Platinum(IV)-mediated nucleophilic addition of 1,3-diphenylguanidine to propiononitrile*

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The reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with diphenylguanidine (DPG) in a molar ratio of 1 : 2 proceeds *via* the nucleophilic addition of DPG to coordinated nitrile and the coordination of DPG to the metal center to form the $[PtCl_4\{NH{=}C(NHPh)_2\}\{NH{=}C(Et)\text{-}N{=}C(NHPh)_2\}]$ complex with the open-chain 1,3,5-triazapentadiene ligand. The latter undergoes chelation in solution (84 h, 50 °C, $CDCl_3$), and the ring closure is accompanied by the replacement of the coordinated chloride and the formation of the cationic complex $[PtCl_3\{NH{=}C(NHPh)_2\}\{NH{=}C(Et)NHC(NHPh){=}NPh\}](Cl)$. The reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with DPG in a molar ratio of 1 : 4 affords the $[PtCl_3\{NH{=}C\text{-}(NHPh)_2\}\{NH{=}C(Et)NC(NHPh){=}NPh\}]$ complex with the chelating 1,3,5-triazapentadienate ligand.

Key words: metal-mediated reactions, 1,3-diphenylguanidine, platinum(IV) nitrile complexes, nucleophilic addition, platinum(IV) 1,3,5-triazapentadiene complexes.

Metal-mediated reactions have found wide use both in preparative chemistry and industry serving as key in metal-complex catalysis. Studies of the reactions of coordinated nitriles giving rise to compounds with new C—C, C—N, C—O, C—P, and C—S bonds, which are difficult to prepare in metal-free organic chemistry, are of importance in this area of chemistry. Among these reactions are nucleophilic and electrophilic additions or a dipolar cycloaddition to the C≡N triple bond.[1—4]

The number of publications on the metal-mediated reactions of nitriles appeared in recent years is rather large, and these studies were devoted mainly to reactions of RCN with such reagents as HO- and HN-nucleophiles.[1] The metal-mediated reactions of nitriles with HN-nucleophiles bearing an sp^3-hybridized nitrogen atom have been studied in sufficient detail. Nucleophiles containing an sp^2-hybridized nitrogen atom (for example, imines) can also serve as reagents for the C—N bond formation. The addition of imines and heteroimines to coordinated nitriles has been investigated in recent years.[5—12]

In continuation of research on reactions of nitriles RCN coordinated to platinum with imines (heteroimines) $HN{=}ER_n$ (ER_n = CPh_2,[5] C(Alkyl)(OAlkyl),[7,12] C(Ar)(NHAr),[10,11] SAr_2,[6] or PPh_3[8]), we investigated the nucleophilic addition reactions of guanidines (ER_n = = $C(NMe_2)_2$,[13] $C(NHPh)_2$[14]) to nitriles activated by coordination to a platinum(II) center. In the present study, we continued research on the metal-mediated reactions of DPG with nitriles. The study included two successive steps. In the first step, we planned to investigate the platinum(IV)-mediated reactions of nitriles with DPG and elucidate the influence of the oxidation state of the metal center on this reaction. In the second step, we developed a procedure for the synthesis of platinum(IV) 1,3,5-triazapentadienyl complexes.

Results and Discussion

The reactions of platinum(IV) nitrile complexes with DPG were studied with the use of *trans*-$[PtCl_4(EtCN)_2]$[15] as the dinitrile precursor. We chose this complex because of its higher solubility in nonpolar solvents (in particular, in CH_2Cl_2) compared to the commonly used nitrile compounds, such as $PtCl_4(RCN)_2$ (R = Me or Ph).

It is known that the platinum(IV) center is one of the best activators of the C≡N bond and is superior in the degree of activation to even such powerful classical activators as the CF_3 group.[16,17] Unlike more labile platinum(II) com-

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plexes,[14] kinetically inert platinum(IV) compounds are much less prone to chelation. This is of interest for investigating the reaction mechanism of the addition of guanidines to coordinated nitriles.

Platinum(IV)-mediated addition of 1,3-diphenylguanidine to propiononitrile. We found that the reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with DPG in a molar ratio of 1 : 2 afforded compound **1a** (Scheme 1, path *a*) as a result of two reactions: (*i*) the replacement of one nitrile ligand EtCN with diphenylguanidine; (*ii*) the nucleophilic addition of the HN=C group to the C≡N bond of the second nitrile.

Under analogous conditions, DPG does not react with uncoordinated nitriles RCN (R = Et or Ph). This is evidence that the nucleophilic addition of DPG to nitrile is mediated by the platinum(IV) center.

