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# Platinum(IV)-mediated hydrolysis of nitriles giving metal-bound iminols

**Konstantin V. Luzyanin,[a] Matti Haukka,[b] Nadezhda A. Bokach,[a] Maxim L. Kuznetsov,[c] Vadim Yu. Kukushkin*[a] and Armando J. L. Pombeiro*[c]**

[a] *Department of Chemistry, St. Petersburg State University, Universitetsky Pr. 2, 198504 Stary Petergof, Russian Federation. E-mail: kukushkin@VK2100.spb.edu*
[b] *Department of Chemistry, P.O. Box 111, FIN-80101, Joensuu, Finland. E-mail: Matti.Haukka@Joensuu.Fi*
[c] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal. E-mail: pombeiro@ist.utl.pt*

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The platinum(IV) complexes *cis*/*trans*-$[PtCl_4(MeCN)_2]$ and *trans*-$[PtCl_4(EtCN)_2]$ react smoothly and under mild conditions with water, contained in non-dried commercial acetone, to afford *trans*-$[PtCl_4\{N(H)=C(OH)Me\}_2]\cdot Me_2CO$ (**1**) or *trans*-$[PtCl_4\{N(H)=C(OH)Et\}_2]$ (**2**); no hydroxide is required, in contrast to relevant platinum(II) systems, to furnish the metal-bound carboxamides which are stable in the iminol form. In non-dried acetone, reaction between *trans*-$[PtCl_4(EtCN)_2]$ and $MeC(=O)NH_2$ gives a mixture of **1** (derived from substitution) and **2** (derived from the hydrolysis), while in non-dried dichloromethane an isomorphic mixture of *cis*-$[PtCl_4\{N(H)=C(OH)Me\}_2]$ and *cis*-$[PtCl_4\{N(H)=C(OH)Et\}_2]$, *i.e.* *cis*-$[PtCl_4\{Z\text{-}N(H)=C(OH)Me\}_2]_{0.66}\cdot$*cis*-$[PtCl_4\{Z\text{-}N(H)=C(OH)Et\}_2]_{0.33}$ (**3**) is obtained. Complexes **1**–**3** were characterised by elemental analyses (C, H, N), $FAB^+$-MS, IR, $^1H$- and $^{13}C\{^1H\}$-NMR spectroscopy. Complexes **2** and **3** were also characterised by $^{195}Pt$-NMR spectroscopy. Crystal structures of **2** and **3** provide the first examples of structurally characterised platinum(IV) complexes with amides in their iminol form. The equilibrium structures for the geometrical and linkage isomers of the platinum(II) complexes $[Pt^{II}Cl_2\{N(H)=C(OH)Me\}_2]$ and $[Pt^{II}Cl_2\{O=C(NH_2)Me\}_2]$ and the platinum(IV) compounds $[Pt^{IV}Cl_4\{N(H)=C(OH)Me\}_2]$ and $[Pt^{IV}Cl_4\{O=C(NH_2)Me\}_2]$ were calculated at the B3PW91 level of theory and the study shows that the most stable isomers for both platinum(II) and platinum(IV) complexes are the *trans*-(iminol)Pt forms, in accord with the experimental results.

## Introduction

The application of organonitrile transition metal complexes as synthons for making new C–O, C–S and C–N bonds by the addition of nucleophiles — such as water–hydroxide, alcohols, mercaptans or amines — to the carbon atom of the nitrile group has been surveyed in a number of reviews.[1–5] Among the less usual and yet systematically unexplored recent examples of the additions, attention should be drawn to couplings of nitriles with the sulfimide $Ph_2S=NH$[6] or the imine $Ph_2C=NH$,[7] catalytic hydrolytic amidation of unactivated organonitriles involving metal complexes,[8] coupling of 1,2-bis(diphenylphosphino)-ethane and nitriles bound to a $[Mo_2]^{4+}$ core,[9] dimerisation and trimerisation of nitriles at a metal centre giving new C–C bonds,[10] and copper-mediated addition of bis(pyrazolyl)borate species to acetonitrile.[11]

