

Article

# Cleavage of the Pt-I bond in a Primary Cycloplatinated Amine by Chelation

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**Abstract:** In the square-planar cycloplatinated complex of *R*-phenylethylamine, both additional substituents, an anionic iodo and a neutral donor ligand, have been replaced by chelating ethylenediamine. A very pronounced *trans* influence is observed in the cationic product complex: Two significantly different bond distances to the chelating ligand are found, the longer in *trans* geometry to the coordinated carbon atom. The positive charge of the monocationic complex is balanced by an uncoordinated iodide. This target solid crystallizes with four independent cations and anions in the unit cell; pairs of complex cations related by pseudo-inversion are stabilized by T stacking. Classical N–H···I hydrogen bonds lead to a layer structure in the (0 1 0) plane.

**Keywords:** cycloplatination; chelation; *ortho*-metalation; pseudo-symmetry

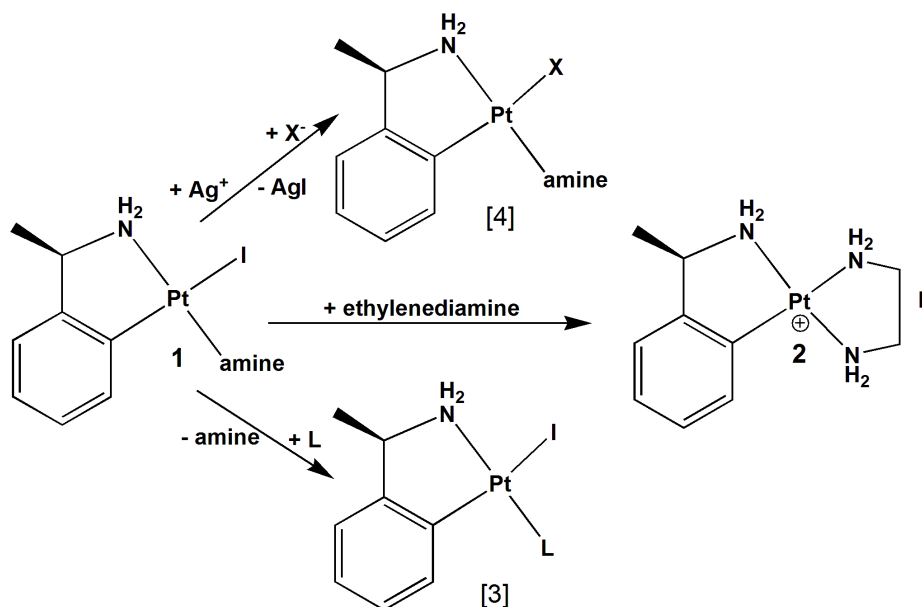
## 1. Introduction

In 1968, the first orthometalation reactions of tertiary benzyl amines with palladium and platinum were conducted by Cope and Friedrich [1]. Up to 2007 little progress was made in the field of cycloplatination of primary amines [2]. In 2008 Calmuschi *et al.* [3] presented the first convenient synthesis of cycloplatinated amines; they also showed that the  $\sigma$  donor ligand (Scheme 1) may be displaced in stoichiometric substitution reactions by strong nucleophiles, such as phosphanes or pyridines. In contrast to this reactivity, the iodo ligand proved inert in thermal substitution; no exchange

with radiolabeled iodine was observed after prolonged refluxing in toluene [4]. Substitution—even under mild conditions—is possible, however, via formation of a suitable intermediate: When the iodo ligand is precipitated with silver salts of weakly coordinating anions, a Pt(II) aqua complex is obtained, and the coordinated water molecule is readily displaced by anionic or neutral nucleophiles [4]. In this contribution, we communicate the substitution of both monodentate ligands,  $\sigma$  donor amine and iodo substituent by the well-known chelating ligand ethylenediamine, and we report the crystal structure of the resulting ionic product. Organoplatinum (II) complexes of ethylenediamine derived from substituted rather than primary amines have been published by Kvam *et al.* [5] and Failes *et al.* [6].