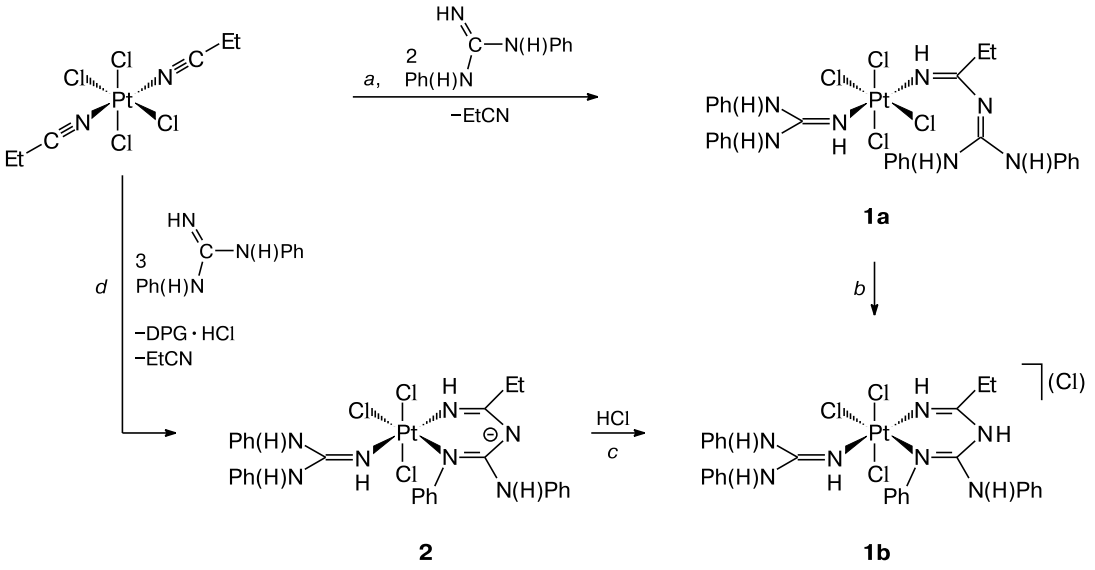
Then the ligand in compound **1a** undergoes chelation in a $CDCl_3$ solution at 50 °C for 84 h, which is accompanied by the replacement of the coordinated chloride to form cationic complex **1b** with the *N,N*-coordinated 1,3,5-triazapentadiene ligand (Scheme 1, path *b*). The transformation of compound **1a** into **1b** was confirmed by ^{1}H NMR spectroscopy (a compound, which was obtained after storage of complex **2** in the solid state in an HCl vapor, was used as a blank sample; see the Experimental section). It should be noted that the reverse reaction, *viz.*, the ring opening giving rise to complex **1a**, does not proceed at room temperature, which is evidence for the intermolecular mechanism of the nucleophilic addition of DPG to propiononitrile coordinated to the platinum(IV) center. The subsequent spontaneous transformation of cationic complex **1b** into neutral complex **2** does not proceed.

The reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with DPG in a molar ratio of 1 : 4 during the same period of time (one day) afforded complex **2** with the bidentate 1,3,5-triazapentadienate ligand. Under the experimental conditions, the intermediate steps of this reaction were not detected. In this chemical transformation, DPG acts as both the nucleophile and the dehydrochlorinating agent. Apparently, the mechanism of formation of complex **2** involves three successive steps *a*—*c* (see Scheme 1).

In the present study, we found that in the case of platinum(IV), the nucleophilic addition proceeds more rapidly than in the case of platinum(II) (for platinum(IV), the reaction is completed in a few minutes; for platinum(II), in a few hours). The observed increase in the reactivity of the platinum(IV) nitrile complex compared to the related platinum(II) complexes can be explained not only in terms of charge-controlled reactions (the larger partial positive charge on the carbon atom of the C≡N bond of coordinated organonitriles in Pt^{IV} complexes compared to Pt^{II} complexes, which facilitates the nucleophilic attack) but also by the nature of the metal center, which determines the orbital control in the reaction (the smaller difference between the levels of HOMO and LUMO of the reactants in the case of Pt^{IV} complexes).[18]

The study of the reaction with the platinum(IV) complex showed that the formation of the 1,3,5-triazapentadiene metallacycle Pt—N(H)=C(Et)NC(N(H)Ph)=NPh proceeds stepwise. As opposed to the previous study dealing with the platinum(II)-mediated nucleophilic addition of DPG to nitriles giving rise to 1,3,5-triazapentadiene chelate complexes (Scheme 2),[14] in the present study we found that the reaction of DPG with EtCN coordinated to platinum(IV) affords *open-chain* 1,3,5-triazapentadiene, which may be indicative of the intermolecular reaction mechanism *a* (see Scheme 1). The formation of chelate **1b** instead of complex **1a** in the reaction *a* (see Scheme 1)

