Preparation and X-ray Crystal Structure of $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$: a Reinvestigation of the Reaction of $S_4N_4H_4$ with $(Ph_3P)_4Pt$

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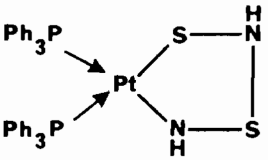
(Received December 19, 1985; revised January 24, 1986)

Abstract

The reaction of $S_4N_4H_4$ with $(Ph_3P)_4Pt$ in toluene produces the yellow complex $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$ shown by X-ray crystallography to contain a five-membered metallathiazene ring with Pt–N = 2.093(9) Å, Pt–S = 2.294(6) Å and two short [1.499(16) and 1.548(12) Å] and one long [1.702(15) Å] S–N bonds. The crystals are triclinic with space group $P\bar{1}$; $a = 11.328(2)$; $b = 12.366(2)$; $c = 16.822(3)$ Å; $\alpha = 94.12(1)$; $\beta = 108.57(1)$; $\gamma = 112.93(1)°$; $V = 2004.8(2)$ Å^3; $Z = 2$. The final R and R_w values were 0.047 and 0.058, respectively. The same complex is obtained from the reactions of $(Ph_3P)_4Pt$ with S_4N_4 or $(Ph_3P)_2PtC_2H_4$ with $S(NSO)_2$. The reaction of $NiCl_2$ with a mixture of $S_4N_4H_4$ and the Wittig reagent, $Ph_3P{=}CH_2$, produces $Ni(S_2N_2H)_2$. The mechanisms of the reactions of $S_4N_4H_4$ and S_4N_4 with electron-rich metal centres are discussed briefly.

Introduction

The coordination chemistry of tetrasulfur tetraimide, $S_4N_4H_4$, is not well developed and only two transition metal derivatives have been structurally characterized, $[Ag(S_4N_4H_4)_2][ClO_4] \cdot 1.5H_2O$ [1] and $(S_4N_4H_4)W(CO)_5$ [2]. In the former complex the silver atom is coordinated to all eight sulfur atoms of two $S_4N_4H_4$ crowns in a sandwich-type structure [1], whereas $S_4N_4H_4$ behaves as a monodentate S-bonded ligand in the latter [2]. The reaction of $S_4N_4H_4$ with tetrakis(triphenylphosphine)-platinum(0), $(Ph_3P)_4Pt$, was reported by Turner and co-workers to give the complex $(Ph_3P)_2PtS_2N_2H_2$, **1** [3], but a subsequent X-ray structural analysis of this material showed it to be $(Ph_3P)_2Pt(OSNH)_2 \cdot 0.5H_2O$, **2***, in which the OSNH ligands were bonded to platinum via oxygen [4, 5].



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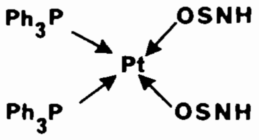

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Turner and co-workers also described the preparation of two poorly characterized compounds, green $(Ph_3P)_2PtS_4N_4$ and brown $(Ph_3P)_2PtS_2N_2$, from the reaction of equimolar quantities of $(Ph_3P)_4Pt$ with tetrasulfur tetranitride, S_4N_4, in benzene [3]. More recently, the reactions of $(Ph_3P)_2PtC_2H_4$ or $(Ph_3P)_3Pt$ with S_4N_4 have been shown by X-ray crystallography to yield the red binuclear complex $(Ph_3P)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$, **3** [6, 7].

As part of a more general survey of the chemistry of $S_4N_4H_4$ we have reinvestigated the reaction of this cyclic sulfur imide with $(Ph_3P)_4Pt$ and we report here the ^{31}P NMR spectrum and X-ray structure of the product, which is the five-membered mononuclear cyclometallathiazene**, $(Ph_3P)_2PtS_2N_2$, **4**. Furthermore, we found that the same product is obtained from the reactions of $(Ph_3P)_4Pt$ with S_4N_4 in methylene dichloride/diethyl ether or $(Ph_3P)_2PtC_2H_4$ with $S(NSO)_2$ in toluene. In view of the unusual redox chemistry exhibited by the $(Ph_3P)_4Pt/S_4N_4H_4$

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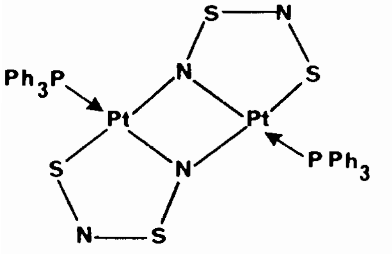
*The positions of the hydrogen atoms were not determined with certainty so the ligands could be either thionylimide, HNSO, or thiazyl-*S*-hydroxide, HOSN. However, the complex is a derivative of Pt(0) rather than Pt(II) as described in refs. 4 and 5, since both these molecules are neutral ligands.

