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The preparation and characterisation of platinum and palladium phosphine thiocarbonate complexes $M(PR_3)_2(CS_3)$ and $Pt(PR_3)_2(CSeS_2)$

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Abstract

Reaction of CS_2 with $NH_3(liq)$ gives the $(CS_3)^{2^-}$ dianion which undergoes in situ reaction with $MCl_2(PR_3)_2$ to give $M(PR_3)_2(CS_3)$. X-ray analysis of four examples (M=Pt, PR₃=PMe₃, PMe₂Ph, PPh₃, dppp) reveals square planar coordination with the $[CS_3]^{2^-}$ dianion being effectively in the same plane as the coordination sphere. The first example of a $[CSeS_2]^{2^-}$ complex is also reported. ©2000 Elsevier Science Ltd All rights reserved.

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1. Introduction

Sulfur donor ligands have been investigated by a number of groups for both academic and industrial reasons including their use in lubricant additives [1], metal specific coordination [2] and bioinorganic chemistry [3]. Although there is a wide range of organosulfur systems [4], and more recently S-P-N-P-S systems [5-8], there is surprisingly little information [9-12] on perhaps the simplest anionic sulfur chelate, $[CS_3]^{2-}$. We have been interested in the incorporation of sulfur-rich ligands into complexes for a number of reasons [13,14], and the thiocarbonate ligand has the attraction of giving complexes with exocyclic sulfur atoms which could be important in the formation of molecular metals as a result of weak interactions to other species in the solid state [15]. There was a recent report on the synthesis of (diphosphine)platinum(II) carbonate complexes [16] and this has prompted us to describe our work on the related thiocarbonate compounds. In this work we describe a facile synthesis of $[CS_3]^{2-}$ together with the formation of a range of $M(PR_3)_2(CS_3)$ (M=Pd, Pt) complexes. The complexes have been characterised by NMR and vibrational spectroscopy; in addition, the X-ray structures of selected examples are reported.

2. Experimental

2.1. General

Diethyl ether, petroleum ether (60–80°C) and tetrahydrofuran were purified by reflux over sodium and distillation under nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Chemicals were purchased from Aldrich and Lancaster and were used as received. The compounds [PdCl₂cod] and [PtCl₂cod] [17] were prepared using literature procedures.

Infrared spectra were recorded from KBr discs on a Perkin-Elmer system 2000 spectrometer; ³¹P NMR spectra were recorded on a Jeol FX90Q operating at 36.21 MHz; ¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker instruments operating at 250, 62.9 and 101.3 MHz, respectively. Fast atom bombardment mass spectra were obtained by the Swansea Mass Spectrometer service.

2.2. Synthesis of 1-8

Carbon disulfide (5–10 ml) was placed into a Schlenk tube and cooled to -78° C. NH₃ was bubbled into the cooled CS₂ until two distinct layers were formed (ca. 10 min), a clear bottom layer and a blood red top layer containing the CS₃^{2–} anion. MCl₂(bis-phosphine), M = Pd, Pt (100–130 mg) was added as a solid and the mixture was stirred magnetically for

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2 h at -78° C and then slowly warmed to room temperature with continual stirring until the excess NH₃ had evaporated. The resulting bright orange residue was placed under vacuum for 1 h then extracted with 3×20 ml portions of dichloromethane. The combined extracts were reduced in volume to approximately 10 ml, and 60–80 petroleum ether (ca. 40 ml) was added slowly to the stirred solution to precipitate the product. The bright yellow solid was collected by suction filtration, washed with a small amount of methanol (5 ml) and diethyl ether (1 ml), and dried overnight in vacuo. Yield 70–90% based on metal used.

