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A General Approach to the Synthesis of Neutral and Cationic Binuclear Trithiocarbonato-Bridged Complexes of Palladium(II) or of Palladium(II)–Platinum(II)

RAFAEL USON*, JUAN FORNIES, MIGUEL A. USON and MARI A. ORTA

Department of Inorganic Chemistry, University of Saragossa, Saragossa, Spain

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Addition (1:2) of Tl_2CS_3 to solutions of perchloratocomplexes of palladium(II) $Pd(OClO_3)(C_6F_5)(PR_3)$ leads to neutral binuclear derivatives of the type $(PR_3)(C_6F_5)Pd(\mu\text{-}S_2CS)Pd(C_6F_5)(PR_3)_2$, whilst the reaction of perchloratocomplexes of palladium(II) or platinum(II) with the neutral $Pd(\eta^2\text{-}CS_3)(PR_3)_2$ affords cationic complexes of the type $[L_2Pd(\mu\text{-}S_2CS)M(C_6F_5)L_2]ClO_4$ (M = Pd or Pt). Spectral data (IR and ^{31}P, NMR) permit the inequivocal structural characterization of both the neutral and the cationic complexes.

Introduction

The field of mononuclear trithiocarbonatocomplexes has been reviewed [1] and further derivatives have since been reported [2–5]. Nevertheless, only six different types of binuclear CS_3-bridged derivatives are so far known [3–7], involving preferently first series transition metals. Only one paper refers to a tetranuclear CS_3-bridged rhenium compound [8], whilst another describes the preparation of polynuclear palladium derivatives [9]. Some of these compounds are the unexpected outcome of reactions [3, 7, 8] between metal carbonyls and CS_2, whereas others were purposefully synthetized, for instance, by the reaction [6] of $NiI(NO)(PPh_3)_2$ with $BaCS_3$ or by addition [4, 5] of electronically and coordinatively unsaturated metal complexes to mononuclear trithiocarbonatoderivatives.

A general preparative approach to the synthesis of binuclear CS_3-bridged complexes has hitherto been lacking, and no second or third series transition metal is present in the reported complexes (with the exception of the unexpectedly obtained Cr–Pt complex [7]).

In the present paper we describe how neutral and cationic CS_3-bridged palladium and palladium–platinum complexes are prepared by methods which can probably also be extended to other cases.

Results and Discussion

Neutral Binuclear CS_3-bridged Palladium(II) Complexes

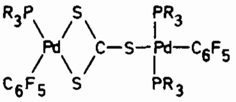
Addition (1:2) of a palladium(II) perchlorato complex to Tl_2CS_3 in benzene solution leads to precipitation of $TlClO_4$ and to formation of a solution of the binuclear complexes (**I**–**IV**) (eqn. 1):

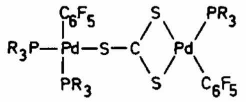
$$2Pd(OClO_3)(C_6F_5)(PR_3)_2 + Tl_2CS_3 \longrightarrow 2TlClO_4\downarrow + PR_3 + Pd_2(\mu\text{-}S_2CS)(C_6F_5)_2(PR_3)_3$$

$$PR_3 = PEt_3(\mathbf{I}),\ PEt_2Ph(\mathbf{II}),\ PMePh_2(\mathbf{III}),\ PPh_3(\mathbf{IV}) \qquad (1)$$

which can be isolated upon vacuum-evaporation of the solvent and eventual recrystallization (yields, elemental analyses and conductivities for complexes **I**–**IV** are listed in Table I).

From a structural point of view five structures (A–E) are plausible, all of them consistent with the analytical and conductance data


(A)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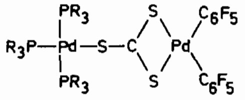
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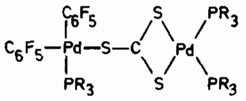
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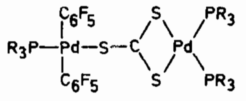
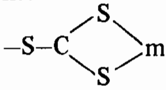

(E)

Only very little information can be drawn from the IR spectra of complexes **I**–**IV**, which show bands arising from the internal vibration [10, 11] of the C_6F_5 group and the neutral ligands. Attending to literature data [4–8], the absorptions due to the  moiety bridging the two metal atoms are

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical Results[a], Conductivity[b] and Yields for the New Complexes.

