Formation of $Pd_2X_2(\mu\text{-S})(\mu\text{-dpm})_2$ by reaction of $PdX_2(dpm)$ with H_2S in the presence of alumina (X = halogen, dpm = diphenylphosphinomethane)

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Abstract

Alumina promotes the reaction of $PdX_2(dpm)$ (**3**) (X = Cl, Br, I) with H_2S to form $Pd_2X_2(\mu\text{-S})(dpm)_2$ (**2**) [1] and HX, with chemisorption of the HX (quantified by titration) providing the driving force; although no intermediate species are detected, the reaction likely proceeds via mercapto species formed via 'alumina activated H_2S'. XPS studies show interactions of species **2** and **3** with alumina, these interactions being weak as demonstrated by recovery of the species on dissolution using an appropriate solvent. For the iodide system, adsorbed HI on alumina undergoes partial photodecomposition to give I_2 and H atoms. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

We reported recently the first homogeneously catalyzed conversion of H_2S to H_2 using dinuclear Pd_2–dpm complexes (dpm = bis(diphenylphosphino)methane) (Scheme 1) [1]. Kinetic and mechanistic studies have been carried out for both the forward ($\mathbf{1} \rightarrow \mathbf{2}$) and reverse ($\mathbf{2} \rightarrow \mathbf{1}$) reactions and, for the forward reaction, hydrido mercapto intermediates were detected in low temperature NMR studies [1–4].

Besides dpm, several reagents (including O-atom donors, and phosphines, CO, CN^-, biphenyl, or butadiene) can remove completely or partially in solution the bridged S in 'coordinated forms' from **2** [3–5]. Reactions with halogens remove the sulfur as elemental S_8 (Eq. (1)) [4,6,7], and these reactions occur under ambient conditions in two kinetically observable stages via a rapid transannular oxidative addition to give (with generation of S_8) a tetrahalo-dipalladium(II) intermediate [8] that subsequently undergoes slower unimolecular decomposition [4,6,7]. (The by-product $PdX_2(Ph_2PCH_2P(S)Ph_2)$,
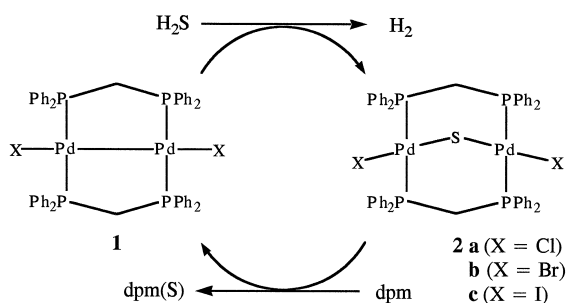

Scheme 1.

crystallographically characterized (with $X = Cl$ or I) and containing a 5-membered (P–S) chelating ring, forms under certain conditions [6,7].)

$$Pd_2X_2(\mu - S)(dpm)_2(\mathbf{2}) + X_2 \rightarrow 2PdX_2(dpm)(\mathbf{3}) + 1/8S_8 \tag{1}$$
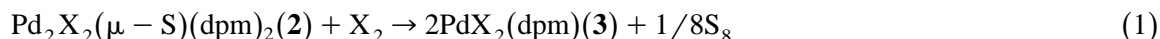
The catalyzed conversion of H_2S to H_2 and elemental sulfur is attractive commercially [1,4], and thus efforts to convert **3** to **2** by reaction with H_2S have been undertaken. This present paper reports on reaction (2) which occurs rapidly and completely under ambient conditions in the presence of γ-alumina. Implications for catalysis can be seen with the iodide system, where combination of reactions (1) and (2), coupled with the known photo-decomposition of HI to generate H_2 and I_2, leads to the net reaction: $H_2S \rightarrow H_2 + 1/8\ S_8$.

$$2PdX_2(dpm)(\mathbf{3}) + H_2S \rightarrow Pd_2X_2(\mu - S)(dpm)_2(\mathbf{2}) + 2HX \tag{2}$$
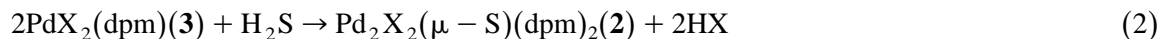
2. Experimental

The materials used, synthetic procedures for the complexes, and instrumentation used for ^{1}H and ^{31}P{^{1}H} NMR and UV–Vis spectroscopies, and gas chromatography, have been largely described previously [1–3]. Complexes **2a–c** [3] and **3a–c** [8–10] were synthesized using established methods. All experiments were performed under Ar unless otherwise specified. Alumina powder and plates were purchased from Fisher (neutral γ-Al_2O_3), Alfa Products (α-Al_2O_3, corundum), and Merck (neutral γ-Al_2O_3 plates, mesh 60, layer thickness 0.2 mm) and were pre-dried at 75 or 150°C for 24 h before use. Finely ground alumina was prepared via a manual grinding process using a mortar and pestle. Aliquots of gases were added to solutions from gas-tight syringes, the volumes referring to 1 atm pressure at ∼ 20°C.

