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Synthesis and characterisation of the amidine complexes *trans*-[PtCl(NH_3){HN=C(NH_2)R}$_2$]Cl (R = Me, Ph, CH_2Ph) derived from addition of NH_3 to the coordinated nitriles in *trans*-[$PtCl_2$(N≡CR)$_2$]

Giovanni Natile [a,*], Francesco P. Intini [a], Roberta Bertani [b,*], Rino A. Michelin [b], Mirto Mozzon [b], Silvia Mazzega Sbovata [b], Alfonso Venzo [c], Roberta Seraglia [c]

[a] *Dipartimento Farmaco-Chimico, Università di Bari, via E. Orabona 4, 70125 Bari, Italy*

[b] *Dipartimento di Processi Chimici dell'Ingegneria, Facoltà di Ingegneria, Università di Padova, Via Marzolo 9, 35131 Padova, Italy*

[c] *Istituto di Scienze e Tecnologie Molecolari, Sezione di Padova, Consiglio Nazionale delle Ricerche, Via Marzolo 1, 35131 Padova, Italy*

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Abstract

The di-nitrile complexes *trans*-[$PtCl_2$(N≡CR)$_2$] (R = Me, Ph, CH_2Ph) react with an excess of gaseous NH_3 in CH_2Cl_2 at −10 °C to form, in high yield, the corresponding di-amidine complexes *trans*-[PtCl(NH_3){HN=C(NH_2)R}$_2$]Cl in which also one chlorine ligand has been displaced by NH_3. The ^1H NMR spectra in DMSO showed the formation of different species which were characterized through NOESY, TOCSY and $^1H/^{13}C$ heteronuclear correlations as *trans*-[Pt(NH_3){HN=C(NH_2)R}$_2$(DMSO)]Cl_2 and *trans*-[PtCl{HN=C(NH_2)R}$_2$(DMSO)]Cl.

Keywords: Platinum; Nitriles; Amidines; Ammonia; Nucleophilic attack

1. Introduction

The coupling of small molecules promoted by a metal center is a relevant feature in biological processes as well as in industrial chemistry [1,2]. In particular, there are many synthetic heterogeneous and homogeneous processes involving NH_3. A first example is the HCN synthesis by the Degussa process, in which a 1:1 mixture of methane and ammonia is passed through a Pt-coated tube-wall reactor, or by the related process using bimetallic gold–platinum cluster cations as catalyst [3]. The use of Pt_3O_4 in the catalytic oxidation of ammonia to NO for the industrial production of nitric acid [4] has also been extensively studied. New hydrophobic fluorinated carbon supported Pt catalysts, promoting the reaction of nitrogen oxides NO_x with NH_3, are investigated in order to develop a very effective post combustion De-NO_x technology for controlling NO_x emissions [5]. The synthesis of methylamines from CO_2, H_2, and NH_3 has been reported to occur over Pt-alumina catalysts, together with significant methane formation [6]. Very recently, Cu^{2+} has been shown to be an efficient catalyst in cycloaddition of nitriles and ammonia to give Cu(I) triazolate derivatives according to the following equation [7]:

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[*] Corresponding authors. Tel.: ++39 49 8275731; fax: ++39 49 8275525.

E-mail address: roberta.bertani@unipd.it (R. Bertani).

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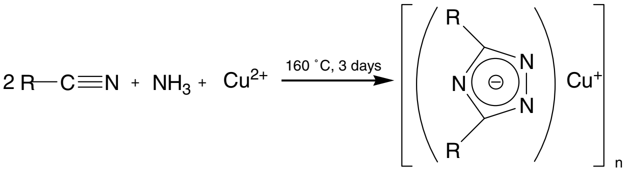
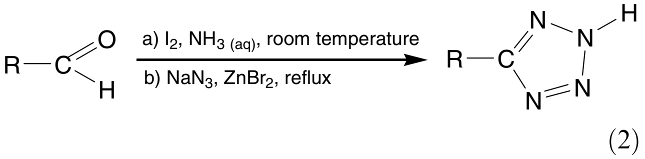


(1)

Tetrazoles and 1,3,5-triazine have also been formed by reaction of an aldehyde with iodine in aqueous ammonia forming a nitrile intermediate which reacts further with sodium azide or dicyandiamine [8] to yield the final product according to the following equation:



(2)

Acetylenic nitriles are reported to give photochemical addition of ammonia to form *E* and *Z* isomers of 3-amino-2-propene nitrile by regioselective addition to the C≡C triple bond [9].