		C	H	Λ_M	Yield
(I)	$(C_6F_5)(PEt_3)_2Pd(\mu\text{-}SCS_2)Pd(PEt_3)(C_6F_5)$	37.55 (36.9)	4.7 (4.5)	nil	58
(II)	$(C_6F_5)(PEt_2Ph)_2Pd(\mu\text{-}SCS_2)Pd(PEt_2Ph)(C_6F_5)$	45.4 (44.75)	4.05 (3.95)	nil	53
(III)	$(C_6F_5)(PMePh_2)_2Pd(\mu\text{-}SCS_2)Pd(PMePh_2)(C_6F_5)$	50.55 (49.75)	3.35 (3.15)	nil	37
(IV)	$(C_6F_5)(PPh_3)_2Pd(\mu\text{-}SCS_2)Pd(PPh_3)(C_6F_5)$	55.8 (55.8)	3.35 (3.15)	nil	65
(V)	$[(C_6F_5)(PEt_3)_2Pd(\mu\text{-}SCS_2)Pd(PEt_3)_2]ClO_4$	34.55 (35.1)	5.55 (5.7)	114	76
(VI)	$[(C_6F_5)(PEt_2Ph)_2Pd(\mu\text{-}SCS_2)Pd(PEt_2Ph)_2]ClO_4$	44.55 (45.05)	4.8 (4.8)	109	83
(VII)	$[(C_6F_5)(PMePh_2)_2Pd(\mu\text{-}SCS_2)Pd(PMePh_2)_2]ClO_4$	51.15 (51.05)	4.05 (3.8)	117	83
(VIII)	$[(C_6F_5)(PPh_3)_2Pd(\mu\text{-}SCS_2)Pd(PPh_3)_2]ClO_4\cdot\frac{1}{2}CH_2Cl_2$	56.85 (56.85)	4.15 (3.65)	114	81
(IX)	$[(C_6F_5)(PEt_3)_2Pt(\mu\text{-}SCS_2)Pd(PEt_3)_2]ClO_4$	32.85 (32.4)	5.2 (5.25)	110	69
(X)	$[(C_6F_5)(PEt_2Ph)_2Pt(\mu\text{-}SCS_2)Pd(PEt_2Ph)_2]ClO_4$	42.85 (42.1)	4.3 (4.5)	111	64
(XI)	$[(C_6F_5)(PMePh_2)_2Pt(\mu\text{-}SCS_2)Pd(PMePh_2)_2]ClO_4$	47.5 (48.0)	3.4 (3.55)	125	80

[a]Calculated values in parentheses. [b]In acetone.

TABLE II. Some I.R. Relevant Data.

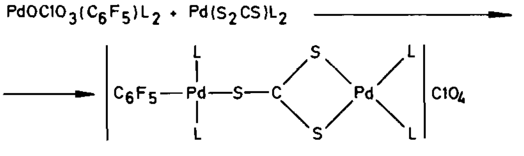
	CS_3 (bridge)	C_6F_5	Phosphine
(I)	1000(vs), 915(s)	1500(vs), 1065(sh), 1060(vs), 1035(vs), 950(vs), 775(s,br)	1095(s,br), 470(w), 410(w,br)
(II)	1000(s), 920(s)	1500(vs), 1055(s), 1045(s), 1030(s), 950(vs), 780(s), 770(s)	1435(vs), 1105(m), 505(m), 495(s)
(III)	995(m), 910(s)	1500(vs), 1060(sh), 1050(s), 1040(s), 945(vs), 775(s,br)	1435(vs), 1100(vs), 980(vs), 970(s), 510(vs), 505(vs), 475(s), 445(s)
(IV)	995(vs), 920(s)	1495(vs), 1055(br,s) 950(vs), 785(s), 770(s)	1445(vs), 1435(vs), 1100(s), 530(s), 520(vs), 510(vs), 495(s,br)
(V)	1010(vs), 1000(vs), 905(m)	1495(s), 1050(m), 1030(s), 955(s), 785(m)	1415(m), 760(s)
(VI)	1000(vs, br), 910(m)	1495(m), 1055(s,sh), 1045(s,sh), 1030(m), 955(s), 770(m)	1435(s), 755(s,sh), 670(s), 500(m)
(VII)	1000(vs,br), 905(m)	1495(s), 1045(s,sh), 1055(s,sh), 955(s), 780(m)	1435(vs), 890(vs,br), 690(vs), 505(s), 485(s), 450(s), 425(w)
(VIII)	1010(vs), 995(vs), 915(m)	1495(s), 1055(s,sh), 1045(s,sh), 955(s), 780(m)	1435(s), 745(s), 740(s), 705(s), 690(vs), 535(s), 525(vs), 515(vs), 500(s)
(IX)	1015(vs), 1005(vs), 910(m)	1500(s), 1065(s), 1035(s) 960(vs), 795(s)	1420(s), 765(vs)
(X)	1005(vs,br), 915(m)	1495(m), 1060(m), 1030(m), 955(s), 795(w)	1435(vs), 770(m), 695(s), 495(m), 465(w)
(XI)	1000(vs,br), 920(m)	1500(s), 1060(m), 955(s), 795(w)	1435(vs), 890(s), 695(s), 505(m), 485(m), 450(w)

