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Synthesis and structure of a thioazobenzene palladacycle: oxygen insertion into the Pd–C bond by *m*-chloroperbenzoic acid

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Abstract

The reaction of *p*-tolyl-*o'*-(2-chloroethylthio)azobenzene (L^1H) with Na_2PdCl_4 affords the complex PdL^1Cl , the structure of which has been determined by X-ray crystallography. The azobenzene ligand acts in the tridentate (C,N,S) fashion and the fourth coordination position is occupied by the chloride ion. In the lattice, the PdL^1Cl molecules are present as loose dimers of parallel $Pd(C,N,S)Cl$ units, the $Pd \cdots Pd$ distance being 3.357(2) Å. Reaction of PdL^1Cl with *m*-chloroperbenzoic acid leads to insertion of oxygen into the Pd–C bond to give the corresponding phenolato complex. The insertion reaction is of first order with respect to each of the reactants, and has a large negative entropy of activation. A plausible mechanism is proposed. The structure and properties of PdL^1Cl are compared with those of related species.

Introduction

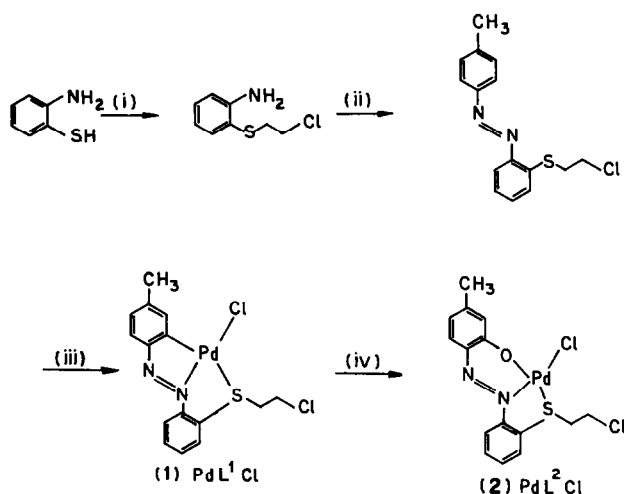
We are engaged in a programme of research on the synthesis and structure of new cyclopalladated azobenzenes and their reactions with organic peracids resulting in regiospecific insertion of oxygen into the Pd–C bond [1–6]. We consider here the case of the complex PdL^1Cl (**1**) (see Scheme 1), and compare the results with those reported for related complexes.

Results and discussion

Synthesis and characterization

The ligand *p*-tolyl-*o'*-(2-chloroethylthio)azobenzene was synthesized from 2-aminothiophenol, 1,2-dichloroethane and *p*-nitrosotoluene and was treated directly with Na_2PdCl_4 in ethanol to give PdL^1Cl . This synthesis reaction and the

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Scheme 1. (i) 1,2-Dichloroethane/EtOH/Na; (ii) $p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}$ /glacial acetic acid; (iii) $\text{Na}_2\text{PdCl}_4/\text{EtOH}$; (iv) $m\text{-CPBA}/\text{CHCl}_3$.

reaction of PdL^1Cl with m -chloroperbenzoic acid ($m\text{-CPBA}$) to give the phenolato complex PdL^2Cl (2), a dark solid, is shown in Scheme 1.

The UV–vis spectral data for PdL^1Cl and PdL^2Cl are listed in Table 1. The UV–vis spectrum of a solution in which 1 is undergoing progressive conversion into 2 by $m\text{-CPBA}$ is shown in Fig. 1. In the IR spectrum, the Pd–Cl stretch in each case is observed as a sharp singlet: PdL^1Cl , 330 cm^{-1} ; PdL^2Cl , 340 cm^{-1} .

X-Ray structure of PdL^1Cl (1)

The X-ray structure of PdL^1Cl was determined in order to establish the bonding mode of the ligand and the nature of intermolecular interactions, if any. A view of the molecule is shown in Fig. 2 and selected bond parameters are listed in Table 2. The azobenzene ligand acts in the tridentate (C,N,S) fashion and a chloride ion completes the planar tetracoordination.

