

## Four- versus Five-coordination in Platinum(II) Complexes of $\alpha$ -Diimines and the Crystal Structure of [PtClMe(i-Pr-N=CHCH=N-i-Pr)]

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(Received June 23, 1987)

### Abstract

The complex [PtClMe(i-Pr-N=CHCH=N-i-Pr)] and its unstable five-coordinate ethylene adduct have been prepared and characterized by  $^1\text{H}$  NMR. The crystal and molecular structure of the former has been determined. The complex crystallizes in the orthorhombic space group  $Pca2_1$ , with  $a = 12.138(6)$ ,  $b = 9.601(6)$ ,  $c = 10.586(6)$  Å,  $Z = 4$ . Refinement converged to a final  $R$  index of 0.059. The geometrical parameters of the structure are compared with those of a related complex and discussed in relation to the stability of the five-coordinate olefin adducts.

### Introduction

The coordination chemistry of  $\alpha$ -diimines has received much attention during the last decade, largely because of the variety of their bonding modes to a metal atom [1]. In platinum chemistry  $\alpha$ -diimines have shown the remarkable ability to stabilize five-coordinate species. The stable complexes have a trigonal bipyramidal structure, with the chelating nitrogen ligand and an olefin in the equatorial plane [2].

During recent studies [2b, 3] aimed to clarify the factors affecting the relative stabilities of related four- and five-coordinate Pt(II) complexes, a series of compounds of the type [PtClMe(N-N)] (N-N = diamine, diimine or di-hydrazone) were prepared, together with the corresponding five-coordinate species [PtClMe( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(N-N)] [3]. In contrast with the previously described dichlorocomplexes [PtCl<sub>2</sub>(N-N)] and [PtCl<sub>2</sub>( $\eta^2$ -olefin)(N-N)] [2], the methyl derivatives displayed the ability to undergo a relatively fast association–dissociation equilibrium, thus allowing a meaningful correlation between the steric

and electronic features of the ligands and the thermodynamic stability of the two coordination states [3]. As a part of our studies on this subject, we found it of interest to attempt the preparation and investigate the properties of the closely related complexes [PtClMe(i-Pr-N=CHCH=N-i-Pr)], [PtClMe(t-Bu-N=CHCH=N-t-Bu)], and their corresponding five-coordinate ethylene adducts.

### Experimental

$^1\text{H}$  NMR spectra were recorded at 60 and 250 MHz on a Varian T-60 A and on a Bruker AM-250 spectrometer, respectively, CDCl<sub>3</sub> was used as solvent and tetramethylsilane as internal standard. Solvents and reagents were of AnalaR grade. Unless otherwise stated, they were used without further purification. The ligands and the platinum complexes were prepared and stored under nitrogen.

### Materials

The ligands i-Pr-N=CHCH=N-i-Pr (**a**) and t-Bu-N=CHCH=N-t-Bu (**b**) were synthesized as previously described [4]. The starting platinum complexes [PtClMe(Me<sub>2</sub>S)<sub>2</sub>] (**1**) [5] and [PtClMe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**3**) [6] were prepared as previously described.

### Preparation of the Complexes

#### [PtClMe(i-Pr-N=CHCH=N-i-Pr)] (**2a**)

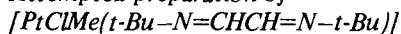
[PtClMe(Me<sub>2</sub>S)<sub>2</sub>] (**1**) (185 mg, 0.50 mmol) was dissolved in methylene chloride (2 ml) and a 2:1 molar excess of i-Pr-N=CHCH=N-i-Pr (**a**) was added. The solution turned rapidly to a dark red colour. After 2 h at room temperature the solvent was evaporated and the residue washed with petroleum ether, giving 175 mg (91% yield) of the crude product, which could be recrystallized from diethyl ether.  $^1\text{H}$  NMR  $\delta$  9.03 (s, 1H, N=CH,  $J(\text{H-Pt}) = 104$  Hz), 8.60 (s, 1H, N=CH,  $J(\text{H-Pt}) = 36$  Hz), 4.79 (m,

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1H, CH), 1.52 (s, 3H, Pt-Me,  $J(\text{H-Pt}) = 79$  Hz), 1.49 (d, 6H, CMe<sub>2</sub>), 1.46 (d, 6H, CMe<sub>2</sub>).

