic sulfur. This report surveys some aspects of this research program.

I. Desulfurization of Polysulfido Complexes

We set out to generate reactive metal sulfides via the desulfurization of sulfur-rich complexes. In this way we sought to generate species that react with organic and small molecule substrates. Since polysulfido complexes were known for most transition metals, we had a broad palate with which to work. The fact that hardly any reactivity studies had been reported on polysulfido complexes suggested that the area was ripe for discovery. As the desulfurization agents, we mainly employed tertiary phosphines. The sulfidation of tertiary phosphines provides about 25 kcal/mol in enthalpy,[14] sufficient to generate reactive L_nMS_x species.

Desulfurization of Cyclopentadienyl Polysulfides. We began by addressing ring contraction reactions of Cp'_2TiS_5 ($Cp' = MeC_5H_4$), one of the most accessible polysulfido complexes. It is interesting to note that our successes owed much to the use of Cp′ (vs $Cp = C_5H_5$), because of improved solubility, crystallizability, and NMR properties for its derivatives. Desulfurization of S_8 by tertiary phosphines does not lead to new homocycles because the strained rings rearrange quickly to regenerate S_8, a reaction that is known to be catalyzed by even weak nucleophiles.[15] The presence of M–S bonds in the ring suppresses this equilibration process as demonstrated by the fact that desulfurization of Cp'_2TiS_5 with phosphines gives 1,5-$[Cp'_2Ti]_2S_6$[16,17] and 1,4-$[Cp'_2Ti]_2S_4$.[18] These species were structurally unprecedented at the time of their synthesis and stimulated the preparation of many new M–S rings.[19,20]

Desulfurization of *mono*cyclopentadienyl metal sulfides leads to clusters, work on the Cp′V case being illustrative. The sequence begins with the thermal conversion of Cp'_2VS_5 into $Cp'_2V_2S_5$ (Scheme 1),[21,22] which in turn undergoes stepwise desulfurizaton to give $Cp'_2V_2S_4$,[23,24] and then to a mixture of $Cp'_4V_4S_4$ and $Cp'_5V_5S_6$ (not shown).[25] The stability of the electron-deficient cubane $Cp'_4V_4S_4$ foreshadowed the synthesis of the 52e cluster $Cp'_4Ti_4S_4$.[26]

(C_5R_5)Ru Platforms for S-Centered Reactivity. The sulfur-rich derivatives of ruthenium proved to be especially revealing with regard to fundamental transformations possible for inorganic sulfur ligands. Prior to our work, the π-donor

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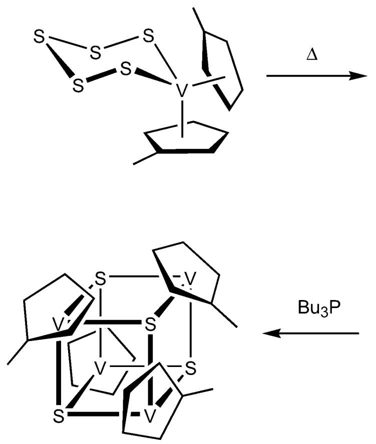
Scheme 1

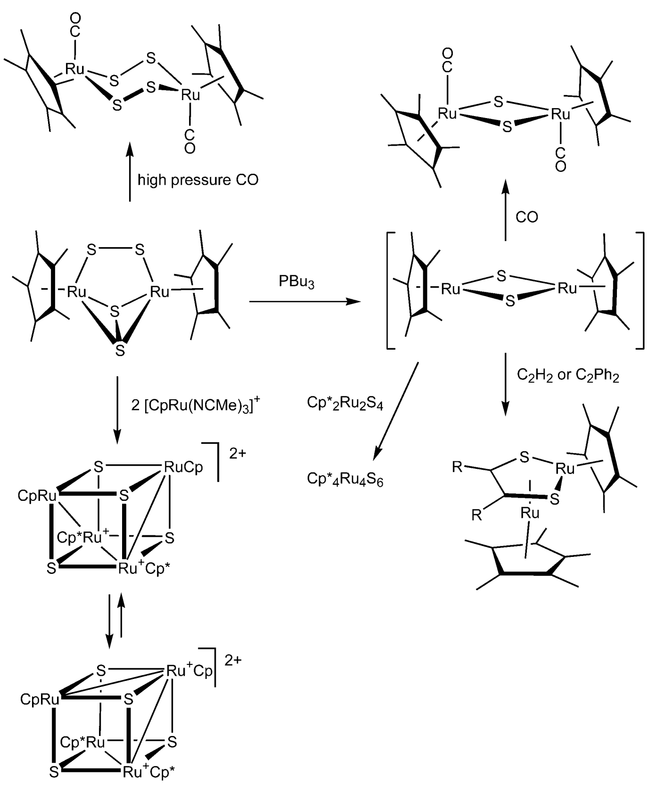


properties of the persulfido (S_2^{n-}) ligand had been established: Taube's $[Ru(NH_3)_5]_2S_2^{4+}$,[27] Kubas's $Cp_2Fe_2(SEt)_2(S_2)$,[28] and Herberhold's $Cp_2Mn_2(CO)_4(S_2)$.[29] The chemistry leading to and emanating from the persulfido ligand blossoms when this sulfur ligand is fitted with the (C_5R_5)Ru substituent.

Desulfurization of $Cp^*{}_2Ru_2S_4$ leads to clusterification, not unlike the $Cp'_2V_2S_4$ case, to give $Cp^*{}_4Ru_4S_6$, which is analogous to sulfur-rich iron−persulfido cuboidal clusters.[30] The formation of $Cp^*{}_4Ru_4S_6$ appears to proceed by the initial formation of the reactive intermediate $Cp^*{}_2Ru_2S_2$, which arises from the attack of PBu_3 on the mildly electrophilic η^1,η^1-persulfide. The resulting $Cp^*{}_2Ru_2S_2$ species then condenses with the $Cp^*{}_2Ru_2S_4$. The proposed intermediate $Cp^*{}_2Ru_2S_2$ could be trapped by alkynes. For example, using C_2H_2 we obtained $Cp^*{}_2Ru_2(\eta^2,\eta^4\text{-}S_2C_2H_2)$,[31] which contains the highly unusual η^4-dithiolene ligand.[32] Further evidence for the intermediacy of $Cp^*{}_2Ru_2S_2$ comes from the finding that the trapping agent (alkyne or CO)[33] must be present *prior* to the addition of the PBu_3 (Scheme 2). The existence of reactive sulfido species was also demonstrated by Bergman in studies on $Cp^*{}_2Rh_2S_2(PR_3)$, which exists in equilibrium with $Cp^*{}_2Rh_2S_2$, which in turn dimerizes to the corresponding 72e cubane $Cp^*{}_4Rh_4S_4$.[34] Further work on the (C_5R_5)M−S compounds led to the discovery of the phenomenon of mobile metal−metal bonds, e.g. in $[Cp^*{}_2Cp_2Ru_4S_4]^{2+}$ (see Scheme 2) and $[Cp^*{}_4Ir_4S_4]^{2+}$.[35−37]

The corresponding chemistry of ruthenium persulfides was explored using the versatile $CpRu(PPh_3)_2$ substituent. Illustrative is the behavior of $CpRu(PPh_3)_2SH$, a simple analogue of $CpRu(PPh_3)_2Cl$. This complex undergoes smooth protonation to give the corresponding H_2S complex, which in turn can be displaced by H_2. This equilibrium models one pathway by which H_2 can regenerate sulfided HDS catalysts. The cationic H_2S complex is readily oxidized to give the green, electroactive persulfide, which can be described within the continuum of resonance structures $[Ru^{III}]_2(S_2^{2-})$ and $[Ru^{II}]_2(S_2^{0})$. More sulfur-rich complexes include the diamagnetic diruthenium derivatives that are bridged by per- and trisulfides (Scheme 3).[19,38−41] Recent work by Matsumoto has demonstrated the C−H activation by Ru_2S_2 centers.[42]

