Sulphonation of Palladium–Carbon Bonds: Synthesis and *X*-Ray Crystal Structures of the Disulphinato Derivatives $[Pd\{S(O)_2CH_2CH_2CH_2CH_2S(O)_2\}(tmen)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) and $[Pd\{S(O)_2Me\}_2(tmen)]$ *

Pietro Diversi, Giovanni Ingrosso, Antonio Lucherini, Tito Lumini, and Fabio Marchetti
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy
Stefano Merlino
Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56100 Pisa, Italy
Victor Adovasio and Mario Nardelli
Istituto di Chimica Generale ed Inorganica dell'Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

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The sulphonation of $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (**1a**) and $[PdMe_2(tmen)]$ (**1b**) (tmen = $Me_2NCH_2CH_2NMe_2$) in CH_2Cl_2 leads to the corresponding disulphinato compounds $[Pd\{S(O)_2CH_2CH_2CH_2CH_2S(O)_2\}(tmen)]$ (**2a**) and $[Pd\{S(O)_2Me\}_2(tmen)]$ (**2b**), while the reaction of (**1a**) and (**1b**) with liquid SO_2 gives the derivatives $[Pd\{S(O)_2CH_2CH_2CH_2CH_2S(O)_2\}(tmen)]\cdot 2SO_2$ (**3a**) and $[Pd\{S(O)_2Me\}_2(tmen)]\cdot 2SO_2$ (**3b**) respectively. On heating under vacuum, (**3a**), and (**3b**) lose SO_2 and revert to the disulphinates (**2a**) and (**2b**), respectively, which give (**3a**) and (**3b**) on reaction with liquid SO_2. The *X*-ray crystal structures of complexes (**2a**) and (**2b**) have been determined: (**2a**), a = 9.259(8), b = 13.380(10), c = 6.213(5) Å, β = 92.96(2)°, space group $P2_1$, Z = 2, R = 0.0325 for 2 619 observed reflections; (**2b**), a = 9.377(2), c = 16.182(3) Å, space group $P4_12_12$, Z = 4, R = 0.0396 for 1 249 observed reflections. The absolute configurations of the two structures have been determined, and the conformations of the two molecules compared. The metal co-ordination in both compounds is square planar with a very small tetrahedral deformation: av. Pd–S 2.288(1) and av. Pd–N 2.168(4) Å. Closure of the $PdS(CH_2)_4S$ chelate ring in compound (**2a**) causes a small increase in the S–Pd–S angle which is 91.3(1)° in (**2a**) and 90.3(1)° in (**2b**), but does not significantly influence the co-ordination of the diamine [av. N–Pd–N 82.9(1)°]. The conformation of the palladadithiaheptane ring in (**2a**) is twisted-boat.

Some time ago we reported the sulphonation reaction of the palladacyclopentane derivative of formula $[Pd(CH_2CH_2CH_2CH_2)(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to give the corresponding disulphinato compound.[1] We have extended this investigation to other palladacyclopentane derivatives, and now report the results of the sulphonation of the metallacycle $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) along with that of the related dimethyl derivative $[PdMe_2(tmen)]$.

Results and Discussion

Reactions of $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (**1a**) *and* $[PdMe_2(tmen)]$ (**1b**) *with* SO_2.—The sulphonation of $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (**1a**) and $[PdMe_2(tmen)]$ (**1b**) follow different courses depending upon the reaction conditions employed. Treatment of (**1a**) and (**1b**) with SO_2 in CH_2Cl_2 gives the complexes (**2a**) and (**2b**) respectively, which are soluble in $CHCl_3$, CH_2Cl_2, and water (see Scheme). Elemental analyses and spectroscopic evidence show that these compounds contain two sulphinato groups bonded to the metal *via* the S atoms. In particular, the i.r. spectra clearly show the presence of bands at 1 180 and 1 048 cm^{-1} in the case of (**2a**) and at 1 187 and 1 050 cm^{-1} in the case of (**2b**), which are close to those observed for similar palladium disulphinates.[2] The ^1H n.m.r. spectrum of complex (**2a**) in D_2O shows two singlets at δ 2.73 and 2.83 (the methyl and methylene groups attached to nitrogen) and two multiplets at δ 2.14 and 3.36 (the methylene groups in β and α positions with respect to the SO_2 groups). That of (**2b**) shows in addition to the two singlets at δ 2.90 and 2.99 (due to the protons of the tmen ligand) a singlet at δ 3.20 which is consistent with a disulphinato structure. The nature of compounds (**2a**) and (**2b**) has been unambiguously determined by *X*-ray determination of their crystal structures (see later).

