Inorganica Chimica Acta, *117* (1986) 17–22

Nucleophilic Attack at the Carbon Atom of a Dithiocarbene Ligand by Coordinated Carbon Disulphide: The Molecular Structure of $[(dppe)IPt(\mu\text{-}C(S)SC(SMe)_2)Pt(dppe)]^+I^-$ (dppe = 1,2-bis(diphenylphosphino)ethane)

STAALE MYRVOLD, OMAR A. NASSIF, GAVIN SEMELHAGO, ALAN WALKER*

Scarborough College Chemical Laboratories, University of Toronto, 1265 Military Trail, Scarborough, Ont., M1C 1A4, Canada

and DAVID H. FARRAR*

Lash Miller Chemical Laboratories, 80 St. George Street, University of Toronto, Toronto, Ont., M5S 1A1, Canada

(Received October 17, 1985)

Abstract

Reaction of the complex $[Pt(\eta^2\text{-}CS_2)(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] with excess methyl iodide results in the formation in high yield of the dimeric complex $[(dppe)IPt(\mu\text{-}C(S)SC(SMe)_2)Pt(dppe)]^+I^-\cdot C_7H_8\cdot Et_2O$, the crystal structure of which has been determined. Crystals of the complex are monoclinic, space group $P2_1/c$, with $Z = 4$, in a unit cell with lattice parameters a = 21.082(4), b = 17.304(3), c = 21.423(3) Å, and β = 116.62(1)°. The structure has been refined to R_1 = 0.054 (R_2 = 0.059) for 4512 unique data and 333 variables. The complex consists of two distorted square-planar Pt fragments which are held together by a novel bridging $CS_2C(SMe)_2$ group. The complex has been independently prepared by the reaction of $[Pt(\eta^2\text{-}CS_2)(dppe)]$ with the carbene complex $[Pt(I)(dppe)\{C(SMe)_2\}]^+I^-$, and has been further characterized by elemental analysis, ^1H, $^{31}P\{^1H\}$ NMR, IR spectroscopy, and conductivity measurements.

Experimental

All reactions were carried out under an atmosphere of nitrogen. IR spectra were determined as KBr discs using a Nicolet 5DX FT-IR spectrometer. Proton and $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ and CH_2Cl_2 respectively using a Varian XL-200 (operating at 200 and 81 MHz) spectrophotometer. Phosphorus-31 chemical shifts were determined with reference to $P(OMe)_3$ but are reported with reference to 85% phosphoric acid; high frequency shifts are positive. Conductivities were measured in $MeNO_2$ using a Beckman RC18 Bridge circuit and microanalyses were performed by Analytische Laboratorien, F.R.G. Melting points (uncorrected) were measured on a Reichert hot-stage microscope.

X-ray Study of $[(dppe)IPt(\mu\text{-}C(S)SC(SMe)_2)Pt(dppe)]I\cdot C_7H_8\cdot Et_2O$

Yellow crystals of $[(dppe)IPt(\mu\text{-}C(S)SC(SMe)_2)Pt(dppe)]I\cdot C_7H_8\cdot Et_2O$ were obtained by recrystallization from toluene/diethylether mixtures. A photographic examination showed the crystals belonged to the monoclinic space group $P2_1/c$, C_{2h}^5, No. 14 [1]. Crystal data are presented in Table I.

TABLE I. Crystal Data and Experimental Conditions Associated with Data Collection

Molecular formula	$C_{47}H_{72}I_2OP_4Pt_2S_4$
Formula weight	1789.46
System	Monoclinic
Space group	$P2_1/c$
Cell constants	a = 21.082(4) Å
	b = 17.304(3) Å
	c = 21.423(3) Å
	β = 116.62(1)°
Cell volume	6986.8 $Å^3$
Density (calc.)	1.70 g cm^{-3}
Z	4
Radiation	Mo Kα, graphite monochromatized
μ(Mo Kα)	51.60 cm^{-1}
Wavelength	0.71073 Å
Temperature	23 °C
Approximate crystal dimensions	0.003 × 0.012 × 0.017 cm
Number and 2θ range of centered reflections	25, $17 < 2\theta < 27°$
Data collected	hkl and $hk\bar{l}$, for $0 < 2\theta < 45$
Scan mode	θ:2θ
Scan width	0.80°
Maximum scan time	70 s
Prescan rate	11 deg min^{-1}
Acceptance ratio $\sigma(I)/I$	0.04

---

*Authors to whom correspondence should be addressed.

