

Note

Two geometrical isomers of the five-coordinate Platinum(II) complex [PtBr(SePh)(2,9-dimethyl-1,10-phenanthroline) (dimethylmaleate)]

Roberto Centore *, Giuseppina Roviello, Angela Tuzi

Dipartimento di Chimica, Università di Napoli "Federico II", Complesso Universitario di Monte S. Angelo, via Cinthia, Napoli I-80126, Italy

Received 24 July 2004; accepted 28 December 2004

Available online 29 January 2005

Abstract

The oxidative addition of phenylselenium bromide to three-coordinate Pt(0) complex [Pt(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)] affords the corresponding five-coordinate Pt(II) complex having trigonal-bipyramidal coordination geometry. The product of the reaction exists as two geometrical isomers (rotamers): in the kinetically favoured compound the olefin substituents are on the same side of the bromide ligand, while the most thermodynamically stable isomer holds the same substituents pointing at the phenylselenenide ligand. The crystal structure of the two isomers is reported and discussed with respect to the reaction mechanism and thermodynamic stability.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Platinum; Selenium; Geometrical isomers; Crystal structure; Hydrogen bonding

1. Introduction

Oxidative addition of electrophilic reagents to three-coordinate Pt(0) complexes of the type [Pt(*N,N*-chelate)(olefin)], with *N,N* bidentate nitrogen ligand, can afford five-coordinate Pt(II) complexes having trigonal-bipyramidal coordination geometry [1a,1b]. With olefin lacking C_{2h} or D_{2h} symmetry, and the axial ligands being different, two stereoisomers can form upon this reaction (two enantiomeric couples if the nitrogen atoms of the equatorial ligand are not equivalent by symmetry) [1b]. Moreover, these are rotamers which differ by rotation of 180° around the metal to olefin bond. The favourable chance of observing and eventually isolating both rotamers depends on several factors. Among these, we may cite the mechanism of the reaction which, as an example, could favour one of the two isomers over the other, and

the energy barrier for rotation around the metal to olefin bond, which is involved in the isomerization process between the two; the barrier of rotation, in turn, is related to several features of the complex (nature of the coordinated olefin, of the axial ligands, of the equatorial bidentate nitrogen ligand, etc. [1b]).

Actually, the formation of both rotamers has been effectively recognized in several cases [2], but always on the basis of NMR analysis (different chemical shifts of olefin protons); in some cases, also the stereochemistry and the molar ratio of the two rotamers were assigned by careful analysis and correlation of NMR spectra within homogeneous classes of five-coordinate compounds. However, in the absence of full structural characterization of both rotamers for a given complex, no explanation of the different thermodynamic stability can be definitively proposed.

Recently, there has been some interest in the oxidative addition of Se–Se and X–Se (X = halogen) to platinum(0) and platinum(II) complexes of general formula

* Corresponding author. Tel.: +39 081 674450; fax: +39 081 674090.
E-mail address: roberto.centore@unina.it (R. Centore).

[Pt(*N,N*-chelate)(olefin)] and [PtR(R')(*N,N*-chelate)] (R, R' = hydrocarbonyl group). These reactions afford, respectively, five coordinate Pt(II) and octahedral Pt(IV) compounds [3,4].

In this communication, we discuss some structural data concerning the products of the oxidative addition of phenylselenium bromide to the three-coordinate complex [Pt(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)]. This reaction affords two stereoisomers (rotamers) of the five-coordinate platinum(II) complex [PtBr(SePh)(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)], shown in Fig. 1.

Both have been isolated and crystallized and fully characterized by single crystal X-ray analysis.