**For a definition of the term cyclometallathiazene see ref. 8.

system, we carried out a preliminary study of the deprotonation of $S_4N_4H_4$ with mild bases e.g. Wittig reagents. The reaction of $NiCl_2$ with a mixture of $S_4N_4H_4$ and $Ph_3P{=}CH_2$ produced $Ni(S_2N_2H)_2$ in 20% yield indicating that the $S_2N_2H^-$ ion is formed *in situ* in this reaction.



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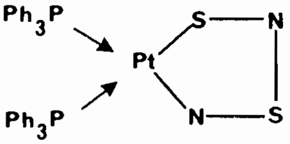

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Experimental

Reagents and General Procedures

$Ph_3P{=}CH_2$ [9], $Ni(S_2N_2H)_2$ [10], $(Ph_3P)_4Pt$ [11], $(Ph_3P)_2PtC_2H_4$ [12], S_4N_4 [13], $S_4N_4H_4$ [14], $S(NSO)_2$ [15] and $Ph_3P{=}NS_3N_3$ [16] were prepared by literature procedures. All solvents were dried and distilled before use: acetone (molecular sieves 4 Å), n-pentane (CaH_2), n-hexane (Na), toluene (Na), diethyl ether (Na/benzophenone), methylene dichloride (P_2O_5).

Infrared spectra were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer (4000–250 cm^{-1}). ^{31}P NMR spectra were obtained by use of a Varian XL-200 spectrometer. ^{31}P NMR chemical shifts are reported relative to external 85% H_3PO_4. Chemical analyses were performed by MHW Laboratories, Tucson, Ariz.

Preparation of $(Ph_3P)_2PtS_2N_2$

(a) From $(Ph_3P)_4Pt$ and $S_4N_4H_4$ under nitrogen

A suspension of $S_4N_4H_4$ (0.106 g, 0.56 mmol) in toluene (10 ml) was added to a yellow–orange solution of $(Ph_3P)_4Pt$ (0.700 g, 0.56 mmol) in toluene (30 ml). The reaction mixture was stirred for 20 h at 23 °C to give a yellow precipitate (0.400 g), which was recrystallized from acetone–hexane (70 ml, 5:2) at –20 °C to give yellow crystals of $(Ph_3P)_2PtS_2N_2$ (0.220 g, 0.27 mmol) melting point (m.p.) 234 °C. *Anal.* Calc. for $C_{36}H_{30}N_2P_2PtS_2$: C, 53.27; H, 3.73; N, 3.45; S, 7.90. Found: C, 53.28; H, 3.83; N, 3.33; S, 8.03%. IR: 1480m, 1440s, 1310w, 1185w, 1160w, 1093m, 1050m, 1030w, 1000w, 750m, 700sh, 692s, 680m, 538m, 520s, 510m, 503m, 492m, 460w, 440w, 420w cm^{-1}. $^{31}P\{^1H\}$ NMR (in CH_2Cl_2): δ +23.7 (d, $^2J_{P-P} = 21.6$ Hz, $^1J_{Pt-P} = 2843$ Hz), +11.7 (d, $^2J_{P-P} = 21.6$ Hz, $^1J_{Pt-P} = 3008$ Hz).

(b) From $(Ph_3P)_4Pt$ and $S_4N_4H_4$ in air

A solution of $S_4N_4H_4$ (0.106 g, 0.56 mmol) in acetone (5 ml) was added by syringe to a solution of $(Ph_3P)_4Pt$ (0.700 g, 0.56 mmol) in benzene (10 ml). After 15 min a yellow precipitate had formed and, after 45 min with stirring, n-hexane (20 ml) was added to the reaction mixture. The product was isolated by filtration, washed with n-hexane (20 ml), and dried in air to give a yellow solid (0.400 g). Recrystallization of this product from acetone–hexane (60 ml, 4:2) at –20 °C gave bright yellow crystals of $(Ph_3P)_2PtS_2N_2$ (0.330 g, 0.41 mmol) m.p. 234 °C after washing with n-pentane (20 ml) and drying in air. The IR spectrum of these crystals was identical with that of $(Ph_3P)_2PtS_2N_2$ prepared in (a) above except for two additional bands at 1710 m and 1220 w cm^{-1}.

