

# Synthesis and Vibrational Spectra of New Bis(alkoxysulfane)-dichloropalladium(II) Complexes and X-Ray Structural Analysis of $[\text{PdCl}_2\{\text{S}(\text{OPr}^i)_2\}_2]^\dagger$

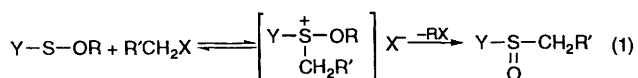
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Reactions of  $\text{L} = (\text{Pr}^i\text{O})_2\text{S}$ ,  $(\text{Pr}^n\text{O})_2\text{S}$ ,  $(\text{MeO})(\text{C}_4\text{H}_8\text{NO})\text{S}$  ( $\text{C}_4\text{H}_8\text{NO} = \text{morpholino}$ ),  $(\text{MeO})(\text{C}_5\text{H}_{10}\text{N})\text{S}$  ( $\text{C}_5\text{H}_{10}\text{N} = \text{piperidino}$ ) or  $(\text{MeO})\text{PhS}$  with  $[\text{PdCl}_2(\text{NCPh})_2]$  in toluene gave five complexes of type  $[\text{PdCl}_2\text{L}_2]$  (yields 40–79%). An X-ray structural analysis of the air-stable, monoclinic crystals of  $[\text{PdCl}_2\{\text{S}(\text{OPr}^i)_2\}_2]$  showed the sulfur atoms to be *cis*-planar co-ordinated. The two co-ordinated dialkoxysulfane ligands are rotational isomers with differing SO torsional angles (+79 and 84° for ligand 1, -106 and +82° for 2). The S–O bond lengths are in the range 1.586–1.611 Å. The infrared and Raman spectra of the five  $[\text{PdCl}_2\text{L}_2]$  complexes demonstrate that the rule of mutual exclusion is not obeyed, indicating a *cis* rather than a *trans* co-ordination in each case.

Alkoxysulfanes  $\text{RO-S-Y}$  ( $\text{Y} = \text{alkoxy}$ ,  $\text{NR}'_2$ ,  $\text{Ph}$ , etc.) may be prepared by a variety of methods.<sup>1–4</sup> These compounds are useful building blocks to synthesize organic sulfinates  $\text{R}'\text{S}(\text{O})\text{OR}$ , sulfinamides  $\text{R}'\text{S}(\text{O})\text{NR}'_2$  and asymmetrical sulfoxides  $\text{RS}(\text{O})\text{R}'$  by means of the thio-Arbuzov reaction<sup>3,5</sup> (1)



( $\text{R} = \text{alkyl}$ ;  $\text{X} = \text{I}$  or  $\text{Br}$ ;  $\text{R}' = \text{H}$ ,  $\text{Me}$ , allyl, etc.). The sulfonium-type intermediate postulated for reaction (1) indicates that alkoxysulfanes show S-donor properties which is confirmed by their function as ligands in transition-metal complexes<sup>6</sup> (see below). Structural information on alkoxysulfanes has become available only recently. The structure of dimethoxysulfane  $(\text{MeO})_2\text{S}$  has been elucidated both in the vapour phase by electron diffraction<sup>7</sup> and in the solid state by X-ray diffraction at low temperatures.<sup>8</sup> In both phases the  $(\text{MeO})_2\text{S}$  molecules are of  $\text{C}_2$  symmetry. The same symmetry was found by *ab-initio* molecular orbital (MO) calculations<sup>9</sup> for the most stable conformer of the related sulfoxylic acid  $(\text{HO})_2\text{S}$  which has not been prepared yet. Photoelectron spectra<sup>10</sup> of  $(\text{MeO})_2\text{S}$  yielded an ionization potential of only 8.8 eV, almost the same as that measured for  $\text{Me}_2\text{S}$  (8.7 eV)<sup>11</sup> and *ca.* 0.7 eV less than found for the related disulfane  $(\text{MeO})_2\text{S}_2$ . Therefore,  $(\text{MeO})_2\text{S}$  and similar dialkoxysulfanes should exhibit good donor properties. The highest occupied molecular orbital (HOMO) of  $(\text{MeO})_2\text{S}$  is basically identical with the sulfur 3p orbital which is perpendicular to the OSO plane. Accurate X-ray diffraction data on crystalline  $(\text{MeO})_2\text{S}$  have made it possible to determine the electron-density distribution of this molecule;<sup>8</sup> the derived deformation density (change of density on molecule formation) shows the shape of the sulfur-centred lone pair occupying the HOMO.