2. Experimental

The complex [PtBr(SePh)(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)] was obtained by reaction of equimolar amounts of [Pt(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)] and Ph–Se–Br in chloroform. A detailed synthetic account is given in [4]. Single crystals were obtained from chloroform solutions, respectively, by cooling at -20°C for **I** and by slow evaporation at room temperature for **II**. An Enraf–Nonius MACH3 diffractometer was used for data collection (graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$). Cell parameters were obtained from least-squares fit [5] of the θ angles of 25 reflections in the range $7.845^{\circ} \leq \theta \leq 10.865^{\circ}$ for **I** and $10.289^{\circ} \leq \theta \leq 11.669^{\circ}$ for **II**. Absorption correction was based on ψ scans for **I** and on DIFABS method for **II**. Structures were solved by the Patterson method, completed by cycles of direct Fourier synthesis and refined by the full matrix least-squares method [6]. Refinement was on F^2 against all independent reflections. C, O, N, Cl, Pt, Br and Se atoms were anisotropic. H atoms of phenyl and heteroaromatic rings were introduced in calculated positions; H atoms of methyl and olefin groups were found in difference Fourier syntheses. Coordinates of alkene H atoms were refined ($U_{\text{iso}} = U_{\text{eq}}$ of the carrier atom) without constraints for **I** and with some restraints for **II**; all other H atoms were refined by the riding model. The largest peaks and holes in the last Fourier difference were (e \AA^{-3}): 0.83, -0.82 for **I** and 1.240 and -1.369 for **II**. Some crystal, collection and refinement data are

reported in Table 1. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Deposition numbers are CCDC 245555 (for **I**) and CCDC 245556 (for **II**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and discussion

The oxidative addition of phenylselenium bromide to the three-coordinate complex [Pt(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)] gives as the first product the rotamer in which the olefin substituents are on the same side of the bromide ligand (rotamer **I**) as it can be seen from Fig. 2 in which the X-ray molecular structure is shown.

If complex **I** is left in solution at room temperature, after few days conversion to rotamer **II** is achieved, in which the olefin substituents are on the same side of the phenylselenide ligand (Fig. 3).¹ Clearly, rotamer **I** is the kinetically favoured product of the reaction and rotamer **II** is the thermodynamically most stable one. The transformation from **I** to **II** can be monitored in solution by NMR spectroscopy [4].

Molecular structures of **I** and **II** share several features. In both cases, the coordination around platinum is trigonal bipyramidal, with the olefin and the bidentate nitrogen ligands occupying the equatorial plane and bromide and phenylselenide ligands in axial position. Within the coordination sphere of the metal, bond lengths and angles are substantially equivalent in the two structures and fall in the ranges reported in the literature for typical bipyramidal trigonal platinum(II) complexes. The orientation of the phenyl ring with respect to the equatorial heteroaromatic ligand is also similar in the two rotamers, and is determined by the valence angle at Se, by the bond C15–Se almost eclipsing the Pt–N2 bond, and by torsion around the bond C15–Se (cf. Figs. 2 and 3). For what concerns the coordinated olefin, the values observed for the bond length C21–C22 are in fair agreement between the two structures and comparable with those found in complexes of similar geometry. A significant bending away from Pt of the four substituents at the double bond is observed.

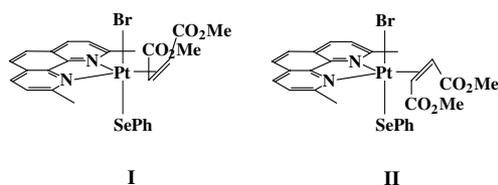


Fig. 1. Chemical diagrams of the two rotamers

¹ It has not escaped our attention the following unusual feature of the crystal structure of rotamer **II**. Most of the electronic density of the molecule (Pt, Br and Se atoms, the equatorial dinitrogen ligand and the two olefin carbons) corresponds to a point symmetry *quasi* C_{2v} . In the crystal, molecules are placed in the cell in such a way that pseudo σ_v planes of the molecules almost coincide with the glide planes of the $P2_1/c$ space group. So, limitedly to this part of the molecule which, however, accounts for a great part of the total electronic density, the structure can be described in the space group $P2_1$ with *c*-axis halved. As a consequence, reflections hkl of the diffraction pattern with odd *l* have intensities systematically lower than those with even *l*.

Table 1
Crystal, collection and refinement data for **I** and **II**

	I	II
Temperature (K)	298	298
Chemical formula	C ₂₆ H ₂₅ BrN ₂ O ₄ SePt · CHCl ₃	
Crystal system	triclinic	monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.72(2)	11.14(1)
<i>b</i> (Å)	12.593(3)	11.363(8)
<i>c</i> (Å)	13.978(2)	23.97(3)
α (°)	63.34(2)	90
β (°)	86.31(4)	101.4(1)
γ (°)	78.93(6)	90
<i>V</i> (Å ³)	1500(3)	2959(2)
<i>Z</i> , <i>D_x</i> (g/cm ³)	2, 1.999	4, 2.027
μ (mm ⁻¹)	7.528	7.630
θ Range	1.63–27.99°	1.74–27.98°
Data/parameters	7232/385	6862/358
<i>R</i> ₁ , on <i>F</i> (<i>I</i> > 2 σ (<i>I</i>))	0.0439	0.0471
<i>R</i> ₁ , <i>wR</i> ₂ (all data) on <i>F</i> ²	0.1027, 0.0821	0.1245, 0.1263

$$R_1 = \frac{\sum \|F_o\| - \|F_c\|}{\sum \|F_o\|}; \quad wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

