3622 *Inorg. Chem.* **1987**, *26*, 3622-3628

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Reaction of Hydrogen Sulfide with Dinuclear Palladium(I) Complexes Containing Bis(diphenylphosphino)methane (dpm) and Conversion of Bridged-Sulfide Derivatives to Bridged-Sulfoxide Species. X-ray Crystal Structure of the Dimetallic Sulfoxide $Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-dpm})_2$, Containing Pyramidal Sulfur

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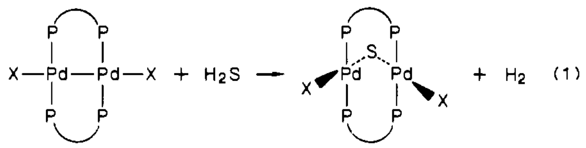
Received April 7, 1987

Hydrogen sulfide reacts with the complexes $Pd_2X_2(\mu\text{-dpm})_2$ (**1**) and the mixed-ligand complex $Pd_2Cl_2(\mu\text{-dpm})(\mu\text{-dpmMe})$ under ambient conditions to yield quantitatively H_2 and the corresponding A-frame, bridged-sulfide complexes such as $Pd_2X_2(\mu\text{-}S)(\mu\text{-dpm})_2$ [X = Cl, Br, I; dpm = bis(diphenylphosphino)methane, dpmMe = 1,1-bis(diphenylphosphino)ethane]. The sulfide complexes can be oxidized by using *m*-chloroperbenzoic acid or H_2O_2 to the corresponding $\mu\text{-}SO_2$ derivatives via intermediate bridged-sulfoxide (μ-SO) species. The complex $Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-dpm})_2$, in which SO acts as a 2-electron donor, with the bonding at S being pyramidal, crystallizes in the tetragonal space group $P4_3$ with $a = b = 21.214$ (1) Å, $c = 14.457$ (1) Å, and $Z = 4$; the data were refined to $R = 0.069$ on the basis of 2452 reflections with $I \geqslant 2.5\sigma(I)$. Two detected isomers of $Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-dpm})(\mu\text{-dpmMe})$ appear to result from differing orientations of the oxygen at the pyramidal sulfur atom. The spontaneous loss of SO_2 from the $\mu\text{-}SO_2$ species regenerates **1** and allows for the two-stage, catalytic process: $H_2S + 2\text{"O"} \rightarrow H_2 + SO_2$. Mechanistic aspects of the reaction of H_2S with $Pd_2Cl_2(\mu\text{-dpm})_2$ are briefly discussed. The complex $PdCl_2(dpm)$ reacts with H_2S under basic conditions to give $Pd_2(SH)_2(\mu\text{-}S)(\mu\text{-dpm})_2$.

Introduction

Research into interaction of H_2S with transition-metal complexes in solution is generally not well developed, despite the industrial[2,3] and biological[4,5] importance of the gas. During our studies on the use of the well-known dinuclear palladium(I) complexes $Pd_2X_2(\mu\text{-dpm})_2$ (X = halides, dpm = $Ph_2PCH_2PPh_2$)[6] for the separation of syngas components,[7] tests were made for reactivity toward H_2S. We discovered reaction 1,[8] which involves quantitative reduction of H_2S to H_2 and S^{2-}; a related reaction, reported more recently,[9] is that shown in eq 2. The H_2 produced



1 **2**

a, X = Cl; **b**, X = Br; **c**, X = I; P⌒P = dpm

$$2Cp'_2Zr(CO)_2 + 2H_2S \rightarrow [Cp'_2Zr(\mu\text{-}S)]_2 + 2H_2 + 4CO \quad (2)$$

$$Cp' = \eta^5\text{-}C_5H_5 \text{ or } \eta^5\text{-}C_5Me_5$$

from reactions of H_2S with (hydrido)phosphine complexes of Ru(II),[10] for example eq 3, is a consequence of the hydride content

$$RuH_2(PPh_3)_4 + H_2S \rightarrow RuH(SH)(PPh_3)_3 + H_2 + PPh_3 \quad (3)$$

of the phosphine complexes, and the net reaction, ignoring a labeling of the hydrogen atoms, is the more usual oxidative addition of H_2S via cleavage of the S–H bond.[3,10b,11] Related reactions, again involving ruthenium complexes, are shown in eq 4 ($P = PPh_3$)[11] and 5,[12] where the net result is the reduction of

$$Ru(CO)_2P_3 \xrightarrow[-P]{H_2S} RuH(SH)(CO)_2P_2 \xrightarrow{H_2S} Ru(SH)_2(CO)_2P_2 + H_2 \quad (4)$$

$$2Ru(NH_3)_5(H_2S)^{2+} \rightarrow 2Ru(SH)(NH_3)_5^{2+} + H_2 \quad (5)$$

two moles of H_2S to H_2 and $2SH^-$. Reaction 5 was suggested tentatively because the precursor H_2S complex was not obtained in a pure state;[12] indeed, in this regard, the only other well-characterized isolated H_2S complex appears to be $W(CO)_5(H_2S)$,[13] although ^1H NMR spectroscopic evidence has been presented for the species $Pt(PPh_3)_2(H_2S)$ en route to formation of a more stable (hydrido)(mercapto) complex.[14] Equation 6, analogous to eq 1 and 2, has been invoked for a solid-state reaction to account for the filling of vacant anionic sites by sulfur in WS_2 lattices[2b]

$$2W^{3+} + H_2S \xrightarrow{\text{anionic site}} 2W^{4+} + S^{2-} + H_2 \quad (6)$$

The studies outlined above show that transition-metal complex/H_2S chemistry clearly has potential from the viewpoints of H_2 recovery and inorganic synthesis, while the use of H_2S for organosulfur compounds has also been considered.[3] This paper reports more fully on the reactions outlined in eq 1 and also on

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Table I. NMR Spectroscopic Data for the Dinuclear Palladium μ-S and μ-SO Complexes

no.	complex	$\delta(^1H)^a$	$\delta(^{31}P)^b$
2a	$Pd_2Cl_2(\mu\text{-}S)(dpm)_2$	2.79[c] (12.56, 3.50)	5.52
		4.73[c] (12.56, 6.08)	
2b	$Pd_2Br_2(\mu\text{-}S)(dpm)_2$	2.86[c] (12.63, 3.41)	5.96
		4.81[c] (12.63, 6.02)	
2c	$Pd_2I_2(\mu\text{-}S)(dpm)_2$	3.04[c] (13.50, 3.30)	6.04
		4.92[c] (13.50, 5.73)	
2d	$Pd_2(SH)_2(\mu\text{-}S)(dpm)_2$[d]	3.14[c] (13.02, 3.47)	14.26
		4.83[c] (13.02, 6.02)	
4	$Pd_2Cl_2(\mu\text{-}S)(dpm)(dpmMe)$	1.07[e] (8.00, 9.20)	*h*
	(*syn*- or *anti*-)	2.81[f] (12.36, 10.57)	
		4.60[f] (12.36, 12.18)	
		5.48[g] (8.00, 7.10)	
3	$Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$	2.30[i] (12.80, 14.00, 8.00[j])	−0.67[k]
		2.50[i] (12.80, 12.60, 5.80[j])	19.09
		3.87[f] (12.60, 9.25)	
		4.68[f] (12.60, 12.40)	
5	$Pd_2Cl_2(\mu\text{-}SO)(dpm)(dpmMe)$		
	major isomer	1.06[e] (7.30, 9.86)	
		2.22[i] (13.87, 12.17, ~7.0[j])	*n*
		3.72[f] (13.87, 9.30)	
		5.43[g] (7.30, 15.02)	
	minor isomer	1.14[e] (8.47, 8.95)	
		2.45[l] (~11.5)	*n*
		4.27[m] (~7.5)	
		4.70[f] (12.26, 12.08)	