(c) From $(Ph_3P)_2PtC_2H_4$ and $S(NSO)_2$

A solution of $S(NSO)_2$ (0.140 g, 0.58 mmol) in toluene (10 ml) was added by syringe with stirring to a solution of $(Ph_3P)_2PtC_2H_4$ (0.660 g, 0.88 mmol) in toluene (60 ml). Gas evolution (SO_2 and C_2H_4) was observed and a yellow precipitate had formed after 15 min. Solvent was removed from the reaction mixture under vacuum to give a brown oil, which was dissolved in acetone (40 ml), filtered and treated with n-hexane (20 ml). After 15 h at –20 °C only a small amount of yellow powder had deposited. This precipitate was removed by filtration and the solution was passed through a layer of silica gel (5 cm, fine porosity frit) and the yellow product was eluted with acetone. Solvent was removed from the eluate under vacuum and the yellow–brown residue was dissolved in chloroform (5 ml). Slow addition of n-hexane (50 ml) to this solution gave a yellow precipitate which was separated by filtration, dried in air, and identified as slightly impure $(Ph_3P)_2PtS_2N_2$ (0.300 g, 0.37 mmol) by IR and ^{31}P NMR spectra: δ = +24.0 and +11.8 ppm.

(d) From $(Ph_3P)_4Pt$ and S_4N_4

A solution of S_4N_4 (0.200 g, 1.09 mmol) in a mixture of diethyl ether (25 ml) and methylene dichloride (25 ml) was added to a solution of $(Ph_3P)_4Pt$ (1.10 g, 0.88 mmol) in a mixture of diethyl ether (75 ml) and methylene dichloride (25 ml). The color of the solution became dark green. After 1 h solvent was removed under vacuum and the green residue was washed with diethyl ether and dissolved methylene dichloride (15 ml). The TLC of this solution showed the presence of $Ph_3P{=}N{-}S_3N_3$ [16] in addition to $(Ph_3P)_2PtS_2N_2$ and unreacted starting materials. This solution was chromatographed on silica gel (10 cm, G3 frit). Unreacted starting materials were eluted with methylene dichloride and the product was eluted with acetone. After removal of solvent under vacuum, the product was washed with diethyl ether to give yellow crystals of $(Ph_3P)_2PtS_2N_2$ (0.230 g, 0.28 mmol). Recrystallization from toluene gave pale yellow crystals suitable for X-ray crystallography.

Preparation of $Ni(S_2N_2H)_2$ *from* $S_4N_4H_4$, $Ph_3P{=}CH_2$ *and* $NiCl_2$

A mixture of $S_4N_4H_4$ (0.570 g, 3.0 mmol) and $Ph_3P{=}CH_2$ (1.66 g, 6.0 mmol) in THF (60 ml) was stirred rapidly at 23 °C. A yellow precipitate formed immediately and the solution became blue. Anhydrous $NiCl_2$ (0.390 g, 3.0 mmol) was added to the reaction mixture. After *ca.* 10 min at 23 °C methanol (100 ml) was added by syringe and the dark-blue solution became red–purple. After 1 h, solvent was removed under vacuum to give a dark red–purple oil which was washed with toluene (100 ml) and dissolved in a 1:1 mixture of acetone/toluene (50 ml). Chromatography on silica gel produced a broad purple band which was eluted with toluene/acetone (1:1) to give $Ni(S_2N_2H)_2$ (0.145 g, 0.59 mmol) as black needles. The IR spectrum of this product was identical with that of an authentic sample prepared from $NiCl_2$ and S_4N_4 in anhydrous methanol by the literature procedure [10].

Crystal Data for $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$

Molecular weight 903.9; triclinic with $a = 11.328(2)$, $b = 12.366(2)$, $c = 16.822(3)$ Å, $\alpha = 94.12(1)$, $\beta = 108.57(1)$, $\gamma = 112.93(1)^\circ$; $V_{calc} = 2004.8$ Å^3; $D_{calc} = 1.497$ g cm^{-3}; $Z = 2$; $F(000) = 900$; space group $P\bar{1}$ (C_i^1, No. 2); Mo Kα radiation, $\lambda = 0.70926$ Å; $\mu_{\mathrm{Mo\,K}\alpha} = 35.6$ cm^{-1}.

X-ray Data Collection

Single crystals suitable for the X-ray work were grown by slow cooling of a hot (70 °C) toluene solution. A yellow crystal of approximate dimensions $0.12 \times 0.15 \times 0.22$ mm was mounted along its extended direction in a thin-walled glass capillary under a nitrogen atmosphere. The crystal was accurately aligned and centered on a Hilger and Watts automated four-circle diffractometer. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 15 high-angle reflections, which were automatically centered at $2\theta_+$ and $2\theta_-$ using Mo Kα radiation ($20 \leqslant 2\theta \leqslant 30^\circ$).