Scheme 1



followed by the ring opening and the formation of compound **1a** with the monodentate ligand seems unlikely in the process with the involvement of the kinetically inert metal center (Pt^{IV}). We suggest that the reaction of 1,3-diphenylguanidine with the propiononitrile ligand in the platinum(IV) nitrile complex *trans*-$[PtCl_4(EtCN)_2]$ proceeds *via* nucleophilic attack on the nitrile carbon atom by the guanidine N atom followed by the proton transfer to the coordinated iminate group that is formed in the course of the coupling. The formation of platinum(II) complexes with the open-chain 1,3,5-triazapentadiene ligands rather than with the chelate ligands (see Scheme 2) was not observed,[14] which is attributed to the higher kinetic lability of platinum(II) compared to platinum(IV). The latter fact, in turn, leads to the ease of the ring closure in platinum(II) complexes compared to platinum(IV) complexes.

Triaza analogs of 1,3-dicarbonyl derivatives, such as 1,3,5-triazapentadienes, are less studied than related 1,3-dicarbonyl compounds. Nevertheless, these compounds deserve special attention because they contain an additional reaction center, *viz.*, the central nitrogen atom, which can be involved in the acid-base equilibrium,[11,19,20] thus imparting pH-dependent properties to these complexes (for example, the luminescence property, which depends on the protolytic form of the reaction center[11]). In spite of evident advantages and potential possible fields of application of chelating systems based on 1,3,5-triazapentadienyls, general preparative methods for the synthesis of chelates based on those compounds are lacking, and the specific methods described in the literature were not systematically studied. Thus, 1,3,5-triazapentadienes unstable in the free state (containing the unsubstituted NH group and/or donor substituents at carbon atoms) are generally produced by metal-mediated reactions, such as (*i*) reactions of amidines with nitriles electrophilically activated by coordination to M^{II} (Pt^{II},[10,11,21] Pd^{II},[21,22] Ni^{II},[23] or Pt^{IV} (see Ref. 10)), the nucleophilic addition of DPG to nitriles electrophilically activated by coordination to Pt^{II} (see Ref. 14 and Scheme 2), the coupling of two adjacent nitriles in the platinum(II) *cis*-nitrile complexes *cis*-$[PtCl_2(RCN)_2]$ by the reaction with DPG;[14] (*ii*) copper-[24,25] or nickel-mediated[26] hydrolytic transformations of 1,3,5-triazine[24,26] or 1,3,5-tris(2-pyridyl)-2,4,6-triazine;[25] (*iii*) the hydrolytic transformation of nitriles mediated by the dinuclear nickel(II) complex $[Ni_2(\mu\text{-}OH)_2(tpa)_2](ClO_4)_2$ (tpa is tris(2-pyridylmethyl)-amine)[27] or Ni^{II} acetate;[28] (*iv*) the reaction of $NiCl_2 \cdot 6H_2O$ with acetamidine in MeOH;[29] and (*v*) the oxime-mediated transformation of nitriles with the involvement of Pt^{II} (see Ref. 30) or Ni^{II}.[19,20] In the present study, we report the first example of the platinum(IV)-mediated nucleophilic addition of guanidine to nitrile and the simple procedure for the synthesis of 1,3,5-triazapentadiene derivatives of Pt^{IV}.

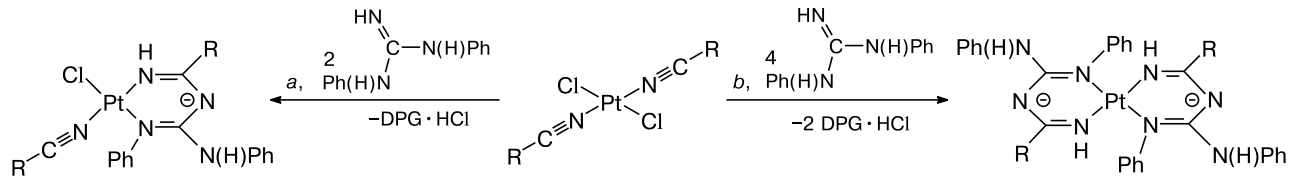
Structures of (1,3,5-triazapentadienate)Pt^{IV} complexes. A comparison of the IR spectra of compounds **1a**, **1b**, and **2** with the IR spectrum of the starting platinum(IV) dinitrile complex *trans*-$[PtCl_4(EtCN)_2]$ shows that stretching bands of the C≡N triple bond are absent in the spectra of the reaction products, but these spectra contain intense stretching bands of C=N and C=C double bonds in the 1636—1442 cm^{-1} region, as well as N—H stretching bands observed at higher frequencies (3396—3043 cm^{-1}).

