Synthetic and Structural Studies of Heteroleptic Platinum(II) and Palladium(II) Complexes Containing Thiacrown and Monodentate Phosphane Ligands

Trevor P. Latendresse^{#,€}, Steven J. Adams^{#,€}, Gregory J. Grant[#], John P. Lee^{*,#}, and Allen G. Oliver[^]

* To Whom Inquiries should be addressed

Department of Chemistry, The University of Tennessee at Chattanooga

^ Department of Chemistry, The University of Notre Dame

€ Undergraduate Research Student

Graphical Abstract

The thiacrown, ([9]aneS₃), forms elongated square pyramidal complexes of the type [S₂P₂+S₁] or [S₂PCl+S₁] with Pd(II) and Pt(II) where the M-S₁ axial distance elongates and shortens with the σ -donor ability of the phosphane and chlorido ligands.

We wish to report the syntheses, spectroscopic, and structural properties for six new Pt(II) and Pd(II) heteroleptic complexes containing the monodentate phosphane ligands PTA (1,3,5-triaza-7-phosphaadamantane) or PMe_3 (trimethylphosphane) and the crown trithioether [9]ane S_3 (1,4,7-trithiacyclononane). All six reported complexes have the general formula $[\text{M}([\text{9]aneS}_3)(\text{P}_2)](\text{PF}_6)_2$ or $[\text{M}([\text{9]aneS}_3)(\text{P})(\text{Cl})](\text{PF}_6)$ where $\text{M} = \text{Pt(II)}$ or Pd(II) and P is the monodentate phosphane ligand. All six complexes form similar structures in which the metal center is surrounded by two sulfur atoms from the trithioether ligand and a *cis* arrangement of either the two phosphorus donors or the chlorido and phosphorus donor. The third sulfur from the [9]ane S_3 interacts with the metal at a greater distance (2.711(2) Å – 3.078(8) Å), resulting in elongated square pyramidal geometries. These axial distances are controlled by the donor abilities of the phosphane ligand with PTA and PMe_3 serving as stronger donors. The two chlorido complexes show longer metal-sulfur interactions, consistent with the strong donor properties of the anionic chlorido ligand. Although the symmetrical *bis* complexes display typical ^1H and ^{13}C NMR behavior in the [9]ane S_3 region, the less symmetrical *chlorido* complexes show a more complex pattern in their spectra. The ^{195}Pt NMR chemical shifts are consistent with the presence of $[\text{S}_2\text{P}_2+\text{S}_1]$ or $[\text{S}_2\text{PCl}+\text{S}_1]$ coordination environments.

Keywords: Thioether complexes, Platinum complexes, Palladium complexes, Trithiacyclononane, Platinum nuclear magnetic resonance, Phosphane complexes, Crown thioethers

1. Introduction

Our group and others have previously reported on Pt(II) and Pd(II) complexes with the thiacycrown ligand, 1,4,7-trithiacyclononane ([9]aneS₃) and related macrocyclic ligands [1-3]. The complexes show an interesting array of unusual properties including the stabilization of rare mononuclear trivalent oxidation states [4-10], C-H bond activation [12], anion recognition [13], photophysical properties [14, 15], antimony-carbon bond activation [16], geometric distortions in five coordination [17], different intermolecular π - π stacking motifs [18], and uncommon metal-metal bond formation [19]. Heteroleptic Pt(II) and Pd(II) complexes with trithiacrowns form geometries best described as elongated square pyramids, with two of the three sulfur donors lying in the square plane while the third forms a long distance axial interaction. These can vary widely depending upon the donor abilities of the ancillary ligand, surprisingly varying over 0.8 Å [1]. Although a number of different ancillary ligands have now been used to form [9]aneS₃ complexes with both metal ions, monodentate and bidentate phosphanes certainly constitute one of the most important series of ligands studied [20, 21]. One of the goals of our current work is to use the measured M-S axial distances to probe donor properties of previously unstudied phosphanes. Phosphane ligands have a long history in homogenous catalysis, and a key factor controlling catalysis is the metal diphosphane P-M-P bite angle [22, 23]. In this report, the two monodentate phosphane ligands of focus are PTA (1,3,5-triaza-7-phosphaadamantane) and trimethylphosphane, PMe₃. The former has been studied extensively due to its property as a water-soluble phosphane ligand [24-27]. The latter phosphane is a strongly donating ligand which should impart interesting properties into its Pt(II) and Pd(II) [9]aneS₃ complexes. The behavior of the trimethylphosphane complexes will provide an interesting contrast with those of the previously studied monodentate triphenylphosphane [20, 28, 29]. We include in this report the syntheses and characterizations, including five crystal structures, for the following new heteroleptic phosphane complexes with [9]aneS₃:

M = Pt(II) or Pd(II): [M([9]aneS₃)(PTA)Cl](PF₆), [M([9]aneS₃)(PTA)₂](PF₆)₂, and
[M([9]aneS₃)(PMe₃)₂](PF₆)₂

2. Results and Discussion

2.1. Syntheses

The preparation of the Pt(II) and Pd(II) [9]aneS₃ phosphane complexes invariably starts with the [M([9]aneS₃)Cl₂] complex. Improved methods for the preparation of these two important synthons have recently been reported by our group [30]. If the monophosphane-chlorido complexes are desired, one equivalent of phosphane is employed. Alternatively, two equivalents of phosphane result in the displacement of both chlorido ligands, and thereby the *bis*(phosphane) complexes. In both cases, metathesis with hexafluorophosphate yields crystalline products in good yields. The synthetic routes are shown in Scheme 1 below.

