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# Synthesis, characterization, and crystal structure of platinum(II) and palladium(II) chlorides with an acidic α-diimine ligand

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## Abstract

Reaction of the symmetrical α-diimine ligand **L** with either $PtCl_2$ or $PdCl_2(C_6H_5CN)_2$ affords the square planar $d^8$ complexes **1** and **2**, respectively. Both complexes were characterized by NMR spectroscopy and elemental analysis. The solid-state structure of **1**, which crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.688(2)$ Å, $b = 13.840(2)$ Å, $c = 14.136(2)$ Å, $\alpha = 111.346(14)°$, $\beta = 103.82(2)°$, and $\gamma = 102.69(2)°$, was established by X-ray crystallography.

*Keywords:* Diazabutadiene ligands; Platinum(II) complex; Palladium(II) complex

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## 1. Introduction

Late transition metal complexes of 1,4-diazabutadiene ligands have lately received renewed attention, primarily due to their utility as homogeneous polymerization catalysts [1]. As a result, the reaction chemistry of this class of diimine ligand with a variety of transition metals has become well established [2]. Recently we communicated our efforts at forming hydrophilic 1,4-diazabutadiene and related unsymmetrical pyridine-imine ligands for use in aqueous organometallic chemistry [3]. Coordination of these ligands to low-valent Pt(0) and Pd(0) metal centers was shown to stabilize the imine functionality towards hydrolysis. Despite a growing interest in the chemistry of water-soluble organometallic complexes and their potential application as recoverable "green" catalysts [4,5], the use of diimine complexes in this area of research has remained relatively unexplored. Herein, we describe the preparation of divalent platinum and palladium compounds with an acidic 1,4-diazabutadiene ligand and the structure of the Pt(II) species as determined in the solid-state by X-ray crystallography.

## 2. Experimental

Transition metal starting materials $PdCl_2(C_6H_5CN)_2$ and $PtCl_2$ were obtained from Strem Chemicals, Inc. (Newburyport, MA) and used without further purification. Other reagents were obtained from commercial sources and used as received. All of the reactions and manipulations involving transition metal compounds were performed under $N_2$ using standard inert-atmosphere and Schlenk techniques [6,7]. Solvents were dried and distilled by standard procedures. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on a JEOL Eclipse 400 NMR in DMF-$d_7$ at 400 and 100 MHz, respectively. Chemical shifts are reported downfield in ppm ($\delta$) relative to tetramethylsilane by reference to residual protonated solvent signals with the following abbreviations: d = doublet, s = singlet, and br = broad signal. Melting points were recorded in open capillary tubes. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

### 2.1. Synthesis of 1,4-bis(4-$CO_2HC_6H_4$)-2,3-dimethyl-1,4-diazabutadiene, L

4-Aminobenzoic acid (2.88 g, 21 mmol) was dissolved in dry MeOH (10 ml). Formic acid (90%, 4 drops) was added, followed by the dropwise addition of 2,

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3-butanedione (0.88 ml, 10 mmol). The solution was stirred at ambient temperature for 24 h. The pale yellow precipitate that resulted was isolated by filtration and washed with cold methanol. Yield 1.1 g (33%). $^1$H NMR (DMF-$d_7$): $\delta$ 13.1 (br, 2H), 8.09 (d, 4H), 7.00 (d, 4H), 2.15 (s, 6H). $^{13}$C{$^1$H} NMR (DMF-$d_7$): $\delta$ 168.4, 167.5, 156.0, 130.9, 127.2, 118.8, 15.0.

### 2.2. Synthesis of $PtCl_2$(**L**), **1**

A 125-ml Schlenk flask equipped with a magnetic stir bar was charged with $PtCl_2$ (0.100 g, 0.38 mmol) and 0.134 g (0.41 mmol) of the diazabutadiene ligand **L** and flushed with nitrogen. THF (30 ml) was added by syringe, and the resulting solution was sealed under nitrogen, heated to 50 °C, and stirred for 48 h to complete transformation to the desired product. The orange solid that precipitated from solution upon cooling to ambient temperature was isolated by filtration, washed with THF, and dried under vacuum. Yield 0.130 g (59%). $^1$H NMR (DMF-$d_7$): $\delta$ 13.2 (br, 2H), 8.19 (d, 4H), 7.37 (d, 4H), 2.02 (s, 6H). $^{13}$C{$^1$H} NMR (DMF-$d_7$): $\delta$ 181.3, 166.9, 149.5, 130.7, 130.1, 124.1, 20.6. Decomposed 330 °C. Anal. calc. for $C_{18}H_{16}Cl_2N_2O_4Pt$: C, 36.62%; H, 2.73%; N, 4.75%. Found: C, 36.13%; H, 2.45%; N, 4.83%.