X-ray photoelectron spectra (XPS) were measured with a Leybold MAX200 spectrometer using a non-monochromatized Mg K_α excitation source (1235.6 eV) which was operated at 10 kV and 20 mA; the emitted photoelectrons were collected from a 2×4 mm^2 area. Survey spectra were measured with the pass energy set at 192 eV, while the higher resolution (narrow scan) spectra were measured with a 48 eV pass energy. The binding energies for assignments in the XPS spectra are referenced to the C 1s peak for adventitious carbon at 285.0 eV. It took approximately 4 h to take samples from atmospheric pressure to the system operating pressure at 4×10^{-9} mbar at room temperature (r.t.) at which these spectra were recorded.

2.1. Heterogeneous alumina systems

Alumina (15 mg) or an alumina plate (1.0×1.0 cm^2), with or without added reagents, was placed either in an NMR tube fitted with a PTFE J. Young valve or septum, or in a Schlenk tube fitted with a septum. CDCl$_3$ (0.7 or 1.0 ml) was added, and the systems were either shaken or stirred and left at r.t. for up to 72 h before analysis; the added reagents were **3a** (5 mg, 0.0089 mmol), gaseous H$_2$S (110 μl or 0.5 ml, 0.0045 or 0.021 mmol, respectively, gaseous HCl (0.5 ml, 0.021 mmol), or S$_8$ (12 mg, 0.047 mmol) as required. In experiments where both **3a** and H$_2$S were used, **3a** was introduced (as a 0.3 ml CDCl$_3$ solution) either before or after the addition of H$_2$S, with 0.4 or 0.7 ml CDCl$_3$ initially being placed in the NMR or Schlenk tube, respectively. Analyses were carried out using NMR spectroscopy on the liquid phases, and XPS on the alumina plates after drying them for a few minutes at r.t. under a flow of Ar.

In some cases, an H$_2$S solution-pretreated alumina plate was dried under Ar, and placed in another Schlenk tube for reaction with a 1.0 ml CDCl$_3$ solution of **3a** prior to analysis.

2.2. Homogeneous systems

PdCl$_2$(dpm) (**3a**, 10 mg, 0.018 mmol) was dissolved in CHCl$_3$ (10 ml), and an MeOH solution (10 ml) of NaSH (1.0 mg, 0.018 mmol) was added dropwise over 30 min. The solvents of the resulting yellow solution were removed, and the remaining yellow residue was dried in vacuo and dissolved in CDCl$_3$ (0.5 ml) for analysis by NMR spectroscopy.

2.3. Low temperature studies

A single, low temperature NMR study was carried out in which H$_2$S (0.25 ml, 0.010 mmol) was injected into a septum-sealed NMR tube containing a 0.5 ml CDCl$_3$ solution of **3a** (5 mg, 0.0089 mmol) and finely ground alumina (15 mg) in a MeCN/liquid N$_2$ slush bath (-42°C). The sample was analyzed at -50°C 1 h later using NMR spectroscopy, and then placed at r.t. for 24 h and re-analyzed.

2.4. Synthetic-scale studies

In a Schlenk tube fitted with a septum were placed 25.0 mg PdX$_2$(dpm) (**3a**, 0.045 mmol; **3b**, 0.038 mmol; **3c**, 0.034 mmol), 75.0 mg finely ground alumina, and 2.5 ml CHCl$_3$. The mixture was rapidly stirred and H$_2$S (5 ml, 0.20 mmol) was injected. The initial yellow (**3a**, **3b**) or orange (**3c**) solution turned brown within seconds. The mixture was stirred continuously for 4 h before being reduced in volume (to ~ 0.5 ml) with evacuation of the H$_2$S. CH$_2$Cl$_2$ (20 ml) was then added to dissolve all Pd species, and the alumina was filtered out, washed with CH$_2$Cl$_2$ (2×10 ml), MeOH (10 ml) (thereby eluting all absorbed Pd species), and CH$_2$Cl$_2$ (10 ml), and then dried in vacuo. The solvents from the filtrates and washings were removed by rotary evaporation, and the resulting residue was dissolved in CDCl$_3$ (~ 0.5 ml) and analyzed by NMR spectroscopy. Yield of Pd$_2$X$_2$(μ-S)(dpm)$_2$: **2a**, 24.0 mg ($> 99\%$); **2b**, 22.0 mg (98%); **2c**, 21.0 mg (99%). The isolated alumina was placed in a flask, and 10 ml H$_2$O and a few drops of phenolphthalein indicator were added for titration with a NaOH solution (0.010 M). For the iodide system, the isolated alumina from a repeat experiment was placed with ~ 0.7 ml CDCl$_3$ in an NMR tube fitted with a J. Young valve. The resulting mixture was then placed in the presence of light (laboratory, sunlight, or that from an 18 W TLC Hg vapour lamp)

for up to 4 days, and the system then analyzed for H_2 in the head-space (using NMR and GC) and I_2 in solution (using UV–Vis); the alumina was subsequently filtered off, washed with MeOH, and the washings analyzed using UV–Vis and titrated with NaOH solution. Blank titrations were also performed using unused alumina, and alumina isolated from the above procedure for the chloride system when H_2S was not used.