As part of our continuing interest in ligand reactivity in general,[12–14] and in reactions of coordinated nitriles[15–17] in particular we have recently observed an unusual coupling between nitriles bound to the platinum(IV) centre in $[PtCl_4(RCN)_2]$ and oximes $HON=CR^1R^2$[15,16] or nitrones $^-ON^+(R^3)=CR^1R^2$[18] (the latter can be viewed as the "frozen", by alkylation, form of the other oxime tautomer) to give $[PtCl_4\{HN=C(R)ON=CR^1R^2\}_2]$ due to the addition[15,16] or $\Delta^4$-1,2,4-oxadiazoline compounds $[PtCl_4\{\overline{N=C(Me)O-N(R^3)-C(R^1)(R^2)}\}_2]$ as a result of a [2 + 3] cycloaddition.[18] The additions of oximes[15,16] containing donor substituents, $R^1R^2$, proceed rapidly in *non-dried* solvents to give the products in almost quantitative yield. However, when oximes with acceptor substituents, *e.g.* $R^1$ = Cl, are employed[19] we observed a significant retardation of the reaction rate and a loss of the selectivity reflected in the appearance of some by-products. Later, the same by-products were observed in addition of either alcohols[20] or hydroxamic acids[21] to nitriles in $[PtCl_4(RCN)_2]$ complexes and we assumed that their formation is associated with a facile hydrolysis of the metal-bound RCN species by *traces of water* in the solvents applied. In the chemistry of platinum, to date only the hydroxide-promoted hydrolysis of organonitriles has been described.[22–27] Hence, a separate study on the addition of water to organonitriles mediated by a platinum(IV) centre was thought to be timely.

Besides the practical interest in the identification of the hydrolysis products, we attempted to enhance the basic knowledge on platinum organonitrile systems and to (i) compare the reactivity of (nitrile)Pt(IV) complexes towards hydrolysis with that of the corresponding platinum(II) nitrile compounds and (ii) investigate how the increase of the oxidation state of the metal centre, on going from Pt(II) to Pt(IV), affects the coordination mode of the carboxamides formed. We now report on the hydrolysis of nitriles ligated to the platinum(IV) centre along with the structural characterisation of amides, coordinated to Pt(IV) in their iminol form, and also present results of a theoretical study on the relative stabilities of N- and O-bonded amides in both platinum(II) and platinum(IV) complexes.

## Results and discussion

### Hydrolysis studies

Hydrolysis of organonitriles represents one of the principal pathways for generation of amides which exhibit a high syn-

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thetic utility and also have industrial applications and pharmacological interest. In the vast majority of cases, a base-catalysed hydrolytic conversion of RCN leads to a carboxylate salt, whereas in acidic media the conversion of amides to carboxylic acids is faster than the conversion of nitriles to amides and the reaction thus proceeds to the final hydration product rather than terminating at the amide stage.[28] Moreover, in some instances in acidic solutions the ratio of the rates is concentration dependent.[29] These difficulties can be overcome with the use of metal ions as powerful activators of RCN towards nucleophilic attack by $OH^-/H_2O$. This activation can result in enhancement of the rate of the hydrolysis commonly in the range of $10^6$ to $10^{10}$.[30] Throughout the last decade, metal-catalysed or metal-promoted hydrolysis of nitrile ligands have experienced a rapid growth in two main directions, namely (i) the homogeneous *catalytic* hydrolysis when the amides formed are expelled from the coordination sphere of the metal ions and (ii) the metal-*promoted* hydrolysis giving amides which remain ligated. The former direction is strongly motivated by practical applications and the latter one gives useful information about structures, coordination modes of metal-bound amides and stereochemistry of plausible intermediates involved in the catalytic hydration. From that viewpoint, kinetically inert platinum(II) complexes[31] were proven to be excellent subjects for the study of base-hydrolysis and also for trapping amides in their iminol form[22–27] or, in one case, in the O-bonded form which then undergoes O-to-N linkage isomerisation.[32] In addition, these studies contribute greatly to investigations of biologically active platinum blues.[33]

Despite a significant number of studies on the platinum(II)-mediated hydrolysis of organonitriles, similar reactions of (nitrile)Pt(IV) complexes have only received limited attention. To date there is only one reported study on the reaction between [Cp*RhPtCl$_6$] and [Cp*Rh(NCMe)$_3$]$^{2+}$ (Cp* = $\eta^5$-$C_5Me_5$) in acetonitrile giving the carboxamide platinum(IV) complex [(Cp*Rh)$_2$($\mu$-Cl)$_3$][PtCl$_5${N(H)=C(OH)Me}].[34] The authors[34] suggested that the carboxamide is formed due to hydrolysis of a Pt-bound acetonitrile with traces of water. However, the presence of the rhodium(III) centre makes the interpretation somehow ambiguous.

