Coordination chemistry, and catalytic conversions, of H_2S

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Abstract: Some reactions of H_2S with solutions of Pd- and Ru-phosphine complexes are described. The Pd systems involve sulfur abstraction and generation of H_2, catalytic conversions of H_2S to H_2, and attempts to catalyse the (H_2S → H_2 + ‘S’) reaction. The Ru studies have led to crystallographic characterisation of a reversibly formed H_2S complex, as well as more familiar oxidative addition-type chemistry of H_2S. This lecture/review naturally emphasises work carried out at this University (UBC).

INTRODUCTION

Research into the interaction of H_2S with transition metal complexes in solution is generally not well developed, despite the relevance of such chemistry in the biological sulfur cycle, in the formation of ores, in hydrodesulfurisation (HDS) catalysis, and in the conversion of H_2S to a source of H_2 and elemental sulfur (or organosulfur compounds). Literature dealing with these topics is plentiful and can be traced through refs.1-6.

My research group became interested in transition metal-H_2S chemistry during studies on the use of the well known dinuclear complexes Pd_2X_2(μ-dpm)_2 (X = halogen, dpm = Ph_PCH_PPh) for the separation of syngas components by efficient reversible binding of the CO (ref. 7); tests were made for reactivity toward the possible contaminant H_2S, and we discovered serendipitously the solution reaction (1) [see also reaction (8)], which shows quantitative reduction of H_2S to H_2 and a bridged-sulfide within the well known, A-frame type complex (ref. 8).

Pd_2X_2(μ-dpm)_2 + H_2S → Pd_2X_2(μ-S)(μ-dpm)_2 + H_2 (1)

2W_3+ + H_2S + anionic site → 2W^{4+} + S^{2−} + H_2 (2)

Ru(H)_2(PPh)_4 + H_2S → RuH(SH)(PPh)_3 + H_2 + PPh_3 (3)

2[Ru(NH_3)_2(SH)_2]^2+ → 2[Ru(SH)(NH_3)_2]^2+ + H_2 (4)

Reaction (1) was the first to demonstrate (in 1985) the 1:1 H_2S:H_2 stoichiometry at a metal centre, although reaction (2) had been invoked earlier to account for the filling of vacant anionic sites by sulfur in WS_2 lattices (ref. 9). In earlier work also, the H_2 produced in reaction (3) was a consequence of the hydride content of the reactant complex (ref. 10), while detection of some H_2 during decomposition of [Ru(NH_3)_2(SH)_2]^2+ had been tentatively attributed to reaction (4) (ref. 11). Since 1985, there have been several more reports of H_2 generation from H_2S with concomitant formation of bridged- or terminal-sulfide species: e.g. via H_2S reaction with carbonyl complexes of metallocenes of Ti and Zr (ref. 12), W-phosphine complexes (ref. 13), and homo- and heterobimetallic complexes of Ir, Rh, and Re containing μ-dpm ligands (ref. 2).

Attempts to isolate and characterise a metal complex containing H_2S itself (a likely, but presumably not essential, species en route to oxidative addition) have been and remain a considerable challenge and, to my
knowledge, only two such crystallographically characterised complexes have been reported, both recently (refs. 5, 16; see below).

PALLADIUM SYSTEMS

Reactions of Pd₂X₄(μ-dpm)₂ with H₂S

Detailed kinetic and spectroscopic studies (refs. 17, 18) on the non-reversible reaction (1) in CH₂Cl₂ from -15 to 25°C led to the overall mechanism shown below in (8). The dinuclear hydrido(mercapt0) intermediate (I) was detected at low temperature for each of the X = Cl, Br, I, systems by ¹H and ³¹P{¹H}

\[
\begin{align*}
Pd & \quad \text{Pd} & \quad \text{Pd} & \quad \text{X} & \quad + & \quad H₂S & \quad \xrightarrow{K} & \quad H₂ & \quad \xrightarrow{k₂} & \quad Pd & \quad \text{Pd} & \quad \text{X} & \quad \xrightarrow{K} & \quad H₂S & \quad \xrightarrow{k₁} & \quad Pd & \quad \text{Pd} & \quad \text{X} & \quad \xrightarrow{K} & \quad H₂S
\end{align*}
\]