Possible reactivity of **3a** with S_8 in the presence of alumina was investigated. A mixture of **3a** (25.0 mg, 0.045 mmol), finely ground alumina (75.0 mg), S_8 (14 mg, 0.45 mmol), and $CHCl_3$ (2.5 ml) was rapidly stirred for 4 h in a Schlenk tube, when the initially white alumina gradually turned orange although the colour of the supernatant remained unchanged (yellow). CH_2Cl_2 (20 ml) was then added to dissolve all Pd species, and the mixture was filtered to separate out the alumina, which was subsequently washed with CH_2Cl_2 (2×10 ml), MeOH (10 ml), and CH_2Cl_2 (10 ml). The solvents from the filtrate and washing were removed by evaporation, and the resulting residue was dissolved in $CDCl_3$ (~ 0.5 ml) and analyzed using NMR spectroscopy.

Possible decomposition of H_2S on alumina was also investigated. An alumina plate (1.0×10.0 cm^2), $CHCl_3$ (20 ml), and 1 atm H_2S in a Schlenk tube were left at r.t. for 4 h when the plate was taken out and dried in air. The alumina was then removed from the plate, washed with $CHCl_3$ (~ 5 ml), and the washings collected and analyzed by UV–Vis. A control experiment was also carried out using alumina in the absence of H_2S.

2.5. Photodecomposition of HI (see also Section 2.4)

Photodecomposition of HI(aq.) in the presence of alumina in $CDCl_3$ was studied qualitatively. Alumina (15 mg) was placed in an NMR tube fitted with a J. Young valve. Then (a) $CDCl_3$ (0.5 ml) was added followed by HI(aq.) (2 μl, 0.016 mmol) and the mixture left in laboratory light for 24 h prior to analysis for H_2 and I_2 (see Section 2.4), and (b) HI(aq.) (2 μl of a 7.58 M solution, 0.016 mmol) was added first, with the head space analyzed 'immediately' or after 4 days, followed by addition of $CDCl_3$ (0.5 ml) with the mixture again left in laboratory light for 24 h prior to analysis. A control sample of I_2 (0.01 mg, 0.052 μmol), alumina (15 mg), and $CDCl_3$ (0.5 ml) was placed at r.t. for 24 h in the presence of laboratory light before being analyzed using UV–Vis spectroscopy.

2.6. Hydrogenation of cis-cyclooctene

A synthetic-scale reaction was repeated for the iodide system (see Section 2.4), and the isolated alumina (washed and dried in vacuo) was placed under an atmosphere of Ar in a septum-sealed NMR tube. The sample was then irradiated using the TLC Hg vapour lamp for 24 h. *Cis*-cyclooctene (2 μl, 1.5×10^{-5} mol) was then injected, and the NMR tube was shaken. The sample was then left at r.t. for 24 h before being analyzed. Control studies using irradiated and non-irradiated, 'unreacted' alumina (i.e., samples not subjected to reaction (2)) were also performed.

3. Results

Table 1 summarizes NMR data for the well characterized complexes $Pd_2X_2(\mu$-S$)(dpm)_2$ (**2**) and $PdX_2(dpm)$ (**3**). The $^{31}P\{^1H\}$ NMR spectra of **2a–c** reveal a singlet at δ 5.5–6.1 for the four equivalent P atoms, and singlets are seen for the two equivalent P atoms of **3a–c** in the δ -55 to

Table 1
NMR data for the palladium complexes

Compound[a]	δ (^{1}H)[b]	δ (^{31}P{^{1}H})[c]
$Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**)	2.79[d,e] (12.6, 3.5)	5.52[d]
	4.73[e] (12.6, 6.1)	
$Pd_2Br_2(\mu\text{-}S)(dpm)_2$ (**2b**)	2.88[d,e] (12.8, 3.2) (2.90)	5.96[d]
	4.83[e] (12.8, 7.6)	6.14
$Pd_2I_2(\mu\text{-}S)(dpm)_2$ (**2c**)	3.06[d,e] (14.0, 3.0)	6.08[d]
	4.95[e] (14.0, 6.0)	
$PdCl_2(dpm)$ (**3a**)	4.21[f] (10.8)	-54.7
$PdBr_2(dpm)$ (**3b**)	4.37[f] (10.5)	-56.2
$PdI_2(dpm)$ (**3c**)	4.42[f] (10.0)	-63.2

[a] For convenience, μ-dpm in **2a–c** is written as dpm.
[b] In $CDCl_3$, unless stated otherwise, at 20°C with respect to TMS; J_{HH} and/or J_{PH} values in Hz are given in parentheses; signals for CH_2 protons.
[c] Unless otherwise stated, singlets in $CDCl_3$ at 20°C with respect to 85% H_3PO_4, downfield being positive.
[d] In CD_2Cl_2.
[e] Doublets of quintets for each of two sets of CH_2 protons.
[f] Triplet.