The positions of the N—H stretching bands in the IR spectrum of complex **2** are similar to those in the spectrum of DPG. The IR spectrum of compound **2** shows intense ν(C=N) and/or ν(C=C) bands at 1639—1462 cm^{-1} and ν(N—H) bands in the region from 3401 to 3244 cm^{-1}. These frequencies agree well with those for ν(C=N) and/or ν(C=C) (1636—1442 cm^{-1}) and ν(N—H) (3422—3338 cm^{-1}) bands in the spectra of the (1,3,5-triazapentadiene)Pt^{II} and/or (1,3,5-triazapentadienato)Pt^{II} complexes, *viz.*, [PtCl(NCR){NH=C(R)NC(N(H)Ph)=N(Ph)}] and [Pt{NH=C(R)NC(N(H)Ph)=N(Ph)}$_2$] (Et, CH_2Ph, or Ph).[14]

In the ^1H NMR spectrum of compound **2**, the chemical shifts and the multiplicities of the proton signals of the phenyl groups at δ 7.90—6.90 differ from those observed in the spectrum of free DPG. The ^1H NMR spectra of complexes **1a**, **1b**, and **2** at δ 5.00—3.90 are characterized by the presence of a singlet + doublet with the spin-spin coupling constant with ^{195}Pt at 13—14 Hz assigned to the proton of the N—H group.

The ^1H NMR spectra of complexes **1a**, **1b**, and **2** display four singlets (**1b**) or one singlet (**1a** and **2**) at δ 13.30—7.50 and one (**1b**), two (**1a**), or three singlets (**2**) belonging to H—N protons at δ 6.30—5.85. Therefore, the protonation of the chelating 1,3,5-triazapentadiene ligand in complex **2** giving rise to cationic complex **1b** leads to substantial downfield shifts of the signals for the H—N protons. The transformation from the open-chain

Scheme 2



to the cyclic neutral form of the 1,3,5-triazapentadiene ligand as a result of chelation is accompanied by upfield shifts of the signals for the aromatic protons (signals for twelve of twenty protons shift to frequencies lower than 7 ppm). The formation of the anionic form of the chelating 1,3,5-triazapentadiene ligand as a result of elimination of HCl is accompanied by the opposite effect. In this case, the signals for ten of twelve phenyl protons shift downfield (to a region higher than 7 ppm). On the contrary, the deprotonation of the cyclic neutral form of the 1,3,5-triazapentadiene ligand leads to upfield shifts of the signals of the ethyl substituent.

Compound **2** was characterized by X-ray diffraction (Fig. 1). The coordination polyhedron of complex **2** is a distorted octahedron formed by three N atoms and three Cl atoms at the Pt atom. The atoms of the metallacycle Pt(1)N(1)C(1)N(2)C(4)N(3) lie in a single plane (the average deviation from the plane is 0.078(3) Å). In the metallacycle, the CN double and single bonds are clearly differentiated. The N(1)—C(1) bond length is 1.298(4) Å. This value is more similar to the characteristics of the C=N double bond and is comparable with the lengths of the corresponding C=N double bonds in the monochelate and bischelate (1,3,5-triazapentadiene)Pt^{II} and/or (1,3,5-triazapentadienato)Pt^{II} complexes, *viz.*, [PtCl{NH=C(Et)NC(N(H)Ph)=NPh)}(EtCN)] (1.313(4) Å) and [Pt{NH=C(Et)NC(N(H)Ph)=NPh)}$_2$] (1.306(3) Å), respectively.[14] The N(2)—C(1) and N(2)—C(4) bond lengths (1.337(5) and 1.338(4) Å, respectively) are similar to the N—C bond lengths in Pt^{II} complexes containing the same structural fragment Pt—NH=C(Et)NC(N(H)-Ph)=NPh, *viz.*, [PtCl{NH=C(Et)NC(N(H)Ph)=NPh)}-(EtCN)] (1.333(4) and 1.346(4) Å, respectively) and [Pt{NH=C(Et)NC(N(H)Ph)=NPh)}$_2$] (1.344(3) and 1.332(3) Å, respectively).[14] The N(3)—C(4) interatomic distance (1.337(4) Å) is shorter than the corresponding N=C double bonds in the complexes containing the (1,3,5-triazapentadiene)M and/or (1,3,5-triazapentadienato)M structural unit (M = Pt^{II} or Ni^{II}),[10,14,19] which is apparently attributed to the influence of the N(H)Ph group. However, this interatomic distance is typical (within 3σ) of this type of 1,3,5-triazapentadiene- and/or 1,3,5-triazapentadienato-containing metallacycles and is comparable with the lengths of the corresponding C=N double bonds in the monochelate and bischelate (1,3,5-triazapentadiene)Pt^{II} and/or (1,3,5-triazapentadienato)Pt^{II} complexes [PtCl{NH=C(Et)NC(N(H)Ph)=NPh)}(EtCN)] (1.330(4) Å) and [Pt{NH=C(Et)NC(N(H)Ph)=NPh)}$_2$] (1.339(3) Å), respectively.[14] The N=C double bond lengths and the N—C single bond lengths in the metallacycle, as opposed to the complexes of the types (1,3,5-triazapentadiene)M and/or (1,3,5-triazapentadienato)M (M = Pt^{II} or Ni^{II}),[10,14,19] are indicative of a higher degree of delocalization in the chelate metallacycle. The N(4)—C(4) bond length (1.370(5) Å) is similar to the length of the corresponding N—C single bond in Pt^{II} complexes containing the analogous structural fragment Pt—NH=C(Et)NC-(N(H)Ph)=NPh, such as [PtCl{NH=C(Et)NC(N(H)-Ph)=NPh)}(EtCN)] (1.370(4) Å) and [Pt{NH=C(Et)NC-(N(H)Ph)=NPh)}$_2$] (1.381(3) Å).[14]