[a] In CD_2Cl_2 at 25 °C. δ for the aliphatic protons of the μ-diphosphine ligand with respect to TMS; *J* values in hertz are given in parentheses (J_{HH}, J_{PH}). [b] In CD_2Cl_2 at 25 °C. Shifts relative to external 85% H_3PO_4, downfield being positive; peaks are singlets, unless stated otherwise. [c] Doublet of quintets (dqn) for each of two sets of methylene protons. [d] $\delta = -1.60$ qn ($J_{PH} = 5.47$ Hz) for –SH ligand. For the complex $Pd_2Cl(SH)(\mu\text{-}S)(dpm)_2$ formed in situ in $CDCl_3$ (see text): δ (multiplets) at −1.40 (S*H*), 2.95, and ~4.80 (CH_2). [e] Doublet of triplets (dt) for the CH_3 protons. [f] dt for one methylene proton. [g] Triplet of quartets (tq) for the CH proton. [h] AA′BB′ multiplet (cf. the corresponding spectrum for $Pd_2Cl_2(dpm)(dpmMe)$ (Figure 6 in ref 16) and Figure 3 for complex **3**). [i] Doublet of triplet of triplets for one methylene proton. [j] J_{HP} long-range coupling to the two remote P atoms. [k] AA′BB′ multiplet with $J_{AA'} = 89.9$, $J_{AB} = J_{A'B'} = 359.3$, $J_{AB'} = J_{A'B} = -3.2$, and $J_{BB'} = 24.79$ Hz. [l] Multiplet for the CH proton. [m] Multiplet for one methylene proton. [n] Complex; mixture of isomers yields two AA′BB′ patterns (see footnotes *h* and *k*).

the subsequent oxidation of **2a** to the bridged-sulfoxide complex $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ (**3**), which has been fully characterized both spectroscopically and crystallographically. Oxidation of **2a** to the bridged-SO_2 derivative has been reported previously by Balch's group.[15] The recently synthesized[16] mixed-ligand complex $Pd_2Cl_2(dpm)(dpmMe)$ (dpmMe, representing monomethylated dpm, = 1,1-bis(diphenylphosphino)ethane) also forms, via a reaction akin to (1), a μ-S derivative that is similarly oxidized, while the monomer $PdCl_2(dpm)$[17] reacts with H_2S in basic solution only to yield $Pd_2(SH)_2(\mu\text{-}S)(dpm)_2$.

Experimental Section

General Data. The palladium complexes $Pd_2X_2(dpm)_2$ (X = Cl, Br, I),[18] $Pd_2Cl_2(dpm)(dpmMe)$,[16] and $PdCl_2(dpm)$[17] were prepared by published procedures. Hydrogen sulfide (Matheson, C.P. grade), *m*-chloroperbenzoic acid (Aldrich), and hydrogen peroxide (BDH, 30%) were used as supplied. Dimethylacetamide (DMA) (Aldrich) was distilled and dried over CaH_2 prior to use. ^1H (5-mm tubes, 400 MHz) and ^{31}P (10-mm tubes, 32.44 MHz) NMR spectra were recorded at room temperature (25 °C) on Bruker WH-400 and WP-80 FT instruments, respectively; ^{31}P NMR shifts are given relative to external 85% H_3PO_4, downfield being positive, while simulation of ^1H and ^{31}P spectra were performed by using the iterative routine of a Bruker ASPECT 2000 NMR PANIC program. IR spectra were recorded as Nujol mulls on a Nicolet 50X FT spectrometer. UV/vis spectra were recorded on a thermostated Perkin-Elmer 552A spectrophotometer using a specially designed tonometer consisting of a 1-cm path length cell attached by a side arm to a reservoir bulb and fitted with a Teflon stopcock and an O-ring joint for attachment to a vacuum line;[19] CH_2Cl_2 saturated with H_2S could be added from a gastight syringe via a septum.

The quoted reaction times in the synthetic procedures (reactions involving H_2S, H_2O_2, or *m*-chloroperbenzoic acid) were determined by monitoring the reactions with TLC, particularly for the disappearance of the starting Pd complex [Merck Kieselgel 60 F_{254} plates, CH_2Cl_2/ethyl acetate (6:1 v/v) as eluent]. Syntheses were carried out by using Schlenk glassware in well-ventilated fume hoods.

Formation of $Pd_2(\mu\text{-}S)$ Complexes Using H_2S. $Pd_2X_2(\mu\text{-}S)(dpm)_2$ (2). $Pd_2Cl_2(dpm)_2$ (**1a**) (300 mg, 0.29 mmol) was dissolved in 40 mL of CH_2Cl_2, and H_2S was bubbled through the solution for 20 min at 20 °C; the color changed from orange-red to brown with accompanying precipitation of a brown solid that was completed by gradual addition of 100 mL ether. Filtering and vacuum-drying gave 300 mg (97%) of the known complex $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**) as identified by ^1H and $^{31}P\{^1H\}$ (see Table I, which lists NMR spectroscopic data for all of the isolated complexes). The corresponding bromide **2b** was prepared in 87% yield by treating a CH_2Cl_2 solution of **1b** with H_2S overnight in a capped Schlenk tube. Anal. Calcd for $C_{50}H_{44}P_4Br_2SPd_2$: C, 51.13; H, 3.78; S, 2.73. Found: C, 51.16; H, 3.71; S, 2.85. Formation of the iodo complex $Pd_2I_2(\mu\text{-}S)(dpm)_2$ (**2c**) from **1c** and H_2S is relatively slow and was only about 25% complete after 24 h. Complex **2c** could be isolated, however, in high yields by stirring a solution of **2a** (200 mg, 0.28 mmol in 30 mL of CH_2Cl_2/10 mL of MeOH) with 10 mL saturated aqueous NaI for 20 min; reduction in volume by rotovap yielded brown crystals that were collected, redissolved in 20 mL CH_2Cl_2, and reprecipitated with 50 mL of MeOH; yield, after filtering and drying, 227 mg (97%). Anal. Calcd for $C_{50}H_{44}P_4I_2SPd_2$: C, 47.34; H, 3.50; S, 2.53. Found: C, 47.48; H, 3.52; S, 2.66.

$Pd_2Cl_2(\mu\text{-}S)(dpm)(dpmMe)$ (4). H_2S was bubbled for 5 min through 30 mL of CH_2Cl_2 containing $Pd_2Cl_2(dpm)(dpmMe)$ (250 mg, 0.23 mmol) in a Schlenk tube; the tube was then capped and the solution stirred for 3 h at 20 °C. Addition of 40 mL of MeOH precipitated a brown product that was filtered off, redissolved in 20 mL of $CHCl_3$, and reprecipitated by addition of 40 mL of MeOH. Filtering and drying under vacuum yielded 221 mg (87%). Anal. Calcd for $C_{51}H_{46}P_4Cl_2SPd_2$: C, 55.76; H, 4.22; S, 2.92. Found: C, 55.53; H, 4.05; S, 2.88.

$Pd_2(SH)_2(\mu\text{-}S)(dpm)_2$ (2d). (a) To 25 mL of CH_2Cl_2 containing **1a** (300 mg, 0.29 mmol) was added 20 mL of $MeOH/H_2O$ (1:1 v/v) containing 500 mg of NaSH (8.9 mmol), and the mixture was stirred for 1 h at 20 °C, when the color rapidly changed from orange-red to brown. A further 25 mL of $MeOH/H_2O$ was then added, and the CH_2Cl_2 was removed by evaporation. The resulting brown solid was collected, dissolved in CH_2Cl_2 and precipitated by addition of ether (twice). Drying under vacuum yielded 250 mg (81%) of **2d**. Anal. Calcd for $C_{50}H_{46}P_4S_3Pd_2$: C, 55.61; H, 4.29; S, 8.91. Found: C, 54.49; H, 4.30; S, 8.29.