Scheme 2



We anticipate that the fruitful chemistry based on the (C_5R_5)Ru platform will be extended to diiron systems, and the synthesis of $(TACN)_2Fe_2(S_2)_3$ (TACN = 1,4,7-triazacyclononane, Figure 1) provides a lead in this direction.[43,44]

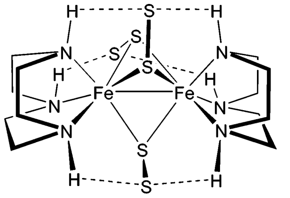


Figure 1. Structure of $Fe_2(S_2)_3(TACN)_2$.[43,44]

From $[IrS_{16}]^{3-}$ to $Ir_2S_2(PPh_3)_4$. In our initial studies on the desulfurization of polysulfido complexes, we assumed that face-capping ligands (e.g., Cp, 1,4,7-triazacyclononane[43])

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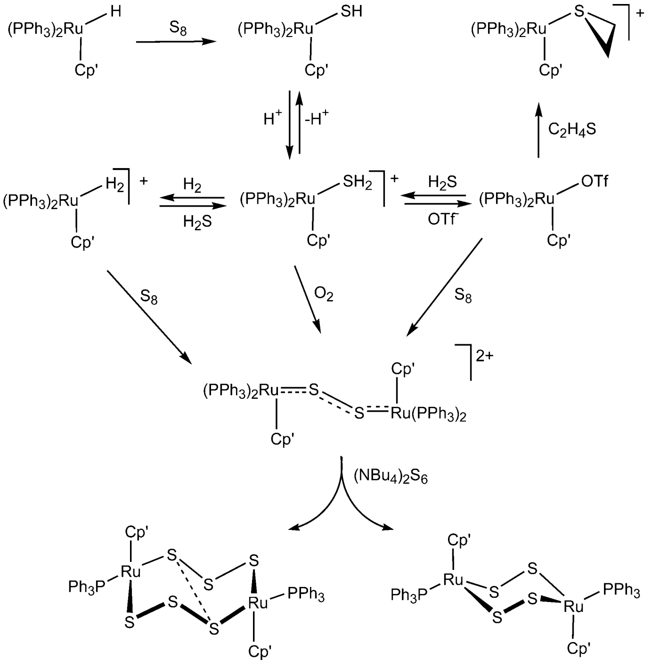
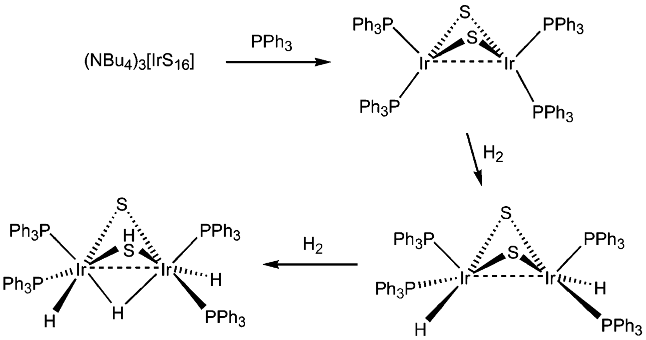
Scheme 3



were required to avoid formation of polymeric products. This concern is apparently unfounded, and the desulfurization of anionic sulfur-rich complexes is a promising route to numerous interesting species. A striking example is the desulfurization of $[Ir(S_6)_2(S_4)]^{3-}$, which had recently been structurally characterized.[45] Treatment of the MeCN-soluble $(NBu_4)_3[IrS_{16}]$ with PPh_3 produces neutral $Ir_2S_2(PPh_3)_4$,[46] which conveniently crystallizes from the reaction solvent. In this transformation, the PPh_3 serves both as a desulfurization agent and as a stabilizing ligand. $Ir_2S_2(PPh_3)_4$ is the singular example of an Ir(II) sulfide, and it exhibits correspondingly singular reactivity.

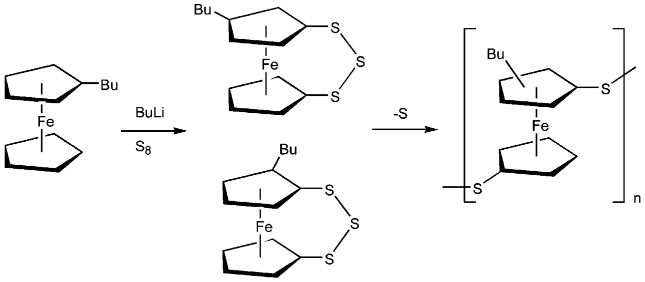
Solutions of $Ir_2S_2(PPh_3)_4$ absorb two equiv of H_2 to give $H_3Ir^{III}{}_2S(SH)(PPh_3)_4$. The double hydrogenation of $Ir_2S_2(PPh_3)_4$ formally entails both homolytic addition of H_2 (to give a dihydride) and heterolytic addition of H_2 (to give the sulfhydryl−hydride). Spectroscopic studies show that the first step leads to the formation of $H_2Ir_2S_2(PPh_3)_4$, a net oxidative addition to both metal centers. This reaction is reversible. The $[Ir^{III}]_2$ dihydride then adds a second equivalent of H_2 to give $H_3Ir_2S(SH)(PPh_3)_4$, which was originally prepared by addition of H_2S to $[H_2Ir(PPh_3)_2(Me_2CO)_2]^+$ (Scheme 4).[47] Interestingly, labeling experiments show that it is an oversimplification to label the second step as purely heterolytic since addition of D_2 to the intermediate dihydride gives a fully equilibrated mixture with the deuterium located equally in all four sites, i.e. the three hydride and the sulfhydryl positions.

Scheme 4



Polyferrocenylenepersulfides. Our desulfurization studies led to the preparation of a new class of organometallic polymers wherein the organometallic subunits are connected by persulfide linkers. Our approach was based on two well-known facts: (i) inorganic sulfur in organic polysulfides can generally be removed using PR_3 under mild conditions, but (ii) C−S bonds are relatively inert.[48] These facts guided our studies on $Fe(C_5H_4)_2S_3$, the rich chemistry of which was then being developed by Herberhold.[49] Initial experiments showed that treatment of a solution of $Fe(C_5H_4)_2S_3$ with PBu_3 produced orange $[Fe(C_5H_4S)_2]_n$. Soluble derivatives were prepared from the related butylferrocene derivatives. Thus, butylferrocene was converted into a ∼5:1 mixture of 1,2,1′- and 1,3,1′-$Fe(BuC_5H_3)(C_5H_4)S_3$ via a lithiation−sulfidization sequence (Scheme 5).[50,51]

Scheme 5



We were concerned that the use of stereoisomeric trisulfides (two chiral regioisomers) would overly complicate the ensuing polymer chemistry, but this concern proved unfounded. Desulfurization of $Fe(BuC_5H_3)(C_5H_4)S_3$ produced soluble polymers with molecular weights of 200000−400000 as verified by size exclusion chromatography and light scattering experiments.[51,52] Polymerization is proposed to proceed via the formation of zwitterionic thiophosphonium−ferrocenylthiolato intermediates. Evidence implicating the transient formation of thiolato anions was provided by the observation that addition of CH_2Cl_2 to the polymerization mixture produced $Fe(RC_5H_3S)_2CH_2$, where the two rings are connected by methanedithiolate.

Polyferrocenes had been heavily examined prior to our work, but previous examples were insoluble and very poorly characterized with respect to electrochemistry, molecular weight, and microstructure. Polyferrocenylenepersulfide polymers on the other hand exhibit excellent stability, film-forming, and handling properties. The polymer $[Fe(BuC_5H_3S)$-

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$(C_5H_4S)]_n$ oxidizes in two steps ($\Delta E \sim 150$ mV), indicating that oxidation of an individual Fe center diminishes the oxidizability of the flanking Fe centers. The intermetallic communication implied by this measurement indicates the particular ability of *per*sulfides to promote strong electronic coupling, a theme observed repeatedly in our work.[40] Reduction of the polymer cleaves the S−S bonds leading to monomeric ferrocenedithiolates.