0020-1693/86/$3.50

A crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Three standard reflections, monitored every 3.8 h, showed no decomposition had occurred during data acquisition. Details of the experimental conditions are summarized in Table I. The crystal faces were identified as {100}, {010}, (101), $(0\bar{1}\bar{1})$, and $(01\bar{1})$. A total of 7971 reflections were measured. The recorded intensities were corrected for Lorentz and polarization effects and a standard deviation $\sigma(I)$ was assigned to each intensity (I), using the data reduction program of the Enraf-Nonius SDP package [2]* An empirical absorption correction was applied to the data based on psi scans for six reflections with varying 2θ values [3]. Transmission coefficients varied from 0.809 to 1.00. Of the data collected 4512 unique data with $I > 3\sigma(I)$ were available for the determination of the structure.

The positional coordinates for the Pt atoms were obtained from a three-dimensional Patterson synthesis. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 66 non-hydrogen atoms, associated with the two ions. After several cycles of full-matrix least-squares refinement on F the model converged at $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o| = 0.067$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2} = 0.099$. A subsequent difference Fourier synthesis revealed two areas of electron density in which a toluene and a highly disordered diethylether solvent molecule were located. Although the geometry of the disordered diethylether solvent molecule is unusual, we were able to refine the model and it accounted for the majority of the electron density in that region of the unit cell. H-atoms were located for the cation only and they were included in subsequent calculations with idealized positional coordinates (either sp^2 or sp^3 geometries and a C–H bond distance of 0.95 or 1.0 Å respectively) but not refined. The refinement converged at $R_1 = 0.054$ and $R_2 = 0.059$ (4512 observations and 333 variables, Pt, I, S and P atoms refined with anisotropic thermal parameters and all remaining non-H atoms refined isotropically). In the final cycle no shift exceeded 0.11 of its standard deviation. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 1.07 e Å^{-3}, associated with the disordered diethylether solvent molecule at fractional coordinates (1.000, 0.033, 0.295). Final positional and B(iso) thermal parameters for the non-H atoms are given in Table II (see also 'Supplementary Material').

TABLE II. Positional and B_{iso} (Å^2) Thermal Parameters for the Non-hydrogen Atoms[a]

