Reactivity of Coordinated Nitriles − Formation of the Acetamidine Complex *cis*-[$(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]^+$ from the 1-Methylthyminate Compound *cis*-[$(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$ − Synthesis, Characterisation, and X-ray Structures

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1-Methylthymine (1-MeTy) reacts reversibly with the hydroxo complexes *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2X_2$ ($X^- = NO_3$; ClO_4) in various solvents (S = CH_3CN, H_2O, DMSO) to give the thyminate derivatives *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(S)]X$ that have been isolated as pure compounds when S is CH_3CN. The single-crystal X-ray structure of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$ shows that the N(3)-platinated nucleobase acts as a monodentate ligand and a molecule of CH_3CN completes the coordination sphere of the metal. Crystals of the acetamidine derivative *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]X$ were isolated from an acetonitrile solution of this complex, in the presence of small amounts of water, after several months at room temperature, separated in 5–10% yield. The X-ray analysis of the perchlorate salt shows a configuration of the amidine ligand consistent with a formal *trans* addition of NH_3 to the CN triple bond of the coordinated nitrile. The acetamidine complex was formed in high yield (70%), in a few weeks, when aqueous solution of NH_3 was added to *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$ dissolved in CH_3CN. Side products of this reaction are the ammonia complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]^+$, which was also obtained as pure compound, acetamide, and other platinum containing species. All the isolated complexes were characterised by elemental analysis, IR, and multinuclear NMR spectroscopy.

Introduction

The coordination of nitriles to electron-withdrawing transition metals results in an enhanced electrophilicity of the nitrile carbon, making it susceptible to nucleophilic attack. Reactions of nitriles with protic nucleophiles such as water, alcohols, and ammonia (or amines) generate the corresponding amides, $H_2N-C(O)R$, imino esters (or imino ethers), $HN=C(OR')R$, and amidines, $HN=C(R)NH_2$, respectively.[1,2]

The products of the reactions of Pt^{II}-coordinated nitriles with water and alcohols have been investigated in details, whereas only a few reports deal with the characterization of amidine complexes.[3−5] The first example of structurally authenticated acetamidine [$HN=C(CH_3)NH_2$] complex of platinum was the dication *trans*-$[Pt(NH_3)_2\{CH_3C(NH)NH_2\}_2]^{2+}$, initially formulated as the octahedral species *trans*-$[Pt(NH_3)_4(CH_3CN)_2]^{2+}$.[6] Very recently, Bertani and co-workers have reported the characterisation of the bis-amidine *trans*-$[PtCl_2\{CH_3C(NH)NHMe\}_2]$, obtained by reacting the acetonitrile complex *trans*-$[PtCl_2(CH_3CN)_2]$ with the primary amine $MeNH_2$, under very mild conditions.[7]

Following our interest in the study of model nucleobases with phosphane analogues of *cis-platin*,[8−14] we came across the nitrile complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$, **1**, containing the N(3)-deprotonated 1-methylthymine ligand [1-MeTy(−H)]. Complex **1** is formed by condensation of the dinuclear hydroxo compound *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2^{2+}$ with N(1)-substituted methylthymine (1-MeTy), in acetonitrile. We found that when this cationic acetonitrile complex was left in the reaction mixture for several months at room temperature, the acetamidine derivative *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]^+$, **2**, separated as pure colourless crystalline solid, whereas the solution became yellow. Such a transformation, which implies the formal addition of NH_3 to the coordinated acetonitrile, occurred in low yield (5−10%) and was accompanied by the formation, in addition to free acetamide, of the ammonia complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]^+$, **3**, and other platinum-containing products.

In this paper we report on the synthesis and the characterisation of these new thyminate complexes showing that the acetamidine derivative **2** can be conveniently prepared by addition of aqueous NH_3 to the acetonitrile complex **1**.

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Along with a detailed multinuclear NMR analysis of the isolated compounds, the X-ray structures of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$ and *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]ClO_4$ were obtained, defining the stereochemistry of the amidine ligand in solution as well as in the solid state.

Results and Discussion

Synthesis and Characterisation of the Thyminate Complexes *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]X$ ($X^- = ClO_4$, **1a**; NO_3, **1b**)

The dinuclear hydroxo complex *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2^{2+}$ reacted with a stoichiometric amount of 1-MeTy in H_2O, DMSO, or CH_3CN, to give the mononuclear species *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(S)]^+$ (S = solvent molecule), resulting from the deprotonation of the nucleobase, according to the following reaction [Equation (1)]:

$$^1/_2\ cis\text{-}[(PMe_3)_2Pt(\mu\text{-}OH)]_2^{2+} + 1\text{-}MeTy + S \rightleftarrows cis\text{-}[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(S)]^+ + H_2O \quad (1)$$

The reaction occurred at room temperature in a few hours and was essentially quantitative when anhydrous acetonitrile was used as the solvent, whereas it was incomplete in dimethylsulfoxide or water. The position of the equilibrium could be easily deduced from the ^{31}P NMR spectrum of the reaction mixture since the reagent is characterized by a sharp singlet at δ ca. −25, flanked by the ^{195}Pt satellites, which was substituted by an AB multiplet when the product was formed. The chemical shifts and the coupling constants are dependent on the solvent, as shown in Table 1.

Table 1. ^{31}P NMR spectroscopic data of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(S)]^+$ (S = solvent molecule)

Solvent S	δ_P; $^1J_{PPt}$ (Hz)	δ_P; $^1J_{PPt}$ (Hz)	$^2J_{PP}$ (Hz)
CD_3CN	−31.10 (2944)	−29.59 (3809)	27.5
$[D_6]$DMSO	−23.16 (3169)	−29.12 (3892)	25.6
D_2O	−26.05 (3171)	−30.11 (3885)	26.4

Thus, the ^{31}P NMR spectrum of a $5\cdot10^{-2}$ M solution of the perchlorate salt *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ in CD_3CN containing the nucleobase in 1:2 molar ratio, after equilibration (a few hours at ambient conditions), showed the complete disappearance of the resonance at δ = −25.6, which was replaced by a sharp AB multiplet at δ = −29.6 ($^1J_{PPt}$ = 3810 Hz) and −31.1 ($^1J_{PPt}$ = 2944 Hz) with $^2J_{PP}$ 27.5 Hz, attributable to the thyminato complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$, **1a**.