A variety of modified perchalcogenido polymers were examined, each demonstrating a different aspect of these new materials. ^{77}Se NMR studies on $[Fe(BuC_5H_3Se)(C_5H_4Se)]_n$ established the microstructure of these polymers, showing that head-to-tail linkages predominated.[52] $[Fe(t\text{-}BuC_5H_3S)(C_5H_4S)]_n$ provided only the 1,3,1′-isomers, further simplifying stereochemical analysis. Finally the species $Fe(t\text{-}BuC_5H_2)(C_5H_3)(S_3)_2$ allowed us to generate high MW cross-linked gel-forming solids, demonstrating advantage of the cross-linking enabled by the four C−S bonds.[53] Contemporaneously with our initial work, Manners described and subsequently powerfully developed the corresponding chemistry of the polyferrocenylenesilanes.[54]

II. Synthesis via the L−M−S_8 Reaction

Given their technological importance, metal sulfides have been the subject of numerous studies. Standard syntheses of the binary and ternary phases involve the reaction between a metal powder and elemental sulfur. We reasoned that donor solvents should influence this redox reaction and perhaps allow for the interception of reactive intermediates. Metal sulfides typically do not form adducts with Lewis bases; thus any metal sulfido intermediates trapped by Lewis bases would be novel.

The L−Cu−S_8 Reaction. This project began with studies on the reaction of copper powder and elemental sulfur, which my colleague John Bailar had demonstrated to me as an example of a low-temperature solid-state reaction: one simply grinds the powders at room temperature to obtain the black CuS (covellite). Pyridine was found to accelerate the formation of CuS from toluene suspensions of Cu and sulfur, leading to a more crystalline product than that obtained in the absence of the donor ligand. An intermediate could be isolated in low yield upon treatment of a mixture of copper powder and elemental sulfur with pyridine (py) at room temperature. This intermediate proved to be the cuprous polysulfide cluster $Cu_4(S_5)_2py_4$. The donor strength of the solvent significantly influences the reaction: Cu metal dissolves in 1-methylimidazole (MeIm) at 0 °C upon addition of sulfur to give the corresponding $Cu_4(S_5)_2(MeIm)_4$ in high yield.[55] The donor ligands in these clusters are labile: treatment of $Cu_4(S_5)_2py_4$ with MeIm gives $Cu_4(S_5)_2(MeIm)_4$. These clusters adopt a particularly beautiful polycyclic S_4-symmetric structure (Figure 2). When the $Cu_4(S_5)_2L_4$ cluster is gently heated either in solution or as solids, one obtains CuS quantitatively. The transformations are quite clean because the cluster lacks counterions or other nonvolatile components that would leave a residue.

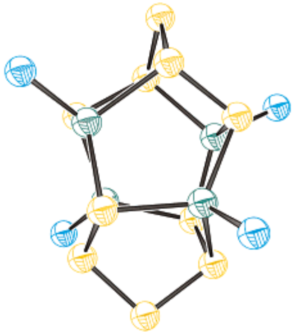

Figure 2. Structure of $Cu_4S_{10}py_4$ with carbon and hydrogen omitted for clarity (yellow = S, green = Cu, blue = N).

Our studies on ligand-induced sulfidation of metals provide insights into the fundamental processes by which elemental sulfur converts a metal into its sulfides, i.e. that the formation to a monosulfide proceeds via sulfur-rich (polysulfido) intermediates. Such polysulfido intermediates provide a structural and conceptual link between cyclo-S_8 and the solid-state products (eq 1).

$$M \xrightarrow{S_8} MS_x \xrightarrow{-(x-1)S} MS \qquad (1)$$

Generalization of the MeIm−M−S_8 Reaction. Success with the Cu−S_8 reaction led to expanded research on what we call "L−M−X" method, where L is a donor ligand, often methylimidazole used neat as the reaction solvent, M is a metal powder (but extendable to metal carbonyls[56]), and X is the oxidant, which in our hands was usually elemental sulfur. In principle many donor ligands could be employed, but obviously the donor ligand and the oxidant must be mutually compatible: this restriction precludes the use of phosphines and elemental sulfur, which would only afford the phosphine sulfide. A key aspect is the use of MeIm, the donor properties of which remain under-appreciated in comparison with pyridine. MeIm is ∼10× more basic than pyridine and enjoys a significantly smaller steric profile, as demonstrated by the paucity and instability of $[M(py)_6]^{n+}$ species vs the robustness of the corresponding $[M(RIm)_6]^{n+}$. Illustrative of the ready ability of MeIm to form hexasubstituted derivatives, the reactions of Mn, Fe, and Ni in MeIm/S_8 solutions generate $[M(MeIm)_6]S_8$, where the $[M(MeIm)_6]^{2+}$ in essence serves as a counterion stabilizing the acyclic $S_8{}^{2-}$ counterion.[57] The fact that one obtains $[S_8]^{2-}$ from the reduction of S_8 is of no mechanistic significance as polysulfido anions readily redistribute in solution.[58]

In place of metal powders, metal carbonyls are highly reactive substrates. Thus a solution of $Fe(CO)_5$ in MeIm reacts rapidly upon addition of S_8 to afford $[Fe(MeIm)_6]S_8$. Different products are produced when one varies the donor solvent or chalcogen. For example, the MeIm/$Fe(CO)_5$/Se_8 reaction affords $[Fe(Se_4)_2(CO)_2]^{2-}$.[56] The basic approach is complementary to Kolis's oxidative decarbonylation of metal carbonyls by polychalcogenide anions.[59] For more electronegative metalloids, polysulfide anions generated in situ from the reaction of Mg and S_8 in MeIm provided novel products, e.g. $[Sb_2S_{15}]^{2-}$ and $[In(S_4)_2(MeIm)]^{-}$ (Figure 3).[60]

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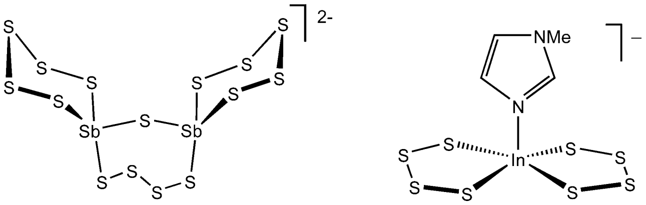


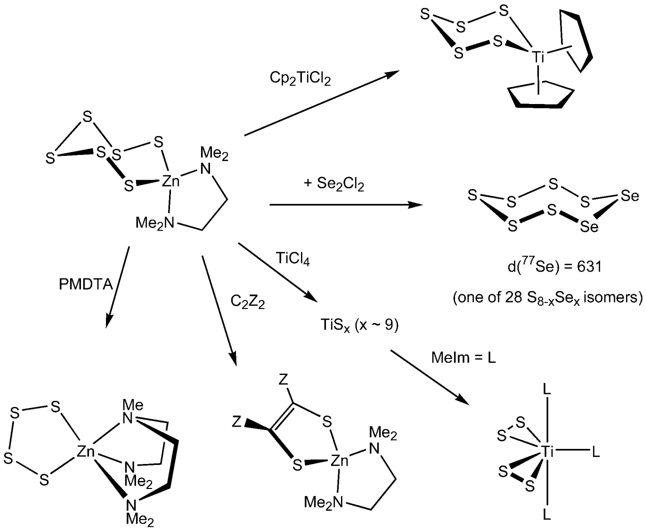
Figure 3. Structures of $[Sb_2S_{15}]^{2-}$ and $[InS_8(MeIm)]^-$, which arise from the MeIm-assisted reaction of S_8, Mg, and the metalloid.