Atom	x	y	z	B
Pt(1)	0.79794(4)	0.44413(5)	0.50779(4)	2.59(2)
Pt(2)	0.74199(4)	0.71576(5)	0.57401(4)	2.62(2)
I(1)	0.92735(7)	0.49923(9)	0.54869(8)	4.37(4)
I(2)	0.66228(9)	0.0807(1)	0.3741(1)	6.02(5)
S(1)	0.7908(3)	0.5366(3)	0.6324(3)	3.8(1)
S(2)	0.7507(3)	0.6212(3)	0.5027(3)	3.8(1)
S(3)	0.8578(3)	0.6614(3)	0.7318(3)	4.2(2)
S(4)	0.7073(3)	0.6289(3)	0.6863(3)	4.3(2)
P(1)	0.6869(3)	0.3993(3)	0.4673(3)	3.0(1)
P(2)	0.8186(3)	0.3364(3)	0.4575(3)	3.1(1)
P(3)	0.7196(3)	0.8147(3)	0.6310(3)	3.1(1)
P(4)	0.7159(3)	0.8047(3)	0.4861(3)	3.2(1)
C(1)	0.778(1)	0.542(1)	0.5503(9)	3.3(5)
C(2)	0.7751(9)	0.637(1)	0.6574(9)	2.8(4)
C(3)	0.917(1)	0.677(1)	0.691(1)	6.4(7)
C(4)	0.740(1)	0.555(2)	0.753(1)	6.6(7)
C(5)	0.6855(9)	0.299(1)	0.4395(9)	3.1(4)
C(6)	0.733(1)	0.296(1)	0.4000(9)	3.6(5)
C(7)	0.724(1)	0.904(1)	0.5884(9)	3.2(4)
C(8)	0.681(1)	0.891(1)	0.508(1)	3.9(5)
C(11)	0.647(1)	0.401(1)	0.527(1)	3.7(5)
C(12)	0.613(1)	0.465(1)	0.531(1)	3.6(5)
C(13)	0.585(1)	0.468(1)	0.578(1)	6.3(7)
C(14)	0.592(1)	0.412(2)	0.622(1)	6.7(7)
C(15)	0.625(1)	0.346(2)	0.619(1)	7.1(7)
C(16)	0.652(1)	0.337(2)	0.570(1)	6.7(7)
C(21)	0.6230(9)	0.449(1)	0.3918(8)	2.4(4)
C(22)	0.650(1)	0.507(1)	0.362(1)	4.4(5)
C(23)	0.598(1)	0.542(1)	0.301(1)	4.6(5)
C(24)	0.527(1)	0.522(1)	0.273(1)	6.1(7)
C(25)	0.505(1)	0.465(1)	0.300(1)	5.2(6)
C(26)	0.551(1)	0.427(1)	0.361(1)	4.9(6)
C(31)	0.868(1)	0.261(1)	0.516(1)	4.4(5)
C(32)	0.843(1)	0.185(1)	0.510(1)	4.2(5)
C(33)	0.887(1)	0.131(1)	0.563(1)	6.4(7)
C(34)	0.953(1)	0.147(1)	0.610(1)	6.0(6)
C(35)	0.978(1)	0.222(2)	0.615(1)	6.7(7)
C(36)	0.939(1)	0.282(1)	0.567(1)	6.3(7)
C(41)	0.860(1)	0.351(1)	0.401(1)	4.1(5)
C(42)	0.839(1)	0.421(1)	0.360(1)	6.3(7)
C(43)	0.869(1)	0.424(2)	0.310(1)	7.1(7)
C(44)	0.913(1)	0.371(1)	0.305(1)	5.5(6)
C(45)	0.929(1)	0.308(2)	0.346(1)	6.6(7)
C(46)	0.905(1)	0.300(1)	0.395(1)	6.1(7)
C(51)	0.775(1)	0.832(1)	0.723(1)	4.2(5)
C(52)	0.745(1)	0.827(1)	0.770(1)	4.7(6)
C(53)	0.792(1)	0.846(1)	0.841(1)	6.0(7)
C(54)	0.861(1)	0.871(1)	0.860(1)	6.0(6)
C(55)	0.888(1)	0.876(2)	0.814(1)	6.7(7)
C(56)	0.843(1)	0.859(1)	0.742(1)	4.7(5)
C(61)	0.629(1)	0.813(1)	0.6172(9)	3.1(4)
C(62)	0.585(1)	0.750(1)	0.579(1)	4.1(5)
C(63)	0.512(1)	0.754(1)	0.563(1)	5.2(6)
C(64)	0.486(1)	0.813(1)	0.582(1)	5.9(6)
C(65)	0.525(1)	0.874(1)	0.616(1)	4.7(6)
C(66)	0.597(1)	0.877(1)	0.631(1)	4.3(5)

(continued)

---

*Run on a DEC PDP-11/23 computer.

TABLE II. *(continued)*

Atom	x	y	z	B
C(71)	0.647(1)	0.781(1)	0.400(1)	4.1(5)
C(72)	0.655(1)	0.799(1)	0.339(1)	4.1(5)
C(73)	0.596(1)	0.779(1)	0.273(1)	5.8(6)
C(74)	0.537(1)	0.748(1)	0.270(1)	5.0(6)
C(75)	0.533(1)	0.729(1)	0.329(1)	6.5(7)
C(76)	0.587(1)	0.743(1)	0.393(1)	5.4(6)
C(81)	0.792(1)	0.833(1)	0.474(1)	4.2(5)
C(82)	0.848(1)	0.783(1)	0.496(1)	4.8(5)
C(83)	0.908(1)	0.804(2)	0.488(1)	7.5(8)
C(84)	0.911(1)	0.881(2)	0.464(1)	7.2(7)
C(85)	0.855(1)	0.932(1)	0.445(1)	6.6(7)
C(86)	0.795(1)	0.908(1)	0.450(1)	4.9(6)
C(91)	0.681(2)	0.385(2)	0.107(2)	16(1)
C(92)	0.618(1)	0.407(2)	0.072(1)	8.5(8)
C(93)	0.552(2)	0.418(2)	0.078(2)	11(1)
C(94)	0.547(2)	0.398(2)	0.137(2)	13(1)
C(95)	0.622(2)	0.373(2)	0.186(2)	13(1)
C(96)	0.683(2)	0.363(2)	0.182(2)	12(1)
C(97)	0.746(2)	0.371(2)	0.122(2)	12(1)
O	0.930(2)	0.084(2)	0.345(2)	18(1)
C(101)	0.801(3)	0.153(4)	0.238(3)	12(2)
C(102)	0.846(2)	0.110(3)	0.315(2)	6(1)
C(103)	0.864(3)	0.140(3)	0.255(3)	21(2)
C(104)	0.958(2)	0.094(2)	0.266(2)	16(1)
C(105)	0.900(2)	0.136(3)	0.219(2)	7(1)
C(106)	0.015(3)	0.062(3)	0.332(3)	9(2)