Scheme 1. Preparation of [M([9]aneS₃)(PTA)Cl](PF₆), [M([9]aneS₃)(PTA)₂](PF₆)₂, and [M([9]aneS₃)(PMe₃)₂](PF₆)₂ where M = Pd(II) or Pt(II)

In the case of the trimethylphosphane complexes, the ligand efficacy of PMe₃ makes the preparation of the mono-phosphane complexes problematic. We were never able to isolate pure samples of the mono-phosphane complexes, but rather always found significant amounts of the *bis* phosphane complex also present. ¹H and ³¹P NMR spectroscopy confirmed the presence of a mixture of both phosphane complexes. For this reason, the last two complexes of the complete family of eight -- [M([9]aneS₃)(PMe₃)Cl]⁺ -- are not included in this report. Furthermore, we had attempted to prepare Pt(II) [9]aneS₃ complexes with the understudied and intriguing bidentate diphosphane, *cis*-P,P-diphenyl-1,4-diphospha-cyclohexane, 6P2, [31, 32]. However, attempts employing a variety of multiple routes always resulted in displacement of the thiacycrown, and the formation of the *bis* 6P2 Pt(II) complex, illustrating the robust complexation ability of the diphosphane.

2.2 Spectroscopy

Proton NMR spectra for all Pt(II) and Pd(II) [9]aneS₃ phosphane complexes show the correct number of peaks, peak intensities, and splitting patterns. Their ¹³C NMR spectra are similarly consistent, and further support the structures. Complexation of the metal center by the [9]aneS₃ ligands is confirmed using NMR spectroscopy where the coordinated [9]aneS₃ ligand typically displays its characteristic AA'BB' "butterfly" pattern for the proton NMR spectrum and a single resonance in its ¹³C carbon NMR spectrum [1]. Illustrative ¹H and ¹³C NMR spectra for the complex [Pt([9]aneS₃)(PTA)₂](PF₆)₂ are presented in Figure 1. We observe these features in all four of the *bis* phosphane complexes. However, both the Pt(II) and Pd(II) PTA chlorido complexes display a broad, complex [9]aneS₃ peak in their ¹H NMR spectrum (see ESI S1) and further display a broadened and unsymmetrical ¹³C NMR resonance for the thiacycrown. Certainly, the less symmetrical [S₂ + PCI] coordination environment, which contrasts with the [S₂ + P₂] environment of the *bis* complexes, is a key factor. Nevertheless, it is not the only contributor. We would note that all [9]aneS₃ complexes of Pt(II), Pd(II), and Au(III) with cyclometallating nitrogen-containing ligands, such as phenylpyridine, also contain a "unsymmetrical" [S₂ + NC] coordination environment, but in contrast display a AA'BB' proton pattern [7, 33, 34], the same as the *bis* phosphane complexes reported here. We suggest that coupling involving the ³¹P nucleus is playing a role. In support of this hypothesis, we would note that Pt(II) and Pd(II) complexes involving cyclometallating phosphane ligands, such as tri(o-tolyl)phosphane, also show broad, complex [9]aneS₃ resonances [7].

Figure 1. ^1H (top) and ^{13}C (bottom) NMR spectra of [9]aneS₃ region for [Pt([9]aneS₃)(PTA)₂](PF₆)₂. Measured in CD₃NO₂. Note AA'BB' "butterfly" in proton spectrum. A water impurity peak is present in the ^1H NMR spectrum, and the [9]aneS₃ region is shown in the insert for both spectra.

Table 1 presents ^{31}P and ^{195}Pt NMR data for the six new complexes as well as some comparative data for relevant reported [9]aneS₃ phosphane complexes. Our group and others have reported these NMR data for twenty-one Pt(II) complexes and twelve Pd(II) complexes so a solid library exists for comparative data [1]. In all of the complexes, the ^{31}P NMR resonance is shifted downfield relative to the free ligands (-100 ppm for PTA, -62 ppm for PMe₃) [35]. Due to their strong electron-donating

abilities, the chemical shifts of complexes with these two ligands are observed upfield relative to other monodentate phosphanes such as PPh₃. Indeed, the *bis* PTA complex exhibits the second most shielded ³¹P NMR resonance among Pd(II) [9]aneS₃ complexes (only the highly strained dp^{pm} (1,1'-bis(diphenyl)phosphinomethane) complex is larger) [20]. One of the Pt(II) [9]aneS₃ complexes included in the report, the complex *bis* PTA (**2**), is similarly noteworthy in that both their ³¹P and ¹⁹⁵Pt nuclei are highly shielded. Indeed, the *bis* PTA complex shows the most upfield ³¹P and ¹⁹⁵Pt resonances among any in these data. The large degree of shielding of the nuclei by strong donor phosphanes is further seen in the related chlorido/monophosphane complexes where the PTA complexes again show upfield shifts. Within the data in Table 1, the ¹⁹⁵Pt-³¹P coupling in the *bis* PTA is very small (2910 Hz), with only the dppe complex showing a smaller value and all other complexes showing ¹⁹⁵Pt-³¹P coupling greater than 3100 Hz. This small coupling occurs despite a relatively large P-Pt-P angle (93.45(3)°) [21]. We suggest the small coupling could be due to the distortions of the complex towards a trigonal bipyramidal geometry. We also observe interesting fine structure in several of the ¹H and ¹³C NMR spectra due to coupling to the ¹⁹⁵Pt or ³¹P NMR nuclei. For example, ³¹P-coupled and decoupled ¹H NMR experiments for [Pt([9]aneS₃)(PMe₃)₂](PF₆)₂ clearly show ⁴J coupling between the two nuclei (See ESI S2).