Amine-Stabilized Zinc Sulfides. Fruitful extensions of the $L-M-S_8$ reaction involved studies on zinc derivatives. Elemental sulfur and zinc powder have long been known to react, explosively in fact, and this exothermic reaction is even employed as a propellant in toy rockets. In the presence of donor solvents the $Zn + S_8$ reaction proceeds with greater control allowing the isolation of well-defined soluble derivatives. Thus the MeIm-mediated reaction of Zn and S_8 efficiently affords the corresponding $ZnS_6(MeIm)_2$,[61] exhibiting the ZnS_2N_2 coordination environment commonly found in Nature.[62] Tetramethylethylenediamine (tmeda) also induces a reaction between elemental sulfur and zinc to afford ZnS_6(tmeda), which exhibits convenient solubility and stability properties.[63] ZnS_6(tmeda) adopts a spirocycle structurally related to $[Zn(S_6)_2]^{2-}$.[64] Partial desulfurization of ZnS_6(tmeda) affords free tmeda and ZnS, indicating the inability of tmeda to compete with the bridging tendency of S^{2-}, which in turn is more basic than the corresponding $S_6{}^{2-}$.

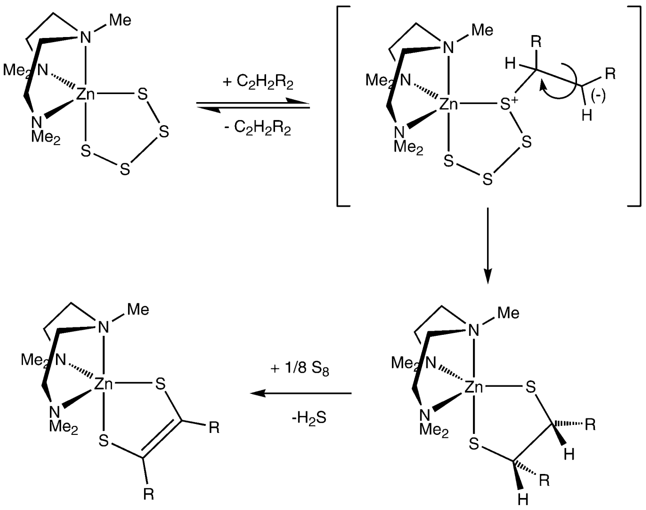
To some extent ZnS_6(tmeda) resembles Cp_2TiS_5 (see above), a time-honored polysulfide group transfer agent popularized by the groups of Schmidt and Steudel.[65,66] In fact ZnS_6(tmeda) is an excellent polysulfide transfer agent, shown by its ability to convert Cp_2TiCl_2 to Cp_2TiS_5. Evidence for the ability of ZnS_6(tmeda) to transfer $S_6{}^{2-}$ intact was provided by its reaction with Se_2Cl_2 to give cyclo-1,2,-Se_2S_6.[67] Treatment of ZnS_6(tmeda) with alkynes affords dithiolenes, which can be readily transferred to other softer electrophiles.

The diamine in ZnS_6(tmeda) can be displaced by other ligands. Otherwise, few polysulfido complexes exist with displaceable coligands. Treatment of ZnS_6(tmeda) with pentamethyldiethylenetriamine (pmdta) gives ZnS_4(pmdta),[68] where, consistent with known patterns, the polysulfido chain length contracts to accommodate the higher coordination number at the metal. In this pentacoordinate complex, the polysulfide is demonstrably more nucleophilic than its precursor hexasulfido derivative (Scheme 7). One unusual reaction effected by the tetrasulfide is the addition of alkenes to give dithiolene complexes, a net dehydrogenation. For example, treatment of ZnS_4(pmdta) with methylacrylate affords $Zn[S_2C_2(CO_2Me)H](pmdta)$, which can be independently synthesized via the reaction of the tetrasulfide with the alkyne HC_2CO_2Me.[69]

Scheme 6



Scheme 7



III. Organic and Organometallic Chemistry of Tetrathiometalates

Tetrathiometalates received focused attention following Müller's demonstration that these previously neglected anions are versatile precursors to diverse metal sulfide aggregates, many of which arise from S−S coupling reactions.[70] Our interest in thiomolybdates stemmed their potential relevance to MoS_2-based HDS catalysis. HDS embodies technologically key transformations, such as H_2 activation and the reactions of strong C−S bonds, so we sought to develop homogeneous compounds exhibiting these catalytic abilities.

Organometallic Derivatives of the Tetrathiometalates. As a continuation of our use of organometallic platforms for inorganic ligands, we examined the binding of $[MS_4]^{2-}$

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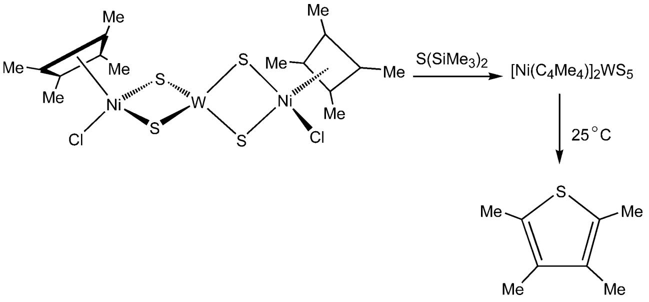
Scheme 8



by organometallic cations. Compounds prepared in this effort include $WS_4[RuCp(PPh_3)]_2$, $MS_4[Rh(C_8H_{12})]_2$, and $[MS_4Mo(CO)_4]^{2-}$ (M = Mo, W).[71–73] The WS_4^{2-} ligand engages in a M′-to-W σ-donor interaction that complements the S-to-M′ σ-donor interactions (M′ = d^6, d^8, d^{10} metal center). Consistent with this qualitative picture, tetrathiometalates exhibit electron acceptor properties; consequently $[MS_4]^{2-}$ rarely if ever binds to d^0 metals. The rarity of the κ^1-$[MS_4]^{n-}$ bonding mode can be similarly rationalized because this bonding mode precludes the stabilization arising from the dative M′→M (M = Mo, W, Re) bonding. An example of κ^1-complexation is $[CpRu(PR_3)_2(\kappa^1\text{-SReS}_3)]$, which owes its stability to the excellent π-donor properties of the Ru(II) center.[74] Significantly, $[CpRu(PR_3)_2(\kappa^1\text{-SReS}_3)]$ is reactive toward a range of small molecule substrates presaging the rich chemistry of $[ReS_4]^-$ itself (see below). The ability of tetrathiometalates to promote relatively long-range communication, presumed to be propagated by direct M- - -M bonding, is demonstrated by the observation that carbonylation of $WS_4[RuCp(PPh_3)]_2$ affords exclusively the monocarbonyl $WS_4[RuCp(PPh_3)][RuCp(CO)]$.

Given that MoS_2 is key to HDS catalysis, it is logical to expect that clusters derived from $[MoS_4]^{2-}$ would provide molecular-level insights into HDS catalysis.[75] In fact we suggest that the chemistry of $[MoS_4]^{2-}$ simulates the behavior of sulfur-rich (i.e. *inhibited*) catalysts; desulfurization catalysis occurs at sulfur-*deficient* metal sites. Catalysis by MoS_x-based HDS catalysts involves a cycling of the metal centers through sulfur-deficient states capable of abstracting sulfur from organosulfur substrates concomitant with formation of a sulfur-rich state, which requires hydrogen-dependent desulfurization to reestablish the sulfur-deficient state required for desulfurization. This logic indicates that tetrathiometalate-derived clusters should in fact be capable of *sulfiding* organic substrates, quite the reverse of HDS. We demonstrated this effect through studies on the tetramethylcyclobutadiene complex $WS_4[NiCl(C_4Me_4)]_2$.[76] Sulfiding this species with $S(tms)_2$ gives the organometallic solid $WNi_2S_5(C_4Me_4)_2$, which releases tetramethylthiophene already at room temperature (Scheme 8). These experiments show that sulfur-rich complexes make thiophenes, the exact opposite of what is sought in HDS catalysis.

Organic Derivatives of the Tetrathiorhenate. The chemistry of $[MoS_4]^{2-}$ essentially revolves around its ability to undergo S-based redox and its affinity for other metals.[70,77] But in contrast to $(C_5R_5)_2Mo_2S_4$,[78,79] $[MoS_4]^{2-}$ is unreactive, showing little or no affinity for dihydrogen or unsaturated substrates. The low reactivity of $[MoS_4]^{2-}$ is related to its highly negative reduction potential: the binding of an alkene to a pair of sulfur atoms would generate adducts $[Mo^{IV}(SR)_2S_2]^{2-}$, which would be excessively electron-rich. This logic led us to examine $[ReS_4]^-$, which is more easily reduced than the other thiometalates,[80] and its reactivity toward unsaturated substrates is correspondingly greater.

