Theoretical study of the relative stability of isomeric forms of platinum carboxamide complexes

ARTICLE *in* INORGANICA CHIMICA ACTA · JULY 2003

Impact Factor: 2.05 · DOI: 10.1016/S0020-1693(02)01512-8

5 AUTHORS, INCLUDING:

Maxim L. Kuznetsov
University of Lisbon
105 PUBLICATIONS **1,963** CITATIONS
SEE PROFILE

Matti Haukka
University of Jyväskylä
468 PUBLICATIONS **6,254** CITATIONS
SEE PROFILE

Alexey Nazarov
Lomonosov Moscow State University
62 PUBLICATIONS **1,629** CITATIONS
SEE PROFILE

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 350 (2003) 245–251
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Theoretical study of the relative stability of isomeric forms of platinum carboxamide complexes

Maxim L. Kuznetsov [a,b], Matti Haukka [c], Armando J.L. Pombeiro [a,*], Alexey A. Nazarov [b], Vadim Yu. Kukushkin [d,*]

[a] Centro de Química Estrutural Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisbon, Portugal
[b] Department of Chemistry, Moscow Pedagogical State University, 3, Nesvigskiy per., Moscow 119021, Russia
[c] Department of Chemistry, P.O. Box 111, FIN-80101 Joensuu, Finland
[d] Department of Chemistry, St. Petersburg State University, Universitetsky Pr. 2, 198904 Stary Petergof, Russia

Received 25 June 2002; accepted 12 September 2002

Dedicated to Professor Pierre Braunstein.

Abstract

The relative stability of the *trans*- and *cis*-isomers of both *N*-iminol and *O*-carboxamide forms of the carboxamide chloro-complexes of Pt(II) and Pt(IV) has been theoretically studied at HF//HF, MP2//HF and B3PW91 levels of theory. For the two latter approaches, the *trans*-*N*-iminol forms appear to be the most stable ones for both the Pt(II) and Pt(IV) series of complexes. The difference between the total energies of the most stable *N*-iminol and *O*-amide forms is only slightly higher for the Pt(II) than for the Pt(IV) species despite the significant variation of the hardness of the metal center.

Keywords: Platinum complexes; Carboxamides; Nitriles; Hydrolysis; Isomerism; Quantum–chemical calculations

1. Introduction

The hydrolysis of organonitriles has great basic and applied significance, for instance, due to its usage for the large-scale production of amides, e.g. acrylamide and nicotinamide, with their industrial and pharmacological importance [1–7]. In general, the hydrolysis of non-coordinated nitriles proceeds under acid- or base-catalyzed conditions. However, such processes are quite environmentally unfriendly, often require drastic conditions and, therefore, lead to products contaminated by the corresponding carboxylic acids formed upon further hydrolysis of carboxamides generated in the first step of the process. It is now well-documented [8–10] that the hydrolysis can be performed under mild conditions and without the presence of the acid or base when it involves transition metal ions and their complexes. The first group of such reactions includes the metal-catalyzed processes (involving enzymatic hydration with nitrile hydratases [8]), that are mainly feasible for labile metal-containing species, and this group of reactions is successfully used for the production of carboxamides. The second group of reactions—more typical for inert metal-based systems—is the metal-mediated hydrolysis, when carboxamides remain ligated to the metal center and their liberation requires additional chemical steps. Development of the former group of reactions is greatly motivated by industrial demands, while the latter processes provide a useful tool for the investigation, e.g. theoretical, of reaction mechanisms, structures, coordination modes of metal-bound amides as possible intermediates in the hydrolysis.

Owing to our well established interest in organonitrile ligands reactivity—a topic that has been recently reviewed by two of us [8]—we have studied both metal-catalyzed [11] and metal-mediated [12] conver-

* Corresponding authors. Fax: +351-21-846 4455 (A.J.L.P.); fax: +7-812-428 6939 (V.Y.K.).
E-mail addresses: inorgchem@mtu-net.ru (M. Kuznetsov), matti.haukka@joensuu.fi (M. Haukka), pombeiro@ist.utl.pt (A.L. Pombeiro), kukushkin@vk2100.spb.edu (V. Kukushkin).