### 2.3. Synthesis of $PdCl_2$(**L**), **2**

A 125-ml Schlenk flask equipped with a magnetic stir bar was charged with $PdCl_2(C_6H_5CN)_2$ (0.100 g, 0.26 mmol) and 0.092 g (0.28 mmol) of the diazabutadiene ligand **L** and flushed with nitrogen. THF (30 ml) was added by syringe, and the resulting solution was sealed under nitrogen, heated to 50 °C, and stirred for 24 h to complete transformation to the desired product. The yellow-orange solid that precipitated from solution upon cooling to ambient temperature was isolated by filtration, washed with THF (3 × 3 ml), and dried under vacuum. Yield 0.109 g (83%). $^1$H NMR (DMF-$d_7$): $\delta$ 13.2 (br, 2H), 8.14 (d, 4H), 7.30 (d, 4H), 2.33 (s, 6H). $^{13}$C{$^1$H} NMR (DMF-$d_7$): $\delta$ 182.0, 166.9, 149.5, 130.2, 130.1, 123.4, 21.1. Decomposed 308 °C. Anal. calc. for $C_{18}H_{16}Cl_2N_2O_4Pd$: C, 43.10%; H, 3.21%; N, 5.58%. Found: C, 42.84%; H, 3.22%; N, 5.55%.

### 2.4. Structure determination

X-ray quality crystals of **1** were grown by slow evaporation of DMF solvent at ambient temperature. An orange prism, approximately 0.37 mm × 0.37 mm × 0.25 mm in size, was chosen by size, habit, and polarized light microscopy and mounted on a glass fiber. Intensity

Table 1
Crystallographic data for $PtCl_2$(**L**), **1**

| | |
|---|---|
| Formula | $C_{18}H_{16}Cl_2N_2O_4Pt \cdot C_6H_{14}N_2O_2$ |
| Formula weight | 1473.02 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 8.688(2) |
| $b$ (Å) | 13.840(2) |
| $c$ (Å) | 14.136(2) |
| $\alpha$ (°) | 111.346(14) |
| $\beta$ (°) | 103.82(2) |
| $\gamma$ (°) | 102.69(2) |
| $V$ (Å$^3$) | 1446.32 |
| $Z$ | 2 |
| $d_{calc}$ (g cm$^{-3}$) | 1.691 |
| $\mu$ (mm$^{-1}$) | 5.08 |
| $\lambda$ (Å) | 0.71073 |
| Crystal dimensions (mm) | 0.37 × 0.37 × 0.25 |
| $T$ (K) | 295 |
| Scan method | $\omega/2\theta$ |
| $F_{000}$ | 724 e |
| Total no. of reflections | 5553 |
| No. of reflections [$I > 3\sigma(I)$] | 4533 |
| Structural parameters | 339 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| $R_1$[a] [$F_o > 4\sigma(F_o)$] | 0.0739 |
| $R_1$[a], $wR_2$[b] (all data) | 0.0845, 0.1938 |
| GOF[c] | 1.049 |

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

[c] Goodness-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})]^{1/2}$, based on all data.

data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromated Mo-$K_\alpha$ radiation. The unit cell was determined and refined from 25 reflections with $1° < 2\theta < 25°$. Reflection data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92) [8] and refined with SHELXL 97 [9]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions on parent atoms in the final refinement. The largest unassigned peak in the final difference map was 3.44 e/Å$^3$ located 0.91 Å from the Pt atom. Details of the crystal parameters, data collection, and structure refinement are given in Table 1.

## 3. Results and discussion

The condensation reaction between 2,3-butanedione and 4-aminobenzoic acid was initially attempted by refluxing a 1:2 mixture of these reagents in ethanol, with benzene (10%, v/v) added to promote azeotropic removal of water byproduct. All efforts to form the desired diimine product **L** by this method were unsuccessful. The addition of molecular sieves to the reaction mixture in an attempt to further dry the solution and promote product formation was also ineffective. Thus, the catalytic method employed by Eisenberg and others for the formation of similar diimine ligands was used [10,11]. Reaction of 2,3-butanedione with two mole equivalents of 4-aminobenzoic acid in a minimum amount of dry methanol with a catalytic amount of formic acid affords the symmetrical 1,4-disubstituted-2,3-dimethyl-1,4-diazabutadiene ligand **L** (Fig. 1) in moderate isolated yield. $^1$H and $^{13}$C NMR signals are consistent with formation of the diimine compound. Specifically, generation of the diimine can be assessed from the $^{13}$C NMR spectrum of **L** where a singlet resonance at 167.5 ppm attributed to the imine carbons is observed with a corresponding absence of a ketone carbonyl resonance from the starting 2,3-butanedione.