In this paper we describe the reaction of gaseous NH_3 with the coordinated nitrile ligands in platinum(II) complexes of the type *trans*-$[PtCl_2(N{\equiv}CR)_2]$ (R = CH_3, Ph, CH_2Ph) [10]. At our knowledge, only very few examples of such reactions have been previously reported. For instance, liquid NH_3 was reacted with $[Pt(N{\equiv}CNMe_2)(dien)][CF_3SO_3]_2$ (dien = diethylentriamine) to form quantitatively a guanidine complex according to the following equation [11]:

$$[Pt(N{\equiv}CNMe_2)(dien)]^{2+} + 2NH_{3(l)} \rightarrow [Pt\{HN{=}C(NH_2)NMe_2\}(dien)]^{2+} \qquad (3)$$

Crystals of the acetamide derivative *cis*-$[Pt\{1\text{-}MeTy(H)\}\{MeC(NH){=}NH_2\}(PMe_3)_2][X]$ (1-MeTy = 1-methylthymine; X = NO_3, ClO_4) were isolated from an acetonitrile solution of *cis*-$[Pt\{\mu\text{-}OH)(PMe_3)_2]_2[X]_2$ (X = NO_3, ClO_4) and 1-MeTy in the presence of a small amount of water, due to the addition of in situ formed NH_3 to the coordinated MeCN [12].

Diffusion of ammonia into a solution of *mer*-$[RhCl_3(PhCH_2CN)_3]$ in neat benzyl cyanide was reported to afford in high yield the amidine complex *mer*-$[RhCl_3\{HN{=}C(NH_2)CH_2Ph\}_3]$ [13].

The addition of primary and secondary aliphatic amines HNR′R″ (R′ = H, Me, Et; R″ = Me, Et, *t*-Bu), but not of ammonia, to *cis*- and *trans*-$[PtCl_2(N{\equiv}CR)_2]$ (R = Me, Ph) to give mono- or di-amidine derivatives of the type $[PtCl_2(N{\equiv}CR)\{HN{=}C(R)NR'R''\}]$ and $[PtCl_2\{HN{=}C(R)NR'R''\}_2]$, respectively, has previously been reported [14]. In particular, primary amines add to *cis*- and *trans*-$[PtCl_2(N{\equiv}CMe)_2]$ affording the di-amidine complexes having exclusively *Z* conformation of the ligands both in solution and in the solid state [14]. This appears to be a consequence of the low steric hindrance of the NHR″ group, which can be easily accomodated *cis* to the platinum moiety, with respect to the C=N double bond. In the solid state the *Z* conformation could also be stabilized by strong intramolecular Pt–Cl–H–N hydrogen bonds forming pseudo six-membered metallacycles [14]. In contrast, secondary amines give rise to *E* amidines, which represent a more thermodinamically stable configuration, placing the bulky NR′R″ group *trans* to the platinum moiety with respect to the C=N double bond. In the case of the benzonitrile derivatives, the addition of secondary amines usually leads to a mixture of *Z* and *E* isomers because of the comparable size of the two substituents on the azomethine carbon atom (Ph and NR′R″). Similar considerations have been made in the case of addition of alcohols to coordinated nitriles to yield iminoether derivatives [15]. The reactions of *cis*- and *trans*-$[PtCl_2(N{\equiv}CPh)_2]$ with *N*,*N*′-di-*tert*-butylethylenediamine were also studied in detail [16] and found to yield *cis*-$[PtCl_2\{HN{=}C(Ph)N(t\text{-}Bu)CH_2CH_2NH(t\text{-}Bu)\}(N{\equiv}CPh)]$ and $[Pt\{HN{=}C(Ph)N(t\text{-}Bu)CH_2CH_2NH(t\text{-}Bu)\}Cl(N{\equiv}CPh)]Cl$, respectively. The X-ray structure of *cis*-$[PtCl_2\{HN{=}C(Ph)N(t\text{-}Bu)CH_2CH_2NH(t\text{-}Bu)\}(N{\equiv}CPh)]$ showed the amino-amidine ligand to have *E* configuration with an extensive electron delocalisation within the amidine group. The same compound undergoes, in solution, facile *E*–*Z* isomerisation about the azomethine double bond.

2. Results and discussion

2.1. Synthesis

trans-$[PtCl_2(N{\equiv}CR)_2]$ (R = Me, Ph, CH_2Ph) react with NH_3 (excess) in CH_2Cl_2 at −10 °C to afford, in high yield, the corresponding di-amidine derivatives according to the following equation:

$$trans\text{-}[PtCl_2(N{\equiv}CR)_2] \xrightarrow{NH_3(exc),\ -10\ ^\circ C} trans\text{-}[PtCl(NH_3)\{HN{=}C(NH_2)R\}_2]Cl \qquad (4)$$
$$(R = Me,\ \mathbf{1};\ Ph,\ \mathbf{2};\ CH_2Ph,\ \mathbf{3})$$

Compounds **1**–**3** are white solids, which exhibit good solubility in water, but are poorly soluble in common organic solvents such as CH_2Cl_2. They have been characterised by elemental analysis, IR and NMR spectroscopy. The IR spectra show C=N absorption bands in the range 1639–1652 cm^{-1} characteristic of amidine ligands and complete absence of bands assignable to C≡N stretchings. N–H stretchings appear in the range 3511–3167 cm^{-1}.

The reaction of $[PtCl_2(N{\equiv}CMe)_2]$ with NH_3 was reported long time ago [17] to afford a compound of formula $[Pt(NH_3)_4(N{\equiv}CMe)_2]Cl_2 \cdot H_2O$ (known as