[a]Estimated standard deviations in the least significant figs. are given in parentheses in this and all subsequent tables. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Preparation of the Complex [(dppe)IPt(μ-C(S)SC(SMe)$_2$)Pt(dppe)]$^+$I$^-$·2C$_7$H$_8$

Method (a)

The complex [Pt(η^2-CS$_2$)(dppe)] (0.10 g) was placed in a 50 cm^3 flask and methyl iodide (10 cm^3) added. The solid quickly dissolved to yield a dark red solution which rapidly changed colour to orange and after 2 min to a bright yellow solution. At this stage petroleum ether (75 cm^3; boiling range 60–80 °C) was added precipitating a yellow–green solid which was filtered off and washed with more petroleum ether. This crude product was redissolved in a minimum of acetone (5 cm^3) and toluene (15 cm^3), petroleum ether (2 cm^3, boiling range 100–120 °C), and absolute ethanol (1 cm^3) added. The final product crystallized overnight as a di-toluene solvate in the form of yellow–green plates. Yield 0.115 g (85%), melting point (m.p.) 175–178 °C. (*Anal.* Calc. for $C_{70}H_{70}I_2P_4Pt_2S_4$: C, 46.51; H, 3.90; I, 14.04; S, 7.10. Found: C, 46.36; H, 3.92; I, 13.88; S, 7.16%).

It should be noted that our X-ray sample contained 1 mol of toluene and 1 mol of diethyl ether in the crystal lattice.

Method (b)

The complex [PtI(dppe){C(SMe)$_2$}]$^+$I$^-$ was prepared as previously described [4]. A solution of this complex was prepared by dissolving 0.070 g (0.073 mmol) in CH$_2$Cl$_2$ (25 cm^3) to which was added [Pt(η^2-CS$_2$)(dppe)] (0.0492 g, 0.073 mmol). The initial colour of the solution was orange but changed to yellow after a few seconds and was then stirred for 30 min. Petroleum ether (100 cm^3, boiling range 60–80 °C) was then added and the yellow solid which precipitated was filtered off and washed with more petroleum ether. This solid was dissolved in acetone (5 cm^3) and toluene (15 cm^3) and petroleum ether (2 cm^3, boiling range 100–120 °C) was added. The product crystallized overnight as a di-toluene solvate in the form of yellow–green plates. Yield 0.118 g (89%), m.p. 175–178 °C.

Introduction

For a number of years we have been interested in the metal promoted activation of carbon disulphide and similar molecules. In this connection it has been observed that electrophilic attack at sulphur can result in the formation of dithioesters [5] and dithiocarbenes [6] from η^2-coordinated carbon disulphide, while nucleophilic attack at the carbon atom results in low temperature C–S bond fission [4, 7]. In this paper we report some unexpected results obtained by investigating the reaction chemistry of the complex [Pt(η^2-CS$_2$)(dppe)] recently prepared in our laboratories [4]

Results and Discussion

When the pink complex [Pt(η^2-CS$_2$)(dppe)] was treated with excess MeI in varying ratios an initial deep red solution was always formed, the colour of which changed rapidly over a period of 2 min from deep red to orange to bright yellow. It was anticipated from our previous experience [6] with η^2-CS$_2$ complexes of platinum that the yellow product isolated from this solution would have been the cationic dithiocarbene complex [Pt(I)(dppe){C(SMe)$_2$}]$^+$I$^-$. Elemental analysis of the product did not however support this formulation but was correct for a toluene solvate of a dithioester. In addition since the ^{31}P{^{1}H} NMR spectrum was very complex, indicating the presence of dimeric platinum species, a single crystal X-ray structural determination was carried out which showed the product to be the dinuclear complex [(dppe)IPt(μ-C(S)SC(SMe)$_2$)Pt(dppe)]$^+$I$^-$.