Reaction of $PtCl_2$ with one equivalent of **L** in THF at 50 °C resulted in the formation of the Pt(II) coordination compound **1**. For comparison with this Pt dichloride, the Pd(II) analogue **2** was synthesized by reaction of **L** with $PdCl_2(C_6H_5CN)_2$. Diagnostic of chelating ligand coordination in these complexes is an overall downfield shift of signals in the $^1$H NMR spectra by about 0.1–0.4 ppm for Pt and 0.05–0.3 ppm for Pd. Not surprisingly, the aromatic protons *ortho*- to the imine nitrogen atoms ($\delta$ 7.00 in **L**) are influenced to a greater extent by metal coordination than the protons in the *meta*-positions for both complexes. Similar resonance shifts have been observed in related compounds [10,12]. Curiously the signals for the $–CH_3$ protons in complex **1** have shifted upfield by 0.13 ppm relative to the free ligand whereas the corresponding protons in **2** experience a downfield shift of 0.18 ppm. The reason for this sole difference in the NMR data is not fully understood; however, a similar effect has been observed for the imine protons in related compounds [10]. Also consistent with ligand coordination in solution in each of these complexes is a downfield shift of signals in the $^{13}$C NMR spectra by 5.6–6.1 and 12.9–13.6 ppm for the $–CH_3$ and $–CO_2H$ carbons, respectively. Compounds **1** and **2** are stable in air and readily soluble in polar organic solvents such as methanol, DMSO, and DMF, but are insoluble in water. Addition of NaOH to a suspension of either **1** or **2** in $H_2O$ results in immediate dissolution of the transition metal complex, presumably as a result of anion formation via deprotonation of $–CO_2H$ groups. Unfortunately, neither **1** nor **2** are stable under these alkaline conditions, and both slowly decompose to untraced products.

Single crystals of $\mathbf{1} \cdot 2(C_3H_7NO)$ suitable for X-ray analysis were grown by slow evaporation of DMF solvent at ambient temperature. The molecular structure of **1** and the associated atom-numbering scheme are depicted in Fig. 2 with selected bond lengths and angles given in Table 2. The geometry around the d$^8$ Pt center in **1** is that of a distorted square plane, where the relatively small N(1)–Pt(1)–N(2) bond angle of 77.4(4)° is a result of chelating ligand steric constraints. The bond angles around the Pt atom, which sum to 359.94(58)°,

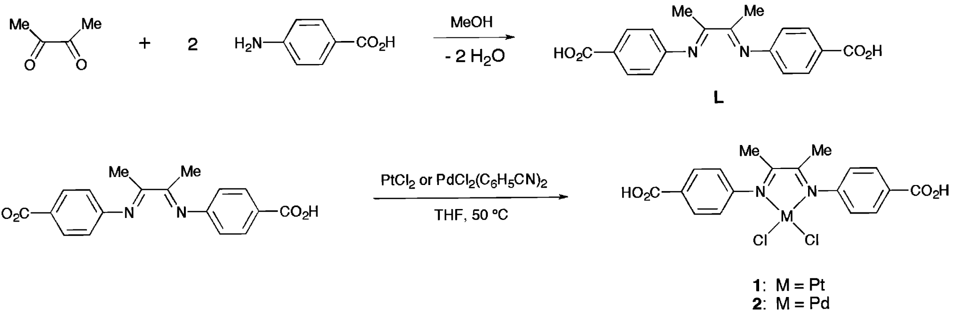

Fig. 1. Synthetic scheme for the preparation of Pt(II) and Pd(II) dichloride complexes **1** and **2**.

