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# Synthesis and characterization of Pt(II) and Pd(II) PTA and DAPTA complexes

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ABSTRACT

A series of four-coordinate air stable and water soluble *cis*- and *trans*-Pt(II) and Pd(II) complexes containing two PTA or DAPTA ligands (PTA = 1,3,5-triaza-7-phosphaadamantane; DAPTA = 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) with the general formulas, $[PtR_2(PTA)_2]$, $[M(Me)X(PTA)_2]$, $[Pt(Et)X(PTA)_2]$, $[MR_2(DAPTA)_2]$, $[MX_2(DAPTA)_2]$, and $[M(Me)X(DAPTA)_2]$ (where M = Pt or Pd; R = Me, Et, C≡CR (R = Ph, $SiMe_3$); X = Cl, Br, I) were prepared by ligand displacement starting from $[M(R)_2(COD)]$, $[M(R)(X)(COD)]$ or precursors or metathesis reactions utilizing $[MCl_2(PR_3)_2]$ precursors in good yields (63%–90%). The complexes were characterized by multinuclear NMR, IR, MS, and elemental analysis experiments and in some cases by X-ray crystallography studies. Complexes, *cis*-$[PtMe_2(PTA)_2]$ (*cis*-**1**), *trans*-$[Pt(Me)Cl(PTA)_2]$ (*trans*-**3a**), *trans*-$[PtCl_2(PTA)_2]$ (*trans*-**4**), *trans*-$[Pt(C{\equiv}CPh)_2(PTA)_2]$ (*trans*-**6**), and *trans*-$[PtI_2(DAPTA)_2]$ (*trans*-**13c**) were characterized by X-ray crystallography. The molecular structures reveal, in general, distorted square planar geometries at the metal center. For the DAPTA complexes, both syn- and anti-conformations of the DAPTA rings were observed depending upon the nature of the groups at the metal center.



## 1. Introduction

Transition metal complexes containing the phosphane ligands, 1,3,5-triaza-7-phosphaadamantane (PTA) [1] have attracted considerable attention in recent years [2]. Transition metal complexes containing the PTA ligand have been reported for nearly all of the metals from Groups 6–12 and binding is predominantly observed through the phosphorus center [2]. More recently the coordination chemistry of the related phosphane, 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) [3–5] has been explored. Both PTA and DAPTA have strongly basic phosphorus centers ($pK_a$ of the protonated form ~5.7–6.0) [6] due to the presence of the nitrogen heteroatoms and in addition, they are air stable, water soluble, resistant to oxidation and are relatively small in size. The Tolman cone angle for PTA (ca. 115°) [7–9] is similar to that for $PMe_3$ (118°) [10] whereas the cone angle for DAPTA [4] was reported to be smaller (102°). Transition-metal PTA complexes have been investigated for catalytic activity for a variety of processes such as hydrogenation, [11a–b] hydroformylation, [11a] hydroamination, [11c–d] as well as in Aza-Morita–Baylis–Hillman reactions, [11e] Suzuki [12] and Sonogashira coupling reactions using water as the solvent or utilizing an aqueous biphasic system [2]. In addition, medicinal diagnostic and therapeutic applications of metal–PTA complexes (primarily Ru systems) are intensely active areas of research [2]. Romereosa and coworkers have investigated the synthesis, characterization, and biological activity of platinum–PTA and DAPTA containing complexes [13]. The preparation and anti-cancer applications of photoluminescent gold–PTA and DAPTA complexes have also been investigated [2,4]. The synthesis and reactivity of metal–DAPTA complexes is relatively unexplored, however complexes are known with the following transition metals: Cr, W, Pd, Pt, Ag, and Au [2]. Phosphane complexes of palladium and platinum have played an extraordinary role in the development of homogeneous catalysis, especially the use of palladium catalysts for carbon–carbon coupling reactions. The synthesis, development, and applications of complexes of the nickel triad with PTA and DAPTA ligands have been increasing recently [2]. Herein we report the synthesis and characterization of a series of tetracoordinate platinum(II) and palladium(II) complexes containing PTA and DAPTA ligands.