The Pd^{II}–S(thioether) distances normally lie in the range 2.260–2.310 Å [7]. The Pd–S distance in 1 is significantly longer, 2.410(2) Å, and this is ascribed to the trans influence of the metallated carbon atom [8]. The entire metallated azobenzene ligand except for the $-\text{CH}_2\text{CH}_2\text{Cl}$ fragment is approximately planar, with a mean deviation of 0.10 Å. There is a small fold of 3.1° between the two chelate rings.

Table 1
UV–vis spectral data^a

Compound	λ_{max} (nm) (ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$))
PdL^1Cl (1)	530 ^b (4500), 490 (5830), 415 (9000), 370 ^b (10 000) 355 (11 090), 320 ^b (9770), 270 ^b (10 338)
PdL^2Cl (2)	530 (7100), 370 ^b (10 800), 340 (13 500)

^a In dichloromethane solution at 298 K. ^b Shoulder.

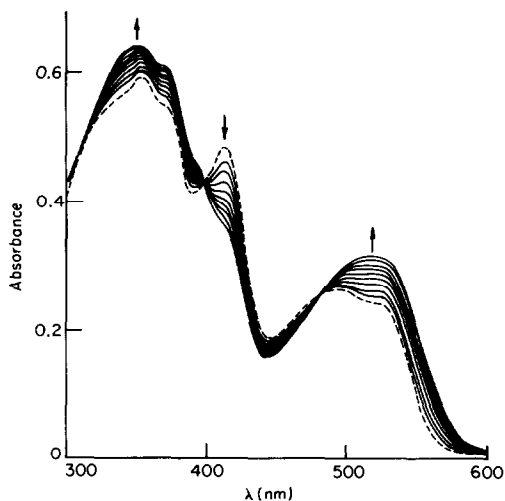


Fig. 1. Spectra of a reaction mixture of PdL^1Cl and *m*-CPBA (—) at 298 K in CHCl_3 solution at various times. The arrows indicate increase and decrease of band intensities as the reaction proceeds; the spectrum of pure PdL^1Cl is also shown (---).

The packing of PdL^1Cl molecules in the lattice involves a characteristic intermolecular interaction. A view down the *b*-axis is shown in Fig. 3. The planar $[\text{Pd}(\text{C},\text{N},\text{S})\text{Cl}]$ fragments lie in parallel pairs, the interplanar distance within each pair being 3.497 Å; the $\text{Pd} \cdots \text{Pd}$ distance within the pair is 3.357(2) Å. The lattice thus consists of loose dimers. The interplanar separation within the dimer essentially corresponds to the van der Waals distance in crystals of planar aromatic molecules [9,10].

The X-ray structure of two other $[\text{Pd}(\text{C},\text{N},\text{S})\text{Cl}]$ complexes, **3** [3] and **4** [2], and that of the binuclear complex, **5** [1] have been reported previously. The metal-ligand and other distances in all four complexes within the **1**, **3**, **4** and **5** are in good agreement. The packing behaviour of **1**, however, is quite distinct from those of **3**