When the reaction was carried out in $[D_6]$DMSO, at the equilibrium ca. 10% of the starting hydroxo complex remained unchanged, suggesting a relatively lower stability of the thyminate complex in this solvent. In line with the presence of different types of donor atoms *trans* to the PMe_3 ligands, the ^{31}P NMR spectrum of the product shows well separated doublets ($^2J_{PP}$ = 25.6 Hz), at δ = −23.1 ($^1J_{PPt}$ = 3169 Hz) and −29.1 ($^1J_{PPt}$ = 3892 Hz). The deprotonation of the nucleobase is evidenced in the proton spectrum by the disappearance of the N(3)H resonance at δ = 11.2 and the concomitant shift to higher field of the H(6) resonance, which is observed as a 1:3:3:1 quadruplet ($^4J_{HH} \approx 1$ Hz) at δ = 7.40, slightly shielded with respect to the free base (δ = 7.49).[9]

Although to a minor extent, the deprotonation of the thymine occurs also in aqueous solution. In this solvent, the perchlorate is insoluble and therefore the corresponding nitrato salt was used. The stoichiometric amount of 1-MeTy added to a $4.1\cdot10^{-2}$ M solution of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ in D_2O dissolved in 2.5 h at ambient temperature. The ^{31}P NMR spectrum of the resulting colourless solution exhibits an intense AB pattern (Table 1), tentatively attributed to the aqua complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(H_2O)]^+$, and the singlet of the unchanged hydroxo complex having an intensity of about 18% of the total resonances. In addition, at the equilibrium, very weak resonances in the range δ = −25 to −32 are detectable. Since the thyminate ion can also act as a bidentate ligand,[15] these signals could be due to the presence of small concentrations of polynuclear complexes of the type *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}]_n^{n+}$ or, alternatively, to other species related to the acidic character of the water molecule coordinated to the metal centre. It is worth noting that addition of a small amount of CH_3CN (1−2%) to the D_2O solution resulted in the immediate appearance of the multiplet due to the complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$ as the only detectable species.

As anticipated, in anhydrous CH_3CN the reaction 1 was essentially complete and the solvent complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$ could be isolated by addition of diethyl ether. The IR spectrum of the perchlorate salt, **1a**, shows the weak absorptions at 2332 and 2371 cm^{-1}, typical values for the η^1-coordinated CH_3CN in platinum(II) complexes, and the carbonyl bands of the thyminate ligand at 1653 and 1591 cm^{-1}. The $\{^1H\}$-^{31}PNMR spectrum (at 161 MHz) in CD_3CN shows an AB system at δ = −29.6 and −31.1 (Table 1), flanked by the ^{195}Pt satellites, due to the chemical non-equivalence of the phosphane ligands. In the corresponding ^1H NMR spectrum the PMe_3 resonances are observed as two doublets at δ = 1.78 ($^2J_{HP}$ = 11.3 Hz; $^3J_{HPt}$ = 30 Hz) and δ = 1.63 ($^2J_{HP}$ = 11.8 Hz; $^3J_{HPt}$ = 42 Hz). The first resonance is attributable to the methyl groups of the phosphane resonating at higher field, as deduced from inverse detection experiments. However, attempts to discriminate between the two PMe_3 ligands with respect to the nucleobase, through NOE experiments, were unsuccessful. The nitrile methyl resonance (δ = 2.03) does not differ significantly from the value of the free ligand indicating that replacement of the CH_3CN molecule by the solvent upon dissolution of compound had occurred. The lability of the acetonitrile ligand was confirmed by dissolving the complex in $[D_6]$DMSO. In this solvent the ^{31}P NMR spectrum of **1a** displays a main set of resonances due to the species *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(DMSO)]^+$ (Table 1) and a weak AB multiplet ($^2J_{PP}$ = 25.9 Hz) at δ = −29.4 ($^1J_{PPt}$ = 3960 Hz) and −30.9

($^1J_{PPt}$ = 2985 Hz), which accounts for ca. 5% of the mixture, attributable to the incomplete replacement of the nitrile molecule on the coordination sphere of the metal. Moreover, as a consequence of the reversibility of reaction (1), **1a** decomposes immediately in water with precipitation of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ that is, unlike the nitrate salt, insoluble in water.

The dissolution of the acetonitrile complexes **1a** and **1b** in [D_6]DMSO or D_2O (for **1b**) caused a remarkable shift to lower field of one of the two PMe_3 resonances in the ^{31}P NMR spectra, while the second one changed only slightly (Table 1). Whereas these changes are in agreement with the replacement of the labile CH_3CN ligand by the solvent, the attribution of the resonances is not obvious. It is generally assumed that in square-planar Pt^{II} complexes the phosphane *trans* to a labile ligand experiences the highest value of the one-bond $^{31}P-^{195}Pt$ coupling. For the complexes *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(S)]^+$ (Table 1) we found that the larger value of $^1J_{PPt}$ was associated with the less shielded phosphane in the case of CD_3CN (δ = 29.6, $^1J_{PPt}$ = 3809 Hz) but in [D_6]DMSO and D_2O the opposite was observed.

Characterisation of the Acetamidine Complexes *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]X$ (X = ClO_4, 2a; NO_3, 2b)

When the reaction mixture of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (ca. 0.1 M) and 1-MeTy in CH_3CN [Equation (1)] was left at room temperature for several weeks, the colourless solution, became yellow, and colourless crystals started to precipitate. In some months (4−7) small amounts (5−10%) of the new complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]ClO_4$, **2a**, were formed as a crystalline solid that was characterised by elemental analysis, multinuclear NMR spectroscopy, and single-crystal X-ray diffraction methods. The compound was insoluble in acetonitrile and in chlorinated solvents, whereas it dissolved in DMSO and water. The proton spectrum (400 MHz) in [D_6]DMSO exhibits the resonances of the phosphane methyl groups as doublets (δ = 1.58 and 1.48, $^2J_{HP}$ = 11 Hz) with unresolved Pt-satellites and a single set of resonances for the thymine and the amidine ligands. The acetamidine resonances are observed as broad singlets at δ = 7.37 for the imino proton, at δ = 7.24 and 6.95 for the amino protons, and as a sharp singlet at δ = 1.93 for the CH_3 group. The assignments of the NH resonances were obtained through inverse detected $^1H,^{15}N$ heteronuclear multiple quantum coherence experiments (HMQC).[16]

As shown in Figure 1, a, the two NH resonances at higher field correlate with the same ^{15}N resonance at δ = −274 ($^1J_{NH}$ = 90 Hz), whereas that at δ = 7.37, partially overlapping with the thymine H(6) multiplet, correlates with a second ^{15}N resonance at δ = −241 ($^1J_{NH}$ = 80 Hz). This latter ^{15}N resonance displays (Figure 1, b) an additional splitting (ca. 60 Hz) due to the coupling with the ^{31}P nucleus in *trans* position. Moreover, the imino proton displays an H,H coupling (3 Hz) with the NH_2 proton at δ = 7.24, as confirmed through a COSY experiment. This finding suggests a *trans* relationship between the NH_2 group and the imino proton and, in particular, a zigzag arrangement between the imino proton and the NH_2 proton at δ = 7.24.