Intensity data were collected at 20 °C in the coupled θ(crystal)–2θ(counter) scan mode with use of graphite-monochromated Mo Kα radiation. The scan time was varied from 60 s (weak reflections) to 5 s (strong reflections). Backgrounds were measured at each end of the scan for 25% of the scan time. Very weak reflections for which a quick point measurement at the K_{α^1} position gave $I < 3.5 \times I_{\mathrm{background}}$ were neglected. Attenuators were inserted whenever the counting rate exceeded 10000 counts s^{-1}. Three approximately mutually orthogonal check reflections were remeasured after each batch of 97 reflections in order to monitor the direct-beam intensity and extent of crystal damage. Their measurement exhibited no significant fluctuation nor decay of the intensity.

A total of 3060 unique reflections were collected in the range $6^\circ \leqslant 2\theta \leqslant 50^\circ$. Intensities were corrected for the direct-beam polarisation and for the usual Lorentz factor. A spherical absorption correction for $\mu r = 0.4$ would result in less than a 1% correction to the observed intensities, and consequently none was applied.

Solution and Refinement of the Structure

All calculations were performed on a Siemens main frame computer employing the SHELX crystal structure package [17]. Interpretation of the three-dimensional Patterson function gave the position of the heavy atom platinum. The remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. Throughout the refinement process, hydrogen atoms of the phenyl rings were included in calculated positions based upon d(C–H) 1.08 Å and the appropriate trigonal planar geometry ($U_H = 0.10$ Å^2). These positions were not refined, but were continuously updated with respect to their attached carbon atoms. During the procedure of refinement it became obvious that one phenyl group was disordered. Two ring positions (site occupation factors 0.7 and 0.3) could be refined. In addition two disordered toluene molecules (site occupation factor 0.5) were found in one half of the unit cell. Full-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms except for C(71) to C(121) (disordered phenyl ring; site occupation factor 0.3) and C(37) to C(50) (two disordered toluenes; site occupation factor 0.5) led to convergence with the following discrepancy indices for all 3060 data: $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.047$; $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.058$. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $1/w = \{\sigma(|F_o|\}^2 + \{0.001|F_o|\}^2$. The six atoms of the phenyl rings were all refined assuming a regular hexagon with d(C–C) 1.395 Å; thus 351 parameters were refined. No systematic trends of F_c/F_o as a function of $\sin\theta$ or F_o were observed. A final electron-density difference synthesis showed a maximum of 1.4 and a minimum of -1.6 e Å^{-3} in the region of the plati-

