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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$_2$Ph) derived from addition of NH$_3$ to the coordinated nitriles in *trans*-[PtCl$_2$(N≡CR)$_2$]

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Abstract

The di-nitrile complexes *trans*-[PtCl$_2$(N≡CR)$_2$] (R = Me, Ph, CH$_2$Ph) react with an excess of gaseous NH$_3$ in CH$_2$Cl$_2$ 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 ^{1}H NMR spectra in DMSO showed the formation of different species which were characterized through NOESY, TOCSY and ^{1}H/^{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$_3$O$_4$ 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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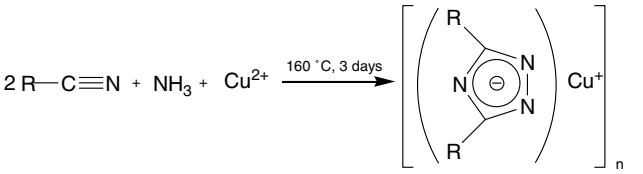
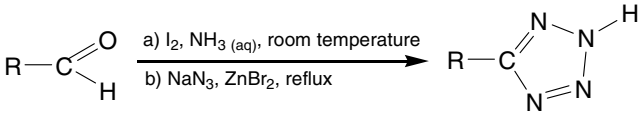


(1)

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]:

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

Crystals of the acetamide derivative *cis*-[Pt{1-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:

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

Tschugaev's salt). Later on this compound was shown by X-ray crystallography to be an amidine complex of formula $[Pt(NH_3)_2\{HN{=}C(NH_2)Me\}]Cl_2 \cdot H_2O$ [18].

Therefore, the main difference between our compounds and the Tschugaev's salt is the number of chlorine ligands substituted by ammonia molecules, one in our case, both of them in the case of Tschugaev's salt. Ammonia is known to be a good ligand for platinum [19] with whom it forms a wide variety of compounds some of which are good antiviral [20] and antitumor [21] drugs.

When we started this investigation we hypothesized that, lowering the temperature to −10 °C, could have retarded the substitution of chloride by the ammine, while still allowing the nucleophilic addition of the ammonia to the coordinated nitrile. However, this has not been the case and even at −10 °C one chloride is substituted by the ammine.

2.2. NMR characterisation

Due to their poor solubility in common organic solvents, NMR spectra suitable for detailed analysis have been recorded in DMSO. The most significant feature for compounds **1**–**3** is the formation in solution of different solvated species, whose relative abundance changes with time. Through NOESY, TOCSY and $^1H/^{13}C$ heteronuclear correlations it was possible to assign the signals to the different species as reported in Table 1.

In all complexes the amidine ligand can be assumed to have the *Z* configuration since it has already been demonstrated that even with primary amines, which are bulkier than ammonia, the kinetically favoured *Z* configuration is also more stable thermodinamically. Furthermore, the X-ray structure of the Tschugaev's salt, as determined by Stephenson, shows the amidine ligand to have *Z* configuration [18a]. Analogous *Z* configuration was found in the X-ray structure of *trans*-$[PtCl_4\{HN{=}C(NH_2)Me\}_2]$ reported by Kukushkin and co-workers [18b]. The *Z* configuration of the acetamidine in compound **1** is also supported by the relatively high field of the methyl proton resonance (δ = 1.93 ppm). A methyl signals at lower field (δ > 2.3 ppm) has been observed in the case of amidines having *E* configuration [14,22].