Table 1. ³¹P and ¹⁹⁵Pt NMR data for heteroleptic Pt(II) and Pd(II) [9]aneS₃/phosphane complexes. All complexes are hexafluorophosphate salts. All NMR data obtained in CD₃NO₂ except (**3**) where CD₃CN is the solvent.

Complex	δ ¹⁹⁵ Pt, ppm	δ ³¹ P, ppm	¹ J (¹⁹⁵ Pt- ³¹ P), Hz	[REF]
Pt(II) Complexes				
[Pt([9]aneS ₃)(PTA)Cl] ⁺ (1)	-4601	-51.5	3160	^b PW
[Pt([9]aneS ₃)(PTA) ₂] ²⁺ (2)	-4659	-61.8	2910	PW
[Pt([9]aneS ₃)(PMe ₃) ₂] ²⁺ (3)	-4454	-28.1	3150	PW
^a [Pt([9]aneS ₃)(dp ^{pv})] ²⁺	-4681	-42.1	3224	[21]
[Pt([9]aneS ₃)(PPh ₃) ₂] ²⁺	-4359	-12.0	3365	[28]
[Pt([9]aneS ₃)(PPh ₃) ₃ Cl] ⁺	-4080	-16.0	3387	[27]
^a [Pt([9]aneS ₃)(dp ^{pe})] ⁺	-4068	-51.8	2740	[21]
[Pt([10]aneS ₃)(PPh ₃)Cl] ⁺	-4603	35.2	3219	[27]

Pd(II) Complexes

[Pd([9]aneS ₃)(PTA)Cl] ⁺ (4)	NA	-20.8	NA	PW
[Pd([9]aneS ₃)(PTA) ₂] ²⁺ (5)	NA	-28.4	NA	PW
[Pd([9]aneS ₃)(PMe ₃) ₂] ²⁺ (6)	NA	-4.19	NA	PW
[Pd([9]aneS ₃)(PPh) ₃ Cl] ⁺	NA	28.9	NA	[20]
^a [Pd([9]aneS ₃)(dppm)] ²⁺	NA	-37.7	NA	[20]

a. dppv = cis-1,2-bis(diphenylphosphino)ethylene; dppe = 1,2-bis(diphenylphosphino)ethane; dppm = 1,2-bis(diphenylphosphino)methane.

b. PW is present work

We have measured the electronic spectra of the complexes in acetonitrile and observe only very intense transitions in the 240 – 300 nm range. These transitions are assigned as a $\pi \rightarrow \pi^*$ transition of the phosphane. Similar observations have been reported for other diphosphane Pt(II) complexes with [9]aneS₃ [21]. The Pd(II) complexes are generally red-shifted relative to the analogous Pt(II) complexes.

2.3 X-ray Structures

A summary of data collection and refinement for six structures, Complexes **1** – **4** and **6**, are presented in Table 2. Anisotropic thermal displacement ellipsoid diagrams of Complexes **1-4**, and **6** are shown in Figures 2-6. A summary of bond distances and other crystallographic data are found in Table 3.

Table 2a. Crystal data, data collection, and refinement parameters for [Pt([9]aneS₃)(PTA)Cl](PF₆) (**1**), [Pt([9]aneS₃)(PTA)₂](PF₆)₂•CH₃NO₂ (**2**), and [Pt([9]aneS₃)(PMe₃)₂](PF₆)₂•CH₃NO₂ (**3**).

Compound	1	2	3
Formula	C ₁₂ H ₂₄ ClF ₆ N ₃ P ₂ PtS ₃	C ₁₉ H ₃₉ F ₁₂ N ₇ O ₂ P ₄ PtS ₃	C ₂₅ H ₆₃ F ₂₄ NO ₂ P ₈ Pt ₂ S ₆
Habit, color	block, orange	block, yellow	block, yellow
Lattice type	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.556(15)	16.805(3)	22.426(4)
<i>b</i> , Å	11.1283(12)	15.994(3)	10.3727(15)
<i>c</i> , Å	18.741(2)	24.295(5)	25.236(4)
α , deg	90	90	90
β , deg	97.352(4)	90	107.786(5)
γ , deg	90	90	90

V, Å ³	2178.7(5)	6530(2)	5589.9(15)
Z	4	8	4
Temperature (K)	200(1)	120(2)	200(1)
Fwt., g mol ⁻¹	712.99	1040.72	1696.06
D _c , Mg m ⁻³	2.174	2.117	2.015
μ, mm ⁻¹	7.052	4.790	3.296
Reflections collected	21717	151102	59178
Unique reflections	3867(R _{int} =0.0673)	8207(R _{int} =0.0332)	9882(R _{int} = 0.0510)
Data, restraints, parameters	3867/253/0	8207/434/0	9882/0/626
R ₁ , wR ₂ (I > 2σ(I))	0.0365, 0.0986	0.0229, 0.0543	0.0279, 0.0608
R ₁ , wR ₂ (all data)	0.0410, 0.1019	0.0278, 0.0569	0.0386, 0.0654
Goodness-of-fit (F ²)	1.055	1.020	1.023
largest diff. peak, hole, e Å ⁻³	1.436, -1.613	1.615, -1.453	1.04, -0.75

Table 2b. Crystal data, data collection, and refinement parameters for [Pd[9]aneS₃](PTA)Cl(PF₆) (4) and [Pd([9]aneS₃)(PMe₃)₂](PF₆)₂ (6).