The S-donor properties of dialkoxysulfanes manifest them-

selves most convincingly in reactions with palladium(II) and platinum(II) halides or halogeno complexes. On reaction of diisopropoxysulfane with  $\text{PdCl}_2$ ,  $[\text{NH}_4]_2[\text{PdX}_4]$ ,  $[\text{NH}_4]_2[\text{PtX}_4]$  or  $[\text{PdX}_2(\text{NCPh})_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) the stable compounds  $[\text{PdX}_2\{\text{S}(\text{OPr}^i)_2\}_2]$  and  $[\text{PtX}_2\{\text{S}(\text{OPr}^i)_2\}_2]$ , respectively, were obtained.<sup>6</sup> In this work we report on the first structural characterization of a complex containing dialkoxysulfane ligands and on the synthesis, vibrational and NMR spectra of new palladium(II) complexes using  $(\text{Pr}^n\text{O})_2\text{S}$ ,  $(\text{MeO})\text{PhS}$ ,  $(\text{MeO})(\text{C}_4\text{H}_8\text{NO})\text{S}$  ( $\text{C}_4\text{H}_8\text{NO} = \text{morpholino}$ ) and  $(\text{MeO})(\text{C}_5\text{H}_{10}\text{N})\text{S}$  ( $\text{C}_5\text{H}_{10}\text{N} = \text{piperidino}$ ) as ligands.

## Experimental

The starting materials were prepared by the following published methods:  $[\text{PdCl}_2(\text{NCPh})_2]$ ,<sup>12</sup>  $(\text{Pr}^i\text{O})_2\text{S}$ ,<sup>1</sup>  $(\text{Pr}^n\text{O})_2\text{S}$ ,<sup>1</sup>  $(\text{MeO})(\text{C}_4\text{H}_8\text{NO})\text{S}$ ,<sup>2</sup>  $(\text{MeO})(\text{C}_5\text{H}_{10}\text{N})\text{S}$ <sup>2</sup> and  $(\text{MeO})\text{PhS}$ .<sup>3,4</sup> Complexes 1–5 (see Table 1) were obtained as follows. Toluene was dried (Na, benzophenone) and distilled, and all following operations were carried out under an atmosphere of argon using Schlenk tubes (100 cm<sup>3</sup>). To  $[\text{PdCl}_2(\text{NCPh})_2]$  (2.61 mmol), dissolved in toluene (30 cm<sup>3</sup>) was added dropwise a solution of the sulfane (5.22 mmol) dissolved in toluene (10 cm<sup>3</sup>). After stirring for 12 h at 20 °C, complex formation was observable by the colour change to orange. The volume of the solution was reduced to 15 cm<sup>3</sup> whereupon 3 and 5 crystallized, while 1, 2 and 4 required the addition of hexane to initiate precipitation. The solids were filtered off, washed with cold hexane and dried in a vacuum.

Proton NMR spectra were measured with a Bruker AM300 spectrometer (samples dissolved in deuterated benzene), Raman spectra of the free ligands with an Instruments S.A. spectrometer which is based on a Jobin Yvon U1000 double monochromator and controlled by a MAC80 computer (resolution and accuracy 1 cm<sup>-1</sup>). Raman scattering was excited with a Spectra Physics krypton-ion laser (647.1 nm) and measured by a Hamamatsu R943-02 GaAs photomultiplier. To prevent thermal or photolytic decomposition, the Raman samples were cooled using a self-made cryostat in which the vapour of boiling liquid nitrogen was used as a coolant, controlled by a Pt100 temperature sensor which was contained in a glass capillary

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV  $\approx 1.60 \times 10^{-19}$  J.

inside a glass Dewar vessel. Raman spectra of the palladium complexes 1–5 were obtained with a Bruker FT-IR-IFS66-spectrometer, equipped with FRA106 Raman module and Nd:YAG laser (100 mW). From 100 to 200 spectra for each were accumulated (resolution 4 cm<sup>-1</sup>). Infrared spectra of 1–5 (Nujol mulls supported by CsI discs) were recorded with a Nicolet FT-IR Magna 750 spectrometer (observed range 145–800 cm<sup>-1</sup>).