When the sulphonation of complexes (**1a**) and (**1b**) is carried out in liquid SO_2, two disulphinates, (**3a**) and (**3b**), differing from (**2a**) and (**2b**) respectively, are obtained as finely divided glasses, insoluble in all common organic solvents, very soluble in water, and highly hygroscopic. Attempts to obtain (**3a**) and (**3b**) in a crystalline form have thus far been unsuccessful. The ^1H n.m.r. spectra in D_2O are those expected for disulphinato complexes. That of (**3a**) shows two singlets at δ 3.05 and 3.68 due to the methyl and methylene groups of the tmen ligand, and two broad multiplets centred at δ 2.11 and 3.13 due to the methylenes in the β and α positions to the SO_2 groups, respectively. The spectrum of (**3b**) is particularly simple, showing three singlets at δ 2.90, 3.05, and 3.70 attributable to the methylsulphinato groups and to the methyl and methylene groups of the tmen ligand, respectively. In both cases the spectra

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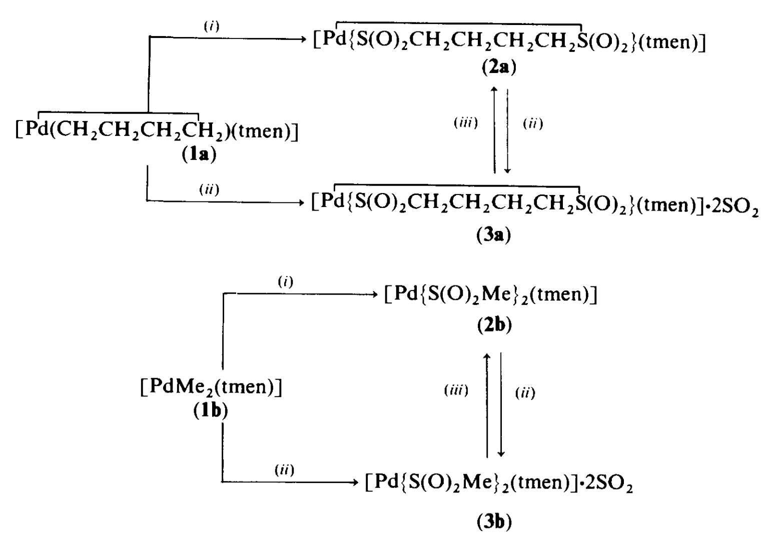
* (Butane-1,4-disulphinato-*SS'*)(*N,N,N',N'*-tetramethylethylenediamine)palladium(II) and bis(methanesulphinato-*S*)(*N,N,N',N'*-tetramethylethylenediamine)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme. (*i*) SO_2, CH_2Cl_2; (*ii*) liquid SO_2; (*iii*) heat

show clearly that symmetric structures have been formed, therefore two SO_2 molecules must have been inserted into the two metal–carbon bonds.

Unfortunately, i.r. spectroscopy, which is generally diagnostic for the mode of bonding of the sulphinato group,[3] was of little utility in these cases. Indeed, the spectra of (**3a**) and (**3b**) were very complicated in the SO_2 absorption region showing many superimposed bands. Some bands can, however, be recognised at 1 150, 1 030, 1 015, 980, and 960 cm^{-1} in the case of (**3a**), and at 1 150, 1 046, 1 012, and 972 cm^{-1} in the case of (**3b**). These bands could be diagnostic for the formulation of (**3a**) and (**3b**) as *S*-bonded rather than the less common *O*-bonded sulphinates, although they are at somewhat lower frequency when compared with values for known disulphinato-*S* palladium derivatives.[2] In the same region however several other bands attributable to other S–O bond modes are present, thus suggesting that more SO_2 groups are present in addition to the inserted SO_2 molecules. The results of the elemental analysis are in agreement with this hypothesis, showing sulphur percentages which are consistent with the presence of four SO_2 groups. Upon prolonged heating under vacuum, complexes (**3a**) and (**3b**) slowly lose SO_2 and are converted into the disulphinates (**2a**) and (**2b**). The separation of these compounds from unreacted (**3a**) and (**3b**) is easily accomplished by simple extraction of the crude reaction products with CH_2Cl_2 or $CHCl_3$. It is interesting that (**2a**) and (**2b**) can be converted into (**3a**) and (**3b**), respectively, by reaction with liquid SO_2: this again substantiates the presence of additional SO_2 groups in (**3a**) and (**3b**).

Crystal Structure Analysis of Complexes (**2a**) *and* (**2b**).—The atomic co-ordinates are given in Table 1 together with the isotropic equivalent thermal parameters[4] and the ratios, $r_{max.}/r_{min.}$, of the maximum and minimum principal axes of the thermal ellipsoids. Figure 1 shows the ORTEP drawings of the two compounds and Table 2 gives the most relevant distances and angles. It appears that most affected by anisotropic thermal motion are the methyl groups and the oxygen atoms. The analysis of thermal motion, carried out in terms of the LTS rigid-body model of Schomaker and Trueblood,[5] gives quite satisfactory results when the internal motions are taken into account according to the one-parameter model of Dunitz and White,[6,7] as shown by the data in Table 3.

The co-ordination about Pd is square planar with a small tetrahedral deformation, more pronounced in the case of compound (**2b**). Chelation of the diamine ligand is practically the same in the two compounds and the conformation of the chelate ring is half-chair with a two-fold axis running through Pd and the middle of the C–C bond. This two-fold axis is pseudo for compound (**2a**) and crystallographic in the case of compound (**2b**), the tetramethylene chain of the sulphinato ligand being responsible for the lack of two-fold crystallographic symmetry in (**2a**).

