Dithiocarbonate and Trithiocarbonate Complexes of Palladium(II); Crystal Structure of Pd(Ph₃P)₂(CS₂O)·CH₂Cl₂

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Dithiocarbonate, Trithiocarbonate, Palladium(II), Crystal Structure

Di- and trithiocarbonate complexes of palladium(II) have been prepared by the action of O₂ or S₈ on PdL₂(η²-CS₂) in the presence of excess L (L = phosphine ligand). ³¹P NMR data for Pd(Ph₃P)₂(CS₂O) are consistent with the presence in solution of both S,S and S,Q coordinated dithiocarbonate. An X-ray crystal structure of the dichloromethane solvate [Pd(PPh₃)₂(CS₂O)CH₂Cl₂] suggests that an equivalent disorder may occur in the solid state.

Introduction

Dithiocarbonato complexes have been synthesised by many different methods: (i) by cleaving xanthato derivatives with tertiary phosphines [1-3]; (ii) treatment of the palladium or platinum isocyanate complexes [M(PPh₃)₂(NCO)] with CS₂ and methanol (via the in situ formation of the methylxanthato ion and thus the corresponding xanthato complex, which instantaneously rearranges) [4,5]; (iii) M(PPPh₃)₂(CS₂O) (M = Pd or Pt) by reacting the corresponding dioxygen derivatives with CS₂ (via a perthiocarbonato intermediate - stable for M = Pt - which is then reduced by triphenylphosphine) [6]; (iv) Pt(PPPh₃)₂(CS₂O) by oxidation of coordinated CS₂ with SO₂ [7]; (v) Pd(PR₃)₂(CS₂O) derivatives by reacting Pd(PR₃)₄ with COS or [(PMe₃)₃PdH]BPh₄ with COS [8]; (vi) [(triphos)Co(CS₂O)] by treating [(triphos)Co(κ₂₈-S)] with alkoxide ions (RO⁻) in the presence of oxygen [9].

The preparation of trithiocarbonato complexes has generally been accomplished by treatment of the appropriate metal compounds with alkaline trithiocarbonate [1, 10] or with an excess of CS₂ [11-13]; alternatively, treatment of [(triphos)Co(κ₂₈-S)] with RO⁻ in the presence of S₈ leads to the formation of the corresponding neutral trithiocarbonate [9].

In the present paper, we describe the preparation of palladium dithio- and trithiocarbonato complexes by the reaction of PdL₂(η²-CS₂) derivatives with O₂ or S₈ in the presence of an excess of the ligand L. An X-ray diffraction study of Pd(Ph₃P)₂(CS₂O) suggests a formulation as a mixture of S,S- and S,Q-dithiocarbonato isomers.

Results and Discussion

The following reactions (1) and (2) in benzene/CS₂ lead to the isolation of the corresponding dithio- or trithiocarbonato complexes

\[ \text{PdL}_2(\eta^2-\text{CS}_2) + O_2 \rightarrow \text{PdL}_2(\text{CS}_2\text{O}) + OL \]  
L = PPh₃, PEtPh₂, PCy₃  

(1)

\[ \text{PdL}_2(\eta^2-\text{CS}_2) + S_8 \rightarrow [\text{PdL}_2(\text{S}_8\text{CS}_2)] + L \]  
PdL₂(S₈CS) + SL  
L = PPh₃, PEtPh₂; L₂ = dpe, dpb  

(2)

In the first case the resulting dithiocarbonato compounds are mixed with OL, as may be seen from their IR spectra, which in the 1200 cm⁻¹ region show absorptions characteristic of the stretching vibration ν(O=P) [14]. The separation can be accomplished by repeatedly washing with diethyl ether, in which the palladium complex is insoluble. As may be seen from the following, the isolated complexes (I-III), whose elemental analyses are
given in Table I, seem to be a mixture of Ρ,索尼- and Ρ,索尼- S0-dithiocarbonates which even by chromatographic methods could not be resolved.

Their IR spectra show absorptions assignable to the Ρ,索尼-dithiocarbonato ligand, which are in excellent agreement with literature data [6], with other absorptions in the 1060–1050 and 860–850 cm⁻¹ region which are not assignable to internal vibrations of the neutral ligand L. The first band can be assigned to the stretching vibration ν(C–S) (see below under trithiocarbonato complexes) thus indicating a mixture of Ρ,索尼- and Ρ,索尼-O-dithiocarbonates as a result of reaction (1).

The 31P NMR spectrum of Pd(PPh₃)₃(CS₂O) shows three different groups of signals with very close chemical shifts: a singlet at δ 33.7 and an AB system (J 36 Hz; δ 31.1, 32.1 ppm) (referred to 85% H₃PO₄) which should correspond to two coupled phosphorus nuclei in very similar environments. This would be in accordance with the presence of a mixture of Ρ,索尼- and Ρ,索尼-O-dithiocarbonato isomers.