**Crystallography.**—Single crystals of complex 1, obtained from toluene–hexane solution, were sealed in nitrogen-filled capillaries for the X-ray diffraction analysis.

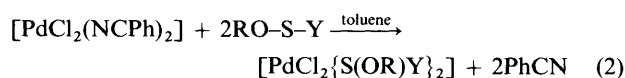
**Crystal data.** [PdCl<sub>2</sub>{S(OPr<sup>i</sup>)<sub>2</sub>}<sub>2</sub>], *M* = 477.81, monoclinic space group *P*2<sub>1</sub>/*c*, *a* = 10.147(4), *b* = 14.265(4), *c* = 14.636(7) Å, β = 96.51(3)°, *U* = 2104.73 Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 21 automatically centred reflections), λ = 0.710 69 Å, *Z* = 4, *D*<sub>c</sub> = 1.5078 g cm<sup>-3</sup>, *F*(000) = 976. Deep yellow, air- and moisture-sensitive crystals. Crystal dimensions (from face to face): 0.4 × 0.4 × 0.3 mm, μ(Mo-Kα) = 1.33 mm<sup>-1</sup>.

**Data collection and processing.** <sup>13</sup>Syntex P2<sub>1</sub> diffractometer, ω scan with θ<sub>max</sub> = 30°, Mo-Kα radiation (λ = 0.710 69 Å); 5342 reflections measured (0 ≤ *h* ≤ 13, 0 ≤ *k* ≤ 18, -19 ≤ *l* ≤ 18), 4338 independent (*R*<sub>int</sub> = 0.0188), 3178 observed with *I* ≥ 2σ(*I*). Intensities were monitored with three check reflections every 100, σ(*F*<sub>o</sub>) < 4%.

**Structure analysis and refinement.** Heavy atom method (found Pd and one Cl atom) followed by repeated Fourier-difference synthesis. Empirical absorption correction<sup>14</sup> (minimum, maximum: 0.985, 1.004) after isotropic full-matrix least-squares refinement of all non-hydrogen atoms. Anisotropic full-matrix least-squares refinement for all non-hydrogen atoms (remaining electron density minimum, maximum: -0.7387, 0.7303 e Å<sup>-3</sup>), hydrogens in calculated positions (assumed C–H 108 pm, thermal parameters refined). Final *R* = 0.0562 by using unit weights for 242 parameters refined. Programs and computers used and source of atom scattering factors are given in ref. 13.

## Results and Discussion

**Synthesis.**—Bis(benzonitrile)dichloropalladium(II) reacts under mild conditions with stoichiometric amounts of various alkoxy sulfanes RO–S–Y with ligand exchange to give the corresponding bis(alkoxy sulfane) complexes according to equation (2). It is remarkable that this reaction proceeds in high yield regardless of the nature of Y which may be an alkoxy, morpholino, piperidino, or phenyl group (isolated yields 40–79%, see Table 1). While the bis(diisopropoxy sulfane) complex 1 has been prepared before,<sup>6</sup> the other four 2–5 are new. Complexes 1, 2 and 5 decompose only very slowly on standing in air, but 3 and 4 should be stored under argon at 4 °C with exclusion of light. The solubility of 3 and 4 in ordinary organic solvents is poor; 1, 2 and 5 are soluble in acetone and benzene. Complexes 3–5 are the first known with monoalkoxy sulfane ligands.



	R	Y
1	Pr <sup>i</sup>	Pr <sup>i</sup>
2	Pr <sup>n</sup>	Pr <sup>n</sup>
3	Me	C <sub>4</sub> H <sub>8</sub> NO
4	Me	C <sub>5</sub> H <sub>10</sub> N
5	Me	Ph

**Structure.**—Earlier vibrational spectroscopic investigations of [PdX<sub>2</sub>{S(OPr<sup>i</sup>)<sub>2</sub>}<sub>2</sub>] with X = Cl or Br had indicated that the two sulfane ligands are in *cis* position to each other.<sup>6</sup> To confirm this result and to study the impact of complex formation on the bond lengths and angles of the ligands we have carried out a single-crystal X-ray diffraction analysis of [PdCl<sub>2</sub>{S(OPr<sup>i</sup>)<sub>2</sub>}<sub>2</sub>] 1 at 21 °C.

