

[ReH(SH)₂(PMe₃)₄]: A Catalyst for Fundamental Transformations Involving H₂ and H₂S**

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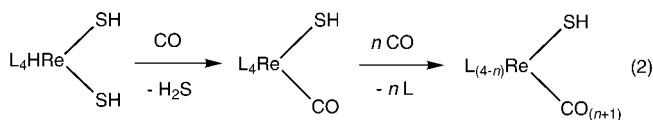
While sulfur is often described as a catalyst poison, many of nature's most remarkable enzymes feature metals embedded in a sulfur-rich coordination sphere. This is especially true for the biological processing of dihydrogen, dinitrogen, and carbon monoxide.^[1–3] In the industrial sector, metal sulfides are used to activate H₂ in the hydrosulfurization (HDS) process.^[4, 5] Inspired by these precedents, there is much interest in metal sulfides that interact with H₂. Three types of metal complexes are known to do so,^[6, 7] and one, [Cp₂Mo₂S₄] (Cp = cyclopentadienyl), exhibits a range of catalytic properties.^[8] Encouraged by rich organic chemistry of the [ReS₄][–] ion^[9] and [Re₂S₇]^[10] we have probed the activation of dihydrogen by rhenium sulfido complexes.

Initial studies revealed that the reaction of [ReS₄][–] ions with PMe₃ affords diverse compounds because PMe₃ serves as both a desulfurization agent and a trapping ligand. When MeCN solutions of [NEt₄][ReS₄] are allowed to react with excess PMe₃ under an atmosphere of H₂S, we obtained a 75 % isolated yield of beige crystals of [ReH(SH)₂(PMe₃)₄] (**1**). The synthesis is proposed to proceed according to Equation (1).



This unusual synthesis involves a complete revision of the ligand set and metal oxidation state. Preliminary experiments demonstrate that this PMe₃/H₂S 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 H₂S with PMe₃ to give SPMe₃ and H₂.^[11] Because M–SH groups are typically nucleophilic, S-atom transfer from M–SH to PMe₃ 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)(PMe₃)₄], [ReSH(CO)₂(PMe₃)₃],^[12] and [ReSH(CO)₃(PMe₃)₂]^[13] [Eq. (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

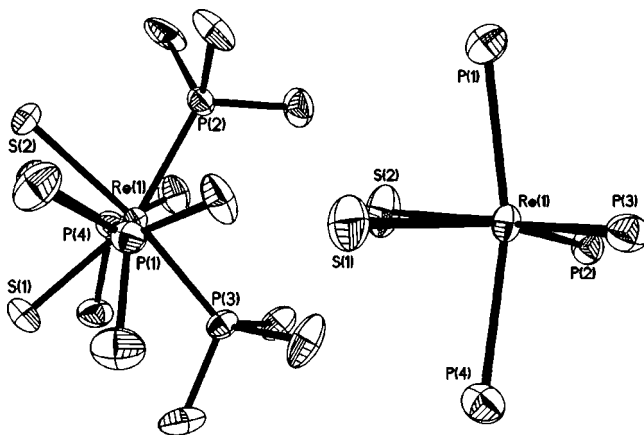


Figure 1. Two views of the molecular structure of **1**, (thermal ellipsoids set at the 50 % probability level). Average selected bond lengths [Å] and angles [°]: Re–S 2.52, Re–P_{eq} 2.37, Re–P_{ax} 2.42; P_{eq}–Re–P_{eq} 110.0, P_{ax}–Re–P_{ax} 163.8, P_{ax}–Re–P_{eq} 95.5, S–Re–S 83.0, P_{ax}–Re–S 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 (PMe₃)_{eq} groups. The ¹H and ³¹P NMR spectra support the crystallographic results, that is, both the SH and ReH protons are coupled to ³¹P nuclei, the former giving rise to a doublet of triplets and the latter a triplet of triplets. At –10 °C ([D₆]-Me₂CO), the ³¹P NMR spectrum of **1** consists of two triplets.

Treatment of **1** with dmpe (Me₂PCH₂CH₂PMe₂) gave [ReH(SH)₂(PMe₃)₂(dmpe)] (**2**), which is characterized by distinctive ³¹P and ¹H 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} = T₁^{–1} for SH). Whereas **1** undergoes complete exchange with P(CD₃)₃ upon mixing (25 °C), **2** exchanges with P(CD₃)₃ only over the course of hours.