The anion[82] $[ReS_4]^-$ reacts with a wide range of organic substrates[83,84] (Scheme 9). In its simplest reaction, the anion forms adducts with alkenes, including ethene.[85] These alkene adducts, rare examples of tetrahedral d^2 complexes, represent analogues of alkene adducts invoked in the OsO_4-catalyzed dihydroxylation reaction.[86] Furthermore, an isoelectronic relationship between $[MnO_4]^-$ and $[ReS_4]^-$ is reinforced by the close resemblance in their optical spectra.[81]

Alkene adducts of $[ReS_4]^-$, e.g. the metastable ethene derivative $[ReS_2(S_2C_2H_4)]^-$, add RSH (R = H, alkyl, aryl) across one of the two Re=S bonds to afford isolable derivatives that are square pyramidal, a highly favored geometry for d^2 metal centers. The finding that *H_2S enhances the binding of ethene* contrasts with the usual prejudice that H_2S is a universal catalyst poison. RSH-enhanced alkene binding is but one of several reactions of metal sulfides that are induced by proton donors (see below).[87] Other processes that generate square pyramidal products from $[ReS_4]^-$ also afford stable derivatives. Thus, in the presence of mild O-donor reagents such as amine oxides, $[ReS_4]^-$ binds alkenes to form the bis(dithiolates) $[ReO(S_2C_2R_4)_2]^-$. An unusual extension of this reaction genre entails the S_8-induced addition of nitriles to $[ReS_4]^-$ to give adducts $[ReS(S_4)(S_2NCR)]^-$ (R = $C_6H_4NO_2$, $C_6H_4CO_2Me$, CF_3, Me) wherein both S−C and S−N bonds have formed.[88] Tatsumi has shown that the phospha-alkyne *t*-BuCP adds to $[Cp^*WS_3]^-$ to give the corresponding WS_2PC cycle.[89] Isonitriles add in a 1,1-sense to give dithiocarbodiimidates,[90] analogous to the

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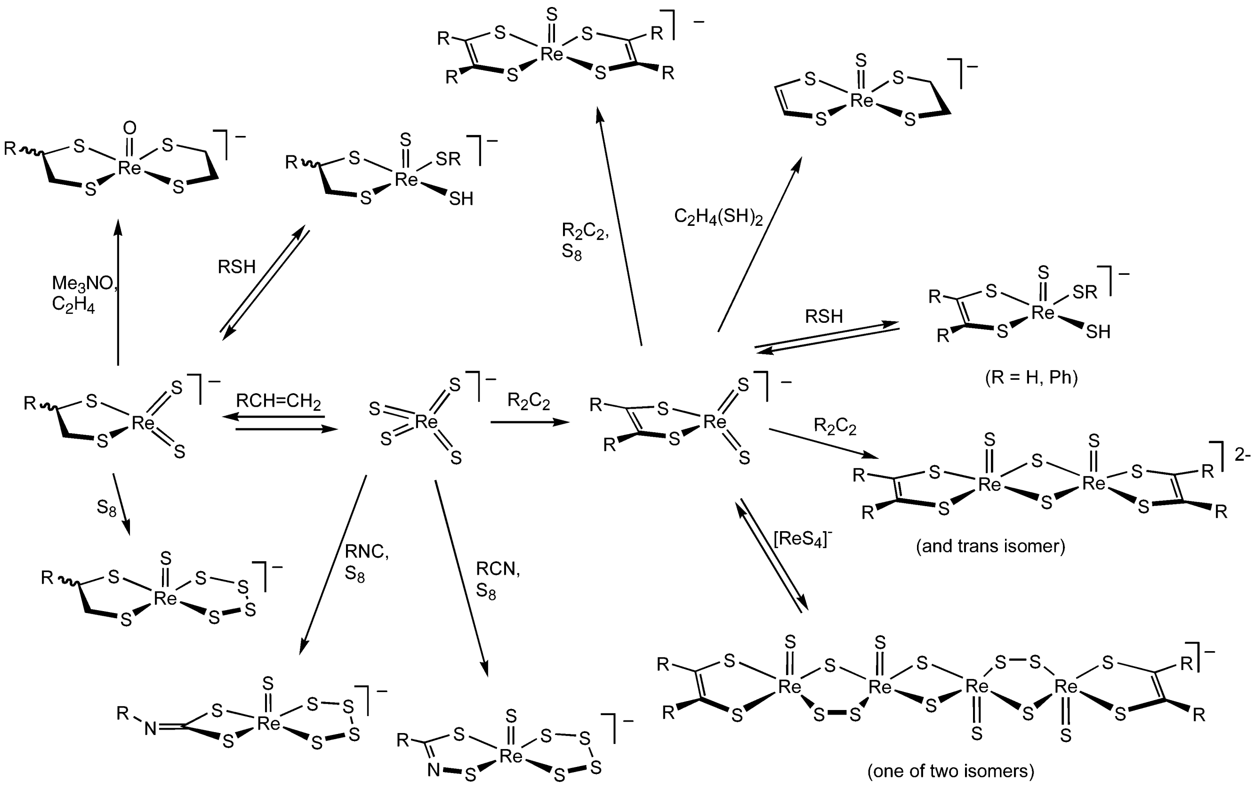
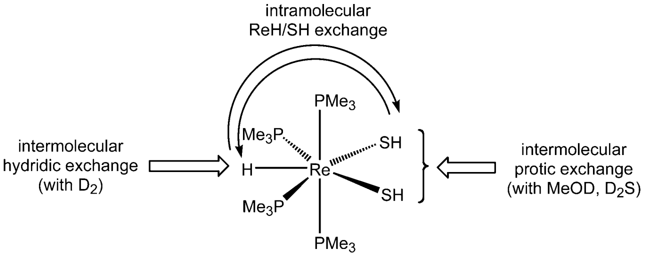
Scheme 9



RNC + $Cp_2Mo_2S_4$ reaction described by Rakowski DuBois.[91] Such experiments show that sulfur-localized substrate binding can be relevant to the catalytic properties of sulfur-rich catalysts, possibly including nitrogenase.

M−S−PMe$_3$ Catalysts Derived from the Tetrathiometalates. Analogous to the corresponding reactions of metal polysulfido complexes, desulfurization of the tetrathiometalates represents a fruitful route to novel metal sulfido complexes. These complicated reactions afford compounds that would be difficult to anticipate and difficult to synthesize by alternative routes. Optimizing these reactions often provides unexpected synthetic and mechanistic insights. For example we found that the desulfurization of thiometalates is highly sensitive to the presence of proton donors such as NH_4^+ and H_2S, nominally because desulfurization generates species with relatively high charge densities. Illustrative is the reaction of $[ReS_4]^-$ with PMe_3 in the presence of H_2S which affords $ReH(SH)_2(PMe_3)_4$, $[Re_2S_4(SH)(PMe_3)_3]^-$, or $Re(SH)_2(PMe_3)_4$, depending on conditions.[76] The species $ReH(SH)_2(PMe_3)_4$ catalyzes a variety of H−D exchange reactions. An interesting exchange involves H_2S and D_2,[92] which arises because $ReH(SH)_2(PMe_3)_4$ features both hydridic and protic centers that can exchange with these two reagents. The catalytic loop is closed via an intramolecular exchange process,[93] e.g. the interconversion of $ReD(SH)_2(PMe_3)_4$ and $ReH(SH)(SD)(PMe_3)_4$ (Scheme 10). These experiments demonstrate the rich chemistry that arises when both hydridic (Re*H*) and protic (ReS*H*) sites are present in the same metal complex, a theme of potential relevance to hydrogenase catalysis. This work illustrates, as is abundantly clear from biological precedents, that sulfur ligands are entirely compatible with, indeed enabling for, catalysis.