The monoclinic crystals of complex 1 contain four molecules of C<sub>1</sub> symmetry in the unit cell. The co-ordination of the metal atom is approximately square planar (Fig. 1). As expected, ligands of the same type are in *cis* position. The dialkoxy sulfane ligands are co-ordinated *via* the sulfur atoms which thus acquire a pyramidal surrounding. Atomic co-ordinates, internuclear distances and valence angles are given in Tables 2 and 3. The angle Cl(1)–Pd–Cl(2) of 92 °C is close to the ideal value for square-planar co-ordination (90°), while the opposite angle S(1)–Pd–S(2) of 102° seems to be the result of steric hindrance of the bulky alkyl groups. As a consequence, the two S–Pd–Cl angles (82 and 84°) are forced to be considerably smaller than the ideal value. The degree of planarity in the co-ordination

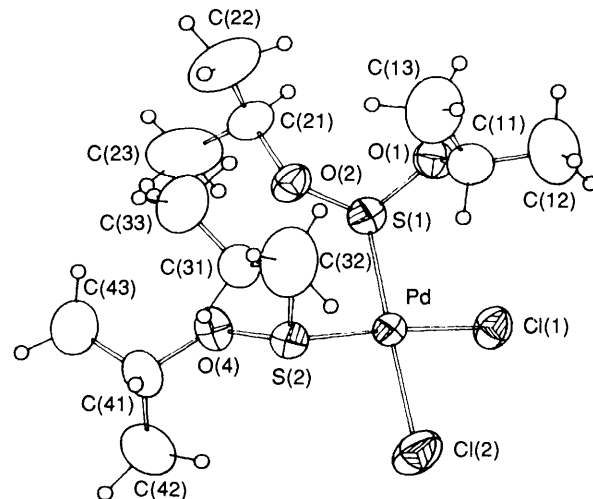


Fig. 1 Molecular structure of [PdCl<sub>2</sub>{S(OPr<sup>i</sup>)<sub>2</sub>}<sub>2</sub>] and numbering of atoms; O(3) is located behind C(32)

Table 1 Properties and analytical data of the palladium(II) complexes 1–5

Compound	Colour	<i>M</i> (calc.)	Yield (%)	Analysis (%) <sup>*</sup>				
				C	H	N	S	Cl
1 [PdCl <sub>2</sub> {S(OPr <sup>i</sup> ) <sub>2</sub> } <sub>2</sub> ]	Lemon yellow	477.8	40	30.95 (30.15)	5.95 (5.90)	—	13.05 (13.40)	14.85 (14.85)
2 [PdCl <sub>2</sub> {S(OPr <sup>n</sup> ) <sub>2</sub> } <sub>2</sub> ]	Pale yellow	477.8	72	31.05 (30.15)	5.90 (5.90)	—	13.40 (13.40)	15.15 (14.85)
3 [PdCl <sub>2</sub> {S(NOC <sub>4</sub> H <sub>8</sub> )OMe} <sub>2</sub> ]	Brown	475.7	79	25.30 (25.25)	4.55 (4.65)	6.00 (5.90)	13.75 (13.50)	14.90 (14.90)
4 [PdCl <sub>2</sub> {S(NC <sub>5</sub> H <sub>10</sub> )OMe} <sub>2</sub> ]	Pale brown	471.8	46	30.55 (30.55)	5.55 (5.55)	6.05 (5.95)	13.90 (13.60)	14.95 (15.05)
5 [PdCl <sub>2</sub> {SPh(OMe) <sub>2</sub> } <sub>2</sub> ]	Orange	457.7	67	37.50 (36.75)	3.50 (3.50)	—	14.10 (14.00)	15.65 (15.50)

<sup>\*</sup> Calculated values in parentheses.