NMR spectroscopy. The general rate-law for such systems corresponds to typical saturation kinetics with a rate = \( k₂K[Pd]_{\text{tot}}[H₂S]/(1 + K[H₂S]) \), the dependence on [H₂S] going from first- to zero-order with increasing [H₂S]; standard (Lineweaver-Burk) double reciprocal plots allow for estimation of \( k₂ \) and \( K \). Qualitatively the rates measured at ambient conditions decrease in the order X = Cl > Br > I. For the Cl system, both thermodynamic and activation parameters were determined (for \( K, \Delta H^o = -20 \text{ kJ mol}^{-1} \) and \( \Delta S^o = -68 \text{ J K}^{-1} \text{ mol}^{-1} \); for \( k₂, \Delta H^o = 61 \text{ kJ mol}^{-1} \) and \( \Delta S^o = -63 \text{ J K}^{-1} \text{ mol}^{-1} \)); extrapolation of the kinetically determined \( K \) values to -78°C gave \( K = 53 \text{ M}^{-1} \), while an experimental value determined by NMR at this temperature was 48 M⁻¹, remarkably good agreement and offering strong support for the proposed mechanism. For the X = Br system, the \( K \) value is significantly smaller, such that the kinetics unfortunately remain first-order in [H₂S] even at the highest [H₂S] used (0.5 M), and only the combined constant \( k₂K \) can be determined for which \( \Delta H^o = 56 \text{ kJ} \) and \( \Delta S^o = -115 \text{ J K}^{-1} \) (where \( \Delta H^o = \Delta H^f + \Delta H^o \), and \( \Delta S^o = \Delta S^f + \Delta S^o \)). One rationale for the data is that the Pd-H and Pd-SH bonds are weaker when trans to Br (vs. Cl), this resulting in a less exothermic \( \Delta H^o \) value and a less favourable contribution for the overall forward reaction. Attempts to extend the quantitative studies to the X = I system were thwarted by its photosensitivity.

Generation of the bridged-sulfide product and H₂ via I is envisaged as deprotonation of coordinated SH⁻ with subsequent protonation of the coordinated hydride. The chemistry has analogies, for example, in H₂S reactivity at a Pt(111) surface (ref. 19) and addition of H₂S to Pt₆(μ₃-CO)(μ-dpm)₆ (ref. 20), while reaction (9) (ref. 21, triphos = MeC(CH₂PPh₂)₃) and reaction (10) (ref. 13) provide direct evidence for production of H₂ from coordinated H and SH⁻.

\[
\begin{align*}
\text{RhH(triphos)}_3(\mu-SH)₂ & \quad \text{= [Rh(triphos)}_3(\mu-S) + 2H₂ \quad \text{(9)}
\text{W(PMe₃)}_4(\text{H})₂(\text{SH})₂ & \quad \text{= W(PMe₃)}_4(\text{S})₂ + 2H₂ \quad \text{(10)}
\end{align*}
\]

Reactions of Pd₂Cl₄(μ-dpm)₂ with H₂X (X = Se, Te, O) and HX (X = Cl, Br)

Solutions of Pd₂Cl₄(μ-dpm)₂ react also with H₂Se (refs. 22, 23) and H₂Te (ref. 24) with formation of the bridged-chalcogenide and liberation of H₂ (cf. reaction (1)), although there is accompanying replacement of one or both of the chloride ligands, for example, by SeH₂; this presumably being related to the higher acidity of H₂Se compared to that of H₂S. Pd₂Cl₄(μ-dpm)₂ in CH₂Cl₂/MeOH also reacts with H₂O to give a complex mixture of products, but the μ-oxo species Pd₂Cl₄(μ-O)(μ-dpm)₂ may well be formed initially (ref. 22); in related chemistry, reaction of H₂O with a zirconocene species gives a μ-oxo derivative with H₂ evolution, and the suggested mechanism involves oxidative addition of H₂O and a subsequent proton transfer (ref. 25) (cf. eq. (8)).