0020-1693/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0020-1693(02)01512-8

sions of organonitriles to carboxamides and carboxamide metal complexes. In particular, we focused our attention on hydrolysis occurred at platinum centers. Indeed, platinum complexes are unique systems which, depending on ligand environment and oxidation state of the metal, can display either high lability providing catalytic properties toward hydrolysis of organonitriles [13–16] or, on the contrary, great inertness which allows the isolation and characterization of (carboxamide)Pt complexes. The latter, in turn, give an intrinsic information on possible intermediates in the metal-catalyzed hydrolysis.

Recently, we have been studying the facile hydrolysis of nitriles in platinum(IV) complexes furnishing metal-bound carboxamides [12]. It was shown that the coordination favors the stabilization of the *N*-iminol tautomeric form, i.e. HN=C(OH)R, which is unstable for the free amides where the amide form, i.e. $NH_2C(=O)R$, is dominated. Moreover, an insignificant change in the reaction conditions (e.g. performance of the reaction in acetone instead of dichloromethane) can lead to the isolation of different (either *trans*- or *cis*-) isomeric forms of the hydrolysis product $[PtCl_4\{N(H)=C(OH)R\}_2]$ and the factors governing the preferential isomeric formation have not yet been elucidated. In particular, the experimental methods did not answer the question about the relative stability of the final products, a matter of recognized pharmacological significance in view of the different biological activity, e.g. as antitumor agents, of the isomers [17]. Conventional platinum drugs are based on the *cis*-isomers, but a higher activity has been recognized, in a few cases, for the *trans*-imine complexes and there is a current growing search for unconventional drugs such as Pt(IV) complexes with the *trans*-geometry [18,19].

We herein report the results of the quantum–chemical calculations of the carboxamide chloro-complexes of Pt(II) and Pt(IV) with the aim to investigate the relative stability of the possible isomers in particular in the absence of solvent, i.e. *trans*- and *cis*-isomers of both *N*-iminol and *O*-amide forms, and the probability of the isomerization/tautomerization processes from the thermodynamic viewpoint.

2. Computational details

The full geometry optimization of all structures has been carried out at both the restricted Hartree–Fock and DFT levels of theory using effective core potentials (ECPs) [20,21] with the help of the GAMESS [22] and GAUSSIAN-98 [23] program packages. The DFT calculations have been performed using Becke's three-parameter hybrid exchange functional [24] in combination with the gradient-corrected correlation functional of Perdew and Wang [25] (B3PW91). Symmetry operations were not applied. The single-point calculations at the MP2 [26,27] level on the basis of the equilibrium Hartree–Fock geometries also have been performed. For the Hartree–Fock and MP2 calculations, a quasi-relativistic Stuttgart pseudopotential described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d] for the platinum atom [28] were used. The standard basis set of Gauss functions 6-31G [29–31] was selected for all other atoms and d-type of polarization functions with exponent 0.75 [31,32] were added for the Cl atoms. For DFT calculations, also the Stuttgart ECP and basis set augmented by the polarization function of p-type with exponent of 0.086 [33] for the Pt atom, and the standard 6-311+G* basis set [34,35] for other atoms were applied. The Hessian matrix was calculated for all structures, numerically for the HF calculations and analytically for DFT calculations in order to prove the location of correct minima (all structures have no imaginary frequencies) and the zero-point vibrational energies have been estimated.

3. Results and discussion

For a better understanding of the relative stabilities of the *trans*- and *cis*-isomers of the *N*-iminol and *O*-amide ligands in both platinum(II) and platinum(IV) complexes, the equilibrium structures for the isomers of the platinum(II) complexes $[Pt^{II}Cl_2\{N(H)=C(OH)Me\}_2]$ (*trans*-**IM1** and *cis*-**IM1**) and $[Pt^{II}Cl_2\{O=C(NH_2)Me\}_2]$ (*trans*-**CARB1** and *cis*-**CARB1**) and the platinum(IV) compounds $[Pt^{IV}Cl_4\{N(H)=C(OH)Me\}_2]$ (*trans*-**IM2** and *cis*-**IM2**) and $[Pt^{IV}Cl_4\{O=C(NH_2)Me\}_2]$ (*trans*-**CARB2** and *cis*-**CARB2**) with the ligands in the *N*-iminol and *O*-amide forms (Fig. 1) were calculated at DFT and, for comparison, at Hartree–Fock levels of theory.