The N(5)—C(17) bond length (1.310(4) Å) in coordinated DPG in complex **2** is consistent (within 3σ) with the lengths of the N=C double bonds in compounds containing the C_{Ar}—C=N—C fragment (aver., 1.279(8) Å)[31]

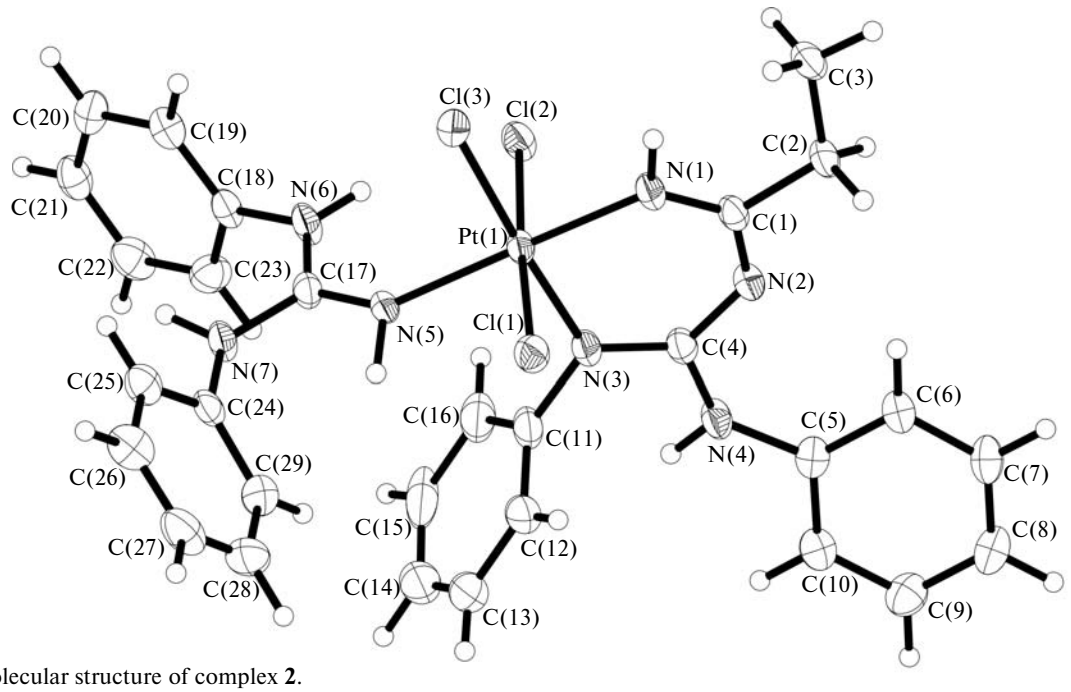


Fig. 1. Molecular structure of complex **2**.

and the lengths of the corresponding CN bond in coordinated 1,2,3-triphenylguanidine $PhN{=}C(NHPh)_2$ in the $[CoCl_2\{PhN{=}C(NHPh)_2\}_2]$ (1.312(8) and 1.295(8) Å) and $[Ag\{PhN{=}C(NHPh)_2\}_2][SO_3CF_3]$ (1.32(1) Å) complexes.[32] Compound **2** is the first structurally characterized transition metal complex with 1,3-diphenylguanidine serving as the neutral monodentate ligand.