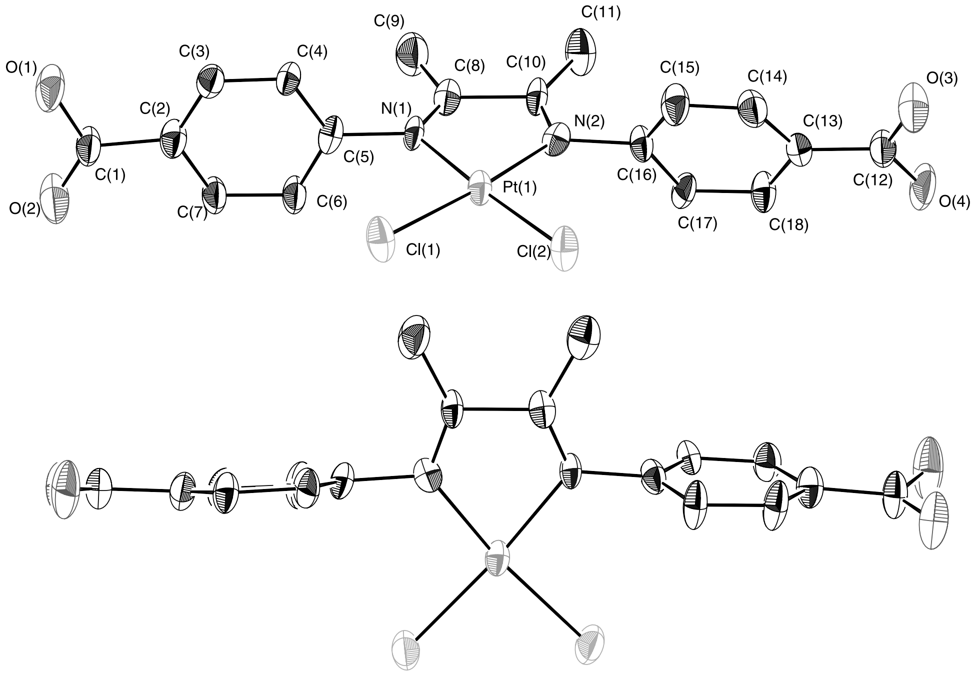

Fig. 2. ORTEP representations of the molecular structure of complex **1** with 50% probability ellipsoids (H atoms and DMF solvent molecules omitted for clarity).

Table 2
Selected bond distances (Å) and angles (°) for $PtCl_2(\mathbf{L})$, **1**

| Bond distances (Å) | | Bond angles (°) | |
|---|---|---|---|
| Pt(1)–N(1) | 2.017(10) | N(1)–Pt(1)–N(2) | 77.4(4) |
| Pt(1)–N(2) | 1.975(10) | Cl(1)–Pt(1)–Cl(2) | 89.54(15) |
| Pt(1)–Cl(1) | 2.276(4) | N(1)–Pt(1)–Cl(1) | 95.8(3) |
| Pt(1)–Cl(2) | 2.275(4) | N(2)–Pt(1)–Cl(2) | 97.2(3) |
| N(1)–C(8) | 1.26(2) | C(8)–N(1)–Pt(1) | 116.4(8) |
| N(2)–C(10) | 1.26(2) | C(10)–N(2)–Pt(1) | 121.4(8) |
| N(1)–C(5) | 1.44(2) | C(8)–C(10)–N(2) | 109.5(11) |
| N(2)–C(16) | 1.49(2) | C(10)–C(8)–N(1) | 115.1(11) |
| C(8)–C(10) | 1.54(2) | C(5)–N(1)–Pt(1) | 123.5(8) |
| C(1)–O(1) | 1.33(2) | C(16)–N(2)–Pt(1) | 124.6(8) |
| C(1)–O(2) | 1.20(2) | O(1)–C(1)–O(2) | 120.0(12) |
| C(12)–O(3) | 1.29(2) | O(3)–C(12)–O(4) | 123.4(13) |
| C(12)–O(4) | 1.26(2) | | |

are consistent with a planar geometry. A mean plane analysis of the five atoms comprising the transition metal square plane reveals a maximum deviation from ideality of 0.0184(25) Å for Pt(1). The aryl-ring that includes C(2)–C(7) is nearly perpendicular to this metal–ligand plane with a calculated angle between the two planes of 88.12(42)°. By way of contrast, the ring containing C(13)–C(18) has a torsion angle with the metal–ligand plane of only 73.82(43)° and is thus tilted relative to the other aryl-ring. A mean plane angle of 19.27(65)° has been calculated between the two aryl-rings. While the aryl-rings on diimine ligands may be expected to lie perpendicular to the metal–ligand plane based on steric repulsions, as observed previously [10,13], square planar Pd and Pt complexes of diazabutadiene ligands with widely disparate torsion angles have been reported [14,15]. Generally speaking, 1,4-diaryl diazabutadiene ligands without sterically demanding groups in the *ortho*-positions of the aromatic rings tend to favor a broader range of plane angles than similar compounds with greater steric repulsion, but factors such as the other ligands bound to the metal center also play a crucial role in determining the overall geometry. The bond distances and angles for **1** are very similar to those of other square-planar platinum diimine compounds [10,16,17]. Single crystals of **2** were also grown by slow evaporation of DMF solvent. Unfortunately, final refinement of the X-ray structure data was not fully satisfactory ($R_1 = 0.1381$) due to the presence of solvent molecules with random occupancy in the crystal lattice. Calculated Pd–Cl (2.2501(31) and 2.2645(29) Å) and Pd–N (2.0578(60) and 2.0581(90) Å) bond distances in **2** are nearly identical to those of related compounds [13,18]. As with the Pt(II) complex **1**, the aryl-rings in **2** are rotated 88.12(34)° and 73.23(33)° relative to the metal–chelate ring. A mean plane angle of 19.48(49) is calculated between the two aryl-rings in **2**. The reaction chemistry of these metal complexes and related water-soluble species is currently under investigation.

## Supplementary materials

Crystallographic data for the structural analysis of **1** in CIF format has been deposited with the Cambridge Crystallographic Data Center under CCDC no. 199729. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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