The S–Pd–S angle, which is very near 90° in compound (**2b**), is a little larger in compound (**2a**) where the sulphinato ligand forms a ring with the metal, while all the N–Pd–S angles are larger than 90° in both molecules. In compound (**2a**) the angle S(1)–Pd–N(2) is significantly larger [$\Delta = 3.2(2)°$] than S(2)–Pd–N(1), probably as a consequence of the interactions between the tmen methyls and the oxygen atoms, which are not equal in the two parts of the molecule. Indeed, while the C(2)$\cdots$O(3) 3.075(8) Å contact is not so different from C(4)$\cdots$O(2) 3.024(10) Å the C(3)$\cdots$O(1) 4.475(10) Å distance is much larger than C(1)$\cdots$O(4) 3.322(9) Å, due to the differences in the mutual orientation of the $N(CH_3)_2$ and SO_2 groups in the two parts of the molecule, as shown by Figure 1(*a*). This orientation is essentially conditioned by C–H$\cdots$O interactions which can be considered as weak hydrogen bonds.[8,9] These interactions have a remarkable influence on the conformations about the Pd–S bonds in (**2a**), as shown by the Newman projections of Figure 2(*a*) and (*b*). No significant differences are observed between corresponding distances in the ligands in each compound and in the two compounds, while several significant differences are observed for the angles, particularly Pd–S–O and Pd–N–C, indicating that conformational deformations occur, mainly attributable to steric effects.

The conformation of the seven-membered $PdS(C)_4S$ ring is described by the parameters in Figure 3. Cremer and Pople's[10] total puckering amplitude, $Q = 1.563(5)$ Å, and the minimum-displacement asymmetry parameter,[11] $\Delta_2^{C(9)} = 0.038\,2(19)$, indicates the presence of a pseudo-two-fold axis running through C(9) and the middle of the Pd–S(1) bond, corresponding to a twist-boat (t.b.) conformation which according to Hendrickson[12] can be described by the symbol $A^{C(9)}$ $(-++\;)-$. It is worth noting that the pseudo-two-fold axis does not run through Pd, and that the endocyclic bond angles at S(1) and S(2) are remarkably different. As a consequence of the narrowing of the angle at Pd (it is reduced by 23.7° with respect to the value of 115° expected for a t.b. regular cycloheptane), the angle at S(1) is also narrowed (by 8.3°), while for the other endocyclic bond angles at the C atoms the variation ranges from

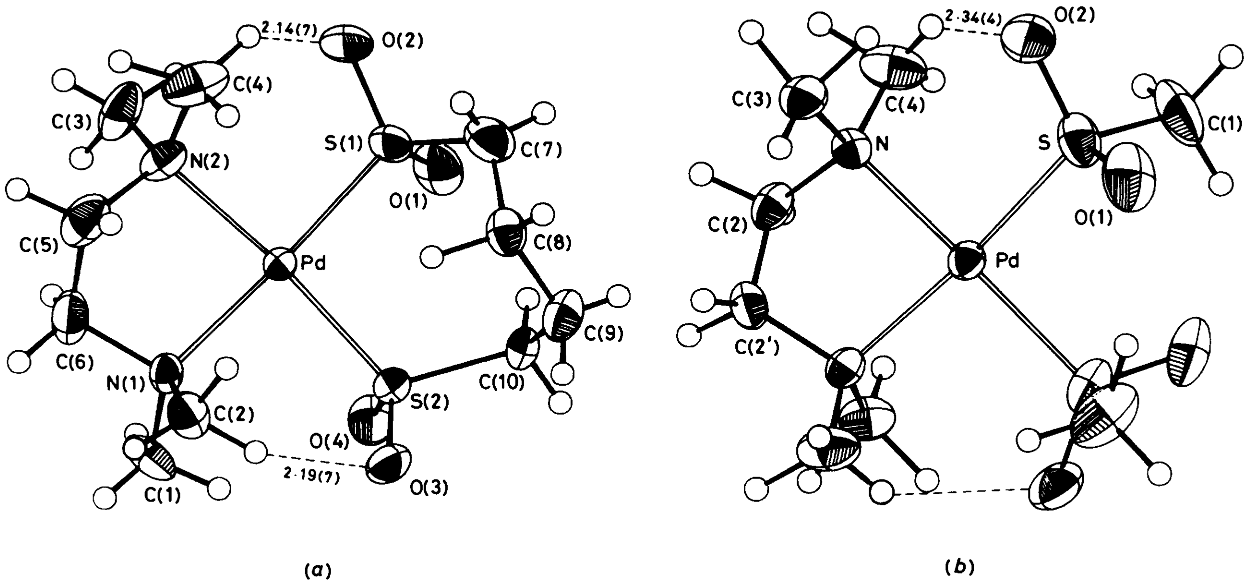


Figure 1. ORTEP drawings of complexes (**2a**) (*a*) and (**2b**) (*b*). Ellipsoids at 50% probability