2.3. Synthesis of 9 and 10

Tetrabutylammonium borohydride (0.144 g, 0.560 mmol) and elemental selenium (0.022 g, 0.279 mmol) were heated to 40° C under a nitrogen atmosphere in dry thf (50 cm^3) for 4 h or until the reaction mixture was colourless. The mixture was then cooled to -78° C (cardice/acetone) and 11.9 cm³ of a 1.78×10^{-3} M solution of CS₂ in thf (0.021 g, 0.276 mmol) was added and the solution stirred for 30 min, resulting in a bright red coloured solution. To this was added solid $PtCl_2(PMe_2Ph)_2$ (0.151 g, 0.278 mmol) and the mixture was stirred for 1 h at -78° C and 1 h at room temperature, giving a bright orange solution containing a light colourless precipitate. The precipitate was removed by filtration through celite and the filtrate was evaporated to dryness leaving an oily dark orange residue. The crude product was taken up into a small volume of dichloromethane $(1.5-2 \text{ cm}^3)$ and diethyl ether (40 cm³) was added with stirring to give an orange precipitate. The product was collected by suction filtration, washed with ice cold methanol (2 cm^3) followed by diethyl ether $(2 \times 5 \text{ cm}^3)$ and dried in vacuo. Yield 0.091 g, 52%.

2.4. X-ray crystallography

Details of the structure determination of 1–5 are given in Table 1. X-ray diffraction measurements were made with graphite-monochromated Mo K α X-radiation ($\lambda = 0.71073$ Å) using a Siemens SMART diffractometer or with Cu K α radiation and a Rigaku AFC7S serial diffractometer. For the SMART data, intensity data were collected using 0.3° or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT [18] program) and for the Rigaku AFC7S data were collected by ω scans over a single quadrant of reciprocal space. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F (teXsan) or F^2 (SHELXTL) for all data with $I > 3\sigma(I)$ with weights w set equal to $(\sigma_{\rm c}^2(F_{\rm o}^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_{\rm o}^2, 0) + bP]^{-1}$ $2F_{c}^{2}$]/3. The parameter x, of the form $k[1+0.001xF_{c}^{2}1^{3}/$ $\sin(2q)$]^{0.25} was refined for the SMART/SHELXTL [19] structures; the weighting scheme for the Rigaku/teXsan [20] was as previously reported [21]. All hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. Refinements converged to residuals given in Table 1. High electron densities in the final difference maps were located close to the heavy metal centre in all the determinations. In 10 the S/Se disorder of the metal bonded sites in the $[CSeS_2]^{2-}$ was refined using 50% occupancy, using anisotropic refinements with the sulfur and selenium atoms on each site sharing common coordinates. There was no indication of any contribution from a selenium occupancy for the terminal sulfur atom. All calculations were made with SHELXTL [19] or teXsan [20].

Table 1		
Details of the crystal	data and	refinements

	1	3	4	5
Empirical formula	$C_7H_{18}P_2PtS_3$	C ₁₇ H ₂₂ P ₂ PtS ₃	C _{37.5} H ₃₁ ClP ₂ PtS ₃	$C_{28}H_{26}P_2PtS_3$
Formula weight	455.4	579.6	870.3	715.7
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	<i>P</i> -1	P-1
a (Å)	9.0048(5)	11.108(1)	11.0763(2)	10.665(1)
<i>b</i> (Å)	11.0771(6)	11.427(2)	13.6100(2)	12.675(2)
c (Å)	15.2897(8)	9.053(1)	13.7719(1)	10.505(1)
α (°)		104.33(1)	81.936(1)	102.03(1)
β(°)	105.32(1)	110.86(1)	86.775(1)	103.05(1)
γ (°)		85.27(1)	66.92(1)	85.55(1)
Volume (Å ³)	1471	1040	1891	1352
Ζ	4	2	2	2
Density (calc.) $(g \text{ cm}^{-3})$	2.057	1.850	1.53	1.76
$\mu (\mathrm{mm}^{-1})$	10.15	16.3 ^a	4.05	12.7*
F(000)	864	560	858	700
Independent reflections/observed reflections	2094/1633	3101/2635	5388/4565	4021/3547
Final R_1/wR_2	0.0662/0.1863	0.050/0.047	0.0374/0.0905	0.047/0.049

^a Cu radiation. Pt(dppp)(CS₂Se), space group $P2_1/n$, a = 10.842(1), b = 15.713(1), c = 15.257(1) Å, $\beta = 106.37(1)^\circ$.

3. Results and discussion

The $(CS_3)^{2-}$ dianion is well established but not particularly well investigated. Typically the dianion is prepared by reaction of a base such as KOH with CS_2 in an inert solvent such as dimethylformamide [9]. We have found liquid ammonia to be a very useful solvent for a range of reactions [22]. Here we report a simple reaction for the preparation of $(NH_4)_2(CS_3)$ as well as for a range of $M(PR_3)_2(CS_3)$ complexes (M=Pd, Pt). Furthermore, we have determined the X-ray crystal structures of four Pt(PR_3)_2(CS_3)_2 complexes for comparison with the $(CO_3)^{2-}$ complex which was recently reported [16].