**Table 2** Fractional atomic coordinates for  $[\text{PdCl}_2\{\text{S}(\text{OPr}^i)_2\}_2]$  with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Pd	0.136 90(6)	0.170 89(4)	0.241 97(4)
Cl(1)	0.140 8(2)	0.332 5(2)	0.256 5(2)
Cl(2)	-0.084 0(3)	0.163 3(2)	0.267 7(3)
S(1)	0.355 6(2)	0.192 6(1)	0.230 2(1)
S(2)	0.120 3(2)	0.014 2(1)	0.234 0(1)
O(1)	0.371 8(6)	0.245 4(5)	0.136 8(4)
O(2)	0.417 8(6)	0.091 8(4)	0.217 5(4)
O(3)	0.182 1(6)	-0.014 2(4)	0.142 7(4)
O(4)	0.228 5(6)	-0.019 7(4)	0.316 5(4)
C(11)	0.281(1)	0.227 4(9)	0.052 9(7)
C(12)	0.256(2)	0.320(1)	0.010 3(9)
C(13)	0.337(2)	0.157(1)	-0.006(1)
C(21)	0.563 9(9)	0.086 1(8)	0.238 6(7)
C(22)	0.612(1)	0.023(1)	0.169(1)
C(23)	0.595(1)	0.051(2)	0.332(1)
C(31)	0.162(1)	-0.114 4(7)	0.112 6(7)
C(32)	0.081(2)	-0.115(1)	0.022(1)
C(33)	0.297(1)	-0.156(1)	0.117(1)
C(41)	0.194(1)	-0.104 9(7)	0.366 3(7)
C(42)	0.113(1)	-0.079(1)	0.440 2(9)
C(43)	0.324(1)	-0.149(1)	0.401(1)

sphere of the palladium atom can be seen from the angles of various bonds with the mean planes through the other atoms. For instance, the angle between the bond Pd-S(1) and the plane defined by Pd, Cl(1), Cl(2) and S(2) is only 4°. All other bonds originating from the Pd atom form angles of 1° or less with this plane.

The two dialkoxysulfane ligands are not equivalent as can be seen from the two Pd-S distances [2.266(2) at S(1) and 2.244(2) Å at S(2)] which differ by as much as 0.02 Å whereas the two Pd-Cl bonds are of equal length [2.316(3) Å]. Three of the S-O internuclear distances are equal within the limits of error: 1.589(6) Å; the distance S(2)-O(4) amounts to 1.611(6) Å, obviously as a result of the differing S-O torsional angle (see below). The S-O bond distance of free (Pr<sup>i</sup>O)<sub>2</sub>S is not known but in (MeO)<sub>2</sub>S the S-O bonds are 1.625 (vapour)<sup>7</sup> and 1.621 Å (solid),<sup>8</sup> respectively. The C-O bond lengths are also considerably affected by the co-ordination. In complex **1** they are found in the range 1.47(1)-1.50(1) Å while in (MeO)<sub>2</sub>S 1.426 (vapour)<sup>7</sup> and 1.444 Å (solid)<sup>8</sup> have been observed. In contrast, the O-S-O angles are almost identical in **1** (104.3 and 104.7°) and in (MeO)<sub>2</sub>S (vapour, 103; solid, 104.8°).<sup>7,8</sup> The same holds for three of the four C-O-S angles of **1** which are in the narrow range 115.2(6)-115.8(6)° compared to 115.9 and 115.8° in gaseous and solid (MeO)<sub>2</sub>S. However, the fourth angle [C(11)-O(1)-S(1)] is 121.3(6)°. For this high value no intramolecular reason can be found. It therefore has to be assumed that packing effects are responsible. The angles Pd-S-O are larger at S(1) (106.9 and 109.2°) than at S(2) (102.7 and 105.2°).

An interesting structural parameter in compounds of divalent chalcogens is the torsion angle at the chalcogen-chalcogen bonds. In the present case the C-O-S-O dihedral angles are 78.5 and 83.5° at ligand **1** [containing S(1)] compared to 81.8° in solid (MeO)<sub>2</sub>S.<sup>8</sup> Ligand **1**, therefore, has a C-O-S-O-C backbone of approximate C<sub>2</sub> symmetry as does (MeO)<sub>2</sub>S. However, for ligand **2** the C-O-S(2)-O torsional angles are -105.5° and +82.3° which means that the two ligands represent two rotational isomers of diisopropoxysulfane. Ligand **2** has a C-O-S-O-C backbone of C<sub>1</sub> rather than C<sub>2</sub> symmetry [if the absolute value of the two torsional angles at S(2) were the same the symmetry would be C<sub>s</sub>]. This difference in symmetry may be the reason for the slightly differing Pd-S, S-O and C-O bond distances and Pd-S-O angles of the two dialkoxysulfane ligands. Selected torsional angles of **1** are given in Table 3. These data show that O(2) is practically located in the PdS<sub>2</sub>Cl<sub>2</sub> plane.