-63 region [3,8–10]. In the ^{1}H NMR spectra, the CH_2 resonances of **2a–c** appear as AB doublets with additional coupling to the four P atoms, while those of **3a–c** appear as 1:2:1 triplets [3,8–10].

^{1}H NMR analysis of a suspension of γ-alumina (mesh size ~ 200) in $CDCl_3$ reveals a broad, unresolved signal at δ 1.2 (presumably due to surface OH groups). With H_2S added, the expected ^{1}H singlet at δ 0.82 for free H_2S [2] is not observed because this species is adsorbed onto the alumina (see Section 4). Addition of **3a** to a suspension of alumina causes over ~ 1 h a gradual colour change in the alumina from white to orange; NMR analysis of the filtrate shows only the presence of **3a**. Subsequent introduction of a stoichiometric amount of H_2S (see Eq. (2), H_2S:**3a** $= 0.5$) resulted in an immediate colour change of the alumina to orange–brown and the solution to a brown–yellow colour. ^{1}H and ^{31}P{^{1}H} NMR spectra here show, in addition to unreacted **3a**, trace amounts of $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**). Reversing the order of addition, i.e., adding **3a** to a $CDCl_3$ suspension of alumina already treated with a stoichiometric amount of H_2S, also yielded an immediate colour change, both the alumina and solvent turning orange–brown, but **2a** was now formed in $\sim 10\%$ yield (determined from the relative integrated areas of the respective CH_2 proton signals), or $\sim 60\%$ if the alumina was pre-dried at 150 instead of 75°C. No **2a** was formed, however, if the alumina was isolated after the addition of H_2S and, prior to the addition of **3a**, placed in fresh, H_2S-free $CDCl_3$, because H_2S desorbs from the alumina during the isolation process (see Section 4). A quantitative yield of **2a** can be affected using alumina of lower mesh size. For example, NMR analyses show, that after 4 h at r.t., **3a** was completely converted to **2a** when alumina of mesh size 60 (i.e., from a TLC plate) or a finely ground ~ 200 mesh size was used. Use of corundum (α-alumina) with an extremely low mesh size of -100 gave only a 10% yield after 24 h and reached a maximum 50% yield after 72 h (Fig. 1).

XPS analysis of γ-alumina reveals signals arising from Al 2p, Al 2s, and O 1s photoelectrons with corresponding binding energies of 74.5, 119.8, and 531.8 eV. Additional signals arising from adventitious carbon and nitrogen are also observed, the C 1s and N 1s photoelectrons, for instance, having binding energies of 285.0 and 399.3 eV, respectively; the data are similar to those found in the literature [11]. With **3a** adsorbed on the alumina, the XPS spectrum also shows the Cl 2p, Pd $3d_{5/2}$, and Pd $3d_{3/2}$ photoelectron signals with binding energies of 198.2, 337.0, and 342.5 eV, respectively (Figs. 2 and 3). For alumina isolated from reaction (2), two additional signals are also seen, namely,
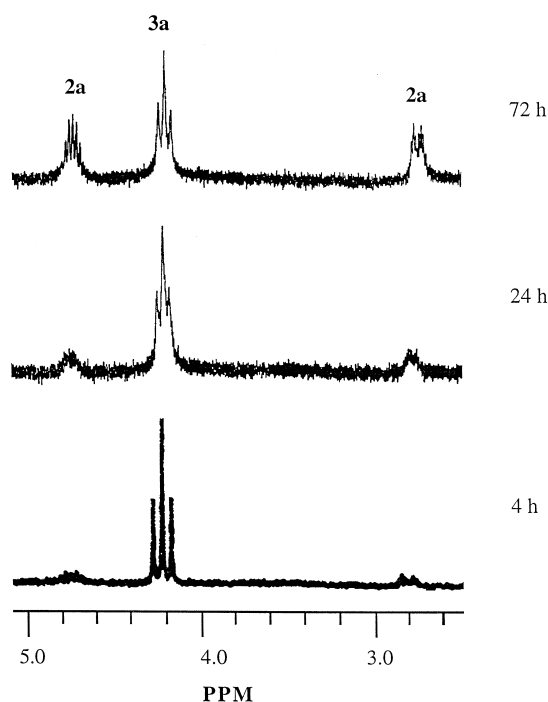
Fig. 1. ^{1}H NMR spectra (300 MHz) showing the conversion of PdCl$_2$(dpm) (**3a**, 8.9×10^{-3} M) with 2.5 mole equivalent H$_2$S to Pd$_2$Cl$_2$(μ-S)(dpm)$_2$ (**2a**) in CDCl$_3$ in the presence of corundum (α-alumina) (15 mg) at room temperature.

the S 2p signals at 161.9 and 169.1 eV (Fig. 3). XPS analyses of alumina exposed to HCl(g), H$_2$S(g), or S$_8$ show a Cl 2p signal at 199.5 eV for the HCl sample, and one broad weak S 2p signal at 169.1 eV for the H$_2$S or S$_8$ samples (Fig. 4). Of note, some decomposition of H$_2$S to elemental sulfur over γ-alumina was observed; for example, alumina previously exposed to H$_2$S for 4 h was washed with CHCl$_3$, and the eluate was analyzed using UV–Vis spectroscopy which revealed the presence of S$_8$ (λ_{max} 244, 266 nm; $\varepsilon = 830$ and 910 M^{-1} cm^{-1}, respectively [6]).