Solutions of **1** catalyze the conversion of H₂ and

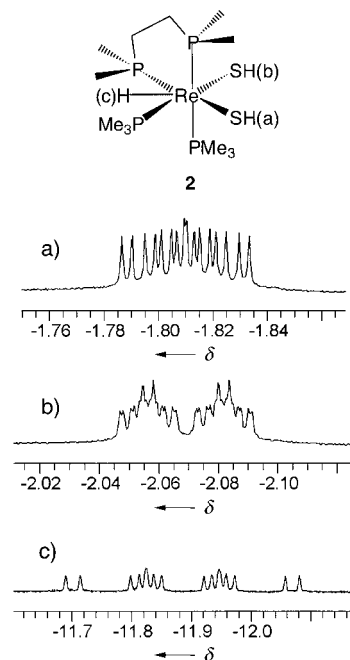


Figure 2. Selected regions of the 500 MHz ¹H NMR spectrum of **2** (C₆D₆ solution).

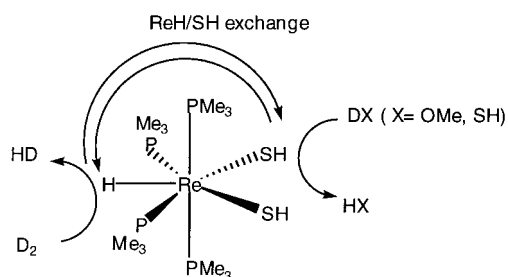
D₂ into HD (monitored by ¹H NMR spectroscopy). Relevant to this process, solutions of **1** react with D₂ to give [ReD(SH)₂-(PMe₃)₄] within a few minutes at 25 °C. Under the same conditions, the reaction of D₂ (1 atm) with the dmpe derivative **2** is slow (*t*_{1/2} > 3.5 h). We conclude that H/D exchange proceeds via the intermediate 16e⁻ species [ReH(SH)₂(PR₃)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 CD₃OD 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-(PMe₃)₄] into [ReH(SD)(SH)(PMe₃)₄] (*k* = 7.10(8) × 10⁻⁵ s⁻¹ at 20 °C). At equilibrium the deuterium in [D₁]**1** (and in [D₂]**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)(PPh₃)₃], is well established.^[14]

Solutions of **1** catalyze isotopic exchange between D₂ and H₂S 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 D₂S, intramolecular H/D exchange between the ReSD and ReH sites, and exchange of the ReD site with H₂.

In contrast to the high reactivity of **1**, the corresponding trihydride [ReH₃(PMe₃)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 SH and ReH with D₂, but by different mechanisms. In [Cp₂^{*}Ti(SH)(H)],^[7] both SH and TiH exchange together and dissociatively (by elimination of H₂) whereas in **1**, the ReH exchanges (associatively) with D₂, independent of ReSH

exchange. The importance of our results is that HDS catalysts use H₂, and it is exciting to see that the M–SH group is an electronically important spectator in the H₂ activation process. Compound **1** is a singular example of a L_nM(H)(SH) compound where the hydride site undergoes exchange with D₂ at a faster rate than the SH site.

Experimental Section

1: To (300 mg, 0.67 mmol) of [Et₄N][ReS₄] frozen in MeCN (10 mL) was condensed PMe₃ (0.7 mL, 6.8 mmol) and H₂S (310 mg, 9.1 mmol). The frozen vessel was evacuated, sealed, and warmed to room temperature. After stirring for 7 h, the solution was evaporated. Vacuum sublimation at 50 °C removed (277 mg, 2.56 mmol) of SPMe₃ (³¹P NMR in C₆D₆): δ = 28.3. The residue was extracted with 5 % THF in Et₂O (100 mL). The extracts were evaporated and the crude product was extracted from the remaining solid by washing with 3 % THF in hexanes (100 mL). These extracts were concentrated to ~25 mL and cooled to -78 °C to give 283 mg (75 %) of beige crystals. Field desorption mass spectroscopy (FD-MS): *m/z* = 556.1 [*M*⁺], 482.1 [*M*⁺ – PMe₃]; elemental analysis (%) calcd for C₁₂H₃₉P₄ReS₂: C 25.84, H 7.05, S 11.50; found: C 26.03, H 6.76, S 11.28; IR (KBr): ν̄ = 2049 (Re–H), 2520 (SH); ¹H NMR (500 MHz, 298 K, C₆D₆): δ = 1.41 (m, 18H), 1.39 (m, 18H), -1.46 (dt, 2H; *T*₁ = 8 s), -11.98 (tt, 1H; *T*₁ = 2.2 s); ³¹P NMR (C₆D₆, 298 K): δ = -47.28 (brs, 2P), -51.81 (brs, 2P); ³¹P NMR ([D₆]Me₂CO, 263 K): δ = -45.5 (t, *J* = 24 Hz), -50.7 (t, *J* = 24 Hz), *T*₁ is the spin–lattice relaxation time. Solutions of **1** are stable in THF and hydrocarbon solvents, less so in MeCN.