In the solid state, the hydrogen atom of the N(H)Ph fragment of the coordinated diphenylguanidine and the adjacent equatorial Cl atom are linked by a hydrogen bond (N(6)—H(6A)···Cl(2), 2.30 Å). The plane of diphenylguanidine N(5)N(6)N(7)C(17) (the average deviation from the plane is 0.007(3) Å) is perpendicular to the plane of the metallacycle Pt(1)N(1)C(1)N(2)C(4)N(3) (the angle between these planes is 89.37(17)°).

Hence, we performed the platinum(IV)-mediated nucleophilic addition of 1,3-diphenylguanidine to propiononitrile giving rise to 1,3,5-triazapentadiene complexes. The results of the present study can be considered in three aspects. First, DPG was demonstrated to be involved in the metal-mediated nucleophilic addition to the nitrile ligand in the *trans*-$[PtCl_4(EtCN)_2]$ complex. Second, it was found that the coordination mode of 1,3,5-triazapentadiene ligands substantially depends on the oxidation state of the metal center. Thus, in the platinum(IV) complexes, the 1,3,5-triazapentadiene ligand exists in the open-chain form, whereas the chelate forms of 1,3,5-triazapentadiene are observed in the platinum(II) complexes (see Scheme 2).[14] Third, the reaction provides a simple method for synthesizing 1,3,5-triazapentadienyl complexes.

Experimental

The elemental analysis was carried out on a 185B Carbon Hydrogen Nitrogen Analyzer Hewlett Packard instrument by burning samples in an air flow according to a known procedure.[33] The IR spectra were recorded in KBr pellets on a Shimadzu FTIR-8400S spectrophotometer in the 4000—400 cm^{-1} region. The ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker DPX 300 spectrometer at room temperature. The chemical shifts in the ^1H ($CDCl_3$, 7.27 ppm) and $^{13}C\{^1H\}$ ($CDCl_3$, 77.4 ppm) NMR spectra were measured relative to the signals of the corresponding solvents. The positive-ion fast atom bombardment (FAB^+) mass spectra were obtained on a Trio 2000 instrument using 3-nitrobenzyl alcohol as the matrix; samples were bombarded with Xe atoms. Thin-layer chromatography was carried out on Al plates precoated with a layer of silica gel Merck 60 F_{254}. Thermogravimetric studies of compound **2** were carried out on a Mettler—Toledo TGA85 derivatograph in aluminum crucibles at a heating rate of 8 K min^{-1} (the temperature range was 20—1000 °C, the rate of air flow was 3 L h^{-1}, the weight of samples was 5—10 mg).

Reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with HN=C(NHPh)$_2$ in a molar ratio of 1 : 2. Diphenylguanidine (46.7 mg, 0.22 mmol) was added to a suspension of the *trans*-$[PtCl_4(EtCN)_2]$ complex (0.10 mmol) in CH_2Cl_2 (1 mL) at room temperature. The reaction mixture turned orange for 1—2 min. After 1 day, the solvent was evaporated to dryness, and the dark-orange oily residue was dissolved in $CHCl_3$ (0.75 mL). Complex **1a** was separated and purified by silica gel column chromatography (Silicagel 60 F_{254}, 0.063—0.200 mm, Merck; ethyl acetate:chloroform = 1 : 20 as the eluent, R_f = 0.58, the first bright-yellow fraction) and then dried in air at 20—25 °C.

The heating of a solution of complex **1a** in $CDCl_3$ at 50 °C for 84 h afforded complex **1b**.