Compound	4	6
Formula	C ₁₂ H ₂₄ ClF ₆ N ₃ P ₂ PdS ₃	C ₁₂ H ₃₀ F ₁₂ P ₄ PdS ₃
Habit, color	block, orange	block, orange
Lattice type	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.5189(7)	12.0108(4)
<i>b</i> , Å	11.1714(8)	10.7371(3)
<i>c</i> , Å	18.8228(14)	20.3239(7)
α, deg	90	90
β, deg	97.837(2)	90.3830(10)
γ, deg	90	90
V, Å ³	2191.2(3)	2620.94(15)
Z	4	4
Temperature (K)	200(1)	200(1)
Fwt., g mol ⁻¹	624.31	728.82
D _c , Mg m ⁻³	1.892	1.847
μ, mm ⁻¹	1.456	1.278
Reflections collected	40189	28051
Unique reflections	3860(R _{int} = 0.0459) 0.0459, R _{sigma} = 0.02151	4619(R _{int} =0.0404)
Data, restraints, parameters	3860/0/253	4619/0/205
R ₁ , wR ₂ (I > 2σ(I))	0.0424, 0.1069	0.0286, 0.0637
R ₁ , wR ₂ (all data)	0.0476, 0.1102	0.0361, 0.0673

Goodness-of-fit (F^2)	1.043	1.039
largest diff. peak, hole, e $\text{\AA}^{-3}$	1.77, -0.99	0.39, -0.45

As expected, all complexes form elongated square pyramidal geometries with similar structural features. Each complex contains a Pd(II) or Pt(II) square planar center bonded to two of the three sulfur atoms of the [9]aneS₃ ligand. The remaining two coordination sites contain either two phosphorus donors from two monodentate phosphanes, [S₂P₂ + S₁] coordination environment or one phosphorus and one chloride donor, [S₂PCl + S₁] coordination environment) in the case of complexes with a single monodentate phosphane. The third sulfur of the trithiacrown exhibits a long distance between the Pt(II) or Pd(II) center to form a *pseudo*-five coordinate geometry that is best described as an elongated square pyramid. As noted previously, in virtually all complexes containing d^8 metals the preferred *endodentate* conformation (*i.e.*, all three sulfurs facing the metal center) of [9]aneS₃ gives rise to these elongated square pyramidal structures with axial interactions [36]. To our knowledge, there are over sixty Pt(II) [9]aneS₃ complexes structurally characterized with twelve (20%) involving some type of phosphane ligand [37]. Similarly, there are forty structurally characterized Pd(II) [9]aneS₃ complexes of which eight (20%) contain at least one phosphane ligand.

Table 3a. Selected bond lengths ($\text{\AA}$) with esds in parentheses for Pt(II) complexes; [Pt([9]aneS₃)(PTA)Cl](PF₆) (1), [Pt([9]aneS₃)(PTA)₂](PF₆)₂•CH₃NO₂ (2), and [Pt([9]aneS₃)(PMe₃)₂](PF₆)₂•CH₃NO₂ (3), and related literature complexes.

	1	2	3	[Pt([9]aneS ₃ (PPh ₃) ₂] ²⁺ ^a	Pt([9]aneS ₃ (PPh ₃)Cl] ⁺ ^b
Pt-S _{eq} <i>trans</i> to P	2.3414(17)	2.3525(8), 2.3489(8)	2.3518(12), 2.3668(12)	2.358(2), 2.485(3)	2.3365(8)
Pt-S _{eq} <i>trans</i> to Cl	2.2698(15)	NA	NA	NA	2.2609(9)
Pt-S _{ax}	2.9075(19)	2.7588(8)	2.7761(13)	2.638(3)	3.0778(8)
Pt-P	2.2582(16)	2.2639(8), 2.2628(8)	2.3120(13), 2.3092(12)	2.288(2), 2.304(2)	2.838(8)
<i>Sum of M-S dist</i>	7.537	7.562	7.545	7.545	7.545
Pt-Cl	2.3389(17)	NA	NA	NA	2.3434(8)
τ^c	0.02	0.28	0.03	0.58	0.07

a. [29]

b. [28]

c. [39]

Table 3b. Selected bond lengths (Å) with esds in parentheses for Pd(II) complexes;
[Pd([9]aneS₃)(PTA)Cl](PF₆) (4), **[Pd([9]aneS₃)(PTA)₂](PF₆)₂ (5)**,
[Pd([9]aneS₃)(PMe₃)₂](PF₆)₂•CH₃NO₂ (6), and related literature complexes.

	4	5	6	Pd([9]aneS ₃ (PPh ₃) ₂) ²⁺ ^a	[Pd[9]aneS ₃ (PPh ₃)Cl] ⁺ ^a
M-S _{eq} <i>trans</i> to P	2.3507(13)	2.3900(14), 2.3821(14)	2.3554(7), 2.4153(8)	2.358(2), 2.485(3)	2.3365(8)
M-S _{eq} <i>trans</i> to Cl	2.3044(12)	NA	NA	NA	2.2609(9)
M-S _{ax}	2.8608(14)	2.7561(13)	2.7594(8)	2.638(3)	3.0778(8)
M-P	2.25727(12)	2.2819(14), 2.2965(13)	2.2946(7), 2.3032(8)	2.288(2), 2.304(2)	2.838(8)
<i>Sum of M-S dist</i>	7.537	7.562	7.545	7.545	7.545
M-Cl	2.3372(13)	NA	NA	NA	2.3434(8)
τ ^b	0.02	0.14	0.26	0.27	0.15

a. [20]

b. [39]