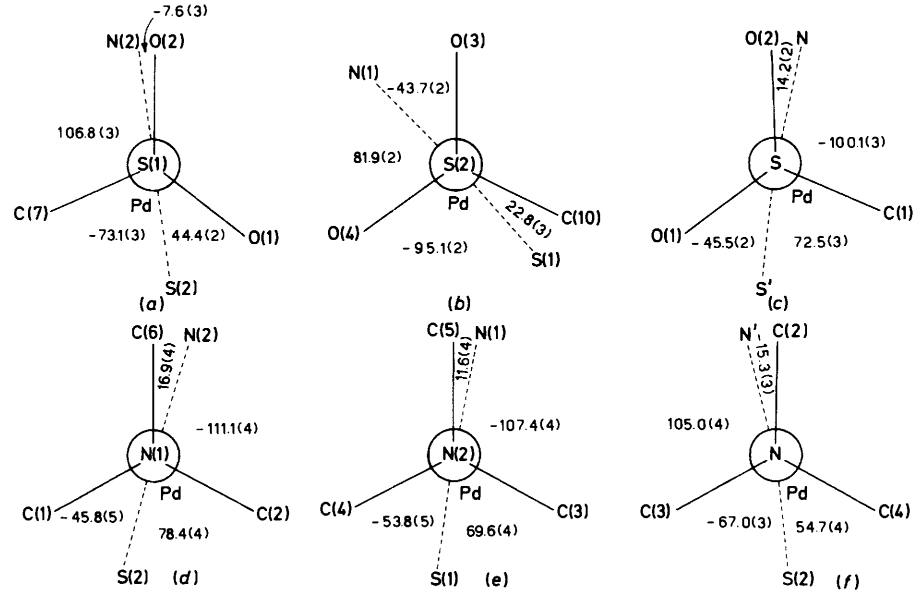


Figure 2. Newman projections showing the conformations about the Pd–S and Pd–N bonds (angles in °) in complexes (**2a**) and (**2b**); (*a*), (*b*), (*d*), and (*e*) refer to (**2a**); (*c*) and (*f*) to (**2b**)

-1 to 2°. The angle at S(2) is very close to the theoretical value.

From the Newman projections of Figure 2 it appears that in compound (**2a**) the chirality about the S(1)–Pd bond is opposite to that about S(2)–Pd which is equal to that about the S–Pd bond in (**2b**).

The conformation of the five-membered $\overline{\mathrm{PdN(C)_2N}}$ ring formed by the tmen ligand is described by the parameters in Figure 3(*b*) and (*c*). The total puckering amplitude is a little higher in compound (**2b**), $Q = 0.485(6)$ Å, than in (**2a**) [$Q = 0.454(8)$ Å]. The pseudo-two-fold axis, running through Pd and the middle of the C(5)–C(6) bond in the ring of compound (**2a**), is indicated by the minimum asymmetry parameter $\Delta_2^{\mathrm{Pd}} = 0.020\,1(26)$. The conformation of the ring is δ for compound (**2a**) and λ for (**2b**). In accord with these opposite conformations are the chiralities about the N(1)–Pd and N(2)–Pd bonds which are equal in (**2a**) and opposite of that about N–Pd in (**2b**), as shown by the Newman projections of Figure 2. The packing in both crystals is determined by C–H • • • O interactions which can be considered as weak hydrogen bonds.[8,9]

Conclusions

The disulphinato complexes of $\mathrm{Pd^{II}}$ described are amongst the very few examples of insertion products of two SO_2 molecules in Group 8 metal alkyls[1,13] and the only ones fully characterized by *X*-ray crystal-structure determination. Other disulphinato palladium derivatives have been reported but they were all

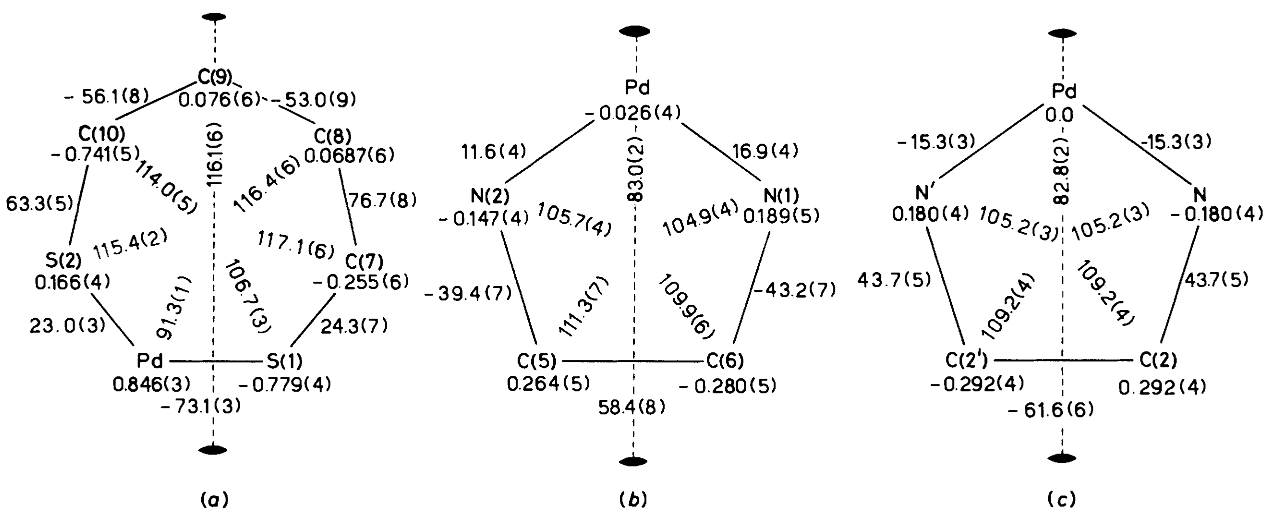


Figure 3. Relevant parameters defining the conformations of the chelate rings: (*a*) $PdS(CH_2)_4S$, (*b*) $PdN(CH_2)_2N$ in complex (**2a**); (*c*) $PdN(CH_2)_2N$ in complex (**2b**). The values at the sides of the polygons are for the torsion angles (°), those under the atom labels are for the distances (Å) of the atoms from the mean planes through the rings; those inside the polygons are for the endocyclic angles (°)