**Table 3** Bond lengths (Å), angles and torsion angles (°) for  $[\text{PdCl}_2\{\text{S}(\text{OPr}^i)_2\}_2]$  with e.s.d.s in parentheses

Pd-Cl(1)	2.315(2)	O(3)-C(31)	1.503(12)
Pd-Cl(2)	2.317(3)	O(4)-C(41)	1.480(12)
Pd-S(1)	2.266(2)	C(11)-C(12)	1.47(2)
Pd-S(2)	2.244(2)	C(11)-C(13)	1.48(2)
S(1)-O(1)	1.586(6)	C(21)-C(22)	1.48(2)
S(1)-O(2)	1.589(6)	C(21)-C(23)	1.46(2)
S(2)-O(3)	1.592(6)	C(31)-C(32)	1.48(2)
S(2)-O(4)	1.611(6)	C(31)-C(33)	1.486(18)
O(1)-C(11)	1.472(12)	C(41)-C(42)	1.477(18)
O(2)-C(21)	1.482(11)	C(41)-C(43)	1.496(18)
Cl(1)-Pd-Cl(2)	92.20(9)	S(2)-O(3)-C(31)	115.8(5)
Cl(1)-Pd-S(1)	82.20(8)	S(2)-O(4)-C(41)	115.8(6)
Cl(1)-Pd-S(2)	175.76(8)	O(1)-C(11)-C(12)	105.1(10)
Cl(2)-Pd-S(1)	172.87(11)	O(1)-C(11)-C(13)	111.2(10)
Cl(2)-Pd-S(2)	83.89(9)	C(12)-C(11)-C(13)	115.1(11)
S(1)-Pd-S(2)	101.56(8)	O(2)-C(21)-C(22)	106.9(9)
Pd-S(1)-O(1)	109.2(2)	O(2)-C(21)-C(23)	108.8(9)
Pd-S(1)-O(2)	106.9(2)	C(22)-C(21)-C(23)	112.3(14)
O(1)-S(1)-O(2)	104.3(3)	O(3)-C(31)-C(32)	108.1(9)
Pd-S(2)-O(3)	105.2(2)	O(3)-C(31)-C(33)	105.9(9)
Pd-S(2)-O(4)	102.7(2)	C(32)-C(31)-C(33)	116.8(11)
O(3)-S(2)-O(4)	104.7(3)	O(4)-C(41)-C(42)	109.6(9)
S(1)-O(1)-C(11)	121.3(6)	O(4)-C(41)-C(43)	104.9(9)
S(1)-O(2)-C(21)	115.2(6)	C(42)-C(41)-C(43)	113.6(10)
Cl(1)-Pd-S(1)-O(1)	-67.9(3)		
Cl(1)-Pd-S(1)-O(2)	179.8(2)		
S(2)-Pd-S(1)-O(1)	114.1(3)		
S(2)-Pd-S(1)-O(2)	1.8(3)		
Cl(2)-Pd-S(2)-O(3)	131.3(3)		
Cl(2)-Pd-S(2)-O(4)	-119.5(3)		
Pd-S(1)-O(1)-C(11)	-35.5(8)		
O(2)-S(1)-O(1)-C(11)	78.5(7)		
Pd-S(1)-O(2)-C(21)	-160.9(5)		
O(1)-S(1)-O(2)-C(21)	83.5(6)		
Pd-S(2)-O(3)-C(31)	-169.9(5)		
O(4)-S(2)-O(3)-C(31)	82.3(6)		
Pd-S(2)-O(4)-C(41)	144.8(5)		
O(3)-S(2)-O(4)-C(41)	-105.5(6)		

**Proton NMR Spectra.**—The two dichlorobis(dialkoxysulfane)palladium(II) complexes **1** and **2** were chosen for the NMR investigation because of their good solubility in deuteriated benzene and their simple <sup>1</sup>H NMR spectra. The co-ordination of the dialkoxysulfane molecules to the metal atom affects the electron-density distribution within the ligands and probably also their symmetry. Therefore, the spectra of the co-ordinated and free sulfanes differ both in the multiplicity of the signals and in their chemical shifts.