We have shown that the metal-sulfur axial distance in [9]aneS₃ complexes is very sensitive to the relative donor abilities of the ancillary ligand [1]. In virtually every Pt(II) and Pd [9]aneS₃ complex, the axial metal-sulfur distance is considerably less than the sum of the Van Der Waals radii, indicating some form of intramolecular interaction is occurring between the two atoms [38]. Due to increasing electron density on the metal center, better donor ligands result in longer axial distances while poor donor ligands will have shorter ones. As expected, the axial metal-sulfur distance increases when an anionic chlorido ligand replaces a neutral monodentate phosphane. This is seen here in the set of PTA complexes for both metal ions where the M-S axial distance increases from 2.7588(8) Å to 2.9075(19) Å and 2.7561(13) Å to 2.8608(14) Å for Pt(II) and Pd(II), respectively. Another important structural feature we observe in both chlorido complexes is the strong *trans* influence of the chlorido ligand. As observed in Table 3, the metal-sulfur bonds, which are *trans* to the chlorido ligand, are considerably shorter than the ones that lie *trans* to the phosphane donor. There are no discernible trends in comparing bond distances between the two metal ions. There is an interesting structural contrast between the *bis* phosphane and the two chlorido-monophosphane complexes. The latter show the metal ion only slightly raised above the mean square plane of the four ligating atoms (Pt(II) = 0.090 Å, Pd(II)

= 0.097 Å). However, the metal ion lies much further out of the mean square plane in the *bis* phosphanes, ranging from 0.161 Å in **3** to 0.262 Å in **6**.

Figure 2. Thermal ellipsoid perspective of the cation in [Pt([9]aneS₃)(PTA)Cl](PF₆) (**1**) (50% probability, H atoms omitted for clarity).

Figure 3. Thermal ellipsoid perspective of the cation in [Pt([9]aneS₃)(PTA)₂](PF₆)₂ (**2**) (50% probability, H atoms omitted for clarity).

Figure 4. Thermal ellipsoid perspective of the cation in $[\text{Pt}([\text{9}] \text{aneS}_3)(\text{PMe}_3)_2](\text{PF}_6)_2$ (**3**) (50% probability, H atoms omitted for clarity).

Figure 5. Thermal ellipsoid perspective of the cation in $[\text{Pd}([\text{9}] \text{aneS}_3)(\text{PTA})\text{Cl}](\text{PF}_6)$ (**4**) (50% probability, H atoms omitted for clarity).

Figure 6. Thermal ellipsoid perspective of the cation in $[\text{Pd}([\text{9}] \text{aneS}_3)(\text{PMe}_3)_2](\text{PF}_6)_2$ (**6**) (50% probability, H atoms omitted for clarity).

A key goal of our study is the examination of the relative donor abilities of the phosphane ligands. Data presented in Table 3 clearly demonstrate that the metal-sulfur axial distances increase as one proceeds through the series: *bis*-PPh₃ < *bis*-PTA < *bis*-PMe₃. The same trend is observed regardless of which metal ion is used or whether the complexes are chlorido/monodentate phosphanes or *bis* phosphanes. Our data suggest that the PMe₃ ligand is the best donor among the three, somewhat better than the PTA ligand, while the triphenylphosphane is the poorest. Indeed, the trimethylphosphane and PTA monodentate phosphanes resemble bidentate phosphane ligands in terms of where their axial metal-sulfur distances fall, suggesting comparable donor behavior. A final structural point noted is the degree of distortion that the complex displays away from the anticipated ideal square pyramidal geometry towards a trigonal bipyramidal geometry (see τ parameter in Table 3) [39]. Our group had previously highlighted that complexes such as $[\text{Pt}([\text{9}] \text{aneS}_3)(\text{PPh}_3)_2]^{2+}$ show a high degree of distortion towards a trigonal bipyramidal shape which was attributed to intramolecular π - π stacking interactions [17]. Among the Pt(II) complexes presented here, the *bis* PTA shows the highest degree of distortion while the other Pt(II) complexes show little distortion. Since the complexes in this report lack the π - π stacking interactions of *bis* triarylphosphanes and related ligands, we propose that the distortion arises from steric interactions. Interestingly, among the Pd complexes, the PMe₃ shows the greatest degree of distortion although the *bis* PTA complex again shows a degree of distortion.

3. Conclusions

The monodentate phosphane ligands PMe_3 or PTA readily displace chlorido ligands from $[\text{M}([\text{9}] \text{aneS}_3)\text{Cl}_2]$ starting complexes. Stoichiometric control allows for the preparation of monophosphane-chlorido complexes ($[\text{S}_2\text{PCl} + \text{S}_1]$ coordination environment) or *bis* phosphane complexes ($[\text{S}_2\text{P}_2 + \text{S}_1]$ coordination environment). The complexes display an elongated square pyramidal geometry around the metal center with long distance interactions between the Pt(II) or Pd(II) center and the third sulfur of the $[\text{9}] \text{aneS}_3$ ligand. These distances are strongly dependent upon the donor abilities of the ancillary ligands present with better donors displaying longer axial metal-sulfur distances. Axial distances in chlorido/monophosphane complexes are over 0.1 Å longer than the related *bis* phosphane complexes, consistent with the good donor quality of Cl^- . Among monodentate phosphane ligands, the increasing axial distance, *bis*- $\text{PPh}_3 < \text{bis}$ -PTA $< \text{bis}$ - PMe_3 is observed due to their increasingly poorer donor qualities. We also note *trans* influence in bond distances in the mixed phosphane/chlorido complexes where the equatorial metal-sulfur bond *trans* to the chloride ligand is always shorter. The less symmetrical *chlorido* complexes show more complex ^1H and ^{13}C NMR spectra in the $[\text{9}] \text{aneS}_3$ region, and contrast the symmetrical *bis* complexes which display the anticipated AA'BB' pattern in their proton NMR spectra and a single resonance for the six $[\text{9}] \text{aneS}_3$ methylene carbons. The ^{195}Pt NMR shifts for these complexes fall in the range of -4400 to -4700 ppm, consistent with the proposed coordination environments. Replacement of a chlorido ligand by a phosphane results in an upfield shift in the ^{95}Pt resonance.