The new $[CS_3]^{2-}$ complexes were obtained by reaction of CS_2 with excess $NH_3(liq)$ followed by the appropriate $MCl_2(PR_3)_2$ species. All of the compounds gave satisfactory microanalyses and FAB mass spectra (with the expected isotopomer distributions, Table 2). In **1–8** (Tables 3 and 4) the ν (C=S) vibrations were observed at ca. 1050, and the ν (M–S) all lie close to 337 cm⁻¹ which is in accord with previous observations for related systems [10]. In the ³¹P NMR spectra the platinum complexes have δ values which are ca. 8 ppm to higher frequency than the analogous carbonate complexes [16].

The ${}^{1}J({}^{31}P-{}^{195}Pt)$ coupling constants observed for the Pt(PR₃)₂(CS₃) complexes lie in the range 2590–3145 Hz for the dppm and PPh₃ complexes, respectively and as such are generally ca. 500 Hz smaller in magnitude than those observed for the analogous carbonate complexes. The values observed here are relatively high for sulfur donor systems though there are few dianionic examples that are directly comparable.

X-ray analysis of four $Pt(PR_3)_2(CS_3)$ complexes reveals (Table 5, Fig. 1) the expected square planar geometry at platinum. The Pt–S distances appear independent of the *trans* phosphine (range 2.336(3)–2.358(2) Å), though as expected the Pt–P distances vary with the nature of the phosphine, with the PPh₃ complex having the longest Pt–P bond length. Interestingly, in Pt(dppp)(CS₃) (**5**) the Pt–P bond lengths (2.263(3), 2.266(3) Å) are substantially longer than those [16] in Pt(dppp)(CO₃) (2.216(5), 2.2149(5) Å).

Table 2

Microanalytical data (expected values in parentheses) and mass spectral data for $1\!-\!8$

Complex	С	Н	m/z
$1 [Pt(PMe_3)_2 \{CS_3\}]$	18.6 (18.5)	3.9 (4.0)	455
2 [Pt(PEt ₃) ₂ {CS ₃ }]	29.4 (28.9)	5.4 (5.6)	540
3 [Pt(PMe ₂ Ph) ₂ {CS ₃ }]	36.7 (36.2)	3.9 (3.8)	580
$4 [Pt(PPh_3)_2 \{CS_3\}]$	53.9 (53.7)	3.8 (3.7)	828
5 [Pt(dppp){ CS_3 }]	46.6 (47.0)	3.4 (3.7)	715
6 [Pt(dppm){ CS_3 }]	44.9 (45.4)	3.3 (3.2)	688
7 [Pd(dppe){ CS_3 }]	52.6 (52.9)	3.7 (3.9)	611
8 [Pd(PEt ₃) ₂ {CS ₃ }]	32.8 (34.6)	6.6 (6.7)	451
9 [Pt(PMe ₂ Ph) ₂ {CS ₂ Se}]	32.4 (32.6)	3.6 (3.5)	627
10 [Pt(dppp){ CS_2Se }]	44.4 (44.0)	3.2 (3.4)	763

Table 3 $^{31}\text{P}\{^1\text{H}\}$ NMR (36.2 MHz) and selected IR data for 1--8

Complex	δ _P (ppm)	¹ J(P–Pt) (Hz)	$\nu(C=S)$ (cm ⁻¹)	$\nu(M-S)$ (cm ⁻¹)
1	-29.4	2969	1052(vs)	395(w), 337(w)
2	5.2	3013	1057(vs)	385(w), 336(w)
3	- 19.1	3018	1060(vs)	387(w), 339(w)
4	17.9	3145	1061(vs)	386(w), 339(w)
5	-4.2	2881	1050(vs)	387(w), 339(w)
6	-51.7	2590	1047(vs)	386(w), 338(w)
7	52.0		1047(vs)	390(w), 337(w)
8	18.6		1039(vs)	375(w), 332(w)