The starting geometries for *trans*-**IM1**, *trans*-**IM2** and *cis*-**IM2** correspond to the experimental X-ray structures for *trans*-$[PtCl_2\{N(H)=C(OH)Me\}_2]$ [36], *trans*-$[PtCl_4\{N(H)=C(OH)Et\}_2]$ and *cis*-$[PtCl_4\{N(H)=C(OH)Me\}_2]$ [12]. The initial geometry for *cis*-**IM1** was chosen on the basis of the equilibrium structure obtained for *cis*-**IM2** by removing the two axial Cl atoms. The starting conformations of the *O*-amide forms were built on the basis of the found equilibrium geometries of the corresponding iminol structures by swapping of the NH and O atoms. The iminol structures were calculated in their *Z*-conformation which is the only one so far observed, in a number of X-ray experiments for (iminol)Pt complexes [36–44]. For the *O*-amide forms, the conformation of the ligand applied for the calculations corresponds to that observed experimentally for [Pt(diethylenetriamine)$\{O$-MeC$(=O)NH_2\}](CF_3SO_3)_2$ [45]. Another conformation, i.e.

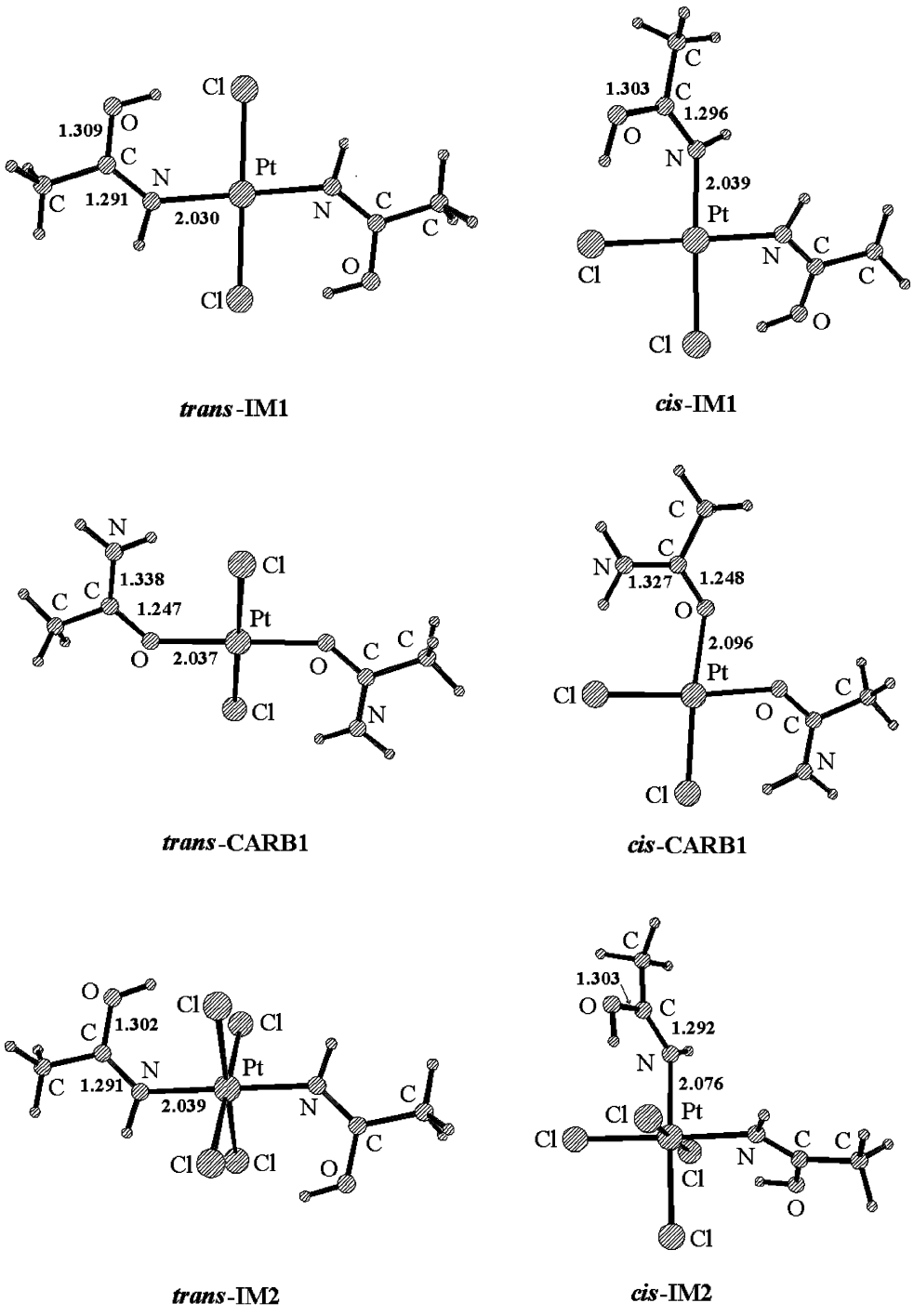

Fig. 1. The calculated structures of the *trans*- and *cis*-isomers of $[PtCl_n\{N(H)=C(OH)Me\}_2]$ and $[PtCl_n\{O=C(NH_2)Me\}_2]$ ($n = 2, 4$).