expected to appear in the 1050–900 cm^{-1} region, and the four complexes exhibit two absorptions (at 1000–995(vs) and 920–910(s) cm^{-1}) assignable to this ligand (see Table II). Since bands due to the C_6F_5 group are also located in the 1050–1030 and 950 cm^{-1} regions it cannot entirely be ruled out that some absorptions due to (μ-CS_3) could be masked by those arising from the perhaloaryl group; however, the absorption band at ~950 cm^{-1} is sharp and presents neither an asymmetry nor a shoulder.

The ^{31}P NMR spectrum of complex **I** presents more conclusive information, showing two signals (multiplets) of relative intensities (2:1) at $\delta_1 = 24.2$ and $\delta_2 = 17.0$ ppm. The complexity of both signals, arising from the coupling with the ^{19}F nuclei of the C_6F_5 ligands, requires that each Pd atom must be linked to a C_6F_5 group, thus ruling out structures C, D and E. Besides, the signal at higher field is caused by two mutually *trans*, magnetically equivalent ^{31}P nuclei, thus excluding structure B. Therefore, structure A can unambiguously be assigned to complexes (I–IV).

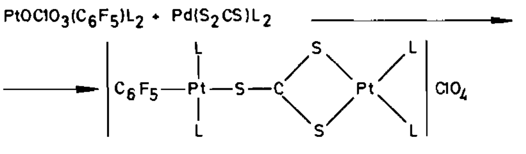
Cationic Binuclear CS_3-bridged Pd(II) or Pd(II)–Pt(II) Complexes

The S_2CS ligand when acting as a chelate in mononuclear palladium(II) complexes of the type $Pd(S_2CS)L_2$ still has an exocyclic S atom which, owing to its nucleophilic character, is a potential donor. Therefore it can be used to displace the weak -OClO_3 ligand in perchloratocomplexes of palladium(II) or platinum(II) to give cationic homo- or heteronuclear binuclear CS_3-bridged complexes, as represented in eqns. 2 and 3:



(2)

L = PEt$_3$(V), PEt$_2$Ph(VI), PMePh$_2$(VII), PPh$_3$(VIII)



(3)

L = PEt$_3$(IX), PEt$_2$Ph(X), PMePh$_2$(XI)

Addition of the neutral monomeric trithiocarbonates to *in situ* prepared solutions (in benzene for Pd and in dichloromethane for Pt derivatives) of the perchlorato complexes leads to the formation of the cationic complexes. Yields, elemental analyses and conductivities (corresponding to 1:1 electrolytes in acetone) for complexes (V–XI) are collected in Table I.

Table II lists the two or three absorption bands in the 1000–900 cm^{-1} region assignable to the bridging CS_3 moiety, along with the most important and characteristic absorptions due to the C_6F_5 group and the neutral ligand. Moreover, all the complexes show absorptions at 1090(vs,br) and 620(s–m) cm^{-1} arising from the ClO_4^- (T_d) [12], confirming the displacement of the $OClO_3$ ligand (C_{3v}) in reactions 2 and 3. The very strong absorptions at ~1000 cm^{-1}, assignable to ν(C=S), are shifted towards lower energies relative to their location in the parent compound owing to the weakening of the $C-S_{(exo)}$ bond upon coordination.