Table 1. Fractional co-ordinates ($\times 10^4$) and isotropic equivalent thermal parameters ($\times 10^4$) ($U_{equiv.}$ = one third trace of the diagonalized matrix) for compounds (**2a**) and (**2b**), and ratios, $r_{max.}/r_{min.}$, of the maximum and minimum principal axes of the thermal ellipsoids. Standard deviations are given in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	$U_{equiv.}$	$r_{max.}/r_{min.}$
Compound (**2a**)					
Pd	−1 973.5(4)	−2 500.0(−)	−2 938.0(5)	223(1)	1.42
S(1)	−4 435(1)	−2 403(2)	−3 391(2)	359(5)	2.47
S(2)	−1 701(2)	−1 116(1)	−5 041(2)	275(4)	1.50
O(1)	−4 882(5)	−2 205(3)	−5 649(8)	492(16)	2.56
O(2)	−5 182(5)	−3 266(4)	−2 498(11)	547(20)	4.67
O(3)	−537(5)	−494(3)	−4 064(8)	417(14)	2.89
O(4)	−1 474(5)	−1 428(3)	−7 254(7)	419(15)	2.56
N(1)	358(5)	−2 701(3)	−2 566(7)	257(15)	1.84
N(2)	−1 996(6)	−3 813(4)	−902(8)	359(18)	2.31
C(1)	1 199(6)	−2 616(9)	−4 557(11)	440(29)	3.70
C(2)	979(8)	−1 984(5)	−930(12)	373(20)	2.08
C(3)	−2 495(10)	−4 691(5)	−2 212(14)	508(28)	4.63
C(4)	−2 889(10)	−3 725(7)	1 004(13)	554(30)	3.02
C(5)	−487(9)	−3 954(6)	−74(13)	516(25)	2.81
C(6)	558(9)	−3 739(6)	−1 776(16)	462(25)	3.03
C(7)	−5 000(9)	−1 338(6)	−1 772(16)	484(28)	2.22
C(8)	−3 893(7)	−532(5)	−1 289(10)	355(20)	1.63
C(9)	−3 613(9)	188(5)	−3 112(12)	422(23)	2.34
C(10)	−3 238(7)	−287(5)	−5 251(11)	337(19)	2.58
Compound (**2b**)					
Pd	909.8(5)	909.8(5)	0(−)	265(1)	1.45
S	1 441(2)	2 813(2)	831(1)	422(7)	2.48
O(1)	2 938(5)	2 858(5)	1 006(3)	604(20)	3.50
O(2)	536(5)	2 850(4)	1 581(2)	530(19)	3.14
N	−1 082(5)	453(4)	622(2)	266(16)	1.61
C(1)	1 016(11)	4 427(6)	335(4)	646(32)	5.15
C(2)	−1 769(5)	−666(6)	120(4)	343(21)	2.10
C(3)	−850(7)	−49(6)	1 483(3)	386(22)	2.53
C(4)	−2 046(7)	1 681(8)	659(4)	507(31)	2.62

prepared by metathesis reactions of dihalogeno complexes with sodium alkanesulphinato derivatives.[2] As far as the precise nature of complexes (**3a**) and (**3b**) is concerned, we cannot draw definitive conclusions, since it is difficult to think of plausible structures in which, in addition to the tmen and the two RSO_2 ligands, two SO_2 groups are co-ordinated to the palladium atom, except for ionic complexes. We are inclined to discard the latter hypothesis because all efforts to obtain crystalline forms of (**3a**) and (**3b**) by addition of large anions have thus far been unsuccessful.

Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen. Solvents were dried in the usual manner and distilled and stored under an inert atmosphere. The complexes $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (**1a**), and $[PdMe_2(tmen)]$ (**1b**) were prepared as described.[1] Sulphur dioxide was purchased from Matheson and used after passing through concentrated H_2SO_4. Hydrogen-1 n.m.r. spectra were recorded using a Varian T60 or XL100 spectrometer. Microanalyses were by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. I.r. spectra were obtained on a Perkin-Elmer 283-B instrument.