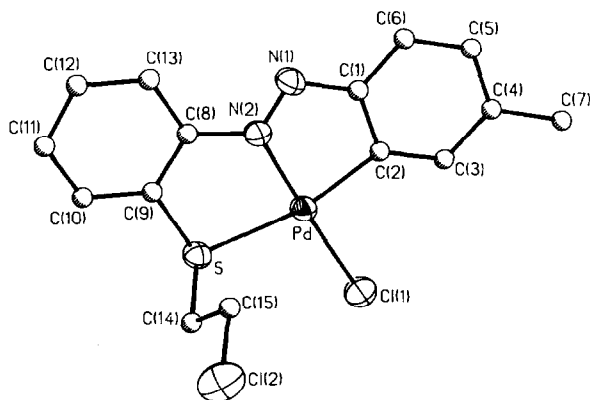


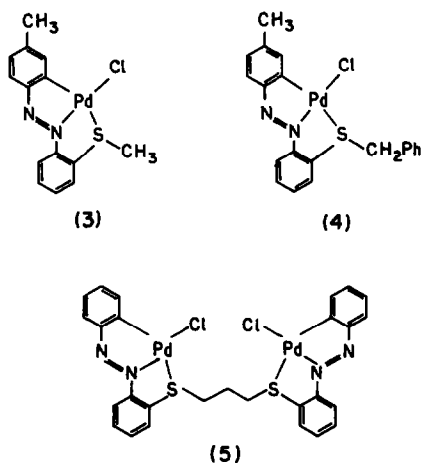
Fig. 2. Molecular structure and numbering scheme for PdL^1Cl .

Table 2

Selected bond lengths (Å) and angles (deg) in PdL¹Cl (1)

Pd–C(2)	1.983(5)
Pd–S	2.410(2)
Pd–Cl(1)	2.311(2)
Pd–N(2)	1.984(4)
N(1)–N(2)	1.266(6)
Pd...Pd	3.357(2)
C(2)–Pd–S	165.5(1)
S–Pd–Cl(1)	98.6(1)
S–Pd–N(2)	85.0(1)
Cl(1)–Pd–N(2)	174.2(1)
Cl(1)–Pd–C(2)	96.7(2)
N(2)–Pd–C(2)	79.5(2)
Pd–S–C(13)	95.8(2)
Pd–S–C(14)	105.3(1)
C(14)–S–C(13)	100.3(3)

and 4. In the lattice of 3, adjacent molecules display S...S interactions of length 3.429(1) Å, but there are no such interactions in crystals of 4. In the lattice of 5, an interaction similar to that in 1 is present between adjacent halves of adjacent molecules.



Reaction of PdL¹Cl with *m*-CPBA

The reaction of PdL¹Cl with *m*-CPBA proceeds smoothly in chloroform. The colour of the solution changes progressively from orange-red to violet. PdL²Cl was isolated from the violet solution (Scheme 1).

The rate of conversion of PdL¹Cl into PdL²Cl by *m*-CPBA was determined spectrophotometrically. Well defined isosbestic points are observed (Fig. 1). The change in absorption (A_t) at 530 nm was monitored as function of time (t). In the presence of excess of the oxidant, the plot of $-\ln(A_\infty - A_t)$ against t is linear up

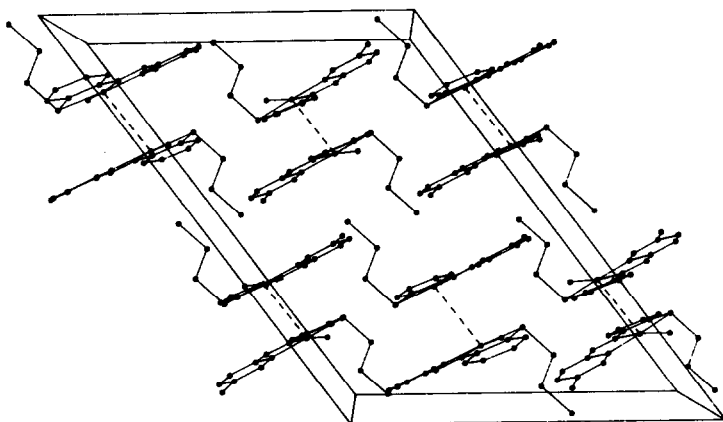


Fig. 3. Packing diagram of PdL^1Cl viewed down the b axis.

to at least 85% of the reaction. The constant k_{obs} (eq. 1) was found to vary linearly with the concentration of m -CPBA (Fig. 4), leading to the rate law shown in eq. 2.

$$\text{Rate} = d[\text{PdL}^2\text{Cl}]/dt = k_{\text{obs}}[\text{PdL}^1\text{Cl}] \quad (1)$$

$$d[\text{PdL}^2\text{Cl}]/dt = k[\text{PdL}^1\text{Cl}][m\text{-CPBA}] \quad (2)$$

