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Synthesis and Crystallographic Characterization of a Novel Platinocycle

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Summary: The efficient synthesis and characterization of the trans-platinum complex $(Ph_3P)_2Pt(C_{25}H_{13}N)$ by coupling the dialkyne 3,5-bis-(2-ethynyl-phenylethynyl)-pyridine with cis-$PtCl_2(PPh_3)_2$ is described. The X-ray crystal structure shows that the platinum center is essentially square planar with the two phosphine ligands mutually perpendicular to the planar organic ligand.

Introduction

The synthesis of platinum acetylides has recently been directed toward the preparation of specialty materials including nonlinear optical materials,[1] building blocks in the preparation of large organoplatinum macrocycles,[2] liquid crystalline materials,[3] or the synthesis of conjugated metal-containing polymers.[4] Our current research efforts are directed to the synthesis of metal-containing macrocycles. In this paper we describe the synthesis and characterization of a small, strained, platinocycle formed by coupling of a preformed dialkynyl ligand with *cis*-bis(triphenylphosphine)platinum dichloride in an amine as solvent and base.[5] Small platinocycles have recently been synthesized using a similar platinum σ-acetylide motif. Thus Haley[6] reported the synthesis and crystallographic characterization of a strained cyclic *trans*-platinum diacetylide complex while Youngs[7] reported the characterization of a relatively unstrained cyclic *cis*-platinum diacetylide. The methodology has been extended to the synthesis of larger macrocycles; for example Takahashi[8] synthesized a macrocycle containing four *trans*-palladium diacetylides. Stang[9] and Youngs[10] independently utilized four *cis*-platinum diacetylide moieties in the synthesis of different large organometallic macrocycles.

Results and Discussion

The synthesis of the platinum complex **5** is shown in Scheme 1. The dialkynyl ligand **4** was synthesized by repetitive applications of the Sonagshira coupling[11] of aryl halides with terminal alkynes. Thus palladium-catalyzed coupling of 3,5-dibromopyridine with 2.2 equiv of trimethylsilylacetylene in refluxing triethylamine followed by basic hydrolysis yielded 3,5-diethynylpyrindine, **2**, in 86% overall isolated yield. Compound **2** was coupled with an excess (3.5 equiv) of 1,2-diiodobenzene to form 3,5-bis(2-iodophenylethynyl)pyridine, **3**, in modest yield (63%). Palladium-catalyzed coupling of diiodide **3** with trimethylsilylacetylene followed by basic hydrolysis, as before, afforded the organic ligand 3,5-bis-(2-ethynylphenylethynyl)pyridine, **4**, in moderate yield (77%). The dialkyne **4** was then reacted with 1 equiv of bis(triphenylphosphine)platinum dichloride at a concentration of 1.6×10^{-3} M in refluxing diethylamine for 10 h. The solvent was concentrated, diluted with hexane, and passed through a short silica column to yield essentially pure complex **5** in 74% yield.[12] The colorless solid yielded crystals suitable for X-ray analysis when recrystallized from hexane.[13]

Although the reaction utilized *cis*-bis(triphenylphosphine)platinum dichloride, the resultant product **5** has mutually trans phosphine ligands as shown in Figure 1. In this regard it should be noted that although there are several examples of stereospecific syntheses of platinum diacetylides, i.e., *cis*-platinum dichlorides yielding cis products,[14] other reports indicate that cis/trans mixtures are obtained when diethylamine is used

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[12] TLC Analysis indicated that a single product was formed, and we found no evidence for the formation of oligomeric or polymeric products. Future studies will consider the role of concentration on the nature of the products formed.

[13] Crystal data: **5** ($C_{61}H_{41}NP_2Pt$), M = 1044.98, triclinic space group P-1, a = 10.8302(16), b = 14.743(2), and c = 16.083(2) Å, α = 81.856(2), β = 80.155(2), and γ = 68.650 (2)°, V = 2347.7(6) Å^3, Z = 2, D_{calcd} = 1.478 Mg/m^3, λ = 0.71073 Å, T = 173(2) K.