In the case of (Pr<sup>i</sup>O)<sub>2</sub>S the OCH<sub>2</sub> group of the free sulfane results in a triplet at δ 4.04, but in the spectrum of complex **2** a symmetrical multiplet of 12 narrow lines is observed at δ 3.98-4.29 representing the AB part of an ABXYZ<sub>3</sub> spin system. This multiplet consists of four signals for the AB system formed by the two diastereotopic hydrogen atoms. Chemical shift values can be calculated for H<sub>A</sub> (δ 4.02) and H<sub>B</sub> (δ 4.25) and a geminal coupling constant of <sup>2</sup>J = 9.65 Hz is determined. Each of the four signals is split into a triplet by vicinal coupling (<sup>3</sup>J = 6.6 Hz).

In the case of (Pr<sup>i</sup>O)<sub>2</sub>S the methyl groups of the free sulfane result in a doublet at δ 1.25, while the ligands of complex **1** give rise to two doublets at δ 1.10 and 1.19 (<sup>3</sup>J = 6.2 Hz). In solid **1** the two (RO)<sub>2</sub>S ligands are of different conformation, but we assume that in solution the rotation about the S-O bonds will not be seriously hindered making the two ligands equivalent on the NMR time-scale. The two doublets for the methyl groups of co-ordinated (Pr<sup>i</sup>O)<sub>2</sub>S may then be explained as a result of the new prochiral centre which is created by the Pd-S bond and which renders the methyl groups diastereotopic. The methine

**Table 4** Infrared and Raman spectral data ( $\text{cm}^{-1}$ ) for the solid palladium complexes **1–5** (ranges: IR 145–800  $\text{cm}^{-1}$ , Raman 50–800  $\text{cm}^{-1}$ ; sample temperature 20 °C; br = broad, sh = shoulder)

<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>		<b>5</b>	
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
	89w		97vw		85w		82w		
146m	152vs		154m		134m		111m		102s
	191vw		221(sh)	179w	154s	147w	148s	152w	152m
212w	215vs		238m	209m	185s	177m	176m	174w	181w
310vs	309(sh)			237m		204m		207m	212m
322vs	324vs	314vs(br)	310s	256w	236m	229m	222m	238w	253w
350vw	350vw	361w	318(sh)	301s	308vs	246w	243vw		291(sh)
402vw	404vw			363s		293m	301vs	311vs	308vs
424vw	425vw		381vw	408vw	409w	386m	385vw	343s	346w
456vw	461vw			456m	453w	449s	449vw	402m	363s
				478vw	480(sh)			447m	441w
479w	481vw			492w	492w	494s	493w	459w	458(sh)
501m	496vw	499m	502w					489s	
513w	514vw			590m	591w	544s	545w	501s	502w
				678s	681m	658s		593m	613w
722s	719w			696s	691(sh)	668s	673m	610w	613w
740(sh)	743w	720s	714w	721m		688vs	688(sh)	680s	694w
759vw	760w		785vw			721w		710w	706w
								731s	728m
								742w	
								760m	759vw

**Table 5** Vibrational spectral data ( $\text{cm}^{-1}$ ) for the free alkoxy-sulfane used in complexes **1**, **2** and **5** (sample temperatures given in parentheses; ranges recorded IR 350–800, Raman 100–800  $\text{cm}^{-1}$ )

$(\text{Pr}^i\text{O})_2\text{S}$		$(\text{Pr}^o\text{O})_2\text{S}$	$(\text{MeO})\text{PhS}$
IR (20 °C)	Raman (–100 °C)	Raman (–80 °C)	Raman (20 °C)
(liquid on KBr)	182s		193w
	270m	266m(br)	
	344m	297m(br)	317ms
	368w		
	434ms		
450w(br)	458w	470(sh)	
	473w	478m	
501w	507s		615w, $\nu(\text{CS})$
700w	734vs, $\nu(\text{SO})$	701s, $\nu(\text{SO})$	
740m	750s, $\nu(\text{SO})$	723vs, $\nu(\text{SO})$	725w, $\nu(\text{SO})$
		783ms	

hydrogen atom of free  $(\text{Pr}^i\text{O})_2\text{S}$  is observed as a septet at  $\delta$  4.13; on co-ordination the signal is shifted to lower field and occurs for **1** at  $\delta$  4.83.