Variable temperature (296–306 K) rate data are listed in Table 3, along with activation parameters. The enthalpy of activation is small and positive and the

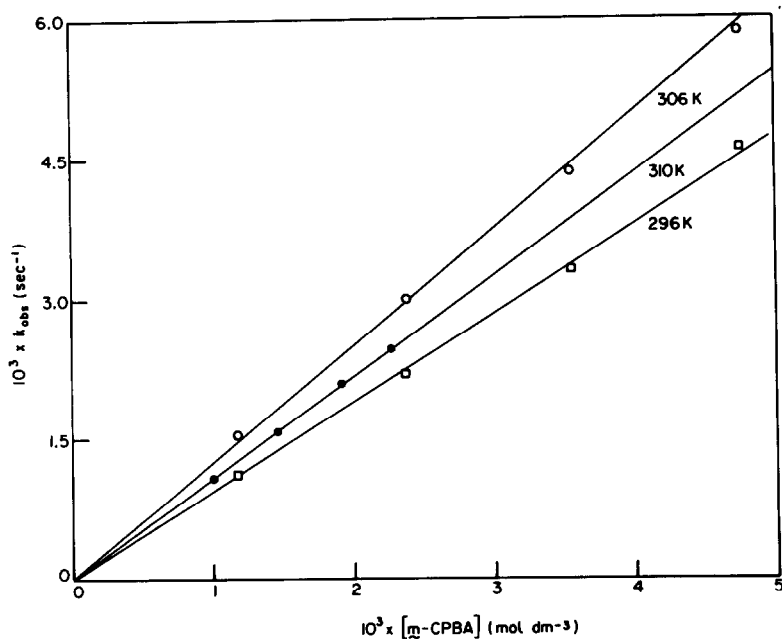


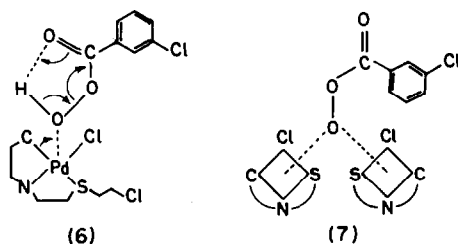
Fig. 4. Variable temperature linear plots of observed rate constant (k_{obs}) versus $[m\text{-CPBA}]$ implying $k_{\text{obs}} = k[m\text{-CPBA}]$ (zero intercept).

Table 3

Rate constants and activation parameters for oxygen insertion into the Pd-C bond of PdL¹Cl (1) by *m*-CPBA

Compound	<i>T</i> (K)	10 ³ [<i>m</i> -CPBA] (mol dm ⁻³)	10 ³ <i>k</i> _{obs} (s ⁻¹)	10 ³ <i>k</i> (mol s ⁻¹)	<i>H</i> [‡] (kcal mol ⁻¹)	<i>S</i> [‡] (e.u.)
PdL ¹ Cl (1)	296	1.188	1.110(10)	0.973(14)	3.37(14)	-47(5)
		2.375	2.194(15)			
		3.563	3.301(9)			
		4.750	4.593(21)			
	301	0.972	1.085(11)	1.078(18)		
		1.453	1.597(8)			
		1.910	2.135(14)			
		2.270	2.467(20)			
306	1.188	1.529(10)	1.211(6)			
		2.375	2.946(18)			
		3.563	4.356(9)			
		4.750	5.852(22)			

entropy of activation large and negative. The transition state 6 is proposed [4,6,11]. The electron movements shown in 6 correspond to heterolytic cleavage of the O-O bond and electrophilic insertion of an oxygen atom into the Pd-C bond.



Previously we reported [1,6,11] oxygen insertion into the Pd-C bond of complexes of type 3, 4 and 5. The gross features of the mechanism are the same in all cases but there are certain differences of detail. For example, the reactions of 3 and 4 show third order behaviour, first order with respect to *m*-CPBA and second order with respect to the complex. This was rationalized in terms of an intermediate of type 7. Such a complication is absent in the cases of 1 and 5, in which each metal binds to a single *m*-CPBA molecule in the activated state. The origin of this difference is unclear at present.