that with the opposite position of the NH_2 group and the metal fragment relative to the double C=O bond, also has been calculated but appeared to be less stable.

In the equilibrium structures, the coordination polyhedra of the platinum atoms are square planar or octahedral for the Pt(II) or Pt(IV) complexes, respectively. The general features, found by calculations, of *trans*-**IM1**, *trans*-**IM2** and *cis*-**IM2** are in agreement with experimental data. For the HF approach, in all *trans*-complexes and in *cis*-**CARB1**, the two {N(H)=C(O)C} (or {O=C(N)C}) fragments are almost coplanar (the angle between their planes is not larger than 13.9°, the value found for *trans*-**IM1**) which is in agreement with the experimental X-ray data for *trans*-$[PtCl_2\{N(H)=C(OH)Me\}_2]$ [36] and *trans*-$[PtCl_4\{N(H)=C(OH)Et\}_2]$ [12]. In the remaining three *cis*-structures, the corresponding fragments are not coplanar, displaying the angle between the planes of 48.0°

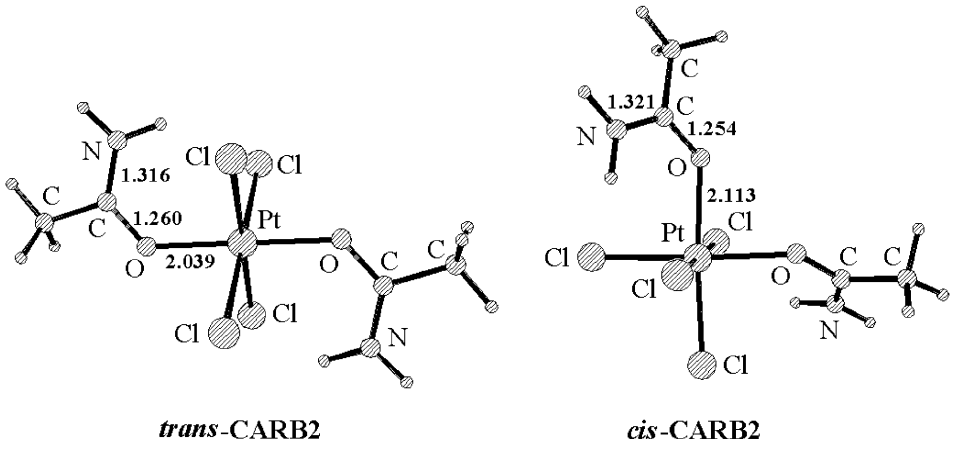

Fig. 1 (*Continued*)

