Note

Antimony–Carbon bond activation in a Pt(II) complex: The crystal structure of [Pt(9S3)(SbPh$_3$)(Ph)](PF$_6$)·CH$_3$NO$_2$

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ABSTRACT

The complex [Pt(9S3)(SbPh$_3$)(Ph)](PF$_6$) forms directly from [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$ during the room temperature crystallization of the latter in nitromethane. The crystal structure shows a five-coordinate Pt(II) center containing the tridentate thiacrown ligand, a Sb donor from the triphenylstibine ligand, and a σ-coordinating phenyl group. The phenyl group forms via Sb–C bond cleavage from one of the SbPh$_3$ ligands in the bis complex.

1. Introduction

The cleavage of a phenyl group via Sb–C bond activation has been reported in several transition metal complexes containing triphenylstibine as a ligand [1–8]. Adams and co-workers have recently noted the formation of dirhenium complexes with σ-coordinated phenyl rings formed from a coordinated SbPh$_3$ ligand [1]. Other examples of Sb–C bond cleavage of triphenylstibene in metal complexes include a triruthenium cluster [2], a triosmium cluster [3], a rhodium(II) dimer [4], hexaruthenium and osmium clusters [5], a stibine–gallium mononuclear complex [6], the formation of a nonanuclear organostiboxane cage via Sb–C bond cleavage [7], and carbon–antimony bond cleavage in a mononuclear Pd(II) complex [8]. Reid and co-workers have similarly reported carbon–antimony bond activation in bidentate Sb donor ligands which were coordinated to Rh(I) [9] while the Levason group reported photoactivation of a Sb–C bond in a binuclear Pd(II) complex [10]. Our group has been interested in probing periodic effects in heteroleptic Pt(II) and Pd(II) complexes involving the thiacrown ligand, 1,4,7-trithiacyclononane (9S3) and a variety of Group 15 donor ligands. In that regard, we have recently published two papers describing these complexes [11,12], and the second paper includes two complexes containing the ligand triphenylstibine, [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$ (1) and [Pt(9S3)(SbPh$_3$)(Cl)](PF$_6$). During the crystallization of Compound 1, we simultaneously isolated a second crystalline product was suitable for a crystal structure

determination and was found to contain a σ-coordinated phenyl ring to the Pt(II) center. The current report describes that compound and some of its properties.

2. Results and discussion

2.1. Syntheses and spectroscopy

Slow crystallization (multiday) of an analytically pure sample of [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$ (1) via ether diffusion into nitromethane yields two distinctive crystalline habits, red chips and yellow needles. The partial conversion occurs over a period of several days during which the solution is exposed to normal laboratory lighting. Single crystal X-ray diffraction confirms the former to be the bis SbPh$_3$ complex (1) while the latter proved to be [Pt(9S3)-(SbPh$_3$)(Ph)](PF$_6$) (2), which is isolated as a mono nitromethane solvate. The proton and carbon-13 NMR spectra of complex 2 show the correct number of peaks, splittings, and intensities associated with the three organic components; the 9S3 macrocyclic ligand, the triphenylstibine, and the σ-bound phenyl ring. In mixtures of the two, the phenyl-coordinated Pt complex (2) is readily differentiated from complex 1 via the chemical shift difference in the ^{13}C NMR spectra for their fluxional 9S3 ligands (37.54 vs. 34.98 ppm for 1 and 2, respectively). The formation of complex 2 is further supported by a combustion analysis. Although it is fairly stable in the solid state, complex 2 does degrade in solution making protracted NMR data acquisitions problematic. The electronic spectrum of complex 2 shows one well-defined transition at 373 nm along with three shoulders in the ultraviolet of higher intensity.

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The replacement of the weaker field SbPh₃ ligand with a strong field phenyl ligand causes the low energy transition in complex **2** to become blue-shifted by approximately 80 nm, compared to the same transition in complex **1**. This blue-shift is also consistent with the relative colors of both compounds.