Scheme 10



As a hint of further rewarding chemistry—again proton-dependent—with the corresponding thiomolybdates,[94] $(Et_4N)_2MoS_4$ was found to catalyze the extrusion of H_2 from H_2S using PMe_3 whereas treatment of $(NH_4)_2MoS_4$ with PMe_3 gives Parkin's $MoS_2(PMe_3)_4$.[95]

IV. Bio-Organometallic Chemistry and Small Molecule Activation

The field of bio-organometallic chemistry was energized by the structural elucidation of the Fe-only hydrogenases (Fe H_2-ases).[4] The hydrogenases, which also comprise the more common NiFe-containing and the rare metal-free enzymes, efficiently catalyze the interconversion of protons and dihydrogen, although a typical enzyme does not catalyze both directions. These biocatalysts are attractive base metal

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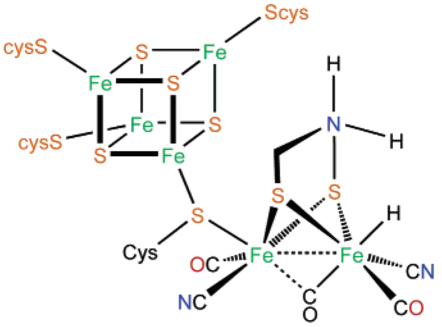
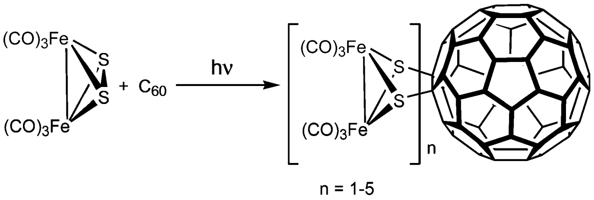


Figure 4. Schematic structure for the H-cluster of the iron-only hydrogenase active site.

alternatives to platinum metal catalysts typical for hydrogen oxidation.[96,97] The Fe H_2-ases have several unexpected design features including CO and CN^- as supporting ligands and Fe−Fe bonding (Figure 4). Furthermore the crystallographic results provide clear hints about how this site activates hydrogenic substrates. One coordination site approximately trans to the Fe−Fe bond can be occupied with CO;[98] it is likely that dihydrogen as well as hydride bind at this same site.

Synthesis of First Generation Models for the Fe-Only Hydrogenases. The binuclear active site of the Fe H_2-ases bears an obvious structural resemblance to the iron carbonyl thiolates $Fe_2(SR)_2(CO)_6$, which we[99,100] and many others[101,102] had previously studied (e.g., eq 2).[99] Soon after Peters's report on the structure of the *C. pasteurianum* Fe H_2-ase, we undertook the synthesis of models in the form of cyano derivatives of $Fe_2(SR)_2(CO)_6$. These studies coincided with our ongoing work on cyanometalate cages,[103−105] which provided relevant experience with organometallic cyanide chemistry. We (and others[106,107]) found that treatment of MeCN solutions of the propanedithiolate $Fe_2(S_2C_3H_6)(CO)_6$ with two equiv of Et_4NCN gives the deep-red $(Et_4N)_2[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$ in excellent yield. We used this method to characterize several salts of $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$,[108] three isomers of which have been observed crystallographically, suggesting that these isomers are of comparable energy.[108] With respect to ν_{CO}, the IR spectra of these dicyanides bear sufficient resemblance to the reduced enzymes[109] to support the proposition that Fe(I) is biologically relevant.



(2)

Synthetic studies on $[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ revealed a mechanistic puzzle: treatment of the hexacarbonyl with one equiv of Et_4NCN gives only traces of $[Fe_2(S_2C_3H_6)(CN)(CO)_5]^-$, the major product being the *di*cyanide. Normally, of course, nucleophilic substitutions occur stepwise, with each successive step proceeding more slowly than the preceding one, a pattern that reflects a fundamental relationship between molecular charge and electrophilicity. This mechanistic puzzle was resolved through the surprising finding that independently prepared $Et_4N[Fe_2(S_2C_3H_6)(CN)(CO)_5]$[108] is *not* an intermediate in the dicyanation of the hexacarbonyl: it reacts more slowly with Et_4NCN than does $Fe_2(S_2C_3H_6)(CO)_6$. Pickett et al.'s evidence for the 36e $Fe_2(SR)_2(\mu\text{-}CO)(CO)_4(L)(CN)]$ intermediates in ligand substitution of these diiron species[110] accommodates the computationally anticipated migration of CO from a terminal to a bridging position.[111]

A useful consequence of (and support for) our mechanistic model was the development of the cyanide-induced phosphine substitution of the parent hexacarbonyl. Thus, treatment of $Fe_2(S_2C_3H_6)(CO)_6$ with Et_4NCN in the presence of PMe_3 efficiently affords $(Et_4N)[Fe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)]$. The reactive intermediate $[Fe_2(S_2C_3H_6)(CN)(CO)_6]^-$ is proposed to undergo attack by PMe_3 (Scheme 11).

The binuclear active site features a μ-CO functionality, although the degree of bridging depends on the oxidation state of the binuclear center. The μ-CO functional group has proven difficult to replicate in $[Fe^I]_2$ models. Thermally unstable intermediates with μ-CO ligands have been observed upon oxidation of specially substituted derivatives of $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$.[112] These results encouraged us to investigate diiron dithiolates in higher oxidation states, which might stabilize bridging carbonyl ligands thereby providing opportunities to observe H_2-binding at the diiron center. The enzyme's $(CN)_2(CO)_3(H_x)[(\mu\text{-}SR)(Fe_4S_4(SR)_3]$ donor set might be reasonably simulated by a homoleptic set of ligands with donor strength intermediate between CO and CN^-. MeNC was selected for this purpose, especially as its rodlike structure also mimics that of the natural diatomic ligands.

Whereas most donor ligands only substitute two CO groups on $Fe_2(S_2C_nH_{2n})(CO)_6$, tetrasubstitution can be effected with MeNC. The species $Fe_2(S_2C_nH_{2n})(CO)_2(CNMe)_4$ are relatively electron-rich as indicated by IR measurements and their susceptibility to protonation. Oxidation of Fe_2-

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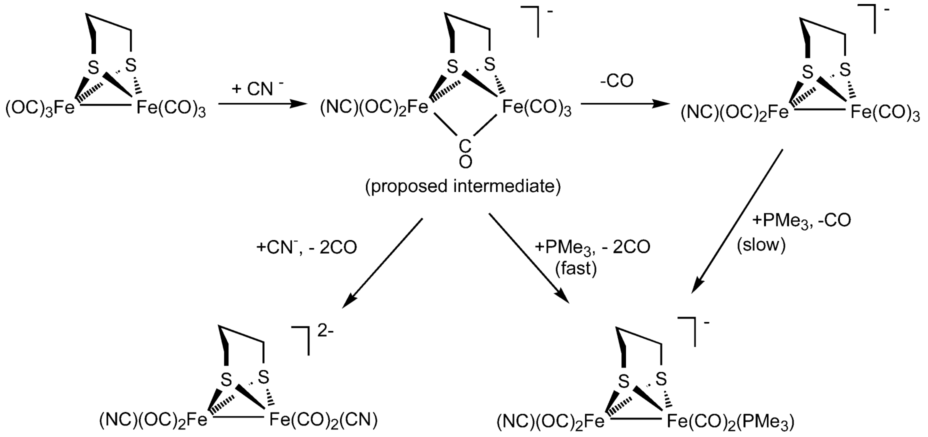
Scheme 11



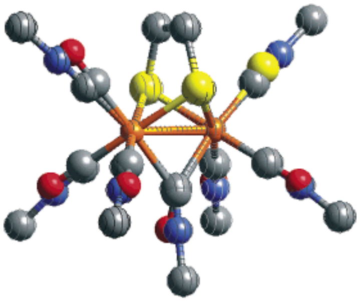
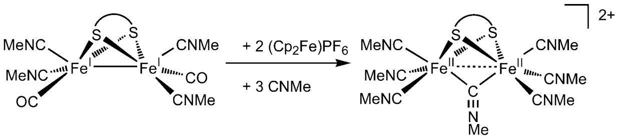


Figure 5. Overlay of the crystallographic models of the dication in $[Fe_2(S_2C_2H_4)(CNMe)_7]^{2+}$ with the binuclear active site of the CO inhibited form of the *C. pasteurianum* (CpI) Fe-only hydrogenase,[114] where all diatomic ligands were modeled as CO in the H-cluster (orange, Fe; yellow, S; red, O; blue, N; gray, C). The atoms and bonds of the dication are shown with solid lines. The hydrogen atoms and the unidentified light atoms bridging the sulfur atoms in the H-cluster have been omitted.