(*cis*-**IM1**), 73.2° (*cis*-**CARB2**) and 95.9° (*cis*-**IM2**), what agrees well with the experimental results obtained [12] for *cis*-[$PtCl_4${N(H)=C(OH)Me}$_2$]. The optimization at the B3PW91 level results in similar configurations of the fragments with the dihedral angles of 34.8° for *cis*-**IM1**, 92.8° for *cis*-**CARB2** and 75.7° for *cis*-**IM2** and not larger than 14.1° for the other structures (except of the *trans*-**IM2** structure where their orthogonal orientation appears to be more stable).

Most of the calculated bond lengths for *trans*-**IM1** and *cis*-**IM2** (Table 1) are coherent with the experimentally observed parameters except the values found for the Pt–Cl and Pt–N bond lengths which deviate by 0.099 Å for Pt–Cl of *trans*-**IM1** and by 0.011–0.047 Å for the others at the HF approach. The calculations at the B3PW91 level lead to noticeable shortening of the Pt–Cl and Pt–L bonds for Pt(II) species in comparison with the HF level, whereas for the Pt(IV) complexes these bonds are slightly elongated. The difference between the theoretical and experimental values for the other bond lengths is in the range 0.001–0.021 Å for HF and 0.002–0.030 Å for B3PW91. The deviation between the theoretical and experimental bond lengths for *trans*-**IM2** is significant, what is accounted for by the unusual X-ray structural parameters of *trans*-[$PtCl_4${N(H)=C(OH)Et}$_2$] [12] in comparison with the structures of other iminol-Pt complexes (*trans*-**IM1** and *cis*-**IM2**).

The vibrational frequencies calculated at the HF level are overestimated in comparison with the experimental values by 20–25% but the DFT frequencies are much closer to the experimental ones. For the latter approach, the stretching ν(NH) and ν(OH) modes are found at 3564–3588, 3177–3286 cm^{-1} (the experimental values, in KBr pellets, are 3270, 3220 cm^{-1} for *trans*-IM1 [36], 3497, 3281 cm^{-1} for *trans*-[$PtCl_4${N(H)=C(OH)Et}$_2$] and 3443, 3282 cm^{-1} for the isomorphic mixture *cis*-[$PtCl_4${N(H)=C(OH)Me}$_2]_{0.66}$·*cis*-[$PtCl_4${N(H)=C(OH)Et}$_2]_{0.33}$ [12]). For these complexes, the ν(C=N) vibrations are calculated at 1694–1719 cm^{-1} (exp. 1638 cm^{-1}) and the C–O stretching modes, which are mixed with bend vibrations δ(NHCOH), are displayed at 1249–1264 cm^{-1} (exp. 1200–1211 cm^{-1}).

The calculations at the B3PW91 level (Table 2 and Fig. 2) indicate that the *trans*-*N*-iminol isomers are the most stable ones for both Pt(II) and Pt(IV) complexes what is in agreement with the experimentally observed iminol structures. The second most stable structures are the *cis*-isomers of the *N*-iminol forms which are less stable than the corresponding *trans* forms by 10.99 and 7.84 kcal mol^{-1}, respectively, and the least stable isomers are the *trans*-**CARB** forms. The zero-point energy correction slightly decreases the values of the relative energies although the order of the relative stability remains the same. In contrast to the DFT method, the calculations at the HF//HF level of theory give another order of stabilities. Within the latter approach, the most stable isomers are *cis*-**CARB1** or *cis*-**CARB2** for the Pt(II) or Pt(IV) series, respectively, being more stable than the corresponding *trans*-*N*-iminol complexes (which are the most stable at B3PW91 level) by 1.83 or 2.37 kcal mol^{-1}. However, the calculations at the MP2//HF level are coherent with the DFT calculations and also indicate the higher stability for the *trans*-*N*-iminol isomers thus demonstrating the great importance of the electron correlation effects for this type of systems.