Alternatively, the complex could be obtained by adding a slight excess of the diimine **a** to a methylene chloride solution of [PtClMe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**3**) at room temperature. The solution turned immediately to a dark red colour, and the required complex could be obtained in 90% yield by evaporating the solvent and washing the residue with petroleum ether.

#### Attempted preparation of



By reacting **1** with the ligand **b**, using the same procedure as above described for complex **2a** (both at room temperature and under reflux), the starting complex **1** was recovered unaltered. Treatment of **1** with a large excess of the ligand **b** in boiling toluene for 20 min resulted in extensive decomposition to unidentified products.

In an alternative attempt, complex **4b** (see later) was recovered unaltered in 80% yield after boiling in chloroform for 30 min. Boiling **4b** in toluene for 30 min led to extensive decomposition to unidentified products.



The chloride-bridged dimer [PtClMe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**3**) was suspended (partially dissolved) in anhydrous diethyl ether (0.3 mmol/ml) at -40 °C under ethylene atmosphere, and the stoichiometric amount of the diimine **a**, dissolved in anhydrous diethyl ether (0.3 mmol/ml) was added dropwise under stirring. An orange precipitate formed, which could be filtered and stored at -30 °C, but rapidly decomposed with loss of ethylene if warmed at room temperature, giving the four-coordinate complex **2a**. <sup>1</sup>H NMR (-40 °C) δ 8.67 (s, 2H, N=CHCH=N,  $J(\text{H-Pt}) = 37$  Hz), 4.12 (m, 2H, CH), 2.83 (d, 2H, CH=CH,  $J(\text{H-Pt}) = 80$  Hz), 2.07 (d, 2H, CH=CH,  $J(\text{H-Pt}) = 55$  Hz), 1.60 (d, 6H, 2C-Me), 1.43 (d, 6H, 2C-Me), -0.20 (s, 3H, Pt-Me,  $J(\text{H-Pt}) = 72$  Hz).

The NMR data (in particular the very high field shifts of the ethylene resonances) are consistent with a trigonal bipyramidal structure, as found for similar complexes [3].



This complex was prepared as previously described [3], using the same procedure as for **4a** at room temperature. The <sup>1</sup>H NMR spectrum has been reported [3].

#### X-ray Data Collection and Structure Determination

Dark violet-red crystals of [PtClMe(i-Pr-N=CHCH=N-i-Pr)] (**2a**), suitable for X-ray analysis, were obtained by slow evaporation of a diethyl ether-hexane (5:1) solution of the complex. A selected crystal was mounted on a Philips PW 100

computer controlled four-circle diffractometer equipped with a graphite monochromator. Standard centering and auto-indexing procedures were used. The orientation matrix and accurate unit cell dimensions were determined from a least-square fit of 25 symmetry-related reflections ( $10 < 2\theta < 23^\circ$ ). Intensity data were collected at 24 °C using the  $\theta-2\theta$  scan method. The intensities were corrected for Lorentz and polarization factors and scaled to give 864 independent  $F_{hkl}$  values with  $I > 3\sigma(I)$ . Crystal data and details of data collection are reported in Table I.