Table 4

Table 5

 $^{31}P{^{1}H} NMR (36.2 \text{ MHz})$ and selected IR data for 9 and 10

Complex	Chemical shift (ppm)		Coupling constant (Hz)		
	$\delta({\rm P_A})$	$\delta(P_B)$	$^{1}J(\text{Pt}-P_{A})$	$^{1}J(\text{Pt}-\text{P}_{\text{B}})$	${}^{2}J(P_{A}-P_{B})$
9	- 19.5	- 17.8	3005	3028	23
10	2.8	3.4	2865	2886	33

Selected bond lengths (Å) an	d angles (°) for	$[Pt(PR_3)]$	$\{CS_3\}$	complexes

	PMe ₃ 1	PMe ₂ Ph 3	PPh ₃ 4	dppp 5
Pt-P(1)	2.263(3)	2.265(3)	2.303(2)	2.263(3)
Pt-P(2)	2.2669(4)	2.265(3)	2.280(2)	2.266(3)
Pt-S(1)	2.342(4)	2.336(3)	2.358(2)	2.47(3)
Pt-S(2)	2.354(4)	2.349(4)	2.337(2)	2.346(3)
S(1) - C(1)	1.70(2)	1.69(1)	1.731(8)	1.76(1)
S(2)-C(1)	1.756(12)	1.71(1)	1.762(7)	1.71(1)
S(3)-C(1)	1.655(12)	1.67(1)	1.630(7)	1.64(1)
S(1)-Pt- $S(2)$	73.8(2)	73.3(1)	73.74(7)	73.6(1)
P(1) - Pt - P(2)	98.7(1)	95.4(1)	98.99(6)	93.2(1)
S(1)-C(1)-S(3)	127.7(8)	125.4(8)	126.9(5)	1257(6)
S(2)-C(1)-S(3)	123.1(9)	124.1(8)	125.6(5)	126.1(6)
S(1)-C(1)-S(2)	109.2(7)	110.5(7)	107.5(4)	108.1(5)
Pt-S(1)-C(1)	89.3(4)	88.6(4)	89.3(2)	88.6(3)
Pt-S(2)-C(1)	87.6(5)	87.6(5)	89.2(3)	89.7(3)



Fig. 1. The X-ray structure of $Pt(PPh_3)_2(CS_3)$ (4).

This is presumably a consequence of the greater electronegativity of the carbonate ligand that enables the dppp to behave as a better σ donor; the same effect would also explain the difference in the ${}^{1}J({}^{31}P-{}^{195}Pt)$ coupling constants. The S-Pt-S angle in 5 $(73.6(1)^{\circ})$ is significantly less strained than the O–Pt–O angle $(65.3(5)^{\circ})$ in the carbonate complex [16]. The C–S bond lengths in the $[CS_3]^{2-}$ ligand are longer for the coordinated sulfur atoms than for the exocyclic sulfur which is as anticipated. Within the PtS₂C rings the Pt-S-C and S-C-S angles are in the range 87.6(5)-89.7(3)° and $107.5(4) - 110.5(7)^{\circ}$, respectively, reflecting the ability that sulfur has to adapt to greater angular distortion. In all of the structures the $(CS_3)^{2-}$ ligand is effectively coplanar with the coordination plane (maximum deviation for S(3) 0.29 Å in 4). There are no significant intermolecular interactions in the solid state for any of the structures.

We have also developed a synthesis of the previously unknown $[CS_2Se]^{2-}$ dianion according to Scheme 1. We made no attempt to isolate the $[Bu_4N]_2[CS_2Se]$ but used it in situ to form complexes **9** and **10**. The NMR of **9** and **10** are the expected AB type with ${}^{1}J({}^{31}P^{-195}Pt)$ couplings which are appropriate for the *trans* coordination of sulfur or selenium. Although very similar, the δ values can be assigned to phosphorus *trans* to sulfur and selenium by comparison with the δ values/coupling constants in complexes **3** and **5**. The X-ray diffraction studies on **10** clearly indicate the presence of a 50% disordered $[CS_2Se]^{2-}$ group with the selenium being bound to the platinum; however, no meaningful bond lengths and angles can be derived because of the disorder.

Supplementary data

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.





ac.uk or www:http://www.ccdc.cam.ac.uk. Any request to CCDC for this material should quote the full literature citation and the reference number 135551–135554.

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