The Pd$_2$X$_2$(μ-S)(dpm)$_2$ products (**2**) from reaction (2) were recovered in quantitative yields ($> 98\%$) from synthetic-scale experiments, while the amounts of HX (adsorbed on the alumina) determined by titration were 5.2, 3.4, and 3.4×10^{-5} mol ($\pm 0.2 \times 10^{-5}$ mol) for the Cl$^-$, Br$^-$, and
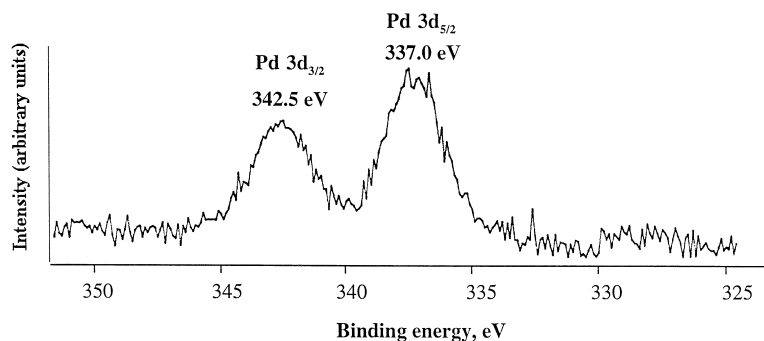

Fig. 2. X-ray photoelectron spectrum (Mg K_α, r.t.) showing the Pd 3d photoelectron signals resulting from adsorption of PdCl$_2$(dpm) (**3a**) and/or Pd$_2$Cl$_2$(μ-S)(dpm)$_2$ (**2a**) on alumina.
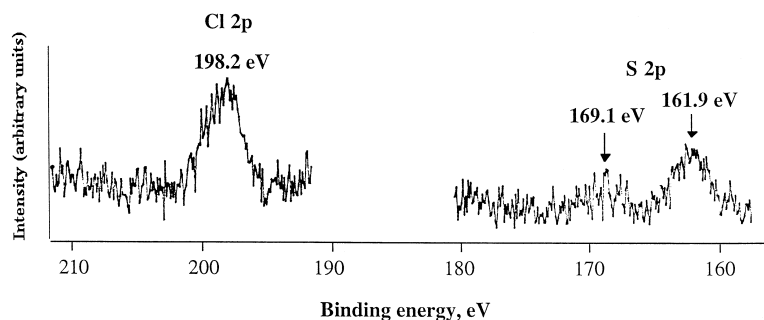
Fig. 3. X-ray photoelectron spectrum (Mg K_α, r.t.) showing the Cl 2p and S 2p photoelectron signals resulting from adsorption of PdCl$_2$(dpm) (**3a**) and/or Pd$_2$Cl$_2$(μ-S)(dpm)$_2$ (**2a**) on alumina; the signal at 169.1 eV is due to S$_8$ (see text).

I$^-$ systems, respectively, allowing for blank titrations giving $1.1(\pm 0.1) \times 10^{-5}$ mol acid. These titration results are in good agreement with the theoretical values of 4.5, 3.8, and 3.4×10^{-5} mol for the respective systems. In the 4-day laboratory/sunlight photochemical experiment with the iodide system, the alumina acquired a yellow colour but the CDCl$_3$ solvent remained colourless. Subsequent exposure to 254 nm light for 4 h led to the alumina becoming orange and the solvent purple. UV–Vis analysis of the solvent revealed an absorption band at 512 nm indicating the presence of I$_2$ ($\sim 1 \times 10^{-7}$ mol) [6], but GC and NMR analyses revealed no detectable H$_2$. The MeOH washing from the orange alumina contained 1.8×10^{-6} mol I$_3^-$ (i.e., 5.4×10^{-6} mol I$^-$) as determined by UV–Vis on comparison with an authentic sample of I$_3^-$ (λ_{max} 292, 360 nm; $\varepsilon = 2.89 \times 10^4$ and 1.66×10^4 M^{-1} cm^{-1}, respectively [6]) (Fig. 5). The filtered alumina was then found by titration to contain 2.8×10^{-5} mol acid, and the total number of moles of I$^-$ (or HI) generated equals $[2.8 + 0.54 + 2(0.01)] \times 10^{-5}$, i.e., $\sim 3.4 \times 10^{-5}$ mol, in excellent agreement with the total iodide available (see above). Of note, some I$_3^-$ also forms from addition of a CHCl$_3$ solution of I$_2$ to alumina without prior exposure to light.