(b) The monomer $PdCl_2(dpm)$ (600 mg, 0.57 mmol) was added to 20 mL of C_6H_6 containing Et_3N (0.5 mL, 3.6 mmol), and H_2S was bubbled through the mixture for 1 h at 20 °C, the initial yellow suspension rapidly turning red-brown. The mixture of solids (containing Et_3NHCl) was collected, washed successively with C_6H_6 and hexane, and then stirred for 3 h in 10 mL of H_2O/CH_2Cl_2 (1:1 v/v); the organic layer was then separated and the product precipitated by addition of ether. The mixed-solvent procedure was repeated twice to give finally 260 mg (42%) of **2d**. The monomer is unreactive toward H_2S in the absence of a base.

(c) $PdCl_2(dpm)$ (300 mg, 0.29 mmol) was dissolved in 40 mL of CH_2Cl_2 and stirred for 1 h at 20 °C with 15 mL of H_2O/MeOH (2:1 v/v) containing NaSH (600 mg, 10.7 mmol). A further 50 mL of H_2O/MeOH was then added, and the CH_2Cl_2 was removed by evaporation. The resulting brown solid was collected, dissolved in CH_2Cl_2, and precipitated by addition of ether (twice); yield 140 mg (46%).

(d) Complex **2d** could be obtained also from $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**) by using either (i) the identical procedure described above in part c, when 300 mg **2a** yielded 200 mg of **2d** (66%), or (ii) an H_2S/NEt_3 procedure similar to that described in part b, when 200 mg of **2a** yielded 110 mg of **2d** (55%).

Detection of H_2 Generated from H_2S. A Carle Analytical gas chromatograph (Model 311) in the thermal conductivity mode was used in conjunction with a 12-ft Porapak Q column (Waters Associates, Inc., 80–100 mesh); injector and column temperatures were maintained at 30 °C, while a He gas stream flowed at 20 psi. DMA, because of its low vapor pressure at 30 °C, proved to be a convenient solvent for studying the H_2 production from reaction 1. Calibration was effected by first saturating with H_2S at 1 atm a previously evacuated 50-mL Schlenk tube containing 10 mL of DMA; 10 mL of H_2 and 1 mL of CO_2 (as internal standard) were injected via a serum cap into the gas phase of the tube, and the solvent was then stirred for $^1/_2$ h. The average integration area

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Table II. Crystallographic Data[a]

compd	$(\mu\text{-SO})(\mu\text{-dpm})_2Pd_2Cl_2{\cdot}xCH_2Cl_2{\cdot}y(C_2H_5)_2O$
formula	$C_{50}H_{44}Cl_2OP_4Pd_2S{\cdot}xCH_2Cl_2{\cdot}yC_4H_{10}O$
fw	1100.56 + solvent
cryst syst	tetragonal
space group	$P4_3$
a, Å	21.214 (1)
c, Å	14.457 (1)
V, Å^3	6506.2 (7)
Z	4
D_{calcd}, g/cm^3	1.363[b]
$F(000)$	2679.7[b]
μ(Mo K_α), cm^{-1}	10.2[b]
cryst dimens, mm	0.18 × 0.20 × 0.54
transmissn factors	0.820–0.852
scan type	ω–2θ
scan range, deg in ω	$0.60 + 0.35 \tan \theta$
scan speed, deg/min	0.91–10.06
data collcd	$+h,+k,+l$
$2\theta_{max}$, deg	50
no. of unique reflcns	5942
no. of reflcns with $I \geq 2.5\sigma(I)$	2452
no. of variables	283
R	0.069
R_w	0.071
GOF	2.166
mean Δ/σ (final cycle)	0.04
max Δ/σ (final cycle)	0.83
residual density, e/Å^3	−2.3 to +1.7 (both near Pd atoms)

[a] Temperature 22 °C, Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.70930, $\lambda_{K\alpha_2}$ = 0.713 59 Å), graphite monochromator, takeoff angle 2.7°, aperture $(2.0 + \tan\theta) \times 4.0$ mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (S = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 2.5\sigma(I)$. [b] These numbers, calculated with $x = 2.76$ and $y = 0$, represent minimum values for the respective parameters.

on the GC for CO_2:H_2 in the gas phase was 3.47 (five runs). To study reaction 1, $Pd_2Cl_2(dpm)_2$ (500 mg, 0.475 mmol) was suspended in 10 mL of DMA in the same Schlenk tube, and the system was evacuated, prior to saturation with H_2S (1 atm) and addition of 1 mL of CO_2. Sampling of the gas phase after $^1/_2$ h of stirring gave an average CO_2:H_2 = 3.30 (five runs), which thus corresponds to 10.51 mL of H_2. The theoretical amount of liberated H_2 for a quantitative reaction at 25 °C for 500 mg **1a** is 11.61 mL, and thus the yield in H_2 is about 90%. As measured, this estimation is independent of the solubility of H_2 in DMA; in any case, this reported solubility (1.76×10^{-3} M atm^{-1} at 25 °C)[20] shows that the amount of H_2 in the solution phase will be negligible (<1%). The reaction as monitored by ^{1}H or ^{31}P NMR showed complete conversion of, for example, **1a** to **2a**.

Oxidation of Bridged-Sulfide Complexes to the Bridged-Sulfoxide Derivatives. $Pd_2Cl_2(\mu\text{-SO})(dpm)_2$ (3). (a) Complex **2a** (400 mg, 0.37 mmol) was dissolved in 40 mL of CH_2Cl_2, and 40 mL of 30% aqueous H_2O_2 and 10 mL of MeOH were added. The mixture was vigorously stirred at room temperature for 2 h, after which time the orange CH_2Cl_2 layer was removed and concentrated to 10 mL. Addition of 50 mL of MeOH precipitated an orange solid that was filtered off and vacuum dried; yield 385 mg (95%). Anal. Calcd for $C_{50}H_{44}OP_4Cl_2SPd_2$: C, 54.57; H, 4.03; S, 2.91; O, 1.45. Found: C, 54.51; H, 4.06; S, 2.75; O, 1.52. ν(SO) = 985 cm^{-1}.

(b) Complex **2a** (308 mg, 0.284 mmol) was dissolved in 40 mL of CH_2Cl_2 at −20 °C, and a similarly cooled CH_2Cl_2 solution (5 mL) of *m*-chloroperbenzoic acid (59 mg, 0.29 mmol) was added with stirring over a period of 10 min. The solution was stirred for a further 5 min, warmed to room temperature, and concentrated to 10 mL by rotovap; addition of 100 mL of ether precipitated the pure orange product that was collected and vacuum dried; yield 270 mg (86%).