For the current study we addressed the platinum(IV) complexes *cis*/*trans*-[PtCl$_4$(MeCN)$_2$][15] and *trans*-[PtCl$_4$(EtCN)$_2$] (for its characterisation see the Experimental) which were shown to exhibit a high reactivity towards nucleophilic additions and cycloadditions.[15,16,18] We have now observed that their reaction with water, contained in non-dried commercial acetone, proceeds at *ca.* 35 °C for 8–10 h and, in contrast to relevant platinum(II) systems, no hydroxide is required to furnish the metal-bound carboxamides. In either case, evaporation of the solvent allows the isolation of a product which, based on the analytical data displayed below, is formulated as [PtCl$_4$-{N(H)=C(OH)Me}$_2$]·Me$_2$CO (**1**) or [PtCl$_4${N(H)=C(OH)Et}$_2$] (**2**), respectively, eqn. (1).

$$[PtCl_4(N{\equiv}CR)_2] + 2\ H_2O \longrightarrow [PtCl_4\{N(H){=}C(OH)R\}_2] \quad (1)$$

The IR spectra of the complexes do not display the C≡N stretching vibrations but show very strong $\nu$(C=N) vibrations and the appearance of both N–H and O–H stretching vibrations. In the spectrum of **1**, the $\nu$(C=O) stretch of Me$_2$CO overlaps with the $\nu$(C=N) vibrations; however, acetone was identified in the $^1$H NMR spectrum. In the $^1$H NMR spectra of both **1** and **2**, signals from the NH and OH protons were clearly observed, while in the $^{13}$C{$^1$H} NMR spectra signals from the imino carbon were detected. The crystal structure of **2** disclosed its *trans*-configuration and will be discussed below. Although we were unable to obtain suitable crystals of **1** for the X-ray experiment, this complex is tentatively ascribed to the *trans*-form based upon indirect arguments such as the different $^1$H NMR and TLC characteristics for *cis*-[PtCl$_4${N(H)=C(OH)-Me}$_2$] (see below). No isomerisation of both **1** and **2** was detected upon heating these complexes in acetone solutions at 35–38 °C for 12 h.

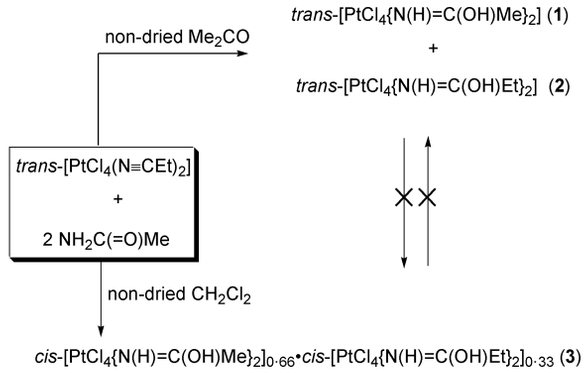
For an estimate of the relative stabilities of the *cis*- and *trans*-isomers in both platinum(II) and platinum(IV) complexes, the equilibrium structures of *cis*- and *trans*-[Pt$^{II}$Cl$_2${N(H)=C(OH)-Me}$_2$] and *cis*- and *trans*-[Pt$^{IV}$Cl$_4${N(H)=C(OH)Me}$_2$] with the ligands in the N-iminol form were calculated at the DFT level of theory. The main bond lengths calculated for *trans*-[Pt$^{II}$Cl$_2$-{N(H)=C(OH)Me}$_2$] and *cis*-[Pt$^{IV}$Cl$_4${N(H)=C(OH)Me}$_2$] are in a good agreement with the X-ray experimental data (ref. 22 and this work) for these complexes. The deviation between the theoretical and experimental bond lengths for *trans*-[Pt$^{IV}$Cl$_4${N(H)=C(OH)Me}$_2$] is significant, which is accounted for by the unusual X-ray structural parameters of *trans*-[PtCl$_4${N(H)=C(OH)Et}$_2$] (see the Structural section below). The analysis of the total energies of the structures calculated at the B3PW91 level of theory shows that the *trans*-isomers of the iminol form are expected to be more stable than the *cis*-isomers by 10.34 and 7.68 kcal mol$^{-1}$. We anticipate that the experimentally obtained geometrical isomeric forms of the complexes depend on a delicate balance of experimental factors and, although the products of the hydrolysis in acetone appear as the *trans* isomers in accord with the predicted higher stability of these isomers for both the Pt(IV) and the Pt(II) systems, the *cis* isomers are the ones obtained by the more direct synthesis of the products on reaction of the Pt(IV) species with a carboxamide in $CH_2Cl_2$. Once a particular isomer formed no isomerisation to the expected more favourable one was observed, suggesting a significant kinetic barrier for the geometrical rearrangement.