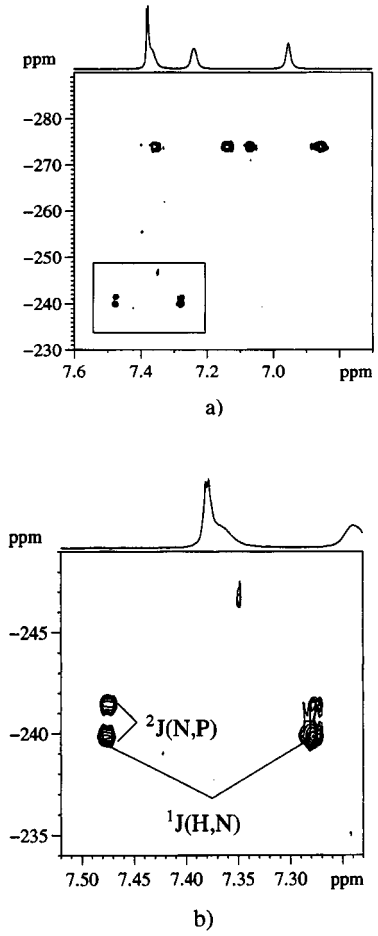

Figure 1. Inverse-detected $^1H,^{15}N$ shift-correlated spectrum of **2a** in [D_6]DMSO obtained with a HMQC experiment without decoupling during the acquisition: a) complete spectrum of the NH region; b) expanded region corresponding to the imino proton

In the inverse detected $^1H,^{195}Pt$ heteronuclear multiple bond correlation experiment (HMBC),[17] the imino proton at δ = 7.37 shows a correlation with the ^{195}Pt signal at δ = −4633 (Figure 2, a), confirming the involvement of the imino group in the coordination to the metal centre.

Figure 2, b, displays that the same ^{195}Pt resonance is also detected through the phosphane proton resonances, demonstrating that the imino nitrogen and the phosphane ligands are bonded to the same metal centre. The left trace in Figure 2 represents the $\{^1H\}$-^{195}Pt spectrum obtained by direct acquisition and, due to the low resolution used in the experimental conditions, the resonance appears as a triplet, whereas the $\{^1H\}$-^{31}P spectrum allowed us to detect two different $^1J_{PPt}$ coupling constants. The phosphane resonances exhibit, in fact, very similar chemical shifts and coupling constants (δ = −28.80 and −29.25; $^1J_{PPt}$ = 3088 and 3125 Hz, respectively) in agreement with the presence of similarly hybridized nitrogen atoms in a *trans* position. As shown in Figure 3, the ^{195}Pt satellites, in spite of the rela-

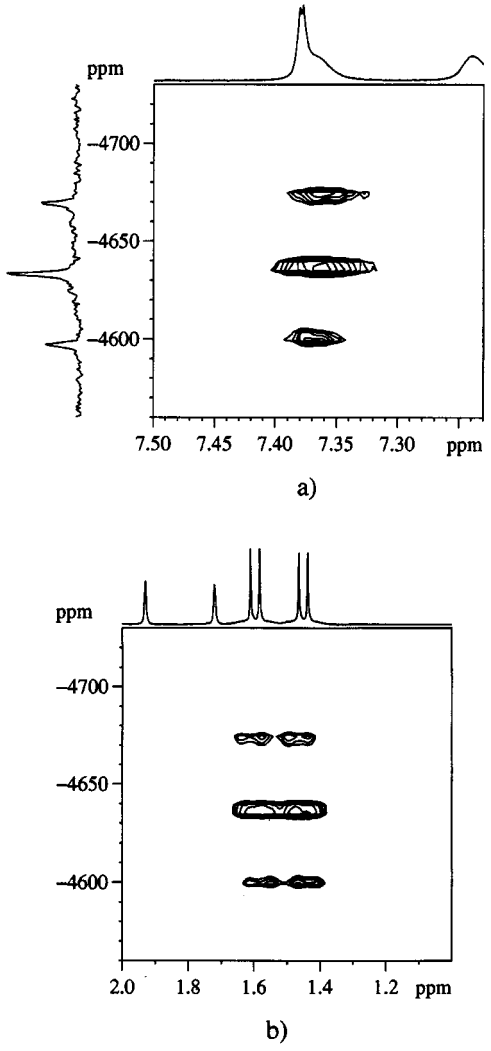

Figure 2. Inverse-detected ^{1}H,^{195}Pt shift-correlated spectrum of **2a** in [D_6]DMSO obtained through a HMBC experiment without decoupling during the acquisition: a) imino proton region and b) phosphane methyl region. The upper trace corresponds to the proton spectrum and the left trace corresponds to the ^{195}Pt spectrum

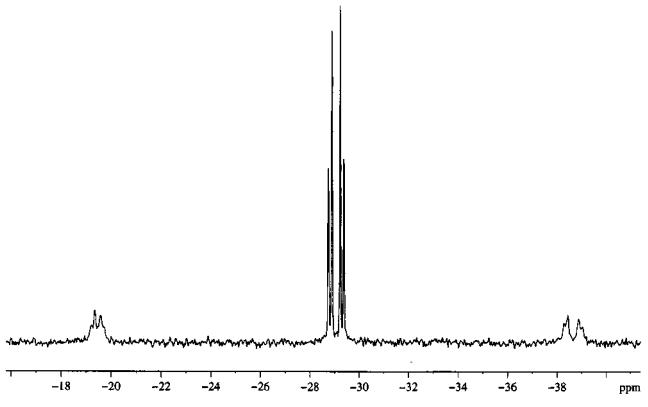

Figure 3. $\{^{1}H\}$-^{31}P NMR at 162 MHz of *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}{$CH_3C(NH)NH_2$}]ClO_4 (**2a**) in [D_6]DMSO

tively high field used (162 MHz), were particularly well resolved.