$Pd_2Cl_2(\mu\text{-SO})(dpm)(dpmMe)$ (5). *m*-Chloroperbenzoic acid (62 mg, 0.30 mmol) in 15 mL of CH_2Cl_2, cooled at 0 °C, was added dropwise over $^1/_2$ h into a CH_2Cl_2 solution (40 mL) of **4** (300 mg, 0.277 mmol),

Table III. Final Positional (Fractional ×10^4, Pd ×10^5) and Isotropic Thermal Parameters (Å^2 × 10^3) with Estimated Standard Deviations in Parentheses[a]

atom	x	x	z	U_{eq} or U_{iso}
Pd(1)	49113 (10)	21882 (10)	78000	36
Pd(2)	56995 (10)	11180 (9)	67175 (20)	37
Cl(1)	3948 (3)	2791 (3)	7848 (6)	55
Cl(2)	5713 (4)	464 (3)	5370 (6)	62
S	5843 (4)	1689 (3)	8035 (5)	47
P(1)	5475 (3)	2972 (3)	7009 (5)	37
P(2)	6141 (4)	1946 (3)	5870 (5)	41
P(3)	4394 (4)	1351 (3)	8512 (5)	38
P(4)	5245 (3)	338 (3)	7643 (5)	37
Cl(3)	7128 (10)	2690 (13)	10393 (21)	350
Cl(4)	5906 (7)	2683 (8)	10747 (15)	238
Cl(5)[a]	7684 (18)	1193 (18)	8014 (26)	352
Cl(6)[a]	7763 (16)	815 (33)	9698 (27)	539
Cl(7)[a]	8032 (19)	1697 (14)	2298 (19)	305
Cl(8)[a]	7566 (14)	2912 (26)	2950 (35)	460
Cl(9)[b]	7941 (37)	−560 (23)	5199 (38)	395
Cl(10)[b]	8825 (24)	−321 (25)	4807 (73)	499
C(1)	6210 (11)	2693 (11)	6474 (14)	29
C(2)	4854 (11)	652 (12)	8701 (16)	35
O(1)[c]	6419 (14)	2049 (14)	8164 (21)	42 (9)
O(1′)[b]	5925 (18)	1401 (18)	8852 (29)	47 (12)
C(3)	6461 (22)	2728 (20)	9838 (31)	125 (16)
C(4)[a]	7412 (33)	785 (30)	8936 (55)	126 (25)
C(1a)	5754 (8)	3568 (7)	7838 (12)	36 (7)
C(2a)	5366 (7)	3723 (8)	8581 (14)	49 (8)
C(3a)	5554 (9)	4185 (9)	9208 (11)	77 (10)
C(4a)	6129 (10)	4491 (8)	9092 (13)	80 (11)
C(5a)	6516 (7)	4335 (9)	8349 (15)	66 (10)
C(6a)	6329 (8)	3874 (9)	7722 (12)	48 (8)
C(1b)	5090 (9)	3401 (8)	6089 (11)	41 (8)
C(2b)	4519 (9)	3193 (7)	5727 (13)	46 (8)
C(3b)	4265 (7)	3485 (10)	4949 (14)	80 (12)
C(4b)	4581 (9)	3985 (9)	4533 (11)	64 (9)
C(5b)	5153 (9)	4193 (7)	4895 (14)	64 (10)
C(6b)	5407 (7)	3901 (9)	5673 (14)	56 (9)
C(1c)	6944 (10)	1812 (16)	5506 (24)	102 (13)
C(2c)	7446 (17)	2129 (11)	5915 (18)	106 (14)
C(3c)	8063 (13)	1967 (15)	5688 (22)	134 (17)
C(4c)	8177 (12)	1488 (17)	5052 (25)	131 (16)
C(5c)	7675 (20)	1171 (13)	4642 (21)	244 (29)
C(6c)	7058 (16)	1333 (15)	4869 (24)	208 (26)
C(1d)	5721 (9)	2158 (9)	4830 (12)	49 (8)
C(2d)	5134 (9)	1894 (8)	4643 (13)	54 (9)
C(3d)	4795 (7)	2087 (10)	3869 (15)	73 (10)
C(4d)	5043 (10)	2544 (10)	3282 (12)	67 (10)
C(5d)	5630 (11)	2808 (8)	3468 (14)	90 (12)
C(6d)	5969 (7)	2615 (10)	4243 (16)	67 (10)
C(1e)	3702 (8)	1069 (9)	7950 (14)	54 (9)
C(2e)	3365 (10)	569 (9)	8330 (12)	69 (10)
C(3e)	2865 (9)	303 (8)	7844 (17)	75 (10)
C(4e)	2702 (8)	537 (11)	6976 (17)	97 (13)
C(5e)	3039 (11)	1037 (11)	6596 (12)	88 (11)
C(6e)	3539 (9)	1303 (8)	7083 (15)	61 (9)
C(1f)	4136 (10)	1551 (9)	9653 (12)	46 (8)
C(2f)	3545 (9)	1823 (9)	9775 (13)	75 (11)
C(3f)	3350 (7)	2006 (9)	10654 (17)	73 (11)
C(4f)	3746 (11)	1916 (10)	11411 (12)	82 (11)
C(5f)	4337 (10)	1643 (10)	11289 (13)	80 (11)
C(6f)	4532 (7)	1461 (8)	10409 (17)	62 (9)
C(1g)	5837 (8)	−180 (8)	8112 (15)	50 (9)
C(2g)	6333 (11)	−319 (9)	7516 (12)	67 (10)
C(3g)	6820 (9)	−711 (11)	7808 (17)	93 (11)
C(4g)	6811 (9)	−964 (9)	8696 (18)	89 (12)
C(5g)	6315 (11)	−825 (10)	9292 (13)	83 (11)
C(6g)	5828 (9)	−433 (10)	9000 (14)	70 (10)
C(1h)	4675 (7)	−183 (8)	7177 (13)	38 (7)
C(2h)	4516 (9)	−723 (9)	7671 (11)	53 (8)
C(3h)	4050 (9)	−1125 (7)	7338 (15)	75 (11)
C(4h)	3743 (8)	−987 (9)	6511 (16)	74 (11)
C(5h)	3902 (9)	−447 (11)	6018 (11)	83 (11)
C(6h)	4368 (10)	−45 (7)	6351 (13)	53 (9)

[a] C(1a)–C(6h) are the carbon atoms of phenyl rings refined as rigid groups. Usperscripts refer to the following occupancy factors: a, 0.66; b, 0.44; c 0.56.

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Table IV. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

Pd(1)–Cl(1)	2.411 (7)	P(1)–C(1b)	1.81 (2)
Pd(1)–S	2.268 (8)	P(1)–C(1)	1.84 (2)
Pd(1)–P(1)	2.346 (7)	P(2)–C(1c)	1.80 (2)
Pd(1)–P(3)	2.328 (7)	P(2)–C(1d)	1.81 (2)
Pd(2)–Cl(2)	2.393 (8)	P(2)–C(1)	1.82 (2)
Pd(2)–S	2.277 (8)	P(3)–C(1e)	1.78 (2)
Pd(2)–P(2)	2.337 (8)	P(3)–C(1f)	1.79 (2)
Pd(2)–P(4)	2.337 (7)	P(3)–C(2)	1.80 (3)
S–O(1)	1.45 (3)	P(4)–C(1g)	1.80 (2)
S–O(1′)	1.34 (4)	P(4)–C(1h)	1.77 (2)
P(1)–C(1a)	1.84 (2)	P(4)–C(2)	1.86 (2)

