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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 ($H_2S \rightarrow H_2$ + '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 $Pd_2X_2(\mu\text{-dpm})_2$ (X = halogen, dpm = $Ph_2PCH_2PPh_2$) 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).

$$Pd_2X_2(\mu\text{-dpm})_2 + H_2S \rightarrow Pd_2X_2(\mu\text{-S})(\mu\text{-dpm})_2 + H_2 \quad (1)$$

$$2W^{3+} + H_2S + \text{anionic site} \rightarrow 2W^{4+} + S^{2-} + H_2 \quad (2)$$

$$Ru(H)_2(PPh_3)_4 + H_2S \rightarrow RuH(SH)(PPh_3)_3 + H_2 + PPh_3 \quad (3)$$

$$2[Ru(NH_3)_5(SH_2)]^{2+} \rightarrow 2[Ru(SH)(NH_3)_5]^{2+} + H_2 \quad (4)$$

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 $[Ru(NH_3)_5(SH_2)]^{2+}$ 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).

As we shall see later, reactions that generate H_2 from H_2S involve oxidative addition to give hydrido(mercapto) intermediates, and 'simple' examples of such chemistry have been known since the mid-1960s, e.g. reaction (5) (ref. 14), and reactions (6) and (7) (ref. 15).

$$Pt(PPh_3)_4 + H_2S \rightarrow Pt(H)(SH)(PPh_3)_2 + 2PPh_3 \quad (5)$$

$$IrCl(CO)(PPh_3)_2 + H_2S \rightarrow IrCl(H)(SH)CO(PPh_3)_2 \quad (6)$$

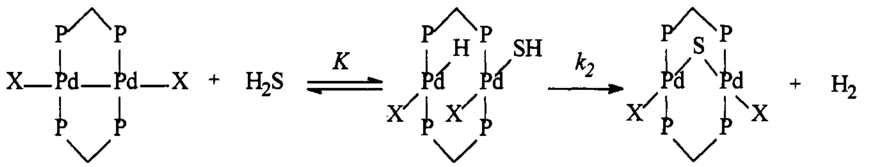
$$2RhCl(PPh_3)_3 + 2H_2S \rightarrow [RhCl(H)(PPh_3)_2]_2(\mu\text{-SH})_2 + 2PPh_3 \quad (7)$$

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 $Pd_2X_2(\mu\text{-dpm})_2$ with H_2S

Detailed kinetic and spectroscopic studies (refs. 17, 18) on the non-reversible reaction (1) in CH_2Cl_2 from -15 to 25°C led to the overall mechanism shown below in (8). The dinuclear hydrido(mercapto) intermediate (**I**) was detected at low temperature for each of the X = Cl, Br, I, systems by ^1H and $^{31}P\{^1H\}$



(8)

(I)

NMR spectroscopy. The general rate-law for such systems corresponds to typical saturation kinetics with a rate = $k_2K[\mathrm{Pd}]_{\mathrm{total}}[H_2S]/(1 + K[H_2S])$, the dependence on $[H_2S]$ going from first- to zero-order with increasing $[H_2S]$; standard (Lineweaver-Burk) double reciprocal plots allow for estimation of k_2 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, $\Delta H^\circ = -20$ kJ mol^{-1} and $\Delta S^\circ = -68$ J K^{-1} mol^{-1}; for k_2, $\Delta H^\neq = 61$ kJ mol^{-1} and $\Delta S^\neq = -63$ J K^{-1} mol^{-1}); extrapolation of the kinetically determined K values to -78°C gave $K = 53$ 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 $[H_2S]$ even at the highest $[H_2S]$ used (0.5 M), and only the combined constant k_2K can be determined for which $\Delta H^\neq_{obs} = 56$ kJ and $\Delta S^\neq_{obs} = -115$ J K^{-1} (where $\Delta H^\neq_{obs} = \Delta H^\circ + \Delta H^\neq$, and $\Delta S^\neq_{obs} = \Delta S^\circ + \Delta S^\neq$). 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 ΔH° 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 H_2 via **I** is envisaged as deprotonation of coordinated SH^- with subsequent protonation of the coordinated hydride. The chemistry has analogies, for example, in H_2S reactivity at a Pt(111) surface (ref. 19) and addition of H_2S to $Pt_3(\mu_3\text{-CO})(\mu\text{-dpm})_3^{2+}$ (ref. 20), while reaction (9) (ref. 21, triphos = $MeC(CH_2PPh_2)_3$) and reaction (10) (ref. 13) provide direct evidence for production of H_2 from coordinated H^- and SH^-.

