[ReH(SH)$_2$(PMe$_3$)$_4$]: A Catalyst for Fundamental Transformations Involving H$_2$ and H$_2$S**

Daniel E. Schwarz, Joel A. Dopke, Thomas B. Rauchfuss,* and Scott R. Wilson

While sulfur is often described as a catalyst poison, many of nature's most remarkable enzymes feature metals embedded in a sulfur-rich coordination sphere. This is especially true for the biological processing of dihydrogen, dinitrogen, and carbon monoxide.[1–3] In the industrial sector, metal sulfides are used to activate H$_2$ in the hydrodesulfurization (HDS) process.[4, 5] Inspired by these precedents, there is much interest in metal sulfides that interact with H$_2$. Three types of metal complexes are known to do so,[6, 7] and one, [Cp$_2$Mo$_2$S$_4$] (Cp = cyclopentadienyl), exhibits a range of catalytic properties.[8] Encouraged by rich organic chemistry of the [ReS$_4$]$^-$ion[9] and [Re$_2$S$_7$][10] we have probed the activation of dihydrogen by rhenium sulfido complexes.

Initial studies revealed that the reaction of [ReS$_4$]$^-$ ions with PMe$_3$ affords diverse compounds because PMe$_3$ serves as both a desulfurization agent and a trapping ligand. When MeCN solutions of [NEt$_4$][ReS$_4$] are allowed to react with excess PMe$_3$ under an atmosphere of H$_2$S, we obtained a 75% isolated yield of beige crystals of [ReH(SH)$_2$(PMe$_3$)$_4$] (**1**). The synthesis is proposed to proceed according to Equation (1).

$$[ReS_4]^- + 8\,PMe_3 + 3\,H_2S \ \rightarrow \\ [ReH(SH)_2(PMe_3)_4] + SH^- + H_2 + 4\,SPMe_3 \tag{1}$$

This unusual synthesis involves a complete revision of the ligand set and metal oxidation state. Preliminary experiments demonstrate that this PMe$_3$/H$_2$S reaction can be used to convert other thiometallates into novel M−SH complexes (M = metal center).

As suggested by Equation (1), **1** is a room temperature catalyst for the unusual reaction of H$_2$S with PMe$_3$ to give SPMe$_3$ and H$_2$.[11] Because M−SH groups are typically nucleophilic, S-atom transfer from M−SH to PMe$_3$ is unexpected. S-atom transfer is, however, typical for sulfido complexes. This reasoning suggests that the S-atom transfer may proceed via the reversible formation of a Re=S species. The kinetic lability of **1** is also indicated by its rapid reaction with CO (1 atm, 25 °C) to give cis-[ReSH(CO)(PMe$_3$)$_4$], [ReSH(CO)$_2$(PMe$_3$)$_3$],[12] and [ReSH(CO)$_3$(PMe$_3$)$_2$][13] [Eq. (2)].

$$\tag{2}$$
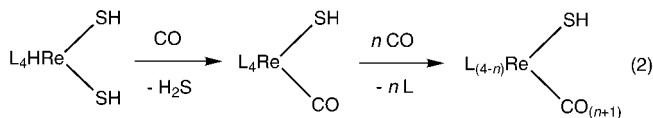
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Crystallographic characterization reveals that **1** has a pentagonal bipyramidal geometry with idealized C_{2v} symmetry (Figure 1). The sulfur-bound H atoms were not observed crystallographically but Re=S bonds are ruled out by the bond length Re−S of 2.52 Å, which is consistent with a single Re−S
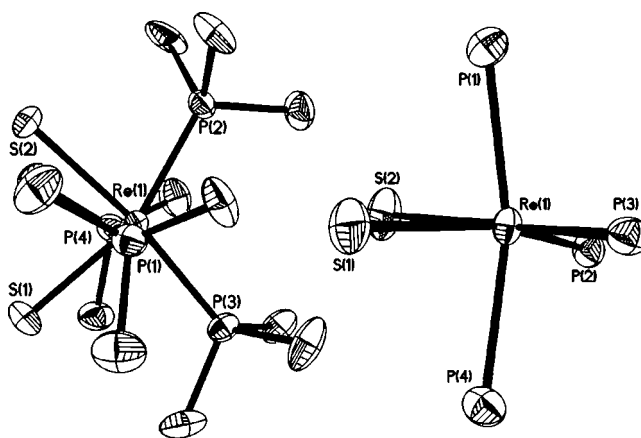

Figure 1. Two views of the molecular structure of **1**, (thermal ellipsoids set at the 50% probability level). Average selected bond lengths [Å] and angles [°]: Re-S 2.52, Re-P$_{eq}$ 2.37, Re-P$_{ax}$ 2.42; P$_{eq}$-Re-P$_{eq}$ 110.0, P$_{ax}$-Re-P$_{ax}$ 163.8, P$_{ax}$-Re-P$_{eq}$ 95.5, S-Re-S 83.0, P$_{ax}$-Re-S 85.0, P$_{eq}$-Re-S 89.15, 77.88.

bond. The position of the hydride ligand between the equatorial phosphane ligands is inferred from the expanded P-Re-P angle (110°) as well as a nuclear Overhauser enhancement effect (NOE) interaction between the Re−H and (PMe$_3$)$_{eq}$ groups. The ^{1}H and ^{31}P NMR spectra support the crystallographic results, that is, both the SH and ReH protons are coupled to ^{31}P nuclei, the former giving rise to a doublet of triplets and the latter a triplet of triplets. At −10 °C ([D$_6$]-Me$_2$CO), the ^{31}P NMR spectrum of **1** consists of two triplets.