Reaction of $[Pd(CH_2CH_2CH_2CH_2)(tmen)]$ (**1a**) *with* SO_2 *in* CH_2Cl_2: *Preparation of* $[Pd\{S(O)_2CH_2CH_2CH_2CH_2S(O)_2\}(tmen)]$ (**2a**).—Sulphur dioxide was bubbled into a solution of complex (**1a**) (0.52 g, 1.87 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C for 1 h. The solvent was removed to give a solid residue which was extracted with CH_2Cl_2 and crystallized from methanol to give yellow crystals of (**2a**) (50% yield), m.p. 160 °C (decomp.) (Found: C, 29.20; H, 5.90; N, 6.90. $C_{10}H_{24}N_2O_4PdS_2$ requires C, 29.50; H, 5.90; N, 6.90%). ^1H N.m.r.: (60 MHz, $CDCl_3$, relative to $SiMe_4$) δ 2.06 (m, 4 H, CCH_2C), 2.76 (s, 4 H, CH_2N), 2.83 (s, 12 H, MeN), and 3.55 (m, 4 H, CH_2S); (100 MHz, D_2O, relative to sodium 3-trimethylsilyl[$^2H_4$]propionate) δ 2.14 (m, 4 H, CCH_2C), 2.73 (s, 12 H, MeN), 2.83 (s, 4 H, CH_2N), and 3.36 (m, 4 H, CH_2S). I.r. (KBr): 1 180, 1 048, and 950 cm^{-1}.

Reaction of $[PdMe_2(tmen)]$ (**1b**) *with* SO_2 *in* CH_2Cl_2: *Preparation of* $[Pd\{S(O)_2Me\}_2(tmen)]$ (**2b**).—Sulphur dioxide was bubbled into a solution of complex (**1b**) (0.41 g, 1.63 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C for 1 h. On removal of the solvent the solid residue was extracted with $CHCl_3$ and crystallized from methanol to give (**2b**) (0.32 g, 53% yield) as yellow crystals, m.p. 195 °C (decomp.) (Found: C, 25.05; H, 5.65; N, 7.85; S, 16.35. $C_8H_{22}N_2O_4PdS_2$ requires C, 25.25; H, 5.80; N, 7.35; S, 16.8%). ^1H N.m.r.: (60 MHz, $CDCl_3$, relative to $SiMe_4$) δ 2.73 (s, 4 H,

Table 2. Comparison of bond lengths (Å) and angles (°) in complexes (**2a**) and (**2b**). Values corrected for rigid-body thermal motion are shown in square brackets. The weighted averages of these values were calculated by assigning to them the estimated standard deviations of the corresponding uncorrected values

	(**2a**)		(**2b**)	Av.
Pd–S(1)	2.286(2) [2.292]	Pd–S	2.290(2) [2.298]	2.288(1) [2.295]
Pd–S(2)	2.288(2) [2.294]		—	
Pd–N(1)	2.176(5) [2.182]	Pd–N	2.164(4) [2.172]	2.168(4) [2.174]
Pd–N(2)	2.165(5) [2.171]		—	
S(1)–O(1)	1.466(5) [1.470]	S–O(1)	1.433(5) [1.438]	1.465(7) [1.469]
S(1)–O(2)	1.470(6) [1.475]	S–O(2)	1.481(4) [1.486]	
S(2)–O(3)	1.468(5) [1.472]		—	
S(2)–O(4)	1.462(5) [1.466]		—	
S(1)–C(7)	1.835(10) [1.840]	S–C(1)	1.759(6) [1.764]	1.788(21) [1.731]
S(2)–C(10)	1.805(7) [1.808]		—	
N(1)–C(1)	1.499(8) [1.504]	N–C(3)	1.486(6) [1.489]	1.486(4) [1.490]
N(1)–C(2)	1.491(8) [1.495]	N–C(4)	1.466(8) [1.471]	
N(2)–C(3)	1.490(9) [1.493]		—	
N(2)–C(4)	1.483(10) [1.488]		—	
N(1)–C(6)	1.482(10) [1.486]	N–C(2)	1.476(7) [1.481]	1.477(5) [1.482]
N(2)–C(5)	1.476(10) [1.480]		—	
C(5)–C(6)	1.497(12) [1.502]	C(2)–C(2′)	1.513(8) [1.519]	1.514(5) [1.519]
C(7)–C(8)	1.508(11) [1.512]		—	
C(8)–C(9)	1.519(10) [1.523]		—	
C(9)–C(10)	1.529(10) [1.533]		—	
S(1)–Pd–S(2)	91.3(1)	S–Pd–S′	90.3(1)	90.8(5)
S(1)–Pd–N(2)	94.5(2)	S–Pd–N	93.9(1)	92.8(10)
S(2)–Pd–N(1)	91.3(1)		—	
N(1)–Pd–N(2)	83.0(2)	N–Pd–N′	82.8(2)	82.9(1)
Pd–S(1)–O(1)	111.0(2)	Pd–S–O(1)	110.6(2)	110.8(7)
Pd–S(1)–O(2)	113.2(2)	Pd–S–O(2)	112.0(2)	
Pd–S(2)–O(3)	108.8(2)		—	
Pd–S(2)–O(4)	109.4(2)		—	
Pd–S(1)–C(7)	106.7(3)	Pd–S–C(1)	110.7(2)	111.9(23)
Pd–S(2)–C(10)	115.4(2)		—	
Pd–N(1)–C(1)	117.2(4)	Pd–N–C(3)	111.9(4)	112.6(12)
Pd–N(1)–C(2)	109.8(4)	Pd–N–C(4)	113.3(4)	
Pd–N(2)–C(3)	109.4(4)		—	
Pd–N(2)–C(4)	115.1(5)		—	
Pd–N(1)–C(6)	104.9(4)	Pd–N–C(2)	105.2(3)	105.2(2)
Pd–N(2)–C(5)	105.7(4)		—	
O–S–O (av.)	113.6(8)		113.5(3)	
O–S–C (av.)	105.1(8)		104.8(19)	
S–C–C (av.)	115.3(15)		—	
N–C–C (av.)	110.5(7)		109.2(4)	
C–N–C (av.)	108.6(6)		108.8(10)	
C–C–C (av.)	116.2(4)			

Primes indicate symmetry-equivalent position *y*, *x*, −*z*.