Table V. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

Cl(1)–Pd(1)–S	169.0 (3)	C(1a)–P(1)–C(1)	102.9 (9)
Cl(1)–Pd(1)–P(1)	94.0 (3)	C(1b)–P(1)–C(1)	103.6 (8)
Cl(1)–Pd(1)–P(3)	89.6 (3)	Pd(2)–P(2)–C(1c)	114.4 (11)
S–Pd(1)–P(1)	87.7 (3)	Pd(2)–P(2)–C(1d)	115.2 (6)
S–Pd(1)–P(3)	89.3 (3)	Pd(2)–P(2)–C(1)	115.9 (8)
P(1)–Pd(1)–P(3)	175.4 (3)	C(1c)–P(2)–C(1d)	105.2 (12)
Cl(2)–Pd(2)–S	171.1 (3)	C(1c)–P(2)–C(1)	101.6 (13)
Cl(2)–Pd(2)–P(2)	90.2 (3)	C(1d)–P(2)–C(1)	102.8 (9)
Cl(2)–Pd(2)–P(4)	93.5 (3)	Pd(1)–P(3)–C(1e)	116.3 (6)
S–Pd(2)–P(2)	89.1 (3)	Pd(1)–P(3)–C(1f)	111.8 (6)
S–Pd(2)–P(4)	87.3 (3)	Pd(1)–P(3)–C(2)	116.1 (8)
P(2)–Pd(2)–P(4)	176.2 (3)	C(1e)–P(3)–C(1f)	104.4 (9)
Pd(1)–S–Pd(2)	90.4 (3)	C(1e)–P(3)–C(2)	103.9 (11)
Pd(1)–S–O(1)	120.4 (12)	C(1f)–P(3)–C(2)	102.8 (12)
Pd(1)–S–O(1′)	117 (2)	Pd(2)–P(4)–C(1g)	111.0 (6)
Pd(2)–S–O(1)	120.0 (13)	Pd(2)–P(4)–C(1h)	120.4 (6)
Pd(2)–S–O(1′)	121 (2)	Pd(2)–P(4)–C(2)	113.6 (8)
O(1)–S–O(1′)	91 (2)	C(1g)–P(4)–C(1h)	103.8 (8)
Pd(1)–P(1)–C(1a)	109.5 (5)	C(1g)–P(4)–C(2)	102.7 (12)
Pd(1)–P(1)–C(1b)	119.0 (6)	C(1h)–P(4)–C(2)	103.4 (10)
Pd(1)–P(1)–C(1)	114.2 (8)	P(1)–C(1)–P(2)	114.5 (13)
C(1a)–P(1)–C(1b)	106.2 (7)	P(3)–C(2)–P(4)	114.3 (13)

also at 0 °C. The resulting solution was stirred for $^1/_2$ h and reduced in volume to 30 mL by rotovap; addition of 50 mL of MeOH gave 211 mg of an orange product. Reducing the volume of the mother liquor to about 20 mL led to precipitation of a further 65 mg of product. Redissolving both fractions in 30 mL of CH_2Cl_2 and reprecipitation via addition of 50 mL of MeOH gave 250 mg of collected, dried product. Anal. Calcd for $C_{51}H_{46}OP_4Cl_2SPd_2$: C, 54.96; H, 4.16; S, 2.88; O, 1.44. Found: C, 54.74; H, 4.16; S, 2.90; O, 1.60. ν(SO) = 984 cm^{-1}.

Regeneration of $Pd_2Cl_2(dpm)_2$ (1a) from $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (2a) or $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ (3). The bridged-sulfide complex **2a** (108 mg, 0.1 mmol) was dissolved in 50 mL of CH_2Cl_2 at −20 °C, and 5 mL of CH_2Cl_2 containing *m*-chloroperbenzoic acid (56 mg, 0.28 mmol), also cooled to −20 °C, added rapidly. The resulting solution was stirred at the low temperature for 15 min, when hydrazine (2 mg, 0.06 mmol) in 1 mL CH_2Cl_2 was added. After 5 min the cooling bath was removed, and the violet solution containing the bridged-SO_2 complex[15] was refluxed for 5 min to remove the SO_2. The solution was concentrated under vacuum to 10 mL; addition of 100 mL of ether precipitated red-orange $Pd_2Cl_2(dpm)_2$ that was collected and vacuum dried (80 mg, 76% yield), the product being identified by UV/vis, ^{1}H NMR, and ^{31}P NMR spectroscopy.[15,18] This same complex was isolated in 83% yield from the μ-SO complex **3** by using a similar *m*-chloroperbenzoic acid/hydrazine treatment but with only 1.2 equiv of the oxidant. The mixed complex Pd_2Cl_2(dpm)(dpmMe) could be recovered in high yield from **4** or **5** by the same peracid oxidation procedures. Treatment of **2a** with ozone at −60 °C generated the μ-SO_2 complex directly, but when it was warmed to 20 °C decomposition occurred to give some $PdCl_2$(dpm) and other unidentified products. Use of other oxidants such as OCl^- or $Pb(OCOCH_3)_4$ at 20 °C did not lead to recovery of **1a** from **2a**. Attempts to regenerate **1a** by reacting **2a** with PPh_3 (a known method for removing coordinated chalcogen atoms as $SPPh_3$[21,22]) were unsuccessful: a slow reaction at 20 °C destroyed much of **2a**, and **1a** was never obtained in >20% yield.

X-ray Crystallographic Analysis of $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2 \cdot xCH_2Cl_2 \cdot y(C_2H_5)_2O$ (3). A single crystal of the compound was prepared by placing a test tube containing 10 mL of a saturated CH_2Cl_2 solution of the complex in a closed vessel (400 mL) containing 100 mL of anhydrous diethyl ether; orange-red crystals were formed after 2 days, but they deteriorated rapidly when removed from the solution, even when mounted wet in Lindemann glass capillary tubes. Satisfactory crystal stability was finally achieved by encapsulating a crystal in an epoxy while it was still in solution. Crystallographic data are presented in Table II.

The final unit-cell parameters were obtained by least squares on 2(sin θ)/λ values for 25 reflections (with 2θ = 20–25°) measured with Mo Kα_1 radiation. The intensities of three check reflections, monitored each hour of X-ray exposure time throughout the data collection, showed only small random variations. The data were corrected for absorption by using the Gaussian integration method.[23]

The systematic absences (00*l*, $l \neq 4n$) and the Laue symmetry ($4/m$) indicated the space group $P4_1$ or the enantiomorphic $P4_3$. The coordinates of the Pd, Cl, P, and S atoms of the $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ molecule were determined from the Patterson function, and the refinement was initiated in space group $P4_1$. The remaining non-hydrogen atoms included in the calculations were positioned from subsequent difference maps. Phenyl rings were refined as rigid groups (D_{6h} symmetry, C–C = 1.392 Å). The key atom in this structure, the oxygen atom of the μ-SO ligand, was found to be disordered over two sites. A more serious disorder problem was encountered with lattice-held solvent molecules of CH_2Cl_2 and diethyl ether. Similar problems were noted for the isomorphous structures of $Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-}dam)_2$ (dam = $Ph_2AsCH_2AsPh_2$)[24] and $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$[15] (**2a**). Four separate CH_2Cl_2 sites were identified, one of which is fully occupied or nearly so. The carbon atoms of two of the CH_2Cl_2 molecules were also located (C(3) and C(4)). Regions believed to be occupied by disordered diethyl ether molecules could not be satisfactorily modeled. Occupancy factors for the disordered μ-SO oxygen atoms and the CH_2Cl_2 solvate molecules were initially estimated from relative Fourier peak heights and were subsequently adjusted to give consistent thermal parameters. Occupancy factors for CH_2Cl_2 molecules are relative to that of the molecule containing Cl(3), Cl(4), and C(3), which was assumed to be a fully occupied site.

In the final stages of full-matrix least-squares refinement, the Pd, Cl, P, S, and carbon atoms C(1) and C(2) were refined with anisotropic thermal parameters, and atoms O(1), O(1′), C(3), and C(4) were refined with isotropic thermal parameters. The hydrogen atoms of the $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ complex were fixed in idealized positions (C(sp^2)–H = 0.97, C(sp^3)–H = 0.98 Å). Neutral-atom scattering factors and anomalous scattering corrections for Pd, Cl, P, and S were taken from ref 25. Parallel refinements were carried out in the enantiomorphic space groups $P4_1$ and $P4_3$, the latter giving slightly better agreement factors (R and R_w ratios of 1.006 and 1.007, respectively).

Final atomic coordinates and equivalent isotropic (U_{eq} = one-third of the trace of diagonalized **U**) or isotropic thermal parameters are given in Table III. Selected bond lengths and angles appear in Tables IV and V, respectively. Calculated hydrogen atom parameters, anisotropic thermal parameters, intraannular torsion angles, and measured and calculated structure factors (Tables SI–SIV) are included as supplementary material.

