Heteroleptic Platinum(II) Complexes with Crown Thioether and Phosphine Ligands I: Crystal Structures of [Pt(9S3)(dppm)]$(PF_6)_2$ and [Pt(9S3)$(PPh_3)_2$]$(PF_6)_2\cdot 2CH_3NO_2$

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Introduction

Research into the coordination chemistry of crown thioether ligands, such as 1,4,7-trithiacyclononane (9S3), continues to progress in a number of areas including transition metal complexes, main group compounds, and organometallic complexes.[1−5] One particularly active area of focus involves thioether complexes of platinum(II) because of the high stability of Pt−S bonds.[6−10] These complexes contain some common but unusual structural features. They typically exhibit structures that involve a distorted square planar array of four equatorial ligating atoms around the Pt(II) center. However, there are usually one or two additional long-distance Pt−S interactions involving other sulfur atoms present in the coordinated thioether. These long-distance interactions result in complex structures best described as elongated square pyramids [$S_4 + S_1$] or elongated octahedra [$S_4 + S_2$].[6,8] The platinum-axial sulfur interactions have been described in a variety of ways (weak bonds, nonbonding interactions, agostic interactions, etc.), and their electronic nature is of considerable theoretical interest.[11] It has been shown that these long-distance Pt−S interactions result in unusual spectroscopic and electrochemical properties displayed by platinum−thioether complexes including d−d electronic transitions near 435 nm and a reversible Pt(II)/Pt(III) couple observed near +0.35 V vs Fc/Fc$^+$ in cyclic voltammetric experiments. Additionally, the unusual Pt complex structures have been correlated with the conformational preferences of the individual crown thioether ligands.[12]

Although several homoleptic Pt(II) crown thioether complexes have now been structurally characterized, less well developed are heteroleptic complexes involving these ligands.[13,14] We were particularly interested in the study of phosphine−crown thioether Pt(II) complexes because phosphine ligands are known to be effective catalysts, especially chiral diphosphines as asymmetric catalysts.[15] Moreover, Pt(II) complexes with 9S3 have been used as models for ligand substitution reactions that proceed by associative mechanisms in four coordinate complexes.[16] Phosphines have stronger π-accepting characteristics than do crown thioethers (moderate π acceptors),[17] and in addition, phosphines are good σ donors while thioethers are poor σ donors. Thus, the complexes may have interesting and unusual electronic properties. An elegant study of phosphine−crown thioethers with Pd(II) has recently appeared.[18] We were interested in extending this research to include Pt(II) because platinum should also form very stable complexes of this type and ^{195}Pt is an attractive nucleus for NMR study. Additional data to probe the ligand−Pt interactions can be provided by ^{31}P NMR chemical shifts and $^1J(^{195}\text{Pt}-^{31}\text{P})$ couplings. Furthermore, we were interested in seeing if heteroleptic crown thioether complexes with phosphine ligands will show the unusual properties that have been observed in Pt−thioether homoleptic complexes and heteroleptic complexes with amine and halide ligands.[19,20]

Experimental Section

Materials. All solvents and reagents were purchased from Aldrich Chemical Co. and used as received. The starting complex [Pt(9S3)Cl_2] was prepared by the published method.[21]

Measurements. Elemental analyses were performed by Atlantic Microlab, Inc. of Atlanta, Georgia. Fourier transform infrared spectra were obtained using a Galaxy FT IR 5000 spectrophotometer, and ultraviolet−visible spectra were obtained on a Varian DMS 200 UV−visible spectrophotometer. ^{13}C and ^{1}H NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CD_3NO_2 for both the deuterium lock and reference. All observed carbon resonance connectivity was confirmed via DEPT (distortionless enhancement by polarization transfer) experiments. Platinum-195 NMR spectra were recorded near 64.208 MHz using aqueous solutions of $[PtCl_6]^{2-}$ (0 ppm) as an external reference and using a delay time of 0.01 s. Referencing