Experimental

Disodium tetrachloropalladate(II) was prepared by treating palladium(II) chloride with sodium chloride in water and evaporating the aqueous solution. Commercial *m*-chloroperbenzoic acid was purified as previously reported and used after determination of the active oxygen content by iodometric titration [12,13]. All other chemicals were reagent grade and were used as received. Silica gel (60-120 mesh) (BDH) was used for column chromatography.

UV-vis spectra were recorded on a Hitachi 330 spectrophotometer and IR (4000–200 cm^{-1}) spectra on a Perkin-Elmer 783 spectrophotometer. Elemental analysis were performed with a Perkin-Elmer 240C elemental analyser.

Synthesis

Chloro-(p-tolyl-o'-(2-chloroethylthio)azobenzene-C,N,S)palladium(II) (PdL¹Cl) (1). To a solution of 2-aminothiophenol (5 g, 0.04 mol) in dry ethanol (30 cm^3) were added small pieces of clean metallic sodium (0.90 g, 0.48 mol). The mixture was stirred and heated in order to dissolve the sodium metal. 1,2-Dichloroethane (3.96 g, 0.04 mol) was then added dropwise during 15 min, and the reaction mixture was refluxed for 2 h, cooled, and poured into cold water (50 cm^3). The oil that separated was extracted with diethyl ether. Evaporation of the extract left a brown semi-solid mass which was taken up in glacial acetic acid (20 cm^3), and *p*-nitrosotoluene (4.84 g, 0.04 mol) was added in portions with constant stirring. The mixture was warmed to 323 K for 15 min and then stirred for another 8 h at room temperature. Water was added followed by extraction with a petroleum ether/benzene (3:1, v/v) mixture. The solvent was evaporated *in vacuo* and crude ligand thus obtained was used for complexation.

The crude ligand (1.5 g) in ethanol was added to an ethanol/water (1:1, v/v) solution of Na_2PdCl_4 (1 g). The mixture was stirred for 4 h at 333 K, and the dark precipitate was filtered off and washed with an ethanol/water (1:1, v/v) mixture. This product was chromatographed on a silica gel column prepared with benzene, with acetonitrile/benzene (1:4, v/v) as eluant. An orange-red band was separated and solvent was evaporated *in vacuo*. The solid was recrystallized by slow diffusion of dichloromethane solution into hexane. The yield was 0.44 g, 30% with respect to Na_2PdCl_4 . Anal. Found: C, 41.65; H, 3.20; N, 6.55. $\text{C}_{15}\text{H}_{14}\text{N}_2\text{Cl}_2\text{SPd}$ calc.: C, 41.70; H, 3.24; N, 6.45%.

Preparation of PdL²Cl (2). A solution of *m*-CPBA (90 mg, 0.39 mmol) in chloroform (20 cm^3) was added dropwise with stirring to one of PdL^1Cl (100 mg, 0.23 mmol) in the same solvent (30 cm^3). The mixture was stirred for 4 h, during which the colour of the solution changed from orange-red to pink-violet. After completion of the reaction, the solvent was evaporated off *in vacuo* and the residue thoroughly washed with ethanol/water (1:1, v/v, $5 \times 3 \text{ cm}^3$), and then with diethyl ether ($3 \times 3 \text{ cm}^3$) to remove any unchanged *m*-CPBA and *m*-chlorobenzoic acid. The dichloromethane solution (10 cm^3) of the residue was chromatographed on a silica gel column (45 \times 1 cm) prepared with benzene. The pink-violet band of PdL^2Cl was eluted by an acetonitrile/benzene (1:9, v/v) mixture. Evaporation of the solvent *in vacuo* gave a dark coloured complex in 85% yield. Anal. Found: C, 40.21; H, 3.08; N, 6.35. $\text{C}_{15}\text{H}_{14}\text{N}_2\text{Cl}_2\text{OSPd}$ calc.: C, 40.33; H, 3.14; N, 6.27%.