## 2. Results and Discussion

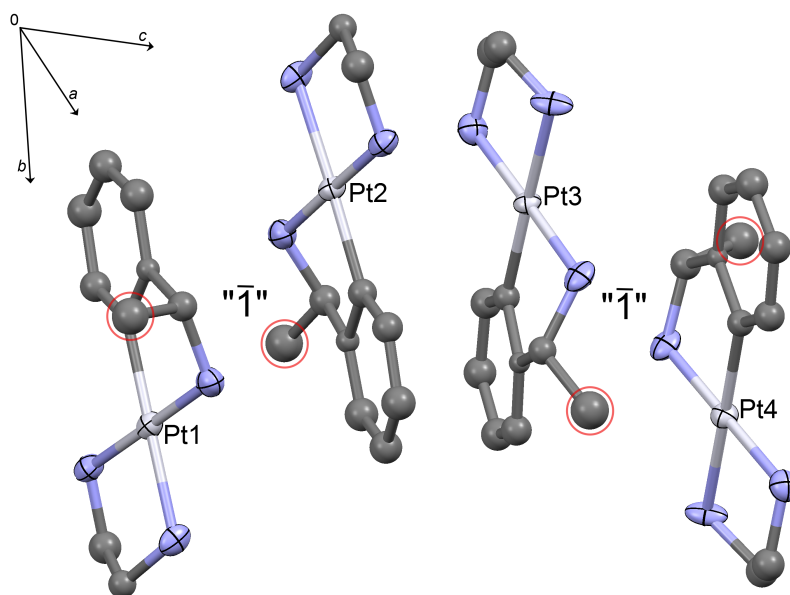
The primary cycloplatination product **1** (Scheme 1, left) was synthesized according to Calmuschi–Cula *et al.* [3]. The one-step reaction with an equimolar amount of ethylenediamine (en) was performed in methanol at 40 °C over a period of 16 h. The rather long reaction time is due to the inertness of the Pt(II) center. As outlined in the Introduction, thermal substitution in **1** is challenging: Exchange of the iodo ligand requires activation by a silver salt, and even displacement of the  $\sigma$  coordinated amine by an alternative donor ligand is sluggish [3]. One may speculate that the latter substitution is the primary step in the reaction reported here; in a second step, the chelating effect of the coordinated en ligand is sufficiently stabilizing to cleave the platinum–iodide bond. The halide thus displaced acts as counteranion to balance the charge. Progress of the reaction may conveniently be monitored by  $^1\text{H}$ -NMR spectroscopy: The doublet associated with the methyl group of the non-cycloplatinated amine at 1.36 ppm disappears, whereas a broad multiplet corresponding to the four methylene H atoms of the en ligand in **2** shows up at 2.71–2.77 ppm. Colorless block-shaped crystals of suitable size and quality for single crystal X-ray diffraction can be obtained by slow evaporation of a solution of **2** in methanol.



**Scheme 1.** The reaction pathway.

## 2.1. Crystal Structure Determination

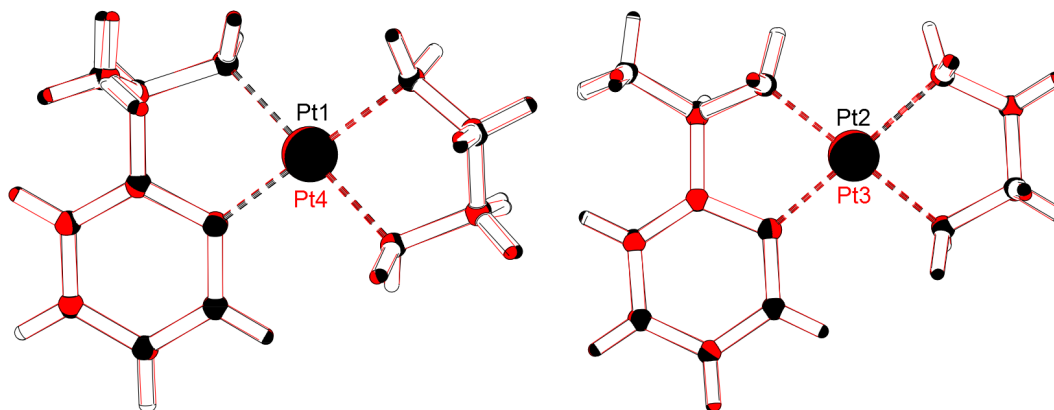
The Cambridge Crystallographic Database [7] contains 295 structures in which ethylenediamine acts as a chelating ligand for Pt, and only two of these involve tertiary cycloplatinated amines [5] or imines [6]. No cycloplatinated primary or secondary amines containing ethylenediamine have been reported to date. Compound **2** crystallizes with four cations and anions in the unit cell which also corresponds to the asymmetric unit in the triclinic space group  $P1$ . Displacement ellipsoid plots for all four symmetrically independent ion pairs are given in the Supporting Information, Figures S1–S4. All independent complex cations agree with respect to the structural *trans* influence: The bond distances between the transition metal cation and the two N atoms of the en ligand differ significantly. In each cation, the Pt–N bond *trans* to carbon is *ca.* 0.1 Å longer (mean value 2.143(6) Å) than the bond *trans* to the amino group (mean value 2.055(6) Å). A strong *trans* influence exerted by the C atom of the cyclometalated ligand has previously been reported for square-planar Pt [8] and Pd [9–16] complexes. Figure 1 shows that the four monocationic platinum complexes are pairwise related by pseudo-inversion. The residues associated with Pt1 and Pt2 form the first, and those associated with Pt3 and Pt4 the second pair. This pseudosymmetry allows to describe 80%–90% of the total electron density in the centrosymmetric super group  $P\bar{1}$  [17]. Although centrosymmetry can be safely excluded because **2** is derived from enantiopure *R*-phenylethylamine, the pseudosymmetry has consequences for the refinement of the structure model; we will come back to these implications in Section 3.4.