TABLE I. Crystal Data and Details of Measurements for **2a**

Molecular formula	C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> ClPt
Molecular weight	386.61
Space group	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> (Å)	12.138(6)
<i>b</i> (Å)	9.601(6)
<i>c</i> (Å)	10.586(6)
<i>V</i> (Å <sup>3</sup> )	1233.7
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.08
Radiation	graphite monochromatized Mo Kα (λ = 0.7107 Å)
Crystal size (mm)	0.10 × 0.15 × 0.10
μ (cm <sup>-1</sup> )	111.1
2θ range (°)	0–45
Scan type and speed	$\theta-2\theta$ ; 2.50–2.35° min <sup>-1</sup>
Reflections collected	2063
Reflections with $I > 3\sigma(I)$	864
<i>R</i>	0.059
<i>R</i> <sub>w</sub>	0.054

The position of Pt and Cl atoms were determined from a three-dimensional Patterson synthesis. The carbon and nitrogen atoms were located from subsequent Fourier maps. The hydrogen atoms, except those of the methyl groups (probably disordered) were also located from the final difference Fourier synthesis, and included in the calculations but not refined. Anisotropic thermal parameters were used only for Pt and the atoms directly bonded to it. Full-matrix least-square refinements were used; they converged to a conventional *R* index of 0.059. The weighting scheme used in the final calculations was of the form  $w^{-1} = a_j |F_o|^j$ . The *a<sub>j</sub>* parameters were calculated using the program PESO [7]. Scattering factors for the atoms were taken from Cromer and Waber [8]; the scattering factors for Pt and Cl were corrected for the real and the imaginary part of the anomalous dispersion using Cromer's values [9] (no absorption corrections have been applied). All computations were carried out on a CDC Cyber 76 computer using the programs of ref. 10. The positional parameters are listed in Table II, the labelling scheme being shown in Fig. 1.

TABLE II. Fractional Atomic Coordinates ( $\times 10^4$ ) for [PtClMe(i-Pr-N=CHCH=N-i-Pr)] (2a)<sup>a</sup>

Atom	<i>x/a</i>	<i>y/a</i>	<i>z/a</i>
Pt	4374(1)	1131(1)	5000(0)
Cl	5244(12)	3203(11)	4975(51)
C	5646(22)	326(20)	6012(23)
N(1)	3054(30)	1774(31)	3768(30)
N(2)	3520(24)	-682(25)	4502(25)
C(1)	2640(34)	-548(37)	3922(39)
C(2)	2352(37)	836(41)	3466(43)
C(3)	3947(25)	-2160(31)	4840(86)
C(4)	3624(46)	-3189(57)	3841(54)
C(5)	3403(59)	-2696(48)	6079(56)
C(6)	2840(30)	3277(37)	3307(37)
C(7)	1595(48)	3739(45)	3247(46)
C(8)	3454(50)	3534(48)	2056(50)
H(1)	2089	-1441	3654
H(2)	1676	898	3313
H(3)	4930	-2008	5037
H(6)	3216	4005	3927

<sup>a</sup>e.s.d.s given in parentheses.

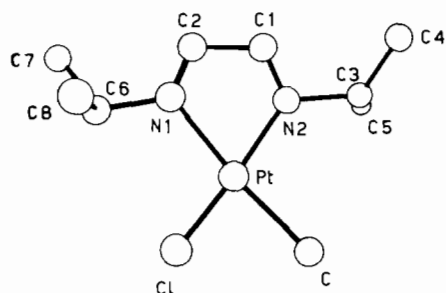
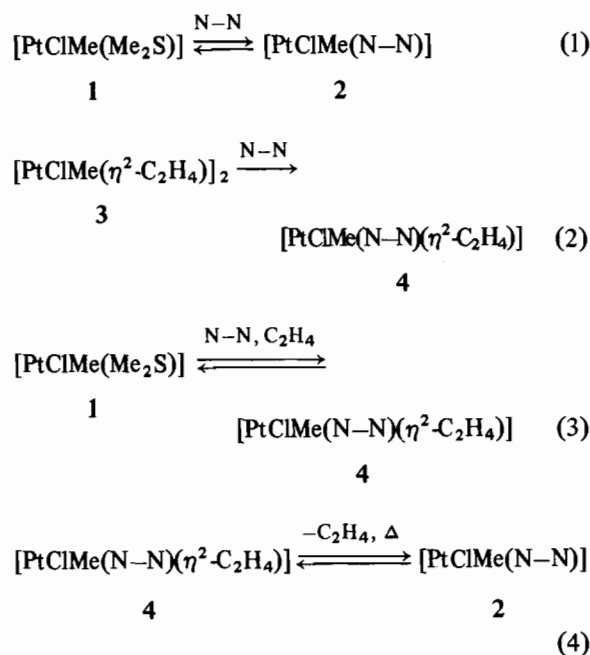