Treatment of **1** with dmpe (Me$_2$PCH$_2$CH$_2$PMe$_2$) gave [ReH(SH)$_2$(PMe$_3$)$_2$(dmpe)] (**2**), which is characterized by distinctive ^{31}P and ^{1}H NMR spectroscopic signatures (Figure 2). Complex **2** is a rare example of a complex with nonequivalent S−H groups, and magnetization transfer experiments show that exchange between these S-bound H sites is slow (< 0.45 s^{-1} = T_1^{-1} for SH). Whereas **1** undergoes complete exchange with P(CD$_3$)$_3$ upon mixing (25 °C), **2** exchanges with P(CD$_3$)$_3$ only over the course of hours.

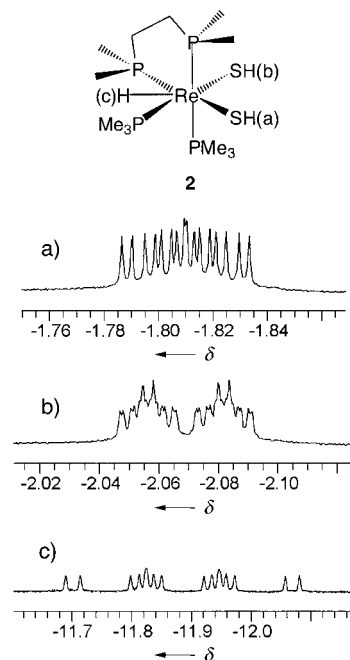Solutions of **1** catalyze the conversion of H$_2$ and

Figure 2. Selected regions of the 500 MHz ^{1}H NMR spectrum of **2** (C$_6$D$_6$ solution).

D_2 into HD (monitored by ^1H NMR spectroscopy). Relevant to this process, solutions of **1** react with D_2 to give [ReD(SH)$_2$-(PMe$_3$)$_4$] within a few minutes at 25°C. Under the same conditions, the reaction of D_2 (1 atm) with the dmpe derivative **2** is slow ($t_{1/2} > 3.5$ h). We conclude that H/D exchange proceeds via the intermediate 16 e$^-$ species [ReH(SH)$_2$(PR$_3$)$_3$], which is more difficult to form from **2**. An important observation is that the Re−H sites are deuterated more quickly than the S−H sites, thus the S−H ligands are not directly involved in HD formation, but are spectators.

The S-bound H groups in **1** and **2** exchange with protic reagents: treatment of benzene solutions of **1** and **2** with excess CD$_3$OD for several minutes, followed by evaporation, resulted in partial deuteration of the S−H sites, as well as significant exchange into the Re−H sites.

Exchange of protons between the M−H and M−SH sites in **1** occurs over the course of several hours at room temperature. This process can be quantitatively analyzed by ^1H NMR spectroscopy by monitoring the conversion of [ReD(SH)$_2$-(PMe$_3$)$_4$] into [ReH(SD)(SH)(PMe$_3$)$_4$] ($k = 7.10(8) \times 10^{-5}$ s^{-1} at 20°C). At equilibrium the deuterium in [D$_1$]**1** (and in [D$_2$]**1**) is approximately equally distributed over the three accessible sites (ReH, and two SH sites). The rate of transfer of D from ReD to ReSH sites in **1** and **2** are approximately the same, consistent with an intramolecular process. The intramolecular H-atom exchange in [M(SH)H] complexes, for example, [Ru(SH)(H)(PPh$_3$)$_3$], is well established.[14]

Solutions of **1** catalyze isotopic exchange between D_2 and H_2S to give HD and DHS, as verified by in situ ^1H NMR spectroscopic measurements. This process can be understood by invoking the three aforementioned exchange processes: H/D exchange between ReSH and D_2S, intramolecular H/D exchange between the ReSD and ReH sites, and exchange of the ReD site with H_2.

In contrast to the high reactivity of **1**, the corresponding trihydride [ReH$_3$(PMe$_3$)$_4$] is kinetically inert.[15] In other words, the usual view that sulfur poisons catalysts is clearly inappropriate in this case: the sulfide ligands are *enabling*. The catalytic properties of **1** result from its bifunctional nature with both protic (SH) and hydridic (ReH) sites that communicate by an intramolecular exchange process (Scheme 1).
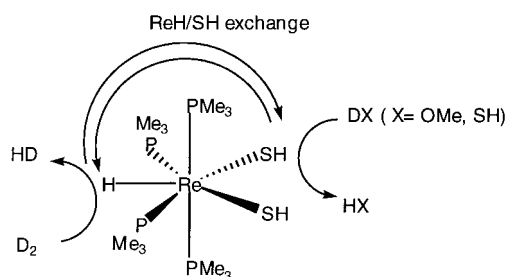
Scheme 1.