A measure of this is given by the two torsion angles H21–C21–C22–C25 (–145° for **I** and 136° for **II**) and H22–C22–C21–C23 (151° for **I** and –128° for **II**), which indicate a significant sp³ character for the olefin carbons [1b,7]. This feature and the significant elongation of the olefinic carbon–carbon bond with respect to the length of the same bond in the free olefin (1.331 Å [8]) can be considered a measure of the π -backdonation from the metal to the olefin [1b]. The conformation of the dimethylmaleate ligand is different in the two rotamers. In **I** the

conformation is *s-trans* around the bond C21–C23 and *s-skew* around C22–C25, in order to release the close contact between alkoxy oxygen atoms (O2···O4 = 2.94 Å). In **II** the conformation is *s-cis* around the bond C22–C25 and *s-skew* around C21–C23 so as to release the contact between carbonyl oxygen atoms (O1···O3 = 3.07 Å).

The first noteworthy feature is the selectivity of the reaction of oxidative addition. Actually, rotamer **I** is formed selectively during the reaction, no trace of **II** being observed in the “fresh” NMR spectrum of the reaction product as obtained, in substantially quantitative yield, after few minutes of reaction. That feature could be related to the reaction mechanism. In particular, in the starting three-coordinate Pt(0) complex the regions above and below the coordination plane of platinum have different sterical encumbrance, the region containing olefin protons being less sterically hindered; so, the selective formation of rotamer **I** could point to a stereocontrol of the reaction driven by the phenylselenenide ligand instead of the bromide ligand. Radical chain mechanism [9], as well as non radical S_N2 type mechanism [10], is compatible with the observed experimental behaviour.

The second feature is concerned with the different thermodynamical stability of the two rotamers, and in particular with the reasons why rotamer **II** is more stable than **I**. In order to get inside this question, we observe preliminarily that since the interconversion of the rotamers takes place in solution, the different stability of the two's is not related to crystal packing effects, but it must come from intramolecular effects. Looking

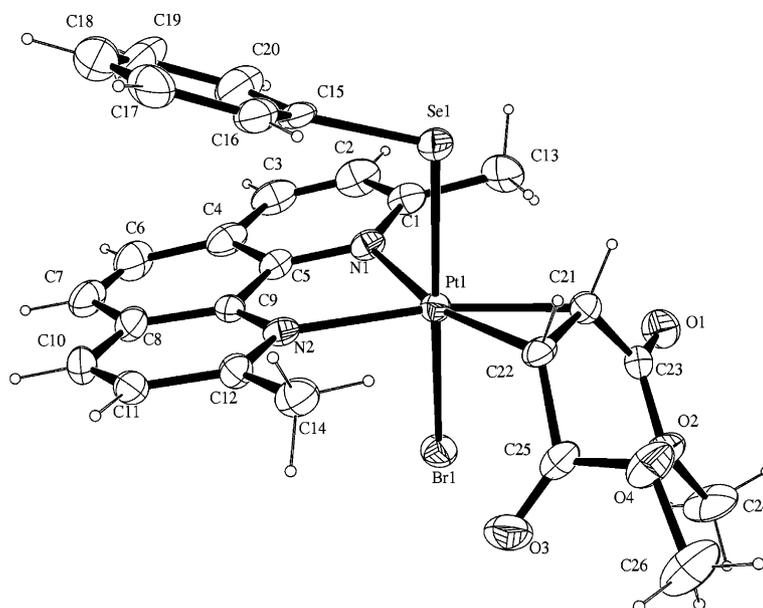


Fig. 2. X-ray molecular structure of **I**. Thermal ellipsoids are drawn at 30% probability level. The chloroform solvent molecule is not shown for clarity. Selected bond lengths (Å), bond angles (°) and torsion angles (°): Pt–N1 2.185(7), Pt–N2 2.177(6), Pt–Se 2.450(2), Pt–Br 2.526(2), C21–C22 1.45(1), C21–C23 1.49(1), C22–C25 1.51(1), N1–Pt–N2 76.2(2), Se–Pt–N1 88.7(2), Se–Pt–N2 93.3(2), Se–Pt–Br 171.54(3), Pt–Se–C15 105.4(2), C20–C15–Se–Pt –79.7(7) N2–Pt–Se–C15 –6.8(3), C22–C21–C23–O1 169.7(7), C21–C22–C25–O3 –102(1).