TABLE I. Positional and Anisotropic Thermal Parameters for Non-hydrogen Atoms of $(Ph_3P)_2PtS_2N_2$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Pt	0.0724(1)	0.0504(1)	0.2775(1)	0.052(1)
P1	−0.0963(4)	0.1168(3)	0.2278(2)	0.054(4)
P2	0.2381(4)	0.2218(3)	0.3735(2)	0.053(4)
S1	0.2143(5)	−0.0438(4)	0.3153(3)	0.090(6)
S2	−0.0266(6)	−0.2085(4)	0.1905(3)	0.105(7)
N1	0.1338(15)	−0.1759(11)	0.2629(9)	0.101(18)
N2	−0.0726(12)	−0.1099(10)	0.1870(8)	0.077(15)
C1	−0.2487(8)	0.0387(8)	0.2539(6)	0.048(14)
C2	−0.2662(8)	−0.0685(8)	0.2811(6)	0.079(19)
C3	−0.3827(8)	−0.1322(8)	0.2996(6)	0.107(25)
C4	−0.4817(8)	−0.0887(8)	0.2909(6)	0.090(22)
C5	−0.4642(8)	0.0185(8)	0.2637(6)	0.077(21)
C6	−0.3477(8)	0.0822(8)	0.2452(6)	0.068(17)
C7	−0.1521(18)	0.1057(24)	0.1109(8)	0.075(38)
C8	−0.0626(18)	0.1019(24)	0.0710(8)	0.136(70)
C9	−0.0990(18)	0.0976(24)	−0.0170(8)	0.119(49)
C10	−0.2249(18)	0.0971(24)	−0.0650(8)	0.117(46)
C11	−0.3144(18)	0.1009(24)	−0.0252(8)	0.095(36)
C12	−0.2780(18)	0.1052(24)	0.0628(8)	0.081(32)
C71	−0.1700(59)	0.0597(52)	0.1074(25)	0.080(25)
C81	−0.0699(59)	0.0976(52)	0.0710(25)	0.074(67)
C91	−0.1080(59)	0.0624(52)	−0.0175(25)	0.149(46)
C101	−0.2462(59)	−0.0108(52)	−0.0697(25)	0.136(28)
C111	−0.3462(59)	−0.0488(52)	−0.0334(25)	0.119(22)
C121	−0.3081(59)	−0.0135(52)	0.0552(25)	0.084(16)
C13	−0.0618(10)	0.2738(7)	0.2597(6)	0.064(17)
C14	−0.0569(10)	0.3151(7)	0.3406(6)	0.064(18)
C15	−0.0251(10)	0.4358(7)	0.3677(6)	0.091(22)
C16	0.0018(10)	0.5153(7)	0.3140(6)	0.117(28)
C17	−0.0030(10)	0.4740(7)	0.2331(6)	0.130(31)
C18	−0.0349(10)	0.3533(7)	0.2059(6)	0.094(22)
C19	0.2078(10)	0.2525(8)	0.4710(5)	0.054(15)
C20	0.0862(10)	0.1718(8)	0.4775(5)	0.078(19)
C21	0.0597(10)	0.1903(8)	0.5516(5)	0.088(22)
C22	0.1547(10)	0.2895(8)	0.6191(5)	0.120(29)
C23	0.2763(10)	0.3703(8)	0.6126(5)	0.103(25}
C24	0.3028(10)	0.3517(8)	0.5385(5)	0.073(19)
C25	0.2738(10)	0.3534(7)	0.3269(6)	0.058(16)
C26	0.2980(10)	0.4671(7)	0.3665(6)	0.065(17)
C27	0.3268(10)	0.5620(7)	0.3246(6)	0.093(23)
C28	0.3314(10)	0.5431(7)	0.2431(6)	0.106(27)
C29	0.3072(10)	0.4294(7)	0.2035(6)	0.085(22)
C30	0.2784(10)	0.3345(7)	0.2454(6)	0.070(18)
C31	0.4118(8)	0.2280(9)	0.4217(6)	0.054(16)
C32	0.5168(8)	0.2953(9)	0.3945(6)	0.080(20)
C33	0.6456(8)	0.2936(9)	0.4273(6)	0.115(29)
C34	0.6694(8)	0.2247(9)	0.4872(6)	0.112(29)
C35	0.5644(8)	0.1574(9)	0.5144(6)	0.089(22)
C36	0.4356(8)	0.1591(9)	0.4816(6)	0.074(19)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

TABLE II. Selected Bond Lengths (Å) and Angles (deg) for $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$[a]

Bond	Length	Atoms	Angle
Pt–P1	2.308(5)	P1–Pt–P2	97.8(1)
Pt–P2	2.259(3)	P1–Pt–N2	84.8(4)
Pt–S1	2.294(6)	P2–Pt–S1	90.8(2)
Pt–N2	2.093(9)	N2–Pt–S1	86.8(4)
		Pt–N2–S2	113.5(7)
S1–N1	1.548(12)	N2–S2–N1	117.5(7)
S2–N1	1.702(15)	S2–N1–S1	113.7(8)
S2–N2	1.499(16)	N1–S1–Pt	108.4(7)
		P2–Pt–N2	176.9(4)
P1–C1	1.830(10)	P1–Pt–S1	171.3(2)
P1–C7	1.841(14)		
P1–C71[b]	1.887(40)	C1–P1–Pt	113.7(3)
P1–C13	1.826(10)	C1–P1–C7	108.9(6)
		C1–P1–C71[b]	101.2(16)
P2–C19	1.823(11)	C1–P1–C13	101.2(5)
P2–C25	1.816(10)	C7–P1–Pt	111.8(6)
P2–C31	1.841(10)	C71–P1–Pt[b]	104.2(17)
		C13–P1–P7	97.4(9)
		C13–P1–C71[b]	112.9(19)
		C13–P1–P2	122.0(4)
		C7–P1–C71[b]	15.8(14)
		C19–P2–Pt	114.6(4)
		C19–P2–C25	109.7(5)
		C19–P2–C31	99.8(5)
		C25–P2–Pt	113.1(3)
		C25–P2–C31	101.7(5)
		C31–P2–Pt	116.5(4)

[a] Estimated standard deviations in parentheses. [b] Disordered phenyl ring.

num atom but much lower values elsewhere (maximum 0.5 e Å^{-3}). Scattering factors and corrections for anomalous dispersion were from ref. 18. Positional and thermal parameters for non-hydrogen atoms of $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$ are given in Table I*.