Description of the Structure

The crystals are built up from discrete ions, incorporating toluene and diethylether in the crystal. The shortest contact between the cation and the anion is 3.05 Å involving I(2) and H(86) at ($x, y - 1, z$) and the shortest inter-cation contact is 2.44 Å between the phenyl H-atoms H(24) and H(65) at (x, $1.5 - y$, $-0.5 + z$). Selected intramolecular distances are presented in Table III. A perspective view of the cation together with the atom numbering scheme is given in Fig. 1. The toluene solvent molecule is numbered C(91) to C(97) and the diethylether molecule is number C(101) to C(106) and O.

TABLE III. Selected Bond Distances and Angles

Bond	Distance (Å)	Bond	Distance (Å)
Pt(1)–I(1)	2.642(2)	Pt(2)–S(2)	2.301(5)
Pt(1)–P(1)	2.240(5)	Pt(2)–P(3)	2.272(5)
Pt(1)–P(2)	2.290(5)	Pt(2)–P(4)	2.299(5)
Pt(1)–C(1)	2.05(2)	Pt(2)–C(2)	2.10(2)
C(1)–S(1)	1.66(2)	C(2)–S(1)	1.89(2)
C(1)–S(2)	1.66(2)	C(2)–S(3)	1.81(2)
		C(2)–S(4)	1.80(2)
S(3)–C(3)	1.83(2)		
S(4)–C(4)	1.82(2)		
Bond	**Angle (deg)**	**Bond**	**Angle (deg)**
P(1)–Pt(1)–P(2)	85.6(2)	P(3)–Pt(2)–P(4)	84.6(2)
I(1)–Pt(1)–P(2)	93.6(1)	P(3)–Pt(2)–C(2)	95.7(5)
I(1)–Pt(1)–C(1)	86.5(5)	P(4)–Pt(2)–S(2)	89.6(2)
P(1)–Pt(1)–C(1)	94.2(5)	C(2)–Pt(2)–S(2)	90.6(5)
Pt(1)–C(1)–S(1)	117(1)	C(1)–S(1)–C(2)	107(1)
Pt(1)–C(1)–S(2)	120(1)	C(1)–S(2)–Pt(2)	107(1)
S(1)–C(1)–S(2)	123(1)		
		Pt(2)–C(2)–S(1)	113(1)
C(2)–S(3)–C(3)	102(1)	Pt(2)–C(2)–S(3)	115(1)
C(2)–S(4)–C(4)	104(1)	Pt(2)–C(2)–S(4)	109(1)
		S(1)–C(2)–S(3)	104(1)
		S(1)–C(2)–S(4)	107(1)
		S(3)–C(2)–S(4)	108(1)

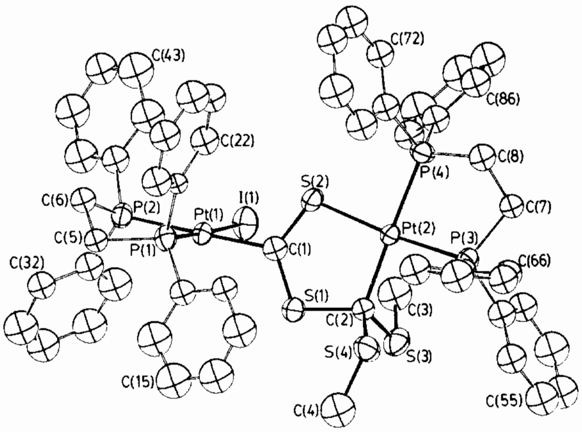

Fig. 1. An ORTEP diagram of the cation with hydrogen atoms omitted. The thermal vibrational elipsoids are represented by 50% probability contours.