Treatment of benzene solutions of compounds of the type PdL₃(eq. 2-CS₂) with S₈ (in N₂ atmosphere) and subsequent addition of an excess of phosphine (eq. (2)) leads to the formation of the trithiocarbonato complexes and phosphine sulphide. The existence of the latter is confirmed by an absorption assignable to ν(P=S) [15] in the 640 cm⁻¹ region of the IR spectrum of the crude product. In most cases, the complexes can be purified by washing with diethylether, which dissolves SPR₂. For L₃ = 1,4-bis(diphenylphosphino)butane, dpb, the product was purified by column chromatography. The analytical results are collected in Table I.

As Coucouvanis and Fackler [16] have shown, addition of 31S to a bis(trithiocarbonato)Ni(II) complex yields only a perthiocarbonato derivative, even with excess sulphur, whilst reduction with an excess of phosphine quantitatively re-forms the starting complexes. In our case, IR spectroscopy proved that addition of sulphur to compounds of the type PdL₃(eq. 2-CS₂) and subsequent reduction with an excess of phosphine also yields only the trithiocarbonato complexes; absorptions assignable to complexes containing CS₂ or CS₃ groups (resulting form a further reduction of the intermediate products) could not be observed. The IR spectra of the trithiocarbonato complexes show, along with vibrations arising from the different ancillary ligands, a strong band at ~1050–1040 cm⁻¹ assignable to ν(C=S exo) together with another absorption at 895–855 cm⁻¹ (medium or weak) which is assignable to the νasym(C=S) stretching vibration of the C and S atoms coordinated to the palladium [1, 3]. The absorptions arising from the symmetric stretching vibration of the C and S atoms of the ring are masked by several bands due to internal vibrations of the neutral ligands L, thus preventing an unambiguous assignment. Pd(PPh₃)₃(CS₂) shows five absorption bands in the 540–480 cm⁻¹ region, one of them due to the stretching vibration ν(C=S) whilst the other four are assignable to internal vibrations of the PPh₃ ligand. This confirms, according to Mastin [17].

Table I. Analytical data for the complexesa.

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<th>Complex</th>
<th>C [%]</th>
<th>H [%]</th>
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<td>Pd(PPh₃)₃(CS₂O)</td>
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<td>4.68 (4.53)</td>
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Notes: a All the complexes contain solvent, which in some cases can be removed by carefully heating in vacuo, whilst in other cases this leads to decomposition.

Table II. 2νas(C=S) ν(C=O) νas(C=S) cm⁻¹ of PdL₃(eq. 2-CS₂) (absorptions of the Ρ,索尼-dithiocarbonato ligand).

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<td>1605 vs</td>
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the cis-position of the two triphenylphosphine molecules.

The $^{31}$P NMR spectrum of Pd(PPh$_3$)$_2$(CS$_2$) shows a signal at 29.7 ppm, which indicates that both phosphines are equivalent.

**Experimental**

C, H analyses were determined with a Perkin-Elmer 240 microanalyzer. IR spectra were recorded (at 4000–200 cm$^{-1}$) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on a Varian FT. 80 A.

**a) Synthesis of PdL$_2$(CS$_2$O)**

(L = PPh$_3$, PPh$_2$PC$_3$)

To a solution of 0.5 mmol of PdL$_2$(η$_2$-CS$_2$) in 10 ml of benzene were added 2 ml of CS$_2$, and O$_2$ was bubbled through for 12 h. After adding 0.5 mmole of L, the resulting solution was evaporated to ~5 ml, and 10 ml of ether were added. The resulting precipitate was filtered off and washed with two portions of ether. The product was recrystallised from dichloromethane/ether. (Yields = 80%, 92%, 75% respectively.)

**b) Synthesis of PdL$_3$(CS$_2$) (L = PPh$_3$, PPh$_2$H$_2$)**

To a solution of 0.5 mmol of PdL$_3$(η$_2$-CS$_2$) in 15 ml of benzene and 3 ml of CS$_2$ was added 0.0321 g (0.125 mmol) of S$_8$. After 5 min stirring 0.5 mmol of L was added and the stirring was continued for 48–72 h.

For L = PPh$_3$ the resulting suspension was filtered and the solid was washed with 3 × 10 ml of Et$_2$O and finally recrystallised from CH$_2$Cl$_2$/ethanol (yield: 70%).