Results and Discussion

Reaction of $S_4N_4H_4$ with $(PH_3P)_4Pt$

The reaction of $S_4N_4H_4$ with $(Ph_3P)_4Pt$ in acetone in the presence of air or under nitrogen in dry solvents proceeds rapidly at 23 °C to give a high yield of a yellow crystalline product. The ^{31}P NMR spectrum of this complex in CH_2Cl_2 at 25 °C shows the presence of two inequivalent phosphorus atoms, $^2J(^{31}P-^{31}P) \sim 22$ Hz, with $^{195}Pt-^{31}P$ couplings of 2843 and 3008 Hz. Structures **1** and **4** are both consistent with the NMR data and elemental analyses do not distinguish between these two possibilities. However, the infrared spectrum of the pure product does not exhibit bands in the 3050–3150 cm^{-1} region attributed by Turner *et al.* to ν(N–H) [4]. The remainder of the infrared spectrum is essentially identical to that reported previously [4]. Thus the spectroscopic evidence favors structure **4** for this

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*See also 'Supplementary Material'.

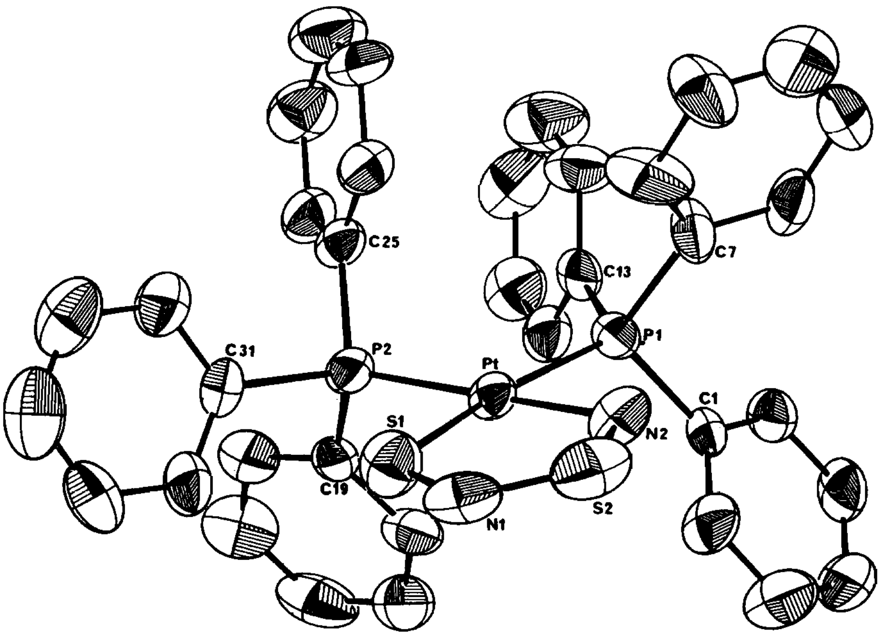


Fig. 1. ORTEP plot (40% probability ellipsoids) for $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$ showing the atomic numbering scheme.

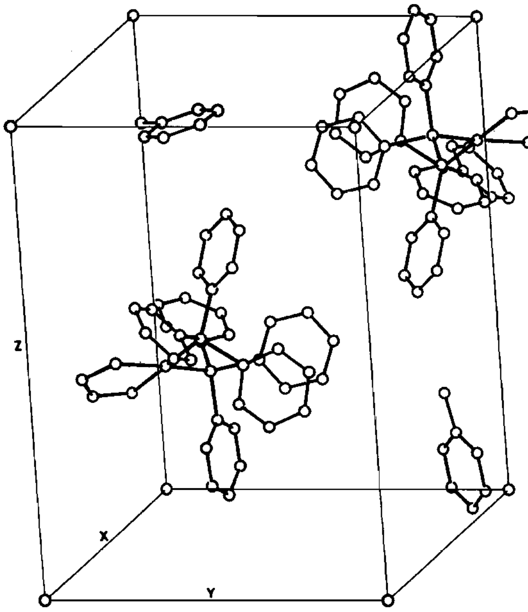


Fig. 2. Unit cell of $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$; only two of the four disordered toluene molecules are shown.

complex and that conclusion has been confirmed by X-ray crystallography.

