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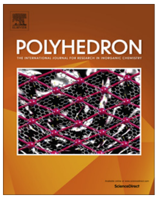

Synthetic and structural studies of heteroleptic platinum(II) and palladium(II) complexes containing thiacrown and monodentate phosphane ligands

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ABSTRACT

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$_3$ (trimethylphosphine) and the crown trithioether [9]aneS$_3$ (1,4,7-trithiacyclononane). All six reported complexes have the general formula [M([9]aneS$_3$)(P$_2$)](PF$_6$)$_2$ or [M([9]aneS$_3$)(P)(Cl)](PF$_6$) where M = 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]aneS$_3$ 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 ^{1}H and ^{13}C NMR behavior in the [9]aneS$_3$ 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 [S$_2$P$_2$+S$_1$] or [S$_2$PCl+S$_1$] coordination environments.

1. Introduction

Our group and others have previously reported on Pt(II) and Pd(II) complexes with the thiacrown ligand, 1,4,7-trithiacyclononane ([9]aneS$_3$) and related macrocyclic ligands [1–3]. The complexes show an interesting array of unusual properties including the stabilization of rare mononuclear trivalent oxidation states [4–11], 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]aneS$_3$ 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, PMe$_3$. 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]aneS$_3$ 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]aneS$_3$:

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M = Pt(II) or Pd(II) : [M([9]aneS_3)(PTA)Cl](PF_6),
[M([9]aneS_3)$(PTA)_2$]$(PF_6)_2$, and [M([9]aneS_3)$(PMe_3)_2$]$(PF_6)_2$

2. Results and discussion

2.1. Syntheses

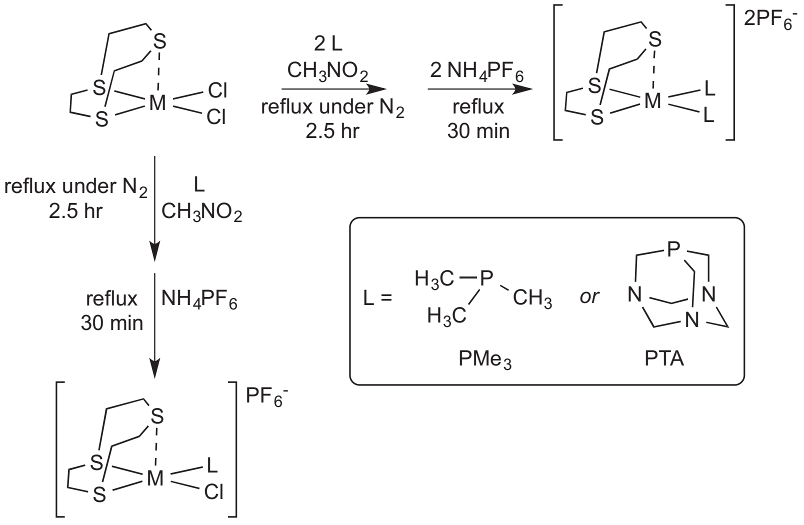
The preparation of the Pt(II) and Pd(II) [9]aneS_3 phosphane complexes invariably starts with the [M([9]aneS_3)Cl_2] complex. Improved methods for the preparation of these two important synthons have recently been reported by our group [30]. If the monophosphane–chlorido complexes are desired, one equivalent 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.

In the case of the trimethylphosphane complexes, the ligand efficacy of PMe_3 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. ^{1}H and ^{31}P 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]aneS_3)(PMe_3)Cl]$^+$ – are not included in this report. Furthermore, we had attempted to prepare Pt(II) [9]aneS_3 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 thiacrown, 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]aneS_3 phosphane complexes show the correct number of peaks, peak intensities, and splitting patterns. Their ^{13}C NMR spectra are similarly consistent, and further support the structures. Complexation of the metal center by the [9]aneS_3 ligands is confirmed using NMR spectroscopy where the coordinated [9]aneS_3 ligand typically displays its characteristic AA′BB′ “butterfly” pattern for the proton NMR spectrum and a single resonance in its ^{13}C carbon NMR spectrum [1]. Illustrative ^{1}H and ^{13}C NMR spectra for the complex [Pt([9]aneS_3)$(PTA)_2$]$(PF_6)_2$ are presented in Fig. 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]aneS_3 peak in their ^{1}H NMR spectrum (see ESI S1) and further display a broadened and unsymmetrical ^{13}C NMR resonance for the thiacrown. Certainly, the less symmetrical [S_2 + PCl] coordination environment, which contrasts with the [S_2 + P_2] environment of the *bis* complexes, is a key factor. Nevertheless, it is not the only contributor. We would note that all [9]aneS_3 complexes of Pt(II), Pd(II), and Au(III) with cyclometallating nitrogen-containing ligands, such as phenylpyridine, also contain a “unsymmetrical” [S_2 + NC] coordination environment, but in contrast display a AA′BB′ proton pattern [7,33], the same as the *bis* phosphane complexes reported here. We suggest that coupling involving the ^{31}P 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]aneS_3 resonances [7].

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]aneS_3 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 PMe_3) [34]. 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 PPh_3. Indeed, the *bis* PTA complex exhibits the second most shielded ^{31}P NMR resonance among Pd(II) [9]aneS_3 complexes (only the highly strained dppm (1,1′-bis(diphenyl)phosphinomethane) complex is larger) [20]. One of the Pt(II) [9]aneS_3 complexes included in the report, the complex *bis* PTA (**2**), is similarly noteworthy in that both their ^{31}P and ^{195}Pt nuclei are highly shielded. Indeed, the *bis* PTA complex shows the most upfield ^{31}P and ^{195}Pt 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 ^{195}Pt–^{31}P coupling in the *bis* PTA is very small (2910 Hz), with only the dppe complex showing a smaller value and all other complexes showing ^{195}Pt–^{31}P coupling greater than 3100 Hz. This small coupling



Scheme 1. Preparation of [M([9]aneS_3)(PTA)Cl](PF_6), [M([9]aneS_3)$(PTA)_2$]$(PF_6)_2$, and [M([9]aneS_3)$(PMe_3)_2$]$(PF_6)_2$ where M = Pd(II) or Pt(II).

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