Four N–H proton resonances are observed in the ^1H NMR spectrum of compound **1** recorded immediately after dissolution in DMSO (resonances A in Fig. 1). The signal at 4.04 ppm is assigned to the ammine protons, the resonance at 6.50 ppm to the iminic proton (C=N–H) and the resonances at 7.17 and 7.03 ppm to the aminic protons (C–NH_2). The initial set of signals decreases rapidly with time simultaneously with the appearance of a new set of signals which becomes dominant after 20 min at 22 °C (signals B in Fig. 1). The new set of signals indicates that the new species still contains a coordinated ammine (signal at 4.53 ppm) and coordinated amidines with signals at 6.82 ppm (C=NH proton) and at 8.21 and 7.63 ppm (C–NH_2 protons). The chemical shift of the C–Me protons (2.09 ppm) also indicates that the amidines have still *Z* configuration. The latter set of signals is assigned to the solvated species *trans*-$[Pt(NH_3)\{HN{=}C(NH_2)Me\}_2(DMSO)]^{2+}$ as confirmed by an NMR experiment performed on the DMSO solution and an ESI mass spectrum performed on a sample of **1** kept in DMSO for the time required to undergo solvolysis, then taken to dryness and the solid residue dissolved in MeOH or *i*-Pr–OH. The NOESY spectrum showed a cross peak between the ammine proton at 4.53 ppm and the C=N–H proton at 6.82 ppm clearly indicating that the ammine is coordinated to platinum and is *cis* to the amidine (see Fig. 2). The ESI mass spectra showed the presence of ions at *m*/*z* 420 and *m*/*z* 449, respectively, corresponding to $[Pt(O–Me)\{HN{=}C(NH_2)Me\}_2(DMSO)]^+$ and $[Pt(O–i\text{-}Pr)\{HN{=}C(NH_2)Me\}_2(DMSO)]^+$, respectively.

Although the molecular ion of $[Pt(DMSO)(NH_3)\{HN{=}C(NH_2)Me\}_2]$ was not observed, this experiment clearly showed that this species contains a coordinated DMSO molecule. Moreover the *trans*-labilizing effect of DMSO can explain why the ammine ligand undergoes substitution by a molecule of alcohol.

Table 1
Selected ^1H and ^{13}C NMR data of **1**–**3** in DMSO (δ in ppm)

Compound	NH_2		Pt–NH	R	NH_3	*C*=N
trans-$[PtCl(NH_3)\{HN{=}C(NH_2)Me\}_2]Cl$, **1**	7.17	7.03	6.50	1.93 (*21.42*)	4.04	166.8
trans-$[Pt(DMSO)(NH_3)\{HN{=}C(NH_2)Me\}_2]Cl_2$	8.21	7.63	6.82	2.01 (*21.58*)	4.53	168.2
trans-$[PtCl(DMSO)\{HN{=}C(NH_2)Me\}_2]Cl$	7.63	7.45	6.72	1.97 (*21.33*)	–	166.8
trans-$[PtCl(NH_3)\{HN{=}C(NH_2)Ph\}_2]Cl$, **2**	8.21	7.89	7.23	–	4.25	166.6
trans-$[Pt(DMSO)(NH_3)\{HN{=}C(NH_2)Ph\}_2]Cl_2$	8.76	8.09	7.20	–	4.74	167.0
trans-$[PtCl(DMSO)\{HN{=}C(NH_2)Ph\}_2]Cl$	8.12	7.87	7.07	–	–	167.8
trans-$[PtCl(NH_3)\{HN{=}C(NH_2)CH_2Ph\}_2]Cl$, **3**	7.86	7.68	7.03	3.58 (*40.85*)	4.14	168.4
trans-$[Pt(DMSO)(NH_3)\{HN{=}C(NH_2)CH_2Ph\}_2]Cl_2$	8.40	7.84	7.15	3.60 (*41.27*)	4.61	169.9
trans-$[PtCl(DMSO)\{HN{=}C(NH_2)CH_2Ph\}_2]Cl$	7.75	7.48	6.95	3.55 (*41.50*)	–	169.1