Fig. 1. Molecular structure of [PtClMe(i-Pr-N=CHCH=N-i-Pr)] (1a) as viewed orthogonally to the coordination plane.

## Results and Discussion

By using the synthetic procedures outlined in Scheme 1, we were able to obtain, as stable species, complexes 2a and 4b only. 4a could be obtained through reaction of the chloride bridged dimer 3 with the diimine a at  $-40^\circ\text{C}$ , according to eqn. (2), as an unstable orange solid, which rapidly decomposed above  $-10^\circ\text{C}$  with loss of ethylene and formation of the deep red 2a according to eqn. (4). 2b could neither be obtained by thermal loss of ethylene from complex 4b (eqn. (4)), nor by displacement of dimethylsulphide from complex 1 (eqn. (1)). In both cases no reaction took place, or extensive decomposition occurred under drastic conditions.

Although the two ligands a and b look rather similar, they actually display a quite different behaviour, the former selectively stabilizing a square-planar species, the latter giving exclusively a trigonal bipyramidal complex. In order to get some direct



(a, N-N = i-Pr-N=CHCH=N-i-Pr;  
b, N-N = t-Bu-N=CHCH=N-t-Bu)

Scheme 1.

evidence about the steric factors affecting the different coordination properties of the two ligands, and to obtain at the same time a structural characterization of a complex belonging to the class [PtClR-(N-N)], we submitted single crystals of 2a to X-ray diffraction analysis.

A molecular model of 2a is shown in Fig. 1. The complex displays the usual arrangement of the ligands around the platinum center, the atoms N(1), N(2), C, Cl, and Pt lying almost in a plane (the averaged deviation from this plane is 0.07 Å). The ligand skeleton C(6)-N(1)-C(2)-C(1)-N(2)-C(3) lies also in a plane, the averaged deviation from which is less than 0.05 Å, and this plane is almost coincident with the coordination plane (dihedral angle  $7^\circ$ ).

Both the isopropyl groups have the bonds C(8)-C(6) and C(5)-C(3) at  $90^\circ$  with respect to the double bonds N(1)-C(2) and N(2)-C(1) respectively; the conformation is nearly 'skew' as usually found in similar cases. The overall conformation of the molecule, excluding Cl and C, is characterized by a pseudo  $C_2$  symmetry, the binary axis passing through Pt and the middle point of the bond C(1)-C(2). Calculations performed exchanging the position of Cl and C proved that there is some degree of statistical vicariance between them, though not numerically evaluable. The isopropyl groups also seem to have a relatively high libration about the C-N bonds; as a consequence of these facts the thermal parameters and the final *R* index are relatively high.

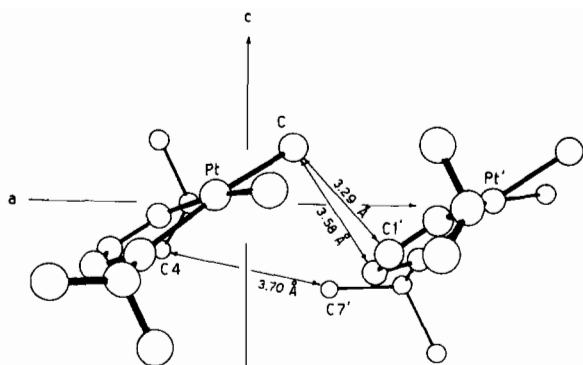


Fig. 2. Two molecules of  $[\text{PtClMe}(\text{i-Pr}-\text{N}=\text{CHCH}=\text{N}-\text{i-Pr})]$  (1a) as viewed down the  $b$  axis, repeated along  $a$  by the glide plane. The shortest intermolecular distances are indicated.