4. Experimental

4.1. Materials and Measurements

All materials were used as received. The ligands $[\text{9}] \text{aneS}_3$, PTA, and PMe_3 as well as NH_4PF_6 were purchased from Aldrich Chemical Company. The platinum starting material, $[\text{Pt}([\text{9}] \text{aneS}_3)\text{Cl}_2]$ was prepared from the commercially available *bis*(benzonitrile)dichloridoplatinum(II) (Alfa Aesar) as previously reported [29]. The palladium starting material, $[\text{Pd}([\text{9}] \text{aneS}_3)\text{Cl}_2]$ was prepared by a similar procedure although the reaction with palladium proceeds *with stirring*. The ligand *cis*-P,P-diphenyl-1,4-diphospha-cyclohexane, 6P2, was a generous gift from the laboratory of Dr. Monte Helm of Pacific Northwest National Laboratory. Analyses were performed by Atlantic Microlab, Inc., of Norcross, Georgia.

UV-vis spectra were obtained on a Varian Cary UV-vis spectrophotometer in acetonitrile using 1 cm quartz cuvettes. All $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra were recorded on a JEOL ECX 400 MHz spectrometer using either CD_3NO_2 (for **1**, **2**, **4** – **6**) or CD_3CN (for **3**) for both the deuterium lock and reference. All ^{31}P NMR spectra were obtained on a JEOL ECX 400 MHz (operating frequency = 161 MHz) spectrometer and externally referenced to 85% H_3PO_4 at 0 ppm. We measured the ^{31}P NMR chemical shift of the PTA ligand in D_2O to be -100 ppm. All ^{195}Pt NMR spectra were obtained on a JEOL ECX 400 MHz (operating frequency = 86.0 MHz) spectrometer at 25 °C and externally referenced to sodium tetrachloridoplatinate(IV) at -1624 ppm [40].

4.2. Crystallography

Table 2 contains crystal data, collection parameters, and refinement criteria for the crystal structures of Complexes **1** – **4** and **6**. All crystals were grown by slow diffusion of diethyl ether into a concentrated solution of the compound in nitromethane.

Crystals of **1**, **3**, and **4** – **6** were mounted on the tip of a Bruker SPINE-pin mount and X-ray intensity data were measured at low temperature using an Oxford Cryosystems Desktop Cooler (200(2) K) for all structures with a graphite monochromated Mo $\kappa\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART X2S Benchtop diffractometer [41]. Data for a crystal of **2** was collected with Mo $\kappa\alpha$ radiation at 120 K on a Kappa X8 4-Circle diffractometer equipped with an APEX-II detector. A hemisphere of data were recorded with 10 seconds per frame at 0.5° sweeps. Structures **1** – **6** were solved (XS) and refined (XL) using Olex2 [42, 43]. A direct-methods solution was calculated that provided the non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms in each structure were placed in ideal positions and refined as riding atoms.

Crystals of **3** show two molecules in the asymmetric unit cell. For complex **5**, significant hexafluorophosphate and solvate (water and nitromethane) disorder was present, which resulted in the R1 value for **5** to be 5.37%. Due to the reduced quality of the structure, **5** is shown only in the ESI, and only the most salient structural features of the inner coordination environment immediately around the Pd center are discussed. For complexes **1** – **6**, the hexafluorophosphate anions showed positional disorder in particular in the fluorine atoms. This disorder was not

modeled, and in all 6 complexes each structure was refined to an $R1 \leq 4.25\%$. Furthermore, there are no resulting Alert Level A or B alerts in the CheckCIF, and no impact on the inner coordination environment of the Pd or Pt other than the esd values.

4.3 Syntheses of Pt(II) and Pd(II) [9]aneS₃ complexes

4.3.1 Preparation of [Pt([9]aneS₃)(PTA)Cl](PF₆) (1).

A mass of [Pt(9S3)(Cl)₂] (0.0753 g, 0.169 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. The ligand PTA (0.0264 g, 0.168 mmol) was added, and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.0332 g, 0.204 mmol) was added to the nearly colorless homogeneous solution and refluxed for an additional 30 minutes. The resulting cloudy yellow solution was cooled to room temperature and filtered through celite. The yellow homogeneous solution was concentrated on a rotary evaporator, and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.1150 g, 94.1% yield). ¹H NMR (CD₃NO₂, δ): 4.65 – 4.46 (12 H, m, PTA, -CH₂) and 3.29 – 3.13 (12 H, unsymmetrical AA'BB', 9S3, -CH₂). ¹³C NMR (CD₃NO₂, δ): 73.8 (d, ³J_{CP} = 7.67 Hz, PTA, -NCH₂-), 51.5 (d, ¹J_{CP} = 24.0 Hz, PTA, -PCH₂-), 36.1 (br s, 9S3, -CH₂). ³¹P NMR (CD₃NO₂, δ): -52.9 (d, ¹J_{PPt} = 3,160 Hz, PTA) and -144.1 (heptet, PF₆⁻). ¹⁹⁵Pt NMR (CD₃NO₂, δ): -4601 (d, ¹J_{PPt} = 3,160 Hz). Anal. Calcd for C₁₂H₂₄ClF₆N₃P₂PtS₃•2CH₃NO₂: C, 20.13; H, 3.60; S, 11.51. Found: C, 19.85; H, 3.51; S, 11.51. UV-Vis (CH₃CN, nm (ε/M⁻¹ cm⁻¹)): 277 (1.66 × 10⁴).