CH_2N), 2.85 (s, 12 H, MeN), and 3.13 (s, 6 H, $MeSO_2$); (60 MHz, D_2O, relative to sodium 3-trimethylsilyl[$^2H_4$]propionate) δ 2.90 (s, 12 H, MeN), 2.99 (s, 4 H, CH_2N), and 3.20 (s, 6 H, $MeSO_2$). I.r. (KBr): 1 187 and 1 050 cm^{-1}.

Reaction of [$Pd(CH_2CH_2CH_2CH_2)$(tmen)] (**1a**) *with Liquid* SO_2: *Formation of* [$Pd\{S(O)_2CH_2CH_2CH_2CH_2S(O)_2\}$(tmen)]·$2SO_2$ (**3a**), *and Its Conversion into* (**2a**).—Sulphur dioxide (5 cm^3, liquid) was introduced into a Schlenk tube containing complex (**1a**) (0.18 g, 0.65 mmol) at −78 °C. After the metallacycle had dissolved, the temperature was raised to −40 °C. The resulting mixture changed from almost colourless to deep burgundy red. After 1 h of stirring the reaction mixture was allowed to warm and the SO_2 was removed under vacuum. The red-orange solid glassy residue was washed repeatedly with diethyl ether and then dried under vacuum to give (**3a**) (0.28 g, 81% yield) (Found: C, 23.70; H, 5.00; N, 5.30; S, 23.0. $C_{10}H_{24}N_2O_8PdS_4$ requires C, 22.45; H, 4.50; N, 5.25; S, 23.95%). ^1H N.m.r. (60 MHz, D_2O, relative to sodium 3-trimethylsilyl[$^2H_4$]propionate) δ 2.11 (m, 4 H, CCH_2C), 3.05 (s, 12 H, MeN), 3.13 (m, 4 H, CH_2SO_2), and 3.68 (s, 4 H, CH_2N). I.r. (Nujol): 1 150, 1 030, 1 015, 980, and 960 cm^{-1}. After heating this solid at 95 °C for 8 h under vacuum (*ca.* 133 Pa) the residue was extracted with CH_2Cl_2. Removal of the solvent under vacuum left a solid which was crystallized from methanol to give yellow crystals of complex (**2a**) (80% yield).

Table 3. Results of thermal motion analysis. The eigenvalues are referred to the molecular inertial frames. $\bar{\Delta}$ = Mean difference in the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms of the molecule; g.l.a. = group libration amplitude in °

		(**2a**)	(**2b**)
g.l.a. for C(7), O(1), O(2)	librating about Pd–S(1)	3.8(11)	—
g.l.a. for C(10), O(3), O(4)	librating about Pd–S(2)	4.2(7)	—
g.l.a. for C(1), C(2), C(6)	librating about Pd–N(1)	5.2(11)	—
g.l.a. for C(3), C(4), C(5)	librating about Pd–N(2)	5.6(11)	—
g.l.a. for C(1), O(1), O(2)	librating about Pd–S	—	6.0(8)
g.l.a. for C(2), C(3), C(4)	librating about Pd–N(1)	—	2.4(21)
L tensor (eigenvalues)$^{\frac{1}{2}}$/°		3.8 3.1 1.5	3.4 2.4 2.4
T tensor (eigenvalues)$^{\frac{1}{2}}$/Å		0.164 0.145 0.137	0.187 0.158 0.153
$\bar{\Delta}$		0.006(7)	0.006(8)
$R_{wU} = [\Sigma(w\Delta U)^2/\Sigma(wU_{obs.})^2]^{\frac{1}{2}}$ where $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$		0.063	0.059
$\sigma(\bar{\Delta}\bar{U}) = [\Sigma w\Delta U)^2/\Sigma w^2]^{\frac{1}{2}}$		0.0011	0.0014
$\sigma(U_{obs.})$		0.0032	0.0034

Table 4. Experimental data for the crystallographic analyses[a]

Compound	$[\text{Pd}\{\text{S(O)}_2(\text{CH}_2)_4\text{S(O)}_2\}(\text{tmen})]$	$[\text{Pd}\{\text{S(O)}_2\text{Me}\}_2(\text{tmen})]$
Formula	$C_{10}H_{24}N_2O_4PdS_2$	$C_8H_{22}N_2O_4PdS_2$
M	406.8	380.8
Space group	$P2_1$	$P4_12_12$
a/Å	9.259(8)	9.377(2)
b/Å	13.380(10)	—
c/Å	6.213(5)	16.182(3)
β/°	92.96(2)	—
U/Å^3	769(1)	1 422.8(5)
Z	2	4
D_c/Mg m^{-3}	1.758	1.778
F(000)	416	776
Crystal size/mm	0.12 × 0.15 × 0.17	0.36 × 0.36 × 0.53
Diffractometer	Philips PW1100	Ital Structures
μ/mm^{-1}	1.462	1.573
Scan speed/° s^{-1}	0.075	0.10
θ range/°	3—26	3—30
h range	−11 to 11	0 to 9
k range	−16 to 16	0 to 9
l range	0 to 7	0 to 16
Standard reflection	4 1 0	2 3 4
No. of measured reflections	3 036	1 625
Condition for observed reflections	$I \geqslant 2\sigma(I)$	$I \geqslant 1.5\sigma(I)$
No. of reflections used in refinement	2 619	1 249
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.0350	0.0239
Max. shift-to-error ratio	0.04	0.50
Min., max. height in final difference map (e Å^{-3})	−0.38, 0.38	−0.88, 0.70
No. of parameters refined	267	89
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0325	0.0396
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0346	0.0278
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$[b]	1.005	2.061