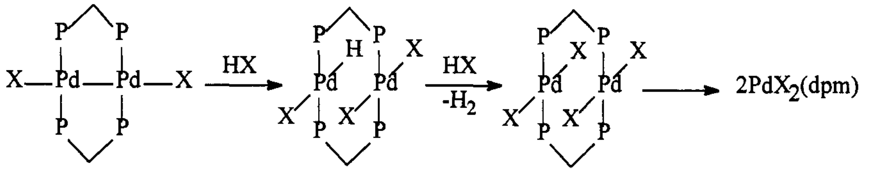
$$[RhH(triphos)]_2(\mu\text{-SH})_2 \rightleftharpoons [Rh(triphos)]_2(\mu\text{-S}) + 2H_2 \qquad (9)$$

$$W(PMe_3)_4(H)_2(SH)_2 \longrightarrow W(PMe_3)_4(S)_2 + 2H_2 \qquad (10)$$

Reactions of $Pd_2Cl_2(\mu\text{-dpm})_2$ with H_2X (X = Se, Te, O) and HX (X = Cl, Br)

Solutions of $Pd_2Cl_2(\mu\text{-dpm})_2$ react also with H_2Se (refs. 22, 23) and H_2Te (ref. 24) with formation of the bridged-chalcogenide and liberation of H_2 (cf. reaction (1)), although there is accompanying replacement of one or both of the chloride ligands, for example, by SeH^-, this presumably being related to the higher acidity of H_2Se compared to that of H_2S. $Pd_2Cl_2(\mu\text{-dpm})_2$ in CH_2Cl_2/MeOH also reacts with H_2O to give a complex mixture of products, but the μ-oxo species $Pd_2Cl_2(\mu\text{-O})(\mu\text{-dpm})_2$ may well be formed initially (ref. 22); in related chemistry, reaction of H_2O with a zirconocene species gives a μ-oxo derivative with H_2 evolution, and the suggested mechanism involves oxidative addition of H_2O and a subsequent proton transfer (ref. 25) (cf. eq. (8)).

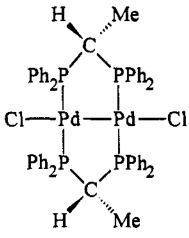
Reactions of $Pd_2X_2(\mu\text{-dpm})_2$ species with HX (X = Cl, Br) in CH_2Cl_2 generate H_2, and these also proceed via initial oxidative addition with subsequent protonation of the coordinated hydride as shown in eq. 11 (ref. 26); both intermediate species were detected spectroscopically (refs. 26, 27).



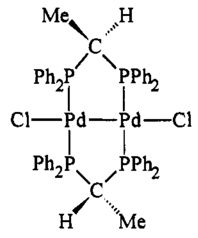
(11)

Related chemistry using Pd_2 dimers containing μ-dpmMe (dpmMe = methylated dpm ; i.e. 1,1-bis(diphenylphosphino)ethane)

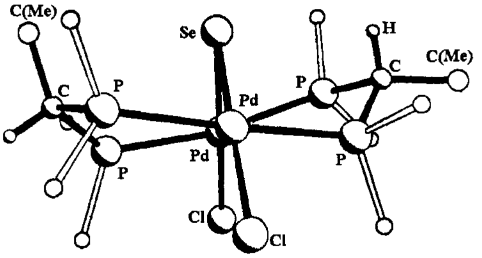
We initially used dpmMe with the aim of modelling a supported $-CH_2CH(PPh_2)_2$ group for immobilizing $Pd_2X_2(\mu\text{-dpm})_2$-type moieties for use in separation of gases, and we synthesised the mixed (μ-dpm)(μ-dpmMe) complex and the *syn*- and *anti*-isomers of the bis(μ-dpmMe) complex (refs. 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 H_2S and H_2Se (and CO which gives the corresponding μ-CO product) decreases in the order: $Pd_2Cl_2(\mu\text{-dpm})_2 > Pd_2Cl_2(\mu\text{-dpm})(\mu\text{-dpmMe}) >$ *syn*-$Pd_2Cl_2(\mu\text{-dpmMe})_2 >>$ *anti*-$Pd_2Cl_2(\mu\text{-dpmMe})_2$, and this is attributed to steric effects within the corresponding A-frame products (cf. eq. (1)) (refs. 8, 23, 28, 29). In the *anti*-form of the reactant complex, the Me groups occupy the less sterically crowded pseudoequatorial positions of the fused five-membered chelate rings that are both in a chair conformation, while the A-frame products adopt boat conformations for both rings and one Me group will be inside a boat, a sterically unfavoured location; nevertheless, such A-frame adducts do exist as demonstrated by the synthesis of *anti*-$Pd_2Cl_2(\mu\text{-Se})(\mu\text{-dpmMe})_2$ (see above), prepared directly from *anti*-$Pd_2Cl_2(\mu\text{-dpmMe})_2$ and elemental Se (ref. 23).