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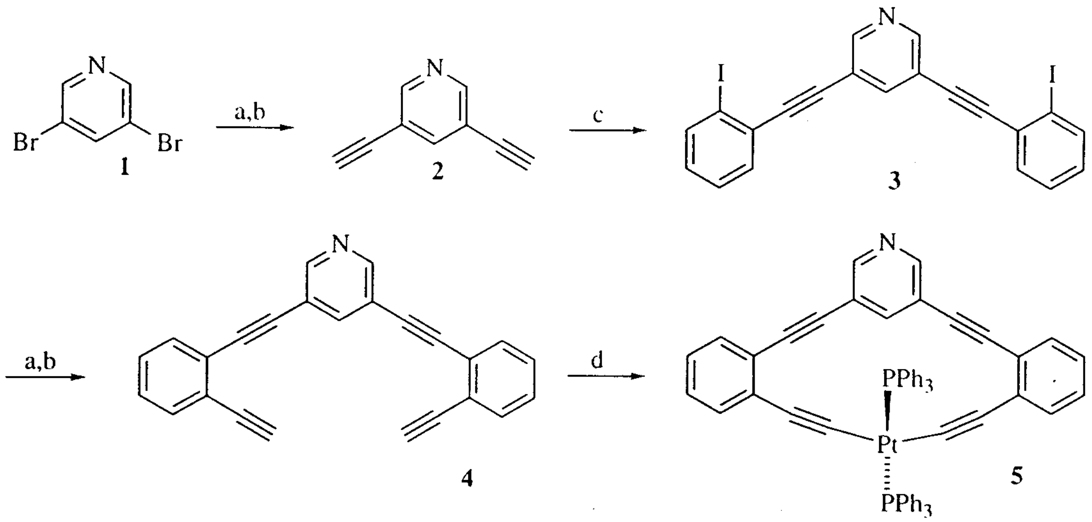
10.1021/om0004904 CCC: $19.00

Scheme 1. Synthesis of Platinum Complex 5[a]



[a] Reaction conditions: (a) 2.2 equiv of $(CH_3)_3SiC_2H$, $PdCl_2(PPh_3)_2$/CuI catalyst, refluxing NEt_3; (b) K_2CO_3/CH_3OH; (c) 3.5 equiv of 1,2-diiodobenzene, $PdCl_2(PPh_3)_2$/CuI catalyst, refluxing NEt_3; (d) $PtCl_2(PPh_3)_2$, catalytic CuI, refluxing Et_2NH.

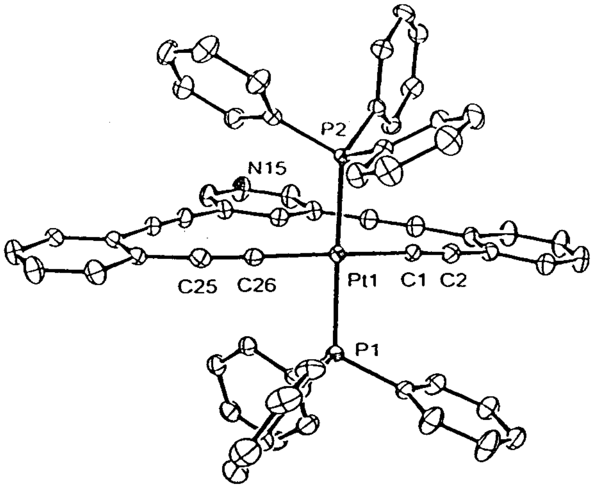


Figure 1. Crystal structure of **5**.[20] The thermal elipsoids are drawn at the 35% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1)–C(26) =1.995(3); Pt(1)–C(1) =1.996(3); C(1)–C(2) = 1.209(5); C(25)–C(26) = 1.215(5); Pt(1)–P(2) = 2.3048(8); Pt(1)–P(1) = 2.3103(9). Selected bond angles (deg): P(1)–Pt(1)–P(2) = 170.68; C(1)–Pt(1)–C(26) = 170.02; C(1)–Pt(1)–P(1) = 90.12; C(3)–C(2)–C(1) = 173.6; C(2)–C(1)–Pt(1) = 169.0; C(24)–C(25)–C(26) = 171.4; C(25)–C(26)–Pt = 167.5.

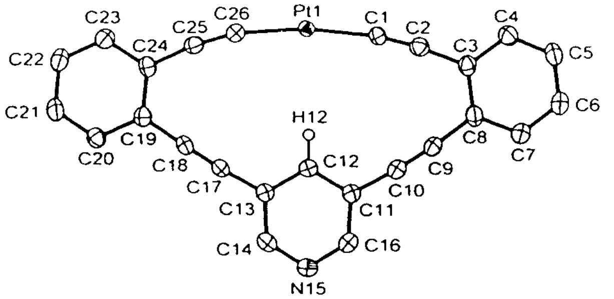


Figure 2. View of the platinum-bound ligand. The two phosphine ligands and all hydrogen atoms except H12 have been omitted for clarity.

as solvent and base.[15] In addition it has been reported that metal salts, including copper iodide, catalyze the isomerization of the less stable *cis*-platinum diacetylides to the corresponding *trans*-platinum diacetylides.[16] In this case we believe, however, that the steric environment of the small dialkyne ligand dictates the formation of the trans compound **5**. Indeed a cis square planar complex would have the phosphine ligands coplanar with the organic ligand and this is prohibited by the large bite angle of the dialkynyl ligand (>120°) and the large cone angle of the triphenylphosphines. Consequently there is significantly less strain when the phosphine ligands are rotated out of the plane of the organic ligand into a trans configuration mutually perpendicular to the organic ligand as shown in Figure 1.