2: To (150 mg, 0.27 mmol) of **1** in MeCN (10 mL) was added (0.045 mL, 0.30 mmol) of dmpe. The solution was stirred under a slow stream of N₂ for 45 min to remove free PMe₃. The solution was then concentrated in vacuo to ~3 mL, and then the MeCN solution was extracted with hexanes (2 × 40 mL). Evaporation of the hexane extracts afforded a tan solid, yield: 128 mg (85 %), elemental analysis (%) calcd for C₁₂H₃₇P₄ReS₂: C 25.94, H 6.71; found: C 26.04, H 6.51; IR (KBr): ν̄ = 2039 (Re–H), 2536 (SH). ¹H NMR (500 MHz, 298 K, C₆D₆): δ = 1.71 (d, *J* = 8.43 Hz, 3H), 1.57 (d, 3H, *J* = 8.82 Hz), 1.44 (d, 9H, *J* = 7.75 Hz), 1.36 (d, *J* = 7.55 Hz, 9H), 1.17 (d, *J* = 8.02 Hz, 3H), 1.08 (d, *J* = 7.13 Hz, 3H), -1.81 (m, *J* = 1.89, 4.20, 7.26, 10.10 Hz; ReSH; *T*₁ = 8 s), -2.07 (m, *J* = 0.58, 1.74, 3.32, 3.79, 12.80 Hz; ReSH; *T*₁ = 8 s), -11.88 (m, *J* = 12.2, 54.0, 61.2, 67.0 Hz; ReH; *T*₁ = 2.2 s); ³¹P NMR (C₆D₆, 298 K): δ = 11.04 (s), 3.44 (d, *J* = 257 Hz), -46.0 (s), -49.1 (d, *J* = 257 Hz). The ¹H NMR spectrum was analyzed by computer simulation.

Deuteration of **1** and **2** with CD₃OD: A solution of **1** (50 mg 8.97 × 10⁻⁵ mol) in THF (5 mL) was treated with CD₃OD (1 g) for 10 min. After removal of the solvent, the residue was dissolved in C₆D₆. ¹H NMR analysis indicated [ReH_{0.75}D_{0.25}(SD_{0.7})₂(SH_{0.3})₂(PMe₃)₄], under identical conditions, **2** gave [ReH_{0.7}D_{0.3}(SD_{0.65})₂(SH_{0.35})₂(PMe₃)₂(dmpe)].

Deuteration of **1** and **2** with D₂: A solution of 50 mg (8.97 × 10⁻⁵ mol) of **1** in THF (10 mL) was treated with a stream of D₂ for 10 min. After removal of the solvent, the product was redissolved in C₆D₆ and analyzed by ¹H NMR spectroscopy which indicated [ReH_{0.1}D_{0.9}(SH)₂(PMe₃)₄] (no deuteration of SH site), similar treatment of **2** with D₂ but for 90 min gave [ReH_{0.8}D_{0.2}(SD_{0.1})₂(SH_{0.9})₂(PMe₃)₂(dmpe)].

Catalyzed exchange between D₂ and H₂S: A solution of **1** in C₆D₆ (0.7 mL) was treated with H₂S (0.5 atm) and D₂ (0.5 atm) and sealed. The mixture was monitored by ¹H NMR spectroscopy, which indicated conversion into a mixture of HD, H₂, HDS, and H₂S.