Reactions of Pd₂X₄(μ-dpm)₂ species with HX (X = Cl, Br) in CH₂Cl₂ generate H₂, and these also proceed via initial oxidative addition with subsequent protonation of the coordinated hydride as shown in eq. 11 (ref. 26); both intermediate species were detected spectroscopically (refs. 26, 27).
Related chemistry using Pd₂ dimers containing μ-dpmMe (dpmMe = methylated dpm; i.e. 1,1-bis(diphenylphosphino)ethane)

We initially used dpmMe with the aim of modelling a supported -CH₂CH(PPh₂)₂ group for immobilizing Pd₃X₃(μ-dpm)₂-type moieties for use in separation of gases, and we synthesised the mixed (μ-dpm)(μ-dpmMe) complex and the syn- and anti-isomers of the bis(μ-dpmMe) complex (refs. 28, 29) [syn and anti refer to the disposition of the Me groups with respect to the Pd-C-Pd plane - see below]. Reactivity of solutions of the complexes toward H₂S and H₂Se (and CO which gives the corresponding μ-CO product)

\[
\text{H}_2\text{S} + 3/2 \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \quad \text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 3\text{S}'
\]

(12)

Reaction (13) is thus a preferred process, but is not practicable under purely thermal conditions because it is thermodynamically unfavourable (e.g. at 298 K, ΔH° = 20 kJ, ΔS° = -43 J K⁻¹, ref. 33); however, the forward reaction has been accomplished thermally at high temperatures (∼1000°C), and by various photo-, plasma- and electrochemical-decomposition methods (refs. 34-37).

\[
\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}'
\]

(13)

Any catalytic process based on the chemistry of reaction (1) requires removal of the bridged-S and regeneration of the Pd₃X₃(μ-PP)₂ species, where PP = dpm or dpmMe. The μ-S species are readily oxidised in solution by H₂O₂ or m-chloroperbenzoic acid (but not O₂) to give successively the μ-SO (with unusual pyramidal geometry at the S) and μ-SO₂ derivatives (eq. (14) where \( \text{Pd}_2 = \text{Pd}_3\text{X}_3(\mu-\text{PP})_2 \), ref. 8), the latter...
readily losing SO₂ reversibly (ref. 38). Thus a two-stage process effecting catalysis of reaction (15) could be realised.

\[ Pd₂(μ-S) → Pd₂(μ-SO) → Pd₂(μ-SO₂) \]

(14)

\[ H₂S + 2 'O' → H₂ + SO₂ \]

(15)

Of a range of other reagents tested for removal of the μ-S and regeneration of PdₓXₙ(μ-PP)₂ species, only dpm or dpmMe is effective (ref. 1); the sulfur is removed as the monosulfide dpm(S), i.e. Ph₃PCH₂P(S)Ph₂, reaction (16), and thus reaction (17) can be accomplished catalytically using the PdₓXₙ(μ-PP)₂ species.

\[ PdₓXₙ(μ-μ-p-dpm) + dpm → PdₓXₙ(μ-dpm)₂ + dpm(S) \]

(16)

\[ H₂S + dpm → H₂ + dpm(S) \]

(17)

Of note, reaction (17), the reverse of an HDS process, is the first reported homogeneous catalytic process utilising H₂S (ref. 1). Detailed kinetic and mechanistic studies on reaction (16) reveal second-order rate constants, that decrease (from 0.09 to ~ 0.01 M⁻¹ s⁻¹) in the order X = Cl > Br > I. Activation parameters show that the differences in reactivity are reflected mainly in differences in the ΔSz values for formation of the suggested 'symmetrical' transition state (A) shown below; this formulation resulted from studies using Ph₃PCD₃Ph₂ and monitoring the product ratios of dpm(S) and d₂-dpm(S) (ref. 1).

The dpm(S) product, synthesised previously from Ph₃P(S) in a two-stage process (ref. 39), can coordinate at metal centres and form five-membered (P-S) chelate ring systems (ref. 40) and, relevant to the catalytic Pd chemistry, the complexes PdCl₄(dpm(S)) and [Pd(dpm(S))₂]Cl₂ have been characterised crystallographically (ref. 41); during the conditions of the catalysis of reaction (17), however, ‘poisoning’ of the catalyst by the dpm(S) product only becomes significant at higher conversions and low dpm : dpm(S) ratios (ref. 41).

Of interest, it is possible to remove the μ-S as precipitated elemental sulfur from solutions of PdₓXₙ(μ-μ-S)(μ-dpm), by treatment with X₂ (X = Br, I), the metal-containing co-products now being mononuclear PdₓXₙ(dpm) (ref. 41). The overall process is exemplified in (18) (cf. eq. (11)); the initial second-order process, and subsequent first-order conversion of the tetrahalo species, are readily monitored by stopped-flow techniques. The activation parameters have been determined for the PdₓI₄(μ-S)(μ-dpm)/I₂ system and discussed in terms of mechanisms involving transition states (B) and (C) shown above (ref. 41).