X-ray Structure of $(Ph_3P)_2PtS_2N_2 \cdot C_7H_8$

An ORTEP drawing of the molecule and a view of the unit cell are shown in Figs. 1 and 2, respectively. Table II contains the pertinent bond lengths and bond angles. One phenyl ring of one of the Ph_3P ligands and the solvent toluene molecules exhibited disorder (details of the refinement are given under 'Experimental'). The molecule consists of an essentially planar five-membered PtS_2N_2 ring. The largest deviation from the least-square plane for $P_2PtS_2N_2$ unit is 0.070 Å for N(2). The geometry around platinum is approximately square planar with bond angles in the range 85–98°. The phosphorus atom *trans* to sulfur forms a longer bond to platinum than the phosphorus atom *trans* to nitrogen (2.308(5) *versus* 2.259(3) Å). There are two short (1.50(2) and 1.55(1) Å) and one long S–N distances (1.70(1) Å) in the MS_2N_2 ring as found for other derivatives (M = Pb [19], C_5H_5Co [20], and in the dimer **3** [6, 7]). In this case, however, the sequence is short-long-short rather than long-short-short.

Reaction of $(Ph_3P)_2PtC_2H_4$ with $S(NSO)_2$

The mononuclear complex **4** can also be prepared by the reaction of $(Ph_3P)_2PtC_2H_4$ with $S(NSO)_2$ in toluene at room temperature.

$$(Ph_3P)_2PtC_2H_4 + S(NSO)_2 \xrightarrow{-SO_2} (Ph_3P)_2PtS_2N_2 + C_2H_4$$

The use of the sulfur–nitrogen oxide $S(NSO)_2$ as a source of the S_2N_2 ligand has been described previously ($TiCl_4 + S(NSO)_2 \rightarrow TiCl_4 \cdot S_2N_2$) [21], but this is the first example of the formation of a cyclometallathiazene from this precursor [8]. The extension of this synthetic approach to other transition metals appears to be a reasonable possibility. In the present case, however, the $(Ph_3P)_4Pt/S_4N_4H_4$ reaction is preferable for the preparation of **4** since it gives a higher yield and a more easily purified product.

Reaction of S_4N_4 with $(Ph_3P)_4Pt$

The reaction of S_4N_4 with $(Ph_3P)_4Pt$ in CH_2Cl_2/Et_2O initially gives a green solution as described by Turner *et al.* [3]. The green product is unstable, however, and work-up of the reaction mixture gave $(Ph_3P)_2PtS_2N_2$, The red compound $Ph_3P{=}N{-}S_3N_3$ was also detected (TLC) in the $(Ph_3P)_4Pt/S_4N_4$ reaction mixtures. It is probably produced by the known reaction of S_4N_4 with triphenylphosphine [16]. These results and those of Ghilardi *et al.* [6] and Woollins *et al.* [7] are summarized in Scheme 1.

Thus the reactions of S_4N_4 with zerovalent platinum complexes involve the following steps: (i) Displacement of C_2H_4 or Ph_3P ligands by S_4N_4 to give the unstable complex $(Ph_3P)_2PtS_4N_4$ (of unknown structure). In the case of $(Ph_3P)_4Pt$, subsequent reaction of the displaced Ph_3P with S_4N_4 produces $Ph_3P{=}N{-}S_3N_3$. (ii) Cleavage of S_4N_4 to S_2N_2 followed by oxidative addition of S_2N_2 to the metal centre to give $(Ph_3P)_2PtS_2N_2$, **4**. This mode of behaviour has been observed for the interaction of S_4N_4 with other electron-rich metal centres, e.g. Co(I) [20], Ir(I) [22], Pd(0) [6, 7], and Ni(0) [6]. (iii) Dissociation of Ph_3P from **4** followed by dimerization to give $[(Ph_3P)PtS_2N_2]_2$, **3**. The last step would be inhibited by the presence of excess triphenylphosphine consistent with the observation that **3** is apparently not formed from $(Ph_3P)_4Pt$ and S_4N_4.