Kinetic measurements

Thermostatted solutions of reactants were mixed and the mixture was diluted to the required volume and transferred to an absorption cell of 1 cm path length. The increase in absorption at 530 nm was digitally recorded as a function of time. The value of A_∞ was read when the intensity change levelled off. In all experiments, the concentration of *m*-CPBA was kept high in order to give pseudo first order kinetics. The values of k_{obs} were obtained from the slopes of the plots of $-\ln(A_\infty - A_t)$ against t . The value of the second order rate constant, k , was

Table 4

Crystallographic data for PdL¹Cl (1)

Formula	C ₁₅ H ₁₄ N ₂ SCl ₂ Pd	No. of centring reflections	25
Formula weight	431.662	Centring 2θ	15–30
Crystal size (mm ³)	0.18 × 0.20 × 0.22	D _c (g cm ⁻³)	1.769
Crystal system	Monoclinic	μ(Mo-K _α) (cm ⁻¹)	16.05
Space group	C2/c	2θ limits	2–55
a (Å)	22.113(16)	h, k, l range	23, 15, ±17
b (Å)	11.152(1)	No. unique reflections	3459
c (Å)	16.051(4)	Observed data I > 3σ(I)	2478
β (°)	126.25(2)	Parameters refined	190
V (Å ³)	3192(1)	R ^a	0.0338
Z	8	R _w ^b	0.0495
		g in weighting scheme ^c	0.001
		Largest peak in final	0.35
		Fourier map (e Å ⁻³)	

^a $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^b $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. ^c $1/[\sigma^2(|F_o|) + g|F_o|^2]$.

obtained from the slope of the plot of k_{obs} against [m-CPBA]. Activation parameters were obtained from Eyring plots. The usual least-squares methods were used for data analysis [14]. At least 30 A_t -t points were used in each calculation.

X-Ray diffraction studies

Crystals suitable for X-ray work were grown by slow diffusion of dichloromethane solution into a hexane solution at 298 K. Data collection was performed on a

Table 5

Atomic coordinates (× 10⁴) for PdL¹Cl

	x	y	z
Pd	1753(1)	2436(1)	5027(1)
S	2257(1)	1181(1)	6523(1)
Cl(1)	1855(1)	4266(1)	5776(1)
Cl(2)	107(1)	1260(1)	6085(1)
N(1)	1248(2)	908(3)	3311(3)
N(2)	1557(2)	907(3)	4274(3)
C(1)	1095(3)	2067(4)	2926(4)
C(2)	1266(3)	3045(4)	3603(3)
C(3)	1080(3)	4180(4)	3193(4)
C(4)	725(3)	4373(5)	2121(5)
C(5)	582(3)	3401(5)	1494(4)
C(6)	755(3)	2250(5)	1877(4)
C(7)	517(4)	5635(5)	1694(5)
C(8)	1714(3)	-216(4)	4775(3)
C(9)	1536(3)	-1311(4)	4262(4)
C(10)	1655(3)	-2368(3)	4792(4)
C(11)	1936(3)	-2358(4)	5821(4)
C(12)	2133(3)	-1291(4)	6352(4)
C(13)	2021(2)	-212(4)	5845(3)
C(14)	1559(3)	1218(4)	6788(3)
C(15)	784(3)	1286(5)	5814(4)

Nicolet R3m/V automated diffractometer using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Relevant crystal data and data collection details are listed in Table 4.

Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was made on the basis of a Ψ -scan [15]. The position of the metal atom was determined by the heavy-atom method. All non-hydrogen atoms were located from subsequent difference Fourier maps and were refined with anisotropic parameters. The hydrogen atoms were included at calculated positions with fixed thermal parameters. Atomic coordinates are listed in Table 5. All calculations for data reduction and structure solutions were performed on a MicroVAX II computer with the SHELXTL-PLUS programs [16].

Tables of H-atom coordinates, thermal parameters, a complete list of bond distances and angles, and lists of structure factors are available from the authors.

Acknowledgments

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