The complex consists of two distorted square-planar Pt fragments which are held together by a bridging C(S)SC(SMe)$_2$ group. The largest deviation from a least-squares plane containing Pt(1) and its inner coordination sphere is 0.101(5) Å while a distance of 0.16(2) Å is observed in the same calculation for Pt(2). The Pt(1) inner coordination sphere contains I(1), the diphosphine ligand P atoms P(1) and P(2) and the carbene C atom of the bridging group, C(1). Two of the sites of the inner coordination sphere of Pt(2) are occupied by atoms associated with the bridging group, C(2) and S(2), with the diphosphine ligand P atoms completing the square plane. The angles subtended at both Pt atoms are consistent with a square planar coordination geometry. Slight deviation from the ideal 90° angles is introduced by the smaller bite angles of the chelating diphosphine ligands, 85.6(2)° at Pt(1) and 84.6(2)° at Pt(2). The Pt(1)–P distances are significantly different, 2.240(5) and 2.290(5) Å for P(1) and P(2), and this is ascribed to the differing nature of the *trans* ligands. The same effect is observed at Pt(2) where the distance to P(3) is 2.272(5) Å while that to P(4) is 2.299(5) Å. The Pt–P values for the two P atoms which are *trans* to C atoms, P(2) and P(4), are equivalent and comparable to the value 2.288(4) Å observed in the complex [Pt{C(NHC$_6$H$_4$CH$_3$)(NHC$_6$H$_3$CH$_3$)}(dppe)]ClO$_4$ [8]. The Pt(1)–C(1) distance, 2.046(18) Å, is not significantly different from the Pt–C(carbene) value 2.044(14) Å reported for the aforementioned complex [8], and is also crystallographically equivalent to the Pt(2)–C(2) (sp^3 carbon) distance, 2.099(18) Å. The Pt(1)–I(1) distance, 2.642(2) Å, is normal [9], as is the Pt(2)–S(2) value, 2.301(5) Å [10].

The bridging ligand C(S)SC(SMe)$_2$ can be formally considered as the condensation product of a CS$_2$ ligand and a C(SMe)$_2$ ligand. While this is the first example of the condensation of a CS$_2$ ligand with a C(SMe)$_2$ ligand the resulting 5-membered ring structure has been previously observed from the coupling of two CS$_2$ moieties [11, 12] and in the trithioanhydride C$_2$S$_3$ ligand [13]. The 5-membered ring is essentially planar with two alternating C and S atoms and a metal atom (largest deviation from a least-squares plane containing Pt(2) and the bridging atoms

C(1), C(2), S(1) and S(2) is 0.04(2) Å). The angles subtended at C(1) are consistent with sp^2 hybridization. The C(1)–S bond lengths are equivalent (1.66(2) Å) and shorter than a normal C–S single bond length suggesting a delocalization of electron density between the S atoms and the sp^2 C atom [10, 14]. The distances and angles associated with C(2) indicate sp^3 hybridization. This results in the S(3) atom being 1.508(7) Å below the plane defined by C(1), C(2), S(1), S(2) and Pt(2) while S(4) is 1.413(7) Å above it. Tetrahedral angles of 102(1) and 104(1)° are found at S(3) and S(4), respectively. All parameters associated with the dppe ligands are normal [8, 15].

The complex exhibits a medium-strong band in its IR spectrum at 999 cm^{-1} attributable to C=S vibrations and thus resembles closely other complexes where the presence of this five membered ring (MC_2S_2) has been structurally characterized [11–13]. The molar conductivity of a solution (10^{-3} mol dm^{-3}) of the complex in CH_3NO_2 is 79 Ω^{-1} cm^2 mol^{-1} which is consistent with 1:1 electrolyte behaviour.

The proton NMR spectrum of a sample of the complex possessing two mol of solvated toluene contained peaks of equal integrated intensity at δ = 2.33 ppm (toluene), superimposed on a broad multiplet due to the methylene groups of the dppe ligands [4], and δ = 1.92 ppm (S–Me) groups. The $^{31}P\{^1H\}$ NMR spectrum was very complex and contained four separate phosphorus resonances at δ = 44.4 (multiplet); 40.4 (unresolved broad singlet); 37.2 (distorted quartet); 35.6 (distorted doublet) ppm. By reference to Fig. 1 these resonances can easily be assigned to particular phosphorus atoms on the basis of either the large value of the ^1J(Pt–P) coupling constant (*trans* to sulphur or iodine rather than carbon [4]) or the size of the coupling to the more distant ^{195}Pt atom (their relative orientation). Thus the resonance at 40.4 ppm [^1J(Pt(1)–P) = 3457 Hz] is assigned to P(1) *trans* to the iodide atom with no observed coupling to Pt(2) except for a broadening of the base. The resonance at 44.4 ppm [^1J(Pt(2)–P) = 3126 Hz; ^4J(Pt(1)–P) = 79 Hz] is assigned to P(3), *trans* to sulphur and Pt(1). The resonance at 37.2 ppm [^1J(Pt((1)–P) = 2137 Hz; ^4J(Pt(2)–P) = 74 Hz] is assigned to P(2) *trans* to carbon(1) and Pt(2), while the remaining resonance at 35.6 ppm [^1J(Pt(2)–P) = 2071 Hz] is assigned to P(4) *trans* to carbon(2) and with no observed coupling to Pt(1) apart from a broadening of the base. The phosphorus–phosphorus coupling is complex but indicates that each of the phosphorus atoms is coupled in varying degrees to the two phosphorus atoms on the other platinum atom but there is no clear evidence for any *cis*-phosphorus coupling within the dppe ligands.