For L = PPh$_2$H$_2$ the solution was evaporated to dryness and the resulting solid was extracted with CH$_2$Cl$_2$ and crystallised by partial evaporation and addition of ethanol. The compound was finally washed with ethanol (yield: 45%).

$L_2 = dpe$, dbp: To a solution of 0.5 mmol of L$_2$Pd(η$_2$-CS$_2$) in 15 ml of benzene and 3 ml of CS$_2$ was added 0.0321 g (0.125 mmol) of S$_8$. The mixture was stirred for 96 or 72 h respectively. The resulting solution was evaporated to dryness and the residue was extracted with 10 ml of CHCl$_3$. 0.6 or 1 mmol respectively of L$_2$ was added whilst the stirring at room temperature was continued for 3 h.

For L$_2 = dpe$ the solution was evaporated to dryness and the residue was treated with 10 ml of acetone. Subsequent filtration and washing of the solid with 2 × 5 ml of ether gave a 75% yield.

For L$_2 = dbp$ the resulting chloroform solution was partially evaporated and 15 ml of Et$_2$O were added to crystallise the compound together with phosphine sulphide. The latter was removed by chromatography in Florisil columns, eluted with a mixture of benzene/dichloromethane (1:2).

**X-ray Structure Determination of Pd(PPh$_3$)$_2$(CS$_2$O) · CH$_2$Cl$_2$**

Red prisms were obtained on recrystallisation from dichloromethane/n-hexane. A crystal 0.7 × 0.3 × 0.1 mm was used to collect 4,943 profile fitted intensities [18] in the range $7^\circ < 2\theta < 45^\circ$ on a Stoe four-circle diffractometer (monochromated MoK$_\alpha$ radiation). After Lp corrections, averaging equivalents gave 4738 unique reflections, 3812 of which with $F > 4\sigma(F)$ were used for all calculations.

Crystal data: triclinic, space group P1, $a = 1103.6(4)$, $b = 1343.4(5)$, $c = 1368.5(5)$ pm, $\alpha =$...
94.77(3), β = 94.57(3), γ = 113.64(3)°, U = 1.8371 nm³, 
Z = 2, μ(MoKα) = 0.7 mm⁻¹.

The structure was solved by the heavy atom 
method and refined to R = 0.059, Rw = 0.057 
(weighting scheme w⁻¹ = σ²(F) + 0.0007 F²). All 
non-hydrogen atoms except solvent C were refined 
anisotropically; phenyl H were included in 
the refinement using a riding model (C–H 96 pm, U(H) = 
1.2 U(C)). Final atom coordinates, thermal pa-
rameters and selected molecular dimensions are given 
in Tables III, IV.

Table III (continued).

Anisotropic temperature factors (pm² × 10⁻¹).

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Table IV. Bond lengths (pm) and angles (deg.).
(Dimensions of phenyl rings omitted.)

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd–S(1)</td>
<td>234.0(4)</td>
</tr>
<tr>
<td>Pd–S(2)</td>
<td>232.0(3)</td>
</tr>
<tr>
<td>P(1)–Pd</td>
<td>230.3(3)</td>
</tr>
<tr>
<td>C(1)–Pd</td>
<td>174.3(8)</td>
</tr>
<tr>
<td>C(1)–O</td>
<td>138.4(11)</td>
</tr>
<tr>
<td>C(1)–Pd</td>
<td>182.3(7)</td>
</tr>
</tbody>
</table>

A notable feature of the structure is the apparent 
asymmetry of the dithiocarbonate ligand; thus 
C–S bond lengths are 174, 178 pm, S–C–O angles 
122, 130°. Furthermore, the C–O bond is unex-
pectedly long (138 pm) and the C and O atoms show 
usually anisotropic thermal parameters (see Fig. 1).

A perspective view of the Pd(Ph₃P)₂(CS₂O) 
molecule; phenyl carbons are shown as circles of 
arbitrary radius, other atoms as 50% probability 
thermal ellipsoids.
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anisotropic O] and K[Rh(PhMe$_2$P)$_2$(CS$_2$O)$_2$]-3H$_2$O [19; C–O 126, 125 pm, S–C–O 123, 126, 123, 126°, C–S 172, 172, 172, 174 pm in two independent molecules, isotropic light atoms]. We would suggest that the deviations from ideal geometry in our Pd(Ph$_3$P)$_2$(CS$_2$O) structure are at least partially to be accounted for by a degree of disorder between S,S and S,O bonding modes of the dithiocarbonate, as observed in the solution NMR spectrum (see above).

The complex shows the expected planar geometry; the Pd atom lies 2 pm out of the S$_2$P$_2$ plane. The thiocarbonate is also planar (max. deviation 0.02 Å) and makes an angle of 7° with the PdS$_2$P$_2$ plane.