Of note, we have discovered that reaction (19) occurs in the presence of γ-alumina (ref. 41); in the absence of alumina, the mononuclear species reacts with H₂S only in the presence of base to yield Pdₓ(SH)(μ-S)(μ-dpm)₂ (ref. 8).

\[ 2PdₓXₙ(dpm)₂ + H₂S (alumina) → PdₓXₙ(μ-S)(μ-dpm)₂ + 2 HX_{adsorbed} \]

(19)

If conditions can be found to give effective photoconversion of, for example, the adsorbed HI (from the X = I system) to give H₂ and I₂, then together with the component equations (18 and 19), the overall net reaction (20) is realised.

\[ H₂S + hv → H₂ + 'S' \]

(20)

An alternative and conceptually more direct approach to effect reaction (20), and considered during the pursuit of the above Pd chemistry following the discovery of reaction (1), is to optimise and 'make
Reactions of H$_2$S

compatible' the known chemistries shown in equation (21), although the HI photochemical reaction has been little studied in solution.

H$_2$S + I$_2$ → 2 HI + 'S' (ref. 42) ; 2HI + hv → H$_2$ + I$_2$ (ref. 43)

(21)

REACTIONS OF RUTHENIUM COMPLEXES WITH H$_2$S

About 10 years ago, we initiated research on the interaction of Ru(0) complexes and/or their dihydride derivatives with a range of S-containing compounds, including H$_2$S; the choice of Ru was dictated partly by the known, high HDS activity of Ru sulfides (ref. 44), and we were also encouraged by our discovery of the conversion of H$_2$S to H$_2$ via the net oxidative addition process at the Pd$_2^+$ centres discussed above (eq. (1)).

Oxidative addition chemistry

At -35°C, H$_2$S oxidatively adds to Ru(CO)$_3$(PPh$_3$)$_2$ in solution to give cis, cis, trans (cct)-RuH(SH)(CO)$_2$(PPh$_3$)$_2$, which can react with further H$_2$S at ambient temperatures (via a presumed protonation of the coordinated hydride, cf. ref. 10) to generate the structurally characterised cct-Ru(SH)$_2$(CO)$_2$(PPh$_3$)$_2$ species and H$_2$, eq. (22); the same chemistry ensues using cct-Ru(H)$_2$(CO)$_2$(PPh$_3$)$_2$ as precursor, following initial loss of H$_2$ (refs. 3, 45, 46).

Similarly, a solution mixture of cis- and trans-Ru(H)$_2$(dpm)$_2$ reacts with H$_2$S to give solely trans-RuH(SH)(dpm)$_2$, which then reacts more slowly with further H$_2$S to give cis- and trans-Ru(SH)$_2$(dpm)$_2$ (refs. 3, 47). Kinetic and mechanistic studies on the cct-Ru(H)$_2$(CO)$_2$(PPh$_3$)$_2$ precursor system for its addition reactions in general (including H$_2$S, thiols, CO and PPh$_3$) imply that the rate-determining step is the initial dissociation of H$_2$, while with the reactant Ru(H)$_2$(dpm)$_2$ mixture, loss of H$_2$ follows a initial protonation step that likely gives the [RuH(η$^2$-H$_2$)(dpm)$_2$]$^+$ intermediate (ref. 47); the differences in mechanisms arise because of the more basic character of the hydrides in Ru(H)$_2$(dpm)$_2$ as demonstrated by rapid exchange of the coordinated hydride in these species with CD$_3$OD. Such exchange is not observed with cct-Ru(H)$_2$(CO)$_2$(PPh$_3$)$_2$ (refs. 3, 47). The mercapto protons of the cct-RuX(SH)(CO)$_2$(PPh$_3$)$_2$ species (X = H, SH) also undergo rapid exchange with CD$_3$OD, and the mechanism suggested is shown in eq. (23); the exchange at the hydride of RuH(SH)(CO)$_2$(PPh$_3$)$_2$ occurs much more slowly than that at the SH moiety,

and an intramolecular process, as suggested previously for RuH(SH)(PPh$_3$)$_3$ (ref.10), was favoured (eq. (24)) (ref. 3).