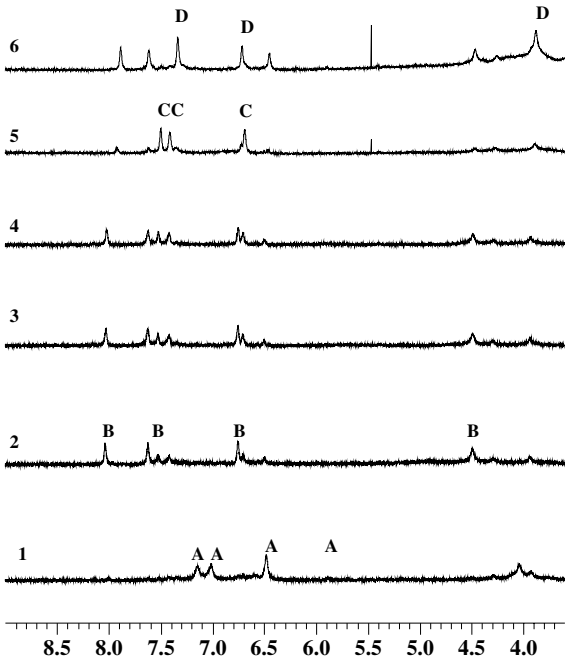
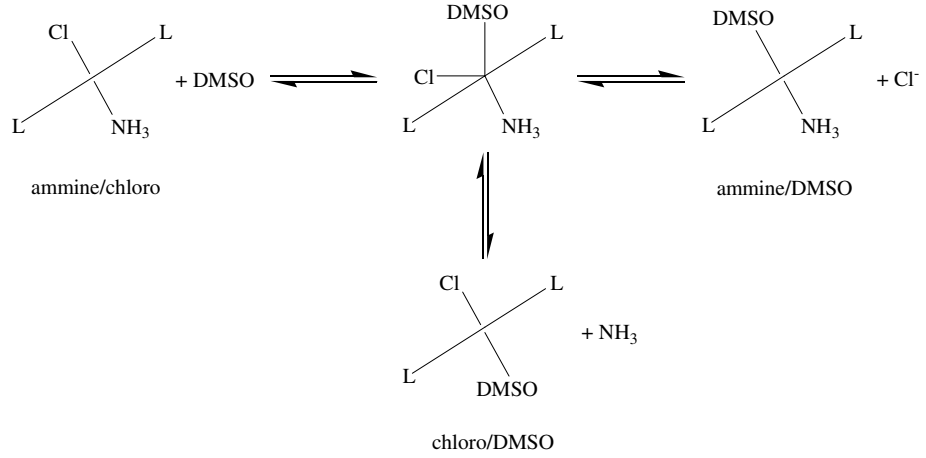


Fig. 1. ^{1}H NMR spectra (in the region 9.0–3.6 ppm) of a solution of compound **1** in DMSO taken soon after dissolution and after standing for 0.2 and 17 days (spectra 1, 2, and 3, respectively), after flashing with argon for 0.25 and 9 h (spectra 4 and 5, respectively), and after addition of gaseous ammonia (spectrum 6). The peaks of the starting substrate *trans*-$[PtCl(NH_3)\{HN{=}C(NH_2)Me\}_2]^+$, of the monosolvated species *trans*-$[Pt(NH_3)\{HN{=}C(NH_2)Me\}_2(DMSO)]^{2+}$ and *trans*-$[PtCl\{HN{=}C(NH_2)Me\}_2(DMSO)]^+$, and of the Tschugaev's cation *trans*-$[Pt(NH_3)_2\{HN{=}C(NH_2)Me\}_2]^{2+}$ are marked A, B, C, and D, respectively.

Substitution of a chloride ligand by a DMSO molecule has been demonstrated to occur readily in solvolysis reactions of *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ [23]. In particular it has been observed that *trans*-$[PtCl(NH_3)_2$-(DMSO)]Cl is the only product formed when *trans*-$[PtCl_2(NH_3)_2]$ is dissolved in DMSO.