Tetrachloro[{*N*-(dianilinomethylene)propanimidamide}-(*N*,*N*′-diphenylguanidine)]platinum(IV), $[PtCl_4\{NH{=}C(NHPh)_2\}\{NH{=}C(Et)N{=}C(NHPh)_2\}]$ (1a). FAB^+ MS, *m/z*: 816 $[M+2H]^+$, 779 $[M-Cl]^+$, 744 $[M-2Cl+H]^+$, 708 $[M-3Cl]^+$, 671 $[M-HCl-3Cl]^+$, 497 $[M-3Cl-NH{=}C(NHPh)_2]^+$, 459 $[M-2HCl-2Cl-NH{=}C(NHPh)_2]^+$. TLC data: R_f = 0.62 (Et_2O : $CHCl_3$, 1 : 10, as the eluent). IR, ν/cm^{-1}: 3545, 3288 ν(N—H); 3057 ν(C—H (Ar)); 2979 ν(C—H (Et)); 1666, 1637 ν(C=N); 1593, 1545, 1496 ν(C=N and/or C=C (Ar)); 754, 694 δ(C—H (Ar)). ^1H NMR ($CDCl_3$), δ: 8.99 (s, 1 H, NH); 7.42—7.32 (m, 15 H, Ph), 7.17 (d, 5 H, Ph); 6.17 (br.s, 2 H), 5.00 (s + d, 1 H, J_{Pt-H} = 13.4 Hz) (NH); 3.14 (q, 2 H, CH_2, J = 7.5 Hz), 1.10 (t, 3 H, CH_3, J = 7.5 Hz) (Et). We failed to obtain a sufficient amount of the compound for C, H, N-elemental analyses and $^{13}C\{^1H\}$ NMR spectroscopy (see Results and Discussion).

Reaction of complex 2 with HCl. Upon the treatment of compound **2** in the solid state (12 mg) with gaseous HCl for 10 min, the color of the compound changed from orange to yellow. Then the compound was dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy, which detected the formation of complex **1b**.

Trichloro[{*N*-(dianilinomethylene)propanimidamide}-(*N*,*N*′-diphenylguanidine)]platinum(IV), $[PtCl_3\{NH{=}C(NHPh)_2\}\{NH{=}C(Et)NHC(NHPh){=}NPh\}](Cl)$ (1b). ^1H NMR ($CDCl_3$), δ: 13.29, 10.25, 8.56, and 7.52 (all br.s, 1 H each, NH); 7.40 (d, 2 H), 7.22 (br.m, 6 H), 6.94 (d, 3 H), 6.81 (d, 4 H), 6.70 (t, 5 H) (Ph); 6.11 (br.s, 1 H), 3.95 (s + d, 1 H, J_{Pt-H} = 14.2 Hz) (NH); 3.05 (q, 2 H, J = 7.1 Hz), 1.50 (t, 3 H, J = 7.1 Hz) (Et).

Reaction of the *trans*-$[PtCl_4(EtCN)_2]$ complex with HN=C(NHPh)$_2$ in a molar ratio of 1 : 3. Diphenylguanidine (88.5 mg, 0.42 mmol) was added to a suspension of the *trans*-$[PtCl_4(EtCN)_2]$ complex (0.10 mmol) in EtCN (2 mL) at room temperature. The reaction mixture turned orange-red during one day. Then the solvent was evaporated to dryness, the red oily residue was dissolved in $CHCl_3$ (0.75 mL), and complex **2** was isolated by silica gel column chromatography (Silicagel 60 F_{254}, 0.063—0.200 mm, Merck; Et_2O : $CHCl_3$ = 1 : 20, as the eluent, R_f = 0.51, the first bright-yellow fraction). The reaction product was dried in air at 20—25 °C. The yield of the analytically pure product was 51 mg (33%) (the reaction mixture contained a broad range of products, including complex **1a**).

Trichloro[{anilino)phenylimino)methyl}(propanimidoyl)-{azanide}(*N*,*N*′-diphenylguanidine)]platinum(IV), $[PtCl_3\{NH{=}C(NHPh)_2\}\{NH{=}C(Et)NC(NHPh){=}NPh\}]$ (2). Found (%): C, 44.75; H, 3.86; N, 12.60. $C_{29}H_{30}N_7Cl_3Pt$. Calculated (%): C, 44.90; H, 3.84; N, 12.20. FAB^+ MS, *m/z*: 778 $[M]^+$, 708 $[M-2Cl+H]^+$, 671 $[M-3Cl]^+$, 497 $[M-2Cl-NH{=}C(NHPh)_2+H]^+$, 460 $[M-3Cl-(NH{=}C(NHPh)_2)]^+$, 405 $[M-HCl-2Cl-NH{=}C(Et)NC(NHPh){=}NPh]^+$. TLC data: R_f = 0.51 (Et_2O : $CHCl_3$, 1 : 20, as the eluent); DTA/TGA: 200 °C (gradual decomposition). IR, ν/cm^{-1}: 3404, 3357, 3215 ν(N—H); 3055 ν(C—H (Ar)); 2933 ν(C—H (Et)); 1693, 1595 ν(C=N); 1577, 1549, 1495, 1473