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was verified vs authentic samples of $[PtCl_4]^{2-}$, which were found to have a chemical shift at −1626 ppm, in agreement with the reported value of −1624 ppm.[22] Phosphorus-31 NMR referencing was done using phosphoric acid (0 ppm) as an external standard.[23] A Biological Analytical Systems 50 analyzer was used for all electrochemical measurements. The supporting electrolyte was 0.1 M $(Bu)_4NBF_4$ in CH_3NO_2, and sample concentrations were 1 mM. All voltammograms were recorded at a scan rate of 100 mV/s. The standard three-electrode configuration was as follows: platinum working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. All potentials were referenced against Fc/Fc^+ couple.

Preparation of $[Pt(9S3)(PPh_3)_2](PF_6)_2{\cdot}2CH_3NO_2$. A mixture of $[Pt(9S3)Cl_2]$ (50.0 mg, 0.112 mmol) and triphenylphosphine (60.0 mg, 0.229 mmol) was refluxed in 25 mL of CH_3NO_2 for 1 h. The resulting solution was allowed to cool slightly, and then NH_4PF_6 (37 mg, 0.227 mmol) was added. The mixture was refluxed for 30 min. The solution was hot-filtered and concentrated to $^2/_3$ of its original volume. Yellow crystals (86 mg, 59%) of $[Pt(9S3)(PPh_3)_2](PF_6)_2{\cdot}2\ CH_3NO_2$ were obtained by diffusion of ether into the solution. Anal. Calcd for $C_{44}H_{48}F_{12}N_2O_4P_4PtS_3$: C, 40.28; H, 3.69; S, 7.21. Found: C, 40.35; H, 3.65; S, 7.41. The electronic absorption spectrum measured in acetonitrile showed two λ_{max}'s at 415 nm ($\epsilon = 750$) and at 277 nm ($\epsilon = 19\,000$). FT-IR (KBr, cm^{-1}): 3064, 3060, 3056, 2973, 2929, 1588, 1520, 1488, 1420, 1415, 1150, 842 (s, PF_6^-), 774, 742, 721, 716, 557, 534. ^1H NMR (CD_3NO_2): δ 7.83, 7.42 ppm (m, PPh_3, 30 H), complex AA′BB′ pattern at 2.84 and 2.45 ppm (9S3, 12 H). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 135.8 (m, 12 C, PPh_3), 134.2 (s, 6 C, PPh_3), 130.8 (m, 12 C, PPh_3), 128.9 (m, 6 C, PPh_3, $^1J_{C-P} = 63$ Hz), 37.3 (s, 9S3, 6 C) ppm. $^{195}Pt\{^1H\}$ NMR (CD_3NO_2): δ ($\nu_{1/2}$) triplet at -4399 ppm (49 Hz) ($^1J_{PtP} = 3369$ Hz). $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ singlet at 12.03 ppm, ^{195}Pt satellite doublet at 25.90 and −1.81 ppm ($^1J_{PtP} = 3365$ Hz) ppm. The complex shows no oxidative electrochemistry but does show an irreversible reduction wave at −1321 mV vs Fc/Fc^+.