In the ^{1}H NMR spectrum of **1** in DMSO, the signals due to the ammine/DMSO solvated species *trans*-$[Pt(NH_3)\{HN{=}C(NH_2)Me\}_2(DMSO)]^{2+}$ decrease slowly with time while a new set of signals gains intensity. The new set of signals has intensity comparable to that of the ammine/DMSO precursor after standing for days in DMSO solution (spectrum 3 in Fig. 1). However, if the solution is flashed with argon the new set of signals increases in intensity and becomes dominant (resonances C in Fig. 1). The new set of signals indicates that the new species does not contain coordinated ammine, but still contains the amidines in their original *Z* configuration (C–Me resonance at 1.97 ppm). Most likely the new species is the product of substitution of the ammine by a chlorine ligand. This has been proved by ESI mass spectrometry showing the presence of a molecular peak at *m*/*z* 431 corresponding to $[PtCl\{HN{=}C(NH_2)Me\}_2(DMSO)]^+$. It is to be noted that in both the ammine/DMSO and chloro/DMSO species the platinum moieties have kept their original *trans* geometry since a *trans* → *cis* isomerisation of the complexes would have lead to non-equivalent amidines (one *trans* to DMSO and the other *trans* to NH_3 or Cl). It has been possible to prove that the slow conversion of the ammine/DMSO into the chloro/DMSO species was not due to a slow rate of the interconversion reaction but to a slow rate of release of gaseus NH_3 from the DMSO solution. In fact addition of gaseous ammonia to the solution containing mainly the chloro/DMSO species converts rapidly this species back to the ammino/DMSO species plus additional formation of a significant amount of the Tschugaev's cation $[Pt(NH_3)_2\{HN{=}C(NH_2)Me\}_2]^{2+}$ (resonances D in Fig. 1). The solvolysis of the amino-chloro species can therefore be represented as shown in the scheme below (L = amidine). It is to be noted that the equilibrium between ammine/DMSO and chloro/DMSO species is shifted towards the ammine/DMSO species even in the presence of a chloride ion concentration twice that of the substrate and a very small amount of free ammonia.



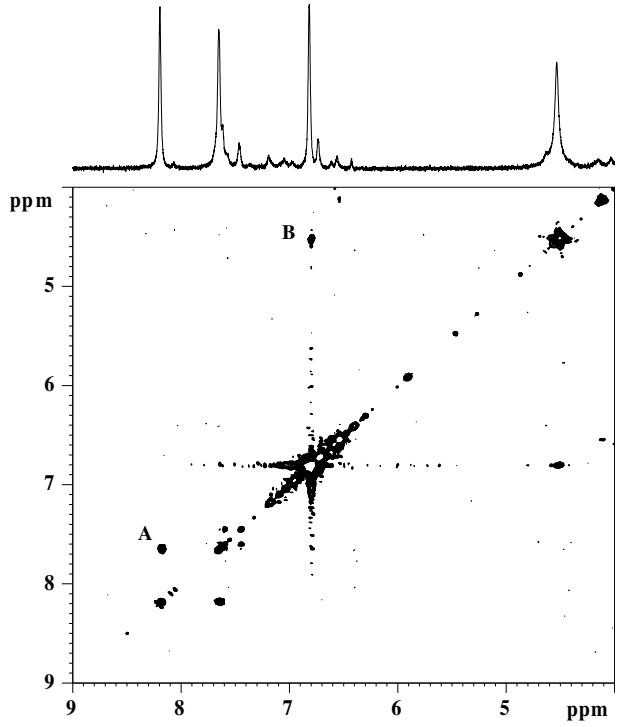


Fig. 2. Low field region of the 2D NOESY spectrum of the *trans*-$[Pt(NH_3)\{HN{=}C(NH_2)Me\}_2(DMSO)]^{2+}$ complex showing the connectivities between the two aminic protons of the amidine (EXY peak, A) and between the NH_3 and the NH iminic proton of the amidine ligands (NOESY peak, B).

Therefore, it can be concluded that the weakening of the trans Pt–NH_3 bond by DMSO in the solvated species, as already reported by some of us [24], is smaller than the weakening of the Pt–Cl bond *trans* to DMSO; this is in accord with Cl competing more for platinum *d* electrons than NH_3.

Similarly to the case of compound **1**, the ^1H NMR spectra of **2** and **3** in DMSO solution also indicate the rapid substitution of the chlorine ligand by DMSO giving rise to formation of the ammine/DMSO species *trans*-$[Pt(NH_3)\{HN{=}C(NH_2)R\}_2(DMSO)]Cl_2$ (R = Ph, CH_2Ph) and subsequent slow formation of the chloro/DMSO species *trans*-$[PtCl\{HN{=}C(NH_2)Me\}_2$-$(DMSO)]Cl$ (R = Ph, CH_2Ph).