The different oxidation state and, therefore, hardness of the metal centers in the Pt(II) and Pt(IV) complexes should provide a greater stability of the iminol form relatively to the *O*-amide form for the Pt(II) than for the Pt(IV) compounds due to the expected lower affinity of the metal to the harder *O*-center in the former case. However, the difference between the total energies of the most stable iminol and *O*-amide forms is only slightly higher for the Pt(II) than for the Pt(IV) species. Indeed, the previous theoretical study [46] of the complexes *trans*-[$PtCl_2(NCMe)_2$] and *trans*-[$PtCl_4(NCMe)_2$]

Table 1
Selected theoretical bond lengths (Å) of the calculated structures

	Pt^{II}				Pt^{IV}			
	IMIN		**CARB**		**IMIN**		**CARB**	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Pt–Cl	2.402, 2.403	2.373	2.390	2.352	2.355, 2.361	2.326, 2.362	2.356–2.358	2.296–2.357
	2.356	**2.341**	**2.342**	**2.309**	**2.346–2.385**	**2.330; 2.365**	**2.363–2.365**	**2.303–2.361**
	[2.301(2)]				[2.319, 2.323(2)]	[2.3143; 2.3173(7)]		
Pt–N	2.077	2.085			2.043	2.072		
	2.030	**2.039**			**2.039–2.040**	**2.076**		
	[2.026(9)]				[2.011(6)]	[2.037(2)]		
Pt–O			2.064	2.105–2.106			2.013	2.074–2.075
			2.037	**2.096**			**2.039**	**2.113–2.114**
C=N	1.279	1.281			1.280	1.283		
	1.291	**1.296**			**1.291**	**1.292**		
	[1.275(13)]				[1.169(10)]	[1.262(4)]		
C–O	1.322	1.319			1.318	1.315		
	1.309	**1.303**			**1.302**	**1.303**		
	[1.321(14)]				[1.510(14)]	[1.313(4)]		
C–C	1.493	1.493	1.497	1.499	1.492	1.493	1.495	1.496
	1.494	**1.495**	**1.492**	**1.503**	**1.493**	**1.493**	**1.498**	**1.500**
	[1.489(13)]				[1.464(11)]	[1.485(4)]		
C=O			1.256	1.255			1.266	1.261
			1.247	**1.248**			**1.260**	**1.254**
C–N			1.320	1.320			1.311	1.316
			1.338	**1.327**			**1.316**	**1.321**
N–H	0.999	0.998			0.998	0.998		
	1.014	**1.013**			**1.013**	**1.013**		

The parameters obtained at the HF level are given as plain text, those for the B3PW91 level are in bold and the experimental parameters for *trans*-**IM1**, *cis*-**IM2** and *trans*-$[PtCl_4\{N(H)=C(OH)Et\}_2]$ are in square brackets.

showed that the Mulliken effective atomic charges on the Pt atoms are very similar. Thus, the expected increase of the effective charge and hardness of the metal due to the growth of its oxidation state should be compensated by a shift of electron density from the two additional electron donor chloride ligands in the Pt(IV) species providing the similarity of the structural properties and, in this case, of the relative isomeric stability of the Pt(II) and Pt(IV) compounds.

The *cis*-isomers of the *O*-carboxamide forms are significantly more stable than the corresponding *trans*-isomers, in accord with our recent experimental data [47] for (formamide)Pt(IV) complexes where only the *cis*-*O*-isomers were isolated. On the contrary, the *trans*-

Table 2
Calculated total energies E_{tot} (Hartree), zero-point energies, ZPE (kcal mol^{-1}) and relative energies, E_{rel} (kcal mol^{-1}), with the most stable isomer as the reference