X-ray Structure Analyses of *cis*-[$(PMe_3)_2$Pt-{1-MeTy(−H)}(CH_3CN)]ClO_4, 1a, and *cis*-[$(PMe_3)_2$Pt-{1-MeTy(−H)}{$CH_3C(NH)NH_2$}]ClO_4, 2a

The identification of the atoms and the molecular structures of **1a** and **2a** are depicted in Figure 4 and Figure 5,

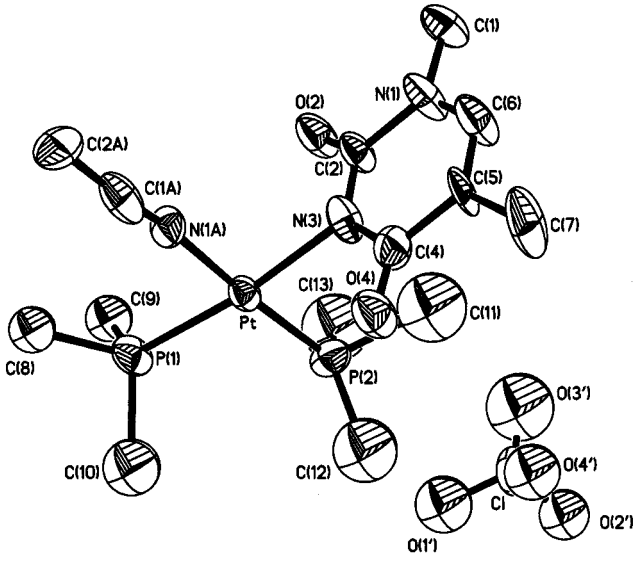

Figure 4. ORTEP drawing of the molecular structure of *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}(CH_3CN)]ClO_4, **1a**, along with atomic numbering system. Non-hydrogen atoms are presented as thermal ellipsoids at 35% probability levels

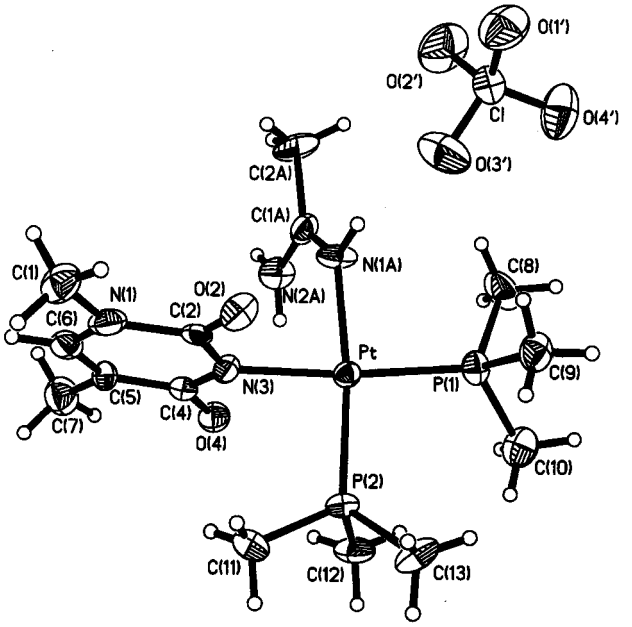

Figure 5. ORTEP drawing of the molecular structure of *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}{$CH_3C(NH)NH_2$}]ClO_4 **2a**, along with atomic numbering system. Non-hydrogen atoms are presented as thermal ellipsoids at 35% probability levels, whereas hydrogen atoms are drawn as spheres of arbitrary size

Table 2. Selected bond lengths [Å], intramolecular separations [Å] and angles [°] in *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}(CH_3CN)]ClO_4, **1a**, and *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}{$CH_3C(NH)NH_2$}]ClO_4 **2a**. Standard deviations are given in parentheses

Compound	**1a**	**2a**
Pt−P(1)	2.268(5)	2.263(3)
Pt−P(2)	2.232(5)	2.259(3)
Pt−N(3)	2.12(1)	2.097(9)
Pt−N(1A)	2.05(1)	2.09(1)
P(1) ··· P(2)	3.347	3.361
P(2) ··· N(3)	3.04	3.07
N(3) ··· N(1A)	2.86	2.81
P(1)−Pt−P(2)	96.1(2)	95.2 (3)
P(1)−Pt−N(3)	173.2(5)	172.0(7)
P(1)−Pt−N(1A)	89.1(4)	90.5(3)
P(2)−Pt−N(3)	88.5(4)	92.6(7)
P(2)−Pt−N(1A)	174.3(4)	173.2(3)
N(3)−Pt−N(1A)	86.5(5)	84.1(5)

respectively, and the main bond lengths and angles are summarised in Table 2.

In both complexes the platinum exhibits a distorted square-planar coordination in which the bond angles around the metal range from 86.5(5) to 96.1(2)° in **1a** and from 84.1(5) to 95.2(3)° in **2a**, their sum being 360.2° and 362.4°, respectively. The common portion of the two structures are roughly superimposable, with an r.m.s. deviation (derived from the BMFIT program)[18] of 0.13 Å when the fitting is performed without the methyl groups. The thymine ring forms a dihedral angle of 89.3(4)° in **1a** and 103.0(3)° in **2a** with the coordination plane, and the acetamidine group in **2a** lies nearly orthogonal to the mean square plane [dihedral angle 111.2(3)°]. In both compounds no effective hydrogen bonds occur and the complexes are built up by the juxtaposition at van der Waals distances of well separated Pt^{II} monocations and perchlorate counter anions. This

Table 3. Geometry of the possible weak hydrogen bonds in **2a**

D−H···A	H···D [Å]	H···A [Å]	D−H···A[°]
N(2A)−H(1AA) ···- O(4)	2.20	2.93	141.3
N(2A)−H(1AB) ···- O(2A)[a]	2.10	2.85	146.1
N(1A)−H(1AC) ···- O(3′)	2.30	3.14	165.5

[a] Refers to the atom in the position x, $y-1$, z.

is despite the fact that the shortest intramolecular (2.93 Å) and intermolecular (2.85 Å) separations in **2a** (Table 3 and Figure 6) seem to be of some significance.