3. Conclusions

The reactivity of the di-nitrile complexes *trans*-$[PtCl_2(N{\equiv}CR)_2]$ (R = Me, Ph, CH_2Ph) with NH_3 has been investigated. The reactions, even performed at low temperature (−10 °C), afford the corresponding diamidine complexes in which also one chlorine ligand has been displaced by NH_3, e.g., *trans*-$[PtCl(NH_3)\{HN{=}C(NH_2)R\}_2]Cl$. By performing the reaction at room temperature Tschugaev obtained the species in which both chlorine ligands were substituted by ammonia molecules. The NMR spectra of the newly synthesized chloro/ammine compounds dissolved in DMSO showed the formation of different solvated species; first the ammine/DMSO species *trans*-$[Pt(NH_3)$-$\{HN{=}C(NH_2)R\}_2(DMSO)]^{2+}$ and *trans*-$[PtCl\{HN{=}$-$C(NH_2)R\}_2(DMSO)]^{+}$. All ^1H NMR signals have been assigned through NOESY, TOCSY and $^1H/^{13}C$ heteronuclear correlation spectra. It is noteworthy that the system of the two *trans*-amidines is stable towards substitution by either DMSO or Cl^- and does not isomerize to *cis*. In contrast, preliminary results indicate that this is not the case for the corresponding *cis*-$[PtCl(NH_3)\{HN{=}C(NH_2)R\}_2]Cl$ derivatives.

4. Experimental

4.1. General procedures and materials

All experiments were carried out under nitrogen atmosphere using standard Schlenck techniques. Solvents were distilled prior to use; CH_2Cl_2 was distilled from CaH_2. Elemental analyses were performed by the Department of Analytical, Inorganic, and Organometallic Chemistry of the University of Padova. The complexes *trans*-$[PtCl_2(N{\equiv}CR)_2]$ (R = Me, Ph, CH_2Ph) were synthesized as previously reported [25], while NH_3 was purchased from SIAD.

4.2. Instrumentation

IR spectra were taken on a FT-IR AVATAR 320 (4000–400 cm^{-1}) or on a FT-IR Nexus (range 600–50 cm^{-1}) of the Nicolet Instrument Corporation (KBr or polyethylene (PE) films) spectrophotometers; the wavenumbers ($\bar{\nu}$) are given in cm^{-1}. ^1H and ^{13}C NMR solution spectra were obtained at 298 K (unless otherwise stated) on Bruker Avance-400 and 300 spectrometers operating at 400.13 and 300.13 MHz, respectively, and a Bruker 200 AC spectrometer operating at 200.13 MHz; δ values (ppm) are relative to internal Me_4Si. Suitable integral values for the proton spectra were obtained by a pre-scan delay of 10 s. The assignments of the proton resonances were performed by standard chemical shift correlations, COSY, TOCSY and NOESY experiments. In the phase-sensitive NOESY measurements (the so-called *Exchange Spectroscopy EXSY* spectra) the presence of intense cross-peaks, *in-phase* with the diagonal, indicates a chemical exchange between the correlated nuclei [26]. The ^{13}C resonances were attributed through 2D-heterocorrelated COSY experiments (HMQC with *bird* sequence [27a] and quadrature along F1 achieved using the TPPI method [27b] for the H-bonded carbon atoms, HMBC [27c] for the quaternary ones.

The electrospray ionisation mass spectra of **1**–**3** were recorded on a LCQ DECA (Finningam MAT) instrument, operating in positive ion mode. The instrumental conditions used were the following: source potential 4 kV, capillary temperature 270 °C, sheath gas (N_2) flow rate 40 arbitrary units. The final solution was directly introduced into the ESI ion source by a syringe pump at a flow rate of 10 μl/min.