The geometry about the platinum is slightly distorted square planar with the phosphine ligands tilted away from the organic ligand. In addition the alkynes are bent away from linearity to act as a pincer to bind the platinum atom as shown in Figure 2. Although the organic ligand is essentially planar the bent alkynes impart strain on the entire ligand, and this is manifest in the bond lengths of the flanking benzene rings. For example the inner benzene bonds C(24)–C(19) and C(3)–C(8) are elongated to 1.419(2) and 1.417(5) Å, respectively and the outer benzene C–C bonds are compressed for example the bond length of C(6)–C(7) is 1.369(5) Å for a difference in bond length around the ring of 4.8 pm. Despite the strain in the organic ligand, the platinum carbon bond lengths, the platinum phosphorus bond lengths, and the platinum-bonded C–C triple bond lengths [C(1)–C(2) = 1.209(5) and C(25)–C(26) = 1.215(5) Å] are similar to those observed in other platinum diacetylides.[17]

It is noteworthy that the distortion of the alkynes holds the platinum atom relatively close to H12 on the

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central pyridine ring as shown in Figure 2. The calculated distance between this proton and the platinum is 3.00 A and this close nonbonded interaction is manifest in a downfield shift of the ^{1}H NMR signal of this proton. This proton is readily identified in the ^{1}H NMR spectrum, appearing as a triplet with $J \approx 2$ Hz[18] and exhibits a chemical shift of 8.35 ppm in complex **5** as compared to a chemical shift of 7.98 ppm in the free ligand **4**.

We intend to extend this study to the preparation of larger platinocycles and also to explore the complexation of other transition metals with the ligand **4** and related dialkynes.

Experimental Section

General. The ^{1}H NMR spectra were recorded at 200 MHz and the ^{13}C NMR spectra were recorded at 50 MHz. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Materials. Diethylamine, triethylamine, 3,5-dibromopyridine, trimethylsilyl acetylene, *cis*-$PtCl_2(PPh_3)_2$, triphenylphosphine copper iodide (ACROS), and 1,2-diiodobenzene (Oakwood) were used as received.

3,5-Diethynylpyridine[19] **(2)** was synthesized according to Sonagshira's[11] coupling procedure. Thus a solution of 3,5-dibromopyridine (2.5 g, 10.6 mmol), trimethylsilyl acetylene (3.2 mL, 23.3 mmol), triphenyl phosphine (120 mg, 0.74 mmol), copper iodide (8 mg, 0.04 mmol), and bis(triphenylphosphine)-palladium(II) chloride (78 mg, 0.11 mmol) in triethylamine (60 mL) was prepared in a pressure flask. Argon was bubbled through the solution for 5 min, and the vessel was sealed with a Teflon stopcock and heated at 70 °C for 8 h. The flask was allowed to cool to room temperature, diluted with hexane:ethyl acetate (1:1), and washed three times with water and finally with saturated aqueous sodium chloride. The organic phase was dried with magnesium sulfate, and the solvent was removed in vacuo to yield an off-white solid. The ^{1}H NMR spectrum indicated that this material was essentially pure 3,5-bis(trimethylsilanylethynyl)pyridine: ^{1}H NMR δ 8.62 (d, $J = 2$ Hz, 2H), 7.83 (t, $J = 2$ Hz, 1H), 0.29 (s, 18H). The solid was thus deprotected without further purification. The crude solid was dissolved in methanol (100 mL), sodium carbonate (0.5 g) was added, and the heterogeneous mixture was stirred at room temperature for 2 h. The mixture was diluted with water and extracted twice with hexane/ethyl acetate (1/1, 2 × 70 mL). The organic extracts were washed with water, saturated aqueous sodium chloride, and dried over magnesium sulfate. The solvent was evaporated in vacuo to yield 3,5-diethynylpyridine as a white solid (1.14 g, 86%): mp 78 °C; IR (KBr) 3280, 3216, 2104, 1581 cm^{-1}; ^{1}H NMR δ 8.61 (d, $J = 2.0$ Hz, 2 H), 7.82 (t, $J = 2.0$ Hz, 1H), 3.24 (s, 2H); ^{13}C NMR δ 150.80, 140.80, 117.88, 80.42, 78.30. Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.66; H, 4.09; N, 10.91.