4.3.2 Preparation of [Pt([9]aneS₃)(PTA)₂](PF₆)₂ (2).

A mass of [Pt(9S3)(Cl)₂] (0.0755 g, 0.169 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. PTA (0.0608 g, 0.387 mmol) was added and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.0610 g, 0.374 mmol) was added to the nearly colorless homogeneous solution and refluxed for an additional 30 minutes. The resulting cloudy yellow solution was cooled to room temperature and filtered through celite. The yellow homogeneous solution was concentrated on a rotary evaporator and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.1034 g, 62.5% yield). ¹H NMR (CD₃NO₂, δ): 4.92 – 4.58 (24 H, m, PTA, -CH₂) and

3.37 – 3.14 (12 H, AA'BB', 9S3, -CH₂). ¹³C NMR (CD₃NO₂, δ): 74.3 (t, ³J_{CP} = 4.31 Hz, PTA, -NCH₂-), 55.3 (t, ¹J_{CP} = 10.5 Hz, PTA, -PCH₂-), 37.5 (s, 9S3, -CH₂). ³¹P NMR (CD₃NO₂, δ): -61.8 (d, ¹J_{Pt} = 2,910 Hz, PTA) and -144.6 (heptet, PF₆⁻). ¹⁹⁵Pt NMR (CD₃NO₂, δ): -4,659 (t, ¹J_{Pt} = 2,910 Hz). Anal. Calcd for C₁₈H₃₆F₁₂N₆P₄PtS₃: C, 22.06; H, 3.68; S, 9.82. Found: C, 21.75; H, 3.65; S, 8.34. UV-Vis (CH₃CN, nm (ε/M⁻¹ cm⁻¹)): 242 (5.49 × 10⁴). For compound **2** the analytical data for S was consistently +/- 1.5% from the theoretical value for multiple samples. Compound **2** consistently showed analytical data within reasonable error for C and H, and has been fully characterized by multi-nuclear NMR spectroscopy and single-crystal X-ray diffraction.

4.3.3 Preparation of [Pt([9]aneS₃)(PMe₃)₂](PF₆)₂ (**3**).

A mass of [Pt(9S3)(Cl)₂] (0.0796 g, 0.178 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. PMe₃ (0.37 mL, 1.0 M in THF, 0.370 mmol) was added, and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.0653 g, 0.401 mmol) was added to the nearly colorless homogeneous solution and refluxed for an additional 30 minutes. The resulting cloudy yellow solution was cooled to room temperature and filtered through celite. The yellow homogeneous solution was concentrated on a rotary evaporator and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.0789 g, 54.1% yield). ¹H NMR (CD₃CN, δ): 3.22 – 2.95 (12 H, AA'BB', 9S3, -CH₂) and 1.84 (18 H, d with Pt satellites, ²J_{HP} = 11.45 Hz, ³J_{HPt} = 32.97 Hz, PMe₃, -CH₃). ¹³C NMR (CD₃CN, δ): 35.3 (s, 9S3, -CH₂) and 18.0 – 17.2 (m, PMe₃, -CH₃). ³¹P NMR (CD₃CN, δ): -28.1 (d, ¹J_{Pt} = 3,150 Hz, PMe₃) and -144.1 (heptet, PF₆⁻). ¹⁹⁵Pt NMR (CD₃CN, δ): -4.454 (t, ¹J_{Pt} = 3,150 Hz). Anal. Calcd for C₁₂H₃₀F₁₂P₄PtS₃: C, 17.63; H, 3.67; S, 11.77. Found: C, 17.77; H, 3.64; S, 11.58. UV-Vis (CH₃CN, nm (ε/M⁻¹ cm⁻¹)): 240 (3.01 × 10⁴).

4.4.4. Preparation of [Pd([9]aneS₃)(PTA)Cl](PF₆) (**4**).

A mass of [Pd(9S3)(Cl)₂] (0.0790 g, 0.221 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. PTA (0.0307 g, 0.195 mmol) was added and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.0543 g, 0.463 mmol) was added to the light orange homogeneous solution and refluxed for an additional 30 minutes.

The resulting cloudy orange solution was cooled to room temperature and filtered through celite. The orange homogeneous solution was concentrated on a rotary evaporator and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.1256 g, 91.1% yield). ^1H NMR (CD_3NO_2 , δ): 4.69 – 4.51 (12 H, m, PTA, $-\text{CH}_2$) and 3.33 – 3.13 (12 H, AA'BB', 9S3, $-\text{CH}_2$). ^{13}C NMR (CD_3NO_2 , δ): 73.6 (d, $^3J_{\text{CP}} = 8.63$ Hz, PTA, $-\text{NCH}_2-$), 53.5 (d, $^1J_{\text{CP}} = 15.3$ Hz, PTA, $-\text{PCH}_2-$), 36.4 (s, 9S3, $-\text{CH}_2$). ^{31}P NMR (CD_3NO_2 , δ): -20.8 (s, PTA) and -144.0 (heptet, PF_6^-). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{ClF}_6\text{N}_3\text{P}_2\text{PdS}_3 \cdot 2\text{CH}_3\text{NO}_2$: C, 22.52; H, 4.02; S, 12.86. Found: C, 22.27; H, 3.95; S, 17.52. UV-Vis (CH_3CN , nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)): 247 (1.82×10^4) and 290 (1.78×10^4). For compound **4** the analytical data for S was consistently $\pm 4\%$ from the theoretical value for multiple samples, which suggests there was a problem with an analysis for this Pd-S compound. Compound **4** consistently showed analytical data within reasonable error for C and H and has been fully characterized by multi-nuclear NMR spectroscopy and single-crystal X-ray diffraction.

