

Quantitative Recovery of Dihydrogen from Hydrogen Sulphide using the Complexes, $[\text{Pd}_2\text{X}_2(\mu\text{-dppm})_2]$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}$; dppm = bis(diphenylphosphino)methane]

Chung-Li Lee,^a Gabor Besenyei,^a Brian R. James,^{*a} David A. Nelson,^{*b} and Michael A. Lilga^b

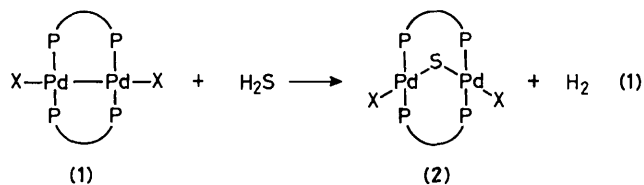
^a Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6

^b Pacific Northwest Laboratory, Richland, Washington, 99352 U.S.A.

The complexes $[\text{Pd}_2\text{X}_2(\mu\text{-dppm})_2]$ (**1**) [$\text{X} = \text{Cl}, \text{Br}, \text{I}$; dppm = bis(diphenylphosphino)methane] abstract sulphur from H_2S under ambient conditions to form $[\text{Pd}_2\text{X}_2(\mu\text{-S})(\mu\text{-dppm})_2]$ (**2**) and H_2 quantitatively; (**2**) can be oxidized in stages to $\mu\text{-SO}$ and $\mu\text{-SO}_2$ derivatives, the latter losing SO_2 spontaneously with regeneration of (**1**).

The interaction of transition metal complexes with H_2S is of interest because of the relevance of the chemistry to metal sulphide hydrodesulphurization catalysts, and the potential use of H_2S as a source of H_2 and organosulphur compounds.^{1,2} We have discovered reaction (1), in which the known^{3,4} metal-metal bonded dimer $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ (**1a**) [dppm = bis(diphenylphosphino)methane] in solution at ambient conditions removes the sulphur from H_2S to form the known, bridged sulphide complex³ with concomitant quantitative generation of H_2 . The reaction is complete in ~15 min on bubbling H_2S through a red CH_2Cl_2 solution of (**1a**) at 10^{-1} – 10^{-2} M; the brown product (**2a**) is readily isolated by addition of diethyl ether and is obtained in 90% recrystallized yield. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ n.m.r. and electronic spectral data are identical to those reported.³ The evolved H_2 was estimated [$>90\%$ per mole of (**1a**)] by g.c. using a 12 ft Porapak column with CO_2 as an internal standard. Complex (**2a**) was made previously by treatment of (**1a**) with elemental sulphur or propylene sulphide.³ The bromo analogue (**1b**) reacted similarly with H_2S but required overnight treatment; the reaction with the iodo complex⁴ was incomplete after one day.† The reverse reaction, liberation of H_2S from the bridged sulphide complexes,^{1,5} does not occur under 1 atm H_2 in refluxing benzene.

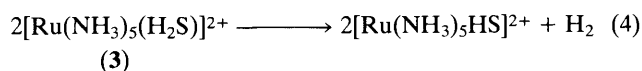
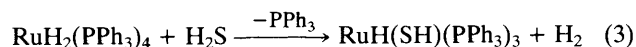
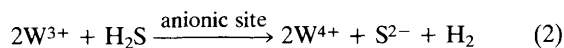
To our knowledge, reaction (1) is the first of its kind showing the 1:1 $\text{H}_2\text{S}:\text{H}_2$ stoichiometry at a metal centre, although reaction (2) has been invoked to account for the filling of vacant anionic sites by S in WS_2 lattices.¹ The H_2 produced in reaction (3) is a consequence of the hydride content of the tetrakisphosphine complex,⁶ and the net result is the more usual oxidative addition of H_2S via cleavage of an S–H bond.^{2,6} Kuehn and Taube⁷ did detect H_2 during



a; X = Cl
b; X = Br
c; X = I

$\text{P} \text{---} \text{P}$ = bis(diphenylphosphino)methane (dppm)

decomposition of (**3**), and tentatively suggested reaction (4), although (**3**) was not obtained in a pure state.



In terms of a potential catalytic recovery of H_2 from H_2S , it should be noted that (**2a**) can be readily reconverted in solution to (**1a**) via the bridged- SO_2 complex that is formed from (**2a**) using *m*-chloroperbenzoic acid;³ the violet $\mu\text{-SO}_2$ species spontaneously loses SO_2 to regenerate (**1a**). On testing a variety of reagents for oxidation of (**2a**) in CH_2Cl_2 , we noted that a two-phase reaction using aqueous-methanolic H_2O_2 at 20 °C gives in quantitative yield the orange, bridged sulph-

† N.m.r. spectral data for (**2b**) and (**2c**) are very similar to those of (**2a**).³

oxide complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-SO})(\mu\text{-dppm})_2]$,[‡] which can be oxidized further with the perbenzoic acid to the $\mu\text{-SO}_2$ species.

Added in proof. The first crystallographically characterized 'dimetallic sulphoxide', $[\text{Mn}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-SO})]$, appeared⁸ after submission of this article.

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[‡] This ($\mu\text{-SO}$) complex has been characterized by: elemental analysis (including oxygen); i.r. $\nu(\text{SO})$ 985 cm^{-1} ; ^1H n.m.r. δ (25°C , CD_2Cl_2) 4.68 (1H, dt, J_{HH} 12.6, J_{PH} 12.4 Hz), 3.87 (1H, dt, J_{HH} 12.5, J_{PH} 9.25 Hz), 2.50 (1H, m), and 2.30 (1H, m); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. δ (from external 85% H_3PO_4) 26.3, 15.0, and 3.5, -7.7 (AA'BB' pattern). Full details, including X-ray crystallographic and e.s.c.a. (S^{2p}) data, will be presented elsewhere.

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