Results and Discussion

μ-S Complexes. Complex $Pd_2Cl_2(\mu\text{-}S)(dpm)_2$ (**2a**) was synthesized previously in up to 55% yield by treating $Pd_2Cl_2(dpm)_2$ (**1a**) with elemental sulfur or propylene sulfide.[15] As shown in the present work, use of H_2S generates **2a** and the corresponding bromide **2b** in almost quantitative yields, while the iodide **2c** is more conveniently prepared from **2a** via halide exchange. In the ^{1}H NMR spectra of **2a**–**2c** (Table I), the methylene resonances appear as AB doublets with additional coupling to four equivalent P atoms.[15]

Complex **1a** is seen to rapidly and quantitatively desulfurize H_2S, which is of key interest in the area of hydrodesulfurization,[2,26,27] and in this regard we found that solutions of

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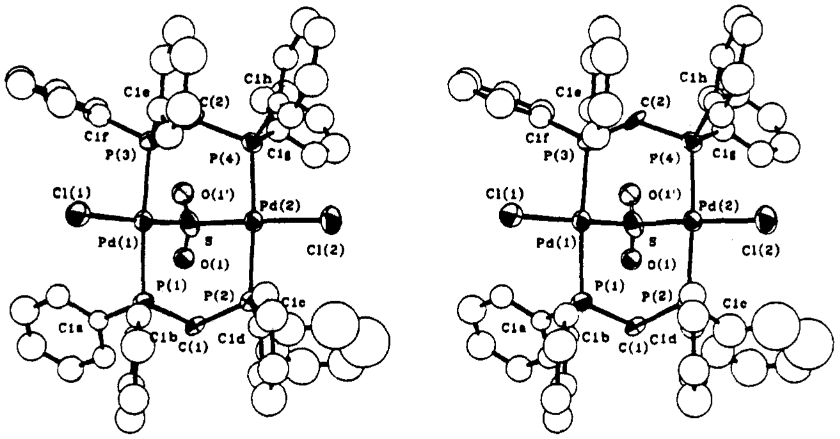


Figure 1. Stereoview of the $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ molecule (3). 50% probability thermal ellipsoids are shown. Both positions of the disordered μ-SO oxygen atoms are also shown.

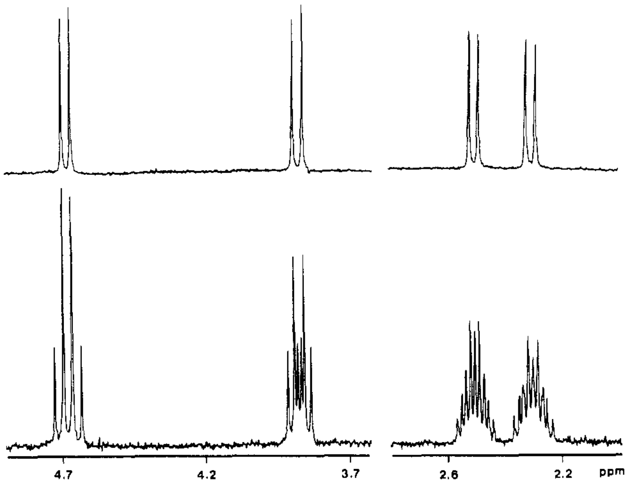


Figure 2. ^1H NMR spectrum of $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ (3) for the four methylene protons (CD_2Cl_2, 25 °C). Upper spectrum shows same region, with broad-band ^{31}P decoupling. The simulated spectra (data in Table I) are identical.

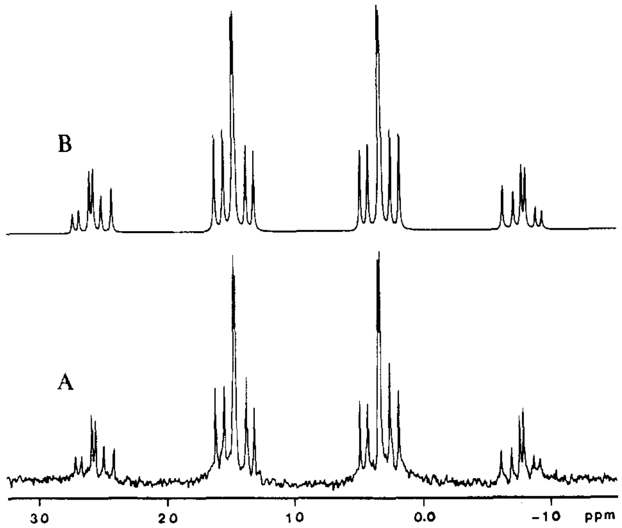
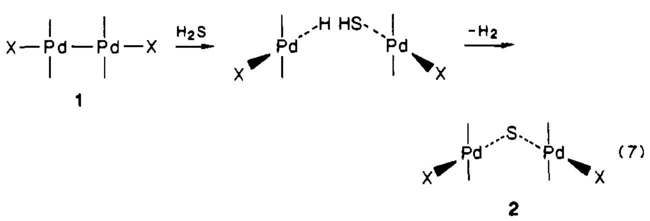


Figure 3. (A) $^{31}P\{^1H\}$ NMR spectrum of $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ (3). (B) Simulated spectrum (data in Table I).

1a up to 70 °C were unreactive toward EtSH, thiophene, and tetrahydrothiophene, and also the μ-S complex **2a** did not react with 1 atm of H_2 in refluxing benzene (i.e. reaction 1 is irreversible).

The mixed-ligand complex $Pd_2Cl_2(dpm)(dpmMe)$, of interest in immobilizing Pd_2 centers on polymers,[16] similarly reacts quantitatively with H_2S to form the μ-S species **4** (Table I). In principle, **4** can exist as two possible isomers with the sulfide bridge and methyl group on the same (syn) or opposite (anti) sides of the Pd–C–Pd plane; the ^1H NMR, however, reveals just four resonances for the methyl, methine, and inequivalent CH_2 protons, as in the precursor mixed-ligand complex,[16] and thus only one isomer is formed. The inequivalence of the trans P atoms rules out any virtual coupling, and the splitting patterns in the ^1H NMR are as expected.[16,28] The $^{31}P\{^1H\}$ NMR spectrum of **4** (and of the μ-SO derivatives **3** (cf. Figure 3) and **5**, Table I) is in accord with an AA'BB' system with large trans coupling.

The mechanistic aspects of the net sulfur abstraction from H_2S, reaction 1, have yet to be elucidated. Preliminary kinetic data on the conveniently studied bromide system, readily ascertained by UV/vis spectrophotometry by monitoring the loss of **1b** at an absorption maximum (425 nm),[7] reveal a first-order dependence on both Pd_2 and H_2S concentrations,[29] which implies direct attack by H_2S rather than SH^- (the latter also displaces the chloride ligands of **2a** to give **2d** (see below)). Oxidative-addition-type reactions for the $Pd_2X_2(dpm)_2$ complexes, in which the metal–metal bond acts as a nucleophile, are well substantiated,[30] and a process depicted in eq 7 seems plausible. The first stage involves



a net oxidative addition, and the second stage could be viewed as deprotonation of the coordinated SH^-, the proton then reacting with coordinated hydride to generate H_2; alternatively, the SH^- and/or H^- in the intermediate could bridge the palladium atoms. The reactivity trend (X = Cl > Br > I) is opposite to that normally encountered and expected, at least for oxidative addition of gas molecules to metal centers, where more basic ancillary ligands promote reaction,[31] although the reverse sequence has been observed in at least one reaction series that involved addition of substituted aryl iodides to Vaska's complex.[32] Within **1**, the metal–metal bond strength is expected to increase in the order

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I < Br < Cl[18] (i.e. the reverse of the trans effects of the halides[33]), and thus the H_2S reactivity trend also is not dominated by differences in the Pd–Pd bond strength.