Reaction (2) was studied at low temperatures, but no intermediate species were detected. For example, for the chloro system at $-42°$C, subsequent NMR analysis at $-50°$C revealed only unreacted **3a** and **2a** in 50% yield. Some mechanistic insight, however, came from reaction of **3a** with
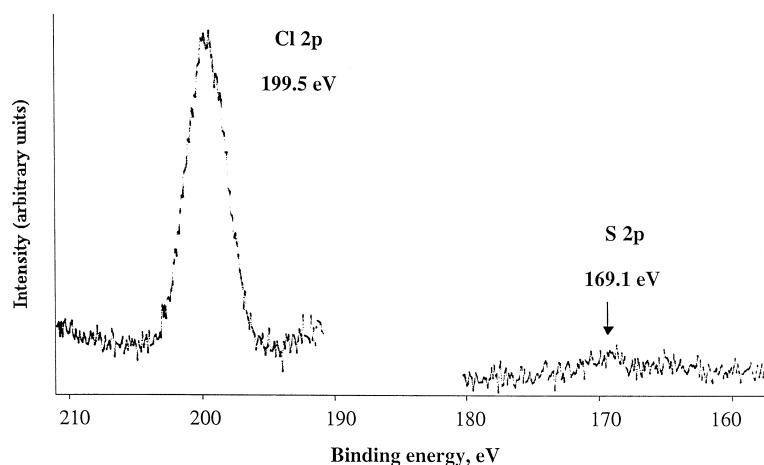

Fig. 4. X-ray photoelectron spectra (Mg K_α, r.t.) showing the S 2p and Cl 2p photoelectron signals resulting from adsorption of H$_2$S, S$_8$, or HCl(g) on alumina.
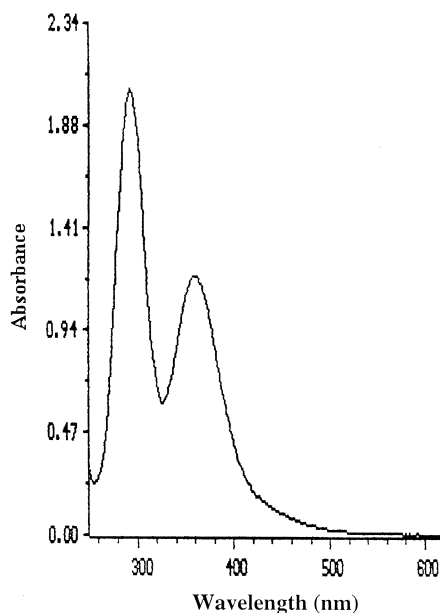
Fig. 5. Electronic spectrum (1 cm cell) of I_3^- (in 25.0 ml MeOH) isolated from synthetic-scale studies.

1 equiv. NaSH in solution which effected complete conversion to **2a**, with liberation of H_2S. Possible reactivity of **3a** with S_8 in the presence of alumina to form **2a** was examined, but NMR analysis revealed only unreacted **3a**.

Qualitative studies showed that an $HI(aq.)/CDCl_3$ solution over alumina photo-decomposes to produce I_2 (within minutes at r.t. in laboratory light) as evidenced by UV–Vis spectroscopy. An orange colour generated in the alumina is due to I_3^- (see above); no H_2 was detected. Of interest, however, ^{1}H NMR analysis revealed that when corundum was used, a broad singlet at δ 5.2 was seen (Fig. 6) and this is attributable to a $CDHX_2$ (X = Cl and/or I) species (see Section 4). Control samples of alumina in $CDCl_3$ with or without I_2 in $CDCl_3$, even using 254 nm light, showed no changes, the alumina remaining white and the I_2 512 nm absorption band remaining constant in intensity.

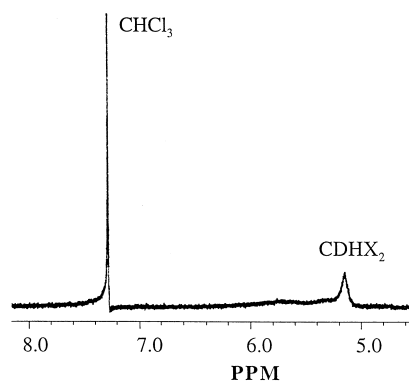

Fig. 6. ^{1}H NMR spectrum (300 MHz) showing the results of the photodecomposition of HI(aq.) (~ 2 μl of a 7.58 M aq. solution) at r.t. in $CDCl_3$ in the presence of corundum (α-alumina) (15 mg); X = Cl and/or I.

There was small but significant conversion (5×10^{-8} mol) to cyclooctane from the added excess cyclooctene using alumina (recovered from reaction (2) for the iodide system) on irradiation under the conditions described in Section 2.6; no conversion was seen with 'blank alumina'.

4. Discussion

The PdX$_2$(dpm) complexes (**3**) react with H$_2$S cleanly and quantitatively within minutes in a heterogeneous system with γ-alumina (low mesh, or finely ground higher mesh) to form Pd$_2$X$_2$(μ-S)(dpm)$_2$ (**2**) and HX (Eq. (2)); no intermediate species were observed. Of note, the reverse reaction using solutions of **2** and HX (in the 'free state') proceeds rapidly and completely, and thus, in the absence of alumina, the forward reaction does not occur [3]. As discussed below, the HX species chemisorbs on the alumina surface during reaction (2) and this provides the driving force for the forward reaction.