**Figure 1.** Pseudosymmetry in the cationic residues of **2**; centers of pseudoinversion have been marked. The methyl carbon atoms (highlighted with a red circle) are attached to homochiral centers and therefore not related by pseudoinversion. H atoms have been omitted for clarity, reprinted with permission from [18].

Closer inspection of a pseudosymmetric pair reveals that the partaking cations interact by T stacking (*cf.* Figure S5, ESI): One of the amino H atoms in each complex points towards the aromatic  $\pi$  system

of the partner cation. The two cations in the same pair differ with respect to the orientation of the methyl groups at the homochiral centers. These moieties can obviously not match inversion and are marked with a red circle in Figure 1; their orientation results in a more and a less planar conformer in each pair. The close correspondence between the less planar complex cations associated with Pt1 and Pt4 on the one hand and the more planar residues associated with Pt2 and Pt3 on the other hand is shown in Figure 2.



**Figure 2.** Superposition of conformationally related (**left**) less planar and (**right**) more planar cations, reprinted with permission from [19].

The distance of the methyl group from the least squares plane defined by the metalated phenyl ring represents a convenient way to measure planarity: This parameter is 1.359(13) and 1.363(13) Å for the less planar cations and 0.418(13) and 0.606(13) Å for the more planar cations.

A total of 24 potential donors for conventional hydrogen bonds exist in the structure of **2**. Four of these, one per cationic residue, are involved in T stacking as mentioned above. The remaining 20 donors are engaged in N–H···I interactions, thus constructing a 2D-network in the (0 1 0) plane. A complete list of all short contacts is available in the Supplementary Information, Tables 1 and 2.

### 3. Experimental Section

#### 3.1. Instrumentation

All measurements were conducted at the Institute for inorganic Chemistry of the RWTH Aachen University. NMR spectra were recorded on a Bruker Avance II Ultrashield Plus 400 (Bruker, Karlsruhe, Germany) ( $^1\text{H}$ -NMR: 400 MHz;  $^{13}\text{C}$ -NMR: 100.6 MHz;  $^{195}\text{Pt}$ -NMR: 86 MHz;  $^1\text{H}$  and  $^{13}\text{C}$  resonances are referenced to TMS and  $^{195}\text{Pt}$  to  $\text{H}_2\text{PtCl}_4$ . Powder diffraction experiments were performed at room temperature on flat samples with a Stoe & Cie STADI P diffractometer (Stoe, Darmstadt, Germany) equipped with an image plate detector with constant  $\omega$ -angle of  $55^\circ$  using germanium-monochromated Cu–K $\alpha$ 1 radiation ( $\lambda = 1.54051$  Å).

### 3.2. Synthesis

56 mg (0.1 mmol) of the primary cycloplatination product **1** and 12 mg (0.2 mmol) ethylenediamine were dissolved in 20 mL methanol and stirred at 40 °C for 16 h. 40 mL of hexane were added to extract **2** and remove the phenylethylamine. **2** was recovered from the methanol phase by slow evaporation. The solid was re-dissolved in methanol; slow evaporation at room temperature afforded colorless block-shaped crystals. Yield 56 mg (0.09 mmol; 88%). Melting point: Decomposition at 230 °C. Phase purity was proven via X-ray powder diffraction.