Akin to the steps suggested in (7), a recent communication[34] describing addition of H_2S to $Pt_3(\mu_3\text{-CO})(\mu\text{-dpm})_3^{2+}$, presents evidence for an intermediate containing a $HPt_3(\mu_3\text{-SH})$ moiety (with a terminal hydride), deprotonation then yielding the isolated product $Pt_3H(\mu_3\text{-S})(\mu\text{-dpm})_3^+$. The liberated proton in this case does not generate H_2, which likely reflects the stronger Pt–H bond compared to the postulated Pd–H bond in reaction 7. The platinum work modeled certain features of the reaction of H_2S with a Pt(111) surface, which, however, yields H_2 as well as a sulfide coat containing $Pt_3(\mu_3\text{-S})$ units.[35]

We do not believe that the methylene protons of the coordinated dpm ligand play any role in these H_2S reactions. The CH_2 group can be deprotonated, but this requires strong bases;[16,30] we have found that $Pd_2Cl_2(dpm)_2$ in CD_2Cl_2/CD_3OD undergoes H/D exchange at the methylene protons (monitored by ^1H NMR), but the exchange at 20 °C is extremely slow ($t_{1/2} \sim 100$ h).

The formation of the sulfur bridge within $Pd_2(SH)_2(\mu\text{-S})(dpm)_2$ (**2d**) in high yield when made from **1a** by treatment with NaSH, or H_2S/Et_3N, could proceed via (i) elimination of H_2S from terminally bound SH^- at each Pd or via (ii) a bridged SH^- group with subsequent proton loss as considered above (H_2S would then be generated from free SH^-). There is ample precedence for bridge sulfide formation from two terminal SH^- ligands[36] (and see below). Formation of **2d** from the monomer $PdCl_2(dpm)$ in 40–50% yield, as described in the Experimental Section, clearly requires basic conditions (H_2S/Et_3N or SH^- as reagent), and must proceed via H_2S elimination from two monomeric Pd–SH moieties. Products from reaction of monomeric Pd complexes with H_2S (sometimes under basic conditions) are more typically monomers with terminal SH^- ligands,[37–41] but trinuclear, μ-S species have been isolated.[38,42] Of note, reaction of $PdCl_2(dpe)$, where dpe = 1,2-bis(diphenylphosphino)ethane, readily forms $Pd(SH)_2(dpe)$;[39,40] presumably the tendency of dpm to bridge[30] promotes formation of $Pd_2(SH)_2(\mu\text{-S})(dpm)_2$ via the nondetected $Pd(SH)_2(dpm)$.

The ^1H NMR spectrum of **2d** (Table I) reveals the coordinated, terminal SH ligands at δ −1.60 with coupling to the four P atoms. The same complex can be obtained also from $Pd_2Cl_2(\mu\text{-S})(dpm)_2$ by ligand exchange with NaSH. It should be noted that an attempted measurement of the ^1H NMR spectrum of **2d** in some $CDCl_3$ samples revealed decomposition of the species into $Pd_2Cl_2(\mu\text{-S})(dpm)_2$ and a species considered to be $Pd_2Cl(SH)(\mu\text{-S})(dpm)_2$; the latter complex has not been isolated, but the ^1H NMR (Table I, footnote d) reveals CH_2 resonances typical of those for a μ-S species and a triplet at δ −1.40 attributable to a single terminal SH ligand. The decomposition results from the presence of acid, presumably HCl, in some vials of $CDCl_3$, because H_2S (δ 0.80 s) is generated also.

Of interest, some allylcyclopentadienylpalladium monomers react with H_2S at −78 °C to generate dimeric allyls containing bridged SH^- ligands with loss of cyclopentadiene; at −60 °C, hydrogen transfer from the μ-SH ligands leads to the formation of olefin and "PdS".[43] In this overall reaction, exemplied in eq 8, the H_2 of the H_2S is consumed in hydrogenation of ancillary

$$PdCp(\eta^3\text{-}C_3H_5) \xrightarrow[-C_5H_6]{H_2S} {}^1/_2[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-SH})_2] \xrightarrow{-C_3H_6} PdS \qquad (8)$$

ligands rather than being liberated as in our Pd_2 systems, but mechanistic similarities via hydrido(mercapto) intermediates (cf. eq 7) are readily envisaged.

Oxygenation of the μ-S Complexes, and the μ-SO Derivatives. The μ-S complexes **2a–c** and **4** are readily oxygenated at the bridging sulfur by using H_2O_2 or *m*-chloroperbenzoic acid. Use of aqueous H_2O_2 in excess at 20 °C generates only μ-SO species (e.g. **3** and **5**) with no further oxygen incorporation—this is true for the present work and the literature reports on a $Fe_3(\mu_3\text{-S})$ moiety;[44] more generally, for the production of μ-SO species from μ-S precursors (see below), other oxidants have been used stoichiometrically, sometimes at low temperatures. The perbenzoic acid even at low temperatures can readily oxidize the $Pd_2(\mu\text{-S})$ moieties through to the μ-SO_2 derivative, and indeed Balch et al.[15] had failed to detect the plausible μ-SO intermediate during such an oxidation. Further, in order to get effective regeneration of, for example, **1a** from **2a** via the μ-SO_2 complex (for potential use in catalysis), we found it necessary to destroy excess peracid with hydrazine at low temperature, because at room temperature the oxidant reacts with the "μ-SO_2 system" to give some $PdCl_2(dpm)$ as well as several unidentified species. This process likely involves equilibrium 9,[15] because it is known that **1a** is readily oxidized.

$$Pd_2(\mu\text{-}SO_2) \rightleftharpoons \underset{\mathbf{1a}}{Pd_2} + SO_2 \qquad (9)$$

For example, even at −50 °C, the perbenzoic acid reacts rapidly with **1a** to give the μ-oxo derivative, but this decomposes at ambient conditions.[28] The problem involved in regenerating **1a** from **2a** via oxidation is resolved by protecting **1a** as the μ-SO_2 species by shifting equilibrium 9 to the left by use of low temperatures. The alternative procedure of performing room-temperature oxidation of the μ-S complex under 1 atm SO_2 can be used, but the oxidant is simultaneously consumed by the SO_2; e.g., a stoichiometric oxidation with the peracid under these conditions gave about a 50% conversion to the μ-SO derivative. The solution regeneration of **1a** from **2a** via the μ-SO_2 species had been alluded to by Balch et al.,[15] but we considered it worthwhile to establish a procedure to recover **1a** as a solid to reveal the quantitative aspects of the various conversions. There seems little doubt that a two-stage process effecting catalysis of reaction 10 could be realized:

$$H_2S + 2\text{"O"} \rightarrow H_2 + SO_2 \qquad (10)$$

The μ-SO complexes **3** and **5** are particularly novel because they contain pyramidal S, the first time such geometry has been documented within a dimetallic sulfoxide. The crystal structure of $Pd_2Cl_2(\mu\text{-SO})(dpm)_2$ consists of well-separated molecules of **3**, CH_2Cl_2, and Et_2O. The A-frame structure of **3** (Figure 1) is very similar to those determined for $Pd_2Cl_2(\mu\text{-S})(dpm)_2$ (**2a**) and $Pd_2Cl_2(\mu\text{-SO}_2)(dpm)_2$,[15] the former being isomorphous with **3**. Common features of the three molecules include boat conformations for the six-membered Pd_2P_2CS chelate rings and tetrahedral distortion of the square-planar coordination geometry at each metal center. Ligand atoms lie alternately above and below the mean coordination plane, being displaced 0.14 Å at Pd(1) and 0.10 Å at Pd(2). The angle between normals to the PdP_2ClS mean planes is 79.6°, and the Pd···Pd distance is 3.225 (4) Å. The mean Pd–S distance (2.273 (5) Å) lies between the corresponding values

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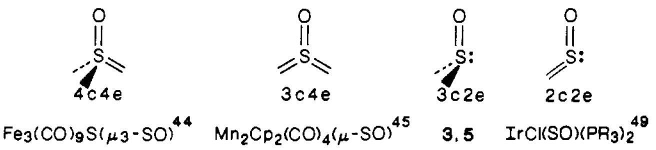
of 2.238 (4) and 2.298 (1) Å observed respectively for the μ-SO_2 and μ-S complexes,[15] while the mean Pd–P distance (2.337 (7) Å) is also intermediate between the values for the μ-SO_2 and μ-S analogues (2.351 (8) and 2.316 (13) Å, respectively). The mean Pd–Cl distance (2.402 (9) Å) is slightly longer than those of the μ-SO_2 and μ-S complexes (2.381 (1) and 2.372 (12) Å, respectively).