Preparation of $[Pt(9S3)(dppm)(PF_6)_2$. The complex was prepared according to the above procedure by refluxing a mixture of $[Pt(9S3)Cl_2]$ (90.0 mg, 0.202 mmol) and dppm (78.0 mg, 0.203 mmol) in 50 mL of CH_3NO_2 for 1 h. Addition of NH_4PF_6 (66 mg, 0.404 mmol) followed by further refluxing for 30 min and concentration to $^2/_3$ volume resulted in the formation of yellow crystals (93 mg, 44%) of $[Pt(9S3)(dppm)](PF_6)_2$ after ether diffusion. Anal. Calcd for $C_{31}H_{34}F_{12}P_4PtS_3$: C, 35.67; H, 3.26; S, 9.16. Found: C 35.66; H, 3.35; S, 9.01. The electronic absorption spectrum measured in acetonitrile showed two λ_{max}'s at 367 nm ($\epsilon = 240$) and at 260 nm ($\epsilon = 25\,000$). FT-IR (KBr, cm^{-1}): 3050, 3020, 2959, 2929, 2923, 1497, 1442, 1350, 1325, 1205, 1173, 1080, 837 (s, PF_6^-), 774, 742, 721, 716, 557, 534. ^1H NMR (CD_3NO_2): δ 7.75, 7.42 (m, PPh_2, 20 H), 3.04, 3.11 (overlapping triplets, PCH_2, 2 H, $^2J_{H-P} = 12$ Hz), complex AA′BB′ pattern at 2.71 and 2.32 (9S3, 12 H) ppm. $^{13}C\{^1H\}$ NMR(CD_3NO_2): δ 136.4 (s, 4 C, PPh_2), 135.5 (m, 8 C, PPh_2), 132.6 (m, 8 C, PPh_2), 130.1 (d, 4 C, PPh_2, $^1J_{C-P} = 61$ Hz), 36.7 (s, 9S3, 6 C), 31.4 (m, PCH_2, 1 C) ppm. $^{195}Pt\{^1H\}$ NMR (CD_3NO_2): δ ($\nu_{1/2}$) triplet at −4601 ppm (49 Hz) ($^1J_{PtP} = 3190$ Hz). $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ singlet at 50.50, ^{195}Pt satellite doublet at 63.62 and 37.37 ($^1J_{PtP} = 3188$ Hz) ppm. The complex shows no oxidative electrochemistry but does show an irreversible reduction wave at −1698 mV vs Fc/Fc^+.

Data Collection and Processing. A summary of key crystallographic details for both structures is presented in Table 1. For $[Pt(9S3)(PPh_3)_2](PF_6)_2{\cdot}2\ CH_3NO_2$, intensity data were collected on a Nonius diffractometer using the $\theta/2\theta$ scan mode.[24,25] The h,k,l ranges used during the structure solution and refinement were −13/12, 0/49, 0/15. For 11 311 measured reflections 9937 were unique. The merging R values on intensities were 0.054. Absorption correction was made by the ω scan technique with minimum and maximum transmission factors of 0.063082 and 0.241 147. The last least-squares cycles were calculated with 112 atoms, 632 parameters, and 7226 out of 9937 reflections. Weights based on counting statistics were used. The residuals were as follows: for significant reflections $R = 0.052$, $R_w = 0.067$, and GoF = 2.08; for all reflections $R = 0.076$, $R_w = 0.070$. The maximum shift/σ ratio was 0.002. In the last D map, the deepest hole was −1.960 e/Å^3 and the highest peak was 1.810 e/Å^3. The secondary extinction coefficient was 0.0607 μm with a σ value of 0.0387.

Table 1. Crystallographic Data for $[Pt(9S3)(PPh_3)_2](PF_6)_2{\cdot}2CH_3NO_2$ and $[Pt(9S3)(dppm)](PF_6)_2$

	$[Pt(9S3)(PPh_3)_2](PF_6)_2{\cdot}$ $2CH_3NO_2$	$[Pt(9S3)(dppm)](PF_6)_2$
empirical formula	$C_{44}H_{42}F_{12}N_2O_4P_4PtS_3$	$C_{31}H_{34}F_{12}P_4PtS_3$
fw, amu	1305.96	1049.73
space group	$P2_1/c$	$Pna2_1$
a, Å	10.5828(18)	20.112(14)
b, Å	39.172(4)	14.827(14)
c, Å	12.7165(14)	14.417(10)
β, deg	106.179(11)	90
V, Å^3	5062.9(11)	4299(5)
Z	4	4
radiation (λ), Å	1.540 56	0.710 73
ρ_{calcd}, g cm^{-3}	1.713	1.621
μ, mm^{-1}	8.39	3.63
temp, °C	22	20
R^a	0.052	0.0504
$R_w{}^b$	0.067	0.1242