The Pt−P distances are comparable to the mean value of 2.27(4) Å derived from 65 Pt−PMe_3 data retrieved from Cambridge Crystallographic Data Base,[19] while the Pt−N(3) distances [2.12(1) and 2.10(1) Å in **1a** and **2a**, respectively] are greater than the value of 2.03 Å found for Pt−N (thyminate or uracilate) distances in four mononuclear, but uncharged, Pt^{II} complexes.[20−23] Similarly, in **1a** the Pt−N(acetonitrile) distance [2.05(1) Å] is remarkably longer than the mean value [1.97(3) Å] derived from 12 X-ray determinations.[19] The Pt−N(acetamidine) distance of **2a** [2.09(1) Å] is also longer than the value of 1.96 Å found in the diamminebis(acetamidine)platinum(II) dichloride.[6]

Reactivity of the Coordinated Nitrile in the Cationic Complex *cis*-[$(PMe_3)_2$Pt{1-MeTy(−H)}(CH_3CN)]$^+$

Amidine complexes are formally derived by nucleophilic attack of amines on metal-coordinated nitriles. It has recently been reported that the neutral acetonitrile complex *trans*-$PtCl_2(CH_3CN)_2$ reacts with $MeNH_2$, under very mild conditions, to give the bis-amidine product *trans*-$PtCl_2${(*Z*)-N(H)=C(NHMe)CH_3}$_2$.[7] The X-ray structure shows that the organic ligands assume the (*Z*) configuration corresponding to the *trans*-addition of the amine fragments to the CN triple bond (Scheme 1).

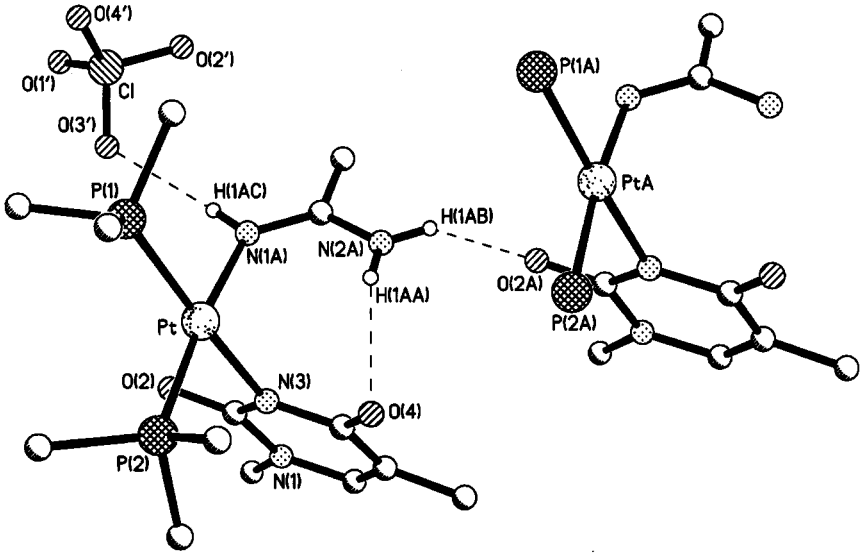

Figure 6. The interactions involving the acetamidine group in **2a**

Scheme 1

The same stereochemistry of the acetamidine groups was early established for the cationic amino complex *trans*-$[Pt(NH_3)_2\{CH_3C(NH)NH_2\}_2]^{2+}$ [6] and is now confirmed for complex **2a** in the solid state as well as in solution.

The separation of the acetamidine compound **2a** as crystalline colourless solid from the reaction mixture of 1-MeTy and *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2^{2+}$ in CH_3CN requires several months at ambient conditions, and the yield is poor. The NMR analysis of the solution, after separation of the solid, removal of the volatiles and dissolution of the yellow residue in $[D_6]$DMSO, indicates the formation of a very complex mixture of products among which acetamide is one of the main components.

Under the experimental conditions in which we observe the conversion of **1** into **2**, the formation of acetamide is easily predictable since the initial solution contains the nitrile molecule, activated through the coordination to the metal centre, and a stoichiometric amount of water resulting from the condensation reaction (1). The hydrolysis of the nitrile to acetamide, therefore, was expected to be the first step of the transformation of the CH_3CN complex into the amidine derivative. The resulting acetamide is likely the source of the ammonia required for the formation of the amidine ligand.

Comparative experiments in which variable amounts of water were added to solutions of **1a** in CH_3CN indicate an increased concentration of acetamide in the reaction mixture after a few weeks, whereas the conversion of complex **1** into **2** had occurred to a small extent (ca. 1−2%). This result is in line with expectations, if we consider the catalytic properties of platinum complexes on the hydrolysis of nitriles to amides.

Amides, in turn, can undergo hydrolysis with formation of free NH_3, or its conjugate acid, depending on the pH. Moreover, the coordination of acetamide to a metal centre, either in the neutral[24] or deprotonated form, is well documented, in particular in the case of platinum.[25] Preliminary experiments indicate that the hydroxo complex *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ does react with $CH_3C(O)NH_2$, leading to the deprotonation of the amide and the coordination of the resulting anion.[26]

Complex **2** can be obtained in relatively good yield by addition of aqueous NH_3 to the acetonitrile complex **1** in CH_3CN. Within a few weeks at room temperature, crystals of the pure **2a** (yield 44%) separated from a solution of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$ containing an excess of NH_3. The NMR analysis of the colourless solution, after removal of the solid **2a**, indicated the complete conversion of **1a** into the amidine derivative **2a** (ca. 70% of the mixture of products, on the basis of the ^{31}P spectrum) together with the ammonia complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]^+$ (ca. 16%) and another species (ca. 14%) that has not yet been fully characterised.