## 2. Experimental section

### 2.1. General methods

All reactions were performed under an inert atmosphere of argon using flame or oven dried glassware on a dual-manifold

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Schlenk line unless otherwise indicated. The solvents, diethyl ether, methylene chloride, methanol, acetone, pentane and hexane were purchased from Fisher Chemical Co, and distilled over appropriate drying agents under nitrogen prior to use then stored over activated molecular sieves. Chloroform-*d*, deuterium oxide and dimethyl sulfoxide-$d_6$ were purchased from Cambridge Isotopes Inc. and dried over activated molecular sieves before use. Phenylacetylene was distilled prior to use. 1,3,5-triaza-7-phosphaadamantane (PTA) was purchased from Sigma–Aldrich and used as received. Other commercially available reagents, were used as received. 3,7-Diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) was prepared following a modified literature procedure using acetone as the solvent instead of water and recrystallized from acetone/pentane [4]. The following compounds were prepared according to a literature (or modified) procedure: [Pt(Me)X(COD)] (X = Cl, Br, I) [16], [Pt(Et)Cl(COD)] [16,17], [Pt(Et)X(COD)] (X = Br, I) [17], [$PdCl_2$(COD)] (COD = $\eta^5$-1,5-cyclooctadiene) [17,26], [$PdBr_2$(COD)] [26,27], [Pd(Me)X(COD)] (X = Cl, Br (Br complex prepared by a modified procedure similar to the preparation of the chloro complex starting from $PdBr_2$(COD)) [18], [$PtX_2$(COD)] (X = Br, I) [26], [Pd(Me)I(COD)] [16], [Pt($C_2$Ph)$_2$(COD)] [23], *cis*-[$PtCl_2$(PTA)$_2$] [11c,20–22], *cis*-[$PdCl_2$(PTA)$_2$] [5,11d,20,22,24], *cis*-[$PtCl_2$(DAPTA)$_2$] [13c], *cis*-[$PdCl_2$(DAPTA)$_2$] [5].

NMR spectra were recorded on Bruker Avance-300 MHz and Bruker ARX-500 MHz instruments at ambient temperature. Spectroscopic data were recorded at 300 MHz or 500 MHz, respectively for $^1$H, 75 MHz and 125 MHz, respectively for $^{13}$C, 121 and 202 MHz for $^{31}$P. Unless otherwise stated, chloroform-*d* was used as the NMR solvent. Proton, carbon, and phosphorus chemical shifts ($\delta$) are reported relative to the residual protio and deuterio solvent resonances, and external $H_3PO_4$, respectively. Chemical shifts are reported in ppm and the coupling constants in Hertz. Melting point determinations were obtained on a Mel-Temp melting point apparatus and are uncorrected. Mass spectral data were obtained in FAB mode with nitrobenzyl alcohol (NBA) on a JEOL MStation-JMS700. Infrared spectra were recorded on a Thermo–Nicolet Avatar 360-FT IR spectrometer. Elemental analysis determinations were performed by Atlantic Microlabs, Inc., Norcross, GA. The X-ray crystallographic data were collected on a Bruker Apex II diffractometer equipped with a CCD area detector.