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

For $[Pt(9S3)(dppm](PF_6)_2$ the crystal was placed in a glass capillary in nitromethane. Data were collected on a Siemens $R3m/V$ automated diffractometer[26] with graphite monochromatized Mo Kα ($\lambda = 0.710\ 73$ Å) radiation to $2\theta = 60°$. An empirical absorption correction[27] was applied to the data with minimum and maximum transmission factors of 0.14 and 0.72. Structures were discovered with SHELXS-90[28] by direct methods. Final models were refined with SHELXL-93[29] and included positions and anisotropic vibrational factors for all non-H atoms with positions and isotropic vibrational factors for the H atoms calculated and contributing, but not refining. Scattering factors were used.[25] The last least-squares cycle was calculated with 461 parameters and all 6435 unique reflections. The final R value was 0.0503 and wR2 = 0.1242 for 2693 reflections for which the intensity exceeded 2 times the standard deviation. The goodness of fit was 0.842, and the final difference map shows features in the range +1.49 to −1.12 e/Å^3.

Results and Discussion

Syntheses and Spectroscopy. The two complexes are readily prepared by a ligand substitution reaction using the appropriate stoichiometric equivalent of phosphine and $[Pt(9S3)Cl_2]$, resulting in chloride ion displacement by the phosphine and subsequent isolation as the hexafluorophosphate salt. Their composition is confirmed using a variety of spectroscopic techniques and elemental analysis. In contrast to bis(trithioether)Pt(II) complexes, electrochemical studies of the two complexes do not show Pt(II)/Pt(III) couples.[6,12] Each complex, however, does show an irreversible reduction wave at −1321 mV vs Fc/Fc^+

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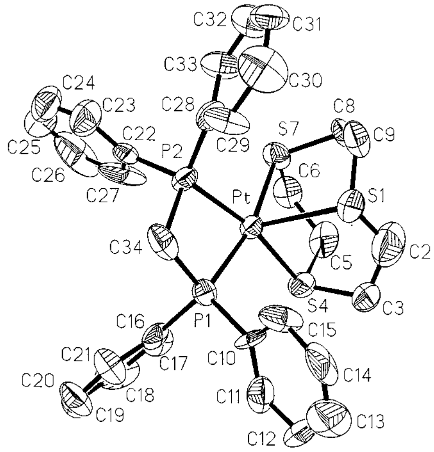

Figure 1. ORTEP perspective of cation in [Pt(9S3)(dppm)](PF$_6$)$_2$].

for the [Pt(9S3)(PPh$_3$)$_2$]$^{2+}$ complex and −1698 mV vs Fc/Fc$^+$ for the dppm complex. Both are assigned to Pt(II)/Pt(0) reductions.

The proton NMR spectrum shows resonances for all phenyl and methylene protons in the appropriate ratios and splittings and a characteristic AA′BB′ splitting pattern of the 12 methylene protons of the 9S3 ligand.[18,21] In addition, ^{13}C DEPT experiments confirm all carbon connectivity. For both complexes, the 9S3 ligand is fluxional in solution, resulting in a single resonance for the thioether ligand and showing all six carbon atoms to be equivalent. The fluxionality of the 9S3 ligand is also seen in the complexity of the ^{1}H NMR spectrum of the dppm methylene protons, which appear as two overlapping triplets due to ^2J phosphorus−hydrogen coupling. The fluxionality is a general property of Pd(II) and Pt(II) complexes with this ligand,[16,18] and the fluxionality has been proposed to occur via rapid intramolecular exchanges of sulfur atoms (1,4-metallotropic shift).[30] The ^{195}Pt NMR spectra show the anticipated triplet splitting pattern (Pt coupled to two ^{31}P donors) centered at −4399 ppm for the PPh$_3$ complex and at −4601 ppm for the dppm complex. The ^{31}P NMR spectra for each complex show one resonance at 12.03 ppm (PPh$_3$) or 50.63 (dppm). Because of the presence of both NMR active and nonactive Pt centers, a doublet of ^{195}Pt satellites appears in the ^{31}P NMR spectrum of the two complexes. The values of $^1J(^{195}\text{Pt}-^{31}\text{P})$ coupling constants occur at 3365 and 3188 Hz, respectively. These differences in coupling constants are correlated with the large variation in the P−Pt−P chelate bite angle, 72.9(2)° for dppm vs 95.6(1)° for (PPh$_3$)$_2$.[31]