The molecules show quite a regular packing except for an intermolecular carbon-carbon distance of 3.30 Å between C and C(1)' of the adjacent molecule, repeated by the glide plane  $a$  (see Fig. 2). This contact occurs between a  $\text{CH}_3$  group and a CH group in a direction almost orthogonal to the  $\text{sp}^2$  plane of C(1): considering that  $\text{CH}_3$  is partially vicariant with Cl this contact does not seem to be critical.

All the bond distances and angles fall in the expected range. In spite of a partial statistical vicariance of the Cl and C atoms, the two Pt-N(1) and Pt-N(2) bond lengths are still significantly different (2.16(3) and 2.09(3) Å respectively), as expected as a consequence of the large *trans*-influence of the  $\sigma$ -bonded methyl group. An independent evidence of the difference in bond strengths of the two Pt-N bonds is given by the large difference in the  $^3J(\text{H}-\text{Pt})$  coupling constants of the two imine protons (104 Hz and 36 Hz respectively) in the  $^1\text{H}$  NMR spectrum of 2a. Such a difference in  $^3J(\text{H}-\text{Pt})$  coupling constants can be useful for stereochemical assignments in the case of unsymmetrical N-N' ligands [3].

Concerning the arrangement of the atoms in the coordination plane, it is interesting to compare the present complex with the recently reported  $[\text{PtClMe}(\text{6-Mepy-2-CH}=\text{N}(\text{S})-\text{CH}(\text{Me})\text{Ph})]$  (5) [3], which is the only other PtCl(alkyl)(diimine) complex whose crystal structure has been determined. The schematic molecular models of the two complexes are shown in Fig. 3, with superimposed Pt-N(2) bonds and viewed along an axis perpendicular to the N(1)-Pt-N(2) plane. Some relevant bond distances and angles are indicated. Going from 5 to 2a the most relevant changes in the coordination geometry are the opening of the C-Pt-N(2) angle ( $101^\circ$  in 2a versus  $94.0^\circ$  in 5), the opening of the C-Pt-Cl angle ( $89^\circ$  in 2a versus  $85.4^\circ$  in 5) and the corresponding contracting of the N(1)-Pt-Cl angle ( $95^\circ$  in 2a versus  $102.0^\circ$  in 5). These changes can be most reasonably ascribed to the absence in 2a of the steric interaction between

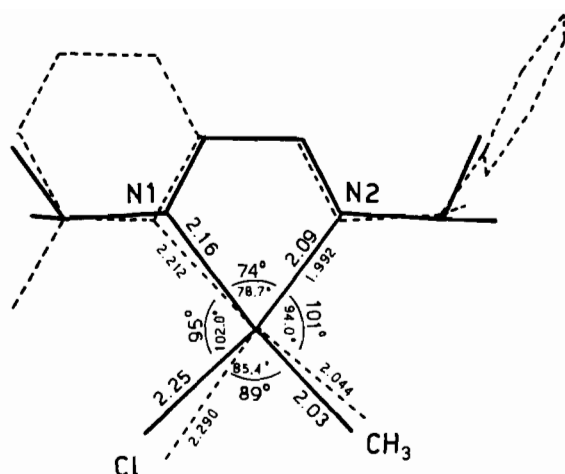


Fig. 3. Comparison of the molecular structures of  $[\text{PtClMe}(\text{i-Pr}-\text{N}=\text{CHCH}=\text{N}-\text{i-Pr})]$  (1a) and  $[\text{PtClMe}(\text{6-Mepy-2-CH}=\text{N}(\text{S})-\text{CH}(\text{Me})\text{Ph})]$  (5), as viewed orthogonally to the plane defined by the Pt, N(1) and N(2) atoms. The Pt atoms and the Pt-N(2) bonds are overlapped.

the 6-Me group and the chloride ligand. Accordingly, the ligands assume a more symmetrical arrangement around the platinum atom, and the resulting molecule is expected to be more stable. Looking at Fig. 3 it can be easily argued that the presence of two additional methyl groups on C(3) and C(6), as it would be in the (hypothetical) complex 2b, would create steric constraints similar to those due to the 6-Me group in 5. These constraints, being on both sides of the molecule, could not be released by pushing the Me and Cl ligands towards one side (as in 5), thus resulting in a severe destabilization of the complex.