### 2.2. Synthesis of the complexes

#### 2.2.1. Synthesis of cis-[$PtMe_2$(PTA)$_2$] (cis-**1**)

A solution of *cis*-[$PtMe_2$(COD)] (0.217 g, 0.651 mmol) in dichloromethane (45 mL) was placed in a 100 mL round bottom flask equipped with a 25 mL addition funnel and a magnetic stir bar. A solution of 1,3,5-triaza-7-phosphaadamantane (PTA) (0.204 g, 1.30 mmol) in methanol (45 mL) was added dropwise with stirring over 10 min. The reaction solution was stirred for 14 h at room temperature. The colorless reaction mixture was then evaporated to dryness on a rotary evaporator and the resulting white residue was washed with diethyl ether (3 × 20 mL). The solid was filtered and dried under vacuum at room temperature for 10 min. Complex *cis*-**1** was obtained as a white solid (0.316 g, 90% yield), Mp 231–233 °C. X-ray quality crystals of *cis*-**1** were obtained by slow diffusion of $Et_2O$ to $CHCl_3$ solution of *cis*-**1** at low temperature. $^1$H NMR (300 MHz): $\delta$ = 4.59, 4.54, 4.49, and 4.45 (br, 12H, $NCH_2$), 4.08 (br, 12H, $PCH_2$), 0.47 (m, $^2J_{PtH}$ = 68 Hz, 6H, Pt–$CH_3$). $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 73.6 (vt, $^3J_{PC}$ = 3 Hz, $NCH_2$), 52.7 (m, $^1J_{PC}$ = 8.6 Hz, $PCH_2$), −0.01 (dd, $^1J_{PtC}$ = 581 Hz, $^2J_{PC(trans)}$ = 94.8 Hz, $^2J_{PC(cis)}$ = 9.5 Hz, Pt–$CH_3$). $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −63.4 (s, $^1J_{PtP}$ = 1608 Hz). HRMS (FAB): *m/z* calcd for $C_{13}H_{27}N_6P_2Pt$, 524.1420; found: 524.1422 [(M–$CH_3$)$^+$]. *Anal.* Calc. for $C_{14}H_{30}N_6P_2Pt$: C, 31.17; H, 5.61. Found: C, 31.26; H, 5.64%.

On extending the reaction time to 20 h, complex *cis*-**1** appears to undergo slow isomerization to give a mixture of *cis*-**1** and *trans*-$PtMe_2$(PTA)$_2$, *trans*-**1** in approximately in 16:1 ratio, respectively. $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −60.4 (s, $^1J_{PtP}$ = 2777 Hz, *trans*-**1**), −63.4 (s, $^1J_{PtP}$ = 1608 Hz, *cis*-**1**).

#### 2.2.2. Synthesis of trans-[PtX(Me)(PTA)$_2$] [X = Cl (trans-**2a**); X = Br (trans-**2b**); X = I (trans-**2c**)]

A representative synthesis is described for complex *trans*-**2a**. To a 100 mL round bottom flask equipped with a 25 mL addition funnel and a magnetic stir bar was placed [Pt(Me)Cl(COD)] (0.067 g, 0.189 mmol) dissolved in 10 mL of dichloromethane. A solution of PTA (0.060 g, 0.382 mmol) in methanol (10 mL) was added dropwise with stirring over 10 min. The reaction solution was stirred for 14–15 h at room temperature. The volatiles were removed *in vacuo* to give a white precipitate that was washed with diethyl ether (3 × 5 mL). The precipitate was filtered and dried *in vacuo* at room temperature. Complex *trans*-**2a** was obtained as a white powder (0.094 g, 86% yield), Mp 278–280 °C. $^1$H NMR (300 MHz): $\delta$ = 4.50 and 4.4 (br, 12H, $NCH_2$), 4.24 (br, 12H, $PCH_2$), 0.30 (t, $^2J_{PtH}$ = 82 Hz, $^3J_{PH}$ = 7.1 Hz, 3H, Pt–$CH_3$). $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −60.4 (s, $^1J_{PtP}$ = 2779 Hz). *Anal.* Calc. for $C_{13}H_{27}N_6P_2ClPt$: C, 27.89; H, 4.86. Found: C, 27.86; H, 4.77%.