syn-$Pd_2Cl_2(\mu\text{-dpmMe})_2$



anti-$Pd_2Cl_2(\mu\text{-dpmMe})_2$



anti-$Pd_2Cl_2(\mu\text{-Se})(\mu\text{-dpmMe})_2$

Catalytic conversions of H_2S to H_2

The recovery of H_2 from H_2S (especially from anthropogenic sources) within a catalytic process is attractive. The two main industrial sources of the obnoxious and poisonous pollutant are from the Kraft wood pulping process (ref. 30), in which the H_2S is recycled as NaSH required in a 'cooking' step, and from HDS in the refinement of petroleum (refs. 9, 31), where the H_2S is usually oxidised to elemental sulfur ('S' = 1/8 S_8), via the 'two-stage' Claus process (see (12), ref. 32); in this process, the energy value of the H_2 is lost.

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O\ ;\ SO_2 + 2H_2S \rightarrow 2H_2O + 3\text{'S'} \tag{12}$$

Reaction (13) is thus a preferred process, but is not practical under purely thermal conditions because it is thermodynamically unfavourable (e.g. at 298 K, $\Delta H^\circ = 20$ kJ, $\Delta S^\circ = -43$ 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).

$$H_2S \rightarrow H_2 + \text{'S'} \tag{13}$$

Any catalytic process based on the chemistry of reaction (1) requires removal of the bridged-S and regeneration of the $Pd_2X_2(\mu\text{-PP})_2$ species, where PP = dpm or dpmMe. The μ-S species are readily oxidised in solution by H_2O_2 or *m*-chloroperbenzoic acid (but not O_2) to give successively the μ-SO (with unusual pyramidal geometry at the S) and μ-SO_2 derivatives (eq. (14) where *Pd2* = $Pd_2X_2(\mu\text{-PP})_2$, ref. 8), the latter readily losing SO_2 reversibly (ref. 38). Thus a two-stage process effecting catalysis of reaction (15) could be realised.

$$Pd_2(\mu\text{-S}) \rightarrow Pd_2(\mu\text{-SO}) \rightarrow Pd_2(\mu\text{-SO}_2) \rightleftharpoons Pd_2 + SO_2 \quad (14)$$

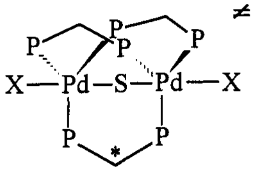
$$H_2S + 2\ \text{'O'} \rightarrow H_2 + SO_2 \quad (15)$$

Of a range of other reagents tested for removal of the μ-S and regeneration of $Pd_2X_2(\mu\text{-PP})_2$ species, only dpm or dpmMe is effective (ref. 1); the sulfur is removed as the monosulfide dpm(S), i.e. $Ph_2PCH_2P(S)Ph_2$, reaction (16), and thus reaction (17) can be accomplished catalytically using the $Pd_2X_2(\mu\text{-PP})_2$ species.