4.3. Syntheses

4.3.1. Synthesis of *trans*-[PtCl(NH$_3$){HN=C(NH$_2$)-Me}$_2$]Cl (**1**)

A suspension of *trans*-[$PtCl_2(MeCN)_2$] (0.56 g, 1.61 mmol) in CH_2Cl_2 (60 ml) was treated with $NH_{3(g)}$ at −10 °C. After 2 h the solution was heated to room temperature and stirred for 4 h. The reaction mixture was concentrated to a small volume and then treated with cold Et_2O (0 °C, 15 ml). A white solid precipitated, which was filtered off, washed with Et_2O (3 × 15 ml) and dried under vacuum. Yield 0.59 g, 91.9%. Anal. Calc. for $C_4H_{15}Cl_2N_5Pt$ (PM = 399.18): C, 12.0; H, 3.8; N, 17.5. Found: C, 11.8; H, 3.8; N, 17.3%. IR ($\bar{\nu}$, KBr film): 3511, 3458, 3353, 3243 (s, br, N–H); 1650 (s, C=N). IR ($\bar{\nu}$, PE film): 333 cm^{-1} (m, Pt–Cl). MS (ESI, *m*/*z*, rel. ab.%): 364 ([PtCl(NH$_3$){HN=C(NH$_2$)Me}$_2$]$^+$, 60%), 347 ([PtCl{HN=C(NH$_2$)Me}$_2$]$^+$, 20%), 311 ([PtCl{HN=C(NH$_2$)Me}$_2$ − HCl]$^+$, 100%).

4.3.2. Synthesis of *trans*-[PtCl(NH$_3$){HN=C(NH$_2$)-Ph}$_2$]Cl (**2**)

A solution of *trans*-[$PtCl_2(PhCN)_2$] (0.60 g, 1.27 mmol) in CH_2Cl_2 (60 ml) was treated with $NH_{3(g)}$ at −10 °C for 2 h and then at room temperature for additional 4 h. The reaction mixture was concentrated to a small volume and then treated with cold Et_2O (0 °C, 15 ml). A white solid precipitated, which was filtered off, washed with Et_2O (3 × 15 ml) and dried under vacuum. Yield 0.55 g, 82.8%. Anal. Calc. for $C_{14}H_{19}Cl_2N_5Pt$ (PM = 523.32): C, 32.1; H, 3.7; N, 13.4. Found: C, 32.2; H, 3.8; N, 13.0%. IR ($\bar{\nu}$, KBr film): 3416, 3293, 3178 (m, br, N–H); 1652 (s, C=N). IR ($\bar{\nu}$, PE film): 335 cm^{-1} (m, Pt–Cl). MS (ESI, *m*/*z*, rel.ab.%): 487 ([PtCl(NH$_3$)-{HN=C(NH$_2$)Ph}$_2$]$^+$, 62%), 470 ([PtCl{HN=C(NH$_2$)-zPh}$_2$]$^+$, 51%), 434 ([PtCl{HN=C(NH$_2$)Ph}$_2$ − HCl]$^+$, 100%).

4.3.3. Synthesis of *trans*-[PtCl(NH$_3$){HN=C(NH$_2$)-CH$_2$Ph}$_2$]Cl (**3**)

A solution of *trans*-[$PtCl_2(NCCH_2Ph_2)_2$] (0.16 g, 0.32 mmol) in CH_2Cl_2 (60 ml) was treated with $NH_{3(g)}$ at −10 °C for 2 h and then at room temperature for additional 4 h. The reaction mixture was concentrated to a small volume and then treated with cold Et_2O (0 °C, 15 ml). A white solid precipitated, which was filtered off, washed with Et_2O (3 × 15 ml) and dried under vacuum. Yield 0.14 g, 84.3%. Anal. Calc. for $C_{16}H_{23}Cl_2N_5Pt$ (PM = 551.38): C, 34.8; H, 4.2; N, 12.7. Found: C, 34.2; H, 4.0; N, 13.0 %. IR ($\bar{\nu}$, KBr film): 3405, 3167 (m, br, N–H); 1639 (s, C=N). IR ($\bar{\nu}$, PE film): 335 cm^{-1} (s, Pt–Cl). MS (ESI, *m*/*z*, rel.ab.%) 515 ([PtCl(NH$_3$){HN=C(NH$_2$)CH$_2$Ph}$_2$]$^+$, 50%), 498 ([PtCl{HN=C(NH$_2$)-CH$_2$Ph}$_2$]$^+$, 18%), 462 ([PtCl{HN=C(NH$_2$)CH$_2$Ph}$_2$ − HCl]$^+$, 100%).

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