**Infrared and Raman Spectra.**—The vibrational spectra of the five palladium complexes were measured in order to answer the question whether all have a *cis* co-ordination of the alkoxy-sulfane ligands. In this case the local symmetry at the metal centre would be  $C_{2v}$  and all fundamental vibrations will be infrared and Raman active. A *trans* co-ordination, on the other hand, would result in a local  $D_{2h}$  symmetry at the metal in which case the rule of mutual exclusion applies and fundamental vibrations can be only infrared or Raman active.

The vibrational spectra of various complexes of type  $[\text{PdCl}_2(\text{SR}_2)_2]^{15,16}$  show that the stretching and bending vibrations of the  $\text{PdCl}_2\text{S}_2$  framework can be expected below 400  $\text{cm}^{-1}$ . In Table 4 the infrared and Raman spectral data for **1–5** in the ranges 145–800 and 50–800  $\text{cm}^{-1}$ , respectively, are listed. It is seen that the rule of mutual exclusion is not obeyed since for each compound several signals are observed both in the infrared and Raman spectra at practically identical wavenumbers. We therefore conclude that compounds **2–5** have

the same *cis* co-ordination as found in the case of **1**. A full assignment of the vibrational spectra is not possible at present since it would require isotopic substitution experiments as well as a normal-coordinate analysis. However, a few specifications can be made. Comparison of the spectra of **1** with those of free diisopropoxy-sulfane (Table 5) shows that the Raman intensity of the SO stretching vibrations (719–760  $\text{cm}^{-1}$ ) dramatically decreases on complex formation. This may be due to the withdrawal of electron density which increases the hardness of the sulfur atom and leaves the SO bonding electrons less polarizable. In addition, the two SO stretching vibrations of  $(\text{Pr}^i\text{O})_2\text{S}$  result in *three* Raman lines for compound **1**, obviously as a result of the two different rotamers co-ordinated to the  $\text{PdCl}_2$  unit (see structural analysis). The spectra of **1** exhibit three signals in the region 300–370  $\text{cm}^{-1}$  which we assign to the four stretching modes of the  $\text{PdCl}_2\text{S}_2$  skeleton (assuming one incidental degeneracy). Similarly, complex **2** also exhibits only three signals in the 300–370  $\text{cm}^{-1}$  region for which there is no counterpart in the Raman spectrum of the free sulfane (Tables 4 and 5). The sharp decrease in the Raman intensity of the SO stretching mode of  $(\text{Pr}^o\text{O})_2\text{S}$  on co-ordination is also observed for **2** which exhibits only one weak signal (at 714  $\text{cm}^{-1}$ ) in the relevant range while the two  $\nu(\text{SO})$  modes of the free sulfane occur at 701 and 723  $\text{cm}^{-1}$ . The spectra of complex **5** confirm the above observations in so far as there are also three rather than four signals in the stretching region of the  $\text{PdCl}_2\text{S}_2$  unit (300–370  $\text{cm}^{-1}$ ). The lines at lower wavenumbers may be assigned to the in- and out-of-plane bending modes of the planar core of this complex. The SO stretching mode of free  $(\text{MeO})\text{PhS}$  observed at 725  $\text{cm}^{-1}$  in the Raman spectrum (Table 5) is shifted to 694 and/or 706  $\text{cm}^{-1}$  on co-ordination, again with a dramatic decrease in intensity (Table 4). For a full vibrational assignment of the related molecule  $(\text{MeO})_2\text{S}$  see ref. 7.

The similarities of the vibrational spectra of complexes **1–5** suggest that in all cases the ligands are co-ordinated *via* the sulfur atoms and that the configuration at the palladium centre is *cis* rather than *trans*.

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