[a] Details common to both: T = 294 K; scan width 1.20° s^{-1}, Mo-K_α radiation; variation of standard reflection, none; scan mode θ—2θ; full-matrix anisotropic least squares; $w = 1/\sigma^2(F_o)$. [b] P = Number of parameters, N = number of observations.

Reaction of Complex (**1b**) *with Liquid* SO_2: *Formation of* $[\text{Pd}\{\text{S(O)}_2\text{Me}\}_2(\text{tmen})]\cdot 2SO_2$ (**3b**) *and Its Conversion into* (**2b**).—Sulphur dioxide (6 cm^3, liquid) was introduced into a Schlenk tube containing complex (**1b**) (0.30 g, 1.19 mmol) at −78 °C. After the dialkyl derivative had dissolved, the temperature was raised to −40 °C and the solution stirred at this temperature for 1 h. After evaporation of SO_2 at room temperature under vacuum, the red-orange glassy residue was repeatedly washed with diethyl ether and then dried under vacuum to give (**3b**) (0.59 g, 98% yield) as an orange, very hygroscopic solid (Found: C, 19.45; H, 5.00; N, 5.65; S, 24.85. $C_8H_{22}N_2O_8PdS_4$ requires C, 18.9; H, 4.35; N, 5.50; S, 25.20%). ^{1}H N.m.r. (60 MHz, D_2O, relative to sodium 3-trimethylsilyl-[$^2H_4$]propionate) δ 2.90 (s, 6 H, $MeSO_2$), 3.05 (s, 12 H, MeN), and 3.70 (s, 4 H, CH_2N). I.r. (Nujol): 1 150, 1 046, 1 012, and 972 cm^{-1}. By heating this solid at 95 °C (*ca.* 133 Pa) a yellow solid was obtained which was extracted with $CHCl_3$. After evaporation of the solvent, crystallization from methanol yielded complex (**2b**) (80%).

Reaction of Complex (**2a**) *or* (**2b**) *with Liquid* SO_2.—Treatment of complex (**2a**) or (**2b**) at −40 °C with liquid SO_2 (5 cm^3) for 2 h gave a product almost quantitatively that was identified as the disulphinate (**3a**) or (**3b**), respectively, by comparison of its i.r. and ^1H n.m.r. spectra with those of an authentic sample.

X-*Ray Analyses.*—Details of the lattice parameters, the data collection, and the structure refinement are summarized in Table 4. The unit-cell dimensions and estimated standard deviations (e.s.d.s) were determined by least-squares fitting of the θ angles of a number of high-angle intense reflections chosen from diverse regions of reciprocal space, considering their α_1 peaks (Mo-$K_{\alpha 1}$ radiation, $\lambda = 0.709\,300$ Å). The reflection intensities were corrected for Lorentz and polarization effects. The structures were solved by Patterson and Fourier techniques and refined by full-matrix least squares using the SHELX 76 program.[14] All the hydrogen atoms were located from Fourier difference syntheses, but were refined isotropically only in the case of compound (**2a**), while for (**2b**) they were kept in calculated positions riding upon the C atoms to which they are bonded. In order to define the absolute configuration of the two compounds, complete refinements were carried out for the enantiomeric structures [for (**2b**) the enantiomeric structure corresponds to the space group $P4_32_12$]. At the end of these refinements the Hamilton test[15] was applied with the following results: (**2a**), $R'(\bar{x}\bar{y}\bar{z})/R'(xyz) = 0.0370/0.0346 = 1.069$; for 2 619 independent F_0 values and 267 variables, $\mathcal{R}_{1,2352,0.005} = 1.002$; (**2b**), $R'(P4_32_12)/R'(P4_12_12) = 0.0297/0.0278 = 1.068$; for 1 249 independent F_0 and 89 variables, $\mathcal{R}_{1,1160,0.005} = 1.0035$. This indicates that, at the 99.5% confidence level, the coordinates of Table 1 correspond to the correct chiralities of the structures.

The atomic scattering factors and anomalous scattering coefficients were taken from ref. 16. The calculations were carried out on the GOULD-SELL 32/77 computer of the 'Centro di Studio per la Strutturistica diffrattometrica del CNR (Parma),' and on the IBM 3081/K of the 'Centro Nazionale Universitario di Calcolo Elettronico del CNR (Pisa).' In addition to the quoted program, PARST,[17] THMV,[18] and ORTEP[19] were used.

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