Complex **1** uniquely undergoes H/D exchange at both S*H* and Re*H* with D_2, but by different mechanisms. In [Cp$_2^*$Ti(SH)(H)],[7] both S*H* and Ti*H* exchange together and dissociatively (by elimination of H_2) whereas in **1**, the Re*H* exchanges (associatively) with D_2, independent of ReS*H*

exchange. The importance of our results is that HDS catalysts use H_2, and it is exciting to see that the M−SH group is an electronically important spectator in the H_2 activation process. Compound **1** is a singular example of a L$_n$M(H)(SH) compound where the hydride site undergoes exchange with D_2 at a faster rate than the SH site.

Experimental Section

were corrected for absorption on the basis of integration. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150678. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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The Hg₃²⁺ Group as a Framework Unit in a Host – Guest Compound: [Hg₁₁As₄](GaBr₄)₄**

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Various inorganic supramolecular compounds with three-dimensional host structures are known.[1] Among them is a separate group of phases in which the three-dimensional network is formed by tetrahedrally coordinated pnicogen and linearly coordinated mercury atoms.[2] In some structures, some or all of the pnicogen atoms are joined into dumbbells

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while keeping their tetrahedral arrangement.[3] Here we report on [Hg₁₁As₄](GaBr₄)₄ (**1**), a novel supramolecular complex in which linear Hg_2^{2+} and Hg_3^{2+} fragments as well as Hg^{2+} cations take part in the formation of the three-dimensional host network. This is the first example of a linear Hg_3^{2+} group serving as a part of a three-dimensional framework.

The crystal structure[4] of **1** consists of a three-dimensional $[Hg_{11}As_4]^{4+}$ host network and tetrahedral $GaBr_4^-$ guest anions, which occupy one-dimensional infinite tunnels of the host framework (Figure 1). Large separations between the
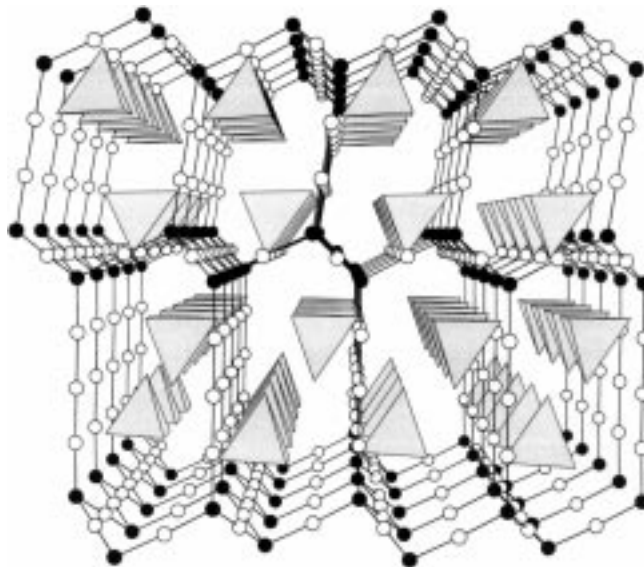

Figure 1. A perspective view of the crystal structure of [Hg₁₁As₄](GaBr₄)₄ (**1**) along the [010] direction of the unit cell. Open circles, mercury; filled circles, arsenic. Polyhedra represent the GaBr₄⁻ ions.

bromine atoms of different GaBr₄ tetrahedra (>3.68 Å), and between the bromine atoms and mercury atoms of the cationic framework (>3.53 Å) allow the guests to be regarded as almost completely isolated from each other and from the host structure. With such separations, the host – guest interactions between the $[Hg_{11}As_4]^{4+}$ framework and the $GaBr_4^-$ anions are apparently limited to weak electrostatic forces.

All the arsenic atoms in the host framework take part in the formation of corrugated layers, composed of edge-linked six-membered As_6 rings in a chair conformation, in which each edge of a chair is centered by a Hg^{2+} cation. These layers are interconnected by linear Hg_2^{2+} and Hg_3^{2+} fragments that alternate along the c axis of the unit cell in such a way that tetrahedral coordination of As is achieved. The ordered alternation of the two mercury polycations leads to the formation of two tunnels of different size that extend along the b axis of the unit cell (Figure 2). The Hg_2^{2+} and Hg_3^{2+} units serve as boundaries for the smaller and larger tunnels, respectively. The Hg–Hg distances in the Hg_2^{2+} (2.57 Å) dumbbell and in the Hg_3^{2+} group (2.58 Å) are typical of those found in various compounds containing mercury in low oxidation states.[5] Note that while Hg_2^{2+} dumbbells are quite common in mercury chemistry, only a few compounds containing Hg_3^{2+} are known. In these, such groups are stabilized by $AlCl_4^-$, AsF_6^-, or $(F_5MOSO_2OMF_5)^{2-}$ (M = Nb,