$(S_2C_nH_{2n})(CO)_2(CNMe)_4$ with Cp_2Fe^+ in the presence of CNMe affords $[Fe_2(S_2C_nH_{2n})(CNMe)_7](PF_6)_2$ ($n = 2, 3$), members of a new class of diferrous dithiolates (eq 3).[113]



(3)

The coordination geometry about the diiron center in such complexes closely matches that for the enzyme active site (Figure 5).

In particular, the binuclear site features a confacial bioctahedron with a μ-CNMe ligand. In the ethanedithiolate derivative the μ-CNMe ligand is symmetrically bridging, whereas in the propanedithiolate derivative the μ-CNMe is unsymmetrical. DFT calculations indicate that the energy difference between the symmetric and unsymmetrical geometries is small, which is relevant to the variable asymmetry of the μ-Fe−CO distances in the enzymes.[115] Ongoing experiments are probing the corresponding CO-substituted derivatives, e.g. $[Fe_2(S_2C_3H_6)(CNMe)_{7-x}(CO)_x]^{2+}$. These mixed ligand species represent superior models of the Fe H_2-ases, and their chemical reactivity promises to open new avenues of research.

Modeling Hydrogen Evolution. In initial experiments, we found that acidification of solutions of $[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ generates some dihydrogen.[116] Unfortunately protonation of the dicyanide is accompanied by irreversible conversion of the diiron species into an intractable solid. The unsuitability of the dicyanide as a catalyst is attributed to its highly reducing character, indicated by its ability to reduce protons directly. Electrochemical measurements also confirm that the dicyanide is a potent reductant.

Monoanion $[Fe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)]^-$ is ca. 0.5 V less reducing than the dicyanide and *proved to be an excellent catalyst for proton reduction*.[117] This observation provided the *first* functional link between organometallic models and proton reduction by Fe-only hydrogenases. Dihydrogen production by the cyano-phosphine, which exists as two isomers in solution, begins with protonation to afford one isomer of $HFe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)$. Spectroscopic and crystallographic characterization established that protonation occurs at the Fe−Fe bond. One guide to the regiochemistry of the protonation is $\Delta\nu_{CO}$, which is ca. 80 cm^{-1} for protonation at metal and ca. 15 cm^{-1} for protonation at CN. The regiochemistry of the protonation depends subtly on the electronic properties of the coligands as illustrated by the fact that $[Fe_2(S_2C_3H_6)(CN)(CO)_4(P(OMe_3))]^-$ protonates at C*N*⁻, not the Fe−Fe bond. Protonation at metal in a metal cyanide is quite rare.[118,119]

Hydride $HFe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)$ further protonates at nitrogen to give $[HFe_2(S_2C_3H_6)(CNH)(CO)_4(PMe_3)]^+$, which behaves as a typical strong Bronsted acid.[120] Reduction of $[HFe_2(S_2C_3H_6)(CNH)(CO)_4(PMe_3)]^+$ occurs irreversibly at $E_p = -0.98$ V concomitant with the formation of H_2. In a preparative scale reaction, this cation catalyzes quantitative proton reduction to H_2 with no decomposition of the catalyst (eq 4).

$$2e^- + 2H^+ \xrightarrow{Fe_2(SR)_2(CO)_4L_2} H_2 \qquad (4)$$

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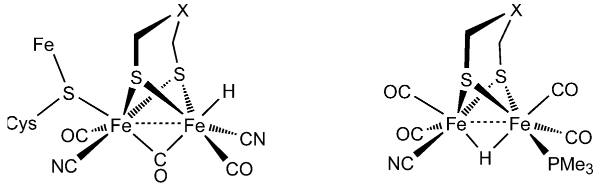
Scheme 12



assumed active site

catalytically active model

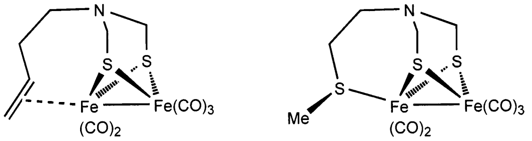
The bisphosphine $Fe_2(S_2C_3H_6)(CO)_4(PMe_3)_2$ protonates at the Fe−Fe bond, as anticipated by Poilblanc et al.,[121] with a pK_a similar to that of $[Fe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)]^-$. The resulting $[HFe_2(S_2C_3H_6)(CO)_4(PMe_3)_2]^+$ is also an electrocatalyst for proton reduction; in fact, it is likely that many $Fe_2(SR)_2(CO)_{6-x}L_x$ species will similarly prove to be catalytically active. There is some evidence that the bisphosphine may be a slower catalyst. For example, the $[HFe_2(S_2C_3H_6)(CO)_4(PMe_3)_2]^{+/0}$ couple appears to be more reversible than the corresponding couples for the reduction of $HFe_2(S_2C_3H_6)(CN)(CO)_4(PMe_3)$ and $[HFe_2(S_2C_3H_6)(CNH)(CO)_4(PMe_3)]^+$.

Whereas the hydride in $HFe_2(S_2C_nH_{2n})(CO)_4L_2$ bridges the Fe centers, the hydride in the enzyme is almost certainly terminal and a CO is bridging. The biological and synthetic catalysts feature isomeric forms of $[HFe_2(SR)_2L_6]$, (Scheme 12). It is unclear if the structural differences between the synthetic models and the active site reflect complex supramolecular interactions within the enzyme. It is also possible that the enzyme and our models differ with respect to their oxidation states.

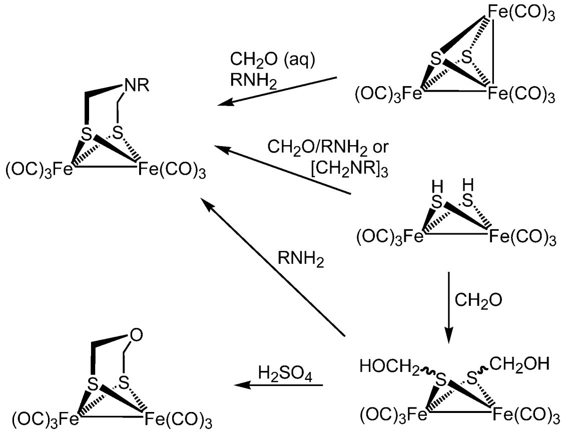
The Azadithiolate Cofactor. Most modeling studies have focused on the metal-centered chemistry of the dinuclear active site, but the dithiolate cofactor is also unique. Cofactors always merit close examination because they are generally critical to catalytic function, and because they can often be readily adapted to model systems. Early crystallographic studies indicated that the diiron centers in the Fe H_2-ases are bridged by 1,3-propanedithiolate, but this proposal has been revised. The prevailing view is that the bridging dithiolate is the azadithiolate $HN(CH_2S^-)_2$.[115] The amine functionality in this azadithiolate would be geometrically restrained from directly coordinating to any metal, but it obviously could complement the catalytic function of the dimetal unit by interacting with flanking ligands. Noncoordinating amine functionalities have been shown to promote deprotonation of H_2 ligands in organometallic complexes.[122−124]

We prepared diiron azadithiolates $Fe_2[(SCH_2)_2NR](CO)_6$ by the reaction of $Li_2[Fe_2(S)_2(CO)_6]$[125] and $(ClCH_2)_2NR$.[126] Although few bis(chloromethyl)amines were known prior to our efforts, several such proligands can be prepared by the reaction of primary amines, formaldehyde, and $SOCl_2$. This versatile methodology allowed us to attach diverse substituents to the amine; in this way we generated alkene- and thioether-functionalized derivatives (Scheme 13).[127]

Scheme 13



Scheme 14



Crystallographic studies of $(Et_4N)_2\{Fe_2[(SCH_2)_2NMe](CN)_2(CO)_4\}$ were particularly revealing because two conformers cocrystallize. In the major conformer, the *N*-methyl group sterically clashes with the underlying CN ligand, manifested by a flattening of the amine. In the minor conformer, the *N*-methyl group is sterically unencumbered and the amine is pyramidal. The implication of these results is that the encumbered conformer must be stabilized electronically; otherwise only the sterically unencumbered isomer would be observed. DFT calculations indicate that this stabilization arises from an anomeric effect, i.e. the interaction of the nitrogen lone pair with the relatively low energy C−S σ^* bonds.