It is also noteworthy to mention that the analysis of the equilibrium structures for the isomers of the platinum(II) complexes [Pt$^{II}$Cl$_2${N(H)=C(OH)Me}$_2$] and [Pt$^{II}$Cl$_2${O=C(NH$_2$)Me}$_2$] and the platinum(IV) compounds [Pt$^{IV}$Cl$_4${N(H)=C(OH)Me}$_2$] and [Pt$^{IV}$Cl$_4${O=C(NH$_2$)Me}$_2$] with the ligands in the N-iminol and O-amide forms, shows that the former are more stable than the latter for each particular *trans*- or *cis*-isomer by 2.17–17.68 kcal mol$^{-1}$. These theoretical results are in full agreement with the experimental ones, since no product with the O-carboxamide form was obtained.

Complexes **1** and **2** have different stabilities. Thus, **2** is stable in the crystalline form for approximately one week in open air and only after that do the crystals start to decompose. In contrast, **1** is unstable as a solid even under dinitrogen in dry conditions and the slow decomposition of crystals occurs soon after isolation of the complex from the reaction mixture. The instability of **1** is reflected in rather poor C, H and N elemental analyses, while FAB-MS, IR and $^1$H NMR data strongly support the formulation. In dried solvents, *e.g.* $CH_2Cl_2$ or $CHCl_3$, **2** is stable for at least 2 d at 40 °C, while **1** gradually decomposes in solution, for example in DMSO-$d_6$ (it is sparingly soluble in the other most common deuterated solvents), and this property does not allow reliable characterisation by $^{195}$Pt NMR spectroscopy. A similar surprising difference in stabilities between the closely related platinum homoleptic complexes was indicated previously for [Pt(NCR)$_4$]$^{2+}$ (R = Me, Et), where the acetonitrile complex is quite unstable, while the propionitrile one displays a rather significant stability.[35]

We also performed the reaction, in non-dried acetone, between *trans*-[PtCl$_4$(EtCN)$_2$] and MeC(=O)NH$_2$ in a 1 : 2 molar ratio which gives a mixture of **1** (derived from substitution) and **2** (derived from the hydrolysis), along with some as yet unidentified products, Scheme 1.

A surprising difference in the reaction path was observed when *trans*-[PtCl$_4$(EtCN)$_2$] was treated with MeC(=O)NH$_2$, in a 1 : 2 molar ratio, in dichloromethane. In this case, we obtained an isomorphic mixture of *cis*-[PtCl$_4${N(H)=C(OH)Me}$_2$] and *cis*-[PtCl$_4${N(H)=C(OH)Et}$_2$], *i.e.* *cis*-[PtCl$_4${*Z*-N(H)=C(OH)-




**Scheme 1**

Me}$_2$]$_{0.66}$·*cis*-[PtCl$_4${*Z*-N(H)=C(OH)Et}$_2$]$_{0.33}$ (**3**) released from the reaction mixture as a solid, isolated in 30% yield (Scheme 1). When **3** is dissolved in acetone and then precipitated by slow addition of diethyl ether the ratio between the components, established by $^1$H NMR integration, remains unchanged. Furthermore, heating of **3** in acetone or dichloromethane at 35–38 °C did not result in *cis*-to-*trans* isomerisation and only a slow overall degradation of the material was observed.

### X-Ray structures of Pt(IV)-bound iminols

The coordination polyhedra of **2** and **3** (Figs. 1 and 2, the latter

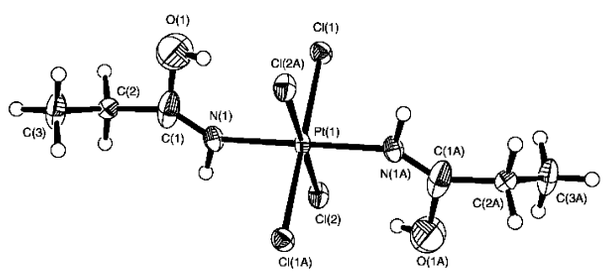



**Fig. 1** ORTEP[54] drawing of *trans*-[PtCl$_4${*Z*-N(H)=C(OH)Et}$_2$] with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformations used to generate equivalent atoms A: $-x$, $-y$, $-z$.