Since the five membered ring (PtC_2S_2) appears to be formed from the condensation of η^2-CS_2 and –C(SMe)$_2$ ligands and the product is formed in high yield no matter what the ratio of MeI to [Pt(η^2-CS_2)(dppe)] used, it seems likely that any dithiocarbene formed initially is subject to fast nucleophilic attack by unreacted [Pt(η^2-CS_2)(dppe)]. In order to test this hypothesis the carbene complex $[PtI(dppe)\{C(SMe)_2\}]^+I^-$ was treated with an equimolar amount of [Pt(η^2-CS_2)(dppe)] in CH_2Cl_2. Reaction occurred immediately and the yellow crystalline product isolated (89% yield) from the reaction had identical physical and spectroscopic properties to the complex $[(dppe)IPt(\mu\text{-}C(S)SC(SMe)_2Pt(dppe)]^+I^-$ described above.

While nucleophilic attack at the carbon atom of dithiocarbene ligands has been well established [4, 16] and the nucleophilic character of sulphur atoms in η^2-CS_2 complexes is also well known [5, 6, 12, 17], the above reaction represents the first report of nucleophilic attack by coordinated CS_2 on a dithiocarbene ligand. Since the reaction results in the formation of an entirely new carbene at C(1) studies are currently in progress to investigate the possibility of further condensation of [Pt(η^2-CS_2)dppe] molecules.

Supplementary Material

The anisotropic thermal parameters, H-atom parameters, some least-squares planes, a description of the solvent molecules, the bond distances and angles for the dppe ligands and the structure amplitudes have been deposited with the Editor-in-Chief.

Acknowledgements

We thank the University of Toronto and the Natural Sciences and Engineering Research Council of Canada for support of this work and N. Plavac for his assistance in recording the NMR spectra.

References

1 'International Tables for X-ray Crystallography', Vol. 1, Kynoch Press, Birmingham, 1969.

2 'Enraf-Nonius Structure Determination Package', Enraf-Nonius, Delft, 1982.

3 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24,* 351 (1968).

4 D. H. Farrar, R. R. Gukathasan, E. Ma, G. Semelhago and A. Walker, *J. Chem. Soc., Dalton Trans.,* 2595 (1985).

5 P. V. Yaneff, *Coord. Chem. Rev., 23,* 183 (1977).

6 D. H. Farrar, R. O. Harris and A. Walker, *J. Organomet. Chem., 124,* 125 (1977).

7 W. M. Hawling, A. Walker and M. A. Woitzik, *J. Chem. Soc., Chem. Commun.,* 11 (1983).

8 D. F. Christian, D. A. Clarke, H. C. Clark, D. H. Farrar and N. C. Payne, *Can. J. Chem., 56,* 2516 (1978).

9 T. J. Giordano and P. G. Rasmussen, *Inorg. Chem., 14,* 1628 (1975).

10 D. H. Farrar, R. R. Gukathasan and S. A. Morris, *Inorg. Chem., 23,* 3258 (1984).

11 M. G. Mason, P. N. Swepston and J. A. Ibers, *Inorg. Chem., 22,* 411 (1983) and refs. therein.

12 M. Cowie and S. K. Dwight, *J. Organomet. Chem., 214,* 233 (1981).

13 V. G. Albano, D. Braga, L. Busetto, M. Monari and V. Zanotti, *J. Chem. Soc., Chem. Commun.,* 1257 (1984).

14 R. E. Wagner, R. A. Jacobson, R. J. Angelici and M. H. Quick, *J. Organomet. Chem., 148,* C35 (1978).

15 D. H. Farrar and G. Ferguson, *J. Crystallogr., Spectrosc. Res., 12,* 465 (1982).

16 Y. S. Yu and R. J. Angelici, *Organometallics, 2,* 1018 (1983), and refs. therein.

17 D. H. Farrar, R. R. Gukathasan and K. Won, *J. Organomet. Chem., 275,* 263 (1984).