4.4.5 Preparation of $[\text{Pd}(\text{9S3})(\text{Cl})_2](\text{PTA})_2(\text{PF}_6)_2$ (**5**).

A mass of $[\text{Pd}(\text{9S3})(\text{Cl})_2]$ (0.0757 g, 0.212 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. PTA (0.0740 g, 0.471 mmol) was added and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.0762 g, 0.467 mmol) was added to the light orange homogeneous solution and refluxed for an additional 30 minutes. The resulting cloudy orange solution was cooled to room temperature and filtered through celite. The pale orange homogeneous solution was concentrated on a rotary evaporator and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.1278 g, 67.8% yield). ^1H NMR (CD_3NO_2 , δ): 4.78 – 4.51 (24 H, m, PTA, $-\text{CH}_2$) and 3.35 – 3.19 (12 H, AA'BB', 9S3, $-\text{CH}_2$). ^{13}C NMR (CD_3NO_2 , δ): 74.4 (t, $^3J_{\text{CP}} = 4.31$ Hz, PTA, $-\text{NCH}_2-$), 56.5 (t, $^1J_{\text{CP}} = 6.71$ Hz, PTA, $-\text{PCH}_2-$), 37.1 (t, $^3J_{\text{CP}} = 33.5$ Hz, 9S3, $-\text{CH}_2$). ^{31}P NMR (CD_3NO_2 , δ): -28.4 (s, PTA) and -144.2 (heptet, PF_6^-). Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{F}_{12}\text{N}_6\text{P}_4\text{PdS}_3 \cdot 2\text{CH}_3\text{NO}_2$: C, 23.70; H, 4.15; S, 9.48. Found: C, 23.41; H, 4.24; S, 6.40. UV-Vis (CH_3CN , nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)): 274 (1.62×10^4) and 293 (1.69×10^4). For compound **5** the analytical data for S was consistently $\pm 3\%$ from the theoretical value for multiple samples, which suggests there was a problem with an analysis for this Pd-S

compound. Compound **5** consistently showed analytical data within reasonable error for C and H and has been fully characterized by multi-nuclear NMR spectroscopy and single-crystal X-ray diffraction.

4.4.6 Preparation of [Pd([9]aneS₃)(PMe₃)₂](PF₆)₂ (**6**).

A mass of [Pd(9S3)(Cl)₂] (0.0754 g, 0.211 mmol) in nitromethane (20 mL) was added to a 50 mL Schlenk flask to give a suspension. The suspension was brought to a gentle reflux under a nitrogen atmosphere at which time it became homogeneous. PMe₃ (0.83 mL, 1.0 M in THF, 0.83 mmol) was added and the mixture was refluxed under nitrogen for 2.5 hours. Ammonium hexafluorophosphate (0.1123 g, 0.6890 mmol) was added to the light orange homogeneous solution and refluxed for an additional 30 minutes. The resulting cloudy orange solution was cooled to room temperature and filtered through celite. The orange homogeneous solution was concentrated on a rotary evaporator and diethyl ether was added. The resulting yellow solid was collected by vacuum filtration, washed with diethyl ether, and dried *in vacuo* (0.1256 g, 91.1% yield). ¹H NMR (CD₃NO₂, δ): 3.38 – 3.21 (12 H, AA'BB', 9S3, -CH₂) and 1.89 (18 H, d, ²J_{HP} = 10.53 Hz, PMe₃, -CH₃). ¹³C NMR (CD₃NO₂, δ): 36.5 (d, ¹J_{CP} = 289.5 Hz, PMe₃, -CH₃), 36.5 (s, 9S3, -CH₂). ³¹P NMR (CD₃NO₂, δ): -4.19 (s, PMe₃) and -144.2 (heptet, PF₆⁻). Anal. Calcd for C₁₂H₃₀F₁₂P₄PdS₃: C, 19.78; H, 4.15; S, 13.20. Found: C, 19.77; H, 4.15; S, 10.82. UV-Vis (CH₃CN, nm (ε/M⁻¹ cm⁻¹)): 250 (3.57 × 10⁴). For compound **6** the analytical data for S was consistently +/- 3% from the theoretical value for multiple samples, which suggests there was a problem with the analysis for this Pd-S compound. Compound **6** consistently showed analytical data within reasonable error for C and H and has been fully characterized by multi-nuclear NMR spectroscopy and single-crystal X-ray diffraction.

Appendix A. Supplementary Data

Crystallographic data for the five structures in this report have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1416996-1417000. Copies of these data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge, CB2 1 EZ UK (Fax: +44-1223-336-033); EMAIL: deposit@ccdc.cam.ac.uk.

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Scheme 1. Preparation of $[\text{M}([\text{9}] \text{aneS}_3)(\text{PTA})\text{Cl}](\text{PF}_6)$, $[\text{M}([\text{9}] \text{aneS}_3)(\text{PTA})_2](\text{PF}_6)_2$, and $[\text{M}([\text{9}] \text{aneS}_3)(\text{PMe}_3)_2](\text{PF}_6)_2$ where $\text{M} = \text{Pd}(\text{II})$ or $\text{Pt}(\text{II})$