Crystal data for **1**: C₁₂H₃₉P₄ReS₂, *M* = 557.63, 193(2) K, monoclinic, space group *P*2₁; *a* = 9.2120(7), *b* = 12.9796(10), *c* = 9.3579(8) Å, β = 90.551(2)°, *V* = 1118.85(15) Å³, *Z* = 2, ρ_{calcd} = 1.655 Mg m⁻³, *F*(000) = 556, 190 parameters: *R*₁ = 0.0443, *wR*₂ = 0.0897, GOF = 1.102 for all 3474 data (*I* > 2σ(*I*)); max./min. residual electron density: 3.137/–1.359 e⁻ Å⁻³. Crystals of **1**, mounted on glass fibers using Paratone-N (Exxon), were analyzed on a Siemens Platform/CCD automated diffractometer at 193 K. Data was processed with SHELXTL. The structure was solved using direct methods and refined using full-matrix least-squares on *F*² using the program SHELXL-93. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.2 times those of the attached carbon atoms. Data

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 pnictogen and linearly coordinated mercury atoms.^[2] In some structures, some or all of the pnictogen atoms are joined into dumbbells

while keeping their tetrahedral arrangement.^[3] Here we report on [Hg₁₁As₄](GaBr₄)₄ (**1**), a novel supramolecular complex in which linear Hg₂²⁺ and Hg₃²⁺ fragments as well as Hg₂²⁺ cations take part in the formation of the three-dimensional host network. This is the first example of a linear Hg₃²⁺ group serving as a part of a three-dimensional framework.

The crystal structure^[4] of **1** consists of a three-dimensional [Hg₁₁As₄]⁴⁺ host network and tetrahedral GaBr₄[−] guest anions, which occupy one-dimensional infinite tunnels of the host framework (Figure 1). Large separations between the

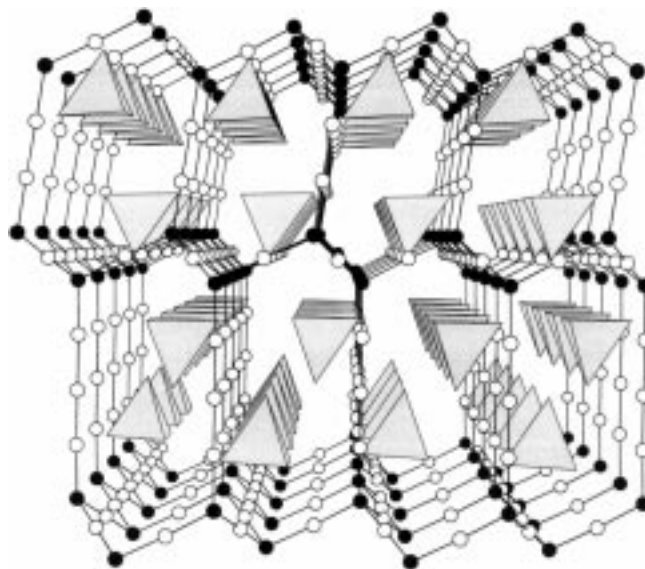


Figure 1. A perspective view of the crystal structure of [Hg₁₁As₄](GaBr₄)₄ (**1**) along the [010] direction of the unit cell. Open circles, mercury; filled circles, arsenic. Polyhedra represent the GaBr₄[−] ions.

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 [Hg₁₁As₄]⁴⁺ framework and the GaBr₄[−] 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 As₆ rings in a chair conformation, in which each edge of a chair is centered by a Hg₂²⁺ cation. These layers are interconnected by linear Hg₂²⁺ and Hg₃²⁺ 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 Hg₂²⁺ and Hg₃²⁺ units serve as boundaries for the smaller and larger tunnels, respectively. The Hg–Hg distances in the Hg₂²⁺ (2.57 Å) dumbbell and in the Hg₃²⁺ group (2.58 Å) are typical of those found in various compounds containing mercury in low oxidation states.^[5] Note that while Hg₂²⁺ dumbbells are quite common in mercury chemistry, only a few compounds containing Hg₃²⁺ are known. In these, such groups are stabilized by AlCl₄[−], AsF₆[−], or (F₅MOSO₂OMF₅)^{2−} (M = Nb,

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