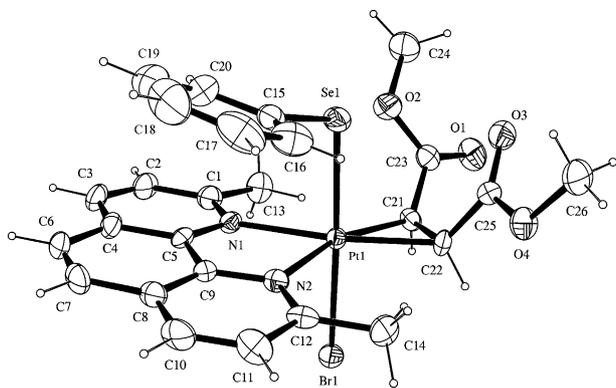


Fig. 3. X-ray molecular structure of **II**. Thermal ellipsoids are drawn at 30% probability level. The chloroform solvent molecule is not shown for clarity. Selected bond lengths (Å), bond angles (°) and torsion angles (°): Pt–N1 2.190(7), Pt–N2 2.189(7), Pt–Se 2.461(3), Pt–Br 2.518(3), C21–C22 1.48(1), C21–C23 1.49(1), C22–C25 1.46(1), N1–Pt–N2 75.5(3), Se–Pt–N1 88.4(2), Se–Pt–N2 91.0(2), Pt–Br–Se 177.17(4), Pt–Se–C15 106.8(3), C20–C15–Se–Pt –99.9(9), N2–Pt–Se–C15 –9.6(4), C22–C21–C23–O1 86(1), C21–C22–C25–O3 2(2).

at the X-ray molecular structure of the rotamers (Figs. 2 and 3), no relevant difference is found in the pattern of bond lengths and angles, as well as in the coordination sphere of the metal, as already noted, so the different stability should probably derive from secondary, non-bonded interactions. In particular, we have noted above that the relative position of the π conjugated systems of the phenyl and of the heteroaromatic chelate ligand is almost the same in the two rotamers and no feature of steric encumbrance is evident in the two compounds so as to allow for their different stability. In this respect, we observe that any different effect of steric crowding between **I** and **II** should necessarily involve contacts among olefin substituents and the axial ligands; however, van der Waals radii of Br and Se are very close (1.85 and 1.90 Å [11]).

Actually, a possibly relevant feature is that in the most stable rotamer the two olefin hydrogens are from the same side of the bromine atom with respect to the equatorial plane.

Recently, it has been recognized that metal bound halogens (M–X with M transition metal) are very good hydrogen bonding acceptors [12], while C–H hydrogens are considered as weak hydrogen bonding donors [12c]. Several cases of “weak” C–H \cdots X (X = halogen) hydrogen bonding have been recently reported [13]. This interaction has been found to play roles in crystal engineering [13a–b] and in stereoselective synthesis [13c–e]. In the present case, although the angles C_{alkene}–H \cdots Br (97° and 101°) and Pt–Br \cdots H (55° and 57°) are smaller as compared with the values reported in the literature for intermolecular bonding [12c] (we note, however, that these angles are somewhat constrained by the intramolecular nature of the contact), nevertheless the distances Br \cdots H are close to the sum of van der Waals radii (H21 \cdots Br1 = 2.88 Å,

H22 \cdots Br2 = 3.03 Å) and in the range reported in the literature [12c,13], so it is reasonable to think that this interaction could play a role in stabilizing **II** with respect to **I**. A further experimental finding, not in contrast with this picture, consists in the observation that in all five-coordinated Pt(II) olefin complexes reported in the literature, which give this type of stereoisomerism and have one halogen as axial ligand, and for which both rotamers have been observed in solution, the most abundant rotamer is the one having more olefin hydrogens from the side of the halogen ligand [2d,2e,2f].