This ammonia complex was isolated as a pure compound with the composition *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]NO_3\cdot H_2O$, **3**, and characterised by multinuclear NMR spectroscopy. It was isolated from a solution of **1b** after addition of excess aqueous NH_3. In the proton spectrum, in $[D_6]$DMSO, the NH_3 resonance is seen as a broad singlet at $\delta = 4.0$, with unresolved platinum satellites. The presence of ammonia in the coordination sphere of the metal was confirmed by means of $^1H,^{15}N$ HMQC experiments in which the ^{15}N signal at $\delta = -381.6$, attributable to the NH_3 ligand, correlates with the proton signal at $\delta = 4.0$, and shows couplings with protons ($^1J_{HN} = 70$ Hz) and ^{31}P nuclei ($^2J_{NP} \approx 50$ Hz; $^3J_{HP} = 5$ Hz). Moreover, in the $^1H,^{195}Pt$ HMBC spectrum the NH_3 and PMe_3 protons correlate with the ^{195}Pt resonance at $\delta = -4653$. The chemical non-equivalence of the phosphanes (in *trans* position to the nucleobase and to the NH_3 ligands, respectively) is proved by the presence of two distinct resonances in the proton spectrum (at $\delta = 1.48$ and 1.66), flanked by well-resolved (90 MHz) ^{195}Pt satellites ($^2J_{HP} = 11.2$; $^3J_{HPt} = 33$ Hz), and by the presence of an AB multiplet [at $\delta = -29.0$ ($^1J_{PPt} = 3237$ Hz) and −32.0 ($^1J_{PPt} = 3084$ Hz) with $^2J_{PP} = 25.6$ Hz] in the ^{31}P spectrum.

Conclusion

In this paper we have reported a further example of reactivity of a dinuclear hydroxo complex of platinum(II) stabilized by phosphanes towards model nucleobases. As previously shown for *N*(1)-methylcytosine,[8,12] *N*(9)-substituted adenine,[11] and guanine,[13] the dimeric species *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2^{2+}$ deprotonates the *N*(1)-substituted thymine, leading to the platination of the nucleobase at the N(3) position. In the isolated complex **1a** the thyminate moiety acts as monodentate ligand leaving the fourth position around the metal centre available for the coordination of a solvent molecule. A similar binding mode of the thymine was early shown in the interaction with the hydroxo complex *cis*-$[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene].[9]

Fortuitous circumstances of leaving the nitrile complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$ in the presence of small amounts of water for a long period of time, allowed the separation of X-ray quality crystals of the amidine derivative *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]ClO_4$. This reaction represents the first example of a direct (i.e. in absence of metal-coordinated[6] or added ammonia) conversion of a nitrile group into an amidine. Such a transformation occurred in low yield with the concomitant formation of a yellow solution containing several not fully characterised products. The ^{31}P NMR spectrum

exhibits a plethora of PMe_3 resonances among which only those of the amidine and ammonia complexes, **2** and **3**, have so far been attributed.

Both **2** and **3** were isolated as pure compounds by simple addition of aqueous NH_3 to acetonitrile solution of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]^+$. The replacement of the acetonitrile ligand by NH_3 in **1** is immediate, and the formation of **3** appears to be quantitative (by ^{31}P NMR). In contrast, the formation of the amidine complex **2** from **1**, in the presence of added ammonia, is a slow process. At room temperature, in fact, the separation of crystals of *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]ClO_4$ requires several weeks (4−6). This is likely due to the high stability of the ammonia complex *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]^+$. We observed that CD_3CN solutions of the isolated compound **3**, warmed at 50 °C for one week, appeared unchanged. Whether this complex is an intermediate in the transformation of the nitrile complex **1** into the acetamidine derivative **2** is, at the moment, an open question.

Experimental Section

Reagents and Chemicals: Reagent grade chemicals were used as received unless otherwise stated. The complex *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ was synthesized as previously reported.[8] 1-MeTy was purchased from Sigma Chemical Company.

Instrumentation: ^1H, ^{31}P, ^{13}C, ^{195}Pt, and ^{15}N NMR spectra were obtained with a Bruker AMX 400-WB spectrometer operating at 400.13, 161.98, 100.61, 85.88, and 40.56 MHz, respectively, and/or on a JEOL 90Q spectrometer. The external references are H_3PO_4 (85% w/w in H_2O) for ^{31}P, Na_2PtCl_4 in D_2O (adjusted to δ = −1628 from Na_2PtCl_6) for ^{195}Pt, CH_3NO_2 in $CDCl_3$ (50% v/v) for ^{15}N. Proton and carbon resonances are referred to internal TMS. The parameters used for HMQC and HMBC experiments are similar to those previously reported.[14] IR spectra in the range 4000−400 cm^{-1} were recorded as KBr pellets with a Perkin−Elmer 283 spectrophotometer.

Syntheses of the Complexes

Preparation of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$: Addition of $NaClO_4{\cdot}H_2O$ (0.20 g, 0.48 mmol) to a solution of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (0.410 g, 0.48 mmol) caused the immediate precipitation of a white solid, which was collected by filtration, washed with H_2O, and dried under vacuum. The yield of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ was 438 mg (98%). − $C_6H_{19}ClO_5P_2Pt$ (463.7): calcd. C 15.54, H 4.13; found C 15.6, H 4.15. The complex, insoluble in water, dissolved in DMSO and CH_3CN; it was slightly soluble in CH_2Cl_2 and $CHCl_3$. ^1H NMR in $[D_6]$DMSO: δ = 3.46 (s, 1 H, OH), 1.52 (d, $^2J_{HP}$ 11.7 Hz, $^3J_{HPt}$ 36 Hz, 18 H, PMe_3). − $\{^1H\}^{31}P$ NMR in $[D_6]$DMSO: δ = −24.4 (s, $^1J_{PPt}$ 3358 Hz); in CD_3CN −25.5 ($^1J_{PPt}$ 3416 Hz).

Caution: The perchlorate is a potential explosive!

***cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$ (1a):** A mixture of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (263 mg, 0.283 mmol) and 1-MeTy (79.4 mg, 0.567 mmol) was dissolved in CH_3CN (12 mL) at room temperature and stirred for 24 h. The resulting solution was filtered to eliminate a trace amount of a black powder, and concentrated to a final volume of 2 mL. Addition of Et_2O afforded a white precipitate, which was recovered by filtration, and recrystallised from CH_3CN/Et_2O. The yield of the pure **1a** was 261 mg (74%). − $C_{14}H_{28}ClN_3O_6P_2Pt$ (626.9): calcd. C 26.82, H 4.47, N 6.70; found C 26.83, H 4.43, N 6.49. − ^1H NMR at 90 MHz in CD_3CN δ = [1-MeTy(−H) resonances] 7.15 [quadruplet, J_{HH} ca 1 Hz, 1 H, H(6)], 3.26 (singlet, 3 H, NCH_3), 1.72 (doublet, J_{HH} ca 1 Hz, 3 H, CH_3); 1.93 (s, 3 H, CH_3CN); 1.59 (d, $^2J_{HP}$ 11.7 Hz, $^3J_{HPt}$ 36 Hz, 9 H, PMe_3); 1.49 (d, $^2J_{HP}$ 11.7 Hz, $^3J_{HPt}$ 36 Hz, 9 H, PMe_3). − $\{^1H\}^{31}P$ NMR at 36.23 Mz in CD_3CN: δ = −29.7 ($^1J_{PPt}$ 3809 Hz) and −31.1 ($^1J_{PPt}$ 2944 Hz) with $^2J_{PP}$ 27 Hz. − ^1H NMR in $[D_6]$DMSO: [1-MeTy(−H) resonances] 7.40, [d $^4J_{HH}$ 1.2 Hz, H(6); 3.20, (s, NCH_3), 1.83 (d, $^4J_{HH}$ 1.2 Hz, $CH_3(5)$] 2.03 (s, 3 H, CH_3CN); 1.59 (d, $^2J_{HP}$ 11.7 Hz, 9 H, PMe_3); 1.53 (d, $^2J_{HP}$ 12 Hz, 9 H, PMe_3). $\{^1H\}^{31}P$ NMR at 36.23 Mz in $[D_6]$DMSO: δ = −23.1 ($^1J_{PPt}$ 3169 Hz) and −29.1 ($^1J_{PPt}$ 3892 Hz) with $^2J_{PP}$ 25.6 Hz. $\{^1H\}^{195}Pt$ in $[D_6]$DMSO: δ = −4695, dd.

***cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]NO_3$ (1b):** With the procedure described for **1a**, the nitrate derivative **1b** was prepared from *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (350 mg, 0.41 mmol) and 1-MeTy (115 mg, 0.82 mmol). The yield of the recrystallised product was 338 mg (70%). − $C_{14}H_{28}N_4O_5P_2Pt$ (589.4): calcd. C 28.53, H 4.79, N 9.50, found C 28.17, H 4.78, N 9.31. The spectroscopic data (^1H and ^{31}P NMR) are the same as those of **1a**. The elemental analysis and the ^{31}P NMR spectrum of the isolated solid indicate the presence of small amounts (ca. 3%) of unchanged *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$.

***cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}\{CH_3C(NH)NH_2\}]ClO_4$ (2a). − a):** A suspension of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (212 mg, 0.23 mmol) and 1-MeTy (64 mg, 0.45 mmol) in CH_3CN (10 mL) was stirred at room temperature for 12 h. The resulting colourless solution was left at room temperature in the dark for 6 months during which time a colourless solid was formed while the solution became yellow. The crystalline product, separated by filtration, washed with CH_3CN, and dried under vacuum, was 26 mg (yield 8.8%). − $C_{14}H_{31}ClN_4O_6P_2Pt$ (643.9): calcd. C 26.11, H 4.85, N 8.70; found C 26.02, H 4.68, N 8.73. − ^1H NMR (400 MHz) in $[D_6]$DMSO δ = [1-MeTy(−H) resonances] 7.38 [q, J_{HH} 1 Hz, 1 H, H(6)], 3.19 (s, 3 H, NCH_3), 1.72 (d, J_{HH} 1 Hz, 3 H, CH_3); [$CH_3C(NH)NH_2$ resonances] 7.37 (broad singlet, 1 H, NH), 7.24, (br. s, 1 H, NH_2), 6.95 (br. s, 1 H, NH_2), 1.93 (s, 3 H, CH_3); 1.58 (d, $^2J_{HP}$ 11 Hz, 9 H, PMe_3) and 1.48 (d, J_{HP} 11 Hz, 9 H, PMe_3). − $\{^1H\}^{31}P$ NMR at 162 MHz in $[D_6]$DMSO: δ = −28.82 ($^1J_{PPt}$ 3100 Hz) and −29.27 ($^1J_{PPt}$ 3119 Hz) with $^2J_{PP}$ 23 Hz. − $^{13}C\{^1H\}$ at 100.6 MHz, in $[D_6]$DMSO δ = [1-MeTy(−H) resonances] 171.0 C(4)O, 154.0 C(2)O, 140.0 C(6), 106.0 C(5); 35.9 NCH_3, 12.5 $CH_3(5)$; PMe_3 14.0 (d, J_{CP} ca 40 Hz); $CH_3C(NH)NH_2$ resonances: 167.0 and 20.8. $\{^1H\}^{195}Pt$: δ = −4633, apparent triplet.

b): A suspension of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (228 mg, 0.245 mmol) and 1-MeTy (68.5 mg, 0.49 mmol) in CH_3CN (8 mL) was stirred at room temperature for a few hours. The resulting solution was then divided in 3 portions (labelled A, B, and C) the first of which was left as a reference. To the fraction B (1 mL) 25.2 mg of H_2O [molar ratio $(H_2O)/(Pt)$ = 20] was added. To the fraction C (2.0 mL) 62.7 mg of an aqueous solution of NH_3 {25% w/w; [molar ratio $(NH_3)/(Pt)$ = 7.5]} was added. After 6 weeks at ca. 20 °C samples A and B appeared as colourless solutions whereas fraction C contained well shaped prismatic crystals of pure **2a** that were separated, washed with CH_3CN and dried under vacuum (35 mg, yield 44%). The mother liquor was evaporated under vacuum, the residue dissolved in $[D_6]$DMSO and analysed by NMR. The ^{31}P spectrum of this residue showed major components to be

the species **2a** (ca. 60%), **3** (14%), and a third species characterised by a broad singlet (line width 8 Hz) at δ = −30.05, flanked by ^{195}Pt satellites ($^1J_{PPt}$ = 2963 Hz), whose relative intensity was 18% of the total resonances. Moreover, a number of very weak resonances in the range δ = −28 to −31 were also detectable. From the corresponding ^{1}H NMR spectrum, the presence of small amounts of free nucleobase and acetamide were also detected.

c): A solution of **1a**, obtained reacting *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(ClO_4)_2$ (137 mg; 0.147 mmol) and 1-MeTy (41 mg, 0.29 mmol) in CH_3CN (5 mL), was divided in 3 portions. One of them was left as reference sample (A), to the second (B) was added water (molar ratio H_2O/Pt = 34) and to the third sample (C) was added aqueous NH_3 (molar ratio: H_2O/Pt = 70; NH_3/Pt = 9.2). After 4 weeks at ca. 30 °C the resulting colourless solutions were evaporated under vacuum and the residues dissolved in [D$_6$]DMSO. The ^{31}P NMR analysis of the reference solution A indicated only a minor conversion of the initial species **1a** into **2a** (1−2%) and the presence of small amounts (a few %) of other platinum containing species. Trace amounts of acetamide were identified in the corresponding ^{1}H spectrum. In the sample B, free acetamide was the major component of the mixture whereas the molar ratio of the complexes **1a** and **2a** was approximately 1.3. Sample C contained the acetamidine complex **2a** as the dominant component (ca. 80%) of the mixture of products, whereas complex **1** appeared to have completely reacted.