The conversion of **1** into complex **2** correlates with the loss of one of SbPh₃ ligands and the rupture of a Sb–C bond of a phenyl ring in the triphenylstibine. The remaining reaction products have not been identified. Our working hypothesis for the formation of the complex is that there is an initial loss of one of the two SbPh₃ ligands which are weakly bound to the platinum center. Next, Sb–C bond activation occurs via the {Pt 9S3 SbPh₃} moiety since the Pt(II) requires a replacement ligand for that vacant coordination site. Both the poor coordinating ability of the SbPh₃ ligands and the weak Sb–C bond strength play important roles in the process. We would note that this Sb–C bond cleavage in SbPh₃ is somewhat unusual in that it readily occurs in a simple, mononuclear complex at room temperature, without heating or the assistance of metal–metal bonds [1–8]. Neither of the two related complexes, [Pt(9S3)(SbPh₃)(Cl)](PF₆) nor [Pt(9S3)(AsPh₃)₂](PF₆)₂ displays this reactivity [12]. We have attempted to convert complex **1** to complex **2** using both controlled thermal and photochemical reactions. However, no reaction occurs when **1** is refluxed in a nitromethane/chloroform mixture for 5 h. We were able to get a partial conversion to complex **2** (monitored via NMR) by a two-hour exposure to ultraviolet light, but a complete conversion to **2** still did not occur. Furthermore, NMR samples of [Pt(9S3)(SbPh₃)₂](PF₆)₂ which are not exposed to light (covered in aluminum foil) for a seven-day period show no conversion to the phenyl-coordinated complex. These experiments suggest that the reaction is photochemically induced. Our complex does not display the robustness of similar systems reported previously [11], as we see degradation in solution of the phenyl complex. In a related paper, Sharma, Carbrera, and co-workers have reported Sb–C bond cleavage in a Pt(II) complex to form a σ-coordinated phenyl ligand along with two SbPh₃ ligands, *trans*-[Pt(SbPh₃)₂(Ph)Br] [13]. However, the starting source of the Sb ligand is the salt [Me₄N][Ph₂SbBr₂], which contains an anionic phenyl group in equilibrium with the neutral Sb species, and the phenyl-coordinated complex forms concurrently during the preparation of *cis*-[Pt(SbPh₃)₂Br₂].

2.2. Crystal structure of [Pt(9S3)(SbPh₃)(Ph)](PF₆)·CH₃NO₂ (*2*)

A thermal ellipsoid perspective of the complex cation is shown in Fig. 1, and crystallographic along with structural data are presented in Tables 1 and 2. The structure includes the Pt complex cation, a hexafluorophosphate counter ion, and one nitromethane solvent molecule. The Pt(II) center is five-coordinate with a [S₃SbC] environment and is surrounded by three sulfur donors from the *facially* coordinating trithiacrown ligand, the Sb donor from the triphenylstibine, and a single σ-coordinated carbon donor from the anionic phenyl ring. Although there are approximately fifty Pt(II) 9S3 crystal structures reported in the literature [14], there is only a single prior example involving a σ-coordinated phenyl ring, that one being reported by Bennett and co-workers for [Pt(9S3)(Ph)₂] [15]. In our structure, the three Pt–S bond lengths are 2.350(2), 2.391(2), and 2.549(2) Å. The pattern contrasts the elongated square pyramidal structures commonly seen in other Pt 9S3 complexes in which the axial and longer Pt–S distance can be as much as 0.7 Å greater than the two equatorial Pt–S bonds. Indeed, our group has highlighted the ability of the 9S3 to adjust its coordination mode to compensate for poorer donor qualities in Group 15 ligands such as Sb donors [12]. In addition, we have noted that *bis* complexes with the formula [Pt(9S3)(EPh₃)₂](PF₆)₂ (E = Ph, As, Sb) all show distortions toward a trigonal bipyramidal structure (and away from a square pyramidal structure) and the

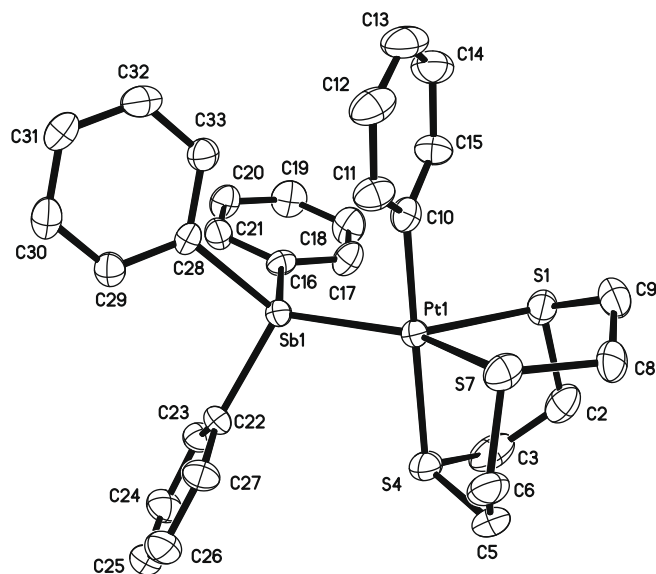**Fig. 1.** Thermal ellipsoid perspective (50% probability) of cation in [Pt(9S3)(SbPh3)-(Ph)]PF₆·CH₃NO₂.