The above arguments can thus explain the observed specificity of  $a$  and  $b$  in stabilizing square planar and trigonal bipyramidal species, respectively, and they could also be used to predict the behaviour of other planar chelating ligands under similar electronic environment. In case of ligands giving (as  $a$ ) weak steric interactions with the *cis* substituents, a square planar species would be unreactive towards the addition of an olefin, and five-coordinate complexes would not generally be formed\*. On the other hand a ligand giving (as  $b$ ) strong steric interactions with the *cis* substituents would form a four-coordinate species reactive towards the addition of an olefin, since the conversion to a trigonal bipyramidal geometry would release the strain in the equatorial plane. In intermediate cases (as for com-

\*The stability of the five-coordinate adduct is however strongly affected by the nature of the olefin, being increased by the presence of electron-withdrawing substituents on the double bond [11]. Thus, a four-coordinate complex which does not bind ethylene could form a stable adduct with for example maleic anhydride [12].

TABLE III. Relevant Geometrical Parameters for [PtClMe(i-Pr-N=CHCH=N-i-Pr)] (2a)<sup>a</sup>

Bond lengths (Å)			
Pt-Cl	2.25(1)	C(6)-C(7)	1.57(3)
Pt-C	2.03(2)	C(6)-C(8)	1.54(2)
Pt-N(1)	2.16(3)	N(2)-C(3)	1.55(3)
Pt-N(2)	2.10(3)	N(2)-C(1)	1.24(3)
N(1)-C(2)	1.28(3)	C(3)-C(4)	1.50(3)
N(1)-C(6)	1.54(2)	C(3)-C(5)	1.55(3)
C(1)-C(2)	1.46(3)		
Bond angles (°)			
Cl-Pt-C	89(1)	N(1)-C(6)-C(8)	110(2)
Cl-Pt-N(1)	95(1)	C(7)-C(6)-C(8)	112(2)
Cl-Pt-N(2)	165(2)	N(1)-C(2)-C(1)	114(2)
C-Pt-N(2)	101(1)	C(2)-C(1)-N(2)	118(3)
C-Pt-N(1)	173(1)	Pt-N(2)-C(1)	118(3)
N(1)-Pt-N(2)	74(1)	Pt-N(2)-C(3)	123(3)
Pt-N(1)-C(2)	116(3)	C(1)-N(2)-C(3)	120(3)
Pt-N(1)-C(6)	126(2)	N(2)-C(3)-C(4)	111(2)
C(2)-N(1)-C(6)	118(3)	N(2)-C(3)-C(5)	111(2)
N(1)-C(6)-C(7)	116(3)	C(4)-C(3)-C(5)	106(3)
Torsion angles (°)			
C(7)-C(6)-N(1)-C(2)	35	C(5)-C(3)-N(2)-C(1)	84
C(8)-C(6)-N(1)-C(2)	94	C(4)-C(3)-N(2)-C(1)	33

<sup>a</sup>e.s.d.s given in parentheses.

plex 5) both the square planar and the trigonal bipyramidal species can be observed [3]. The influence of the coordination environment on their relative stabilities is presently extensively investigated.

### Supplementary Material

Lists of thermal parameters (Table IV) and of the observed and calculated structure factors (Table V) are available from the authors on request.

### Acknowledgements

The authors are indebted to Prof. V. G. Albano for helpful discussions. Financial support by CNR and MPI is gratefully acknowledged.

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