ν(C=N and/or C=C (Ar)); 756, 694 δ(C—H (Ar)). ^{1}H NMR ($CDCl_3$), δ: 8.77 (s, 1 H, NH); 7.46 (d, 2 H), 7.41 (d, 2 H), 7.34 (d, 2 H), 7.27 (d, 5 H), 7.21 (t, 6 H), 7.04 (quint, 1 H), 6.87 (d, 2 H) (Ph); 6.29 (br.s, 1 H), 5.93 (s, 1 H), 5.84 (br.s, 1 H), 4.23 (s + d, 1 H, J_{Pt-H} = 13 Hz) (NH); 2.56 (q, 2 H, CH_2, J = 7.5 Hz), 1.24 (t, 3 H, CH_3, J = 7.5 Hz) (Et). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 165.66 (J = 5.6 Hz), 154.58 (J = 10 Hz), 146.11 (J = 5.6 Hz) (C=N); 143.62, 138.92, 135.80, 134.54, 130.16, 130.11, 129.98, 129.77, 128.33, 128.26, 127.23, 126.83, 125.60, 124.59, 124.17, 123.26 (C=C (Ar)); 33.34 (J = 12.4 Hz, CH_2), 11.57 (CH_3) (Et). Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of complex **2** in a 3 : 1 hexane—chloroform mixture.

X-ray diffraction study. A single crystal of complex **2** was grown by slow evaporation of a solution of this compound in a 3 : 1 hexane : chloroform mixture at 20—25 °C. Before the X-ray data collection, the crystal of complex **2** was mounted in a Nylon loop and soaked in a cryo protectant. The X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer at 120(2) K, (monochromator, Mo-Kα radiation, λ = 0.71073 Å). The unit cell parameters were refined and the X-ray data were merged using the Denzo-Scalepack[34] or EvalCCD[35] program packages. The structure was solved by direct methods with the use of the SIR97,[36] SIR2002,[37] and SHELXS97[38] program packages and the WinGX graphics interface.[39] The absorption correction was applied based on the intensities of equivalent reflections with the use of the XPREP program from the SHELXTL v.6.14-1 program package[40] and the SADABS v.2.10 program[41] (T_{min}/T_{max} was 0.2187/0.3869). The structure was refined using the SHELXL97 program package.[42] The NH hydrogen atoms were located in difference Fourier maps and were not refined. All other hydrogen atoms were positioned geometrically. The atomic coordinates and complete tables of bond lengths and bond angles were deposited with the Cambridge Structural Database. Principal crystallographic parameters are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 1. Crystallographic data for complex **2**

Parameter	Characteristics
Molecular formula	$C_{29}H_{30}Cl_3N_7Pt$
Molecular weight	778.04
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.9851(4)
b/Å	18.1005(7)
c/Å	16.4492(4)
α/deg	90
β/deg	90.720(2)
γ/deg	90
V/Å^3	2972.72(18)
Z	4
d_{calc}/mg m^{-3}	1.738
μ/mm^{-1}	5.022
Scanning range/deg	1.67—27.51
Number of measured reflections	37462
R_{int}	0.0442
R_1 ($I \geq 2\sigma$)	0.0275
wR_2 ($I \geq 2\sigma$)	0.0578

Table 2. Selected bond lengths (d) and bond angles (ω) in complex **2**

Bond	d/Å	Angle	ω/deg
Pt(1)—Cl(1)	2.3261(9)	N(1)—Pt(1)—N(3)	89.66(11)
Pt(1)—Cl(2)	2.3315(9)	N(3)—Pt(1)—N(5)	93.22(11)
Pt(1)—Cl(3)	2.3345(9)	C(1)—N(1)—Pt(1)	126.6(3)
Pt(1)—N(1)	1.986(3)	N(1)—C(1)—N(2)	126.9(3)
N(1)—C(1)	1.298(4)	C(1)—N(2)—C(4)	124.5(3)
N(2)—C(1)	1.337(5)	N(3)—C(4)—N(2)	128.2(3)
N(2)—C(4)	1.338(4)	C(4)—N(3)—Pt(1)	122.9(2)
N(3)—C(4)	1.337(4)	C(4)—N(4)—C(5)	130.8(3)
N(4)—C(4)	1.370(5)	C(17)—N(5)—Pt(1)	137.2(2)
Pt(1)—N(3)	2.023(3)	C(17)—N(6)—C(18)	124.7(3)
Pt(1)—N(5)	2.057(3)	C(17)—N(7)—C(24)	122.3(3)
N(5)—C(17)	1.310(4)	N(5)—C(17)—N(6)	122.6(3)
N(6)—C(17)	1.343(5)	N(5)—C(17)—N(7)	121.4(3)
N(7)—C(17)	1.366(4)	N(6)—C(17)—N(7)	116.0(3)

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