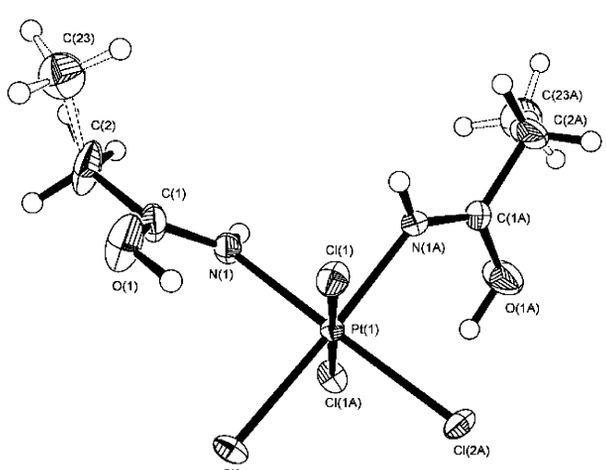



**Fig. 2** ORTEP drawing of *cis*-[PtCl$_4${*Z*-N(H)=C(OH)Me}$_2$]$_{0.66}$·*cis*-[PtCl$_4${*Z*-N(H)=C(OH)Et}$_2$]$_{0.33}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformations used to generate equivalent atoms A: $x$, $y$, $1-z$.

for the methylcarboxamide molecule) are slightly distorted octahedra and the amide ligands are mutually *trans* (in **2**) and *cis* (in **3**). The Pt atom in structure **2** is placed on an inversion center while in **3** Pt is on a two-fold axis. All angles around Pt are normal and the Pt–Cl bond lengths (2.31–2.32 Å; Tables 1 and 2) are within the range of typical values reported for other platinum(IV) chloride complexes.[15,16]

**Table 1** Bond lengths (Å) and angles (°) for *trans*-[PtCl$_4${N(H)=C(OH)Et}$_2$]

| | | | |
|---|---|---|---|
| Pt(1)–N(1) | 2.011(6) | C(1)–C(2) | 1.464(11) |
| Pt(1)–Cl(1) | 2.319(2) | C(1)–O(1) | 1.510(14) |
| Pt(1)–Cl(2) | 2.323(2) | C(2)–C(3) | 1.509(10) |
| N(1)–C(1) | 1.169(10) | | |
| N(1)–Pt(1)–N(1)#1 | 180.0 | C(1)–N(1)–Pt(1) | 146.0(7) |
| N(1)–Pt(1)–Cl(1) | 89.9(2) | N(1)–C(1)–C(2) | 141.4(11) |
| Cl(1)–Pt(1)–Cl(1)#1 | 180.0 | N(1)–C(1)–O(1) | 110.5(8) |
| N(1)–Pt(1)–Cl(2) | 87.4(2) | C(2)–C(1)–O(1) | 108.1(7) |
| Cl(1)–Pt(1)–Cl(2) | 89.58(6) | C(1)–C(2)–C(3) | 111.5(7) |

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

**Table 2** Bond lengths (Å) and angles (°) for *cis*-[PtCl$_4${N(H)=C(OH)Me}$_2$] in the isomorphic mixture *cis*-[PtCl$_4${N(H)=C(OH)Me}$_2$]$_{0.66}$·*cis*-[PtCl$_4${N(H)=C(OH)Et}$_2$]$_{0.33}$

| | | | |
|---|---|---|---|
| Pt(1)–N(1) | 2.037(2) | O(1)–C(1) | 1.313(4) |
| Pt(1)–Cl(2) | 2.3143(7) | N(1)–C(1) | 1.262(4) |
| Pt(1)–Cl(1) | 2.3173(7) | C(1)–C(2) | 1.485(4) |
| N(1)–Pt(1)–N(1)#1 | 87.00(14) | N(1)–Pt(1)–Cl(1) | 93.45(8) |
| N(1)–Pt(1)–Cl(2)#1 | 176.37(8) | Cl(1)#1–Pt(1)–Cl(1) | 178.70(4) |
| N(1)–Pt(1)–Cl(2) | 91.05(7) | C(1)–N(1)–Pt(1) | 133.7(2) |
| Cl(2)#1–Pt(1)–Cl(2) | 91.06(4) | N(1)–C(1)–O(1) | 123.5(3) |
| N(1)–Pt(1)–Cl(1)#1 | 87.49(8) | N(1)–C(1)–C(2) | 123.5(3) |
| Cl(2)#1–Pt(1)–Cl(1)#1 | 89.58(3) | O(1)–C(1)–C(2) | 113.0(3) |
| Cl(2)–Pt(1)–Cl(1)#1 | 89.52(3) | | |

Symmetry transformations used to generate equivalent atoms: #1 $x$, $y$, $1-z$.

In *cis*-[PtCl$_4${*Z*-N(H)=C(OH)Me}$_2$]$_{0.66}$·*cis*-[PtCl$_4${*Z*-N(H)=C(OH)Et}$_2$]$_{0.33}$ (**3**), only the dominant molecule, *i.e. cis*-[PtCl$_4${*Z*-N(H)=C(OH)Me}$_2$], was clearly resolved. However, every third molecule of *cis*-[PtCl$_4${*Z*-N(H)=C(OH)Et}$_2$] in the isomorphic mixture was detected by observation of extra electron density near (*ca.* 1.6 Å) the methyl carbon of the *Z*-N(H)=C(OH)Me ligand. This observation agrees well with the unambiguous identification of the ethyl group in $^1$H and $^{13}$C{$^1$H} NMR spectra in solution.