Structures. The complex [Pt(9S3)(dppm)](PF$_6$)$_2$ crystallizes in the space group *Pna*2$_1$ and forms an elongated square pyramidal structure [S$_2$P$_2$ + S$_1$]. An ORTEP perspective is shown in Figure 1, and bond lengths and distances are presented in Table 2. Here two sulfur atoms and two phosphorus atoms form a distorted cis square planar array around the Pt(II) while the third sulfur from the 9S3 (S1) interacts from a much longer distance of 2.666(6) Å. Of particular note is the complexation behavior of the dppm ligand. This ligand is known to complex in several different binding modes including monodentate bridging between two metal centers to form "A-frame" complexes and as a bidentate ligand to a single metal center.[32] In our case, the dppm functions in the latter role, resulting in the formation of a strained four-membered chelate ring and a very small P−Pt−P angle (72.7(2)°. The Pt atom in the structures is 0.20 Å above the square plane defined by S(4), S(7), P(1), and P(2) with an average deviation from the plane of 0.004 Å. The Pt atom is displaced toward the axial sulfur, supporting the idea of a strong interaction between the two atoms. The four-membered chelate ring is slightly bowed (by about 20°) toward the axial sulfur.

Table 2. Selected Bond Distances and Angles for [Pt(9S3)(PΦ3)$_2$](PF$_6$)$_2$ and [Pt(9S3)(dppm)](PF$_6$)$_2$

	[Pt(9S3)(PΦ3)$_2$](PF$_6$)$_2$	[Pt(9S3)(dppm)](PF$_6$)$_2$
	Distances (Å)	
Pt−S$_{eq}$	2.358(2), 2.485(3),	2.350(4), 2.359(4)
Pt−S$_{axial}$	2.638(3)	2.666(6)
Pt−P$_{eq}$	2.288(2), 2.304(2)	2.250(4), 2.256(4)
	Angles (deg)	
S$_{eq}$−Pt−S$_{eq}$	86.06(9)	88.3(2)
P(1)−Pt−P(2)	95.58(7)	72.7(2)
P(1)−Pt−S$_{eq}$	179.62(7), 93.77(7)	166.2(2), 99.7(2)
P(2)−Pt−S$_{eq}$	144.7(2), 84.74(8)	168.3 (2), 97.5(2)
S$_{eq}$−Pt−S$_{axial}$	81.85(11), 84.9(7)	85.9(2), 85.4(2)

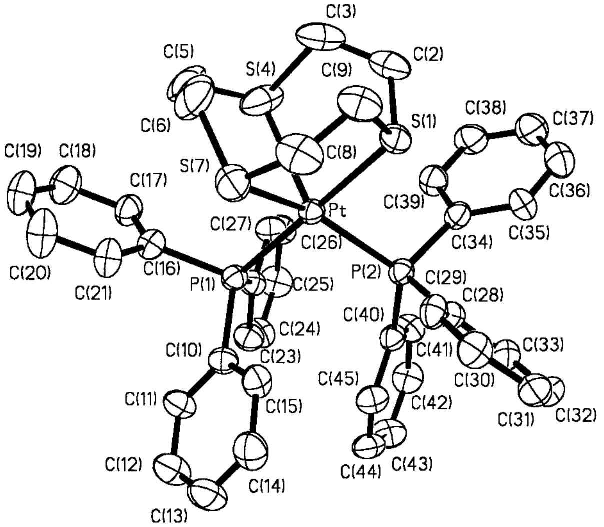

Figure 2. ORTEP perspective of cation in [Pt(9S3)(PPh$_3$)$_2$](PF$_6$)$_2$].