Table 1
Crystallographic data for [Pt(9S3)(SbPh₃)(Ph)](PF₆)·CH₃NO₂ (**2**).

Empirical formula	C₃₁H₃₅F₆NO₂PPtS₃Sb
Formula weight (amu)	1011.59
Lattice	monoclinic
Space group	$P2_1/c$
a (Å)	20.428(4)
b (Å)	10.949(2)
c (Å)	16.610(3)
β (°)	108.16(3)
V (Å³)	3530(1)
Z	4
Radiation (λ) (Å)	0.71073
D_{calc} (g cm⁻³)	1.903
μ (mm⁻¹)	5.008
T (K)	153(2)
Reflections collected	28939
Independent reflections (Rint)	7205
R_1[a]	0.0401
wR_2[b]	0.0951
Goodness-of-fit (GOF)	1.116

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.
[b] $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°)[a] for [Pt(9S3)(SbPh₃)(Ph)](PF₆)·CH₃NO₂ (**2**).

Lengths	
Pt–S₁	2.549(2)
Pt–S₄	2.350(2)
Pt–S₇	2.391(2)
Pt–Sb₁	2.4939(6)
Pt–C₁₀	2.039(6)
Angles	
S₄–Pt–S₇	88.26(6)
S₄–Pt–S₁	86.57(6)
S₇–Pt–S₁	87.37(6)
C₁₀–Pt–S₄	177.8(2)
Sb₁–Pt–S₇	147.16(4)

[a] Estimated standard deviations are given in parentheses.

degree of distortion is surprisingly independent of the Group 15 donor. The distortion is most conveniently defined by the τ parameter developed by Reedijk and co-workers where a value of 0 represents an ideal square pyramid and a trigonal bipyramid has a value of 1 [16]. Complex **2** has a τ value of 0.51 intermediate be-

tween the two extremes indicating some distortion towards trigonal bipyramid, but not to the same degree as the three *bis* pnictogen 9S3 complexes ($\tau = 0.58$) [12]. We have argued that π–π intermolecular interactions between phenyl rings are responsible for the distortion, but these cannot occur here due to the relative orientation of the phenyl and SbPh$_3$ ligands. However, we would note a hydrogen atom (H32) from one of the phenyl rings in the triphenylstibine is directed to the π system of the coordinated phenyl ring and lays only 2.17 Å from its mean-least-squares plane. This is considerably less than the sum of the van Der Waals radii (2.8 Å) and could be the source of the distortion. For over eighty 9S3 complexes with Pt(II) or Pd(II) centers, only the three *bis* EPh$_3$ Pt(II) complexes of 9S3 mentioned above show a greater distortion towards a trigonal bipyramidal geometry than does complex **2**.

The σ-coordinated phenyl ring lays *trans* to S4 (C10–Pt–S4 = 177.8(2) Å) while the Sb donor is nearly *trans* to the centroid between S1 and S7 (Sb–Pt–centroid (S1–S7) = 167.23(6) Å). Due to its strong *trans* directing strength, the shortest Pt–S bond (Pt–S4 = 2.350(2) Å) is also the one that is *trans* to the phenyl group. When the complex is viewed as a distorted trigonal bipyramid, the phenyl group is in an axial position (along with S4). The longest Pt–S bond is Pt–S1 at 2.549(2) Å. Alternatively, if viewed as an elongated square pyramidal shape, the Pt–S1 bond then would correspond to the axial position. The Pt–S distances as well as the Pt–C(phenyl) in **2** are comparable to those reported in the structure of [Pt(9S3)Ph$_2$] [15]. The Pt–C distances in either of these two 9S3/Ph complexes are considerably longer (2.039(6) Å in our case) than those seen in *trans*-[PtBr(Ph)(SbPh$_3$)$_2$] (1.990(2) Å), due to the π-acceptor electronic effects of the 9S3 ligand. The influence of the strongly σ-donating phenyl group on the Pt(II) center is clearly seen in the Pt–Sb bond distance. Here the Pt–Sb bond length (2.4939(6) Å) is 0.05 Å shorter than in the *bis* Complex **1** (Pt–Sb$_{avg}$ = 2.5467(8) Å or [Pt(9S3)(SbPh$_3$)(Cl)](PF$_6$) (Pt–Sb = 2.5304(7) Å) which contains a π-donating chloro group. [12]. The phenyl ring is oriented nearly perpendicular to the mean-least-squares equatorial plane (Sb–S1–S7–Pt) at an angle of 88.7°.