Oxidative addition of H$_2$S at a metal centre is a common reaction (see Introduction and refs. 48-50), but formation of a monomeric mercapto complex is relatively uncommon (refs. 3, 51), in part because of the instability with respect to deprotonation and conversion to μ- or terminal-sulfide species (see above). Other Ru$^n$-hydrido-phosphine complexes reported to react with H$_2$S yield dimeric products with μ-SH ligands (refs. 51-53).
Ru complexes containing \textit{H}_2\textit{S}

As alluded to in the Introduction, the number of reported, isolated transition metal-\textit{H}_2\textit{S} complexes is small, probably about a dozen (refs. 5, 6, 11, 14, 16, 51, 54-58), and in some cases their existence is equivocal (e.g. refs. 55, 56); indeed, only two structurally characterised \textit{H}_2\textit{S} complexes exist, both of Ru (refs. 5, 6, 16). The first structure was that reported by Sellmann et al. for the Ru\textsuperscript{II} complex Ru('S,')(PPh\textsubscript{3})(SH\textsubscript{2})\textsubscript{3}-THF, where 'S,' = the dianionic, macrocyclic S-ligand, 1,2-bis(2-mercaptophenol)thio]ethane (see below); the species was formed by reaction of the [Ru(PPh\textsubscript{3})('S,')]\textsubscript{3} polymer with liquid \textit{H}_2\textit{S} at -70°C (refs. 5, 6). The crystal stability results from intermolecular H-bonding involving the THF solvate and strong S-H...S bridging, the solvate-free complex being labile and not characterised crystallographically. At ~20°C, the \textit{H}_2\textit{S} reaction gives a mixture of the bridged-sulfide complex [Ru(PPh\textsubscript{3})('S,')]\textsubscript{3}(\mu-S\textsubscript{2}) and other uncharacterised products. The \textit{H}_2\textit{S} complex is stable at ambient conditions in the absence of air, but loses \textit{H}_2\textit{S} slowly when stored in vacuo.

Studies at UBC on the design of systems to form \textit{H}_2\textit{S} complexes led to isolation of the extremely reactive, five-coordinate species RuCl\textsubscript{2}(P-N)(PR\textsubscript{3}), where P-N = \textit{o}-diphenylphosphino-N, N-dimethylaniline and R = \textit{p}-tolyl (ref. 59); this complex binds at ambient conditions a range of small molecules including \textit{H}_2\textsubscript{2} (as an \textit{η}^2-moity), N\textsubscript{2}, CO, O\textsubscript{2}, SO\textsubscript{2}, MeOH, MeSH, H\textsubscript{2}O (refs. 59, 60) and, of interest here, \textit{H}_2\textit{S} (ref. 16). The RuCl\textsubscript{2}(P-N)(PR\textsubscript{3})(SH\textsubscript{2}) complex (illustrated above) is formed reversibly in solution at ~20°C using 1 atm \textit{H}_2\textit{S}, and is isolated as an air-sensitive, yellow material. The crystal structure reveals a partially occupied H\textsubscript{2}O site on a two-fold axis, and a THF solvent disordered about a two-fold axis but, in contrast to the Sellmann complex, no ‘stabilising’ H-bonding interactions to the coordinated \textit{H}_2\textit{S} are apparent. The \textit{H}_2\textit{S} adduct is also formed quantitatively by reacting the five-coordinate precursor in the solid state with 1 atm \textit{H}_2\textit{S}, and under vacuum does not lose \textit{H}_2\textit{S} over 24 h at ~20°C. This Ru(P-N) system and Sellmann’s complex provide an opportunity to investigate and develop for the first time the chemistry of coordinated \textit{H}_2\textit{S}.

Systems that with \textit{H}_2\textit{S} give oxidative addition products, such as hydrido(mercapto) species, are sometimes considered to proceed via initial \textit{H}_2\textit{S}-adduct formation, whether mono- or dinuclear metal complex precursors are involved (e.g. refs. 2, 14, 17), but no entirely convincing evidence for such a transformation has yet been published.

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DEDICATION

The lecture on which this paper was based was dedicated to Professor Colin F. J. Lock, who passed away on May 1, 1996; Colin, who had been Chairman of the 18th ICCC meeting held in Toronto, Canada (1972), was a close friend and the most enjoyable of colleagues. He did solve several structures relevant to the Ru systems discussed here (e.g. ref. 3). I dedicate also this review to him.

REFERENCES