The bridgehead Pd–S–Pd angle of 90.4 (3)° is essentially the same as that in the μ-S structure (90.3 (2)°) but is smaller than the values of 98.4 (4)° and 91.9 (4)° given for the two crystallographically independent molecules of the μ-SO_2 compound. Of major interest, however, the sulfur atom within **3** is sp^3 hybridized, the coordination being pyramidal with a mean bond angle of 109.9° at S. In $[MnCp(CO)_2]_2(\mu\text{-}SO)$, the only other μ_2-SO compound that has been structurally characterized,[45] the sulfur atom has a trigonal planar, sp^2-hybridized, geometry, and the μ-SO ligand is thus considered to act as a 4-electron donor. The pyramidal geometry within **3** implies that here μ-SO acts as a 2-electron donor. Consistent with the differences in geometry, where the S–O bond will have more double bond character in the sp^2-hybridized system, ν(SO) is found at higher wavenumbers for the Mn system[45] (1037 vs. 985 cm^{-1}). The disordered oxygen atom in **3** gives considerable uncertainty in the mean S–O distance of 1.40 (6) Å. The S–O distances in the Mn system and in $Pd_2Cl_2(\mu\text{-}SO_2)(dpm)$, which has four IR bands in the 1028–1165-cm^{-1} ν(SO) region,[15] are 1.504 (4) and 1.47 (2) Å, respectively.

Of interest, the Mn complex was stated[45] to exist in an isomeric form containing a 2-electron donor μ-SO moiety: the μ-SO of the structurally characterized isomer was derived by thermolysis of thiirane S-oxide, while the previously synthesized isomer (not structurally characterized) had been made via air oxidation of $[MnCp(CO)_2]_2(\mu\text{-}S)$.[46] However, the two "isomers" give essentially the same IR data in the ν(SO) region (1037[45] and 1045 cm^{-1} [46]), and the only evidence that we can discern is differences in IR relative intensities in the ν(CO) region, which we consider to be inconclusive.

To our knowledge, the Pd and Mn bridged-SO complexes are the only structurally characterized "dimetallic sulfoxides", and they clearly represent two markedly different types of μ-SO bonding modes.

It should be noted that the $Pd_2X_2(\mu\text{-}S)(dpm)_2$ complexes and the mixed diphosphine analogue **4** are quite stable in solution toward O_2, and the only reported examples of O_2 oxidation of coordinated sulfur to sulfoxide appears to be with $[MnCp(CO)_2]_2(\mu\text{-}S)$ (as noted above)[46] and $Mn(\eta^5\text{-}C_5Me_5)(CO)_2(S_2)$.[47] Such oxidations have more generally utilized H_2O_2[44] or *m*-chloroperbenzoic acid[21,48] (as in the present work) or IO_4^- [22], where a range of sulfur-bound sulfur-oxygen moieties (for example μ_3-SO, μ_2-SO, η^2-S_2O, η^2-S_2O_2, and η^1-SO) has been identified. Sulfoxide complexes have been synthesized also via thermolabile molecules such as thiirane *S*-oxide[45,49,50] or epithiostilbene *S*-oxide,[51] the products containing either η^2-S_2O_2, η^1-SO, or μ_2-SO fragments. In *all* of the reported SO complexes,[21,22,44–46,48,49,51] *except* the $Pd_2(\mu\text{-}SO)$ complexes **3** and **5** described in the present work, ν(SO) is found in the 1020–1107-cm^{-1} range, which indicates double-bond character. The recorded S–O bond lengths within SO[44,45,49] or S_2O_2[22] metal complexes are in the range 1.213–1.504 Å, although there is considerable uncertainty in some of these; for example, the quoted 1.213 (19) and 1.438 (14) Å values for the S–O distances within $Ir(dpe)_2(\eta^2\text{-}S_2O_2)^+$ are said to become 1.355 and 1.501 Å after correction for thermal librations.[22] The bond length in free SO, as determined by microwave spectroscopy, is 1.48 Å.[52] It appears at this stage that for the various bonding modes of the SO fragment, a ν(SO) value below 1000 cm^{-1} (as for **3** and **5**) is a sufficient criterion for a 3c2e system, e.g.:



The ¹H NMR spectrum of the μ-SO complex **3** (Table I) is much more complicated than that of the precursor μ-S species **2a**, because the four CH_2 protons, as well as the four P atoms, are now inequivalent (Table I, Figure 2); furthermore, two of the protons are coupled only to the adjacent P atoms, while the other two are coupled also to the remote P atoms via long-range effects. The μ-SO of the mixed ligand complex (**5**) reveals eight resonances for the aliphatic protons, indicating the presence of two stereoisomers formed from **4**, which itself is either a syn or anti isomer (see above). These further isomers must result from differences in the orientation of the oxygen atom attached to the sulfur; this requires the S atom to be sp^3 hybridized (pyramidal), as in the structurally characterized complex **3**. The NMR integrations reveal an isomer ratio of 7:3. The resonances for the isomers are readily assigned (Table I), with again one of the two methylene protons showing coupling to remote P nuclei (as in **3**).

Worth noting also is that the stepwise conversions from the precursor dimers (**1**) to the μ-S, μ-SO, and μ-SO_2 species, and subsequent regeneration of **1** via SO_2 loss, are readily monitored by solution electronic spectroscopy (as noted by Balch et al.,[15] but without access to the μ-SO species). Species such as **1** are reddish orange; e.g., **1a** (CH_2Cl_2) shows λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) at 416 (7550), 347 (16 000), and 293 (25 900).[7,18] The μ-S complexes are brown and have absorption maxima in the 485–470-, 350–325-, and 280-nm regions;[15] e.g., the new complex **4** (CH_2Cl_2) shows λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) at 483 (1000), 327 (20 460), and 278 (36 900). The μ-SO complexes are orange; e.g., **5** (CH_2Cl_2) shows λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) at 440 (14 450), 389 (5780), 310 sh (20 700), and 263 (31 120). The μ-SO_2 species are violet and are characterized by a band in the 510–530-nm region (ϵ ~ 8000 M^{-1} cm^{-1}).[15] Finally, the binding energy of the S $2p_{3/2}$ state in $Pd_2Cl_2(\mu\text{-}SO)(dpm)_2$ as determined by ESCA[53] is, as expected, intermediate between the values reported by Balch's group for the μ-S and μ-SO_2 species.[54]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Morgantown Energy Technology Center, U.S. Department of Energy, for financial support, Professor J. Trotter for use of crystallographic facilities, and Johnson Matthey Ltd. for loan of the palladium. C.-L.L. thanks the Izaak Killam Foundation for a postdoctoral fellowship, administered by the University of British Columbia.

Supplementary Material Available: Table SI–SIII, listing derived hydrogen positions and isotropic thermal parameters, anisotropic thermal parameters, and intraannular torsion angles (3 pages); Table SIV, listing measured and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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