The complex [Pt(9S3)(PPh$_3$)$_2$](PF$_6$)$_2$·2 CH$_3$NO$_2$ crystallizes in the space group *P*2$_1$/*c*. An ORTEP perspective of the complex cation is shown in Figure 2, and selected bond lengths are given in Table 2. Two nitromethane solvent molecules are also incorporated into the crystal lattice. The complex also forms an elongated square pyramidal structure, which is common for heteroleptic crown thioether complexes of Pt(II) and Pd(II).[16,20] However, this structure is much more distorted than analogous ones with a much greater variation in the Pt−S bond lengths (2.358(2) and 2.485(2) Å for the two equatorial Pt−S bonds).[33] The shorter equatorial Pt−S bond is trans to the shorter Pt−P bond. Also, as noted above, the change between the two phosphine ligands results in an increase in over 20° in the

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(33) The structure bears some resemblence to a highly distorted trigonal bipyramidal geometry. Four atoms, the platinum center, the two phosphorus atoms, and S1 define the equatorial plane. They are all coplanar within ±0.05 Å. The atom S4 lies 1.96(2) Å above the equatorial plane, while S7 lies 1.39(2) Å below the equatorial plane to form the trigonal bipyramidal structure. For a discussion of distortions among five-coordinate geometries, see the following. Muetterties, E. L.; Guggenerger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

P−Pt−P chelate bind angle due to the small ring size of the dppm and the bulky phenyl rings of the triphenyl phosphine. Research efforts are underway to see if less sterically hindered trialkylphosphines will show similar structural results. The phenyl rings on each PPh_3 ligand show a staggered conformation.

As was true for the Pd analogues, the dppm structure has shorter average Pt−S distances because of the increased basicity of the dppm (better σ donor ligand) and its large ring strain.[18] These features result not only in the shorter Pt−P and Pt−S bonds observed crystallographically but also in a downfield ^{31}P NMR chemical shift and a corresponding upfield ^{195}Pt NMR chemical shift. The NMR spectra show a more deshielded phosphorus and a more shielded platinum in the dppm complex. Consistent with a more electron-rich Pt(II) center, the electrochemical results show that the dppm complex is indeed more difficult to reduce.

Conclusions

The two phosphine ligands, dppm and PPh_3, readily react with $[Pt(9S3)Cl_2]$ to form heteroleptic thioether−phosphine complexes with an elongated square pyramidal structure $[S_2P_2 + S_1]$ in the solid state. Their solution NMR data are also similar, and both exhibit fluxional 9S3 ligands. The enhanced basicity and ring strain of the dppm ligand over PPh_3 is observed structurally, electrochemically, and spectroscopically, resulting in characteristic chemical shift changes in the ^{31}P and ^{195}Pt NMR spectra of the two complexes. Large changes in the value of the ^{1}J coupling between the platinum and phosphorus correlate with changes in the P−Pt−P chelate bite angle. The electrochemical and spectroscopic behavior of the two complexes contrasts with that of homoleptic crown thioether and related complexes of platinum(II).

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Supporting Information Available: Complete listings for $[Pt(9S3)(PPh_3)_2](PF_6)_2 \cdot 2\ CH_3NO_2$ showing general details of crystallographic data (pp S1, S2), positional parameters (pp S2−S5), bond distances and angles (pp S6−S11), atomic coordinates and equivalent isotropic displacement coefficients (pp S12−S14), and anisotropic displacement coefficients and hydrogen atom coordinates (pp S14−S16); and listings for $[Pt(9S3)(dppm)](PF_6)_2$ showing general details of crystallographic data, (pp S17, S18), atomic coordinates and equivalent isotropic displacement parameters (pp S19, S20), bond distances and angles (pp S21−S24), and anisotropic displacement coefficients and hydrogen atom coordinates (pp S25−S27). This material is available free of charge via the Internet at http://pubs.acs.org.

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