We found that $Fe_2(SH)_2(CO)_6$ efficiently condenses with formaldehyde in the presence of primary amines to give the corresponding azadithiolates (Scheme 14).[128] Alkyl and arylamines also participate in this reaction to give $Fe_2[(SCH_2)_2NR](CO)_6$ where R = *t*-Bu, Bn, and Ph. The otherwise very stable cluster $Fe_3S_2(CO)_9$ also reacts with aqueous formaldehyde and amines or ammonia to give $Fe_2[(SCH_2)_2NR](CO)_6$. To synthesize $Fe_2[(SCH_2)_2NH](CO)_6$, which contains the proposed secondary amine, we employed $(NH_4)_2CO_3$ as a source of ammonia.

With regard to the mechanism of these multicomponent reactions, $Fe_2(SH)_2(CO)_6$ reacts with aqueous formaldehyde in the absence of amines to afford $Fe_2(SCH_2OH)_2(CO)_6$, which reacts at room temperature with amines to give the corresponding azadithiolates. Since amines and formaldehyde condense to give imines, it is not surprising that $Fe_2(SH)_2(CO)_6$ condenses efficiently with 1,3,5-$(CH_2)_3(NR)_3$ to afford $Fe_2[(SCH_2)_2NR](CO)_6$ (R = Me, Ph). The NH derivative also arises via the reaction of $Fe_2(SH)_2(CO)_6$ and hexamethylenetetramine, $(CH_2)_6N_4$. $Fe_2(SCH_2OH)_2(CO)_6$ undergoes

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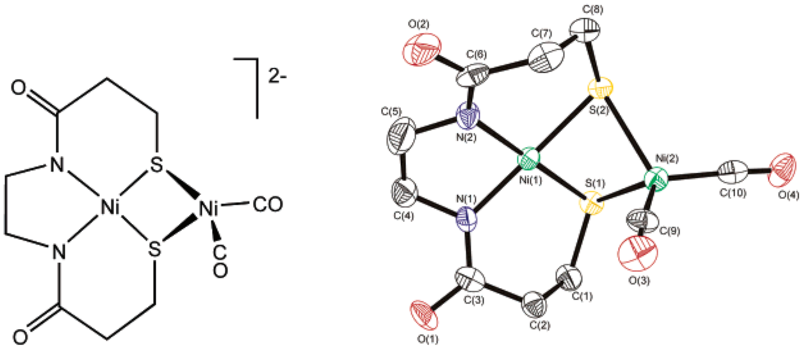
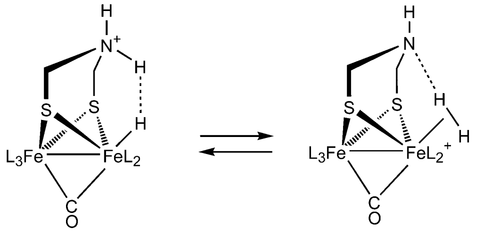


Figure 6. Structure of the "Ni-Ni" model for the proposed active form of the binuclear active site of acetyl coenzyme A synthase.

Scheme 15



acid-catalyzed condensation to give $Fe_2[(SCH_2)_2O](CO)_6$, the backbone of which is also consistent with the results from protein crystallography, i.e. a chain of three carbon-like atoms, the central one of which could interact with a cysteinyl SH.

The hydroxymethyl derivative $Fe_2(SCH_2OH)_2(CO)_6$ is interesting in part because little has been published on the interaction of metal sulfides with C-1 compounds.[5] The interaction of small carbon compounds with metal sulfides are conceivably relevant to the formation of biocatalysts in the primordial era.[129] Although $Fe_2(SCH_2OH)_2(CO)_6$ was not fully characterized, the corresponding glyoxal derivative $Fe_2[S_2(CHOH)_2](CO)_6$ is more stable.

The structure of $(Et_4N)_2\{Fe_2[(SCH_2)_2NH](CN)_2(CO)_4\}$ established that the N−H is axial, the orientation favored by the anomeric effect, and the amine is pyramidal. The amine in $Fe_2[(SCH_2)_2NH](CO)_6$ can be protonated by HOTf as indicated by $\Delta\nu_{CO(avg)} = 17\ cm^{-1}$, but the resulting ammonium ion is deprotonated by water, which indicates a $pK_a < 1$. Such an acidic ammonium center should be capable of protonating even weakly basic iron hydrides to give coordinated H_2.

The natural selection of the azadithiolate cofactor might have been favored for any of several reasons. Azadithiolates might be evolutionarily advantaged because of their easy biosynthesis, which as shown above requires only simple components (formaldehyde equivalent, ammonia, H_2S). Of course, most intriguing of all, the amine in the cofactor could participate in the activation of dihydrogen as shown in Scheme 15. Dihydrogen oxidation probably occurs via conversion of an incipient dihydrogen complex to a terminal hydride, which is susceptible to oxidation and loss as a proton. Amine-modified diphosphines have recently been shown to effect H−D exchange reactions characteristic of hydrogenase enzymes.[130]

Beyond the Hydrogenases: Models for Acetyl Co-A Synthase. Our work on bio-organometallics has recently extended beyond hydrogenase models to include acetyl coenzyme-A synthase (ACS), a key enzyme for CO processing.

Recent crystallographic studies have elucidated remarkable structures for these enzymes, which motivated us to undertake syntheses of models for the ACS bimetallic subunit. Like the Fe H_2-ase, the ACS enzyme is a bridged assembly, consisting of well-defined subunits linked by coordination bonds.[131] We prepared bimetallic systems bearing a stoichiometric and structural resemblance to the bimetallic site of the proposed[10] functional form of ACS (Figure 6).[132] Our strategy entailed complexation of nickel diamino/diamidodithiolates to sources of low valence Cu and Ni to test for their ability to bind CO. Of particular note is the finding that Ni−Ni model forms a CO adduct, whereas related Ni−Cu derivatives do not. Our efforts provide the first models for a biological role for nickel carbonyls.

V. Summary

Research on sulfur-rich metal complexes has proven to be fruitful with respect to novel structures, methods development, and chemical transformations, including catalytic processes. The extensive role of metal sulfides in bio- and industrial catalysis indicates that this area holds tremendous potential for continued theoretical advances and practical applications. Especially encouraging are advances in structural biology that have defined targets for synthesis and catalysis.

This review surveyed selected areas of chemistry studied by our group over the past 15 years or so. An effort is made to show the connections, logical and historical, between the various research themes. For the sake of space, results are not presented for all of the major research topics that have attracted our attention, e.g., carbon sulfides,[133] the organometallic chemistry of thiophene[134] and related π-heterocycles,[135] and our ongoing work on cyanometalate cages.[136]

Acknowledgment. Through the citations in this review, I have endeavored to acknowledge the accomplishments of

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undergraduate, graduate, and postdoctoral co-workers who have helped conceive and implement these research projects. I have also tried to recognize other research groups that have contributed to the evolution of these research themes through their insights and shared values. Not explicitly discussed, but of tremendous importance, are the many contributions from my colleagues in the School of Chemical Sciences. Our research has been sponsored by the Department of Energy, the National Institutes of Health, and the National Science Foundation.

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