The NMR and XPS data show that adsorption of **2**, **3** and H$_2$S occurs on alumina, but the interactions are relatively weak. For H$_2$S, desorption readily takes place when the alumina is removed from the H$_2$S environment, and this is evident from non-reactivity, i.e., within reaction (2), when such alumina was subsequently treated with a solution of **3a**. Species **2** and **3** readily elute with solvent, implying physisorption rather than chemisorption as seen for HX (see below). XPS measurements and recovery of the Pd species on elution indicate that the complexes remain unchanged when adsorbed onto the alumina. Thus the observed Pd 3d$_{5/2}$ binding energy of 337.0 eV corresponds to those found for PdX$_2$(phosphine)$_2$ (337–338 eV) [12] and the observed Cl 2p binding energy of 198.2 eV is in the range of those reported for chloro complexes (197–199 eV) [13]. The presence of **2** on alumina is further defined by the S 2p signal at 161.9 eV, in the range of 160–162 eV seen for S^{2-} in metal sulfides [14].
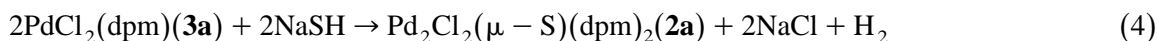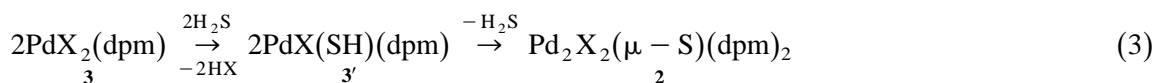
Although facile desorption of H$_2$S is evident, XPS analyses of alumina isolated from reaction (2) reveal a weak, second S 2p photoelectron signal at 169.1 eV that is also observed in control studies of alumina treated only with H$_2$S or S$_8$; UV–Vis data furthermore show that S$_8$ (which can be eluted from the alumina with corresponding loss of the 169.1 eV signal) can be formed from decomposition of H$_2$S. These studies show that the 169.1 eV signal results from the presence of elemental sulfur (the S 2p binding energy associated with non-adsorbed solid S$_8$ is 164 eV [14]). The 169.1 eV binding energy is close to that of S in 'free' SO$_4^{2-}$ (168.8 eV) [14], suggesting that the environment of surface O-atoms shifts the S$_8$ signal to the higher 169.1 eV value. Decomposition of H$_2$S to S$_8$ over alumina is reported, but the mechanism is poorly understood [15,16].

Chemisorption of hydrohalic acids by transition aluminas is known [17]. One component of the XPS Cl 2p signal centered at 198.2 eV noted for the chloride system is the Cl 2p signal of HCl; a control sample of alumina treated with HCl(g) shows a signal at 199.5 eV.
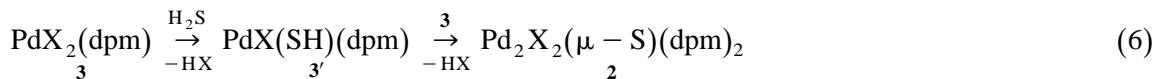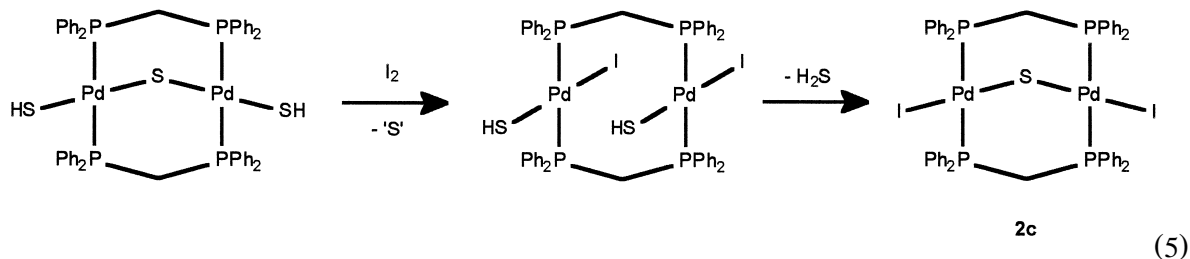
Reaction (2) proceeds largely via initial H$_2$S activation on alumina (probably via an S–H moiety), as seen from only trace conversion to **2** when adsorption of **3** occurred prior to addition of H$_2$S, and more obviously when **3** was introduced following desorption of H$_2$S during isolation of the alumina. Surprisingly, use of corundum with an extremely low mesh size of -100 yielded only 50% conversion (after 72 h) and, as noted below, the absence of 'active' sites here for S–H bond activation hinders the progress of reaction (2). Improved conversions (up to quantitative) of **3** to **2** were realized with use of lower mesh or more finely ground γ-alumina, where presumably more active sites are available; the detailed nature of the sites involved (acid–base or H-bonding [17–19]) remains unknown. Involvement of such active sites is supported by: (i) increased conversion to **2** on drying the