### 3.3. Characterization

Nuclear magnetic resonance spectroscopy:  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  = 1.46 (d, 3H,  $\text{CH}_3$ ); 2.71–2.77 (b, 4H,  $\text{CH}_2\text{CH}_2$ ); 4.18–4.23 (q, 1H, CH); 6.81–6.85 (m, 1H,  $\text{sp}^2\text{-H}$ ); 6.88–6.93 (m, 2H,  $\text{sp}^2\text{-H}$ ); 7.02–7.04 (m, 1H,  $\text{sp}^2\text{-H}$ ) ppm.  $^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}$ ):  $\delta$  = 22.69 (1C,  $\text{CH}_3$ ); 44.22 (C, En-C); 47.08 (C, En-C); 60.26 (1C, CH); 121.94 (1C,  $\text{sp}^2\text{-C}$ ); 124.55 (1C,  $\text{sp}^2\text{-C}$ ); 124.61 (1C,  $\text{sp}^2\text{-C}$ ); 125.74 (1C,  $\text{sp}^2\text{-C}$ ); 125.80 (1C,  $\text{sp}^2\text{-C}$ ); 133.27 (1C,  $\text{sp}^2\text{-C}$ ) ppm.  $^{195}\text{Pt}$ -NMR ( $\text{D}_2\text{O}$ ):  $\delta$  = −3362.4 ppm. All NMR spectra are depicted as Figures S6–S8 for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{195}\text{Pt}$ , respectively. The powder diffractogram is visualized in Figure S9; all available in the Supplementary Information.

### 3.4. X-ray Data Collection and Structure Refinement

Intensity data were collected with a Bruker D8 goniometer equipped with an APEX CCD area detector and an Incoatec microsource (Mo- $\text{K}_\alpha$  radiation,  $\lambda$  = 0.71073 Å, multilayer optics) at 100 K (Oxford Cryostream 700 instrument, Oxfordshire, UK). Data were integrated with SAINT [20] and corrected for absorption by multi-scan methods [21]. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least squares procedures based on  $F^2$ , as implemented in SHELXL-13 [22]. **2** was synthesized from enantiopure *R*-phenylethylamine, and therefore crystallization in a chiral space group was expected. The decision for  $P1$  over its centrosymmetric super group  $P\bar{1}$  was confirmed by intensity statistics: The average value for  $\langle E^2-1 \rangle$  amounted to 0.722, in close agreement with the expectation for an acentric distribution. In the absence of crystallographic inversion, pseudo-inversion was encountered (see Results and Discussion). Correlation between displacement parameters of atoms related by pseudo-inversion prevented refinement of a conventional structure model with anisotropic displacement parameters (adps) for all non-hydrogen atoms. In order to maintain a high ratio between observations and variables and to ensure physically meaningful displacement parameters, the following refinement strategy was employed: For Pt and I atoms individual adps were refined; N atoms related by pseudo-inversion were constrained to common adps; C atoms related by pseudo-inversion were constrained to share common isotropic displacement parameters; a total of 52 displacement parameter constraints was thus established; C atoms associated with the chiral centers and their methyl substituents were assigned individual isotropic displacement parameters. Hydrogen atoms were treated as riding with N–H = 0.99 Å, C–H = 0.98 Å for  $\text{CH}_3$ , C–H = 0.95 Å for aryl–CH and C–H = 0.99 Å for alkyl–CH groups

and assigned isotropic displacement parameters constrained to  $U_{iso}(H) = -1.5U_{eq}(C)$  for methyl groups or  $U_{iso}(H) = -1.2U_{eq}(C,N)$  otherwise.

CCDC reference number: 1061196. Copies of the data can be freely obtained on application: deposit@ccdc.cam.ac.uk. Crystal data.  $C_{10}H_{18}N_3IPt$ , 502.26 g/mol. Triclinic,  $P1$  (no.1);  $a = 9.3309(9)$ ,  $b = 10.6319(10)$ ,  $c = 15.8037(15)$  Å;  $\alpha = 78.6270(12)$ ,  $\beta = 75.6680(12)$ ,  $\gamma = 64.4590(13)^\circ$ ;  $V = 1363.2(2)$  Å<sup>3</sup>;  $Z = 4$ ; 11,239 reflections, of which are 10,657 independent;  $R_{int} = 0.0358$ ;  $F(000) = 920$ ;  $\mu = 12.53$  mm<sup>-1</sup>;  $\rho_{calc} = 2.447$  g/cm<sup>3</sup>; 293 refined parameters.  $R_{1(all)} = 0.0400$ ;  $wR_2 = 0.0838$ ;  $S_{all} = 1.020$ ;  $\Delta\rho(\text{min/max})$ :  $-1.68/2.53$  e/Å<sup>3</sup>; Flack parameter: 0.028(6), determined by Parsons' method using 4820 quotients [23].

#### 4. Conclusions

Both monodentate ligands in a cycloplatinated primary amine have been replaced by the chelating ligand ethylenediamine in a single reaction; under these conditions, the otherwise inert platinum–iodine bond has been cleaved. The crystal structure of this new organoplatinum compound confirms the pronounced *trans* influence of the carbon atom attached to platinum.

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#### Author Contributions

Synthesis and characterization were carried out by William Raven and Irmgard Kalf. The crystallographic study was executed by William Raven. Ulli Englert is the leading scientist of the group.

#### Conflicts of Interest

The authors declare no conflict of interest.

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