3. Conclusions

Cleavage of an antimony–carbon bond in the complex [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$ results in the formation of [Pt(9S3)(SbPh$_3$)-(Ph)](PF$_6$) which contains a σ-coordinating phenyl ligand. The structure of the phenyl bound complex shows a high degree of distortion towards a trigonal bipyramidal geometry with a S$_3$SbC(phenyl ring) environment around the Pt(II) center.

4. Experimental

4.1. Materials and measurements

Complex **1**, [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$, was prepared by the literature method [12]. All solvents and other reagents were used as received. Analyses were performed by Atlantic Microlab, Atlanta, GA. All ^{13}C{^{1}H} and ^{1}H NMR spectra were recorded on a JEOL ECX-400 NMR spectrometer using CD$_3$NO$_2$ for both the deuterium lock and internal reference. UV–Vis. spectra were obtained in acetonitrile using a Varian Cary 100-Bio UV–Vis. spectrophotometer. A Rayomet MGR-100 circular UV lamp operating at 50 watts was used for photochemical reactions.

4.2. Isolation of [Pt(9S3)(SbPh$_3$)(Ph)](PF$_6$)·CH$_3$NO$_2$ (**2**)

Slow diffusion (1 wk) of diethyl ether into a nitromethane concentrate of Complex **1** produced two sets of crystals – red chips of **1** and yellow needles of **2**. These are mechanically separated and

found to be in an approximate 1/4 ratio (complex **1**/complex **2**) by mass. Anal. *Calc*. for C$_{31}$H$_{35}$F$_6$NO$_2$PPtS$_3$Sb: C, 36.81; H, 3.49; S, 9.51. Found: C, 36.80; H, 3.29; S, 9.51%. **2**: ^{1}H NMR (CD$_3$NO$_2$) δ (ppm): complex multiplets at 7.46–7.34 (15 H, Sb(C$_6$H$_5$)$_3$), 7.54–7.49 (2 H, *Ph, o*-H), 6.84–6.75 (3 H *Ph, m, p*-H), symmetrical multiplet at 3.10–2.97 (12 H, 9S3). ^{13}C {^{1}H} NMR (CD$_3$NO$_2$): δ (ppm): 141.85, 136.79, 132.16, 130.78 (Sb(C$_6$H$_5$)$_3$); 136.36, 130.01, 126.52, 125.00 (*Ph*); 34.98 (9S3). We have not been able to observe a ^{195}Pt-{^{1}H} NMR resonance for the compound, possibly due to line broadening by the quadrupolar Sb nuclei and/or sample degradation in solution. The electronic absorption spectrum measured in acetonitrile showed one peak with λ_{max} at 373 nm (ε = 468 M^{-1} cm^{-1}) and shoulders at 292 nm (ε = 7000 M^{-1} cm^{-1}), 253 nm (ε = 12,000 M^{-1} cm^{-1}) and 235 nm (ε = 35,000 M^{-1} cm^{-1}). Solutions of [Pt(9S3)(SbPh$_3$)$_2$](PF$_6$)$_2$ in CD$_3$NO$_2$, which were kept in the dark by covering the NMR tube in aluminum foil, were unchanged after a seven-day period as measured using NMR.

4.3. Data collection and processing

The intensity data for these were measured at low temperature with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Rigaku AFC8S diffractometer equipped with a 1 K mercury CCD detector [17,18]. Structure solution, refinement and the calculation of derived results were performed with the SHELXTL package of computer programs [19].

Appendix A. Supplementary material

CCDC 744844 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.010.

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