The amide ligands are in the iminol tautomeric form in its *Z* conformation. Although the C=N [1.262(4) Å] and C–O [1.313(4) Å] bond lengths in **3** are within normal values,[22–27] in **2** they are unusual. Indeed, the C=N bond [1.169(10) Å] is shorter in comparison with the C=N bond in **3**, in the anionic platinum(IV) complex [PtCl$_5${N(H)=C(OH)Me}]$^-$ [1.27(3) Å],[34] in the series of platinum(II) imino complexes *trans*-[PtCl$_2$(N(H)=C(OH)R}$_2$] [1.24–1.28 Å],[22–24] in *cis*-[PtCl$_2${N(H)=C(OH)Bu$^t$}$_2$]$_2$ [1.21(3) and 1.25(3) Å][25] and in the platinum(II) trimer [PtCl$_2${N(H)=C(OH)Bu$^t$}]$_3$ [1.277(22) Å].[36] The bond is also shorter than in the platinum(III) complex [Pt$_2$Cl$_6${N(H)=C(OH)Bu$^t$}$_4$] [1.24(1) Å][37] and much shorter than in {N(H)=C(OH)R}Ni(I) [1.314(7) Å].[38] Concurrently, the C–O bond [1.510(14) Å] is longer than was observed in the other amides in the iminol form (1.32–1.43 Å).[22–27] The deviations found in **2** for the C=N and C–O bonds most likely cannot be attributed to a systematic error since six crystals from different syntheses were subject to the X-ray structure determinations and all data obtained were in good agreement. We believe that at this stage more X-ray structures for (iminol)Pt(IV) complexes are needed to make clear the reason for the deviation.

## Final remarks

These studies indicate that the Pt(IV) centre can readily activate alkanenitriles towards hydrolysis which proceeds smoothly, under mild conditions and in the absence of added hydroxide, a

reagent required in the case of Pt(II) centres.[22–27] In this respect, the behaviour parallels that observed[20] for the addition of alcohols to nitriles to give imino esters but, in contrast with the latter ligands which exhibit a more stable *E*-configuration, the ligated carboxamides of the present work prefer to adopt the *Z*-configuration.

The reaction does not proceed beyond the carboxamide stage and the iminol form of this product is the favourable one for ligation to Pt(IV), as known for Pt(II),[22–27] in spite of the expected harder character of the former centre which could prefer O-binding of the amide.

## Experimental

### Materials and instrumentation

The complex $[PtCl_4(MeCN)_2]$ was prepared in accord with the published method.[15,39] Solvents were obtained from commercial sources and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. For TLC, Merck UV 254 $SiO_2$-plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* $1.28 \times 10^{15}$ J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 $cm^{-1}$) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. $^1H$, $^{13}C\{^1H\}$ and $^{195}Pt$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. $^{195}Pt$ chemical shifts are given relative to $Na_2[PtCl_6]$ by using aqueous $K_2[PtCl_4]$ ($\delta = -1630$ ppm) as a standard, and the half height line width is given in parentheses.

### Synthetic work and characterisation

***trans*-[$PtCl_4(EtCN)_2$].** Was prepared by the passage of $Cl_2$ through a suspension of *trans*-$[PtCl_2(EtCN)_2]$ (0.011 g, 0.034 mmol) in chloroform (3 ml) at room temperature for *ca.* 30 min. The resultant bright yellow powder of *trans*-$[PtCl_4(EtCN)_2]$ was filtered off, washed with diethyl ether (three 3 ml portions) and dried in air at room temperature. Yield: 80%, based on Pt.

Anal. calc. for $C_6H_{10}N_2Cl_4Pt$: C, 16.12; H, 2.25; N, 6.27%. Found: C, 16.05; H, 2.14; N, 5.98%. $FAB^+$-MS, *m*/*z*: 407 [M − Cl], 376 [M − 2Cl], 339 [M − 3Cl]. TLC on $SiO_2$: $R_f$ = 0.39 (eluent $Me_2CO$–$CHCl_3$ = 3 : 1). IR spectrum (selected bands), $cm^{-1}$: 2920 m $\nu$(C–H), 2340 s $\nu$(C≡N). $^1H$ NMR spectrum in DMSO-$d_6$, $\delta$: 1.54 (t, *J* 7.5 Hz, 3H, $CH_2Me$), 3.20 (quartet, *J* 7.5 Hz, 2H, $CH_2Me$). $^{13}C\{^1H\}$ NMR in DMSO-$d_6$, $\delta$: 9.5 ($CH_3$ from Et) and 13.1 ($CH_2$ from Et), 118.8 (N≡C). $^{195}Pt$ NMR in DMSO-$d_6$, $\delta$: −530 (840 Hz).