	HF//HF			MP2//HF		B3PW91//B3PW91		
	E_{tot}	ZPE	E_{rel} [a]	E_{tot}	E_{rel}	E_{tot}	ZPE	E_{rel} [a]
Trans-**IM1**	−1453.278985	106.25	1.25 (1.83)	−1454.490141	0.0	−1458.297137	98.58	0.0 (0.0)
Cis-**IM1**	−1453.257751	105.93	14.57 (14.83)	−1454.474542	9.79	−1458.279619	97.93	10.99 (10.34)
Trans-**CARB1**	−1453.277209	105.78	2.36 (2.47)	−1454.471563	11.66	−1458.267345	97.57	18.69 (17.68)
Cis-**CARB1**	−1453.280970	105.67	0.0 (0.0)	−1454.479639	6.59	−1458.275269	97.37	13.72 (12.51)
Trans-**IM2**	−2372.195689	108.41	1.90 (2.37)	−2373.744931	0.0	−2378.648994	100.38	0.0 (0.0)
Cis-**IM2**	−2372.184723	108.53	8.78 (9.37)	−2373.736454	5.32	−2378.636495	100.22	7.84 (7.68)
Trans-**CARB2**	−2372.193329	108.20	3.38 (3.65)	−2373.725274	12.33	−2378.627511	99.57	13.48 (12.66)
Cis-**CARB2**	−2372.198712	107.94	0.0 (0.0)	−2373.736367	5.37	−2378.631529	99.56	10.96 (10.13)

[a] Values in parentheses include zero-point corrections.

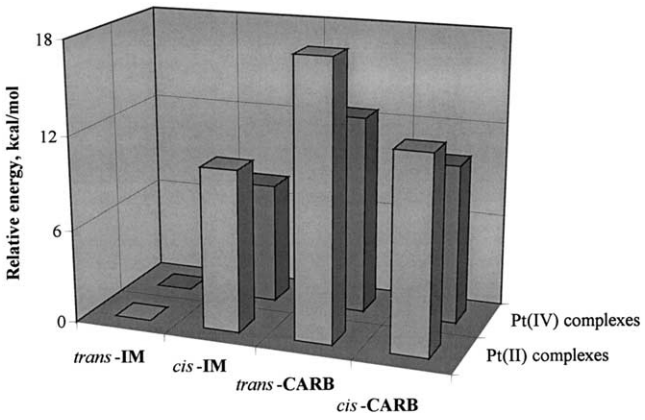

Fig. 2. Relative stability of the calculated structures at B3PW91 level.

isomers of the iminol forms are more stable than the respective *cis*-isomers for all methods. The analysis of the frontier MO composition indicates that virtual π* orbitals of the carboxamide ligands do not give any noticeable contribution in the HOMOs of the complexes for both *N*-iminol and *O*-amide forms. Thus, the bonding situation is similar for both isomeric forms, and their relative stability should be accounted for by other factors.

Acknowledgements

M.L.K. and V.Y.K. are very much obliged to the PRAXIS XXI program (Portugal) for the grants BPD16369/98//BPD/5558/2001 and BCC16428/98, correspondingly. A.J.L.P. and V.Y.K. are grateful to the Foundation for Science and Technology (FCT) and the PRAXIS XXI and POCTI programs for financial support of these studies. V.Y.K. expresses gratitude to the International Science Foundation for the Soros Professorship.