*trans*-[PtBr(Me)(PTA)$_2$] (*trans*-**2b**). Reagents used: [Pt(Me)Br(COD)] (0.064 g, 0.16 mmol) in 10 mL of dichloromethane and PTA (0.052 g, 0.331 mmol) in 10 mL of methanol. Complex *trans*-**2b** was obtained as a white powder (0.090 g, 93% yield), Mp 231 °C (dec). $^1$H NMR (300 MHz): $\delta$ = 4.50 (br, 12H, $NCH_2$), 4.25 (br, 12H, $PCH_2$), 0.36 (t, $^2J_{PtH}$ = 81 Hz, $^3J_{PH}$ = 7 Hz, 3H, Pt–$CH_3$). $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −63.4 (s, $^1J_{PtP}$ = 2748 Hz). HRMS (FAB): *m/z* calcd for $C_{13}H_{28}N_6P_2{}^{79}Br{}^{195}Pt$, 604.0682; found: 604.0697 [(M+H)$^+$]. *Anal.* Calc. for $C_{13}H_{27}N_6P_2BrPt$: C, 25.84; H, 4.50. Found: C, 25.75; H, 4.50%.

*trans*-[PtI(Me)(PTA)$_2$] (*trans*-**2c**). Reagents used: [Pt(Me)I(COD)] (0.040 g, 0.089 mmol) in 10 mL of dichloromethane and PTA (0.028 g, 0.178 mmol) in 10 mL of methanol. Complex *trans*-**2c** was obtained as a pale yellow solid (0.050 g, 88% yield), Mp 261–263 °C. $^1$H NMR (300 MHz): $\delta$ = 4.51 and 4.48 (br, 12H, $NCH_2$), 4.31 (br, 12H, $PCH_2$), 0.47 (t, $^2J_{PtH}$ = 79 Hz, $^3J_{PH}$ = 7.1 Hz, 3H, Pt–$CH_3$). $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −67.9 (s, $^1J_{PtP}$ = 2690 Hz). HRMS (FAB): *m/z* calcd for $C_{13}H_{28}N_6P_2IPt$, 652.0543; found: 652.0518 [(M+H)$^+$]. HRMS (FAB): *m/z* calcd for $C_{12}H_{24}N_6P_2IPt$, 636.0230; found: 636.0242 [(M–$CH_3$)$^+$]. *Anal.* Calc. for $C_{13}H_{27}N_6P_2IPt$: C, 23.97; H, 4.18. Found: C, 23.95; H, 4.25%. When incompletely dried [PtI(Me)(COD)] was used for the reaction, the oxidized product [PtI(Me)(OPTA)$_2$] was produced (see Supporting information).

#### 2.2.3. Synthesis of trans-[PtX(Et)(PTA)$_2$] [X = Cl (trans-**3a**); X = Br (trans-**3b**); X = I (trans-**3c**)]

A representative synthesis is described for complex **3a**. To a 100 mL round-bottom flask equipped with a 25 mL addition funnel and a magnetic stir bar was placed [Pt(Et)Cl(COD)] (0.125 g, 0.340 mmol) in 10 mL of dichloromethane. A solution of PTA (0.106 g, 0.675 mmol) in 10 mL of methanol was added dropwise with stirring over 10 min. The reaction solution was stirred for 14–15 h at room temperature. The resulting colorless solution was evaporated *in vacuo* and the residue was washed with diethyl ether (3 × 5 mL). The white residue was filtered and dried *in vacuo* at room temperature. Complex *trans*-**3a** was obtained as a white solid (0.268 g, 76% yield), Mp 240–242 °C. X-ray quality crystals of *trans*-**3a** were obtained by slow diffusion of diethyl ether to a methylene chloride solution of *trans*-**3a** at low temperature. $^1$H NMR (300 MHz): $\delta$ = 4.49 (br, 12H, $NCH_2$), 4.26 (br, 12H, $PCH_2$), 1.25–0.85 (m, 5H, $PtCH_2CH_3$). $^{31}$P{$^1$H} NMR (121 MHz): $\delta$ = −60.3 (s, $^1J_{PtP}$ = 2961 Hz). HRMS (FAB): *m/z* calcd for $C_{14}H_{30}N_6P_2ClPt$, 574.1343; found: 574.1337 (M+H)$^+$. HRMS(FAB): *m/z* calcd for