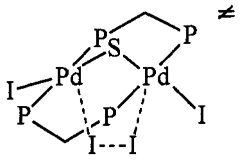
$$Pd_2X_2(\mu\text{-S})(\mu\text{-dpm})_2 + \text{dpm} \rightarrow Pd_2X_2(\mu\text{-dpm})_2 + \text{dpm(S)} \quad (16)$$

$$H_2S + \text{dpm} \rightarrow H_2 + \text{dpm(S)} \quad (17)$$

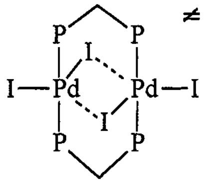
Of note, reaction (17), the reverse of an HDS process, is the first reported homogeneous catalytic process utilising H_2S (ref. 1). Detailed kinetic and mechanistic studies on reaction (16) reveal second-order rate constants, that decrease (from 0.09 to ~ 0.01 $M^{-1}\ s^{-1}$) in the order X = Cl > Br > I. Activation parameters show that the differences in reactivity are reflected mainly in differences in the $\Delta S^{\neq}$ values for formation of the suggested 'symmetrical' transition state (**A**) shown below; this formulation resulted from studies using $Ph_2PCD_2PPh_2$ and monitoring the product ratios of dpm(S) and d_2-dpm(S) (ref. 1).



(**A**)



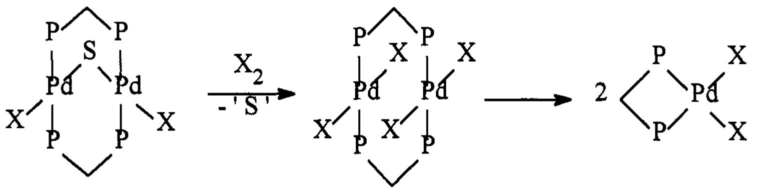
(**B**)



(**C**)

The dpm(S) product, synthesised previously from $Ph_3P(S)$ 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 $PdCl_2(\text{dpm(S)})$ and $[Pd(\text{dpm(S)})_2]Cl_2$ 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 $Pd_2X_2(\mu\text{-S})(\mu\text{-dpm})_2$ by treatment with X_2 (X = Br, I)), the metal-containing co-products now being mononuclear $PdX_2(\text{dpm})$ (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 $Pd_2I_2(\mu\text{-S})(\mu\text{-dpm})_2/I_2$ system and discussed in terms of mechanisms involving transition states (**B**) and (**C**) shown above (ref. 41).



(17)

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 H_2S only in the presence of base to yield $Pd_2(SH)_2(\mu\text{-S})(\mu\text{-dpm})_2$ (ref. 8).

$$2PdX_2(\text{dpm})_2 + H_2S\ (\text{alumina}) \rightarrow Pd_2X_2(\mu\text{-S})(\mu\text{-dpm})_2 + 2\ Hx_{\text{adsorbed}} \quad (19)$$

If conditions can be found to give effective photoconversion of, for example, the adsorbed HI (from the X = I system) to give H_2 and I_2, then together with the component equations (18 and 19), the overall net reaction (20) is realised.

$$H_2S + h\nu \rightarrow H_2 + \text{'S'} \quad (20)$$

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

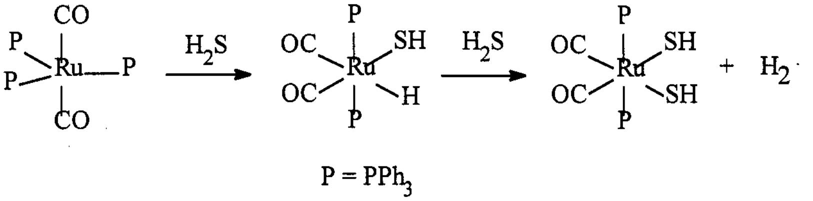
$$H_2S + I_2 \rightarrow 2\ HI + \text{'S'}\ (\text{ref. 42})\ ;\ 2HI + h\nu \rightarrow H_2 + I_2\ (\text{ref. 43}) \qquad (21)$$

REACTIONS OF RUTHENIUM COMPLEXES WITH H_2S

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_2S; 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_2S to H_2 via the net oxidative addition process at the $Pd_2{}^I$ centres discussed above (eq. (1)).

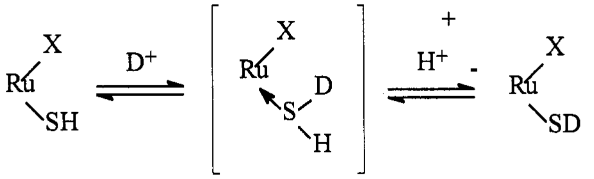
Oxidative addition chemistry

At -35°C, H_2S oxidatively adds to $Ru(CO)_2(PPh_3)_3$ in solution to give *cis, cis, trans* (*cct*)-$RuH(SH)(CO)_2(PPh_3)_2$, which can react with further H_2S 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).