The ^{31}P NMR spectrum of complex (V) shows two signals: one complex multiplet at $\delta = 17.4$ ppm, again assignable to the coupling of the ^{19}F nuclei, along with a singlet at $\delta = 22.3$ ppm corresponding to the P nuclei linked to the Pd atom which does not contain any C_6F_5 group in its coordination sphere. Integration of both signals shows that the same number of ^{31}P nuclei are associated with each Pd atom.

Furthermore, the ^{31}P NMR spectrum of complex (XI) also shows two groups of signals: one, centered at $\delta = 21.7$ ppm with ^{195}Pt satellites ($^5J_{Pt-P} = 15.4$ Hz) assignable to the P nuclei linked to the Pd atom, and another one located at $\delta = 12.1$ ppm with ^{195}Pt satellites ($^1J_{Pt-P} = 1200$ Hz). The signals assigned to the P nuclei linked to Pt do not show any coupling with ^{19}F, in agreement with previous observations for analogous Pt compounds [13, 14].

Experimental

All reactions were carried out at room temperature using solvents purified by standard procedures.

$PdCl_2L_2$ [15], $Pd(C_6F_5)ClL_2$ [16], $Pt(C_6F_5)ClL_2$ [17] and Tl_2CS_3 [18] were prepared as described elsewhere.

C and H analyses were made with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. The ^{31}P NMR spectra were recorded on a Varian FT-80A and phosphoric acid (85%) was used as external standard. Molar conductivities of the binuclear complexes were determined in 5×10^{-4} *M* acetone solution with a Philips PW 9509 conductimeter using a PW 9510 cell.

$Pd(S_2CS)L_2$

Though the preparation of these complexes has already been reported [2d], the following procedure leads to consistently higher yields (>85%). All the complexes give satisfactory analyses and IR spectra.

Under nitrogen $PdCl_2L_2$ (1 mmol) and Tl_2CS_3 (0.5169 g, 1 mmol) in 40 ml of deoxygenated CH_2Cl_2 were stirred for 24 hr. The formed TlCl was filtered off and the filtrate was evaporated to dryness. After extraction with 20 ml of ether the yellow solid was filtered off, washed with 4 ml of ether and vacuum-dried.

$(C_6F_5)LPd(\mu\text{-}S_2CS)PdL_2(C_6F_5)$

In the absence of light $PdL_2(C_6F_5)Cl$ (0.25 mmol) and $AgClO_4$ (0.0518 g, 0.25 mmol) in 30 ml of benzene was stirred for 1 hr. The precipitated AgCl was subsequently filtered off. Tl_2CS_3 (0.064 g, 0.125 mmol) was added and left to react for 72 hr. The formed precipitate was filtered off, and the filtrate was vacuum-concentrated to dryness. The residue was extracted with chloroform, the solution was concentrated and 3 ml of ethanol was added. The formed yellow solid was filtered off and vacuum-dried.

$[L_2Pd(\mu\text{-}S_2CS)PdL_2(C_6F_5)]ClO_4$

In the absence of light $Pd(C_6F_5)ClL_2$ (0.25 mmol) and $AgClO_4$ (0.0518 g, 0.25 mmol) in 25 ml of benzene was stirred for 1 hr. The formed AgCl was removed by filtration and 0.25 mmol of $Pd(S_2CS)L_2$ was added to the filtrate and stirred for 3 hr. After evaporating to dryness 20 ml of ether was added and the yellow residue was filtered off, washed with 3 ml of ether and vacuum-dried.

L = PEt_3 was recrystallized from acetone/ether. L = PEt_2Ph from $CHCl_3$/hexane and L = PPh_3 from $CHCl_3$/ethanol.

$[L_2Pd(\mu\text{-}S_2CS)PtL_2(C_6F_5)]ClO_4$

Protected from light, $Pt(C_6F_5)ClL_2$ (0.25 mmol) in 25 ml of dichloromethane was stirred with $AgClO_4$ (0.0518 g, 0.25 mmol) for 4 hr. After removing the precipitated AgCl, $Pd(S_2CS)L_2$ (0.25 mmol) was added to the filtrate and stirred for 13 hr. The solution was concentrated to dryness, the residue was extracted with 20 ml of ether and the resulting yellow solid was washed with two 10 ml portions of ether.

The complex with L = PEt_3 was recrystallized from ethanol/hexane, with L = PEt_2Ph and $PMePh_2$ from acetone/ether.

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