3,5-Bis(2-iodophenylethynyl)pyridine (3). A solution of 3,5-diethynylpyridine (220 mg, 1.7 mmol), 1,2-diiodobenzene (1.78 g, 5.4 mmol), triphenylphosphine (30 mg), copper iodide (5 mg), and bis(triphenylphosphine)palladium(II) chloride (36 mg) in triethylamine (20 mL) in a pressure flask was deaerated as described above, sealed, and heated at 80 °C for 8 h. The tube was allowed to cool to room temperature, diluted with ethyl acetate, and washed with water and saturated aqueous sodium chloride. The organic phase was separated and dried with magnesium sulfate, and the solvent was removed in vacuo. The crude product was subjected to flash chromatography with hexane:ethyl acetate (10:1) as eluant and the desired compound obtained as an off-white solid (581 mg, 63%). The material was recrystallized from ether/hexane as colorless crystals: mp 86 °C; ^{1}H NMR δ 8.76 (d, $J = 2.0$ Hz, 2 H), 8.03 (t, $J = 2.0$ Hz, 1 H), 7.90 (dd, $J = 1{,}2, 7.7$ Hz, 2 H), 7.56 (dd, $J = 1.8, 7.7$ Hz, 2H), 7.36 (dt, $J = 1.8, 7.7$ Hz, 2 H), 7.06 (dt, $J = 1.8, 7.7$ Hz, 2H); ^{13}C NMR δ 150.0, 139.4, 137.8, 131.6, 128.1, 127.8, 126.9, 118.8, 100.1, 94.3, 87.6. Anal. Calcd for $C_{21}H_{11}NI_2$: C, 47.50; H, 2.09; N, 2.64. Found: C, 47.78; H, 2.28; N, 2.41.

3,5-Bis(2-ethynylphenylethynyl)pyridine (4) was synthesized as described for **2** starting with **3** (350 mg, 0.66 mmol) and 2.5 equiv (160 mg, 1.63 mmol) of trimethylsilylacetylene. The intermediate bis-trimethylsilyl-protected compound was essentially pure by ^{1}H NMR: δ 8.72 (d, $J = 2$ Hz, 2H), 7.99 (t, $J = 2$ Hz, 1H), 7.55−7.51 (m, 4H), 7.33−7.28 (m, 4H), 0.29 (S, 18H). After base-promoted deprotection as before an off-white solid was isolated and purified by flash chromatography with hexane:ethyl acetate (10:1) as eluant. Compound **4** was obtained as colorless crystals (189 mg, 77%): mp 151 °C; IR (KBr) 3275, 3031, 1580 cm^{-1}; ^{1}H NMR δ 8.73 (d, $J = 2.0$ Hz, 2 H), 7.98 (t, $J = 2.0$ Hz, 1H), 7.55 (m, 4 H), 7.34 (m, 4H), 3.40 (s, 2H); ^{13}C NMR δ 150.08, 139.62, 131.66, 130.88, 127.61, 124.24, 123.87, 118.97, 90.61, 88.10, 80.84, 80.53. Anal. Calcd for $C_{25}H_{13}N$: C, 91.72; H, 4.00; N, 4.27. Found: C, 91.43; H, 4.03; N, 3.99.

Platinum Complex (5). Bis(triphenylphosphine)platinum dichloride (274 mg, 0.35 mmol) and **4** (118 mg, 0.36 mmol) and were added to dry diethylamine (220 mL) in a round-bottom flask fitted with a Schlenk adapter. Argon was bubbled through the flask for 10 min, a condenser was attached, and the mixture was refluxed under an argon atmosphere for 10 h. A distillation adapter was then fitted, and the diethylamine was distilled until the mixture was concentrated to 70 mL. Hexanes (100 mL) were added to the concentrate, and the resultant heterogeneous mixture was passed through a short column of silica gel. The column was eluted with a mixture of hexane and ethyl acetate (4:1). The solvent was evaporated under vacuum, and the product was isolated as an off-white solid (267 mg, 74%). A sample suitable for crystallographic analysis was recrystallized from hexane: ^{1}H NMR δ 8.42 (d, $J = 2.0$ Hz, 2 H), 8.35 (t, $J = 2.0$ Hz, 1 H), 7.83 (br m, 12 H), 7.35 (m, 2 H), 7.20 (m, 15 H), 7.01 (m, 4 H), 6.74 (m, 2 H); ^{13}C NMR δ 149.18, 145.31, 135.44, 135.32, 132.37, 131.79, 131.20, 130.57, 129.17, 128.35, 128.23, 128.12, 128.02, 125.01, 124.52, 121.47, 95.41, 88.66. Anal. Calcd for $C_{61}H_{41}NP_2Pt$: C, 70.11; H, 3.95. Found: C, 69.84; H, 3.95.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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