Finally, we think that the possible implications that the interaction C_{alkene}–H \cdots X (X = halogen) could play in some important catalytic processes, whose key step involves coordination of an olefin molecule to alkyl-halogen complexes of low valence transition elements, are worth of being investigated.

Acknowledgements

Financial support of MIUR of Italy is acknowledged. We thank the CIMCF of the University of Naples “Federico II” for the Nonius X-ray equipment.

References

- [1] (a) V. De Felice, M. Funicello, A. Panunzi, F. Ruffo, *J. Organomet. Chem.* 403 (1991) 243; (b) V.G. Albano, G. Natile, A. Panunzi, *Coord. Chem. Rev.* 133 (1994) 67.
- [2] (a) H. van der Poel, G. van Koten, *Inorg. Chem.* 20 (1981) 2950; (b) M.E. Cucciolito, V. De Felice, A. Panunzi, A. Vitagliano, *Organometallics* 8 (1989) 1180; (c) V.G. Albano, C. Castellari, M.E. Cucciolito, A. Panunzi, A. Vitagliano, *Organometallics* 9 (1990) 1269; (d) S. Bartolucci, P. Carpinelli, V. De Felice, B. Giovannitti, A. De Renzi, *Inorg. Chim. Acta* 197 (1992) 51; (e) M.L. Ferrara, I. Orabona, F. Ruffo, V. De Felice, *J. Organomet. Chem.* 519 (1996) 75; (f) F. Giordano, F. Ruffo, A. Saporito, A. Panunzi, *Inorg. Chim. Acta* 264 (1997) 231.
- [3] (a) V.G. Albano, M. Monari, I. Orabona, A. Panunzi, F. Ruffo, *J. Am. Chem. Soc.* 123 (2001) 4352; (b) A. Panunzi, G. Roviello, F. Ruffo, *Organometallics* 21 (2002) 3503.
- [4] V.G. Albano, M. Monari, V. De Felice, G. Roviello, F. Ruffo, *Eur. J. Inorg. Chem.* (2005), in press.
- [5] R. Centore, CELLFIT, Università di Napoli “Federico II”, Napoli, Italy, 2002.
- [6] G.M. Sheldrick, *SHELX-97*, University of Göttingen, Göttingen, Germany, 1997.
- [7] (a) J. Chatt, L.A. Duncanson, *J. Chem. Soc.* (1953) 2959; (b) P. Corradini, C. Pedone, A. Sirigu, *Chem. Commun.* (1966) 341; (c) F.R. Hartley, *Angew. Chem., Int. Ed. Engl.* 11 (1972) 596; (d) F.R. Hartley, *J. Organomet. Chem.* 216 (1981) 277.
- [8] Z. Urbanczyk-Lipkowska, P. Gluzinsky, *Supramol. Chem.* 7 (1996) 113.

- [9] T.L. Hall, M.F. Lappert, P.W. Lednor, *J. Chem. Soc., Dalton Trans.* (1979) 1448.
- [10] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry, A Comprehensive Text*, fourth ed., John Wiley and Sons Inc., New York, 1980.
- [11] H. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [12] (a) G.P.A. Yap, A.L. Rheingold, P. Das, R.H. Crabtree, *Inorg. Chem.* 34 (1995) 3474;
(b) G. Aullón, D. Bellamy, L. Brammer, E.A. Bruton, A. Guy Orpen, *Chem. Commun.* (1998) 653;
(c) L. Brammer, E.A. Bruton, P. Sherwood, *Crystal Growth Des.* 1 (2001) 277.
- [13] (a) P.K. Thallapally, A. Nangia, *Cryst. Eng. Commun.* 27 (2001) 1;
(b) J.N. Moorthy, R. Natarajan, P. Mal, P. Venugopalan, *J. Am. Chem. Soc.* 124 (2002) 6530;
(c) E.J. Corey, J.J. Rohde, A. Fisher, M.D. Azimioara, *Tetrahedron Lett.* 38 (1996) 33;
(d) D.J. Parks, W.E. Piers, M. Parvez, R. Atencio, M.J. Zaworotko, *Organometallics* 17 (1998) 1369;
(e) E.J. Corey, T.W. Lee, *Chem. Commun.* (2001) 1321.