Deprotonation of Cyclic Sulphur Imides

The formation of **4** from $(Ph_3P)_4Pt$ and $S_4N_4H_4$ has interesting implications for the redox chemistry of the reaction. The product can be formally regarded as a complex of platinum(II) with the hypothetical $S_2N_2^{2-}$ anion. Accordingly the formal oxidation state of platinum increases by two while those of sulfur and nitrogen remain unchanged at +2 and −3, respectively. The ions $S_2N_2^{2-}$ and $S_2N_2H^-$ are well known in complexes with metals [8], but they have not been isolated as salts of the free anion. Products formulated as $Na_4S_4N_4$ and $Na_2S_4N_4H_2$ were obtained from the reaction of $S_4N_4H_4$ and Ph_3CNa [23]. It is possible that these salts contain the $S_2N_2^{2-}$ and $S_2N_2H^-$ ions, respectively. However, the only product of the deprotonation of $S_4N_4H_4$ to be conclusively identified is $K^+S_3N_3^-$, which is formed on treatment of $S_4N_4H_4$ with potassium hydride [24]. We have shown in this investigation that the $S_2N_2H^-$ ion can be generated *in situ* from $S_4N_4H_4$ on treatment with various bases. For example, the reaction of $S_4N_4H_4$ with $Ph_3P{=}CH_2$ in a 1:2 molar ratio in THF followed by the addition of anhydrous $NiCl_2$ gives $Ni(S_2N_2H)_2$ in 20% yield.

$$S_4N_4H_4 + 2Ph_3P{=}CH_2 \longrightarrow$$

$$2[Ph_3PMe][S_2N_2H] \xrightarrow{NiCl_2} Ni(S_2N_2H)_2$$

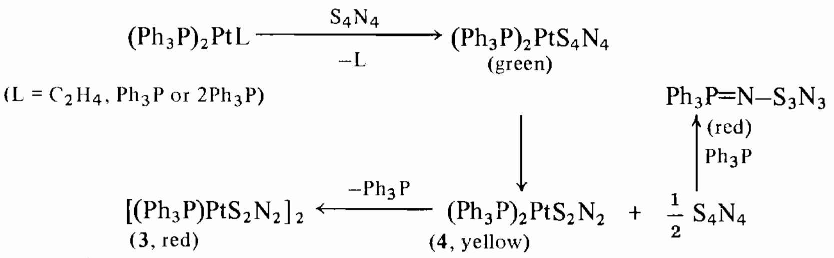
In a related study we have isolated sulfur–nitrogen anions from the deprotonation of cyclic sulfur imides by the Wittig reagent. Thus the reaction of S_7NH with $Ph_3P{=}CH_2$ in acetonitrile gave a high yield of $[Ph_3PMe][S_4N]$ [25]. The recent report of the formation of the complex $(Ph_3PS)CuS_3N$ from the reaction of $(Ph_3P)CuCl$ with S_7NH in methylene dichloride indicates that triphenylphosphine is also capable of deprotonating cyclic sulfur imides [26]. We have confirmed this viewpoint in a separate experiment. The reaction of S_7NH with triphenylphosphine in acetonitrile at 23 °C rapidly produces the blue S_4N^- anion (λ_{max} 582 nm) [27] followed, after *ca.* 5 min, by the orange–red S_3N^- ion (λ_{max} 465 nm) [28]. It seems reasonable to propose, therefore, that $S_4N_4H_4$ is also deprotonated by triphenylphosphine (formed by dissociation of $(Ph_3P)_4Pt$ in solution) in the $S_4N_4H_4/(Ph_3P)_4Pt$ reaction to give Ph_3PH^+ salts of the $S_2N_2H^-$ and/or $S_2N_2^{2-}$ ions. These ions must then undergo a rapid redox reaction with $(Ph_3P)_2Pt$ resulting in the following overall transformation.

$$2(Ph_3P)_4Pt + S_4N_4H_4 \longrightarrow$$

$$2(Ph_3P)_2PtS_2N_2 + 4Ph_3P + 2H_2$$

Summary and Conclusions

The reaction of $(Ph_3P)_4Pt$ with $S_4N_4H_4$ in acetone provides a convenient preparation of the five-membered metallathiazene ring, $(Ph_3P)_2PtS_2N_2$. The



Scheme 1

structurally characterized complex $(Ph_3P)_2$-$Pt(OSNH)_2 \cdot 0.5H_2O$ previously reported to be formed in this reaction may have been the result of the degradation of the initial reaction product by atmospheric moisture and/or oxygen. The rapidity and high yield of the synthesis of the PtS_2N_2 ring from $S_4N_4H_4$ suggests that this cyclic sulfur imide may be a useful precursor for the preparation of other cyclometallathiazenes via the *in situ* generation of S–N anions, e.g. $S_2N_2^{2-}$ or $S_2N_2H^-$.

Supplementary Material

Other X-ray structural data (observed and calculated structure factors, best planes, torsion angles) may be obtained from the authors.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Mr. C. Lensink for obtaining the ^{31}P NMR spectrum.

Note Added in Proof

After this manuscript was submitted, a paper describing the preparation and X-ray structure of $(Ph_3P)_2PtS_2N_2 \cdot 4CHCl_3$ appeared [29].

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