***cis*-[(PMe$_3$)$_2$Pt{1-MeTy(−H)}(NH$_3$)]NO$_3$ (3):** A mixture of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ (161 mg, 0.19 mmol) and 1-MeTy (55 mg, 0.39 mmol) in DMSO (3.5 mL) was stirred at room temperature for 12 h, and the resulting colourless solution, containing trace amounts a black solid, was filtered. Addition of aqueous NH_3 (25% w/w, 50 μL, 0.67 mmol) gave **3** in quantitative yield (by ^{31}P NMR). The compound was isolated by addition of CH_3CN (6 mL) and precipitated with Et_2O (30 mL). The white solid recovered by filtration and dried under vacuum was purified by dissolution in the minimum volume of hot CH_3CN, filtered and left to crystallise at room temperature. The yield of colourless crystals, having the composition $[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(NH_3)]NO_3\cdot H_2O$, was 175 mg, 79%. − $C_{12}H_{30}N_4O_6P_2Pt$ (583.4): calcd. C 24.70, H 5.18, N 9.60; found C 24.71, H 5.08, N 9.46. − ^{1}H NMR (90 MHz) in CD_3CN δ = [1-MeTy(−H)] 7.10 [q, $^4J_{HH}$ 1.4 Hz, 1 H, H(6)], 3.20 (s, 3 H, NCH_3), 1.74 (s, 3 H, CH_3); 3.7 (very broad singlet, 3 H, NH_3); 2.20 (s, 2 H, H_2O); 1.69 (d, $^2J_{PH}$ 11 Hz, $^3J_{HPt}$ 34 Hz, 9 H, PMe_3) and 1.23 (d, J_{PH} 11 Hz, $^3J_{HPt}$ 34.7 Hz, 9 H, PMe_3). − ^{1}H NMR at 400 MHz in in [D$_6$]DMSO: [1-MeTy(−H)] 7.35 [s, H(6)], 3.17 (s, NCH_3), 1.72 (s, CH_3); 4.03 (broad singlet, 3 H, NH_3); 3.31 (s, H_2O); 1.65 (d, $^2J_{PH}$ 11 Hz, 9 H, PMe_3) and 1.48 (d, J_{PH} 11 Hz, 9 H, PMe_3). − $\{^1H\}^{31}$P NMR at 162 MHz in [D$_6$]DMSO: AB multiplet at δ = −29.5 ($^1J_{PPt}$ 3342 Hz) and −32.5 ($^1J_{PPt}$ 3076 Hz) with $^2J_{PP}$ 26 Hz. $\{^1H\}^{195}$Pt NMR in [D$_6$]DMSO: δ = −4653.

X-ray Data Collection, Structure Solution, and Refinement of 1a and 2a:[27] The experimental X-ray data are summarized in Table 4 and some metrical parameters for both structures are reported in Table 2. Further details are provided in Supporting Information. The crystals [milk-white, opaque, wedged-shaped **1a**, and colourless, transparent cuboids **2a**] proved of sufficient size to collect data on a Nicolet R3m/V four-circle diffractometer, using the ω − 2θ technique. Unfortunately, the crystal quality of **1a** was poor and significant crystal decomposition was observed during the course of data collection (up to 20% in intensity). The structures were solved by Patterson methods using the SHELXTL/PC[28] and refined using the SHELXL-93 package.[29] Refinement of the crystal structure of **1a** was not satisfactory and it was hampered by some disorder of the ClO_4^- ions. No disorder model was found to be adequate and consequently some high residual electron density peaks (up to 1.2 e·Å^{-3}) lie in the vicinity of the Cl atom, as evidenced by the final Fourier map. In addition, the phosphane methyl

Table 4. Crystal data and structure refinement for *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}(CH_3CN)]ClO_4$, **1a**, and *cis*-$[(PMe_3)_2Pt\{1\text{-}MeTy(-H)\}]\{CH_3C(NH)NH_2\}]ClO_4$, **2a**

Compound	**1a**	**2a**
Empirical formula	$C_{14}H_{28}ClN_3O_6P_2Pt$	$C_{14}H_{31}ClN_4O_6P_2Pt$
Molecular mass	626.87	643.91
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P\,2_1/c$ (no. 14)	$Pna2_1$ (no. 33)
Unit cell dimensions		
a [Å]	11.184(4)	28.091(6)
b [Å]	16.610(5)	6.731(1)
c [Å]	12.990(4)	12.568(3)
β [°]	106.45(3)	90
V [Å^3]	2314(1)	2376(1)
$D_{calcd.}$ [Mg m^{-3}]; Z	1.799; 4	1.800; 4
Absorption coefficient [mm^{-1}]	6.35	6.19
θ Range for data collection [°]	2.2−24.0	2.2−28.0
Independent reflections	3403	2993
Observed reflections	2293	2034
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ parameters	3403/195	2420/133
Goodness-of-fit on F^2	0.965	0.981
Final R indices [$I > 2\sigma(I)$]	$R1$[a]= 0.066	$R1$[a] = 0.032
	$WR2$[b] = −0.163	$WR2$[b] = 0.072
Largest difference peak and hole [eÅ^{-3}]	1.91, − 3.07	1.08, − 1.07

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = [\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)]]^{1/2}$.

groups carbons of **1a** suffer from high temperature factors (up to 21.7 Å^2) and the P−C distances (comprised in the large range 1.79−1.91 Å) of high e.s.d.'s. Due to the fact that the refinement was not satisfactory, with relatively high values for the *R* indices, only the bond lengths and angles in the coordination sphere around Pt are discussed for the complex **1a**.

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