**Hydrolysis of [$PtCl_4(RCN)_2$].** $[PtCl_4(RCN)_2]$ (0.015 g) was dissolved in non-dried acetone (5 ml for R = Et and 10 ml for R = Me) with stirring at room temperature and left to stand for 8–10 h at 35–38 °C. The resultant bright yellow solution was evaporated to dryness under a flow of $N_2$ and the residue washed with *n*-pentane (five 3 ml portions). Yield: 70 (**1**) and 85% (**2**), based on Pt.

*[$PtCl_4${NH=C(OH)Me}$_2$]·$Me_2CO$ (**1**).* Anal. calc. for $C_7H_{16}N_2Cl_4O_3Pt$: C, 16.39; H, 3.14; N, 5.46%. Found: C, 15.22; H, 2.60; N, 5.19%. $FAB^+$-MS, *m*/*z*: 383 [M − 2Cl − H], 349 [M − 3Cl]. TLC on $SiO_2$: $R_f$ = 0.47 (eluent $Me_2CO$–$CHCl_3$ = 3 : 1). IR spectrum (selected bands), $cm^{-1}$: 3504 m $\nu$(O–H), 3296 mw $\nu$(N–H), 1645 s $\nu$(C=N). $^1H$ NMR spectrum in DMSO-$d_6$, $\delta$: 2.35 (s, 3H, Me), 7.30 (s, br, 1H, NH), 9.11 (s, br, 1H, OH). $^{13}C\{^1H\}$ NMR in acetone-$d_6$, $\delta$: 21.7 ($CH_3$) and 177.7 (HN=C). We were unable to record the $^{195}Pt$ NMR spectrum of **1** due to its instability in DMSO-$d_6$, and poor solubility and moderate stability in acetone-$d_6$.

*trans-[$PtCl_4${NH=C(OH)Et}$_2$] (**2**).* Anal. calc. for $C_6H_{14}N_2Cl_4O_2Pt$: C, 14.92; H, 2.92; N, 5.80%. Found: C, 15.01; H, 2.93; N, 5.00%. $FAB^+$-MS, *m*/*z*: 412 [M − 2Cl], 376 [M − 3Cl − H], 341 [M − 4Cl]. TLC on $SiO_2$: $R_f$ = 0.49 (eluent $Me_2CO$–$CHCl_3$ = 3 : 1). IR spectrum (selected bands), $cm^{-1}$: 3497 m $\nu$(O–H), 3281 mw $\nu$(N–H), 1638 s $\nu$(C=N), 1211 s $\nu$(C–O). $^1H$ NMR spectrum in DMSO-$d_6$, $\delta$: 0.95 (t, *J* 7.5 Hz, 3H, $CH_2Me$), 2.02 (quartet, *J* 7.5 Hz, 2H, $CH_2Me$), 6.93 (s, br, 1H, NH), 10.42 (s, br, 1H, OH). $^{13}C\{^1H\}$ NMR in DMSO-$d_6$, $\delta$: 9.7 ($CH_3$ from Et) and 28.1 ($CH_2$ from Et), 175.3 (HN=C). $^{195}Pt$ NMR in DMSO-$d_6$, $\delta$: 36 (800 Hz).

**Reaction of *trans*-[$PtCl_4(EtCN)_2$] with $MeC(=O)NH_2$ in $CH_2Cl_2$.** The carboxamide (10 mg, 0.22 mmol) was added to a suspension of *trans*-$[PtCl_4(EtCN)_2]$ (50 mg, 0.11 mmol) in $CH_2Cl_2$ (1 ml) and the mixture left to stand at *ca.* 30 °C for 3 d. Large yellow crystals formed which were filtered off and washed with *n*-pentane (five 3 ml portions). Yield: 30%, based on Pt.