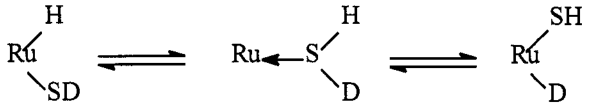
(22)

Similarly, a solution mixture of *cis-* and *trans*-$Ru(H)_2(dpm)_2$ reacts with H_2S to give solely *trans*-$RuH(SH)(dpm)_2$, which then reacts more slowly with further H_2S 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_2S, 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 $[RuH(\eta^2\text{-}H_2)(dpm)_2]^+$ 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_3OD. 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_3OD, 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,



(23)

and an intramolecular process, as suggested previously for $RuH(SH)(PPh_3)_3$ (ref.10), was favoured (eq. (24)) (ref. 3).

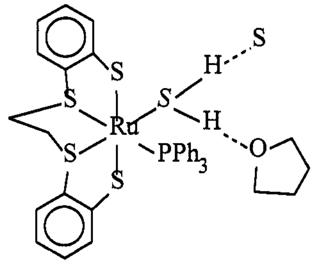


(24)

Oxidative addition of H_2S 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^{II}-hydrido-phosphine complexes reported to react with H_2S yield dimeric products with μ-SH ligands (refs. 51-53).

Ru complexes containing H_2S

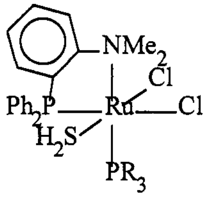
As alluded to in the Introduction, the number of reported, isolated transition metal-H_2S complexes is small, probably about a dozen (refs. 5, 6, 11, 14, 16, 51, 54-58), and in some cases their existence is equivocal (e.g. refs. 55, 56); indeed, only two structurally characterised H_2S complexes exist, both of Ru (refs. 5, 6, 16). The first structure was that reported by Sellmann et al. for the Ru^{II} complex $Ru('S_4')(PPh_3)(SH_2)\cdot THF$, where '$S_4$' = the dianionic, macrocyclic S-ligand, 1,2-bis[(2-mercaptophenol)thio]ethane (see below); the species was formed by reaction of the $[Ru(PPh_3)('S_4')]_x$ polymer with liquid H_2S 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 H_2S reaction gives a mixture of the bridged-sulfide complex $[Ru(PPh_3)('S_4')]_2(\mu\text{-}S_2)$ and other uncharacterised products. The H_2S complex is stable at ambient conditions in the absence of air, but loses H_2S slowly when stored in vacuo.



Sellmann's complex

(Ru-*S* = 2.399, av. *S*-H = 1.20 Å ;

Ru-*S*-H = 102, 121°)



The Ru(P-N)/H_2S complex

(Ru-S = 2.330, S-H = 1.25 Å ;

Ru-S-H = 124.2°)

Studies at UBC on the design of systems to form η^2-H_2 complexes led to isolation of the extremely reactive, five-coordinate species $RuCl_2(P\text{-}N)(PR_3)$, where P-N = *o*-diphenylphosphino-N, N-dimethylaniline and R = *p*-tolyl (ref. 59); this complex binds at ambient conditions a range of small molecules including H_2 (as an η^2-moiety), N_2, CO, O_2, SO_2, MeOH, MeSH, H_2O (refs. 59, 60) and, of interest here, H_2S (ref. 16). The $RuCl_2(P\text{-}N)(PR_3)(SH_2)$ complex (illustrated above) is formed reversibly in solution at ~20°C using 1 atm H_2S, and is isolated as an air-sensitive, yellow material. The crystal structure reveals a partially occupied H_2O 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 H_2S are apparent. The H_2S adduct is also formed quantitatively by reacting the five-coordinate precursor in the solid state with 1 atm H_2S, and under vacuum does not lose H_2S 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 H_2S.

Systems that with H_2S give oxidative addition products, such as hydrido(mercapto) species, are sometimes considered to proceed via initial H_2S-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.

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