References

[1] A.L.J. Beckwith, J. Zabicky, in: J. Zabicky (Ed.), The Chemistry of Amides, Wiley, New York, 1970, p. 105.
[2] D. Dopp, H. Dopp, Houben-Weyl, Methods of Organic Chemistry, Thieme, New York, 1985, p. 934.
[3] B.C. Challis, A.J. Challis, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, vol. 2, Pergamon, Oxford, 1979, p. 964.
[4] G.V. Boyd, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Amidines and Imidates, vol. 2, Wiley, Chichester, 1991, p. 339.
[5] F. Albericio, S.A. Kates, in: S.A. Kates, F. Albericio (Eds.), Solid-Phase Synthesis, Marcel Dekker, New York, 2000, p. 275.
[6] M. North, J. Chem. Soc., Perkin Trans. 1 (1999) 2209.
[7] U.E.W. Lange, B. Schäfer, D. Baucke, E. Buschmann, H. Mack, Tetrahedron Lett. 40 (1999) 7067 (and references therein).
[8] V.Y. Kukushkin, A.J.L. Pombeiro, Chem. Rev. 102 (2002) 1771 (and references therein).
[9] A.W. Parkins, Platinum Met. Rev. 40 (1996) 169.
[10] R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.
[11] M.N. Kopylovich, V.Y. Kukushkin, M.F.C. Guedes da Silva, M. Haukka, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Chem. Soc., Perkin Trans. 1 (2001) 1569.
[12] K.V. Luzyanin, M. Haukka, N.A. Bokach, M.L. Kuznetsov, V. Yu. Kukushkin, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2002) 1882.
[13] T. Ghaffar, A.W. Parkins, J. Mol. Catal. A: Chem. 160 (2000) 249 (and references therein).
[14] T. Ghaffar, A.W. Parkins, Tetrahedron Lett. 36 (1995) 8657.
[15] A.W. Parkins, T. Ghaffar, US Patent 6,133,478 (2000).
[16] C.J. Cobley, M. van den Heuvel, A. Abbadi, J.G. De Vries, Tetrahedron Lett. 41 (2000) 2467.
[17] G. Natile, M. Coluccia, Coord. Chem. Rev. 216–217 (2001) 383 (and references therein).
[18] E. Wong, C.M. Giandomenico, Chem. Rev. 99 (1999) 2451 (and references therein).
[19] N. Rawat, in: H.M. Pinedo, J.H. Schornagel (Eds.), Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy 2, Plenum Press, New York, 1996.
[20] L. Szasz, Pseudopotential Theory of Atoms and Molecules, Wiley, New York, 1985.
[21] M. Krauss, W.J. Stevens, Ann. Rev. Phys. Chem. 35 (1984) 357.
[22] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Peterson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98 (Revision A.9), Gaussian, Pittsburgh, PA, 1998.
[24] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[25] J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B54 (1996) 16533.
[26] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
[27] J.S. Binkley, J.A. Pople, Int. J. Quantum Chem. 9 (1975) 229.
[28] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.
[29] R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724.
[30] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[31] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
[32] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[33] S. Huzinaga (Ed.), Gaussian Basis Sets for Molecular Calculations, Physical Sciences Data 16, Elsevier, Amsterdam, 1984.
[34] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
[35] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.
[36] R. Cini, F.P. Fanizzi, F.P. Intini, G. Natile, C. Pacifico, Inorg. Chim. Acta 251 (1996) 111.
[37] R. Cini, A. Cavaglioni, F.P. Intini, F.P. Fanizzi, C. Pacifico, G. Natile, Polyhedron 18 (1999) 1863.
[38] R. Cini, F.P. Fanizzi, F.P. Intini, C. Pacifico, G. Natile, Inorg. Chim. Acta 264 (1997) 279.

[39] R. Cini, F.P. Fanizzi, F.P. Intini, L. Maresca, G. Natile, J. Am. Chem. Soc. 115 (1993) 5123.
[40] F.P. Intini, M. Lanfranchi, G. Natile, C. Pacifico, G. Natile, Inorg. Chem. 35 (1996) 1715.
[41] A. Erxleben, B. Lippert, J. Chem. Soc., Dalton Trans. (1996) 2329.
[42] A. Erxleben, I. Mutikainen, B. Lippert, J. Chem. Soc., Dalton Trans. (1994) 3667.
[43] F.D. Rochon, P.C. Kong, R. Melanson, Inorg. Chem. 29 (1990) 1352.
[44] F.D. Rochon, R. Melanson, E. Thouin, A.L. Beauchamp, C. Bensimon, Can. J. Chem. 74 (1996) 144.
[45] R. Cini, F.P. Intini, L. Maresca, C. Pacifico, G. Natile, Eur. J. Inorg. Chem. (1998) 1305.
[46] M.L. Kuznetsov, N.A. Bokach, V.Y. Kukushkin, T. Pakkanen, G. Wagner, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2000) 4683.
[47] N.A. Bokach, S.I. Selivanov, V.Y. Kukushkin, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Eur. J. Inorg. Chem. (2001) 2805.