*cis-[$PtCl_4${NH=C(OH)Me}$_2$]$_{0.66}$·cis-[$PtCl_4${NH=C(OH)Et}$_2$]$_{0.33}$ (**3**).* Anal. calc.: C, 12.07; H, 2.46; Cl, 30.54; N, 6.03%. Found: C, 12.11; H, 2.26; N, 5.64%. TLC on $SiO_2$: $R_f$ = 0.43 and 0.31 (eluent $Me_2CO$–$CHCl_3$ = 3 : 1). IR spectrum in KBr, selected bands, $cm^{-1}$: 3443 w $\nu$(O–H), 3282 m $\nu$(N–H), 2930 w $\nu$(C–H), 1638 s $\nu$(C=N), 1200 m $\nu$(C–O). $^1H$ NMR in DMSO-$d_6$, $\delta$: 2.56 and 2.53 (quartet, *J* 7.6 Hz, Et), 1.04 and 1.02 (t, *J* 7.6 Hz, Et), 2.29 and 2.26 (s, $CH_3$), 8.11 (s, br, 3H, NH). $^{13}C\{^1H\}$ NMR in DMSO-$d_6$, $\delta$: 28.9 ($CH_2$ from Et), 10.7 ($CH_3$ from Et), 22.4 and 21.8 ($CH_3$), 178.6 and 175.0 [HN=*C*(Et) and HN=*C*(Me)]. $^{195}Pt$ NMR in DMSO-$d_6$, $\delta$: −202 (660 Hz).

### X-Ray crystallography

The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo-Kα radiation ($\lambda$ = 0.71073 Å) and the Collect[40] data collection program. The Denzo and Scalepack programs[41] were used for cell refinements and data reduction. Both structures **2** and **3** were solved by direct methods using the SHELXS97[42] and SIR97[43] programs, respectively, with the WinGX[44] graphical user interface. Structural refinements were carried out with SHELXL97.[45] The OH-group hydrogen in **2** was located from the difference Fourier map but not refined. The NH and OH hydrogens in **3** were found in the difference Fourier map and refined isotropically. All other hydrogens in **2** and **3** were placed in idealised positions and constrained to ride on their parent atoms. The structure **3** consisted of an isomorphic mixture of *cis*-[$PtCl_4$-{*Z*-N(H)=C(OH)Me}$_2$]$_{0.66}$·*cis*-[$PtCl_4${*Z*-N(H)=C(OH)Et}$_2$]$_{0.33}$. The isomorphic ratio was estimated by refining the population parameters. According to these results the ratio was then fixed at 0.66/0.33. The carbon bonded to C(1) was formally divided into two atoms C(2) and C(22) with different occupancies of 2/3 and 1/3 but the same coordinates and anisotropic parameters. Methyl hydrogens were fixed to ride on C(2) and methylene hydrogens on C(22). Similarly to C(22), C(23) was refined with an occupation factor of 1/3 completing the ethyl group. The crystallographic data are summarised in Table 3. Selected bond lengths and angles in Tables 1 and 2. The molecular structures are shown in Figs. 1 and 2.

CCDC reference numbers 170791 and 170792.

See http://www.rsc.org/suppdata/dt/b1/b108327a/ for crystallographic data in CIF or other electronic format.

### Computational details

The full geometry optimization of all structures has been carried out at the DFT level of theory using effective core potentials (ECPs)[46,47] with the help of the Gaussian-98[48] program package. The calculations have been performed using Becke's three-parameter hybrid exchange functional[49] in combination with the gradient-corrected correlation functional of Perdew and Wang[50] (B3PW91). Symmetry operations were not

**Table 3** Crystal data for **2** and **3**

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_6H_{14}N_2Cl_4O_2Pt$ | $C_{4.67}H_{11.33}Cl_4N_2O_2Pt$ |
| FW | 483.08 | 464.38 |
| $T$/K | 120(2) | 120(2) |
| Space group | $P2_1/n$ (no. 14) | $P4_12_12$ (no. 92) |
| Crystal system | Monoclinic | Tetragonal |
| $a$/Å | 5.9316(1) | 11.2374(1) |
| $b$/Å | 8.9649(3) | 11.2374(1) |
| $c$/Å | 12.2271(4) | 9.6576(1) |
| $\beta$/° | 102.5080(10) | 90 |
| $V$/Å$^3$ | 634.76(3) | 1219.55(2) |
| $Z$ | 2 | 4 |
| $\rho_{calc}$/g cm$^{-3}$ | 2.528 | 2.529 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 11.877 | 12.358 |
| $R_1$ [a] | 0.0262 | 0.0095 |
| $wR_2$ [b] | 0.0657 | 0.0248 |

[a] $I > 2\sigma$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

applied. A quasi-relativistic Stuttgart pseudopotential described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][51] augmented by the p-type polarisation function with an exponent of 0.086[52] were used for the platinum atom. The standard 6–311+G* basis set[53] was applied for the other atoms. The Hessian matrix was calculated analytically for all structures in order to prove the location of correct minima (all structures have no imaginary frequencies) and the zero-point vibrational energies have been estimated.

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