alumina at higher temperatures, and (ii) adsorption of **3** prior to the introduction of H_2S giving only trace amounts of **2**. The drying process presumably exposes more active sites as more H_2O molecules are driven from the surface [20], while occupation of these sites by **3** would explain zero conversion with subsequent addition of H_2S as 'S–H activation' could not take place. The relatively low activity of corundum (of low mesh) corresponds to its general properties; the material is both chromatographically inactive [17] and chemically inert [21], and thus H_2S activation by interaction with polar Al–O bonds in this material is not effective. Not all active sites on γ-alumina activate H_2S for reaction (2), because this reaction is not quite stoichiometric with respect to H_2S (a stoichiometric amount gives only 90% conversion to **2a** from **3a**, and XPS studies reveal slight decomposition of H_2S to S_8).

After activation of H_2S, anionic ligand exchange within **3** could form the mercapto intermediate PdX(SH)(dpm) (**3′**) that could subsequently couple (with elimination of H_2S) to give **2** (Eq. (3)). Although **3′** was not detected by low temperature NMR studies, the observed interaction between **3a** and 1 equiv. of NaSH in solution (Eq. (4)) provides indirect evidence for such an intermediate (X = Cl).

$$2PdX_2(dpm) \underset{\underset{3}{-2HX}}{\overset{2H_2S}{\rightarrow}} 2PdX(SH)(dpm) \underset{3'}{\overset{-H_2S}{\rightarrow}} Pd_2X_2(\mu-S)(dpm)_2 \tag{3}$$
$$32$$

$$2PdCl_2(dpm)(\mathbf{3a}) + 2NaSH \rightarrow Pd_2Cl_2(\mu-S)(dpm)_2(\mathbf{2a}) + 2NaCl + H_2 \tag{4}$$

Previous studies from this laboratory [3] have shown that **3a** with excess NaSH gives exclusively $Pd_2(SH)_2(\mu\text{-}S)(dpm)_2$, which could be formed from **2a** by nucleophilic substitution of both Cl^- ligands, or via coupling of $Pd(SH)_2(dpm)$ with concomitant elimination of H_2S (cf. Eq. (4)). Coupling of **3′** could go via $Pd_2X_2(SH)_2(dpm)_2$, and such species have been detected in low temperature NMR studies of the solution reaction between $Pd_2(SH)_2(\mu\text{-}S)(dpm)_2$ and I_2 [6,7] (Eq. (5)); a deprotonation/protonation process [22,23] then gives **2** and H_2S. The net reaction (2) would then be realized via the steps shown in Eq. (3). Alternatively, PdX(SH)(dpm) could couple with $PdX_2(dpm)$, and the steps in Eq. (6) could constitute reaction (2).

$$\tag{5}$$

$$PdX_2(dpm) \underset{-HX}{\overset{H_2S}{\rightarrow}} PdX(SH)(dpm) \underset{-HX}{\overset{3}{\rightarrow}} Pd_2X_2(\mu-S)(dpm)_2 \tag{6}$$
$$33'2$$

Adsorbed HI on alumina undergoes partial photodecomposition to form I_2, this then reacting with I^- on the surface to form I_3^-, which is readily quantified (following elution) by UV–Vis spectroscopy. Typically, up to 15% photodecomposition was observed with alumina isolated from reaction (2) for the iodide system; the strongly light-absorbing I_3^- appears to limit the extent of photodecomposition of HI. The co-photoproduct (the adsorbed hydrogen) was not detected as H_2, but there is some evidence for the formation of H-atoms. Based on comparison of ^1H NMR data for CH_2Cl_2 (δ 5.2 in $CDCl_3$), the δ 5.2 signal shown in Fig. 6 (for the generally less active α-alumina system) is attributed

to $CDHX_2$ (X = Cl and/or I), which could be formed by reaction of H-atoms with $CDCl_3$ to give initially HCl and $CDCl_2 \cdot$ radicals, with these then reacting with H- or I-atoms to give $CDHCl_2$ or $CDCl_2I$, respectively (note that I-atoms do not react with $CHCl_3$ [24]). Use of γ-alumina gave no formation of this type of species, but in hydrogenation studies using *cis*-cyclooctene, cyclooctane was formed in up to $\sim$ 5% yield based on 15% photodecomposition of HI.

5. Conclusions

Concerning potential catalytic cycles for the conversion of H_2S to H_2 and elemental sulfur, we have shown that the dinuclear bridged-sulfide species $Pd_2X_2(\mu\text{-}S)(dpm)_2$ can be formed from the reaction of H_2S with $PdX_2(dpm)$ on alumina, the reaction being induced by chemisorption of the liberated HX (X = halide). The reaction involves activation of the H_2S on the alumina, and a plausible mechanism via mercapto intermediates is presented. For the iodide system, photodecomposition of the absorbed HI can generate I_2, but not very efficiently, and H_2 is not produced; there is some evidence for formation of H-atoms, but not to the quantitative amount based on the I_2 formed.

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